Full Length Article

Vapor pressure and thermal properties of heavy oil distillation cuts

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ABSTRACT

The vapor pressure, liquid heat capacity, and heat of combustion were measured for distillation cuts obtained from several heavy oils using a deep vacuum fractionation apparatus. Derivatives of fitted vapor pressure equations were used to determine heats of vaporization based on the Clausius–Clapeyron equation. Existing correlations were evaluated against these data and new correlations were proposed including a generalized Cox vapor pressure correlation (as a function of molecular weight and boiling point temperature) and a correlation for the heat of vaporization based on the generalized Cox equation. Two versions of Tsonopoulos correlations were developed for liquid heat capacity: one using the Watson Factor and another using the H/C ratio. In general, the new correlations improved the prediction of heavy cut properties compared with correlations from the literature and performed similarly for light cuts (both for the development dataset and for independent test datasets). In addition, the heats of combustion of some cuts were measured and used to validate the elemental analysis based correlations from the literature.

1. Introduction

The simulation of refining and recovery processes requires models to describe the phase behavior and the associated physical properties of the petroleum fluids within the process. The input to these models is a fluid characterization(s) based on pseudo-components representing the distribution of properties within the fluid(s) [1]. The key properties required to perform a fluid characterization are the normal boiling point, specific gravity and molecular weight. Other properties, such as the critical properties, are usually determined from correlations. However, if vapor pressure and thermal properties (liquid heat capacity, heat of vaporization, and heat of combustion) are available, the modeling can be made more robust and the accuracy of the predictions can be tested and potentially improved.

Vapor pressure constitutes the backbone of thermodynamic equilibrium calculations. It is frequently used together with liquid density to determine equation of state parameters [2,3]. The equilibrium dictated by vapor pressure is required for the design and operation of process units such as distillation columns and separators. Liquid heat capacity and heat of vaporization are

required for energy balances and heat flux calculations for petroleum process units such as distillation columns and heat exchangers. For heavy oil in particular, the liquid heat capacity is required to estimate the amount of heat required to preheat a heavy oil or bitumen before recovery. Heat of combustion are used to identify the quality of the hydrocarbon as a fuel source and also to derive the heat of formation for reaction enthalpy calculations [3,4].

Since these properties are not often available as part of the characterization procedure, their accurate prediction is indispensable for modeling purposes. The most commonly used vapor pressure predictive correlations for pure hydrocarbons and narrow distillation cuts are based on critical properties [5–7]. Maxwell and Bonnell [8] and Riazi [2] developed correlations from petroleum fraction vapor pressure data which are based on measurable physical properties. The latter correlations are recommended when reliable critical property data are not available. There are many correlations available in the literature for liquid heat capacity [3,6,9], heat of vaporization [10–12], and heat of combustion [2,13]. All of these correlations were based on data collected for conventional oils and, in a few cases, including the distillable fraction of heavy oils.

However, only a small fraction (typically about 30 wt.%) of a heavy oil is distillable before the cracking temperature is reached. Hence, the correlations must be extrapolated for most of the heavy

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Table 1
Bulk API, molecular weight, asphaltene content, and distillable fraction of the bitumen and heavy oils used in this study (data from Sánchez-Lemus et al. [16]).

Sample name	Source	API gravity	Molecular weight, g/mol	Asphaltene content, wt.%	wt.% distilled
WC-B-B1	Shell	9.7	559	17.4	51.8
CO-B-A1	Schlumberger	9.2	604	25.8	42.8
MX-HO-A1	Schlumberger	13.2	653	21.2	41.1
CO-B-B1	Schlumberger	10.9	578	22.7	46.0
US-HO-A1	Schlumberger	15.5	548	12.7	53.4
WC-B-D1	Schlumberger	10.4	585	16.2	41.9
RO-HO-A1	Schlumberger	15.4	467	6.5	62.2

oil and, until recently, there were no data with which to validate the extrapolations. A recently developed deep vacuum fractionation procedure [14,15] provided a methodology to extend the distillation to approximately 50 wt.% of a typical heavy oil. Furthermore, the method allows for the collection of physical samples of heavy distillation cuts for property measurements.

Physical properties and their correlations were examined in a previous publication [16]. The objective of this study is to measure the vapor pressure and thermal properties of the distillation cuts obtained from the deep vacuum apparatus. Vapor pressures, heat capacities, and heats of combustion are measured directly. The heat of vaporization cannot be measured directly because heavy oils thermally decompose before reaching their normal boiling point. Instead, the heat of vaporization is calculated from the derivative of a vapor pressure equation fitted to vapor pressure data; the derivative is based on the direct relationship between vapor pressure and heat of vaporization through the Clausius–Clapeyron equation. Although these derived heat of vaporization data cannot be regarded as measured values, these calculated values are the best estimate available for heavy distillation cuts. The vapor pressure and thermal property data are used to tune and modify existing correlations (or propose new correlations) to provide improved predictions for these properties for heavy distillation cuts.

2. Experimental methods

2.1. Materials

Seven different heavy oils and bitumen samples from five geographical regions were provided by Shell Canada Ltd. and Schlumberger. Their bulk API, molecular weight, asphaltene content, and distillable fraction (with the Deep Vacuum Apparatus) are provided in Table 1, and their elemental analysis in Table 2. Their boiling point and physical property distributions are reported elsewhere [16]. The nomenclature for the samples is as follows: the first term indicates the country of origin (WC = Western Canada, CO = Colombia, MX = Mexico, US = United States, RO = Romania); the second term indicates the type of oil (B = bitumen, HO = heavy oil), and the third term indicates the reservoir and sample number.

Prior to distillation, the water content of the samples was measured and, if necessary, the sample was dewatered. Once the water

was removed, the crude oils were deasphalted to facilitate the extended distillation. The deasphalted and water-free crude oils were distilled using both spinning band distillation and deep vacuum fractionation. The distillation cuts obtained from the deep vacuum apparatus were characterized by measuring density, molecular weight, refractive index, elemental analysis, vapor pressure and liquid heat capacity. The physical properties were required as inputs to predict the vapor pressure and thermal properties. The sample preparation, distillation, and physical property measurement procedures are described in detail elsewhere [14–17] as are the physical properties of the cuts including boiling point, density, elemental analysis, molecular weight, and refractive index [16,17]. The experimental methods for vapor pressure and liquid heat capacity are described below.

2.2. Vapor pressure measurement

The vapor pressure of the distillation cuts was measured using a static apparatus and method developed by Castellanos-Díaz et al. [18] that was designed to achieve pressures below 0.1 Pa. The apparatus is shown in Fig. 1 and was designed to perform a series of isothermal flashes on a given sample. To perform an experiment, the sample vessel is isolated and the rest of the apparatus is placed under a vacuum (the base line pressure) at a pressure below the expected vapor pressure. Then, the sample is opened to the vacuum and the pressure (the vapor pressure) is recorded. Finally, the sample is again isolated and the apparatus is brought back to the base line vacuum. This single flash measurement cycle is repeated as required.

Prior to a measurement, the empty apparatus is baked out and the samples degassed to eliminate contaminants that invalidate vapor pressure readings. In order to remove the impurities, several measurement cycles were run until the peak pressure stabilizes. The degassing process was carried out at 313 K to minimize possible fractionation of the cuts. After degassing, the vapor pressure was measured with the following procedure. The liquid sample was placed in the sample vessel and the apparatus was heated up to the desired temperature. The pump was switched on and once the apparatus reached the minimum pressure given by the turbo-molecular pump (or baseline), the vapor pressure was measured at the test section between Valves 1 and 2 in cycles. First, the test section was opened to the pump (open Valve 2 keeping Valve 1 closed) for two minutes. Then the test section was isolated from the pump and opened to the sample (close Valve 2 and open Valve 1) until the pressure reached a constant value. Finally, Valve 1 was closed to isolate the sample and Valve 2 was opened to begin a new cycle. The cycles were repeated until the peak pressures of at least three consecutive cycles were constant. To account for the leak rate, the pressure readings for each cycle were corrected by extrapolating the pressure back to the time when the cycle started.

An error analysis of the vapor pressure measurements using this apparatus was presented elsewhere [18]. The absolute relative deviations for naphthalene and *n*-hexadecane vapor pressures were within 13% and 4%, respectively, of their literature values [19,20]. Hence, the error in the vapor pressure measurements for

Table 2
Elemental analysis (in wt.%) and atomic ratios of the bitumen and heavy oils used in this study (data from Sánchez-Lemus et al. [16]).

Sample name	C	H	N	O	S	H/C	N/C × 100	O/C × 100	S/C × 100
WC-B-B1	82.3	10.1	0.5	0.9	6.0	1.5	0.5	0.8	2.7
CO-B-A1	85.1	10.2	0.7	0.6	3.2	1.4	0.7	0.5	1.4
MX-HO-A1	83.4	10.5	0.6	0.5	5.3	1.5	0.6	0.4	2.4
CO-B-B1	86.1	10.6	0.6	0.6	2.6	1.5	0.6	0.5	1.1
US-HO-A1	84.1	11.1	0.8	1.6	2.4	1.6	0.8	1.4	1.1
WC-B-D1	84.6	10.8	0.4	0.4	3.3	1.5	0.4	0.3	1.4
RO-HO-A1	86.8	11.6	0.8	0.6	0.2	1.6	0.8	0.5	0.1