

Application of a generalized model to the estimation of physical properties and description of the aromatic extraction from a highly paraffinic lubricating oil

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Published on:

Chemical Engineering Science 63 (2008) 711 – 720

[doi:10.1016/j.ces.2007.10.013](https://doi.org/10.1016/j.ces.2007.10.013)

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Abstract

In the lubricating oil manufacturing process, the aromatic content of vacuum distillates is reduced by solvent extraction, frequently with furfural. In this work, a generalized model (based on a reduced number of pseudo-components and the NRTL model) for estimation of activity coefficients is applied to the simulation of the extraction process of aromatics by furfural from a highly paraffinic Argentinian lubricating oil. Such model proposes a linear dependence between the pseudo-component properties and the NRTL parameters with the average boiling point of the distillate used as feed. Physical properties of the mixtures are calculated using the calculated pseudo-component properties. Obtained values are compared to those calculated by other methods reported in the literature, obtaining no remarkable deviations, but showing the influence of the paraffinic content on the accuracy of the predictions. The extraction process is simulated using the calculated pseudo-component properties and the NRTL parameters by means of Aspen Plus[®] commercial software. Good agreement was found between predicted and experimental values of yield, furfural content and composition.

Keywords: Extraction, phase equilibria, separations, simulation, lubricating oil, furfural.

1. Introduction

In the process of manufacturing lubricating oils, the removal of aromatic hydrocarbons from vacuum distillates is required to improve several lubricating properties (Singh et al., 1978; Sequeira, 1994). The residue from the crude oil atmospheric distillation (long residue) is transferred to a vacuum distillation column and separated into different lube oil cuts, characterized by their boiling range and viscosity. Five raw cuts are commonly obtained, called SPD (spindle distillate), LND (light neutral distillate), MND (medium neutral distillate), HND (heavy neutral distillate) and BSD (bright stock distillate).

For many years several works have been focused on looking for selective solvents for aromatic extraction from hydrocarbon mixtures (Vakili-Nezhaad et al., 1999). Furfural is one of the most widely used solvents because its high selectivity towards aromatic compounds which slowly decreases with increasing temperature and is acceptable for both light and heavy vacuum distillates as reported by different authors (De Lucas et al., 1993).

The design of solvent extraction processes has been performed mostly by fully empirical methods (Rahman et al., 1984), requiring large experimental information usually not available.

The rigorous modeling of the liquid-liquid equilibrium (LLE) would be a suitable tool to properly describe the extraction process and consequent design and simulation. However, the involved solvent+lubricating oil mixtures are very complex and difficult to model because it is not possible to identify and quantify all the individual compounds (Hariu and Sage, 1969). The pseudo-component approach based on distillation curves is widely used to represent the complex composition of petroleum fractions in vapor-liquid equilibrium calculations.

This approach is not effective in LLE modelling because chemical structure has a much larger effect than boiling temperature. The “molecule-type” approach is able to represent these differences according to the chemical structure of compounds and it has been applied to describe the LLE in solvent+lubricating oil systems (Vakili-Nezhaad et al., 1999).

Recently, a pseudo-component approach based on the correlation of different properties with the chemical structure and the boiling temperature has been developed. Such approach was successfully applied to solvent+lubricating oil systems (van Grieken et al., 2005; Coto et al., 2006a).

The average composition of such complex mixtures can be experimentally determined by standard test methods. For instance, ASTM D2007 (Annual Book of Standards, 2003) represents composition in terms of average saturates, aromatics and polars. However, these methods are time consuming and composition data are not usually available. Therefore, the characterization of petroleum mixtures is determined through correlations between their physical properties. Commonly only a few properties are experimentally determined, while the rest are estimated by means of the empirical relations between properties reported in the literature.

In this work, density, refractive index and sulphur content were considered, since these properties are commonly used to characterize lubricant mixtures. Gomez (1989) developed a method to calculate the liquid density at a given temperature for petroleum mixtures from their experimental specific gravity and characterization factor. Reported results show the validity of such correlation within the temperature range 313-923K. Riazi and Roomi (2001) reported correlations to calculate both liquid density and refractive index from specific gravity, molecular weight and mean average boiling point. Accurate results were reported for pure compounds and petroleum mixtures with

boiling point up to 575K. However, results for heavier fractions were not reported. The American Petroleum Institute reported different correlations to calculate the density of petroleum fractions with molecular weight ranging from 70 to 700 and boiling point up to 840K (API, 1987a). Riazi et al. (1999) proposed a method to calculate the sulfur content for petroleum mixtures with molecular weight ranging from 75 to 1500 and sulfur contents up to 6%. These authors found a good agreement between calculated and experimental values for a wide range of petroleum mixtures.

Recently, van Grieken et al. (2005) reported a method to correlate average pseudo-component properties, composition (in saturates, aromatics and polars) and physical properties (density, refractive index and sulfur content) of lubricating oil mixtures.

Common thermodynamic models, such as NRTL (Renon and Prausnitz, 1968) and group contribution methods (Abildskov et al., 2004) have been used to describe LLE in solvent+lubricating oil systems. LLE data for the system furfural+hydrocarbon were studied with the thermodynamics models NRTL and UNIQUAC (De Lucas et al. 1993; Letcher et al., 2003; Morawski et al., 2003).

Recently, the NRTL model and a description of the mixture based on three pseudo-components was used to simulate the extraction operation for the systems furfural+HND (van Grieken et al., 2005) and furfural+SPD (Coto et al., 2006a), obtaining good results. The model was generalized and its predictive capability improved by establishing a linear relation between the pseudo-component properties and the NRTL parameters with the average boiling point of the mixture used as feed. Consequently, only a reduced number of properties from the feedstock oil are required to fully predict the LLE (Coto et al., 2006b).

Accurate results were obtained for different systems furfural+lubricating oils (ranging from SPD-HND). However, this generalization was only applied to lubricating products obtained from Arabian Light crude oil.

In this work, single-stage extraction experiments were carried out with a lubricating oil cut called C-30000 obtained from a South American crude oil (Argentina), and with an average boiling temperature within the range SPD-HND. All the involved mixtures (feed, raffinates and extracts) were experimentally characterized in terms of composition (ASTM D2007), specific gravity (ASTM D1298), liquid density (ASTM D1298) and refractive index at 343K and 293K (ASTM D1747), sulfur content (ASTM D4249) and distillation curves (ASTM D2887), respectively (Annual Book of Standards, 2003). Values of density, refractive index and sulfur content were calculated using the pseudo-component method and different methods reported in the literature, obtaining similar results. LLE was described by means of the generalized model with parameters calculated from average boiling point of C-30000 lubricating oil cut. In order to summarize all the parameters needed for the description of the LLE in the extraction operation, a scheme of calculations is shown in Figure 1.

Good results were obtained for the prediction of yields, furfural content and composition of the involved mixtures.

2. Experimental

The highly paraffinic lubricating oil called C-30000, obtained from a South American crude oil from Argentina, was provided by REPSOL-YPF. Furfural was supplied by REPSOL-YPF and distilled before use to remove the oxidation products formed due to air contact.

Experimental results were obtained by using a 0.5L cylindrical stirred glass reactor. Temperature was set by recirculating silicone oil from a thermostatic bath, and

controlled within $\pm 0.1^\circ\text{C}$. A stream of nitrogen was passed to prevent furfural decomposition. Agitation at 430 rpm was maintained for one hour, followed by settling for another hour to achieve a good separation of the two phases (Moreno et al., 1992). Furfural was removed from extracts and raffinates by vacuum distillation. Table 1 shows experimental conditions (temperature and furfural/feed ratio), extraction yields (defined as the percentage in weight of raffinate or extract), furfural content and results for the characterization of the mixtures: Composition (in saturates, aromatics and polars), specific gravity (SG), liquid density at 343K (D_{343}), refractive index at 343K (RI_{343}) and sulfur content ($S\%$) determined by means of ASTM D2007, ASTM D1298, ASTM D1747 and ASTM D4294, respectively (Annual book of standards, 2003). Each mixture is defined by a letter (R, raffinate; E, extract), followed by the corresponding number of the experiment. For some mixtures, the simulated distillation curves were obtained by means of ASTM D2887 (Annual book of standards, 2003) and they are summarized in Table 2.

The quality of experimental data was checked by calculating the feed composition from the composition and yield of raffinates and extracts for each experiment. A comparison of such calculated values with those experimental is shown in Figure 2. Average absolute deviations between experimental and calculated composition values for saturates, aromatics and polars were 1.2%, 1.6% and 0.7%, respectively. Such values are all within the reproducibility limits indicated by the ASTM D2007 standard test method. Therefore, the quality of the experiments may be considered satisfactorily.

As it is shown in Table 1, for experiments performed at the same temperature, higher yields in extract were obtained when increasing furfural/feed ratio: species undergo higher dissolution in furfural, and therefore, the efficiency of the process increases.

The experimental compositions show that furfural mainly dissolves aromatic

compounds, which mostly appear in the extract: 76.7% (T=323K, furfural/feed=1), 75.7% (T=338K, furfural/feed=9), 72.6% (T=353K, furfural/feed=1) and 67.2% (T=353K, furfural/feed=8). On the opposite, saturates are mainly present in the raffinates.

When experiments performed at the same furfural/feed ratio and different temperature are compared, lower temperatures reduce the content of aromatic and other undesirable compounds (mostly sulfur compounds), improving the selectivity of the process. Extraction experiments carried out at higher furfural/feed ratios yield raffinates with lower content of aromatics, showing that extraction of aromatic species increases when furfural/feed ratio becomes higher. As it is shown in Table 1, raffinates of experiments carried out at the same furfural/feed ratio and different temperature do not exhibit significant differences regarding aromatics content. However, the content of saturates in extracts decreases with the temperature, showing that furfural selectivity towards aromatic compounds increases.

The experimental work confirms the suitability of furfural for extracting aromatics, and also sulfur-containing compounds from this kind of distillate. These results are in good agreement with those reported for other lubricating oils (Van Grieken et al., 2005; Coto et al. 2006a).

3. Model

The previously described generalized model (Coto et al., 2006b) for the description of the lubricating oil extraction with furfural was applied to the furfural+C-30000 system. The model is based on a reduced number of pseudo-components (saturates, S, aromatics, A, and polars, P). In the description of the extraction experiments, each mixture is considered to be formed by the solvent and three pseudo-components (Furfural+S+A+P), while the thermodynamic model is the NRTL model. Linear

relations between the pseudo-component properties and the NRTL parameters with $T_{50\%}$ of the lubricant oil used as feed are used. $T_{50\%}$ is obtained from ASTM D1160 distillation curve as the temperature at which 50 % (vol.) is distilled.

3.1 Pseudo-component properties. Different physical properties of pseudo-components (saturates, aromatics and polars) were calculated from the relations proposed by Coto et al. (2006b). Linear dependence between the physical property (SG , D_{343} , RI_{343} and $S\%$) and the $T_{50\%}$ of the lubricant oil used as feed was assumed. Table 3 shows the values for the different pseudo-components properties calculated from $T_{50\%}$ of C-30000 lubricating oil.

3.2 NRTL model. The NRTL model is based on the local composition concept and considers only binary interactions. The well known (Poiling et al., 2001; Prausnitz et al., 2000; Raal and Mühlbauer, 1998) expression for the activity coefficient is given by:

$$\ln \gamma_i = \frac{\sum_{j=1}^c x_j \tau_{ji} G_{ji}}{\sum_{k=1}^c x_k G_{ki}} + \sum_{j=1}^c \left[\frac{x_j G_{ij}}{\sum_{k=1}^c x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^c x_m \tau_{mj} G_{mj}}{\sum_{k=1}^c x_k G_{kj}} \right) \right] \quad (1)$$

$$G_{ij} = \exp \left(-\alpha_{ij} \tau_{ij} \right) \quad (2)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T_{ext}} \quad (3)$$

where x_i is the molar fraction of component i ; α_{ij} is the tendency of species i and j to be randomly distributed, and τ_{ij} is the parameter of interaction between pairs of molecules i and j . τ_{ij} depends on the temperature of extraction (T_{ext}) according to (3) in terms of binary parameters (a_{ij} and b_{ij}) as proposed by Demirel and Gecegörmez (1991). As $\tau_{ii}=0$, $a_{ij} \neq a_{ji}$, $b_{ij} \neq b_{ji}$ and $\alpha_{ij} = \alpha_{ji}$, five binary parameters are considered as model parameters to characterize each binary interaction.

The C-30000 NRTL binary interaction parameters were calculated from the previous correlation between NRTL parameters and $T_{50\%}$ of the feed (Coto et al., 2006b).

Obtained values are shown in Table 4.

No additional parameters are needed for the application of the generalized model and, consequently it was not necessary any further fit of experimental data. For that reason, this model can be considered fully predictive.

4. Results and discussion

4.1 Physical properties. The physical properties of the involved mixtures (feed, raffinates and extracts) can be estimated by means of the method based on pseudo-component properties following the mixing rule (van Grieken et al., 2005):

$$P_{calc} = \left[\frac{X_S}{100} \bar{P}_S + \frac{X_A}{100} \bar{P}_A + \frac{X_P}{100} \bar{P}_P \right] \quad (4)$$

where P_{calc} is the calculated property for each mixture; X_S , X_A and X_P are the compositions (in weight percent) in saturates, aromatics and polars; and \bar{P}_S , \bar{P}_A , \bar{P}_P are the average properties of saturates, aromatics and polars.

This method was applied to the mixtures involved in the present work and reported in Table 1. The physical properties considered were SG , D_{343} , RI_{343} and $S\%$. Equation (4) was applied with composition values (X_S , X_A and X_P) from Table 1 and pseudo-component parameters \bar{P}_S , \bar{P}_A , \bar{P}_P from Table 3.

Experimental and calculated values are compared in Figure 3. Reasonable agreement was obtained in the whole range, with the highest deviations for the highest values of the different properties. Absolute average deviations between experimental and predicted values were determined by using the following expression:

$$\bar{\varepsilon} = \frac{\sum \varepsilon_i}{N} = \frac{\sum |P_{exp} - P_{calc}|}{N} \quad (5)$$

where P_{exp} and P_{calc} are the experimental and calculated values of a given property, respectively; N is the number of mixtures considered and the summatory is extended over the N mixtures. Absolute average deviation values were $\bar{\varepsilon}=0.014$ for SG , $\bar{\varepsilon}=0.012$ for D_{343} and $\bar{\varepsilon}=0.010$ for RI_{343} . The prediction of the sulfur content was less accurate ($\bar{\varepsilon}=0.7$) as expected since it was previously reported as a limitation of the model (Coto et al., 2006b).

In order to check the accuracy of this application of the pseudo-component method with the linear relation between pseudo-component properties and $T_{50\%}$, other methods available in the literature were used to calculate the same properties of the involved mixtures. The methods reported by Riazi and Daubert (1986), Riazi and Roomi (2001), API (1987) and Gomez (1992) were used to calculate the liquid density at 293K. The methods by Riazi and Daubert (1986), and Riazi and Roomi (2001) were used to calculate the refractive index at 293K. The method proposed by Riazi et al. (1999) was used for the estimation of the sulfur content. All these methods require the average boiling point of the mixture obtained from the ASTM D86 distillation curve. In this study, the ASTM D2887 distillation curves presented in Table 2 for each fraction were converted to ASTM D86 by using the method proposed by Daubert (1994) and the average boiling point was calculated following the procedure 2B1.1 (API, 1987).

Table 5 shows the average boiling point (\bar{T}), the liquid density and the refractive index at 293K (D_{293} and RI_{293} , respectively) and the sulfur content ($S\%$) for each mixture calculated by the methods mentioned before. Such results and those ones obtained by the pseudo-component method were compared to the experimental values as shown in Figure 4. D_{293} values for the method reported here were obtained from D_{343} calculated ones by using a relation between densities at different temperatures (Peña,

2000). RI_{293} calculated values for the pseudo-component method were obtained according to the following expression (Altgelt and Boduszynski, 1994):

$$RI_{T_1} = RI_{T_2} + 0.0004 \cdot \Delta T \quad (T_1 < T_2) \quad (6)$$

where $T_1=293\text{K}$ and $T_2=343\text{K}$.

The absolute average deviations were calculated from equation (5) and listed in Table 6 for the prediction of the studied properties.

The predictions for D_{293} by the methods proposed by Riazi-Daubert, Riazi-Roomi, API and the pseudo-component method for mixtures with low density are very similar and in good agreement with the experimental values. For mixtures with high densities, the method based on pseudo-components slightly underestimates the experimental values, while other methods overestimate such values. The different nature of the mixture is only considered in the method by Gomez (through the Watson factor) and in the pseudo-component method reported here (through composition in saturates, aromatics and polars). However, the results obtained with the method proposed by Gomez are superior, as accurate predictions without systematic deviations are obtained. On the opposite, the method reported in this work has the advantage that it is easier to apply and allows to calculate several properties simultaneously.

According to such results, the method proposed by Gomez ($\bar{\varepsilon} = 0.003$) can be used to properly calculate the density for the involved mixtures. The obtained deviations of the other methods (0.009, 0.009, 0.010 and 0.012 for Riazi-Daubert, API, Riazi-Roomi and that reported in this work, respectively), are similar.

Similar results were obtained for the predictions of RI_{293} as it can be seen in Figure 4. All methods provide similar deviations, although those proposed by Riazi-Daubert is the most accurate with $\bar{\varepsilon} = 0.005$ against $\bar{\varepsilon} = 0.007$ for Riazi-Roomi, and $\bar{\varepsilon} = 0.011$ for the method based on pseudo-components.

The predictions for the sulfur content from the method proposed by Riazi et al. and from the pseudo-component method are of similar accuracy, $\bar{\varepsilon} = 0.9$ and 0.7 , respectively. However, in both methods systematic deviations are obtained as it can be observed in Figure 4.

The pseudo-component method was successfully used to estimate D_{293} and RI_{293} of mixtures obtained from lubricating oils with medium content of saturates, whereas the estimation of the sulfur content is less accurate (van Grieken et al., 2005; Coto et al., 2006a and Coto et al., 2006b) However, the results shown in this study reveal that the accuracy of that method decreases when it is applied to mixtures with higher paraffinic content than those previously studied. Despite this limitation, the method used in this work can be considered more predictive than the other ones, since it allows predicting several properties simultaneously, yielding similar deviations.

4.2 Extraction model. Experimental conditions listed in Table 1 were simulated by a single stage decanter where the extraction is carried out followed by two separation units to remove the furfural from both the raffinate and the extract. Figure 5 shows a scheme of this simulation model. The simulation was performed with a commercial simulator, Aspen Plus[®], using $T_{50\%}$ and SG of each pseudo-component (listed in Table 3) and the NRTL (listed in Table 4). The simulation results for C-30000 extraction experiments (extraction yields, furfural content, composition and physical properties for each mixture) are presented in Table 7.

Experimental and predicted values for C-30000 extraction yields and furfural content are compared in Figure 6. Good agreement between predicted and experimental yields was found, confirming the expected distribution of phases. Thus, at medium temperature (333K) and lowest solvent/feed ratio (1), a raffinate yield of 94.3% was predicted, which compares favorably with the 90.2% experimentally obtained. At higher

temperature (353K) and furfural/feed ratio (8), species undergo larger dissolution, and the yield of raffinate decreases. Thus, a yield of 62.6% was predicted, which again shows a good concordance with the 63.7% experimentally obtained. When predicting experiments carried out in conditions near the limit of application of the model, the obtained predictions show higher deviations. At lowest temperature (323K) and furfural/feed ratio (1), a value for raffinate yield of 96.3% was predicted whereas a value of 90.3% was experimentally determined. Likewise, extractions carried out at highest furfural/feed ratios could not be predicted. To determine the accuracy of the predictions of the extraction yields, absolute average deviation was calculated, obtaining a value of 3.1%. The comparison between predicted and experimental values for the furfural content shown in Figure 6 can be considered satisfactorily, with absolute average deviations of 2.5% and 1.9% for raffinates and extracts, respectively.

Figure 7 shows the comparison between experimental and predicted compositions of the involved mixtures (feed, raffinates and extracts). As it is shown, no important deviations were found, although a slight underestimation for the content of saturates and aromatics in extracts can be observed. Such deviations can be related to the high content of saturates in these fractions due to the highly paraffinic nature of the C-30000 lubricating oil. Absolute average deviations of 4.3% for saturates, 3.7% for aromatics and 0.7% for polars were obtained. Such values are all within the limits of reproducibility established by the ASTM D2007 standard test method.

The results obtained show the possibility to correctly apply the generalized model to a highly paraffinic lubricating oil with no remarkable deviations between experimental and calculated values.

A well known limitation of this model (van Grieken et al., 2005; Coto et al., 2006a; Coto et al., 2006b) is the application to experiments carried out at highest temperature

and highest furfural/feed ratio. This limitation was also found for the system furfural+C-30000 lubricating oil. Such experiments can not be simulated because the system is near the miscibility region and no accurate predictions are obtained in these conditions.

However, this limitation is not a big model lack because in the practice these severe conditions are far from common operation.

5. Conclusions

The method based on the pseudo-component properties, obtained from $T_{50\%}$ of the lubricating oil used as feed, allows the correct prediction for properties of different mixtures (feed, raffinates and extracts) obtained from highly paraffinic lubricating oils. Sulfur content predictions show systematic deviations revealing that it is necessary to obtain a new distribution of the sulfur content for the pseudo-components. However, obtained results show similar accuracy than those calculated using other methods reported in the literature.

The high content of paraffinic compounds has further influence on the accuracy of the method applied in this work. However, such method is suitable to predict several properties with acceptable accuracy. Consequently, the predictive capability of this model can be considered higher than that of other proposed models.

The generalized model used in this work can be applied to describe the extraction by furfural using Aspen Plus[®] with the pseudo-component properties and NRTL parameters calculated from $T_{50\%}$ of the lubricating oil used as feed. In this work, no important deviations were found when predicting extraction yields ($\bar{\varepsilon} = 3.1\%$), furfural content ($\bar{\varepsilon} = 2.5\%$ and 1.9% for raffinates and extracts, respectively) and compositions ($\bar{\varepsilon} = 4.3\%$, 3.7% and 0.7% for saturates, aromatics and polars, respectively)

Acknowledgements

The authors thank REPSOL-YPF for providing the lubricant oil samples used in this work and for the financial support through the project “Desarrollo de modelos de simulación de procesos de refino”.

Nomenclature

Symbols

D_{293} : Liquid density at 293K, g/cm³

D_{343} : Liquid density at 343K, g/cm³

E: Extract

F: Furfural

G: NRTL interaction parameter given by eq. 2

N: Number of experiments

P: Studied property such as density, specific gravity or refractive index

\bar{P} : Average property.

R: Raffinate

RI_{293} : Refractive index at 293K

RI_{343} : Refractive index at 343K

SG: Specific gravity at 288K

S%: Sulfur content, w%

T_{ext} : Temperature of extraction, K

\bar{T} : Average boiling point, K.

$T_{50\%}$: Average boiling point of the feed lubricating oil, K

X: Composition, w%

x: Molar fraction.

γ_i : Activity coefficient of component i

α , a, b: NRTL interaction parameters

$\bar{\varepsilon}$: Average absolute deviation, given by eq. 5

τ : NRTL interaction parameter given by eq. 3

Subscripts

A: Aromatics

calc.: Calculated

exp.: Experimental

i, j, k, m: Component i, j k or m.

P: Polars

S: Saturates

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Figure captions

Figure 1. Scheme of calculations.

Figure 2. Material balance of C-30000 extraction experiments.

Line: Experimental feed composition

Symbols: Feed composition calculated from raffinate and extract:

□ , Saturates; ▽ , Aromatics; △ , Polars.

Figure 3. Comparison between experimental and calculated properties from pseudo-component method of C-30000 mixtures (feed, raffinates and extracts).

Figure 4. Comparison between experimental and calculated properties from different methods: ▽ Riazi-Daubert; △ API; □ Riazi-Roomi;

◇ Gomez; ○ Riazi et al.; ■ This work.

Figure 5. Scheme of simulation of the single-stage extraction process.

Figure 6. Comparison between experimental and predicted values of extraction yields and furfural content of C-30000 extraction experiments:○ Raffinates;

● Extracts

Figure 7. Comparison between experimental and predicted compositions of involved mixtures in C-30000 extraction experiments (raffinates and extracts).

Raffinates: □ , Saturates; ▽ , Aromatics; △ , Polars.

Extracts: ■ , Saturates; ▼ , Aromatics; ▲ , Polars.