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Separation of Asphaltenes and Lube Oil from Petroleum Residuum by Supercritical Deasphalting

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Due to the limited global oil reserves, more and more heavy crudes are being processed. These crudes contain large amounts of asphaltenes and resins. The Residuum Oil Supercritical Extraction (ROSE™) process is the premier deasphalting technology available in industry today. This state-of-the-art process extracts high-quality deasphalted oil (DAO) and asphaltenes from atmospheric or vacuum residues and other feedstocks. Depending on the solvent selection, the DAO can be an excellent feedstock for catalytic cracking, hydrocracking, or lube oil blending. The energy consumption in supercritical extraction is considerably lower than in conventional extraction, which requires a higher ratio of solvent to crude. The use of supercritical fluid has some advantages such as higher yield and improved quality of the valuable DAO and asphaltenes product, and recovery of supercritical solvent, reducing significantly operating costs compared to other solvent deasphalting processes. This work presents a new method for petroleum deasphalting. This new proposal involves the extraction of the residue fractions of the vacuum distillation using supercritical pentane as solvent. The development of the deasphaltation technology using supercritical fluid appears as a solution to improve the separation of the deasphalted oil (ODEs) from the asphaltenes. The studied process showed that there was an improvement in both amount and quality of the obtained products (DAO and asphaltenes).

1. Introduction

Petroleum is a mixture of several compounds, mainly hydrocarbons (Mendes et al., 2005). Petroleum must be processed in order to have larger quantity of high added value compounds. In a dispersion medium consisting mainly of hydrocarbons, which can be classified into alkanes, naphthenes and aromatics, there are two groups of dispersed colloidal particles in solution: asphaltenes and petroleum resins. Asphaltenes are hydrocarbons with higher molar masses, and contain the majority of oxygen and sulphur compounds, inorganic and organic salts as well as the main part of the metal compounds. Reduction of asphaltenes and metal content can be achieved by disturbing the solvation equilibrium via addition of suitable solvents, e.g., propane, pentane,

heptane or carbon dioxide, resulting in the flocculation of asphaltenes (Eckermann and Vogelpohl, 1990 *apud* Neuman and Rahimian, 1981).

The solvent deasphaltation treats the residue of the vacuum distillation through a pressurized liquid-liquid extraction, using specific properties of the solvent. The deasphaltation produces the deasphalted oil and the asphalted residue (Mendes et al., 2005)

The Residuum Oil Supercritical Extraction process is the premier deasphalting technology available in industry today. This state-of-art process extracts high-quality deasphalted oil (DAO) from atmospheric or vacuum residues and other feedstocks. The asphalthene products from the ROSE process is often blended to fuel oil, but can also be used in the production of asphaltic blending components, solid fuels, or fuel emulsions. Other possible options for the asphaltenes include use as feedstock to conversion processes such as partial oxidation, cooking, or visbreaking.

Supercritical extraction, in comparison with liquid liquid extraction is more energy-efficient, owing to the possibility of regulating the solubility by a small change of pressure P and temperature T. The solvent is readily regenerated by a stepwise change of its density ρ, making it possible to obtain pure products of the separation (Dadashev and Abdulagatov, 1993).

The development of the deasphaltation technology using supercritical fluid appears as a solution to improve the separation of the deasphalted oil (ODES) from the asphaltenes. The use of supercritical fluid has some advantages like: the difference of the densities between the extraction phase and the refining phase is greater than that obtained by the conventional liquid extraction, becoming the separation between the phases easier; the mass transport is faster using the supercritical fluid; the quantity and the quality of the ODES can be easily controlled adjusting the temperature and the pressure of the extraction system and the efficiency to recover the oil is a function of the density of the supercritical fluid (Rodrigues, 2006 and Mendes et al., 2005).

The knowledge of a proper thermodynamic modeling for mixtures of hydrocarbons in high pressures is extremely important for diverse applications in the petroleum engineering, such as reservoir simulation at high pressures and evaluation of extraction techniques of oil in deep waters.

2. Thermodynamic Modelling of Supercritical Phase Behavior

In this item, it will be described the models capable to predict the phase behaviour of vapour-liquid systems at high pressures. (In this article, the designation vapour will be used synonymously with supercritical fluid).

The behaviour of a SCF is difficult to modelling due to the vicinity of the critical point (a mathematical singular point) and the high asymmetry that have in extraction with supercritical solvents. Regardless of the modelling procedure, the following thermodynamic relationships or their equivalent relationships in terms of chemical potentials must be satisfied for two phases to be in equilibrium.

$$f_i^V\ (T, P, y_i) = f_i^L\ (T, P, x_i) \tag{1}$$

where, f_i^L is the fugacity of component i in the liquid phase, f_i^V is the fugacity of component i in the vapor phase, x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction of component i in the vapor or SCF phase. The most computationally straightforward and thermodynamically consistent method for calculating high-pressure phase behavior is to choose an equation of state to model both the liquid and vapor or SCF phases. With this approach, the fugacity in each phase can be written as:

$$f_i^L(T,P,x_i) = x_i \phi_i^L P \tag{2}$$

$$f_i^V(T,P,y_i) = y_i \phi_i^V P \tag{3}$$

where φ_i^L is the fugacity coefficient of component i in the liquid phase, P is the system pressure, T is the system temperature and φ_i^V is the fugacity coefficient of component i in the vapor phase. This is the φ-φ thermodynamic approach. The γ-φ models (γ being the activity coefficient) can not be used for phase equilibrium with supercritical fluids due to the manner that it treats each phase in different ways; therefore, it can not represent in continuous form the changes that occur in the critical region. This inconsistence is not present in the EOS models (Equation of State), where the fugacity equality for V-L equilibrium is written with φ-φ models. The fugacity coefficients can be calculated from the exact thermodynamic relationships (Praunitz, 1968):

$$\ln \phi_i^V = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq n_i}} - \frac{RT}{V}\right] dV - \ln\left(\frac{Pv^V}{RT}\right) \tag{4}$$

$$\ln \phi_i^L = \frac{1}{RT}\int_{V_L}^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq n_i}} - \frac{RT}{V}\right] dV - \ln\left(\frac{Pv^L}{RT}\right) \tag{5}$$

where R is the gas constant , v^v is the molar volume of the vapor phase, v^L is the molar volume of the liquid phase, and n_i and n_j are the moles of components i and j, respectively.

To determine the analytical form of $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}}$, a single equation of state (EOS) can be used. Fortunately, in many cases, high-pressure phase behavior can be reasonably represented with an EOS if the components in the mixture do not differ substantially in size, structure or shape. The most commonly used cubic EOS are the Soave-Redlich-Kwong (SRK) equations and Peng-Robinson (PR) equations.

In this work, the model used is the Predictive Soave-Redlich-Kwong equation of state (PSRK), which is an extension of the SRK equation of state. This model uses the Holderbaum-Gemehling mixing rules; these rules can predict the binary interactions at any pressure. Using UNIFAC, the PSRK method is predictive for any interaction that can be predicted by UNIFAC at low pressure. The main advantage of using PSRK equation of state is that it is more accurate in prediction of the binary interaction parameters and it gives more satisfactory results for mixtures of non-polar and polar components, as the case of the asphaltenes-oil mixture.

The Holderbaum-Gemehling mixing rules use a relationship between the excess Helmholtz energy and equation-of-state. The goal of these mixing rules is to be able to use binary interaction parameters for activity coefficient models at any pressure. They

do not use a relationship between equation-of-state properties and excess Gibbs energy, as in the Huron-Vidal mixing rules.

2.1 Holderbaum-Gemehling mixing rules for PSRK model

The pressure-explicit expression for the equation-of-state is substituted in the thermodynamic equation:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \tag{6}$$

The Helmholtz energy is calculated by integration A^E is obtained by:

$$A_m^E = A_m - \sum_i x_i A_i^* - RT \sum_i x_i \ln x_i \tag{7}$$

Where both A_i^* and A_m are calculated by using equation 1. A_i^* and A_m are written in terms of equation-of-state parameters. The simplified form of constant packing fraction (V_m/b) is used:

$$\frac{V_i^{*,l}}{b_i} = \frac{V_m^l}{b} \tag{8}$$

with:

$$b = \sum_i x_i b_i \tag{9}$$

Therefore:

$$V_m^E(p = \infty) = 0 \tag{10}$$

The mixing rule is:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{1}{\Lambda'} A_m^E(p) \tag{11}$$

where Λ' is slightly different from Λ for the Huron-Vidal mixing rule:

$$\Lambda' = \frac{1}{\lambda_1 - \lambda_2} \ln\left(\frac{\frac{V_m}{b} + \lambda L_1}{\frac{V_m}{b} + \lambda_2}\right) \tag{12}$$

where, λ_1 and λ_2 depend on the equation-of-state. In general, a cubic equation-of-state can be written as:

$$P = \frac{RT}{V_m - b} - \frac{a}{(V + \lambda_1 b) + (V_m + \lambda_2 b)} \tag{13}$$

If equation (11) is applied at infinite pressure, the packing fraction goes to 1, so $\lambda_1 = 1$ and $\lambda_2 = 0$ for the SRK equation of state. The excess Helmholtz energy is equal to the excess Gibbs energy.

3. Results and Discussion

Simulations were done using the commercial process simulator *Aspen Plus* version 2004.1 in order to obtain the ternary phase behaviour of the asphaltene-oil-pentane mixture at three different conditions. As it is known, crude oil asphaltenes represent a solubility class, not a specific molecular species or family. By this way, there is not a specific molecular structure for asphaltenes, since different chemical structures exist for asphaltenes, depending on the origin of the crude oil, different molar mass between several types of asphaltenes are also reported.

The characterization of the asphaltene component in the process simulator was done based on the molecular structure of the low molar mass asphaltene of Figure 1B. The molecule was characterized with UNIFAC group contribution method.
The lube oil free of asphaltenes is consisted of a mixture of saturates, aromatics and resins. As a representative way, it was selected the paraffin n-eicosane ($C_{20}H_{42}$) as the representative component for oil in the process simulator.
The thermodynamic equilibrium model used in the simulation was PSRK with Holderbaum-Gemehling mixing rules. The binary interaction parameters k_{ij} were well predicted using UNIFAC for all pairs of components.
The ternary diagrams generated with Aspen Plus for the system asphaltenes-oil-pentane are shown in Figure 2.

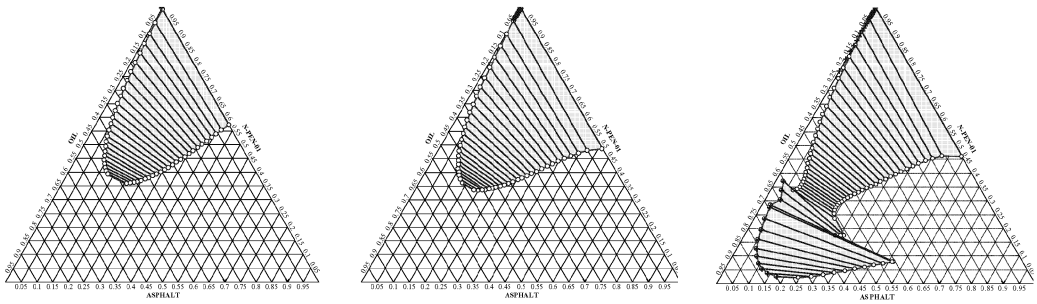

Figure 2– Ternary diagram of the asphalt-oil-pentane mixture at 10 bar, 33 bar and 40 bar.

The principles governing the phase behavior shown in these diagrams are similar to those described by Wilson et al. (1936). At 10 bar (subcritical conditions), pentane is almost entirely miscible with the oil, the oil is almost entirely miscible with the asphalt too, but the pentane is only partially miscible with the asphalt, therefore the asphalt falls out of the solution. This represents the first step of the lube oil refining process.
Figure 2B shows that for a pressure slightly below the critical pressure of pentane (33 bar) the two-phase region of the diagram expands considerably, so liquid pentane is in a much more expanded state than at 10 bar.
If the pressure of the system is increased to a value above the critical pressure of solvent, as shown in Figure 2C, the oil-pentane binary mixture develops an LV region on the oil-pentane axis of the ternary phase diagram and an LLV region appears in the interior of the ternary phase diagram. The LLV behavior occurs because we are in the supercritical state of the pentane, the degree of separation appears to have improved at this temperature for asphalt-oil feed mixtures, as the solubility power of pentane decreases it is possible to separate resins and lighter components of the oil phase. This represents the last step of separation in the oil deasphalting process.

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