Phase Equilibrium Study for Upgrading of Heavy Oils Using Supercritical Water

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ABSTRACT

A flow type apparatus was developed to measure vapor-liquid equilibrium (VLE) data of water and heavy oil mixtures at higher temperatures and pressures. Experiments were carried out bitumen-water systems at 603, 623, 653 K and pressures ranging from 2 to 16 MPa. The heavy oil was divided into 7 fractions. It was revealed that the mixture at 603 K shows VLE behavior and with increasing pressure it attains mixture critical point and then liquid-liquid (LLE) above 16 MPa. The experimental results were correlated by Peng-Robinson EoS in which the critical constants of oil fractions were evaluated by using a group contribution characterization and the binary interaction parameters, $k_{ij,}$ in mixing rules were estimated from a generalized equation derived from related VLE correlations with the literature binary VLE data. The calculation could represent the data within a good accuracy for the process design.

INTRODUCTION

The petroleum oil crises lead us to the diversification in the fuel resources and also to the effective utilization of the super-heavy crude oils, such as bitumen. One possible technology to solve these problems is the decomposition in supercritical water where the operation temperature is above 650 K and the pressure is above 20 MPa. In this technology, water molecules may play role as obstacle for coking hydrocarbon. However, there have been reported no VLE data for the related water-heavy oil mixtures under the operation conditions. Since the heavy crude bitumen is multi-component mixtures, we have to specify the component composition for the phase equilibrium calculation by using equations of states (EOS). Normally the petroleum crude oil is divided into several fractions in terms of boiling point and their fractions are considered as pseudo-components whose critical properties for calculating EOS parameters are estimated from their boiling points and densities. However, there is no way to estimate the intermolecular binary parameters in EOS method for the bitumen mixtures because there have been reported no data of VLE for bitumen-water mixtures at high temperatures and high pressures.

In this work, we developed a flow type apparatus for measuring VLE of heavy oil mixtures at high temperatures and pressures. Bitumen was selected a heavy oil and VLE of water-bitumen mixtures at 603, 623, and 653 K and at pressures ranging 2 ~ 16 MPa. The obtained equilibrium data were correlated by the Peng-Robinson EOS with the binary interaction parameters. The binary parameters were estimated by an empirically derived equation which was developed by correlating the reported VLE data for water-heavy hydrocarbon mixtures at high temperatures and pressures which were collected as many as possible in literatures.

EXPERIMENTAL APPRATUS AND PROCEDURE

Figure 1 shows a schematic diagram of the flow type VLE measurement apparatus developed in this work with following the concept of our previous report [1]. The apparatus is basically composed of a feed system, equilibration system (mixing and cell) and sampling system. The details of oil feed tank and cell are shown in Fig.2. The equilibrium cell, which is equipped with observation windows and also stirring mechanism, has an internal volume of 100 cm^3 and 100 mm height. The heavy oil tank has a float-type liquid level meter and an air pressurizing liquid deliver system. The colored area in Figure 1 was heated by electric heater tapes to prevent the oil components from condensing.

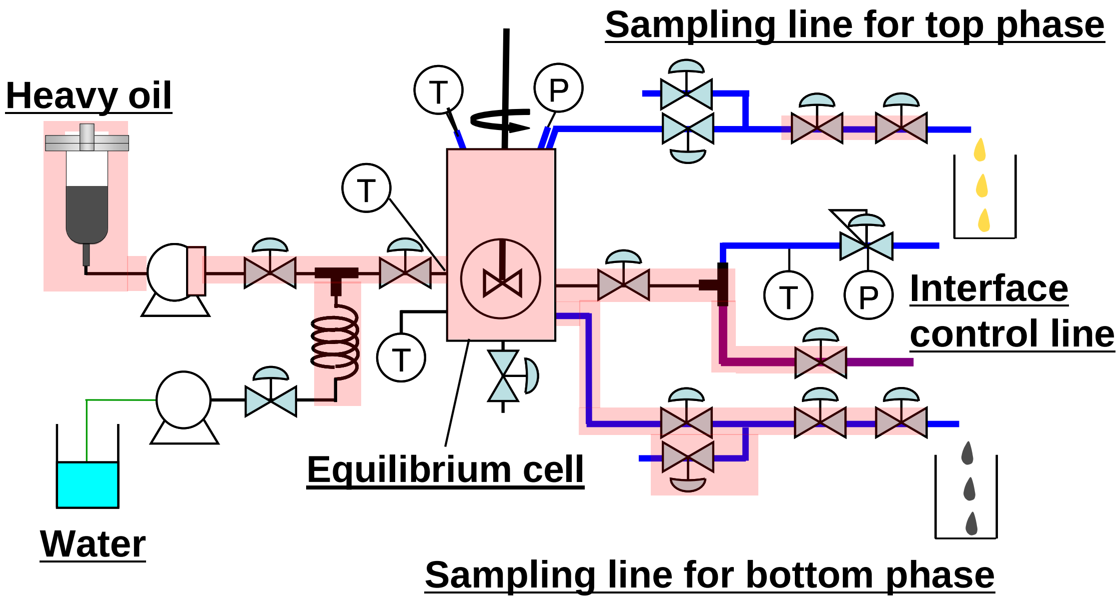


Figure 1 Schematic diagram of experimental apparatus

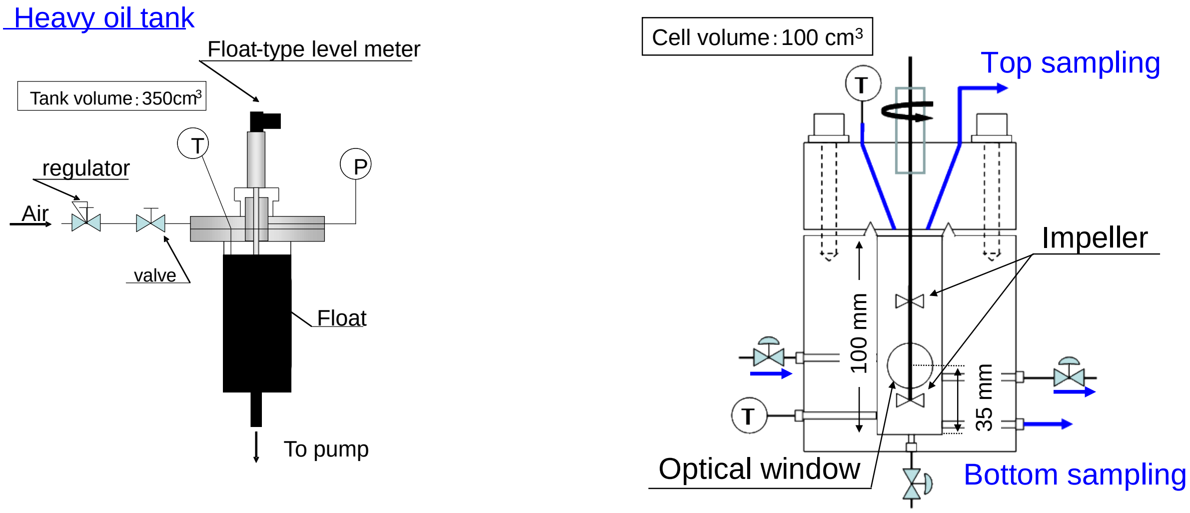


Figure 2 Details of oil feed tank and equilibrium cell

Heavy oil in a heated reservoir tank was fed to a plunger pump by air and pressurized up to a desired pressure. The pressurized oil was merged with water from another plunger pump at the mixing port and flowed into an equilibrium cell where the equilibration and vapour-liquid phase separation was attained. To avoid gas entrainment in the liquid withdrawn from the bottom of the cell and to maintain steady state, the vapour-liquid interface was automatically controlled at the position of a nozzle connected to the overflow line whereas the pressure was maintained by a back pressure regulator. The overflow line was also connected to vent line which was used for preventing the bitumen from flowing to the back pressure regulator.

The liquid phase flowed out constantly from the bottom of the cell through a metering valve, while the vapour phase exited from the top of the cell. A small amount of both vapour and liquid samples were collected in vials. Equilibrium compositions of the collected samples were analyzed by GPC for oil content and by Karl-Fischer for water content.

MATERIALS AND CONDITIONS

Canadian Athabasca bitumen was used as feedstock. The bitumen was separated into 4 fractions and residue by vacuum distillation according to boiling point and the residue was then fractionated into 3 fractions according to solvent solubility; n-pentane-soluble (C5 Maltene), n-pentane-insoluble and n-heptane soluble (C5 Asphaltene), and n-heptane insoluble (C7Asphaltene). All these fractions were characterized by measuring the specific gravity (SG), average boiling temperature (Tb) and average molecular weight. For the residual fractions we could not determine Tb because of thermal decomposition.

Vapor-liquid equilibria were measured isothermally at 603, 623 and 653 K in the pressure range of 2 ~ 16 MPa. Flow rate was determined as less than 5.0 cm^3/min to assure equilibration and also negligible decomposition during measurement. Stirring rate was set to 200 rpm.

RESULTS

Validation experiments were performed for water-tetralin sytem at 573 K by comparing the measured data with the literature values by Christensen and Paulaitis. [2] , and the agreement between both data was found to be good.

Direct observation of phase behaviour of water-bitumen system was carried out at 653 K prior to the VLE measurements. Feed composition was set to water/oil weight ratio as 1/1. Since the objective of this observation was to overview how phase behaviour does change with increasing pressure, the phase boundary pressures were not rigorously determined. Figure 3 is the obtained phase behaviour and typical photos of three regions. As clearly shown, the system showed VLE, then VLLE, and LLE at higher pressure above 20 MPa. The PT-curve in Figure 3 was estimated from the observed sample behaviours but it can be noted that the system may have liquid-liquid phase separation at higher pressures even at 653 K depending on its composition.

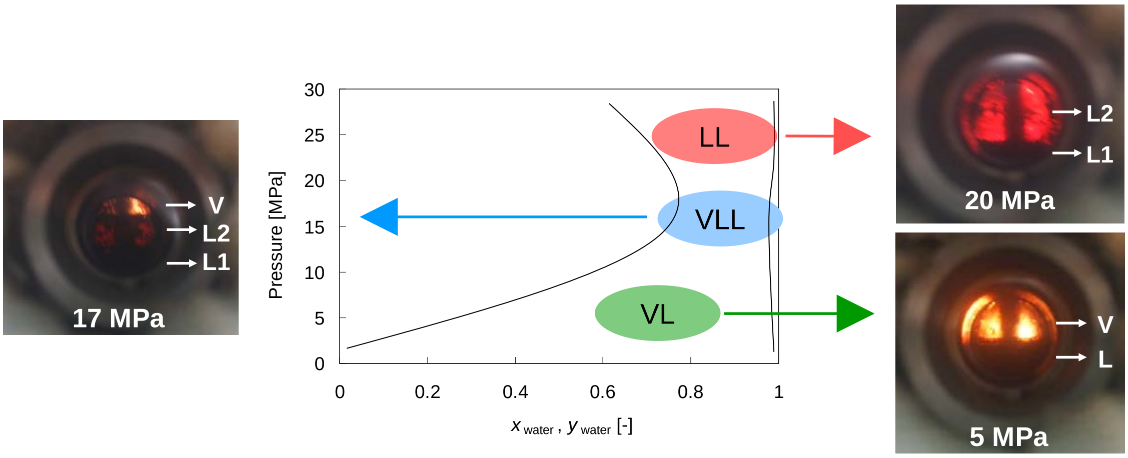


Figure 3 Phase behvior observation results for water-bitumen system at 653 K and photos

Yields of the fractions and their important characteristics are summarized in Table 1. Because heavier fractions (C5MA, C5AS, C7AS) account for about 70% of the characterized bitumen, the bitumen properties depend considerably on their composition. The critical properties were estimated by the group contribution method by Marrero&Gani[3] with using their average molecular structure estimated through H/C by NMR, Mw by GPC, and elementary analyses.

Table 1 Characterization of the fractions of bitumen

		Fr.1	Fr.2	Fr.3	Fr.4	C5MA	C5AS	C7AS
Weight fraction	[wt%]	1.67	7.60	10.7	10.2	54.6	4.48	10.7
T_C	[K]	756.9	776.1	803.1	890.3	1059.5	1319.9	1300.8
P_C	[MPa]	1.89	1.79	1.72	1.51	0.93	0.68	0.70
ω	[-]	0.438	0.400	0.476	0.528	1.141	2.260	2.049

The experimental VLE results for water-bitumen systems are shown on isothermal pressure-composition (PX) diagrams in Figure 4 as pseudo-binary mixtures. In experiments, firstly water/oil ratios were determined from the measured weight and water content from Karl-Fisher analysis and then the composition of each fraction was determined from GPC chromatograph data and the calibration curve between Mw and Tb, which was previously made using standard polymer reagents. Three bottom fractions (C5MA, C5AS, C7AS) were assumed to keep the fraction yield of feed sample in determining the equilibrium composition of both vapor and liquid phases. From Figure 4, it should be noted that vapor-liquid phase separation area for water-bitumen systems becomes wider with increasing

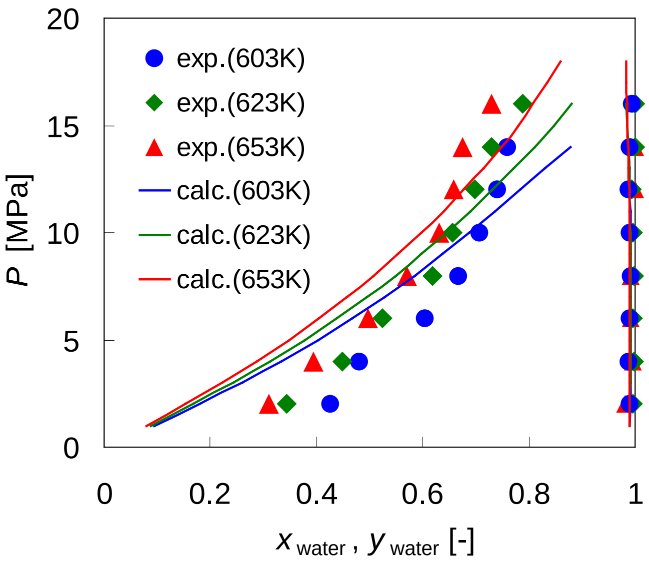
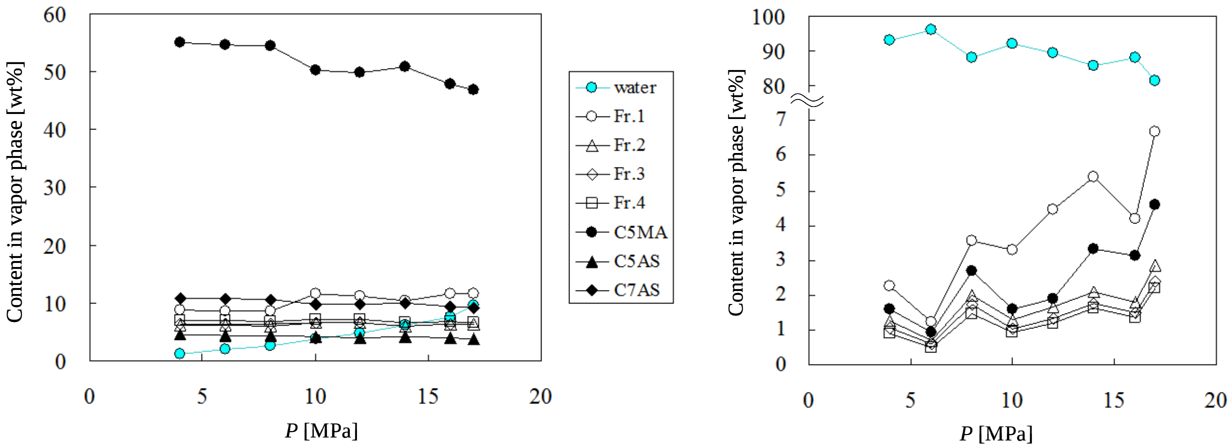


Figure 4 vapor-liquid equiliria for water-bitumen system (W/O=1g/g) temperature and the vapor-phase consists mostly of water. The behaviors of each fraction in equilibrium are shown in Figure 5. The content of C5MA content in liquid phase decreases with increasing pressure while that of water increases. For the vapor phase, it is clearly seen that the fraction-1 and C5MA content increase with increasing pressure although the water content is extremely large as above 85% in the whole pressure range.



(a) Liquid phase (b) Vapor phase

Figure 5 Equilibrium composition of each fraction at 653 K and W/O=1g/g

The solid lines in Figure 4 represent the calculated values for water-bitumen system by the Peng-Robinson equation of state [eq.(1)] and van der Waals mixing rules [eq.(2)]. The binary interation parameters k_{ij} in eq.(2) are generally treated as a fitting parameters in correlations. In this study, the k_{ij} values were predicted by using eq.(3) which was derived from the correlation of literature data of VLE for water-hydrocarbon mixtures at higher temperatures above 573 K. The VLE data used in deriving the correlation are tabulated in Table 2.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \qquad (1)$$

$$a = \sum_i \sum_j x_i x_j (1-k_{ij})\sqrt{a_i a_j}\ , \qquad b = \sum_i x_i b_i \qquad (2)$$

Table 2 VLE data source used in correlations

Water-decalin [5,6]		**Water-dodecane [4]**		**Water-squalane [4]**	
Temp[K]	AAD[%]	Temp[K]	AAD[%]	Temp[K]	AAD[%]
573.2	17.5	603.6	3.2	637.2	6.6
593.2	13.4	633	4.0	642.2	7.4
				653.2	6.2
Water-1-methylnaphthalene[2]		**Water-Tetralin [2]**			
573.2	9.0	573.2	8.9		
623.2	6.0	623.2	1.5		
673.2	3.6	672.9	2.9		

$$k_{ij}(water - bitumen) = 3.2(T_{cr}^{-6.1}) - \frac{1561}{T}\left(T_{cr}^{-6.7}\right) \quad (3) \qquad T_{cr} = \frac{T_{c,bitumen\_fraction}}{T_{c,water}}$$

For hydrocarbon-hydrocarbon components, it was revealed that k_{ij} is very small and could be assumed to be zero through the correlation of related VLE data. The prediction results based on the mentioned above method were plotted as solid lines in Figure 4 and could represent the experimental behaviors at all temperatures although the deviation at lower pressures seems to be large.

CONCLUSION

A newly developed apparatus allowed for us to measure the vapor-liquid equilibrium data for water-bitumen systems at 653 K which can be the reaction condition of supercritical water upgrading of bitumen. The bitumen divided into 7 fractions and the mixtures of water and the 7 fractions was used to predict the VLE of water-bitumen system with using some characterization method for the fraction. The empirical equation for k_{ij} of water-bitumen was developed through the correlation of available binary VLE data and was found to be highly applicable to the prediction of bitumen mixtures. At present, we have been measuring VLE for solvent-bitumen and solvent-AR (atmospheric residual oil) and also have been trying to improve the estimation methodology of k_{ij} for all related binary pairs.

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