J. of Supercritical Fluids 82 (2013) 63–71

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Determination of saturation pressures using experimental data of modified SC-CO_2 extraction of crude oil by consistency test

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ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form 29 May 2013
Accepted 30 May 2013

Keywords:
Consistency test
Activity coefficient
Carbon dioxide

ABSTRACT

The current work aimed to perform a consistency test based on the Gibbs–Duhem equation in order to evaluate experimental results obtained by supercritical carbon dioxide extraction of crude oil modified with several co-solvents in pressures of 20–60 MPa at 60 °C. The collected oil represented a liquid phase fraction while the outgassing losses a vapour phase fraction obtained after extraction. The systems of crude oil and ethanol or methanol modified supercritical carbon dioxide exhibited negative deviations from the Lewis–Randall rule. The unique combinations of saturation vapour pressures that satisfied the consistency tests were determined for the systems with the co-solvents using the criterion of the even distribution of the data about zero line in the plots of area test. The obtained values can be used to determine the thermodynamic conditions where the maximum recoveries can occur and the regions where the multiphases exist.

The current study demonstrates that the consistency test is able to evaluate supercritical carbon dioxide extraction data obtained at high pressures, when using a combination mode.

1. Introduction

Supercritical carbon dioxide (SC-CO_2) possesses strong solvent properties, such as a gas-like penetrating ability and a liquid-like density. As such, in various applications it is used for extraction of many different substances. For instance, numerous papers and patents describe supercritical carbon dioxide extraction of petroleum hydrocarbons at an array of different pressures and temperatures.

Interactions within a CO_2/oil system occur by vapour–liquid (VL), vapour–liquid–liquid (VLL) or liquid–liquid (LL) mechanisms. Greatest recovery of crude oil is obtained upon achievement of a miscibility state in the LL region at the specific pressure determined to be a breakover point on a graph of recovery versus pressure [1]. It is well-known that crude oil recovery increases with rising pressure, but decreases with increasing temperature. Meanwhile, the controversial data about influence of pressure and temperature on hydrocarbon recovery from natural porous matrix is often obtained [2]. The presence of water or the addition of co-solvents to improve oil recovery can also complicate the phase behaviour of the system.

Investigations of crude oil interaction and SC-CO_2 are carried out using different types of batch or continuous flow equipment. In a batch system, gas pressure is gradually increased in a vessel containing oil. The measured crude oil recovery and observed phase transitions are shown in the phase diagrams. Using a rising bubble apparatus, miscibility conditions are determined observing the formation of bubbles.

Flow systems differ significantly from batch systems with regards to operational regime, design, dimensions, orientation of extraction cells, presence of water, geometry of porous matrix, and many other details. The variety of equipment designs, including the slim tube apparatus, traditionally used in the petroleum industry to study crude oil recovery have been well-described by Danesh [3]. The lengths of slim tubes vary from 5 to 40 m; slim tube diameter can also vary (e.g. 6.3 mm or 5 cm). In addition, different gas injection rates are recommended based on the length of the tubes.

Experiments using high pressure extractors can be conducted under static or dynamic modes. In static mode, gas is injected into an extraction cell and interacts with the hydrocarbons for a certain period of time. Afterwards, the extraction cell is opened and only the gas that was contained in the cell transports the extracts into a collection module. Recovery using only a static mode is typically very low. In dynamic mode, gas flows constantly through an extraction cell filled with oil. Improved performances can be achieved by combination of static and dynamic modes; nearly 100% recovery can be attained depending on oil composition, pressure and temperature. A majority of studies report recovery of liquid

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http://dx.doi.org/10.1016/j.supflu.2013.05.021

phase of crude oil. However, a small percentage of extracted oil is not collected due to loss from outgassing. When crude oil is extracted by liquid carbon dioxide from a porous matrix, the total amount of extracted oil is not equal to the amount collected. Fast gas flow upon release and imperfections in the collection system lead to minor oil loss. Additional loss can result from the phase split occurring inside the extractor at elevated temperatures, leading to formation of a vapour. Whether that uncollected vapour should be taken into account when analysing experimental results and considered as part of the system remains to be determined.

Despite the belief that the interaction between CO_2 and crude oil depends solely on oil composition and thermodynamic conditions, the difference of the applied equipment leads to the difference of oil recovery; sharpness and shape of the resulting graphs also vary. Experimental results obtained using slim tubes or high pressure extractors do not always match to the phase or solubility diagrams obtained using batch systems. In addition, the numerical models simulating recovery processes can produce very different results. Therefore, standardised thermodynamic techniques to analyse experimental data are necessary to ensure accurate comparison of results.

Consistency tests based on the Gibbs–Duhem equation [4] are used to analyse experimental phase equilibrium data and show that, for the simple symmetric binary systems, the natural logarithm of the ratio of the activity coefficients of both species (i.e. $\ln(\gamma_1/\gamma_2)$) ranges from 1 to −1 throughout the entire concentration range so that the sum of areas above and below the zero line is equal to null as shown in Fig. 1. Valderrama and Alvarez [5] expanded the test criteria to analyse high pressure data, adding that consistency tests should be able to be used to correlate data within acceptable limits of evenly distributed deviations and to detect erroneous experimental points using all available experimental data including pressure, temperature and fraction of the vapour phase data in any range of concentration. The consistency tests implemented for the analysis of complex systems [5–16], ionic liquids in supercritical carbon dioxide [14], high pressure conditions [4–13], and gas hydrates [15,16] proved to be accurate. Most of the aforementioned investigations used consistency tests to match numerical model to the experimental results. The studies related to the analysis of only experimental data of the complex systems or conditions are rarely reported.

A modified version of the area method based on the Gibbs–Duhem equation was used in the current study to analyse the results of crude oil extraction by pure and modified supercritical carbon dioxide. Specifically, various co-solvents such as methanol, ethanol, seawater and deionised water were added at high pressures, and the experiment was carried out using a combination of static and dynamics modes.

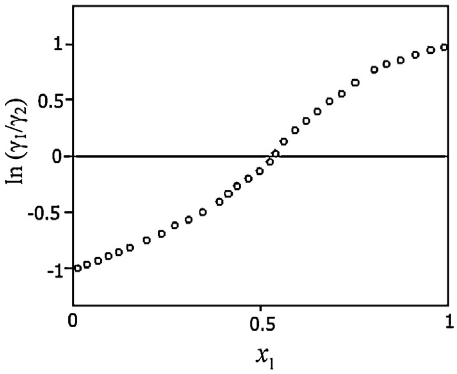

Fig. 1. Traditional area consistency test.

2. Materials and experimental procedure

2.1. Materials

The Halfdan field crude oil was supplied by Maersk Oil Company for experiment. According to ASTM D4052 [17] analysis performed by Saybolt, Division of Core Laboratories Sales N.V., the oil density at 15 °C is 0.8573 kg/L. According to ASTM D445, viscosity $Q = 9.163\ mm^2/s$ at 20 °C. The towels, measuring 9.5 cm × 9.5 cm and 5 g in weight, consisting of 80% viscose × 20% polypropylene used as a carrier for oil were manufactured by Multi Line. Strandmollen A/S, Denmark supplied the 99.9% pure carbon dioxide. Ethanol and methanol, having 99.9% purity, were purchased at VWR Prolab. The seawater of 30 g/L of salinity was taken from the North Sea.

2.2. Preparation of the sample

The towels were used as carriers for crude oil to avoid the oil leaking and to assure that the oil was extracted rather than displaced. In order to achieve proper saturation, the towels were soaked in crude oil for 48 h. The extraction of oil by SC-CO_2 at a fixed temperature value of 60 °C was carried out at nine pressure values within a range from 20 to 60 MPa. The tests were run in a random order. The first experiment was conducted with pure carbon dioxide, whereas the others were performed with the addition of 3 g of mentioned above co-solvents.

2.3. Apparatus description

The extraction experiments were performed using a commercial high-pressure extractor Spe-ed SFE; the scheme of the equipment is shown in Fig. 2 and further operational details can be found in [18–20]. The oven was heated to 60 °C. The inlet (2) and outlet (10) valves were closed. The extractor vessel of 100 mL of volume (7) containing the sample (9) was closed by cap-ends and placed vertically into the oven (8) of the supercritical fluid extractor (SFE). Opening the inlet valve (2), the CO_2 was fed into the system by pump (4) from the storage tank (1) through the pipe connected to the bottom cap-end in order to attain the required pressure. The system was left for the interaction for 30 min in static mode. Afterwards, the inlet (2), outlet (10) as well as the vent valve (11) was opened to collect the extracted oil flowing through the 0.3 mm

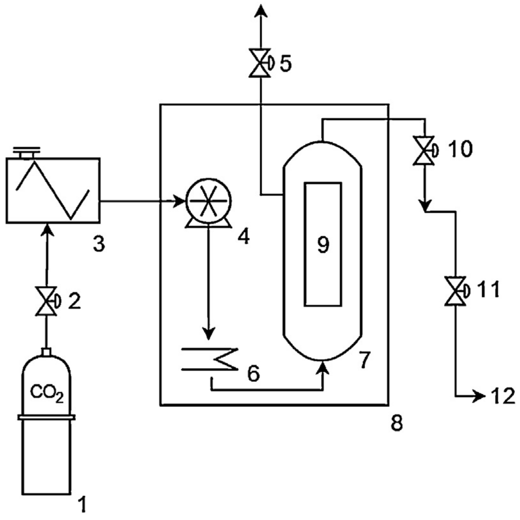

Fig. 2. Scheme of the experimental setup: (1) CO_2 storage tank, (2) CO_2 outlet valve, (3) cooler, (4) pump, (5) vent valve, (6) pre-heat coil, (7) extractor vessel, (8) oven, (9) sample, (10) outlet valve, (11) exit valve, and (12) collection module.