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Prediction of density and refractive index in furfural+lubricating oil systems

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ABSTRACT

Lubricating oil cuts are obtained by vacuum distillation of residues followed by a series of refining processes, such as aromatic removal. The aromatic content of vacuum distillates is reduced by solvent extraction, usually with furfural. Among the different properties of lubricating oils, density and refractive index are key to determine their final quality. In this work, density (D_{20}) and refractive index (n_{20}) at 20 °C of lubricating oil mixtures were determined from a pseudo-component characterization of the fluid using mixing rules. For that purpose, correlations between these properties and the average boiling point of the feedstock ($T_{50\%}$) were determined. These correlations were applied to different feedstock, thus obtaining the corresponding pseudo-component D_{20} and n_{20} values. Finally, D_{20} and n_{20} of the studied mixtures were calculated by using mixing rules relating pseudo-component properties and composition of samples.

Obtained results were compared to those determined by a variety of methods in order to check the reliability of pseudo-component approach. Comparison of D_{20} predictions show that pseudo-component mixing rule exhibits similar accuracy as the best of the methods tested for the studied lubricating oil mixtures. Regarding to n_{20} predictions, the use of a function of refractive index as pseudo-component property, instead of refractive index, clearly improves the prediction accuracy. This modification yields deviations similar to those obtained by the most accurate of the methods tested for the analyzed lubricating oil mixtures. Pseudo-component approach presents as main advantage over tested correlations, that experimental information on refractive index or density are not required.

1. Introduction

Lubricating oils are valuable products obtained from vacuum distillation of the atmospheric distillation residue. Five raw lubricating cuts are commonly obtained according to their boiling point and viscosity: SPD (spindle distillate), LND (light neutral distillate), MND (medium neutral distillate) HND (heavy neutral distillate) and BSD (bright stock distillate) [1,2]. These cuts are further refined in order to achieve the required properties. Among the different refining process, removal of aromatic compounds is mandatory for lubricating oils to obtain adequate variation of viscosity with the temperature. This process is usually carried out by selective extraction operation, in which a good solvent is used to extract the aromatic compounds with high yield. Although there is a wide variety of solvents [3,4], furfural has been widely used because of its good selectivity towards aromatics even at high temperature, being suitable for a number of light and heavy petroleum fractions [5], [6].

Traditionally, design and simulation of solvent extraction processes have been carried out using empirical methods [7], but this approach requires large experimental data, scarcely available, which limits their application. On the other hand, rigorous modeling presents as advantages the possibility of simulating changes in operating conditions or feed quality. However, heavy mixtures present very complex composition and consequently, it is not possible to determine all the individual compounds, which makes their rigorous modeling difficult [8]. Pseudo-component approach allows for modeling complex mixtures according to their distillation curve. Nevertheless, it is not valid in the case of liquid-liquid equilibrium, since chemical nature has bigger effect than boiling temperature. In this case, “molecule-type” approach describing complex mixtures regarding to chemical nature of compounds appears as a useful alternative [9]. A combination of

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both approaches, based on pseudo-component properties according to their boiling temperature and chemical nature, has been successfully applied to describe furfural + lubricating oil systems [1,2,10].

The determination of composition and physical properties of lubricating oil mixtures is a key step to describe the processes in which they are involved [11]. This kind of mixtures present complex composition, which makes impossible their detailed characterization [7,12]. For that reason, composition is usually expressed in terms of hydrocarbon-type. Regarding physical properties, only few of them are usually determined experimentally, being the rest calculated by different correlations.

As well reported in the literature [13–15], density and refractive index are strongly related in hydrocarbon systems and their knowledge allows for the calculation of other properties, such as interfacial tension and viscosity in petroleum systems [14]. In the case of lubricating oils, density and refractive index are some of the most important properties [12,16]. The former is key for the determination of different transport properties and it is an input parameter for simulating processes [14,17]. Refractive index is also important as it is commonly used to check the quality of the fraction as lubricating oil, regarding their aromatic content [16].

There is a large number of correlations to calculate density and refractive index of petroleum fractions. In this work, a first set of correlations based on relations between density or refractive index to independent properties (such as molecular weight, specific gravity and/or boiling point) [18,19] was applied. On the other hand, a second set of correlations relating density to refractive index [14,20–22] was also used.

The objective of this work is to determine density (D_{20}) and refractive index at 20 °C (n_{20}) of lubricating oil systems by using a pseudo-component approach. Firstly, D_{20} and n_{20} of pseudo-components were calculated from the average boiling point of the feedstock by using correlations developed in this work. Thereafter, D_{20} and n_{20} values of the studied mixtures were determined using pseudo-component mixing rules. As a novel aspect of this work, a mixing rule using a function of refractive index (*FRI*) as pseudo-component property was also tested. Finally, D_{20} and n_{20} predictions obtained by pseudo-component correlations were compared to those ones calculated by other methodologies based on different approaches.

2. Dataset section

Previously reported data on aromatic extraction experiments using furfural were used in this work [23]. Table 1 summarizes experimental conditions (temperature and furfural/feed ratio), composition (in terms of saturates, aromatics and polars) and characterization of each fraction: liquid density at 20 °C (D_{20}) and refractive index at 20 °C (n_{20}). In this work, D_{20} values were determined by ASTM D1298 [24]; and n_{20} values were determined from those ones at 70 °C [23], using the following equation [12]:

$$n_{T_1} = n_{T_2} + 0.0004 \cdot \Delta T \quad (T1 < T2) \tag{1}$$

Experimental uncertainties for D_{20} and n_{20} measurements were ±0.0006 g/cm^3 and ±0.0005, respectively.

Table 1
Experimental results for the experiments considered in this work (R: raffinate; E: extract).

Fraction	T[a] (°C)	Furf./Feed[a] (v/v)	Composition[a] (wt %)			D_{20} (g/cm^3)	n_{20}
			X_S	X_A	X_P		
SPD	–	–	50.13	46.14	3.73	0.9121	1.5089
R-1	55	1	59.99	37.65	2.36	0.8810	1.4894
E-1	55	1	13.22	77.33	9.46	1.0096	1.5758
R-2	55	4	71.39	27.22	1.39	0.8567	1.4750
E-2	55	4	22.53	70.43	7.03	0.9818	1.5556
R-3	55	7	76.26	22.65	1.09	0.8482	1.4696
E-3	55	7	30.14	63.91	5.95	0.9647	1.5450
R-4	75	1	62.52	35.16	2.32	0.8815	1.4893
E-4	75	1	21.15	71.44	7.41	0.9818	1.5563
R-5	75	4	75.43	23.34	1.23	0.8539	1.4731
E-5	75	4	32.12	62.18	5.70	0.9533	1.5385
R-8	95	4	77.47	21.40	1.13	0.8510	1.4721
E-8	95	4	42.46	52.94	4.60	0.9238	1.5202
LND	–	–	47.62	48.50	3.88	0.9208	1.5160
R-1	60	1	54.78	41.95	3.27	0.8969	1.5000
E-1	60	1	8.44	84.36	7.20	1.0277	1.5910
R-2	60	4	63.87	33.45	2.68	0.8755	1.4870
E-2	60	4	16.66	77.18	6.16	0.9949	1.5660
R-4	80	7	57.08	39.55	3.37	0.8950	1.5000
E-4	80	7	14.60	79.73	5.66	1.0021	1.5730
R-5	80	1	67.68	29.66	2.66	0.8719	1.4850
E-5	80	1	25.47	69.30	5.22	0.9740	1.5540
R-7	100	1	57.98	38.55	3.47	0.8953	1.5000
E-7	100	1	23.14	72.01	4.84	0.9675	1.5510
R-8	100	4	69.93	27.46	2.60	0.8684	1.4830
E-8	100	4	35.22	60.19	4.59	0.9456	1.5340
MND	–	–	45.49	50.10	4.41	0.9312	1.5192
R-1	60	1	52.12	43.84	4.04	0.9094	1.5043
E-1	60	1	5.89	87.47	6.64	1.0462	1.6000
R-2	60	4	60.79	35.67	3.53	0.8898	1.4923
E-2	60	4	12.65	81.06	6.29	1.0191	1.5801
R-3	60	7	64.78	31.86	3.37	0.8813	1.4866
E-3	60	7	18.78	75.36	5.85	1.0042	1.5688
R-4	80	1	54.34	41.52	4.14	0.9081	1.5038
E-4	80	1	10.93	83.59	5.48	1.0205	1.5831
R-5	80	4	64.60	31.88	3.52	0.8867	1.4898
E-5	80	4	20.75	73.69	5.56	0.9932	1.5632
R-7	100	1	55.52	40.29	4.20	0.9087	1.5042
E-7	100	1	18.44	76.57	4.99	0.9899	1.5610

[a] Taken from Ref. [23].

3. Characterization section

3.1. Pseudo-component approach

The considered approach describes the liquid-liquid equilibrium in furfural + lubricating oil systems by using a reduced number of pseudo-components and the NRTL model [1,2]. The application of this approach is not limited to specific lubricating oil feedstock, since it can be generalized and applied to most of the usual lubricating oil within the range SPD-HND feedstock. For that purpose, pseudo-component properties and NRTL parameters of two reference feedstock are linearly correlated to the average boiling point of the lubricating oil used as feed. Thus, for any feedstock, only distillation curve is needed as experimental information to calculate main variables of the extraction process (extraction yields, furfural content and composition of raffinate and extract phases). Finally, and it is the point of interest in this work, pseudo-component approach allows estimating properties of raffinates and extracts by applying different mixing rules.

In this work, the studied mixtures were characterized in terms of saturates, aromatics and polars, being their properties (D_{20} and n_{20}) calculated by applying the following mixing rules [1]:

$$\left(\frac{1}{D_{20}}\right)_{MIX} = \left[\frac{X_S}{100}\left(\frac{1}{D_{20}}\right)_S + \frac{X_A}{100}\left(\frac{1}{D_{20}}\right)_A + \frac{X_P}{100}\left(\frac{1}{D_{20}}\right)_P\right] \tag{2}$$