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Paraffin solubility curves of diesel fuels from thermodynamic model adjusted through experimental DSC thermograms

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ABSTRACT

DSC and wax solubility curves were measured for two diesel fuel samples. Compositional profiles were also measured for the solubility curve points. The paraffin distributions of the samples were determined and the non-paraffinic components were lumped into pseudocomponents. The liquid phase was modeled using the Peng-Robinson equation of state with the classical van der Waals mixing rule. For the solid phase, the modified UNIQUAC model was employed. The models were fitted to the DSC data by tuning only four multipliers acting on the molecular weights, boiling and critical temperatures of the pseudocomponents as well as on the paraffins' pair interaction energies from the UNIQUAC model. Then the model is used to predict wax appearance temperature, amount and composition of solid deposit as a function of temperature during cooling. Excellent results were obtained for the two samples analyzed. This way, the methodology developed is able to predict adequately the formation of solid paraffin from diesel fuels.

1. Introduction

Diesel fuels are widely used on road, marine and air transports. These fuels are composed in great part by paraffins, which crystallize and form gels when submitted to low temperatures. Consequently, it reduces the fuel flow by plugging the fuel filters [1] and, as the fuel fluid composition is altered by the precipitation, jeopardizes the engine efficiency [2,3]. To avoid these issues, paraffin precipitation is usually controlled by using additives in the fuels [2,3].

Simulation of the diesel phase behavior may help determining how much additive should be used to avoid paraffin solidification in a desired temperature range. Different models have been used to model solid paraffin solubility curves from diesel fuels, as these curves are extremely laborious to measure experimentally. Coutinho et al. [4] and Sansot et al. [5] used an equation of state for the liquid phase and the modified Wilson model for the solid phase. Coutinho et al. [6] and Coutinho [1] employed the combination of the UNIFAC model and the Flory free volume equation for the liquid phase and the modified UNIQUAC model for the solid phase. To tune these models, the wax appearance temperature (WAT) was majorly employed. Nevertheless, all current experimental techniques available to measure the WAT have shortcomings that limits an effective measurement of the thermodynamic equilibrium temperature [7]. The supersaturation unavoidable in WAT measurements due to kinetic effects also imposes limitations to its use in model tuning.

To avoid such interferences, a different approach has been recently proposed [8,9]. In this new approach, the single WAT point commonly used to tune the thermodynamic model is substituted by an entire DSC thermogram, that provides phase equilibria information over a large temperature range. Using an appropriate cooling rate in the DSC experiments, solid-liquid equilibrium data is indirectly provided via the enthalpy variation of the system and can thus be directly calculated through an appropriate thermodynamic model. Nevertheless, this approach has only been applied so far to synthetic systems where the composition was controlled and well known. The aim of the present work is to extend the method do Diesel fuels and improve the reliability of paraffin solubility curves obtained from thermodynamic models.

For that purpose, experimental DSC and experimental solubility data were measured for two different Diesel fuel samples. These samples compositions were then analyzed and characterized by their full

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Nomenclature

h	*molar enthalpy*
T	temperature
P	pressure
N_c	number of components
N_p	number of phases
N_paraf	number of paraffins
N_{pseudo}	number of pseudocomponents
N_{mol}	number of moles
C_p	heat capacity
x	mole fraction
f	fugacity
m	EoS parameter
Kw	Watson factor
r,q	structural parameters
Z	coordination number
R	universal gas constant
Q	heat
t	time

Superscripts and Subscripts

fus	fusion
tr	crystalline transition
sub	sublimation
vap	vaporization
ig	ideal gas
c	critical
b	boiling
L	liquid
S	solid
R	residual
E	excess
exp	experimental
i,j	index
l	pseudocomponents index

Greek letters

Δ	variation
γ	activity coefficient
τ,θ,ϕ	modified UNIQUAC parameters
λ	pair interaction energy
φ	fugacity coefficient
ρ	density
ω	acentric factor
β	phase fraction
ξ	estimated parameter

Accent

$\overline{M}$	average property M (M is a dummy variable)
$\underline{M}$	vector M
$\widehat{M}$	property M in the mixture

Abbreviations

PR-EoS	Peng-Robinson equation of state
SLE	solid-liquid equilibrium
CN	carbon number
MW	molecular weight
SG	specific gravity at 15.5 °C
WAT	wax appearance temperature

paraffin distributions whereas non-paraffinic components were lumped into pseudocomponents. The Peng-Robinson equation of state (PR-EoS) was used to model the liquid phase, as it can be readily applied to high pressures systems and complex fluids like crude oil. For the solid phase, the modified UNIQUAC model was used. The models were tuned using the calorimetric data and the predictions obtained for the solubility and compositional data were analyzed.

2. Experimental

2.1. Diesel samples

The two samples used in this study were supplied by PETROBRAS and used without any further treatment. Density, Flash Point and Sulfur content of the two samples are presented in Table 1.

2.2. DSC measurements

The calorimetric experiments were carried out using a SETARAM Micro DSC 7 evo calorimeter. All experiments were performed using a temperature rate of 0.2 K.min^{-1} in, at least, triplicates. Samples of around 450 mg were weighted with a precision of 0.01 mg. The experiments were conducted at temperatures from 248.15 K to 303.15 K. The equipment was calibrated using Gallium. This reference compound was acquired from Fluka as an ultrapure sample (purity of 99.999%).

2.3. Analysis of the paraffin distributions

The paraffin distribution within the samples were analyzed using gas chromatography. An Agilent 6890 chromatograph equipped with a split/splitless injector, a flame ionization detector (FID) and HP-1 50 m capillary column with an internal diameter of 0.20 mm and a film width of 0.11 μm was used. The carrier gas used was hydrogen at a constant pressure of 25 psi. The injector temperature was kept constant at 573.15 K and a split ratio of 128:1 was used. The detector was kept at a constant temperature of 573.15 K with constant flow of air (450 mL.min^{-1}). The column temperature was raised from 313.15 K to 573.15 K at 2 K.min^{-1} and from there raised to 653 K at 4 K.min^{-1}. The sample was diluted in CS_2 and 1 μL of the solution was injected using an automatic injection system. The retention time of the different *n*-alkanes were calibrated using a standard mixture Polywax 655 from Supelco. Each sample was injected in at least triplicates. The uncertainties calculated from two standard deviations of the results were smaller than 2% for all cases. *n*-alkanes up to C35 were identified.

2.4. Analysis of fluid composition and fluid representation

The total composition of the sample was represented by discretizing the original samples into pseudocomponents characterized by their average carbon number and subtracting from each of them the corresponding concentration of paraffin analyzed.

The method used is based on the ASTM standard 7169. An Agilent 6890 N chromatograph equipped with an on-column injector, a FID

Table 1
Density, Flash Point and Sulfur content of the two samples studied.

Sample	Density (kg.m^{-3})	Flash Point (°C)	Sulfur content (ppm)
1	828.2	68.0	1.6
2	824.5	69.0	0.9