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Phase Behaviour of a Near-Critical Gas Condensate Reservoir Fluid from a Conventional Field in the Niger-Delta Region

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Abstract
Near-critical gas condensate reservoir fluid like near-critical oil has a very complex hydrocarbon phase behavior and is likely to be encountered as deeper formations are been drilled in an extensive search for hydrocarbon deposits. This paper presents an experimental methodology and results of a PVT analysis done on two (2) near-critical gas condensate reservoir fluids from a prolific gas field in the Niger Delta region. The following experiments: Constant Composition expansion (CCE), single stage flash and reservoir fluid composition were carried out using a HPHT visual PVT cell and gas chromatograph. The CCE test performed clearly showed the unusual but unique formation of two liquid phases rather than one liquid phase during the isothermal depressurization below the dew point pressure and the subsequent disappearance of the lower liquid phase, the maximum liquid drop out (LDO) behavior (above 45% condensate dropout) at a small pressure drop of 100-150 psig below the dew point pressure owing to the fact that at the vicinity of the critical point, a marginal change in pressure caused a rapid volumetric change in the single-phase gas. The C_{7+} *mole percent (<12.5%) and the produced gas-oil ratio (>5,000 SCF/STB) were other parameters used to further provide a reasonable insight that the fluid under study is a near-critical gas condensate. In conclusion, proper characterization of a near-critical gas condensate reservoir fluid will greatly aid the reservoir and production engineers to have a better and more robust field development strategy to produce and manage a near-critical gas condensate reservoir.*
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1. Introduction

Over the years the phase behaviour of near-critical fluids has received close attention because of its complex and inconsistent fluid properties. Though there have been series of PVT experiments done on the other reservoir fluid types (ordinary black oils, volatile oils and retrograde gas condensate) but not much PVT studies has been done on a near-critical gas condensate. There are very limited papers that have been published in open literatures on near-critical gas condensate reservoir fluid. Charles Caginard de la Tour was the first to study and report on critical phenomena. His study showed the sudden disappearance of the liquid-vapor meniscus of ether enclosed in a confined glass tube when the temperature is above a certain value (Betrand et al., 2009)

For years, the phase behavior of near critical fluids was conducted mainly on binary or ternary mixtures, while the study of multicomponent reservoir fluid was very limited. In the year 1910, Van der Waals from his studies found out that a saturated vapor of a binary mixture, for example carbon dioxide-nitrobenzene and ethanol-alcohol mixture, gave two liquids instead of the usual single liquid formation due to retrograde condensation as the system undergoes isothermal depressurization at temperatures above the critical temperature (Zheng et al., 2000). Van der Waals was the first to postulate "double retrograde condensation"- a phenomena in which two liquids are condensed in a retrograde process (Zheng et al., 2000). Katz and Kurata (1940) also pointed out that the double retrograde condensation phenomena could occur in high pressure natural gases saturated with heavy hydrocarbons and water vapor, they suggested that the second liquid phase is water condensation.

Yang et al. (1997) studied experimentally the behaviour of naturally occurring reservoir fluid mixture. They measured physical PVT parameters like bubble and dew point around the vicinity of the critical region, the critical point, deviation factor, volume fraction of liquid at the two-phase region and the density of the gas and the liquid phases were all measured. These measurements were made on a real multicomponent reservoir fluid at the near-critical region and they were all measured through PVT experiments. Parra and Remolina (2005) performed PVT phase behaviour study using synthetic-4 component near-critical volatile oil after injection of Nitrogen. The study results showed that the saturation pressure of near-critical volatile oil increase with increasing nitrogen injection ratio. The result also showed that at 40 mole% of nitrogen injection, the near-critical volatile oil fluid transformed into near-critical gas fluid. Zheng et al. (2000) in their phase behaviour study at near critical region on three (3) rich gas condensate gas pools: one was synthetic 6-component rich gas condensate reservoir fluid sample and the other two were samples from real offshore rich gas condensate gas pool and land rich condensate gas pools. In their study, bubble and dew point curve were measured. The critical point, critical opalescence phenomena and the unusual transition at the critical region were all tested and established from the study. The study result shows that the behaviour of synthetic fluid sample at the near-critical region differ from real formation fluid sample and the difference becomes wider with an increase in the paraffinic content of the fluid. The test also shows that two dew points occur at temperatures higher than the critical point and transition between dew point and bubble point at temperatures lower than bubble point.

The phase diagram of a typical near-critical gas condensate is shown in Fig 1. Since the reservoir temperature is close to the critical point where all the quality lines converged, a rapid liquid condensation occurs with small pressure drop (from point 1 to 2) below the dew point pressure. (Ahmed, 2006). Extensive research has been conducted on critical or near-critical phase behaviour majorly for pure substances (synthetic fluids), binary and ternary fluid systems, only a few research has been performed on real multicomponent reservoir fluid at the critical or near-critical region .It is a highly unconventional fluid and lacks adequate characterization approach in the open literature due to its complexity as it is found in a near critical region of hydrocarbon phase envelope of a multi-component system. All known Equations of State models such as Peng Robinson (PR), Soave-Redlich-Kwong (SRK) etc. through the use of compositional simulators such as Eclipse-PVTi, PVTSim and PVTpro have been found to be inadequate in characterizing this fluid. However, in this paper, the phase behaviour study was performed on a real near-critical reservoir fluids using PVT experiments.

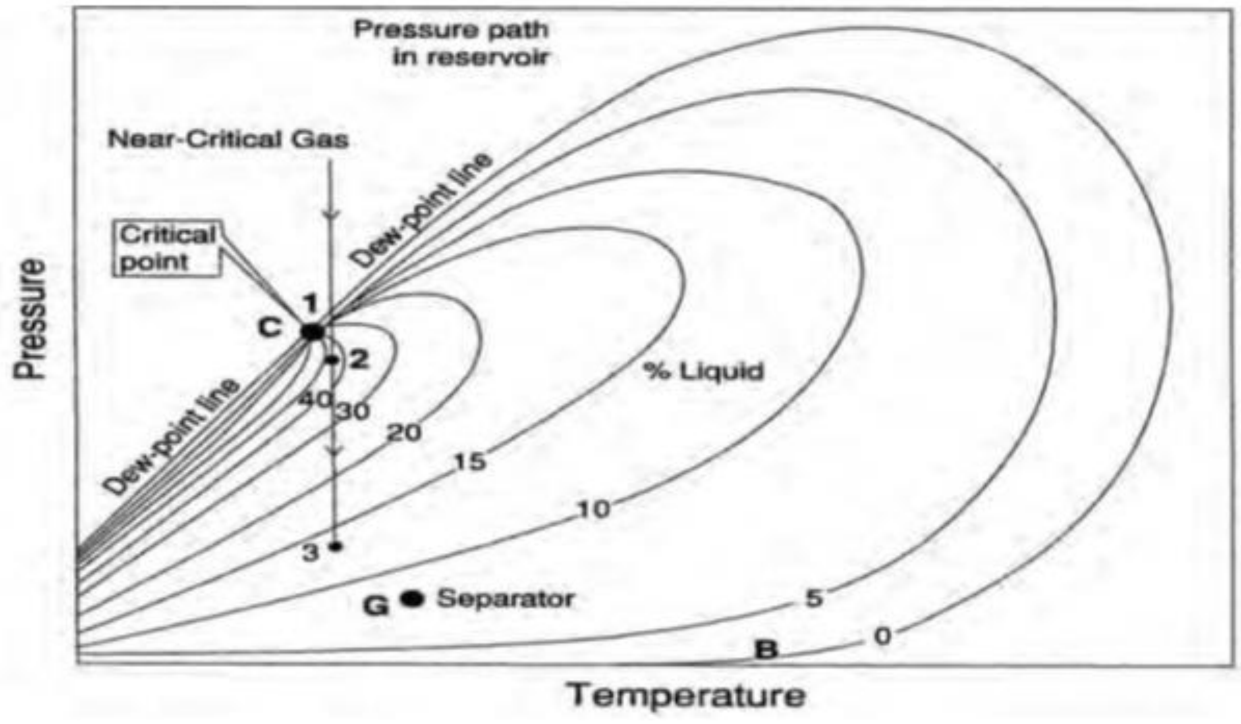


Fig. 1: Pressure-Temperature diagram of a near-critical gas condensate (Ahmed, 2006)

2. Materials and methods

2.1 Equipment

The equipment used to carry out the phase behavior study was a Mercury-free, high pressure, high temperature visual PVT cell manufactured by DB Robinson Design and Manufacturing Limited. The setup is composed of the PVT cell, computer-controlled displacement pumps, pressure sensor, constant temperature air bath and a visual recording system. The piston in the cell is driven by a computer-controlled Jefri displacement pump. The PVT cell maximum operating pressure is 10,000 psig, the maximum operating temperature of the cell is 200 ^{0}C and the cell volume is 130 cc. The Agilent Gas chromatograph was used for compositional analysis.

2.2 Preliminary procedures

Two (2) bottom-hole samples from 1 reservoir were received in our laboratory. The samples were restored to reservoir conditions by continual and simultaneous heating to reservoir temperature and rocking for 48 to 72 hours. The PVT cell was cleaned, vacuumed and heated to reservoir temperature in preparation for the incoming near-critical gas condensate sample. After the sample has been properly restored, a subset of it (about 70cc) was transferred into the PVT cell at the specified reservoir temperature and pressure. The sample in the PVT cell was pressurized to a pressure of at least 2,000 psia higher than the reservoir pressure and maintained at the reservoir temperature of the sample. The preliminary procedures as stated above was performed for the 2 samples at their various reservoir temperatures and pressures. The following experiments were carried out on the near-critical gas condensate samples and their testing purposes were:

2.3 Single-stage flash experiment

This experiment is mainly carried out to determine the reservoir fluid composition and the initial producing gas-oil ratio. A subset of the conditioned sample in the PVT cell was released (flashed) to atmospheric conditions in the laboratory (757 mmHg and 80.9 ^{0}F). The flashed products (gas and oil) were collected and analyzed by gas chromatographic technique to obtain their molecular composition in accordance with GPA 2286 and ASTM D2887 standards respectively. The compositions of the flash products were then mathematically recombined to obtain the reservoir fluid composition through C_{7+}. The flashed gas and oil volumes were measured and used to calculate the initial producing Gas-Oil Ratio (GOR).

2.4 Constant composition expansion experiment (CCE)

The CCE test also known as the pressure-volume (PV) test is carried out to determine the saturation pressure of the sample, in this case, the dew point pressure of the near-critical gas condensate. The test involves stepwise isothermal depressurization from a pressure (of at least 2,000 psia above the reservoir pressure) and at reservoir temperature. This depressurization was continued until two or three pressure steps after the start of re-vaporization of the liquid dropouts (i.e where the relative volume >> 2.0). During this depletion process, pressures and volumes at each step were recorded. Other fluid properties obtained from CCE test were gas deviation factor, relative volume, reservoir fluid density, retrograde liquid dropout behaviour, instantaneous compressibility, etc.

3. Results and discussion

3.1 Reservoir fluid composition

As described earlier, a single stage flash experiment was carried out on the near-critical gas condensate samples. Table 1 shows the experimental data obtained from the flash experiment. The parameters shown on the table includes reservoir fluid composition, produced gas-oil ratio, reservoir fluid molecular weight, and C_{7+} mole percent. The reservoir fluid composition (up to C_{7+}) was obtained by performing a mathematical recombination on the flashed liquid and flashed gas compositions for the two near-critical gas condensate samples. The reservoir fluid composition is clearly shown on Table 1. From the table it was seen that the C_{7+} mole percent for samples A and B were 10.61 mole % and 10.07 mole % respectively all of which are lesser than 12.5 mole percent indicating they are all gaseous reservoir fluids at reservoir conditions. The high percentage moles of C_{7+} also showed that the samples have very high liquid forming components which is an indication that the fluid is close to the critical region, hence a small pressure drop of about a few 100-150 psig below the dew point pressure will result in a large amount of liquid condensing out of the gas.

3.2 Gas-oil ratio (GOR)

The single stage flash experiment performed on the sample produced a gas-oil ratio of 5,119.7 SCF/STB and 5,454.2 SCF/STB for samples A and B as presented on Table 1. Their GOR's are higher than 5,000 SCF/STB which shows that they are not oils but rather gaseous reservoir fluids. At the same time they also exhibits the lowest GOR as compared to other gaseous reservoir fluids like the gas condensate (rich or lean) with GOR (8,000-70,000 SCF/STB), wet gas (60,000-100,000 SCF/STB) and dry gas (> 100,000 SCF/STB). The low GOR is a major characteristic of a near-critical gas condensate reservoir fluid.

3.3 Constant composition expansion

3.3.1 Saturation pressure

For sample A, the saturation (dew point) pressure was observed at 4821 psia, this was indicated by the first appearance of a liquid droplet at the bottom of the PVT cell, and this was seen visually through the window of the PVT cell. This condensed liquid increased in volume as pressure was reduced below 4821 psia. This is an indication that the reservoir fluid was gaseous at reservoir conditions and the dew point pressure was observed to be less than the reservoir pressure (4950 psia) at the time of sampling, this points to the fact that the reservoir was under-saturated (single phase) when the sample was collected. The saturation pressure for sample B is shown on Table 2.

3.3.2 Retrograde liquid dropout behaviour

For sample A, at first pressure step (4680 psia) below the dew point pressure (4821 psia); we observed maximum liquid dropout (LDO) which started retrograding by re-vaporization upon further pressure depletion. This is unique to near critical gas condensate reservoir fluid unlike other gaseous reservoir fluid types that usually experience liquid dropout retrogration at pressures below 2500 psia (far below the dew point pressures). Also, the measured maximum LDO (about 52.06 %) at 4680 psia was the highest when compared to other gaseous reservoir fluid types (that is > 0-5.0 % for lean gas condensate, 5.0 % - 20.0 % for mid-rich and 20.0 - 45.0 % rich gas condensates) (Yisheng et al., 1998). This retrograde liquid dropout behavior is an indication that the fluid is near to the critical point and this behaviour was also observed in sample B as shown on Table 2.

Table 1: Reservoir fluid composition

Composition	Sample A mole (%)	Sample B Mole (%)
N_2	0.36	0.58
CO_2	1.73	0.23
H_2S	0.00	0.00
C_1	65.34	68.00
C_2	7.84	6.32
C_3	6.06	5.00
i-C_4	2.27	2.70
n-C_4	2.45	2.75
i-C_5	1.54	1.98
n-C_5	0.97	1.20
C_6	0.82	1.17
C_{7+}	10.61	10.07
Total	**100**	**100**
MW (g/mol)	39.99	39.14
Mole % C_{7+}	10.61	10.07
GOR (SCF/STB)	5,119.7	5,454.2

3.3.3 Formation of two liquid phases (double retrograde condensation)

During the Constant Composition Expansion experiment on the near-critical gas condensate reservoir fluid, it was observed that two liquid phases were formed during the isothermal depressurization from the dew point pressure of 4821 psia to a pressure of 4400 psia; below the pressure of 4400 psia, the lower liquid at the bottom of the cell disappeared. This liquid behavior is unique to a near-critical gas condensate; this is in contrast with a normal retrograde gas condensate (rich or lean) in which only one liquid phase is formed when the pressure is reduced below the dew point pressure.

3.3.4 Critical opalescence phase behaviour from the constant composition experiment

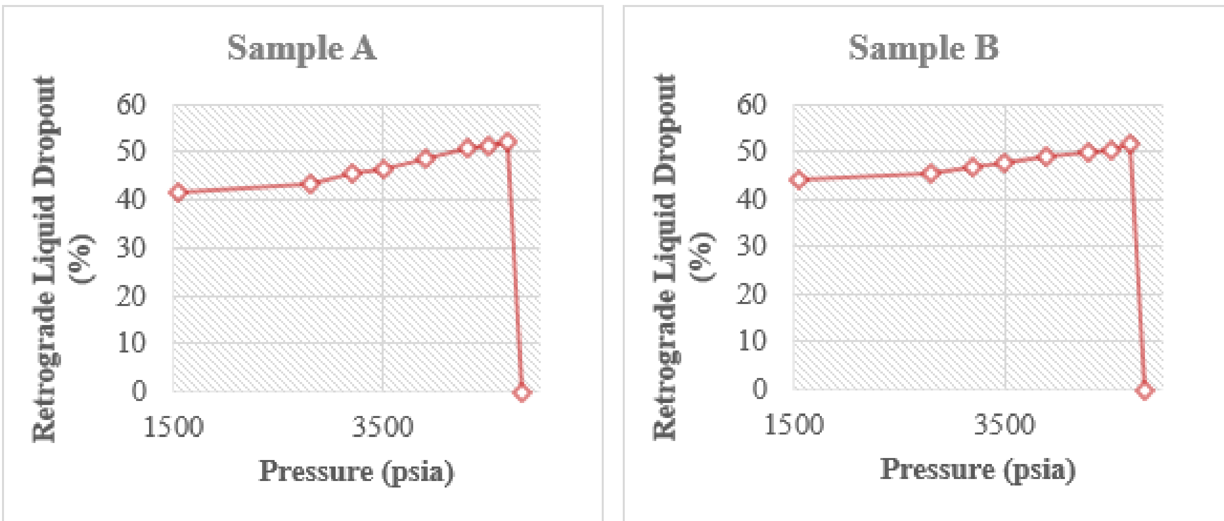
The colour progression that accompanied the measurements were carefully studied and recorded. It was observed that at pressures significantly above saturation pressure, the near-critical gas condensate sample was seen to be bright yellow from the cell window. As pressure depressurization continued, the sample in the cell which is still at single phase started turning from bright yellow to reddish brown progressively. Finally, at saturation pressure the cell became fully dark and at very little pressure drop, the fluid in the cell started going from very dark to reddish brown and finally to bright yellow. This optical phenomenon has also been reported in open literatures by Zheng et al (2000) and Dali et al (2016) and this is clearly shown in figures 3(a)-(o).

Table 2: CCE liquid dropout behaviour using total volume at dew point pressure

Sample A		**Sample B**	
Pressure (psia)	**Retrograde liquid dropout (%)**	**Pressure (psia)**	**Retrograde liquid dropout (%)**
7015	0.00	7015	0.00
6515	0.00	6515	0.00
6015	0.00	6015	0.00
5515	0.00	5515	0.00
5015	0.00	5015	0.00
4950*	0.00	4950*	0.00
4821**	0.00	4735**	0.00
4680	52.06	4680	51.737
4500	51.32	4500	50.332
4300	50.57	4300	49.687
3900	48.56	3900	48.921
3500	46.59	3500	47.523
3200	45.55	3200	46.619
2800	43.41	2800	45.385
1550	39.48	1550	42.487

*Initial reservoir pressure ** Dew point pressure

*Retrograde liquid dropout = (Liquid dropout volume at pressure P/ Total volume at dew point pressure)*100*



(a) **(b)**

Fig. 2: CCE Retrograde liquid dropout plot for (a) sample A and (b) sample B

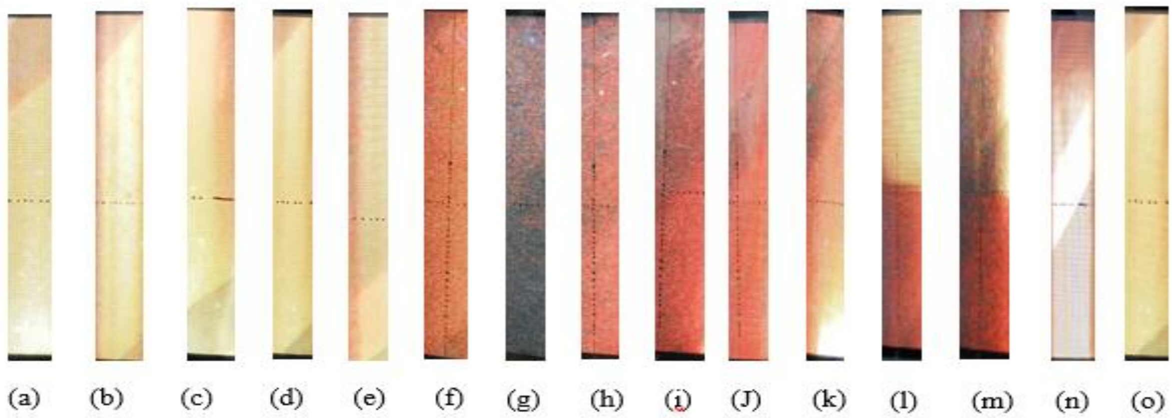


Fig. 3: Critical opalescence phase behaviour phenomena in the Constant Composition Expansion experiment at 101.7 ^{0}C

(a) 7015 psia (b) 6515 psia (c) 6000 psia (d) 5500 psia (e) 5000 psia (f) 4950 psia (g) 4820.5 psia (h) 4680 psia (i) 4500 psia (j) 4300 psia (k) 3900 psia (l) 3500 psia (m) 3200 psia (n) 2800 psia (o) 1550 psia

4. Conclusion

From the experimental results presented in Tables 1 and 2, the following conclusions can be deduced:

1. The two (2) reservoir fluids have C_{7+} mole percent < 12.5 %. This indicates that both fluids are gaseous at reservoir conditions.
2. The fluids under study have the lowest initial producing gas-oil ratio (GOR) compared to other gaseous reservoir fluids (dry gas, wet gas, lean and rich gas condensates)
3. Both fluids have maximum liquid dropout (LDO) > 45 %. This confirms that they are both near-critical gas condensates.
4. Both fluids also exhibit opalescence phase behaviour as well as double retrograde condensation during depressurization below dew point pressure.
5. No commercial PVT software is able to reliably predict the properties of these fluids, hence further improved techniques is recommended in modelling the fluid properties in the near-critical region.

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