

Cloud point prediction of fuels and fuel blends

Fátima I.C. Mirante, João A.P. Coutinho*

Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Received 7 November 2000; accepted 10 January 2001

Abstract

The cloud point temperature, the temperature at which the first wax crystals appear in solution, is one of the most important specifications associated with the low temperature behaviour of a fuel. A database of about 80 fuels and fuel blends was collected and used to assess the performance of the three predictive local composition models (Wilson, NRTL and UNIQUAC) for cloud point prediction. The results indicate that Predictive UNIQUAC can predict the cloud points of the fuels within the experimental uncertainty of the measurements. It could thus be a useful tool in the production of fuels both in the design of refining process and the blend of fuels to meet the low temperature specifications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cloud point; Fuel blends; *n*-Alkane

1. Introduction

The solubility of linear alkanes present in petroleum fluids quickly decreases with temperature. The temperature at which the first crystals appear is called the cloud point and is one of the most important specifications for fuels concerning their low temperature behaviour. The utilisation of a fuel is restricted to temperatures above their cloud point. It must be 6 K above the 10th percentile minimum ambient air temperature for the region in a given time of the year [1]. Below the cloud point, the presence of crystals in suspension impairs the flow plugging fuel filters, and quickly below the cloud point the fluid stops flowing, reaching what is known as pour point.

The exact temperature at which the cloud point is reached depends on the total *n*-alkane content of the fuel, the average size of the *n*-alkane molecules, and their size distribution. This dependence is very complex and although a number of correlations or techniques have been proposed to predict cloud points of fuels or fuel blends [2–6] a reliable method, of wide applicability, can only be based on a thermodynamic approach.

* Corresponding author. Tel.: +351-234-401507; fax: +351-234-370084.

E-mail address: jcoutinho@dq.ua.pt (J.A.P. Coutinho).

Two processes are commonly used to produce fuels with a given specification. The use of additives, such as cloud point depressants, and fuel blending where a fuel with a too high cloud point is mixed with a low cloud point fluid to produce a fuel that meets the specifications. Most often both approaches are used simultaneously, since cloud point depressants have a limited action and are quite expensive [7]. The capacity to predict the cloud point of a mixture would be of importance for the economical optimisation of the fuel production [5].

In previous works, Coutinho [8–10] proposed predictive local composition models for the description of the low temperature behaviour of synthetic mixtures. Recently, Predictive UNIQUAC was applied with success to describe the solid formation in fuels [11,12]. From previous works, it is not clear which would be the best model for cloud point prediction [13]. Although the Wilson equation presents some problems in the description of solid formation at temperatures below the cloud point, since it is unable to deal with the multiple solid phases forming, at the cloud point the solid present must be monophasic and no restrictions exist to the application of the Wilson equation to the description of cloud points. In this work, a large database of fuels and fuel blends was assembled and the performance of three predictive local composition models and the ideal solid phase behaviour approach was compared.

ASTM 2500 [14] or some modification of this method was used to measure most of the cloud points used in this work. This method is a visual inspection technique and as discussed elsewhere [14,15] very dependent on the operator. Since the articles used do not present the precision of the measured data, a thorough statistical study of the adequacy of the model to predict cloud points is not possible. ASTM 2500 reports as repeatability that differences exceed 2 K only in one case in 20 and for reproducibility differences of 4 K in one case in 20. In the following discussion, these values will be used. The results show that both the Predictive Wilson and UNIQUAC models present a very good performance. This holds in particular for the Predictive UNIQUAC model.

2. Thermodynamic model

Since fuels correspond to a very defined distillation cut, only molecules of a restricted size range will be present in the fluid. From these molecules, only the *n*-alkanes are heavy enough to crystallise and are responsible for the solid formation at the cloud point. The cloud point can be described as the temperature of the boundary between the one- and two-phase (solid–liquid) region for the mixture under study. Thermodynamically, it will be modelled as a solid–liquid equilibrium of *n*-alkanes in a hydrocarbon mixture. An equation relating the composition in both phases with the non-ideality of the phases and the thermophysical properties of the pure components, can be written for each component *i* present at the equilibrium [16]

$$\ln \frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} = \frac{\Delta_{\text{fus}} H_i}{RT_{\text{fus},i}} \left(\frac{T_{\text{fus},i}}{T} - 1 \right) + \frac{\Delta_{l2} H_i}{RT_{l2,i}} \left(\frac{T_{l2,i}}{T} - 1 \right) \quad (1)$$

Using the correlation for the pure component thermophysical properties proposed before [11], it is possible to calculate the cloud point as the temperature of the phase boundary at atmospheric pressure using a flash algorithm provided that adequate models for the non-ideality of the solid and liquid phases are available.

3. The liquid phase g^E model

The non-ideality of a hydrocarbon liquid phase arises both from entropic effects such as size differences and free volume effects, and energetic interactions between unlike molecules such as aromatics and aliphatics. The activity coefficient model used is

$$\ln \gamma_i = \ln \gamma_i^{\text{res}} + \ln \gamma_i^{\text{comb-fv}} \quad (2)$$

where the residual contribution for the activity coefficient, γ^{res} , is estimated by the modified UNIFAC model [17] and the Flory-free volume equation [18] provides the combinatorial term

$$\ln \gamma_i^{\text{comb-fv}} = \ln \left(\frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i}, \quad \text{with} \quad \phi_i = \frac{x_i (V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j (V_j^{1/3} - V_{wj}^{1/3})^{3.3}} \quad (3)$$

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

4. The solid phase g^E model

The solid phase non-ideality will be described using four different approaches. First assuming an ideal solid solution and then using three predictive local composition models: Wilson, NRTL and UNIQUAC [9,10,19].

4.1. Wilson model

The Wilson equation used is a modification of the original Wilson equation where the contribution of the molar volumes to the local compositions are not taken into account due to the characteristics of the crystal lattice

$$\frac{g^E}{RT} = - \sum_{i=1}^m x_i \ln \left[\sum_{j=1}^m x_j \exp \left(- \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \right] \quad (4)$$

4.2. NRTL model

The NRTL g^E model was used without modifications

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \sum_{j=1}^n \frac{x_j \exp(-\alpha(\lambda_{ij} - \lambda_{ii})/RT)}{\sum_{k=1}^n x_k \exp(-\alpha(\lambda_{ki} - \lambda_{ii})/RT)} \frac{\lambda_{ij} - \lambda_{ii}}{RT} \quad (5)$$

The parameter α in this model is a measure of the non-randomness of the mixture and has a value of $\alpha = 2/z$. For the solid phase, the coordination number, z has a value of 6.

4.3. UNIQUAC model

The version of the UNIQUAC model used is given in [10]

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{z}{2} \sum_{i=1}^n q_i x_i \ln \left(\frac{\theta_i}{\Phi_i} \right) - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (6)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (7)$$

and using the definition for the structural parameters r and q proposed for the solid phase [10]

$$r_i = \frac{V_w}{109.2} \quad \text{and} \quad q_i = \frac{A_w}{15.0 \times 10^9} \quad (8)$$

where V_w and A_w are respectively the van der Waals volume and surface of the molecules.

For all these models, the assessment of the local compositions are based on the interaction energies between pairs of molecules, λ_{ij} . The predictive local composition concept [19] provides a predictive approach for the estimation of the interaction energies used. The pair interaction energies between two identical molecules are estimated from the enthalpy of sublimation of an orthorhombic crystal of the pure component,

$$\lambda_{ii} = -\frac{2}{z} (\Delta_{\text{sub}} H_i - RT) \quad (9)$$

z being the coordination number with a value of 6 as mentioned above. The enthalpy of sublimation, $\Delta_{\text{sub}} H = \Delta_{\text{vap}} H + \Delta_{\text{fus}} H + \Delta_{f2} H$, are calculated at the melting temperature of the pure component. The heat of vaporisation $\Delta_{\text{vap}} H$ is assessed using the PERT2 correlation by Morgan and Kobayashi [20].

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

$$\lambda_{ij} = \lambda_{jj} \quad (10)$$

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

The approach followed in this work provides a purely predictive estimation of the cloud point once the composition of the fluid is established since the solid liquid equilibrium calculation used to assess the cloud point uses only pure component properties.

5. Results

The calculation of phase boundaries requires a flash algorithm. Due to its simplicity, the algorithm of resolution of the Rachford–Rice equations proposed by Leivovici and Neoschil [21] was used in the calculations.

The n -alkanes composition is experimentally obtained from GC analysis and reported in the original reference for all the fluids used on this study. Whenever information about the aromatics content was available that value was used. For the other cases, an average aromatics content of 20% was assumed. For the description of the mixture, all the n -alkanes were considered. Two pseudo-compounds, one for

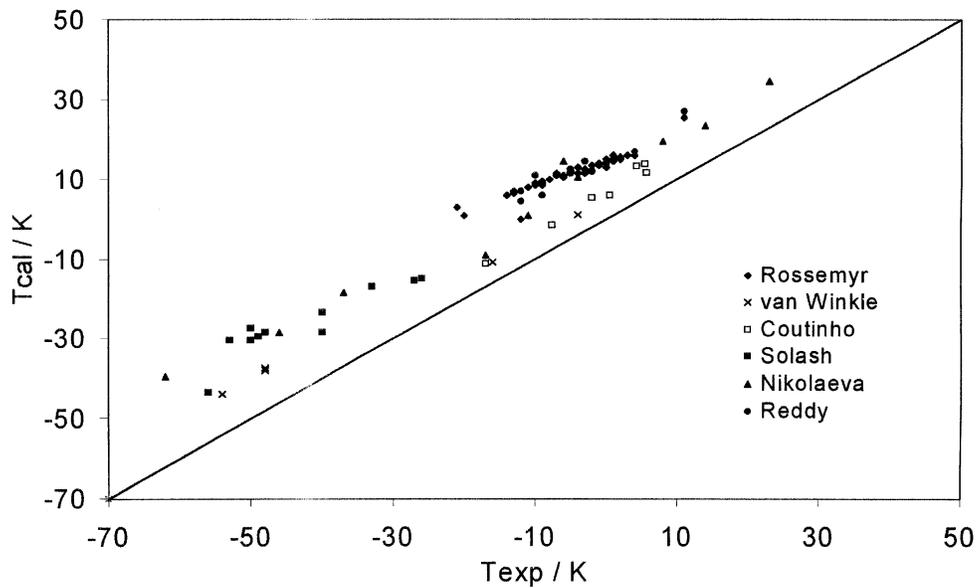


Fig. 1. Comparison between experimental and predicted cloud points assuming ideal solid phase.

the aromatics and other for the saturated molecules, represented the non-*n*-alkanes. As pseudo-aromatic, a molecule with the properties of ethylbenzene was used while a multibranched alkane was employed as saturated pseudo-component. The choice of the saturated pseudo-component was made to make the pseudo-fluid match the average molecular weight of the actual fluid.

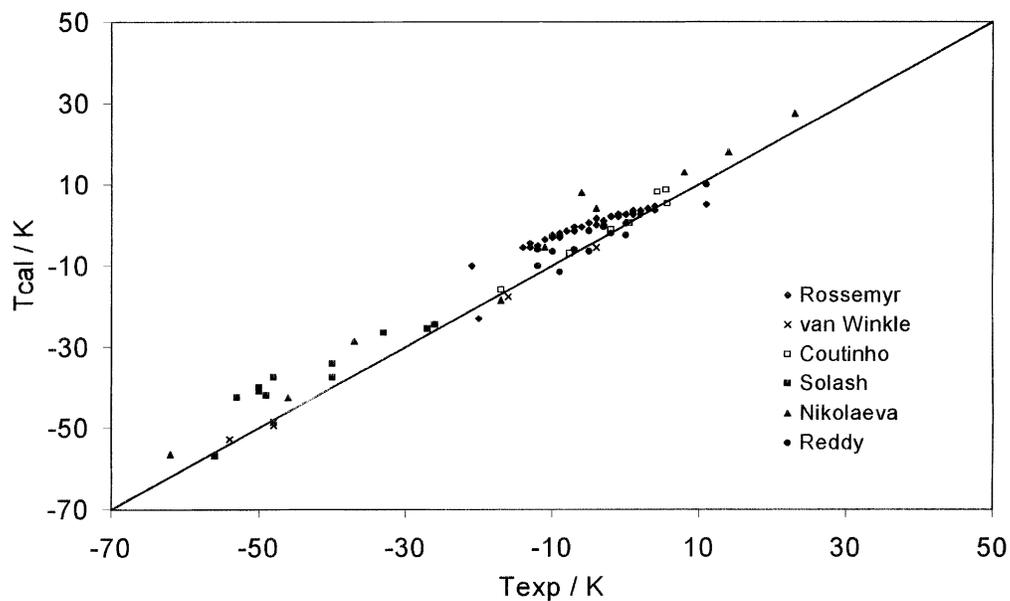


Fig. 2. Comparison between experimental and predicted cloud points using NRTL for the solid phase.

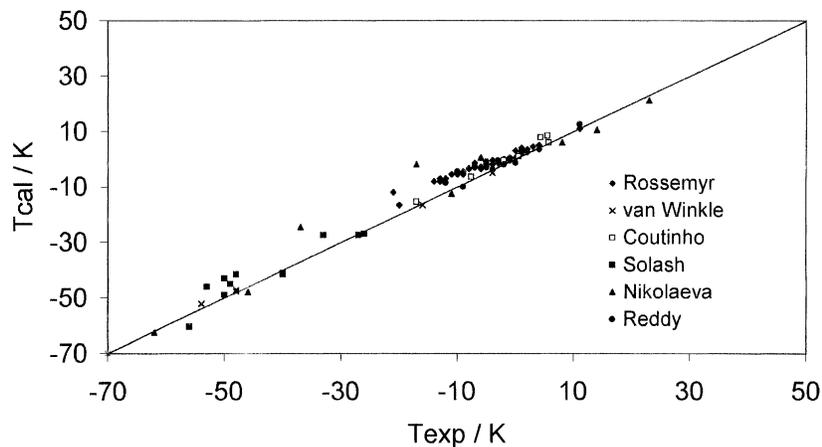


Fig. 3. Comparison between experimental and predicted cloud points using Wilson for the solid phase.

Average molecular weights are reported for some fluids but not for all. However, the ASTM distillation temperatures are reported for most fuels used in this work. Reddy [4] proposed a correlation between the average molecular weight of diesel fuels and the ASTM distillation temperature corresponding to 50% distilled. This correlation was used to estimate the molecular weights for fuels where this value was not reported.

A non-exhaustive bibliographic research provided results for the construction of a database of fuel cloud points. Although many articles on cloud points of fuels are available in the literature [2,3,5,6,22] most of these works do not provide information on the composition of the fuels. The data utilisable was collected from [4,11,23–27]. After a careful analysis, it was decided not to use data from [28,29] since it was found that the cloud points reported were not reliable. In [29], although fuels A, B and D have similar

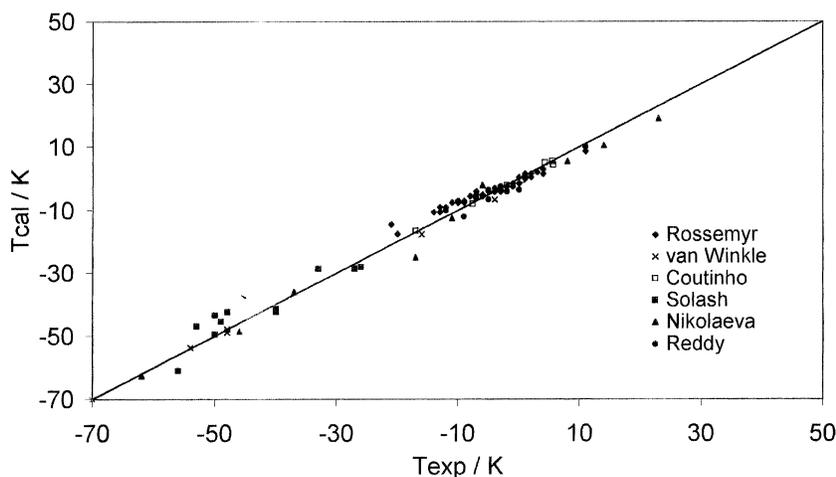


Fig. 4. Comparison between experimental and predicted cloud points using UNIQUAC for the solid phase.

Table 1
Cloud points average absolute deviations and standard deviations for the studied fluids

	Data points	Model	AAD	S.D.
Rossemyr	38	Ideal	16.3	16.5
		Wilson	3.0	3.6
		NRTL	4.6	5.3
		UNIQUAC	1.7	2.2
Solash	11	Ideal	16.6	17.1
		Wilson	3.6	4.4
		NRTL	6.0	7.0
		UNIQUAC	3.5	4.1
Nikolaeva	10	Ideal	14.6	15.3
		Wilson	4.6	6.7
		NRTL	6.0	6.8
		UNIQUAC	2.8	3.5
Reddy	11	Ideal	15.5	16.9
		Wilson	2.6	3.1
		NRTL	2.4	2.8
		UNIQUAC	1.3	2.1
Coutinho	7	Ideal	6.8	7.0
		Wilson	1.6	2.0
		NRTL	1.4	1.9
		UNIQUAC	0.6	0.7
van Winkle	5	Ideal	8.2	8.6
		Wilson	0.9	1.0
		NRTL	1.3	1.3
		UNIQUAC	1.1	1.4
Total	82	Ideal	14.7	15.5
		Wilson	3.0	4.0
		NRTL	4.2	5.2
		UNIQUAC	1.9	2.6

n-alkane distributions, they present large differences in cloud points. Fuel E in spite of having a larger concentration of heavier *n*-alkanes has a reported cloud point lower than fuel C. Similar arguments could be used against the utilisation of data from [28]. This decision was strengthened by the fact that Reddy [4], in a later work on cloud point modelling used some literature data, but not the data he previously reported. Attempts to predict the reported cloud points revealed for these systems deviations much larger than for the other sets of data. Cloud point data could also be found in [30] but compositions for those fuels were only available from a NASA report [31] that was not possible to obtain.

The database compiled for this work consists of 82 fluids, 34 fuels and 48 fuel blends or fuel fractions, with cloud points ranging from 210 to 300 K covering the entire range of fuels commonly employed from jets to fuel oils.

The performance of each solid phase model is presented in Figs. 1–4 where a comparison between the experimental and predicted cloud points is done. Clearly, both the Wilson and UNIQUAC models are

superior to the other two approaches. The large deviations found when considering an ideal solid phase are a clear indication of the stringent requirement to take the non-ideality of the solid phase into account.

A quantification of the deviations presented by each model for the different data sets and the global database are reported in Table 1. Average absolute deviations (AADs) are calculated as

$$\text{AAD} = \frac{\sum_{i=1}^n |T_{\text{calc}} - T_{\text{exp}}|}{n} \quad (11)$$

and the standard deviations as

$$\text{S.D.} = \sqrt{\frac{\sum_{i=1}^n (T_{\text{calc}} - T_{\text{exp}})^2}{n}} \quad (12)$$

From these results, it can be seen that although both the Wilson and UNIQUAC model provide an adequate description of the cloud points temperature, only the UNIQUAC model provides a deviation between experimental and predicted cloud points within the repeatability of the cloud point measurements. It is interesting to note that data measured by methods other than ASTM 2500 [11,23,27] or by an improved ASTM 2500 method [4] present the lowest deviations indicating that in other sets of data the scattering is due to a large extent to the poor accuracy of the experimental data itself.

6. Conclusions

A comparison of the performance of three predictive local composition models (Wilson, NRTL and UNIQUAC) and the ideal solid solution approach for the estimation of fuels cloud points was made. The results stress once more the importance of having an adequate description of the solid phase non-ideality for a correct description of the low temperature behaviour of these fluids. Both Predictive Wilson and UNIQUAC proved to be adequate although this last model reveals some superiority. Predictive UNIQUAC seems to be capable to predict the cloud point of fuels and fuel blends in a very large range of temperatures (cloud points extending from 210 to 300 K were used in this work) within the uncertainty of the experimental data using only information about the fluid composition.

Acknowledgements

This work was founded by Fundação para a Ciência e Tecnologia, Portugal, under the project Praxis/P/EQU/12010/1998.

References

- [1] ASTM D 975-97, Annual Book of ASTM Standards, Vol. 05.01, 1999.
- [2] R.P. Walsh, J.V. Mortimer, *Hydrocarbon Process.* Issue 9 (1971) 153–158.
- [3] K. Petrovic, D. Vitorovic, *J. Inst. Petr.* 59 (1973) 20–26.
- [4] S.R. Reddy, *FUEL* 65 (1986) 1647–1652.
- [5] H.U. Khan, M.M. Mungali, K.M. Agrawal, G.C. Joshi, *Oil Gas J.* 88 (39) (1990) 98–101.
- [6] C.Y. Tsang, V.S.F. Ker, R.D. Miranda, C.J. Wesch, *Oil Gas J.* 86 (12) (1988) 33–38.

- [7] G. Pipenger, *Hydrocarbon Process.* (1997) 63–78.
- [8] J.A.P. Coutinho, V. Ruffier-Meray, *Ind. Eng. Chem. Res.* 36 (1997) 4977.
- [9] J.A.P. Coutinho, *Fluid Phase Equilib.* 158–160 (1999) 447.
- [10] J.A.P. Coutinho, *Ind. Eng. Chem. Res.* 37 (1998) 4870.
- [11] J.A.P. Coutinho, C. Dauphin, J.L. Daridon, *FUEL* 79 (2000) 607–616.
- [12] J.A.P. Coutinho, *Energy and Fuels* 14 (2000) 625–631.
- [13] C. Dauphin, J.L. Daridon, J.A.P. Coutinho, P. Baylère, M. Potin-Gautier, *Fluid Phase Equilib.* 161 (1999) 135.
- [14] ASTM D 2500-98a, *Annual Book of ASTM Standards*, Vol. 05.01, 1999.
- [15] J.L. Lando, H.T. Oakley, *Ind. Eng. Chem. Prod. Res. Dev.* 8 (1969) 310–319.
- [16] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Edition, Prentice-Hall, Englewood Cliffs, NJ, 1999.
- [17] B.L. Larsen, P. Rasmussen, A. Fredenslund, *Ind. Eng. Chem. Res.* 26 (1987) 2274.
- [18] J.A.P. Coutinho, S.I. Andersen, E.H. Stenby, *Fluid Phase Equilib.* 103 (1995) 23.
- [19] J.A.P. Coutinho, K. Knudsen, S.I. Andersen, E.H. Stenby, *Chem. Eng. Sci.* 51 (1996) 3273.
- [20] D.L. Morgan, R. Kobayashi, *Fluid Phase Equilib.* 94 (1994) 51.
- [21] C.F. Leibovici, J. Neoschil, *Fluid Phase Equilib.* 112 (1995) 217–221.
- [22] P. Claudy, J.M. Letoffe, B. Neff, B. Damin, *FUEL* 65 (1986) 861–864.
- [23] A. Queimada, C. Dauphin, I. Marrucho, J.A.P. Coutinho, *Thermochim. Acta*, in press.
- [24] V.G. Nikolaeva, B.A. Englin, S.K. Kyuregyan, T.N. Veretennikova, E.I. Elenskaya, V.A. Kvasova, T.G. Davydova, *Chem. Technol. Fuels Oils* 12 (1976) 417–420.
- [25] J. Solash, R.N. Hazlett, J.M. Hall, C.J. Nowack, *FUEL* 57 (1978) 521–528.
- [26] L.I. Rossemyr, *Ind. Eng. Chem. Prod. Res. Dev.* 18 (1979) 227–230.
- [27] T.L. van Winkle, W.A. Affens, E.J. Beal, G.W. Mushrush, R.N. Hazlett, J. DeGuzman, *FUEL* 66 (1987) 947–953.
- [28] S.R. Reddy, M.L. McMillan, *SAE Trans.* 90 (1981) 3598.
- [29] S.R. Reddy, *SAE Trans.* 93 (1984) 922.
- [30] C.T. Moynihan, M.R. Shahriari, T. Bardakci, *Thermochim. Acta* 52 (1982) 131–141.
- [31] F.J. Stockemer, Report No. CR-159615, NASA-Lewis Research Centre, Cleveland, OH, 1979.