SIMULTANEOUS CONSTRUCTION OF PHASE DIAGRAM AND HYDRATE EQUILIBRIUM CURVE FOR AN IRANIAN GAS CONDENSATE RESERVOIR

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ARTICLEINFO

ABSTRACT

Constructing phase diagram and its subsequent quality lines for gas condensate reservoirs are always demanding but challenging problem in reservoir fluid experimental studies. Phase diagram and quality lines for gas condensate systems defines regions of gas and gas-liquid condensates through phase diagram and this is frequently used as a short-cut method by reservoir engineers to determine reservoir fluid phase behavior in each operating pressure and temperature condition. Moreover, gas production units sometimes are imposed by solid hydrate formation problem due to spatial combination of producing water and gas molecules and to some extent this phenomena complicates fluid phase conditions dramatically. This experimental research introduces simultaneous studying of reservoir fluid phase diagrams parallel with experimental constructing of hydrate stability curves in order to depict different regions of gas, liquid condensate and solid hydrates throughout of phase diagram region. To do so, phase diagram and hydrate stability curve constructed and merged together for an Iranian gas condensate sample and newly obtained curve interpreted completely and different regions of gas, liquid condensate, gas- liquid condensate and solid hydrates regions were pinpointed experimentally.

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NOMENCLATURE

bbl	Barrel
CCE	Constant Composition Expansion
EOS	Equation of State

MMscf	Billion standard cubic feet
P	Pressure (Psia)
T	Temperature (F)
V	Volume (cc)
W	water
L_{HC}	Liquid hydrocarbon
GAS_{PH}	Gaseous Phase(Hydrocarbon Gas+ vapour)
LW	Liquid Water
H	Hydrate
Ice	Solid ice

1. INTRODUCTION

Phase diagrams of hydrocarbon systems always depict phase behaviour of hydrocarbon fluid systems at different pressure and temperature [1]. The main borderline of phase diagram always separate two phase conditions from monophasic criteria. In other words, pressure and temperature conjugates inside the phase diagram correspond to two phase flow region and contour lines in this area are so called quality lines which are drawn to show liquid drop quantities at different pressure and temperature [2]. The critical Point in a phase diagram is an indicator to show the type of fluid. In a gas condensate reservoir, the initial reservoir condition is in the single phase area to the right of the critical point in phase diagram. As reservoir pressure declines, the fluid passes through the dew point and a liquid phase drops out of the gas. The percentage of vapour decreases, but can increase again with continued pressure decline. Presence of heavier components (C4-C7+) expands the phase envelope, so that the reservoir temperature lies between the critical point and cricondentherm in gas condensate reservoirs. Figure 1 shows the typical phase diagram of gas condensate reservoir fluid. As long as reservoir is produced, formation temperature usually doesn't change, but reservoir pressure decreases.
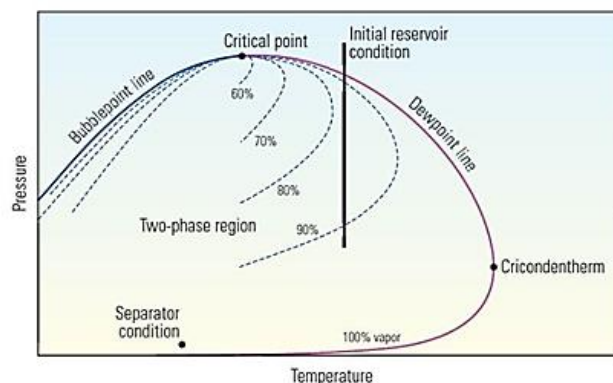

Figure 1: Typical phase diagram of gas condensate reservoir fluid (after [3]).

When the pressure in a gas condensate reservoir decreases to dew point pressure, a liquid phase rich in heavy ends drops out of solution; the gas phase is slightly depleted of heavy ends. As shown in Figure 1, a continued decrease in pressures leads the volume of the liquid phase up to a maximum amount, liquid volume then decreases. When pressure decreases at reservoir temperature, a rich gas forms a higher percentage of liquid than a lean gas. This behaviour can be displayed in a Pressure Volume Temperature (PVT) diagram. Typically a gas condensate system yields from about 30 bbl of condensate per MMscf of gas for lean gas condensate to 300 bbl of condensate per MMscf of gas for

rich gas condensate [3,9].

One of the most important steps in better performance prediction of gas condensate reservoirs is accurate phase behaviour modelling. The phase behaviour of gas condensate mixtures has been extensively studied and reported in literature [4,7]. However, depicting phase diagrams to show phase behaviour, with correspondent quality lines for very high lean gas condensate reservoir fluids is really cumbersome and time-consuming [8].

Moreover, gas condensate production units sometimes suffer from solid hydrate formation in special operating pressures and temperatures due to spatial combination of reservoir connate water and gas molecules. Therefore, this problem necessitates experimental pinpointing of three phase regions of gas, liquid condensate and solid hydrates throughout constructed phase diagram. This study aims to simultaneous constructing of phase diagram and hydrate stability curve for an Iranian lean gas condensate in order to pinpoint fluid phase criteria in each operating temperature and pressure. Combining experimental phase diagram and hydrate equilibrium curves yields to introduce and pinpoint different regions of gas, liquid condensate and solid hydrates in each operating pressure and temperature.

2. EXPERIMENTAL SECTION

2.1 EXPERIMENTAL PROCEDURE FOR CONSTRUCTING PHASE DIAGRAM

In PVT laboratories, different pressure depletion tests are designed and performed in order to monitor thermodynamic properties changes respect to reservoir pressure declination imposed by production scenarios. Each experiment should mimic some real phenomena of reservoir production. Constant Composition Expansion (CCE) or Constant Mass Expansion (CME) test is carried out in virtually all PVT studies irrespective of fluid type. To do so, fixed amount of monophasic subsurface sample or recombined surface sample is transferred into a PVT cell and brought to reservoir temperature and a pressure above the reported initial reservoir pressure. After that pressure is declined gradually and then fixed in some pre-designed pressure steps and fluid parameters such as liquid condensate volume, gas volume, compressibility and densities are recorded very precisely for each pressure step manually or automatically.

The number of pressure reduction steps and the total pressure range covered is generally determined by consultation between the Engineer who commissions the study and the laboratory personnel. For a black oil or volatile oil, the transition from single to a two-phase System is apparent in the plot. For gas condensates the separation of the liquid phase is not readily apparent from the experimental volumetric data and it must be determined visually.

It should be remind that this process is started from one phase condition of real gas condensate sample and phase changes continuously recorded by taking some snapshots from inside the PVT cell periodically. Dew point pressure is one of the most important output parameters of CCE experiment. Dew point pressure is measured by looking inside the PVT cell during pressure depletion process in conventional PVT cells or interpreting recorded pictures during CCE experiment in modern PVT cells. The CME experiment may also be carried out at other temperatures in addition to the reservoir

temperature to help model the producing conditions for subsequent process calculations.

As mentioned above, saturation pressure test was done at pre-defined temperatures so that borderline of the phase diagram could be kept tracked and pinpointed very precisely. Measuring dew point pressure at each temperature led to find a conjugate of pressure and temperature and after finishing of dew point pressure tests, a bunch of pressure and temperature conjugates were obtained.

Table 1 shows the components of reservoir fluid in which the C7+ molar mass in this sample is about 111.9 g/mol. The cricondentherm and cricondenbar points of this sample were measured about 305oF and 3420 psia respectively. Finally all the saturation pressure data were inserted in reservoir fluid simulation software and borderline of the phase diagram were continuously drawn using a well-known reservoir fluid simulator.

Second part of the PVT experiments was allocated to measure experimental data needed for generating quality lines. Hence, some constant composition expansion or CCE experiments were designed and done at pre-defined temperatures. Briefly, CCE experiments is done in order to monitor thermodynamic parameter changes i.e. condensed liquid drop-outs due to pressure depletion process. To do so, CCE experiments were done at five different temperatures and the results showed condensed liquid volumes respect to pressure changes at each predefined temperature.

A magnified snapshot of a typical liquid drop-out formation through CCE experiment has been shown in Figure 2. The results of the CCE experiments were used to generate candidate quality lines. it should be noted that the experimental set up to do PVT tests in this study was designed and developed in DBR-Canada in 2005 which is shown in Figure 3 and all the experimental parts have been calibrated in accompany with DBR experts. It should be remind that calibration tests have been periodically repeated by some skilful technician in lab and it can be claim that quality of all experimental data has been checked many times by teamwork members. This experimental set up is under commercial services for many important phase behaviour studies projects for internal and international companies since 2005.

The visual capability of the hydraulic experimental set up enabled us to measure the hydrate phase equilibrium curve using a high pressure visual cell. The routine procedure for measuring them has already been done through fixed volume pressure depletion. To do so, the hydrocarbon fluid to be tested is introduced to cell and at the same time the cell volume is increased until a desired pressure and volume could be attained.

An HPLC pump is then used to inject water into the base of the cell. While the cell content is being mixed, temperature is lowered to form hydrates. The formation of the hydrates caused a rapid decline in pressure dramatically. Cell temperature is then raised stepwise, allowing at least 3 hours for equilibrium to be reached at each temperature. Temperature and pressure are logged continuously and equilibrium data is plotted on a scatter-gram. The point at which the slope of pressure versus temperature sharply changed is considered as hydrate dissociation point. But visual capacity of the hydrate experimental set up enabled us to measure hydrate formation temperature in each fixed pressure step. In other words, during the experiment tests pressure was kept constant and three different steps were considered to pinpoint hydrate formation temperature with acceptable accuracy. The experimental procedure for determining conjugates of hydrate formation pressures and

temperatures has been described through the following steps:

1-Cooling down and heating up the mixture of connate water and gas sample in a visual cell, just to sub-cool and melt hydrates respectively. During this step, hydrate formation temperature and melting temperature are measure by monitoring visual hydrate cell with +/-1℃. Once forming hydrate, temperature of the cell should be adjusted close to melting temperature to keep hydrate seeds in the water.

2-Sett temperature 4-5℃ below formation temperature and holding this temperature until the time that corresponds to crystal growth (crystal growth effect). Once confirming this part set the temperature back to within 2℃ of the suspected melting temperature immediately. Then, increase the temperature in 0.5℃ steps holding for about 15 minutes after the temperature is stable to confirm that there is no melting. Continue this process until melting is confirmed. Melt most but not all of the hydrate.

3. Set the temperature 2-3℃ below the formation temperature and hold until one can see crystal growth. Once confirming that crystals are growing, set the temperature back to within 2℃ of the suspected melting temperature immediately. Then increase the temperature in 0.2℃ steps holding for about 15 minutes after temperature is stable to confirm that there is no melting and this process should be continued until melting is confirmed.

3. SIMULATION PROCEDURE

Winprop-CMG is a well-known reservoir simulator which is able to predict reservoir fluid phase behaviour based on PVT experimental data. The point is that using reservoir simulators without any precise experimental data is really useless. Therefore it was already tried to measure experimental data as accurate as possible [10].

To perform simulation procedure, CCE experimental data i.e. liquid drops-out volume versus pressure were inserted in regression process of the software in order to tune an EOS for each reservoir fluid and after that some new liquid drop outs data versus pressure and temperature were generated. Hence, the number of reliable liquid drop-outs data versus pressure and temperature were increased considerably and there was possibility of experimental keep tracking of quality lines by interpolating and extrapolating between liquid drop data [11].

Table 1. Reservoir Fluid component.

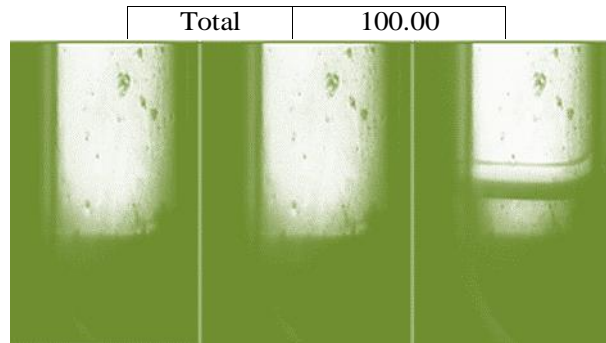| Component	Reservoir Fluid
N_2	5.27
CO_2	0.37
H_2S	0.0005
C_1	86.44
C_2H_6	4.36
C_3	1.47
iC_4	0.33
nC_4	0.45
iC_5	0.21
nC_5	0.15
C_6	0.22
C_{7+}	0.73

Total	100.00

Figure 2: Snapshot of liquid drop-out forming process for lean gas condensates.

Figure 3. PVT apparatus used in this study.

Table 2. 0.5% Vol. Liquid percent.

Pressure(psia)	Temperature(F)
560	15
560	40
580	72
680	104
1100	140
1400	152
1700	155
2950	15
3080	40
3150	72
3020	104
2600	140
2100	155

3.1 CONSTRUCTION OF QUALITY LINES USING EXPERIMENTAL-SIMULATION PROCEDURE

The proposed method involved combination of experimental and simulation data to generate candidate quality lines. To do so, all volumetric liquid drop-outs percent of CCE experiments and simulation process were listed versus pressure and temperature. Finally pressure and temperature conjugates of the same volumetric liquid drop-out percents i.e. 0.5%, 0.7% and 1.3% were picked among all experimental and simulation data. To match the experimental data with simulation values, the Soave-Redlich-Kwong (SRK 1978) equation of state is used. The matching parameters to tune experimental and simulation data were selected as critical pressure (Pc), critical temperature (Tc), acentric factor and also volume shift factor. Smoothed experimental and simulation data have been gathered in Tables 2, 3 and 4 and final construction of quality lines based on achieved

experimental-simulation data has been depicted in Figure 4.

Table 3. 0.7% Vol. Liquid percent.

Pressure(psia)	Temperature(F)
760	15
760	40
780	72
950	104
1250	130
1600	140
1800	142
2750	15
2880	40
2900	72
2700	104
2400	130
2100	140

Table 4: 1.3% Vol. Liquid Percent

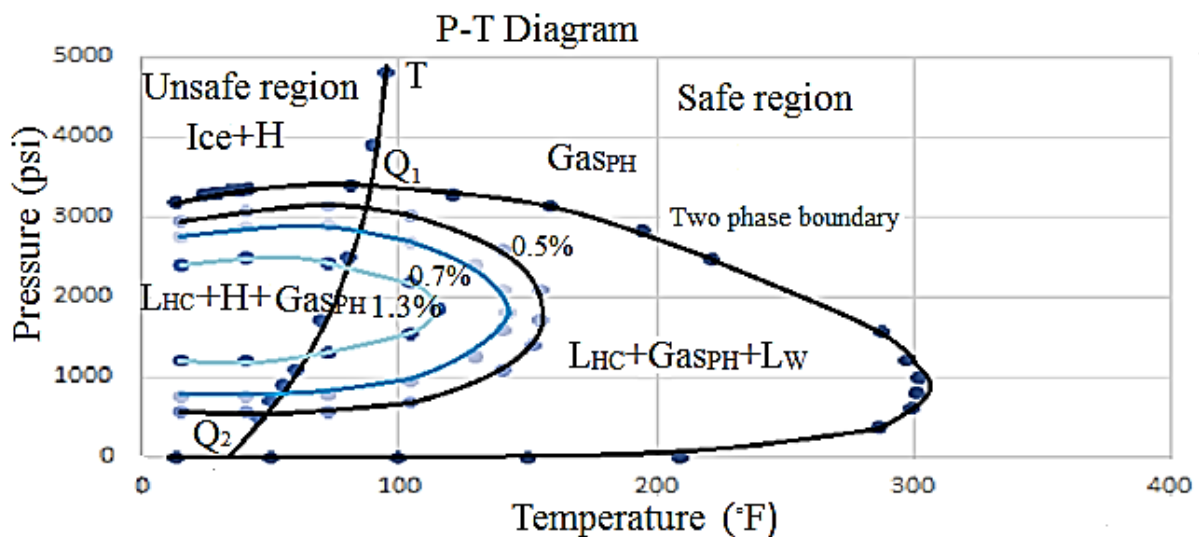| Pressure(psia)	Temperature(F)
1200	15
1200	40
1300	72
1550	104
1850	115
2400	15
2500	40
2430	72
2200	104

Figure 4: Pressure-temperature phase diagram for multicomponent gas condensate systems.

3.2 EXPERIMENTAL SET-UP FOR CONSTRUCTING HYDRATE STABILITY CURVE

The high-pressure visual cell was used to measure the hydrate formation conditions in a static condition. The experimental set up mainly consisted of a high-pressure visual cell. The maximum working pressure and temperature of the high-pressure visual cell was around 1000 Atm and 300°C, respectively. It has been made in Canada by DBR Oil Phase Company.

The high pressure cell has been connected to a high pressure hydraulic pump and therefore the pressure of the cell could be controlled by injecting and withdrawing the hydraulic fluid to the hydraulic side. On the other hand, the high-pressure cell could be stabilized by a digital temperature controller very precisely. The internal volume of high pressure cell was divided into two separated parts. They were separated from each other by a sealed piston. One side of the piston was connected to the hydraulic pump and the other side had been filled with the gas sample and connate water.

In this experimental research, total volume of the visual cell was 100cc and about 25cc of this volume was filled by connate water and the rest (75 cc) was filled by gas reservoir sample. As a rule of thumb, the ratio of connate water volume respect to gas sample volume was 1 to 3 volumetrically. To perform the experiments, the high pressure visual cell was thoroughly cleaned and evacuated before being filled with the sample. The hydrocarbon fluid to be tested was introduced to the cell and at the same time the cell volume was increased until the desired pressure and temperature was attained. A high-pressure pump was then used to inject water into the base of the cell [7].

4. SIMULATION SOFTWARES FOR ESTIMATING HYDRATE STABILITY CURVE

Before experimental measuring the hydrate formation conditions, it is necessary to have an estimate about hydrate formation temperatures in each pre-defined pressure. To do so, we used in-house hydrate simulation software in order to predict the hydraulic formation temperature in each operating pressure.

The hydrate simulation software is user-friendly software and this is able to simulate and predict the hydrate formation conditions with and without using inhibitors. It can predict incipient hydrate formation potentials using detailed algorithm based on a statistical thermodynamic model. The software has been developed form a calculation scheme suggested by Parrish and Prausnitz and this has been modified and extended by Robinson. The Peing Robinson equation of state is used for all property calculations through the structure of the simulator. Before measuring the hydrate formation temperature in each specific pressure, it was necessary to have a rough estimation using available hydrate simulation software.

5. RESULT AND DISCUSSION

The phase behaviour of gas hydrates considerably changes depending on the size and chemical nature of guest molecules. The relationship between microscopic structure, just described, and macroscopic hydrate phase properties can be better understood through the study of phase diagrams. A brief description of phase diagrams for multicomponent systems is thus provided to gain a fundamental insight into the phase equilibrium of hydrate forming systems. The phases are separated by phase boundaries, where phase transitions occur.

Tables 1, 2 and 3 include combination of experimental and simulation data for three important quality lines of the phase diagram and Figure 4 depicts final construction of phase diagram simultaneous with three candidate quality lines. According to the Figure 4, quality lines are really scattered inside the phase diagram since liquid drop volumes are really small in two phase region for

lean gas condensate fluids. In this study three quality lines i.e. 0.5%, 0.7% and 1.3% volumetric percent were constructed using the proposed experimental-simulation method. Needless to say that other quality lines could be roughly interpolated or extrapolated using the available quality lines data. The most important experimental observation of this study is that quality lines in lean gas condensates converge with each other at very low temperature and this temperature is somehow allegorical. In other words, critical points of these fluids could not be detected experimentally due to exclusive phase behaviour of gas condensate reservoir fluids and this only can be estimated by allegorical extrapolating of accessed quality lines.

Depending on pressure and temperature conditions, four stability regions are defined in Figure 4. At high pressures and low temperature, crystallization occurs and the water ice and hydrate (Ice + H) zone appears. At low pressure and low temperature liquid hydrocarbon, hydrate and gas phase including hydrocarbon gas and vapor (LHC + H+ GasPH) zone is formed. The line Q1T separates the region in which water ice and hydrate (Ice + H) exist from the part in which gas phase (GasPH) exist. The line Q1Q2 separates the area in which liquid hydrocarbon, hydrate and gas phse (LHC + H + GasPH) exist from the area in which liquid hydrocarbon, gas phase and liquid water (LHC + GasPH + LW). Point Q1 is a quadruple point. At Q1, four phases are in equilibrium: liquid water, liquid hydrocarbon, gas phse, and solid hydrate. Q2, which occurs at low temperature and zero pressure, is also a quadruple point representing the point at which ice, hydrate, liquid water, and gas condensate exist in equilibrium.

6. CONCLUSION

Due to small amounts of liquid drop-outs in lean gas condensates at reservoir conditions, full experimental constructing of phase diagram and its relevant quality lines is almost impossible for lean gas condensates fluids. Also tuned EOS models of reservoir fluid softwares are often unable to estimate condensed liquid drop-outs at different pressures and temperatures for lean gas condensates. On the other hand, an efficient phase diagram reflects some of the most important production criteria i.e. operating pressure and temperature in surface facilities to achieve optimum production. Therefore the unique procedure introduced in this paper presents a reliable experimental procedure for constructing phase diagrams and correspondent quality lines for lean gas condensates. It should be remind that increasing the number of CCE experiments helps to increase the accuracy of quality lines tracks considerably since the numbers of experimental points are increased and interpolating between experimental points will be more accurate. On the other hand, measuring the hydrate formation temperature in specified pressure led to determine the conjugates of hydrate formation pressure and temperature. Afterwards, the hydrate formation points were depicted for each reservoir fluid sample. Using the experiments, hydrate three phase equilibrium curves were constructed in order to depict safe and unsafe regions of hydrate formation zones.

Also, the results showed that the experimental data are reasonably in good agreement with the simulator results. As it was expected, hydrate zone was detected at high pressures and low temperatures (above the stability curve) and the safe zone (below the stability curve) was depicted at low pressures and high temperatures for each reservoir gas sample. Using the results of the stability

curves, one can determine the possibility of the hydrate formation in different temperatures and pressures. In other words, the stability curves can be used as a rule of thumb in order to design the field operating conditions within the hydrate free zone. Also, determining the hydrate formation conditions using the visual hydraulic experimental set up is a time economizing method to construct the hydrate phase equilibrium curve. Results of the simulation and the experiments are reasonably in good agreement with each other and combining these two experimental curves yields to pinpoint different regions of gas, liquid condensate and solid hydrates in each operating pressure and temperature.

7. AVAILABILITY OF DATA AND MATERIAL

Information used and generated from in this work is available by contacting the corresponding author.

8. ACKNOWLEDGEMENT

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