

Low temperature behaviour of refined products from DSC measurements and their thermodynamical modelling

António J.N. Queimada^a, C. Dauphin^b, Isabel M. Marrucho^a,
João A.P. Coutinho^{a,*}

^a*Departamento de Química da Universidade de Aveiro, 3810 Aveiro, Portugal*

^b*Laboratoire des Fluides Complexes, Université de Pau, 64000 Pau, France*

Received 18 October 2000; accepted 8 January 2001

Abstract

The low temperature behaviour of five distillation cuts (230–375°C) from crude oil from different sources (North Sea, Africa and Middle East) provided by the Portuguese refinery Petrogal, was studied. Precipitation curves for these cuts, showing the evolution of the fraction of solid *n*-alkanes with temperature, were measured by DSC and the compositions of the cuts were analysed by gas chromatography (GC). The measured precipitation curves have been compared with the predictions from a thermodynamical model using the compositional analysis. The model results agree well with the experimental data indicating that the model used can be an adequate tool to predict the low temperature behaviour of refined oil products. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Low temperature behaviour; Thermodynamical model; Paraffinic fuels

1. Introduction

The new European standards for automotive fuels, issued under the Auto-Oil program [1], are changing the way fuels are produced. There is a clear trend towards more paraffinic fuels [2,3], with better combustion habits, and thus more environmental friendly, but that will have a worst behaviour at low temperatures presenting higher cloud and pour points.

The solubilities of the long *n*-alkanes strongly decrease with temperature and, for diesels, below 280 K, the exact temperature depending on the *n*-alkane content and its distribution, crystals of *n*-alkanes start precipitating plugging pipes and fuel

filters. The production fuels that simultaneously conform to the new European standards and the low temperature behaviour restrictions will demand either an increasing use of additives, such as pour point depressants, or the redesign of the distillation to reduce the concentration of *n*-alkanes to an acceptable level. For this purpose, it is important to be able to relate the *n*-alkane crystallisation with the composition of the fluid. This will help to design adequately the production and blend of fuels, and to select the most adequate additives [4].

This work studies the low temperature behaviour of five distillation cuts (230–375°C) from crude oils from different sources (North Sea, Africa and Middle East) obtained from the Petrogal refinery. They were chosen because they are the basis for diesel produced at the refinery and cover the range of *n*-alkane contents

* Corresponding author. Fax: +351-234-370084.
E-mail address: jcountinho@dq.ua.pt (J.A.P. Coutinho).

typically found at the refinery (3–30 wt.%). Precipitation curves for these cuts, showing the temperature dependence of the solid fraction formed, were measured by differential scanning calorimetry (DSC) according to a method proposed before [5,6]. The measured precipitation curves are compared with predictions from a thermodynamical model using a compositional analysis of the fluid by gas chromatography. It will be shown that the model predictions agree very well with the curves obtained from the DSC measurements.

2. Experimental

The samples studied had the *n*-alkane composition measured by gas chromatography and the average molecular weight estimated by freezing point depression. No attempt to obtain any further compositional information, such as a PIONA analysis, was done since, as will be discussed later, the non *n*-alkane compounds do not play a relevant role in the low temperature behaviour of these fluids. The solid formation was assessed by DSC, as described below.

2.1. Gas chromatography

To measure the composition of the samples a Hewlett Packard 6890 equipped with a hydrogen flame ionisation detector was used. The column employed is composed of a pre-column of 1 m (i.d. = 530 μm); two 30 m column: the first was made of an HP 5 MS (i.d. = 320 μm and film thickness 0.5 μm) and the second a HP 5 (i.d. = 320 μm and film thickness 0.25 μm); and a final empty column of about 30 cm. The injection was performed on-column. On this chromatograph both the temperature and the carrier gas flow rate are programmable. To obtain a better separation of the heavy paraffins the gas flow rate was kept at 2 $\text{cm}^3 \text{min}^{-1}$ during the first 100 min and then increased to 3 $\text{cm}^3 \text{min}^{-1}$. Heating started at 333 K, at 2.5 K min^{-1} to 578 K, and then at 2 K min^{-1} up to 593 K. Under these conditions paraffins between decane (*n*-C₁₀) and triacontane (*n*-C₃₀) can be quantified. Nonane (*n*-C₉) (Aldrich >99%) was used as reference material and CS₂ as solvent. A chromatogram for Oso Condensate is shown in Fig. 1. The compositions obtained are presented in Table 1.

2.2. DSC

The calorimetric measurements were performed on a Setaram DSC 141. The sample was initially cooled to 130 K, kept at that temperature for 15 min to stabilise, and then heated up to 320°C at 3 K min^{-1} . This heating rate was chosen as a compromise between a good signal and close to equilibrium conditions. The wax appearance temperatures presented in Table 2 were measured under these conditions and may be slightly over estimated. The thermograms are presented in Fig. 2a–e. They are similar to other DSC measurements for fuel and crude oils previously reported in the literature [6–8]: after a glass transition at around 190 K, there was an exotherm due to the crystallisation of species that did not crystallise on cooling; it was followed by a broad endotherm due to the dissolution of the paraffinic crystals in the liquid matrix. The major problem in the treatment of the DSC results for these fluids is the definition of a base line. As proposed by Claudy and L  toff   [7,8] a polynomial line fitted the liquid region and the base of the exotherm, where the dissolution of the paraffins began, was used as base line. Since there was no way to assess the ‘true’ base line for these fluids this was a fair approach to it. Nevertheless, one must be aware that some uncertainty was introduced in the calculations by its adoption. Using this base line the fraction of solids dissolved was obtained using an approach proposed before [5,6] where the fraction of melted *n*-alkanes was identified with the fraction of total energy required to completely melt the *n*-alkanes obtained from the integration of the energy using the adjusted base line.

3. Modelling the solid formation

The solid formation was described as a solid–liquid equilibrium of *n*-alkanes. The general solid–liquid equilibrium equation relating the compositions with non-ideality of the phases and the pure component thermophysical properties was used [9]

$$\left(\ln \frac{s\gamma^s}{x\gamma^l} = \frac{\Delta h_m}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta h_{tr}}{RT_{tr}} \left(\frac{T_{tr}}{T} - 1 \right) - \frac{\Delta_s^1 C_{p_m}}{R} \left(\ln \frac{T}{T_m} + \frac{T_m}{T} - 1 \right) \right)_i \quad (1)$$

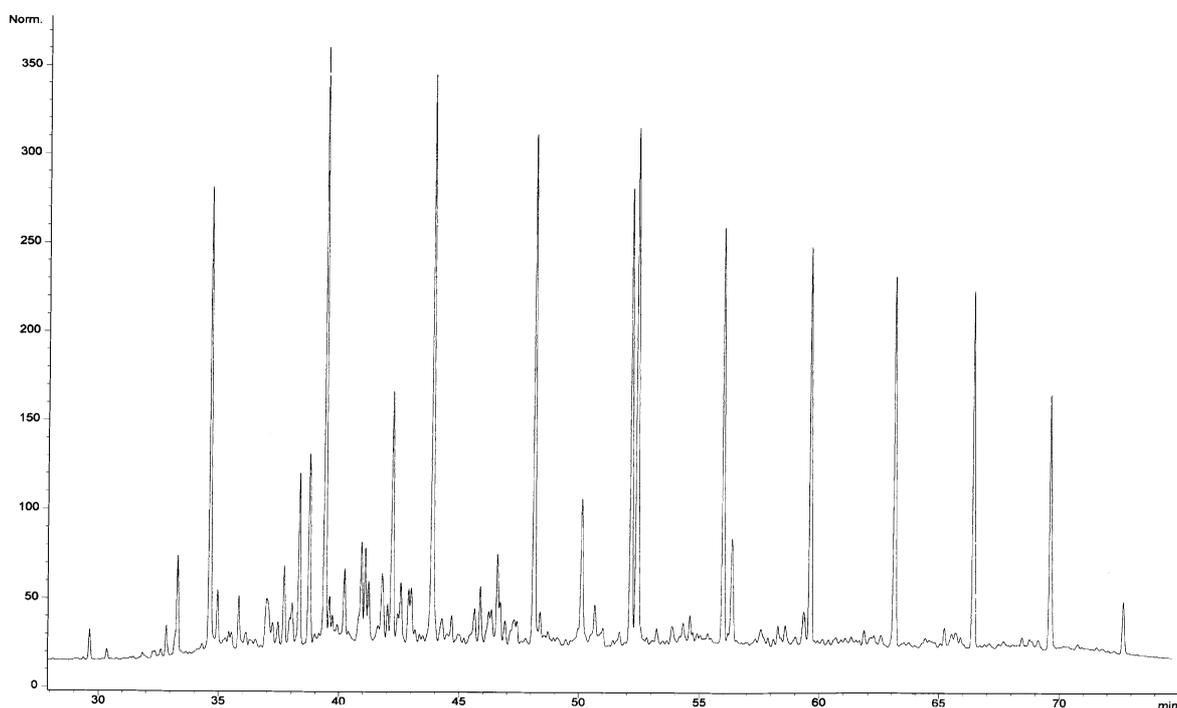


Fig. 1. Gas chromatography analysis of the distillation cut obtained from Oso Condensate. The higher peaks are the *n*-alkanes.

3.1. The liquid phase non-ideality

In previous works the liquid phase was assumed to be non-ideal and modelled using the Flory-free volume equation [10]. The use of this model for the liquid phase required a more detailed knowledge of its composition such as a PIONA analysis or equivalent. However the non-ideality of the liquid phase was not very significant [11] and as discussed in a previous work [12] to consider the solvent composed of 25% of aromatics or being

fully paraffinic does not change the low temperature behaviour of a solution. To simplify the approach, both in calculation and experimental requirements, an ideal liquid phase will be adopted in this work.

3.2. The solid phase non-ideality — predictive UNIQUAC

The solid phase non-ideality will be described by the predictive UNIQUAC model [13,14]. This is a

Table 1
n-alkane composition (wt.%) and average molecular weight of the distillation cuts studied

	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄	Total	<i>M_w</i>
Brent	0.04	0.06	0.36	10.65	13.42	14.43	11.86	9.72	8.3	7.97	8.25	6.97	6.52	1.42		19.55	222.8
Oso Condensate	0.05	0.11	0.56	10.11	12.77	13.61	11.15	9.88	9.01	8.94	8.46	8.04	6.02	1.22	0.04	31.98	226.8
Troll	0.07	0.09	0.28	9.65	14.05	16.36	12.15	9.40	8.63	8.09	8.03	6.32	5.53	1.36		9.79	231.7
DUC			0.07	5.50	13.66	17.30	9.97	7.22	9.52	9.81	11.42	6.19	7.21	2.14		2.79	220.3
Sahara Blend	0.03	0.09	0.53	13.22	14.79	14.94	11.39	10.41	9.07	7.78	7.38	5.54	4.06	0.75	0.02	21.17	235.8
Average distribution	0.05	0.09	0.36	9.83	13.74	15.33	11.30	9.33	8.91	8.52	8.71	6.61	5.87	1.38	0.03		

Table 2
Comparison between measured and predicted WATs

	Measured WAT K ⁻¹	Predicted WAT K ⁻¹	Deviation K ⁻¹
Brent	273.8	272.7	1.1
Oso Condensate	278.9	277.5	1.4
Troll	265.6	265.3	0.3
DUC	256.2	256.6	0.4
Sahara Blend	271.2	271.1	0.1
Average deviation			0.66

version of the original UNIQUAC, where

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (2)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (3)$$

using a new definition for the structural parameters r and q [14].

The predictive local composition concept [13] allowed an estimation of the interaction energies, λ_{ij} , used by these models. The pair interaction energies between two identical molecules were estimated from the heat of sublimation of the pure n -alkane taking the solid phase as an orthorhombic crystal,

$$\lambda_{ii} = -\frac{2}{Z} (\Delta h_{\text{sublm}_i} - RT) \quad (4)$$

where Z is the coordination number and has a value of $Z = 6$ for orthorhombic crystals. The heats of sublimation, $h_{\text{sublm}} = h_{\text{vap}} + h_{\text{m}} + h_{\text{tr}}$, was calculated at the melting temperature of the pure component. The heat of vaporisation, h_{vap} was assessed using the PERT2 correlation of Morgan and Kobayashi [15].

The pair interaction energy between two non-identical molecules is given by

$$\lambda_{ij} = \lambda_{ji} \quad (5)$$

where j is the n -alkane with the shorter chain of the pair ij .

The solid–liquid equilibrium model was, thus, a purely predictive model that used in the calculation of

the phase behaviour nothing, but pure component properties.

3.3. Solvent characterisation

The n -alkanes composition was obtained experimentally from the GC analysis, but no information was available about the composition of the balance of the fluid. As discussed above an ideal liquid phase will be assumed and thus no differentiation was made between aliphatic and aromatic compounds in the liquid phase. A single pseudo-compound will be used to describe the liquid phase. Its concentration is given by the concentration of non n -alkanes obtained from the GC analysis. The choice of the pseudo-compound is done by matching the average molecular weight of the pseudo-solution used in the calculation with the measured average molecular weight.

4. Results

The experimental precipitation curves obtained are presented in Fig. 3a–e. The curves exhibited similar shapes only shifted in temperature with differences that are related to the total n -alkane content. For the samples studied in this work the WATs nicely correlate with the total n -alkane content as shown in Fig. 4. Unfortunately, as has been shown before [16–18], this sort of correlation cannot be generalised to fluids with n -alkane distributions different than those used in the development of the correlation, as the WAT is highly dependent on the n -alkane distribution besides the total content.

Some recent results for crude oils [19,20] show that the total n -alkane content in waxy crude oils is related to the average molecular weight of the fluid. For the distillation cuts studied and other fuels from the literature [6,16], it was found that there was no such relation. The data in Table 1 clearly illustrates this.

The Fig. 3a–e also show the modelling results for each of the studied samples. As can be seen the predictions of the model agree very well with the experimental precipitation curves. Even for very low total n -alkane contents as for the cut from DUC oil, which contains only 2.8 wt.% of n -alkanes, and a WAT of 256 K, an excellent description of the experimental data is obtained. Due to the low n -alkane content the

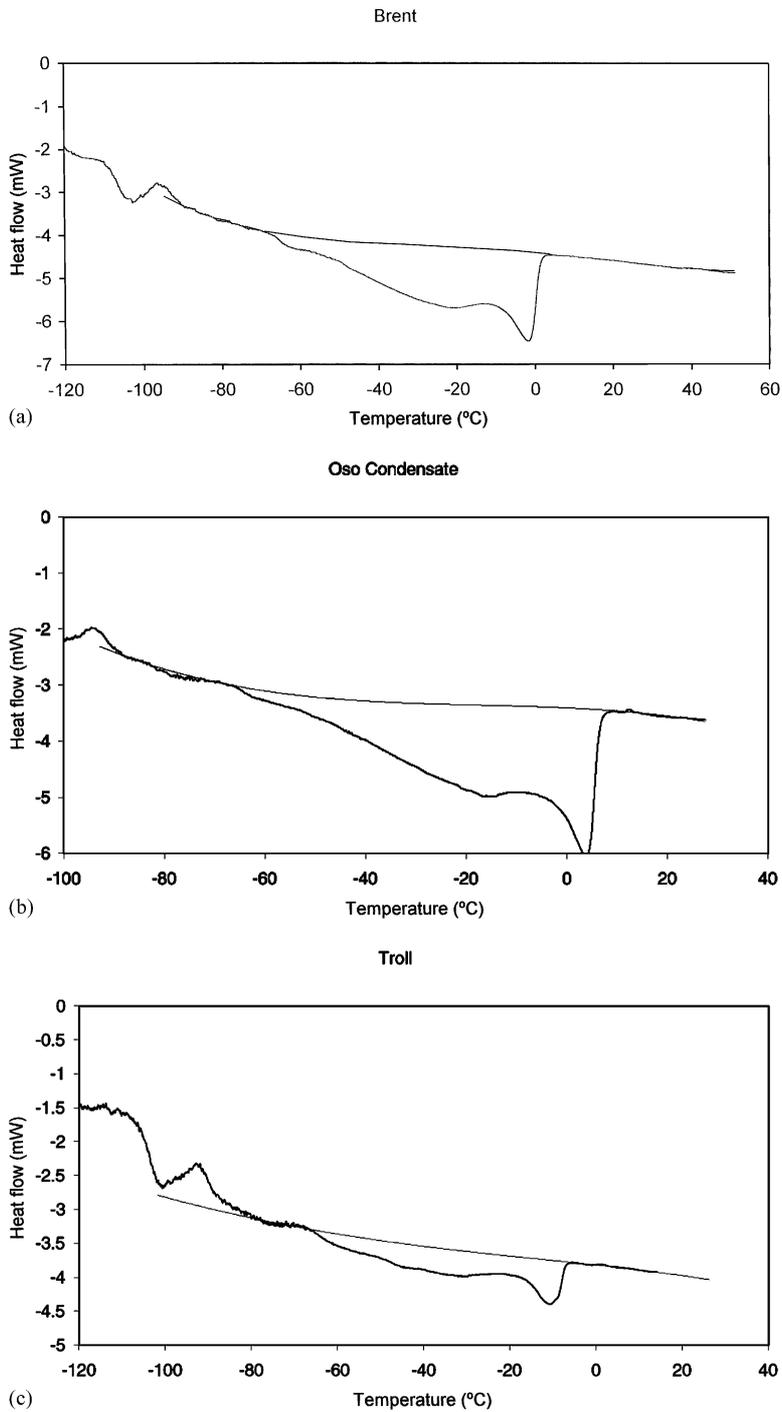


Fig. 2. DSC measurements for distillation cuts from Brent (a); Oso Condensate (b); Troll (c); DUC (d); and Sahara Blend (e).

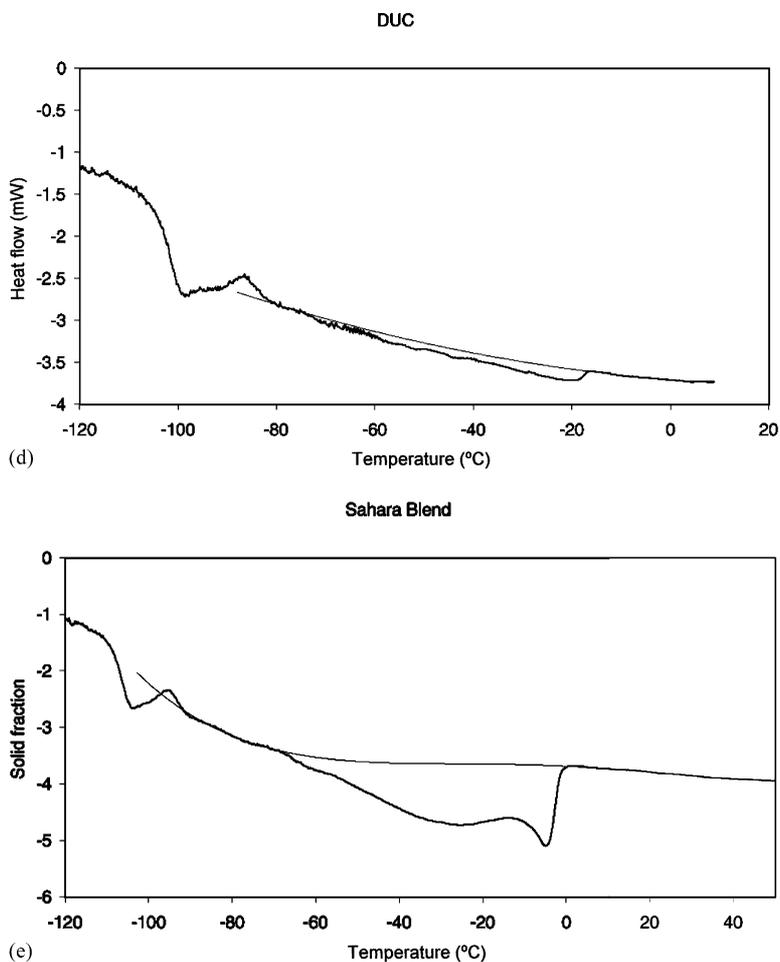


Fig. 2. (Continued).

DSC measurement for this fluid is particularly difficult due to the low intensity of the energy measured and thus, a larger experimental error is associated with this measurement. Generally it seems that the model slightly underestimates the measured precipitation curves. Since the DSC measurements are performed with a heating rate that does not assure that the equilibrium is attained in the sample, the temperatures measured are slightly overestimated and this may explain the deviations between the experimental data and the model predictions. Other reason may reside in the inadequacies of the baseline chosen. Model limitations would also be another obvious explanation given the huge simplifications made in what concerns the sample composition. Nevertheless, and taking into

account all the simplifications used and assumptions made, the model predictions and the experimental data present a surprisingly good agreement. The proposed model, using only the information from GC analysis, can thus provide a quick and reliable estimate of the low temperature behaviour of the fuel and could easily be used to plan fuel blends to meet some given low temperature specifications.

As suggested before for the distillation cuts studied it would be possible to develop a correlation to predict WATs from the total *n*-alkane content. Given the similarity of the *n*-alkane distributions among the studied samples, that appears to be completely independent of the total *n*-alkane content, it would also be possible, from the results presented, to propose an

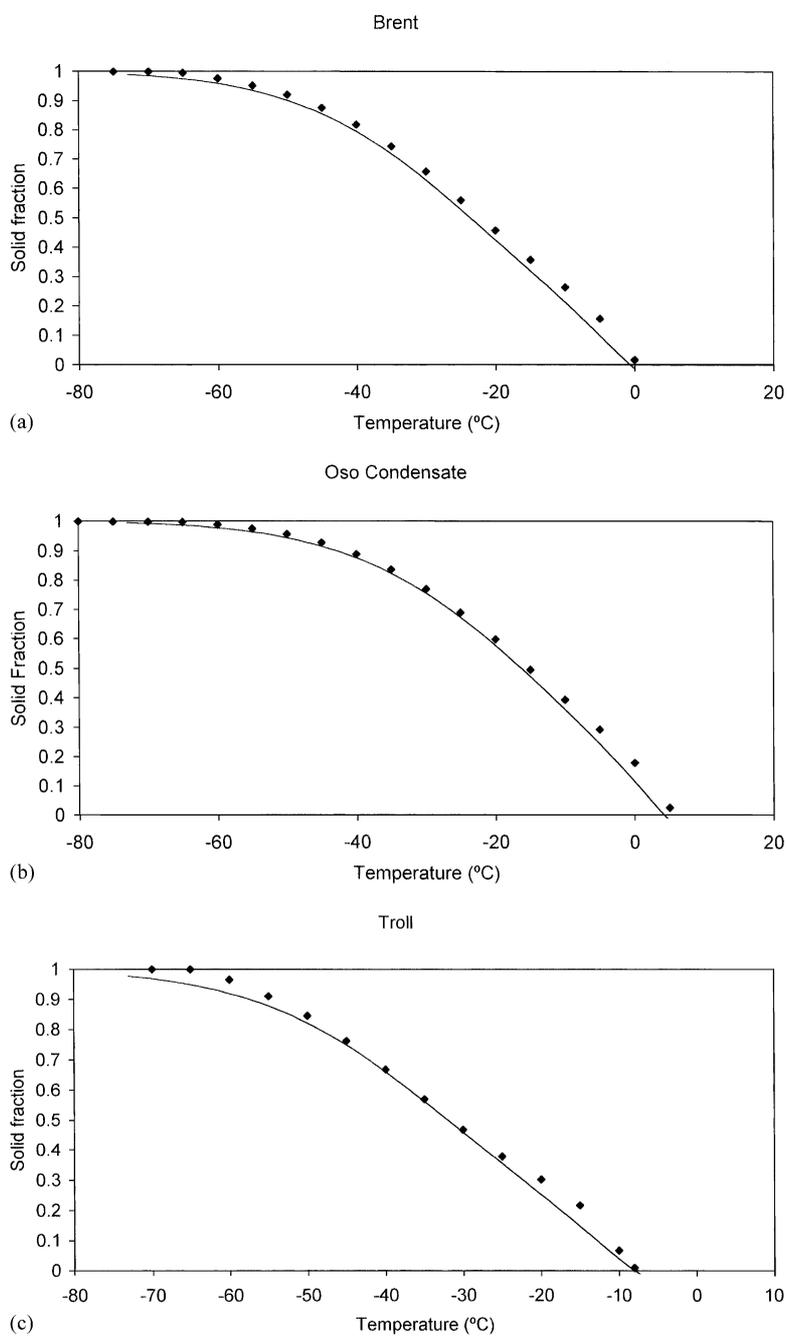


Fig. 3. Measured and predicted precipitation curves for distillation cuts from Brent (a); Oso Condensate (b); Troll (c); DUC (d); and Sahara Blend (e).

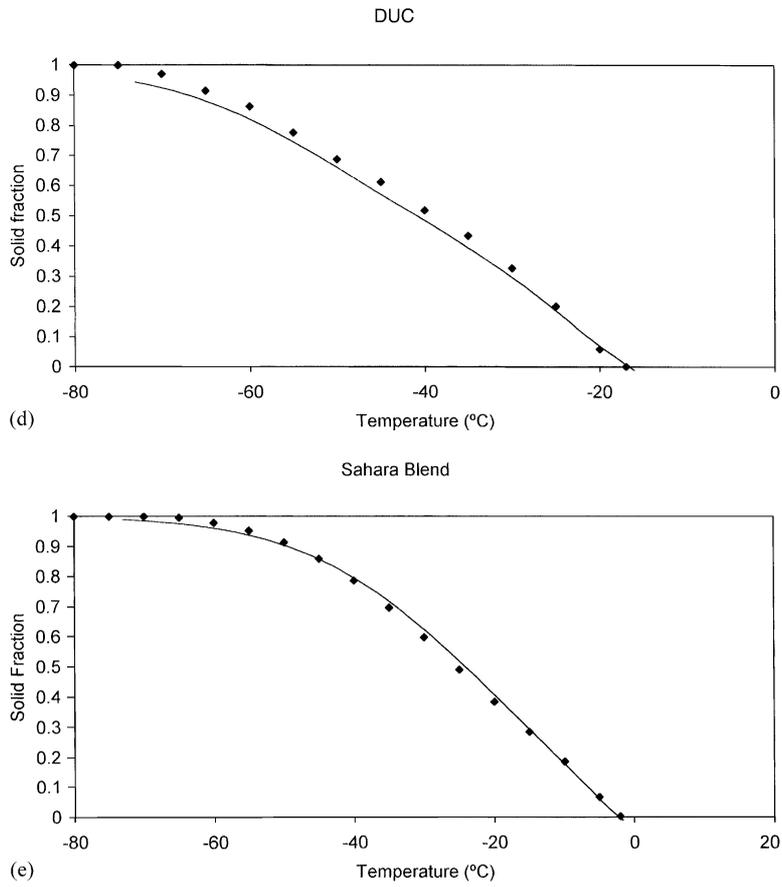
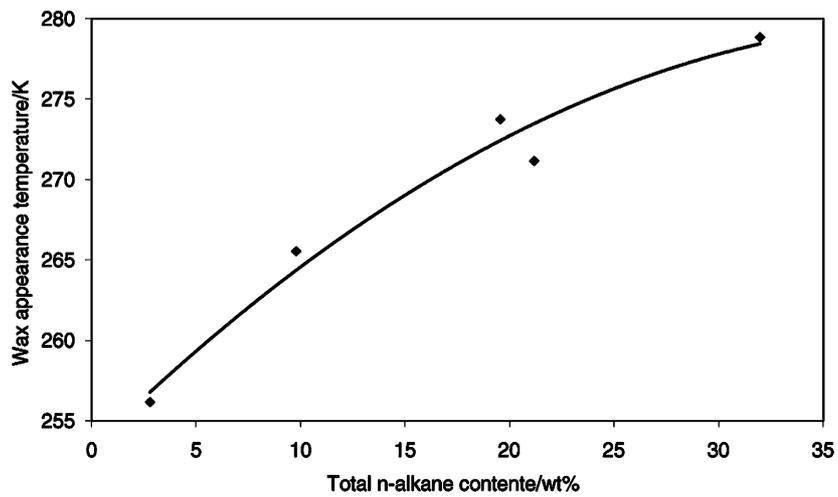


Fig. 3. (Continued).

Fig. 4. Relation between total *n*-alkane content and wax appearance temperatures for the studied cuts.

average *n*-alkane distribution for 230–375°C distillation cuts. Such a distribution is presented in Table 1. By using the average distribution, only a measurement of the total *n*-alkane content would be required to apply the model to obtain a reliable estimate of the low temperature behaviour of the fuel.

5. Conclusion

Distillation cuts from five crude oils commonly used to fuel production, had their low temperature behaviour studied. The composition of the samples was analysed by GC and precipitation curves were measured by DSC and predicted by a thermodynamic model assuming ideal liquid phase and a solid phase which non-ideality is described by the predictive UNIQUAC model. It was shown that the model provides an accurate description of the experimental data and can thus be used for a quick estimate of the low temperature behaviour of a fuel or to plan fuel blends to meet existing regulations.

Acknowledgements

The authors would like to thank Dr. Jorge C. Ribeiro and Petrogal for the distillation cuts and to Mr. Dang Thong at IVC-SEP, Technical University of Denmark for the molecular weight measurements. This work was founded by Fundação para a Ciência e Tecnologia, Portugal, under the project Praxis/P/EQU/12010/1998.

References

- [1] Auto Oil Programme, Doc: COM(96)248, European Commission, Brussels, 1996.
- [2] T. Neale, in: Proceedings of the Euro Sinergy Conference, Brussels, October 1997.
- [3] J. Soares Mota, in: Proceedings of the CHEMPOR'98, Lisbon, September 1998.
- [4] S.L. Wang, A. Flamberg, T. Kikabhai, *Hydrocarbon Processing*, 1999, p. 59.
- [5] J.A.P. Coutinho, S. Calange, V. Ruffier-Meray, *Can. J. Chem. Eng.* 75 (1997) 1075.
- [6] J.A. P. Coutinho, C. Dauphin, J.L. Daridon, *Fuel* 79 (2000) 607.
- [7] J.M. Létoffé, P. Claudy, M. Garcin, J.L. Volle, *Fuel* 74 (1995) 92.
- [8] F. Bosselet, J.M. Létoffé, P. Claudy, P. Valentin, *Thermochim. Acta* 70 (1983) 19.
- [9] J.M. Prausnitz, R.N. Lichtenthaler, Azevedo, E.G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Edition, Prentice-Hall, Englewood Cliffs, NJ, 1999.
- [10] J.A.P. Coutinho, S.I. Andersen, E.H. Stenby, *Fluid Phase Equilibria* 103 (1995) 23.
- [11] D.D. Erikson, V.G. Niessen, T.S. Brown, SPE 26604.
- [12] J.A.P. Coutinho, *Energy and Fuels* 14 (2000) 625.
- [13] J.A.P. Coutinho, E.H. Stenby, *Ind. Eng. Chem. Res.* 35 (1996) 918.
- [14] J.A.P. Coutinho, *Ind. Eng. Chem. Res.* 37 (1998) 4870.
- [15] D.L. Morgan, R. Kobayashi, *Fluid Phase Equilibria* 94 (1994) 51.
- [16] S.R. Reddy, *Fuel* 65 (1986) 4870.
- [17] L.I. Rossmyr, *Ind. Eng. Chem. Prod. Res. Dev.* 18 (1979) 227.
- [18] F. Mirante, J.A.P. Coutinho, *Fluid Phase Equilibria*, Submitted for publication.
- [19] H.P. Ronningsen, B. Bjordal, A.B. Hansen, W.B. Pedersen, *Energy Fuels* 5 (1991) 895.
- [20] K. Delmas, V. Ruffier-Meray, F. Brucy, in: Proceedings of the 2nd International Conference on Petroleum Phase Behaviour and Fouling, August 2000, Copenhagen, Denmark.