

Short Communication

# Cloud and pour points in fuel blends<sup>☆</sup>

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## Abstract

Cloud and pour points are part of the specifications for diesel fuel oils. This work studies the dilution of a diesel with a jet fuel of very low cloud point to produce fuel blends with lower cold characteristics. It is shown that the cloud point of the blend is a highly non-linear combination of the cloud points of the original fuels and is mainly dependent on the cloud point of the heavier fluid. Using a thermodynamic model previously proposed, an accurate description of the cloud point for the fuel blends is achieved. This model also allows an estimation of the amount of solid at the pour point showing that as little as 0.5–1 wt% of solids are enough to gel the fuel. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

At low temperatures crystals of paraffins form in fuels imposing restrictions to its use. A few degrees below the temperature at which these crystals first appear, the cloud point, a crystal network develops in the fluid preventing it from flowing and leading to the pour point. The presence of solids plugs pipes and fuel filters causing the engines to stall. For this reason among the standard specifications for fuels [1] there are the cloud [2] and pour points [3] that are related to the low temperature characteristics of the fuel. The definition of a maximum value for these properties depends on the fuel purpose, the time of the year and the region [1]. To achieve a given value of these properties for a distillate two approaches are followed. The first blends [4] the high cloud or pour point fuel with fuels of lower cloud point. The other uses additives such as cloud and pour point depressants to achieve the desired goal [5,6]. The planning followed in the refineries aims at producing a fuel at the lowest cost but is often quite empirical due to the difficulty to predict the low temperature behaviour for fuel blends.

This communication reports the effect of diluting a diesel, with a jet fuel produced by the same refinery, on the fuel cloud and pour points.

## 2. Experimental

Both the diesel and the jet fuel used on this work are non-additive samples. The *n*-alkane distribution on the diesel was measured by g.c. equipped with f.i.d. using a protocol established in previous studio that proved to be efficient for the analysis of this sort of fluids [7,8]. The column used consisted of a composed by a pre-column of 1 m (i.d. = 530  $\mu$ m), one 60 m Ohio Valley column OV-5 (i.d. = 320  $\mu$ m and film thickness 0.5  $\mu$ m) and a final empty column of about 30 cm. The pre- and post-columns are used for protection of the main column. The post-column protects the main column from the high temperatures of the detector and reduce the noise in the detector due to phase destruction. The pre-column ‘concentrates’ the sample heavy and light components before the main column. It is larger than the main column to reduce the length of the sample before the partition in the main column. It also acts as protection against the heavy compounds that accumulate here. The injection is performed on-column. Both the temperature and the carrier gas flow rate are programmable. To obtain a better separation of the heavy paraffins the gas flow rate is kept at 2 ml/min during the first 100 min and then increased to 3 ml/min. The heating starts at 40 °C, is heated at 2.5 °C/min to 305 °C, and then at 2 °C/min up to 320 °C. Under these conditions paraffins between heptane (*n*-C7) and dotriacontane (*n*-C30) can be quantified. Hexane (*n*-C6) [Aldrich 99.5 + %] was used as reference and CS<sub>2</sub> as solvent. The integration is done base to base

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**Nomenclature**

$g$	Gibbs free energy
$h$	enthalpy
$q$	UNIQUAC structural parameter
$r$	UNIQUAC structural parameter
$R$	universal gas constant
$T$	temperature
$V$	molar volume
$V_w$	van der Waals volume
$x$	liquid molar fraction
$s$	solid molar fraction
$Z$	coordination number

*Greek letters*

$\gamma$	activity coefficient
$\lambda$	pair interaction energy

*Subscripts*

$i$	component $i$
$j$	component $j$
$m$	fusion
$sblm$	sublimation
$tr$	solid phase transition

*Superscripts*

$E$	excess property
$l$	liquid phase
$s$	solid phase

whenever possible. The  $n$ -alkane content above heptane was found to be negligible for the jet fuel. The analysis for the diesel is reported in Table 1 along with the total  $n$ -alkane content and other fuel properties. The concentrations of heptane or larger  $n$ -alkane in the jet fuel were negligible.

The average molecular weight was measured by freezing point depression and the densities at 20 °C were determined using an Anton Paar DMA 58 densimeter.

Blends with compositions of 20, 40, 60 and 80 vol% of the diesel were prepared by mixing measured volumes of diesel and jet fuels to achieve the desired concentration. The cloud, freezing and pour points were measured using the ASTM standard methods: D 2500 for the cloud point [2], D 2386 for the freezing point [9] and D 97 for the pour point [3]. Results are reported in Table 2. Duplicates for each essay were run to check for consistency. Composition for the different blends prepared was obtained by mass balance using the reported densities since the jet fuel acts only as diluents for the diesel  $n$ -alkanes. The average molecular weight is used to calculate the mass fractions, the molar fractions used by the thermodynamic model.

### 2.1. Cloud point modelling

The cloud point is defined as the temperature at which the first crystals appears in the fuel. The crystal formation is treated as a solid liquid equilibrium of paraffins between a solution and a solid phase [10,11]. The general solid–liquid

Table 1  
Properties and composition of the studied fuels

	Diesel (wt%)	Jet
$n$ -C7	0.102	
$n$ -C8	0.508	
$n$ -C9	2.126	
$n$ -C10	6.804	
$n$ -C11	8.765	
$n$ -C12	10.450	
$n$ -C13	11.513	
$n$ -C14	11.421	
$n$ -C15	8.949	
$n$ -C16	6.901	
$n$ -C17	6.934	
$n$ -C18	5.671	
$n$ -C19	4.690	
$n$ -C20	4.191	
$n$ -C21	3.385	
$n$ -C22	2.541	
$n$ -C23	1.668	
$n$ -C24	1.133	
$n$ -C25	0.825	
$n$ -C26	0.601	
$n$ -C27	0.376	
$n$ -C28	0.230	
$n$ -C29	0.148	
$n$ -C30	0.068	
Total $n$ -alkane content	16.45	
Average $M_w$ (g/mol)	193.8	149.9
Density (20 °C)	0.8352	0.8070

equilibrium equation relating the composition in both phases with the non-ideality of the phases and the pure component thermophysical properties is used

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

where  $s$  is the molar fraction of compound  $i$  in the solid phase, and  $x$  in the liquid phase,  $T_m$  and  $T_{tr}$  are the melting and solid–solid transition temperatures, respectively, and  $h_m$  and  $h_{tr}$  the heats of these phase transitions. The correlations for these thermophysical properties used in this work are based on the data presented by Broadhurst [12].

#### 2.1.1. The liquid phase non-ideality

The activity coefficient model used for the liquid phase is the Flory-free volume model [13]:

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}, \quad \text{with} \quad (2)$$

$$\phi_i = \frac{x_i (V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j (V_j^{1/3} - V_{wj}^{1/3})^{3.3}}$$

where  $V_i$  is the molar volume and  $V_{wi}$  is the van der Waals volume of component  $i$ .

Table 2  
Experimental values of cloud, freezing and pour points

Diesel (vol%)	Freezing point (°C)	Cloud point (°C)	Solids at cloud point (wt%)	Pour point (°C)	Solids at pour point (wt%)
0	−62				
20	−16				
40		−11	0.013	−33	1.38
60		−7	0.024	−18	0.71
80		−5	0.051	−12	0.57
100		−3	0.068	−12	1.14

### 2.1.2. The solid phase non-ideality—predictive UNIQUAC

The solid phase non-ideality will be described by the predictive UNIQUAC model [10,11]. This is a version of the original UNIQUAC where

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left( \frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[ \sum_{j=1}^n \theta_j \exp \left( -\frac{\lambda_{ji} - \lambda_{ii}}{q_i RT} \right) \right] \quad (3)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (4)$$

using a new definition for the UNIQUAC structural parameters  $r$  and  $q$  [10].

The predictive local composition concept [10] allows an estimation of the interaction energies,  $\lambda_{ij}$ , used by these models. The pair interaction energies between two identical molecules are estimated from the heat of sublimation of an orthorhombic crystal of the pure component,

$$\lambda_{ii} = -\frac{2}{Z} (\Delta h_{\text{sblm}_i} - RT) \quad (5)$$

where  $Z = 6$  is the coordination number for orthorhombic crystals. The heats of sublimation,  $h_{\text{sblm}} = h_{\text{vap}} + h_{\text{m}} + h_{\text{tr}}$ , are calculated at the melting temperature of the pure component. The heat of vaporisation  $h_{\text{vap}}$  is assessed using a correlation by Morgan and Kobayashi [14].

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

$$\lambda_{ij} = \lambda_{jj} \quad (6)$$

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

The solid–liquid equilibrium model is thus a *purely predictive* model that uses the calculation of the phase behaviour nothing but pure component properties.

### 2.2. Fluid characterisation

For fuels a detailed composition is generally not obtainable. A fluid characterisation is then needed for the modelling. The model used in this work only requires a

good knowledge of the paraffins composition to describe the phase behaviour of a fluid at low temperature. No pseudo-components are used in the paraffins description. With the concentration obtained from the g.c. measurements, here each paraffin is taken as an individual compound.

All the other compounds are considered to be acting as solvent. They are described by a single pseudo-component since, as previously shown [15], the solubility of  $n$ -alkanes is, to a large extent, independent of the nature of the hydrocarbon solvent. The pseudo-component is chosen to match the average molecular weight of the fluid.

For the fuel blends the same principle was adopted. All the  $n$ -alkanes were used in the fluid description with their mole fractions calculated taking into account the dilution performed. The solvent was chosen to match the average molecular weight of the blend estimated taking into account the dilution performed. The match to the molecular weight is required so that the conversion from mass fractions, obtained from g.c. to mol fractions, used by the model, can be performed in a coherent way. To misrepresent the molecular weight of the mixture in the choice of the solvent would result in a change of the total  $n$ -alkane content in the conversion. Note that the match is made to the molecular weight of the mixture and not to the cloud points, these are predicted by the model.

### 3. Results

The model described earlier, together with the fluid characterisation proposed in Section 2, can provide a predictive description of the fluid behaviour at low temperatures. This is a pure predictive description since only information on the fluids composition and pure compound properties are used in the modelling of cloud points. A comparison between the measured and predicted cloud points is presented in Fig. 1. The non- $n$ -alkane compounds were all grouped in a single or two saturated pseudo-compounds chosen to match the measured value for the fuel. The results show that the cloud point of the diesel/jet fuel blend, with the possible exception of the dilute region, is dominated by the composition of the heavier fuel and is a highly non-linear combination of the cloud points of both fuels as

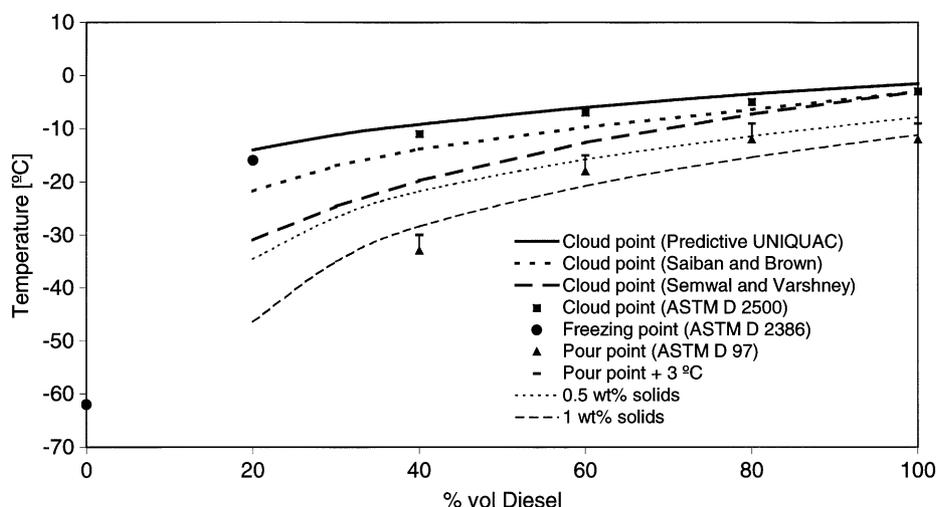


Fig. 1. Experimental and model results for the cloud and pour points of the fuel blends studied.

previously reported by Hu and Burn [16]. It is surprising to note the little effect that dilution has on the cloud point of the diesel. The dilution to 40 vol% of the diesel with a jet fuel with a cloud point 60 °C lower, reduces the cloud point by a mere 8 °C. Nevertheless the model provides a good description of the experimental cloud points with an average deviation of about 1.4 °C, well below the 2 °C of repeatability reported for the method [2]. These results are in good agreement with previously reported results where this model was shown to be able to predict cloud points for fuels and fuel blends within the experimental uncertainty [17]. The fact that the predicted cloud point always overestimate the measured values is another indication of the correctness of the model since the cloud points are determined by visual inspection at each 1 °C as the temperature drops and a finite amount of solid is required to detect the cloud point. The model estimates that at the measured cloud point an amount of solid ranging between 0.02 and 0.05 wt% is present, which must correspond to the minimum amount required for the operator to observe a change in the fuel aspect.

Based on the Hu–Burns model [13] several empirical and semi-empirical blending models have been proposed. Two of these models, Semwal and Varshney [18] and Saiban and Brown [19] are compared with the experimental data in Fig. 1. Both models perform worst than the predictive UNIQUAC model. Semwal–Varshney presents an average deviation of 7.9 °C and Saiban–Brown of 3.2 °C. In both cases these deviations are far greater than the values reported by the authors showing that empirical equations are strongly dependent on the data used for their development unlike purely predictive models such as predictive UNIQUAC.

The pour point is defined as the temperature at which the fuel no longer flows. The solid like aspect of the fluid results from the development of a 3D network of *n*-alkane crystals within the fluid forming a thermoreversible gel [20]. Unlike

the cloud point, it is a property of the fluid and can be rigorously described by a thermodynamic model, the amount of crystals required to achieve that condition depends on the conditions under which they developed such as cooling rate and shear stress [20]. It is nevertheless interesting to use the model to predict the amount of solids formed at the pour point. For the fuel blend studied these values are remarkably low. Both Table 2 and Fig. 1 show that a total solid content between 0.5 and 1% is enough to reach the pour point, i.e. to prevent fuel flowing. This value is in close agreement with the value of 1 wt% of precipitated *n*-alkanes at the pour point reported by Claudy et al. [21]. Using an estimate of 1% of solids it would then be possible to provide a fair, although not rigorous, estimate of the fuel blend pour points. The effect of dilution on the pour point is more significant than on the cloud point. The reduction of the pour point is more than twice the reduction achieved for the cloud point. The results clearly indicate that the temperature drop required to produce the same amount of solids is inversely proportional to the total *n*-alkane content. It is possible to conclude that lower the total *n*-alkane content larger the difference between the cloud point and pour points for a given fuel or fuel blend.

#### 4. Conclusions

It is shown that although cloud points of fuel blends are a highly non-linear function of the cloud points of the fuels used in the blend, the model used can provide a good prediction of the cloud points from the knowledge of the fuel *n*-alkane composition.

Although pour points are not a fluid property but are dependent on the conditions under which the crystals develop, ASTM pour points for the fuel blends studied have as little as 0.5–1% of total solid content and a fair

estimate of the pour points could be obtained assuming 1 wt% of solids required for the pour point to occur.

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### References

- [1] ASTM D 975-97. Annual book of ASTM Standards. vol. 05.01, 1998.
- [2] ASTM D 2500-98a. Annual book of ASTM Standards. vol. 05.01, 1998.
- [3] ASTM D 97-96a. Annual book of ASTM Standards. vol. 05.01, 1998.
- [4] Serpemen Y, Wenzel FW, Hubel A. Oil Gas J 1991;89(11).
- [5] Wang SL, Flamberg A, Kikabhai T. Hydrocarbon Process 1999; February:59.
- [6] Pipenger G. Hydrocarbon Process 1997; February:63.
- [7] Coutinho JAP, Dauphin C, Daridon JL. Fuel 2000;79:607.
- [8] Queimada AJN, Dauphin C, Marrucho IM, Coutinho JAP. Thermochim Acta 2001;372:93.
- [9] ASTM D 2386-97. Annual book of ASTM Standards. vol. 05.01, 1998.
- [10] Coutinho JAP. Ind Engng Chem Res 1998;37:4870.
- [11] Coutinho JAP. Energy Fuels 2000;14:625.
- [12] Broadhurst MG. J Res Nat Bur Stand 1962;66A:241.
- [13] Coutinho JAP, Andersen SI, Stenby EH. Fluid Phase Equilib 1995;103:23.
- [14] Morgan DL, Kobayashi R. Fluid Phase Equilib 1994;94:51.
- [15] Coutinho JAP, Daridon JL. Low pressure modelling of wax formation in crudes. Energy and Fuels 2001;15:1454–60.
- [16] Hu J, Burns AM. Hydrocarbon Process 1970;49:213.
- [17] Mirante FIC, Coutinho JAP. Fluid Phase Equilib 2001;180:247.
- [18] Semwal PB, Varshney RG. Fuel 1995;74:437.
- [19] Saiban S, Brown TC. Fuel 1997;76:1417.
- [20] Lorge O, Djabourov M, Brucy F. Rev Inst Français Petri 1997;52:235.
- [21] Claudy P, Letoffe JM, Bonardi B, Vassilakis D, Damin B. Fuel 1993;72:821.