Simulation of pilot-plant extraction experiments to reduce the aromatic content from lubricating oils

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Published on:

Chemical Engineering and Processing: Process Intesification 47 (2008) 1398–1403

doi:10.1016/j.cep.2007.06.012

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Abstract

In the lubricating oil manufacturing process, the aromatic content from 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 shown. In this generalized model few physical properties of the lubricating oil used as feed are needed as experimental information. In this work, such model was applied to pilot-plant experiments carried out with different lube oils within the range (SPD–HND). The accuracy of the model was checked by simulating multi-stage extractions using AspenPlus©. Calculated and experimental yields, and refractive index of the involved mixtures were compared and a good agreement was obtained for the experiments carried out with the heavier lubricating oil cuts.

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 [1,2]. 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 selectively extracts the aromatic compounds with a high yield. Furfural is one of the most widely used solvents. Its selectivity towards aromatic compounds is high enough and it decreases slowly when increasing temperature, being suitable for both light and heavy vacuum distillates as reported by different authors [3,4].

The design and simulation of solvent extraction processes have been performed mostly by fully empirical methods [5] that require a 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 is needed which should be based on the equilibrium data available for the studied systems. Solvent+lubricating oils are especially difficult systems because of the high number of components in these mixtures [6].

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. For that reason, the “molecules-type” approach should be more convenient since it makes difference according to chemical nature of compounds [7]. However, different authors have successfully applied the pseudo-component approach, based on the chemical nature of the species to predict the LLE for the systems furfural+lubricating oils [8].

In order to describe the LLE in the system solvent+lubricating oils, different thermodynamic models can be used. LLE data for the system furfural+hydrocarbon systems have been adequately correlated by NRTL [9] and UNIQUAC models [10]. LLE data for the system furfural+heavy lubricating oils were correctly described by De Lucas et al. [8].

Recently, a method based on three lumped pseudo-components (saturates, aromatics and polars) together with the NRTL model has been reported to describe LLE in the systems furfural+HND [11] and furfural+SPD lubricating oils [12]. This model has been generalized to any heavy fraction based on a linear relation between the pseudo-components properties and the NRTL parameters with the average boiling point of the mixture used as feed [13].

In this work, the generalized model was applied to pilot-plant extraction experiments carried out with lubricating oil cuts within the range SPD-HND. The extraction experiments have been simulated with Aspen Plus©, using the generalized model. The magnitudes of interest in practice are the extraction yields of the process and the refractive index of the raffinate. In order to check the accuracy of the model, the experimental values were compared to those predicted, obtaining good results for the prediction of yields. The predictions of refractive index at 343K of raffinates showed better agreement with the experimental values coming from the heavier lubricating oils.

2. Experimental Section

Different lubricating oil cuts were provided by REPSOL-YPF from their refinery in Puertollano (SPD, LND) and Cartagena (SPD, LND and MND). Such mixtures were all 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.

Extraction experiments were carried out, for each feeding, modifying the furfural/feed ratio and the temperature of the top and the bottom of the four-stage extraction column [14]. A scheme of the pilot-plant is shown in Figure 1. Both the vacuum distillate (feed) and the solvent (furfural) are stored in tanks and preheated until the desired temperature before reaching the rotatory extraction column. The temperature was set in the column by recirculating oil from a thermostatic bath and controlled within ±0.1°C. In order to improve the quality/yield of the raffinate a profile of temperature between the top and the bottom of the column was fixed. As shown in Figure 1, a mixed raffinate (raffinate+furfural) and extract (furfural+extract) are obtained, respectively, on top and bottom of the column. Afterwards, the solvent is removed by vacuum distillation and refractive index at 343K of the free-solvent raffinates was determined by means of ASTM D1747 [15].

3. Simulation section

The generalized model developed by Coto et al. [13] was used to describe the multi-stage extraction operation. Such model assumes a linear temperature dependence of the pseudo-component properties and the NRTL parameters, being the temperature the one for which 50% (vol.) of the feed is distilled following ASTM D-1160 method [15]. Table 1 and 2 show the pseudo-component properties and the NRTL interaction parameters obtained through the generalized model applied to LND lubricating oil from Puertollano.

Likewise, the calculated composition for this feed in terms of saturates, aromatics and polars shown in Table 1 was calculated by means of the following mixing rule and the iterative procedure reported by Coto et al. [13]:

$$P_{i,calc} = \left[\frac{X_S}{100} \overline{P}_{i,S} + \frac{X_A}{100} \overline{P}_{i,A} + \frac{X_P}{100} \overline{P}_{i,P} \right] \quad (1)$$

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. Figure 2 shows the scheme of application of the generalized model.

The pseudo-component properties, the lumped composition and the NRTL interaction parameters for the other lubricating oils form Puertollano and Cartagena were previously calculated by Coto et al. [12,13], respectively.

4. Results and discussion

To check the quality of the generalized model, the pilot-plant experiments were simulated for the lubricating oil cuts selected in this work by means of Aspen Plus©. The calculated model parameters (pseudo-component properties, NRTL and composition of the feed) and a four stage extraction column were used in the simulation of the different experiments, including the temperature profile along the column. The results for all extraction experiments are shown in Tables 3 and 4 for the lubricating oil cuts from Puertollano and Cartagena, respectively. As it is shown, the generalized model is able to correctly predict phase splitting. Thus, when decreasing the furfural/feed ratio, at the same temperature, the yields in raffinate increase. The species undergo less dissolution and the efficiency of the extraction decreases. Comparing the experiments carried out with SPD and LND from Cartagena at the same furfural/feed ratio, it can be observed that the yield in raffinate decreases when decreasing the

temperature on the top stage of the column due to the lower solubility of the species in these conditions.

To check the accuracy of the different predictions, absolute average deviation ($\bar{\varepsilon}$) was calculated as follows:

$$\bar{\varepsilon} = \frac{\sum \varepsilon_i}{N} = \frac{\sum \left| P_{\exp} - P_{calc} \right|}{N} \quad (2)$$

where N represents the number of mixtures considered, P_{exp} is the experimental value of a property and P_{calc} the calculated one.

Experimental and predicted values for extraction yields are compared in Figures 3 and 4 for the experiments carried out with the lube oils from Puertollano and Cartagena, respectively. As it is shown, except for SPD extractions (from Puertollano and Cartagena), good agreement was found between predictions and the experimental values in all cases with absolute average deviations <4.0%.

Values of the RI_{343} for raffinates were obtained by using expression (1), with the average properties of each pseudo-component (Table 1 for LND from Puertollano, Coto et al. [12] for SPD from Puertollano and Coto et al. [13] for the lube oils from Cartagena) and the predicted compositions in saturates, aromatics an polars (X_S, X_A and X_P) listed in Tables 3 and 4. Experimental and predicted values of RI_{343} for raffinates are compared in Figures 5 and 6 for the lubricating oils from Puertollano and Cartagena, respectively. Calculated values of RI_{343} for extracts are not presented because raffinates are the fractions of interest in the process of manufacturing lubricating oil base stocks. The predictions for the experiments carried out with LND and MND lubricating oil cuts can be considered in good agreement with the experimental values, with absolute average deviations≤0.003. However, the predictions for SPD extraction experiments show a systematic underestimation of the experimental values with higher average

absolute ($\bar{\varepsilon}$=0.011). Table 5 summarizes all the deviations obtained for the predictions of yields and RI_{343}.

According to the obtained predictions for yields and RI_{343}, the generalized model can be successfully used to properly describe the pilot-plant experiments carried out with vacuum distillates heavier than SPD. However, it is not accurate enough for those extractions carried out with lubricating oil cuts with $T_{50\%}$ near the lower limit of application of the generalized model.

5. Conclusions

It is possible to correctly describe the influence of temperature and solvent/feed ratio on the multi-stage extraction process by using a generalized model.

The generalized model can be used to simulate not only single stage experiments, but also pilot-plant experiments carried out with different lubricating cuts.

Good results were obtained for predicting yields and refractive index at 343K for the experiments carried out with the heavier lubricating oil cuts. However, the predictions of such properties showed lower accuracy for experiments carried out with lubricating oil cuts with $T_{50\%}$ close to the lower limit of application of the generalized model.

Acknowledgements

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

Nomenclature

Symbols

a: NRTL interaction parameter.

b: NRTL interaction parameter.

Comp.: Compound.

$D_{343:}$ Liquid density at 343K.

E: Extract.

f: Furfural

p: Polar

P: Studied property such as refractive index.

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

R: Raffinate.

RI_{343}: Refractive index at 343K.

SG: Specific gravity.

S%: Sulfur content, w%.

T: Temperature, K.

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

v/v: volume/volume.

X: Composition of each mixture, w%.

α: NRTL interaction parameter.

Subscripts

A: Aromatics

b: Bottom of the column.

i, j: Component i, j.

P: Polars

S: Saturates

t: Top of the column.

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Figure captions

Figure 1. Scheme of the experimental pilot-plant.

Figure 2. Scheme of calculations using the generalized model.

Figure 3. Comparison between experimental and predicted values of extraction yields for the lubricating oil cuts from Puertollano:

SPD: ▫ Raffinates; ■ Extracts.

LND: △ Raffinates; ▲ Extracts.

Figure 4. Comparison between experimental and predicted values of extraction yields for the lubricating oil cuts from Cartagena:

SPD: ▫ Raffinates; ■ Extracts.

LND: △ Raffinates; ▲ Extracts.

MND: ○ Raffinates; ● Extracts

Figure 5 Comparison between experimental and predicted values of RI_{343} for the raffinates mixtures from Puertollano: ▫ SPD; △ LND.

Figure 6. Comparison between experimental and predicted values of RI_{343} for the raffinates mixtures from Cartagena: ▫ SPD; △ LND; ○ MND.