A Generalized Model to Predict the Liquid-Liquid Equilibrium in the Systems Furfural+Lubricating Oils

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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. These mixtures present very complex composition which makes difficult the description of the liquid-liquid equilibrium involved. In previous studies, the possibility to describe such equilibrium by using a reduced number of pseudo-components and the NRTL model has been stated. In this work, a generalized model to describe the liquid-liquid equilibrium in the systems furfural+lubricating oils is presented. The generalized model is based on a correlation of pseudo-component properties (specific gravity, density, refractive index and sulfur content) and NRTL parameters with the oil average boiling temperature which has been developed from the model description for SPD and HND mixtures. This method allows set up a suitable thermodynamic model for any lubricant oil cut by using as experimental information only the average boiling point and three physical properties (density, refractive index and sulfur content) of the distillate used as feed. The accuracy of the model was checked by simulating single-stage extractions carried out with different lube oil cuts within the range SPD-HND in different experimental conditions. Calculated and experimental yields, furfural content and physical properties of the raffinates and extracts were compared and a good agreement was obtained.

Keywords: Aromatic extraction, furfural, lubricating oils, liquid-liquid equilibrium.

1. Introduction

In the process of manufacturing lubricating oil base stocks, 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).

The aromatic extraction process requires a good solvent which maximize differences in properties between the liquid phases. Furfural is one of the most widely used solvents. Its selectivity towards aromatic compounds is high enough, it decreases slowly when increasing temperature and it is acceptable for both light and heavy vacuum distillates as reported by different authors (Nelson, 1978; Mcketta, 1989; De Lucas et al., 1993).

The design and simulation of solvent extraction processes have been done mostly by fully empirical methods (Rahman et al. 1984) that require wide experimental determination. The application of such approach is limited because the experimental information is not usually available. A more rigorous modeling of the extraction process would be a suitable tool to simulate changes in operating conditions or feed quality. To properly describe the liquid-liquid equilibrium (LLE) established in the extraction operation, a consistent thermodynamic model should be based on the equilibrium data of the studied systems. Solvent+lubricating oils are especially difficult systems because the high number of components in these mixtures, and therefore, simplified methods of calculations are needed.

The pseudo-components approach based on distillation curves, which is widely used to represent the complex composition of petroleum fractions in the vapor-liquid equilibrium calculations, is not effective in LLE modeling because the chemical structure of the compound has much bigger effect than boiling temperatures. De Lucas et al., 1993 have successfully applied the pseudo-component approach to predict the LLE for the systems furfural+lubricating oils.

Recently, Briesen and Marquardt (2004) have reported an adaptive multi-grid strategy based on a discretization to construct correction terms using composition representation. The obtained model, based on molecular information, can be used to describe the LLE.

The composition of such complex mixtures is frequently determined by standard test methods, such as ASTM D2007 (Annual Book of Standards, 2003). However, these methods are time and money consuming and, therefore, composition data are not usually available. For that reason, the composition of petroleum mixtures is related with their physical properties, few of them experimentally determined while the remaining are estimated by known correlations. Different authors have proposed accurate relations to calculate the composition of paraffins, naphthenes and aromatics from the refractive index and the viscosity of the mixture (Riazi and Daubert, 1986). However, the use of most of the developed correlations is limited and, therefore, new methods are needed especially for heavy petroleum fractions. Specific gravity, density, refractive index and sulfur content were selected in this work, since these properties can be successfully correlated with the composition of the lubricant mixtures, obtaining good results for light and heavy lubricant oils (Van Grieken et al., 2005; Coto et al., 2006).

In order to describe the LLE in the system solvent+lubricating oils, different thermodynamic models can be used (Poling et al., 2001; Prausnitz et al., 2000; Raal and Mühlbauer, 1998). NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and

Prausnitz, 1975) methods have been used to correlate LLE data for the system furfural+hydrocarbon systems (Letcher et al., 2003; Morawski et al., 2003).

Recently, a method based on three pseudo-components (saturates, aromatics and polars) together with the NRTL model has been reported to describe LLE in the systems furfural+light (SPD) and furfural+heavy (HND) lubricating oils (Van Grieken et al., 2005; Coto et al., 2006). The application of such model to describe the extraction operation and to predict properties of petroleum fractions (feed, raffinates and extracts) was also reported. The results obtained in the prediction of several physical properties showed similar or even higher accuracy than those calculated by other methods reported in the literature. However, the application of such models is limited to extraction experiments carried out with light or heavy lubricating oils.

In this work, a generalized model was developed from the studies reported for HND and SPD (Van Grieken et al., 2005; Coto et al., 2006). Such generalization is based on the relation between the pseudo-components properties and the NRTL parameters with the average boiling point of the mixture used as feed. The relations between pseudo-component properties and average boiling point can be used to calculate the composition of the lubricant oil, if it is not experimentally available, by means of an iterative method based on the pseudo-components properties, and developed in this work. Thus, the LLE can be described by means of a reduced number of parameters and using as experimental information only the characterization of the lube oil cut used as feed. To check the accuracy of the proposed model, single-stage extraction experiments carried out with lubricating oil cuts (obtained from light Arabia crude oil and within the range SPD-HND) were simulated with Aspen Plus, using the generalized model. Good results were obtained for the prediction of yields and furfural content of the involved mixtures. The predictions of physical properties (specific gravity, density, refractive

index and sulfur content) calculated by using the generalized model showed a good agreement with the experimental values.

2. Experimental Section

Spindle Distillate (SPD), Light Neutral Distillate (LND) and Medium Neutral Distillate (MND) were provided by REPSOL-YPF from their refinery in Cartagena (Spain). Such mixtures were obtained from light Arabia crude oil. Furfural was also supplied by REPSOL-YPF and distilled before use to remove the oxidation products formed due to air contact.

Experimental results for the single-stage extraction experiments were obtained by using a 2L cylindrical stirred glass reactor following the procedure reported by Van Grieken et al. (2005). Temperature was set by recirculating silicone oil from a thermostatic bath, and controlled within ±0.1°C. A gentle 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. Furfural was removed from extracts and raffinates by vacuum distillation. Table 1 shows the temperature at which 50% of the lubricating oil is distilled ($T_{50\%}$) following ASTM D-1160. Specific gravity (SG) and liquid density at 343K (D_{343}) (ASTM D1298), refractive index at 343K (RI_{343}) (ASTM D1747) and sulfur content ($S\%$) (ASTM D4294) of feed, raffinates and extracts were determined by means of the mentioned ASTM procedures (Annual Book of Standards, 2003). Each mixture is denoted by a letter (R, raffinate; E, extract), followed by the corresponding number of the experiment.

From the results shown in Table 1, for experiments at the same temperature, lower yields of extract were obtained when decreasing the furfural/feed ratio: species undergo less dissolution in furfural, and therefore, the efficiency of the extraction is lower.

Consequently, the yield of raffinate is higher. When experiments with the same furfural/feed ratio and different temperature are compared, higher temperatures increase not only aromatic extraction, but also other compounds, reducing the selectivity of the process.

3. Generalized model

A generalized model to describe the extraction operation was developed from the models previously reported for SPD and HND lubricating oil cuts (Van Grieken et al., 2005; Coto et al., 2006). Such models were based on the pseudo-component properties and the NRTL model. The pseudo-component properties for SPD and HND lubricating oil cuts previously reported are shown in Table 2. NRTL parameters calculated for such lubricating oil cuts are presented in Table 3.

In this work, both pseudo-component and NRTL parameters for SPD and HND were linearly correlated with $T_{50\%}$ as follows:

$$P = A \cdot T_{50\%} + B \tag{1}$$

where *P* denotes a pseudo-component property or a NRTL binary interaction parameter, and *A* and *B* are linearly-adjustable parameters.

Figure 1 shows, as an example, the assumed linear dependence between pseudo-component *SG* (for saturates, aromatics and polars) and $T_{50\%}$ of the lubricant oil. In such figure it is possible to check how the $T_{50\%}$ range between the previously studies for HND and SPD is covered.

3.1. Pseudo-component properties. The parameters of equation (1) for the different properties (*SG*, D_{343}, RI_{343} and *%S*) of each pseudo-component are shown in Table 4. According to such correlations, the pseudo-components properties of any vacuum distillate lubricating oil with $T_{50\%}$ within the range SPD-HND (640-801K) can be easily calculated.

The following mixing rule was assumed to relate the physical properties of any lubricating oil mixture to the properties and composition of pseudo-components:

$$P_{i,calc} = \left[\frac{X_S}{100} \overline{P}_{i,S} + \frac{X_A}{100} \overline{P}_{i,A} + \frac{X_P}{100} \overline{P}_{i,P} \right] \quad (2)$$

where $P_{i,calc}$ is the calculated value of property i; $\overline{P_{i,S}}$, $\overline{P_{i,A}}$ and $\overline{P_{i,P}}$ the calculated values of the property i for saturate, aromatic and polar pseudo-component, respectively, and X_S, X_A and X_P the values of composition in saturates, aromatics and polars.

In this work equation (2) was used straightforward to calculate physical properties of any lubricating oil mixture from calculated pseudo-component properties and composition. In addition, such equation was used in a reversed way in order to calculate the composition values in saturates, aromatics and polars for any lubricating oil cut used as feed in the extraction operation.

The calculation procedure to obtain the composition of the feed involves only three properties, D_{343}, RI_{343} and *%S*. For a given unknown lubricating oil cut, the pseudo-component properties are obtained from equation (1) and values for X_s, X_A and X_P are those which minimize the following objective function:

$$F = \sum_i \left| P_{i,\exp} - P_{i,calc} \right| \quad (3)$$

where $P_{i,exp}$ is the experimental value for the considered property, i, and $P_{i,calc}$ is the corresponding one calculated from equation (2). The sum is extended over the three above mentioned properties (D_{343}, RI_{343} and *%S*). Figure 2 shows, as an example, the comparison between the experimental and predicted values of D_{343} for the distillates considered in this work. As it can be observed, no deviation was found, and therefore the calculated values of composition can be successfully considered.

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

$$\ln \gamma_i = \frac{\sum_{j=1}^{c} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{c} x_k G_{ki}} + \sum_{j=1}^{c} \left[\frac{x_j G_{ij}}{\sum_{k=1}^{c} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{c} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{c} x_k G_{kj}} \right) \right] \quad (4)$$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \quad (5)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T_{ext}} \quad (6)$$

where x_i is the molar fraction of component i; α_{ij} is a model parameter related with the tendency of species i and j to be randomly distributed, and τ_{ij} is the model parameter which must be considered for the interaction between pairs of molecules i and j. τ_{ij} is assumed to be temperature dependent (T_{ext}) according to equation (6), for which two binary parameters, a_{ij} and b_{ij}, are defined (Demirel and Gecegörmez, 1991). As τ_{ii}=0, $a_{ij} \neq a_{ji}$, $b_{ij} \neq b_{ji}$ and $\alpha_{ij} = \alpha_{ji}$, five binary parameters should be considered to characterize each binary interaction.

NRTL parameters for SPD and HND shown in Table 3 were used to obtain a $T_{50\%}$-dependent generalized model. Thus, α_{ij} parameters, previously calculated for SPD and HND were correlated with $T_{50\%}$ by means of expression (1) and shown in Table 5. According to expression (6), temperature dependent parameters τ_{ij} and τ_{ji} were estimated for SPD and HND at different temperatures, in this work values of 323, 343 and 363K were selected for T_{ext} as usual temperatures for the extraction operation. Equation (1) was used to correlate τ_{ij} and τ_{ji} at fixed T_{ext} values with $T_{50\%}$. From the dependence of τ_{ij} against $1/T_{ext}$ according to equation (6), values for a_{ij} and b_{ij} can be obtained. Such procedure was also applicable to τ_{ji}. Obtained values are collected in

Table 8. These relations allow calculate NRTL parameters for any lubricant oil using as experimental information only the $T_{50\%}$. The range of application is for lubricating oils with $T_{50\%}$ values within the range SPD-HND (640-801K). Figure 3 summarizes the scheme of application of the generalized model.

4. Results and discussion

In order to check the quality of the generalized model described before, several experiments were carried out with the lubricating oil cuts (within the range SPD-HND) presented in Table 1. Pseudo-components properties and NRTL parameters of such lubricating oil cuts were calculated from their $T_{50\%}$ (Table 1) according to the coefficients listed in Tables 4, 5 and 6. Calculated properties of each pseudo-component for SPD, LND and MND lubricating oil are shown in Table 7. Calculated NRTL parameters for such cuts are shown in Table 8. Experimental conditions given in Table 1 were simulated by means of Aspen Plus® using the generalized model and the results for all extraction experiments are shown in Table 9. The composition of each cut used as feed was estimated following the method described above from the pseudo-components properties and physical properties of the different lubricating oils (SPD, LND and MND).

In order to determine the accuracy of the different predictions, absolute average deviation ($\bar{\varepsilon}$) was calculated as follows:

$$\bar{\varepsilon} = \frac{\sum \varepsilon_i}{N} = \frac{\sum \left| P_{exp} - P_{calc} \right|}{N} \tag{7}$$

where N represents the number of mixtures considered, P_{exp} is the experimental value of a property and P_{calc} the calculated one. Table 10 lists the values of $\bar{\varepsilon}$ for different properties related with the single stage extractions for SPD, LND and MND.

Experimental and predicted yields for all lubricating oil cuts are compared in Figure 4. As it can be observed, no systematic deviations were found in any case, obtaining the expected distribution of phases. Thus, at the lowest temperature and furfural/feed ratio 79.5%, 84.5% and 85.7% in raffinate was predicted for SPD, LND and MND respectively, which is in good concordance with 74.1%, 80.0% and 83.2% experimentally determined for such cuts. When increasing the temperature or the solvent/feed ratio, the yield becomes lower as stated before. Thus, at the same temperature and highest solvent/feed ratio a raffinate yield of 44.0%, 54.1% and 58.1% was calculated for SPD, LND and MND respectively, showing again a good agreement with the 43.8%, 51.5% and 57.8% experimentally obtained. Absolute average deviations of 2.6%, 3.0% and 1.2%, were obtained for the prediction of extraction yields for SPD, LND and MND, respectively.

The comparison between experimental and predicted content of furfural for raffinates and extracts is shown in Figure 5. The model exhibits good accuracy in all experimental conditions, even at the higher values of temperature or furfural/feed ratio. For instance, the predicted values for furfural content in raffinate for MND was 9.1% at the lowest temperature and furfural / feed = 7 and 19.2% at higher temperature and furfural / feed ratio = 1, such values fit well with the experimental ones, 8.0% and 21.6%, respectively. Absolute average deviations of 0.6%, 1.5% and 1.1% were obtained for the prediction of furfural content in raffinate for SPD, LND and MND, respectively.

Physical properties (*SG*, *D*, *RI* and *S%*) of each mixture (feed, raffinates and extracts) for SPD, LND and MND were calculated according to expression (2), using the pseudo-components properties shown in Table 7 and the compositions in saturates, aromatics and polars (X_S, X_A and X_P) obtained by simulation presented in Table 9. As an example, experimental and calculated values for SPD experiments are summarized in Table 11.

The comparison between experimental and calculated values of such properties is shown in Figures 6, 7 and 8 for SPD, LND and MND extraction experiments, respectively. As it can be seen, a good agreement between predicted and experimental values was obtained in all cases. In all cases absolute average deviations were < 0.015 for *SG*, <0.007 for D_{343}, <0.005 for RI_{343} and <0.6 for %S.

As it can be observed in Figures 6, 7 and 8 the prediction of the sulfur content shows systematic deviations. This can be due to a limitation of the model since it is assumed that the sulfur content is zero for saturates, which is true if only tiophenic sulfur (present in aromatic and polar species) is present. It works well for the lightest lube oil cut (SPD). However, for heavier lube oil cuts, other sulfur species present in the saturate compounds should be considered. Although the proportion of this kind of sulfur is not very high, it could affect the predictions obtained by using the proposed model and a new distribution of the sulfur content for the pseudo-components would be needed.

In spite of these limitations, the obtained results reported by Coto et al (2006) using the simplified distribution of the sulfur content present similar accuracy than those obtained using a method proposed by Riazi et al. (1999).

The experiments carried out at highest temperatures and furfural/feed ratio could not be simulated because the system is near the miscibility region. This is a limitation in the application of the model previously indicated (van Grieken et al., 2005) for the system furfural+HND lubricating oils and also found for the system furfural+SPD lubricating oil (Coto et al., 2006). 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 not very usual.

According to all the obtained results, it is possible to correlate the pseudo-components properties and NRTL parameters with the $T_{50\%}$ of the lubricating oil cut to predict extraction yields, furfural content and physical properties of the involved mixtures.

Therefore, the generalized model can be used to describe the LLE in the systems furfural+lubricating oil cuts with $T_{50\%}$ within the range SPD-HND.

5. Conclusions

A thermodynamic model, previously developed for the description of the LLE established in the extraction operation of lubricating oils with furfural, has been extended to other feeds within the range SPD-HND yielding a generalized model version.

Only three pseudo-components (saturates, aromatics and polars) are considered and the NRTL model is used to determine the activity coefficients. In order to reach a predictive model, a procedure has been developed in order to determine both the pseudo-component properties and the NRTL parameters. The $T_{50\%}$ value was chosen as representative of the lubricating oil mixture and a linear dependence was established between pseudo-components properties and NRTL parameters and $T_{50\%}$.

The feed composition was estimated from their physical properties and that estimated for the pseudo-components. Involved properties were D_{343}, RI_{343} and *%S*.

The generalized model was applied to a single-stage extraction experiments carried out with vacuum distillates SPD, MND and LND, all of them within the range SPD-HND. Accurate predictions were obtained for yields and furfural content in the extraction experiments as well as for the physical properties (*SG*, D_{343}, RI_{343} and *%S*) of the involved mixtures (raffinates and extracts). Absolute average deviations were always lower than 3.0% for the yields and lower than 1.5% for the furfural content in raffinates and extracts. Likewise, absolute average deviations for the studied properties were lower than 0.014 for *SG*, around 0.006 for D_{343}, lower than 0.005 for RI_{343} and around 0.5 for the *%S*.

Sulfur content predictions show systematic deviations revealing that it is necessary to obtain a new distribution of the sulfur content for the pseudo-components. No systematic deviations were obtained for the predictions of the other properties in the application of the model to the different feeds, thus concluding that the differences between these feeds can be well established through the different physical properties involved and the $T_{50\%}$ value.

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Nomenclature

Symbols

a: NRTL interaction parameter.

A: Parameter of linear correlation.

b: NRTL interaction parameter.

B: Parameter of linear correlation.

Comp.: Compound.

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

E: Extract.

f: Furfural

F: Objective function.

HND: Heavy neutral distillate.

LND: Light neutral distillate.

p: Polar

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

$\overline{P}$: Average property of pseudo-component.

R: Raffinate.

RI_{343}: Refractive index at 343K.

s: saturate.

SG: Specific gravity.

SPD: Spindle distillate.

S%: Sulfur content, w%.

T: Temperature of extraction, K.

T_t: Temperature on the top of the extractor, K.

T_b: Temperature at the bottom of the extractor, K.

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

v/v: volume/volume.

x: Mole fraction.

X: Composition of each mixture, w%.

α: NRTL interaction parameter.

τ: NRTL interaction parameter given by eq. 4.

Subscripts

A: Aromatics

i, j: Component i, j.

P: Polars

S: Saturates

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Table captions

Table 1. Experimental results for the extractions carried out with SPD, LND and MND.

Table 2. Pseudo-component properties previously reported for SPD (Coto et al., 2006) and HND (van Grieken et al., 2005)

Table 3. NRTL binary interaction parameters previously reported for SPD (Coto et al., 2006) and HND (van Grieken et al., 2005).

Table 4. Correlation between pseudo-component properties and $T_{50\%}$**.**

Table 5. Correlation between α_{ij} and $T_{50\%}$.

Table 6. Correlation between τij and $T_{50\%}$.

Table 7. Pseudo-component properties for the selected lubricating oils.

Table 8. NRTL parameters calculated for the selected lubricating oils.

Table 9. Simulation results for the single-stage extraction experiments.

Table 10. Absolute average deviations for predictions of single stage extractions.

Table 11. Experimental and calculated values of the studied properties for SPD extraction experiments

Figure captions

Figure 1. Relation between SG and $T_{50\%}$ for the studied lubricant oils.

Line: —— Saturates, ····· Aromatics, - - - - Polars

Symbols: ▫ SPD (Coto et al., 2006) and HND (van Grieken et al., 2005)

▼ SPD, ▲ , LND, ● MND, this work

Figure 2. Experimental and calculated D_{343} for the lubricant oils used in this work.

Symbols: ▼ SPD, ▲ , LND, ● MND

Figure 3. Scheme for the application of the generalized model.

Figure 4. Comparison between experimental and predicted values for extraction yields for the single-stage extraction experiments: (a) SPD; (b) LND; (c) MND.

Symbols: ▫ Raffinates; ■ Extracts.

Figure 5. Comparison between experimental and predicted values for the furfural content for the single-stage extraction experiments: (a) SPD; (b) LND; (c) MND.

Symbols: ○ Raffinates; ● Extracts.

Figure 6 Comparison between experimental and predicted properties for SPD mixtures (feed, raffinates and extracts).

Figure 7. Comparison between experimental and predicted properties for LND mixtures (feed, raffinates and extracts).

Figure 8. Comparison between experimental and predicted properties for MND mixtures (feed, raffinates and extracts).