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 to 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.

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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 and Kishore, 1978; Sequeira Jr., 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 spindle distillate (SPD), light neutral distillate (LND), medium neutral distillate (MND), heavy neutral distillate (HND) and bright stock distillate (BSD).

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

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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 (*SG*), density (*D*), refractive index (*RI*) and sulfur content (*S%*) 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 (Coto et al., 2006; Van Grieken et al., 2005). 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 (Coto et al., 2006; Van Grieken et al., 2005). Such generalization is based on the rela-

tion 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 (*SG*, *D*, *RI* and *S%*) calculated by using the generalized model showed a good agreement with the experimental values.

2. Experimental section

SPD, LND and 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 1 h, 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. (*SG*) and *D* at 343 K (D_{343}) (ASTM D1298), *RI* at 343 K (RI_{343}) (ASTM D1747) and *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