Journal of
Applied Sciences

Measurement and Phase Behavior Modeling (Dew Point+Bubble Point) of CO₂ Rich Gas Mixture

[1]Qazi Nasir, [2]K.M. Sabil and [1]Khashayar Nasrifar

[1]Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar,
Tronoh, Perak, 31750, Malaysia

[2]Phase Separation Laboratory, Research Center of CO₂ Capture, Universiti Teknologi PETRONAS, Malaysia

Abstract: Dew point and bubble measurements is carried out using Hydreval and PVT equipment. Experimental data for both dew and bubble point is collect with temperature ranges from -20 to 5°C with pressure of 0 to 10 MPa. Mathematical model based on cubic PR Equation of State (EOS) couple with van der Waals classical mixing rule is applied to these experiment data points, A comparison shows a close match between experimental data point and model prediction with low (%) AADP.

Key words: Dew point, bubble point, Peng-robinson

INTRODUCTION

Natural gas is most powerful, attractive and most vital supply of energy in the world obtained from underground reservoir by the decomposition of organic materials in plants and animals. Natural gas in dry form is purely methane along with other heavier hydrocarbons like ethane, propane, iso-butane, n-butane (AspenTech, 2013 o-ENREF-3). In a raw state, it often contains a considerable amount of non-hydrocarbons like nitrogen, and carbon dioxide, few traces like hydrogen, helium, carbonyl sulphide and various marceptanes are also present. Table 1 contains composition of typical some raw gases.

Natural gas has been consumed as heating source both in industrial and commercial sector. For producing electricity it ranked second after coal having an edge over coal because of its clean burning ability (Alonso, 2010). Other core uses of natural gas are fuel for vehicles and transportation. In the world, Russia has the largest natural gas reserves estimated about 1680 Trillion Cubic Feet (Tcf), covering 30% of world natural gas reserves (Ndefo *et al.*, 2007). Iran holds the world second largest natural gas reserves estimated almost 1000 Tcf (Omidvar, 2007). Qatar rank third in proven natural gas reserves estimated 910 Tcf (EIA, 2008). Among north American countries like Canada, Mexico and USA, United states covers 3% of world natural gas reserves (6th in the world) estimated about 200 Tcf. Canada with 57.9 Tcf natural gas reserves proves to be the 2nd largest natural gas producers in western hemisphere after US. Among southeast Asian economies Malaysia has the largest of natural gas reserves and third amongst Asia Pacific economies and these reserves would be sufficient to last around 43 years with current production rate (Anonymous). In natural gas, non-hydrocarbon gases (CO_2, N_2, and H_2S) can account between 1 to 99% of overall composition (Fong *et al.*, 1996; Avila *et al.*, 2002). With Carbon dioxide (CO_2) presence in natural gas, not only reduces the energy content but because of its acidic property, causing corrosion in pipeline especially with the presence of water. Stringent safety measures are adopted for demonstrating the behavior of non-hydrocarbons gas like CO_2 and H_2S with in the process equipment and in the pipeline. Solid formation e.g., solid CO_2 (Dry ice), hydrate formation in the pipeline not only cause blockage in the pipeline, process equipment but also indulge in the plant shutdown and other safety hazards. CO_2 composition in natural gas varies with different geographical locations, high carbon dioxide (CO_2) concentrations are encountered

Table 1: Typical raw natural gases composition (UnionGas, 2013)

Components	Typical analysis (mole %)	Range (mole %)
Methane	95.20	87.0-96.0
Ethane	2.50	1.5-5.1
Propane	0.20	0.1-1.5
i-butane	0.03	0.01-0.3
n-butane	0.03	0.01-0.3
i-pentane	0.01	Trace-0.14
n-pentane	0.01	Trace-0.04
n-hexane	0.01	Trace-0.06
Nitrogen	1.30	0.7-5.6
Carbon dioxide	0.70	0.1-1.0
Oxygen	0.02	0.01-0.1
Hydrogen	Trace	Trace-0.02

Corresponding Author: K.M. Sabil, Phase Separation Laboratory, Research Center of CO₂ Capture,
Universiti Teknologi PETRONAS, Malaysia Tel: +6053687684

in diverse areas including South China Sea, Gulf of Thailand, Central European Pannonia basin, Australian Cooper-Eromanga basin, Colombian Putumayo basin, Ibleo platform, Sicily, Taranaki basin, New Zealand and North Sea South Viking Graben. The composition of CO_2 can reach as high as 80% in certain natural gas wells such as wells at the LaBarge reservoir in western Wyoming and the Natuna production field in Indonaisa (Kariznovi *et al.,* 2011). Besides, purged gas from a gas-re-injected EOR (Enhanced Oil Recovery) well can contain as much as 90% CO_2. Malaysia is one of major natural gas producers and exporters of natural gas in the world with estimated reserve of 88.0 tscf. These reserves are located at off shore Sarawak (48%), offshore East coast of Peninsular Malaysia (38%) and the remaining at offshore Sabah (14%). These large gas reserves are sufficient to last around 36 years with current production rate. Unfortunately, some of these reservoirs contain very high CO_2 level, as high as 87% in K5 field (Anonymous). This high amount of CO_2 coupled with the deep-water conditions pose new problems for the exploration and production of natural gas including the estimation of the type of the gas in the reservoir, the deep-water transportation of the gas , separation of the CO_2 from the natural gas and storage of CO_2 produced. PETRONAS currently produces about 2 billion SCFD of natural gas in Peninsular Malaysia with their gas plants tolerant to CO_2 content of approximately 8%. These gas plants utilize Benfield process capable to reduce the CO_2 content down to the sales gas specification 60-100 mg m^{-3} (Vinci Technologies, 2013a). With increasing demand PETRONAS, needs to exploit their natural gas reserves with high CO_2 content up to 80%. These untapped gas reserves could significantly meet future gas demand with the capacity of equivalent to 38 years of current production rate (PETRONAS, 2012). However, the current proven technology that is commercially available and economically viable for efficient removal of CO_2 from natural gas to pipeline and cryogenic quality natural gas is only limited to low CO_2 concentration of up to 20%. The available technology limitation is due to some critical issues in the processing of high CO_2 natural gas. CO_2 in the presence of water is highly corrosive which requires special material for handling and transportation. The heating value of natural gas reduces as CO_2 content increases. Moreover, high CO_2 natural gas is more vulnerable to gas hydrate formation which causing blockage in pipeline and upstream processes provided conditions of temperature and pressure suitable for hydrate formation. Without the removal of CO_2, natural gas cannot be further processed, liquefied, transported and commercially sold (Alonso, 2010). Such challenge and

its further estimation, necessitates the importance of phase behavior study of the system, where phase envelope is used to classify either the gas is retrograde gas wet or dry gas. The estimation on the amount of condensate produced from natural gas is also depended on phase behavior of the gas at reservoir condition. Each one of these factors has significant implications on the design of wellbore for exploration of the natural gas. Therefore, accurate representation of the gas and its behavior is required. In transportation, the behavior of the natural gas in the pipeline is important to avoid operation issues such as blockage and corrosion. Currently most of the phase behavior data available in literature for natural gas system is limited to very low concentration of CO_2 (less than 5%). Since phase behavior is very much affected by concentration of components in the systems, these phase equilibrium data is no longer valid for high CO_2 systems. Therefore, studies must be conducted to measure the phase behavior of high CO_2 content natural gas and model must be developed from these data for accurate prediction of phase behavior of the high CO_2 content natural gas. Mathematical model used is based on Peng-Robinson (PR) equation of state (EoS) couple with van der Waals classical mixing rule with improved Binary Interaction Parameter (BIP) (Peng and Robinson, 1976; Avila *et al.*, 2002).

This proposed research work is planned to provide the phase equilibrium data and a model that can accurately predict the phase behavior of natural gas with high CO_2 content. In this proposed work, systematically phase measurement both dew and bubble points have conducted at different pressure, temperature and composition of the natural gas. The range of pressure and temperature selected is based on the pipeline and surface condition of natural gas production. Based on the obtained data, a model will be developed for a high precision phase behavior modeling for high CO_2 natural gas systems.

MATERIALS, APPARATUS AND METHODS

Materials: CO_2 rich natural gas of different composition was purchased from Gas Walker SDN BHD with cylinder capacity of 10 L, Gases are filled at 45 bar and 0.6 m^3 volume. The cylinder is provided with two stages-HP regulator with an outlet pressure of 18 bar. The gas compositions used in this study is stated in Table 2.

Apparatus
Hydreval (Gas hydrate study system): A complete instrument designed mainly to determinate vapor-liquid-hydrate equilibrium condition. In other words it is used to

Table 2: SNG composition used in this study

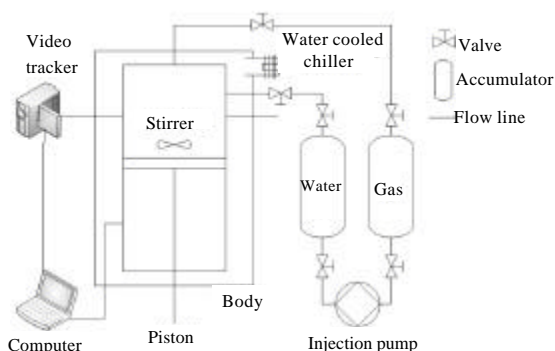| Components	Composition (mole frac)		
	SNG-A	SNG-B	SNG-C
CO_2	69.14	69.37	70.3
Nitrogen	3.10	3.10	3.1
Methane	26.20	26.30	26.6
Ethane	0.93	0.94	-
Propane	0.29	0.29	-
Iso-butane	0.17	-	-
n-butane	0.17	-	-

Fig. 1: Schematic diagram of Hydreval equipment used in this study

identify thermodynamic stability of hydrates. Based on the motor driven PVT equilibrium cell, where cell has maximum capacity of 80 cm³ with maximum operating pressure is 20 Mpa and temperature ranges from -20 to 150°C. A magnetic stirrer is provided for homogenous agitation of fluid sample. Temperature, pressure, volume is recorded in every 2 sec with accuracy of 0.1 K, 0.01 MPa and 0.001 cm³, respectively (Vinci Technologies, 2013bo-ENREF-18).

A camera device is also attached for capturing picture in regular interval. A Hydreval schematic is shown in Fig. 1.

PVT equipment (Fluid eval for PVT study): In this study, Fluid Eval used for measurement is similar to the one used by Kariznovi *et al.* (2011). A schematic diagram of PVT equipment used in this study is shown in Fig. 2. Phase behavior study of hydrocarbon is carried out at various conditions of temperature and pressure. Maximum operating pressure of the equipment is 10 MPa, and temperature ranging from -20 to 175°C, the cell has a volume of 200 cc with a visual volume is 100 cc. Temperature , pressure and volume is recorded with accuracy of 0.5°C , 0.1% full scale and 0.01 mL. Fluid Eval offers full sample visibility from front and back windows with a camera device for recording sample picture in regular intervals (Vinci Technologies, 2013b).
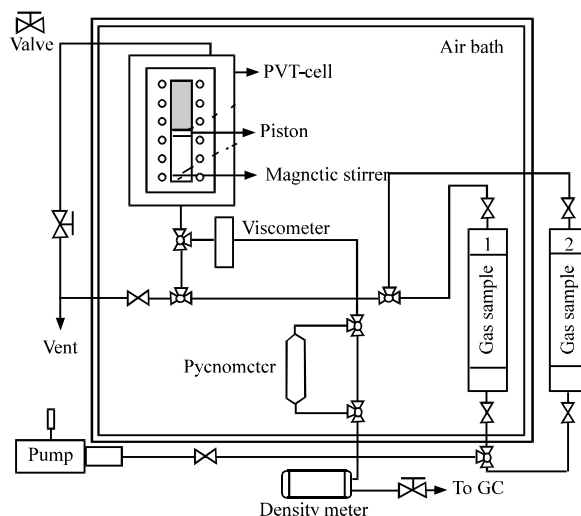

Fig. 2: Schematic diagram of PVT equipment similar to the one above is used in this study

Methods

Measurement of bubble point using PVT equipment: In this study, the mercury free fluid Eval Analyzer is used for phase behavior measurement of Hydrocarbon fluids at reservoir conditions of pressure and temperature. The PVT cell has full sample visibility through front and back windows. Bubble point measurements for high CO_2 natural gas will be measured by using a synthetic method. A known composition sample will be placed in an equilibrium cell (PVT) and the system will be allowed to be at either isothermal or isobaric condition until the system contains gas phase is converted into liquid phase. Then, the pressure of the system was decreased in small steps and any changes on the phases available in the system will be monitored. This step will be at the rate of 0.2°C h⁻¹ or 0.01 Mpa h⁻¹. The slow process of changes is required so that an equilibrium condition will be achieved at every condition imposed on the system. The first point where a gas phase appears or disappears is taken as an equilibrium points or bubble point. A series of these bubble points are achieved at different temperature or different pressure.

Measurement of dew point using hydreval: In this study, Hydreval is used to find the equilibrium points (Dew points) for CO_2 rich synthetic gas mixture. Hydreval is equipped with PVT cell designed particularly to find the thermodynamic stability of hydrate but in this study it is used for dew point measurement by observing visually, the disappearance of last drop of liquid. The sample to be tested in placed in the equilibrium cell, and using either isobaric or isothermal process to change the gas phase

into liquid phase. In this study, the system pressure is decreased where all the liquid phase is disappearing into gas phase and the point where last droplet of liquid is disappear is taken as dew point . Similarly, for different temperature the same process is performed and various data for dew point is gathered.

THERMODYNAMIC MODELING

In the study the model used to evaluate the work is based on Peng-Robinson (PR) cubic Equation of State (EOS) (Peng and Robinson, 1976). The equation can be written as follows:

$$P = RT/(V-b)-\alpha/(v(v+b)+b(v-b))$$

with:

$$\alpha = \alpha.\alpha_c, \alpha = 0.45724. (RTc)^2/P_c$$

$$m = 0.374646+1.54226\omega-0.26992\omega^2$$

$$\alpha = (1+m(1-T_r0.5))^2$$

$$b = 0.07780 (RT_c)/P_c$$

where, P is the pressure in MPa, T is the temperature in°C, R is the gas constant, a and b are the attractive and co-volume parameters, v is the molar volume, Tc, Pc and ω are the critical temperature, pressure and acentric factor. For mixture of gas, mixing rule is employed, in this study van der Waals one fluid mixing rules (vdW1f) is used, which is written as follows:

$$\alpha = 1_i \equiv \Sigma_j \equiv \llbracket x_i \, x_j \, \alpha_{ij} \rrbracket$$

$$\alpha_{ij} = 1(\alpha_i \, \alpha_j \, (1-k_{ij}))$$

$$b = 1_i \equiv \llbracket x_i \, b_i \rrbracket$$

where, K_{ij} is the binary interaction parameter and collected from literature study (AspenTech, 2013o-ENREF-3).

More detail regarding the mathematical model procedure is mentioned elsewhere (Peng and Robinson, 1976).

RESULTS AND DISCUSSION

Data obtained in experimental measurement for SNG-A gas mixture is plotted against the thermodynamic mathematical model, as shown is Fig. 3. A series of data
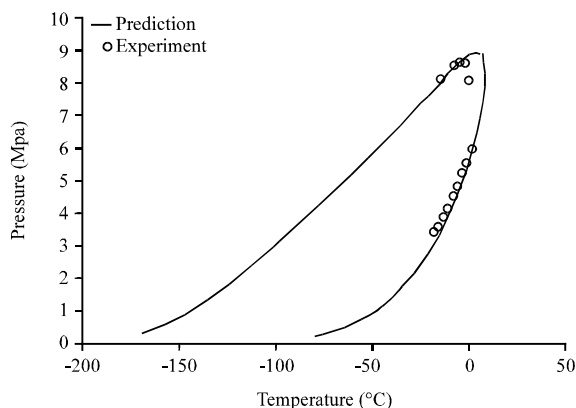

Fig. 3: Comparison between model prediction and experimental data point, (-) PR-EOS, experimental results of SNG-A
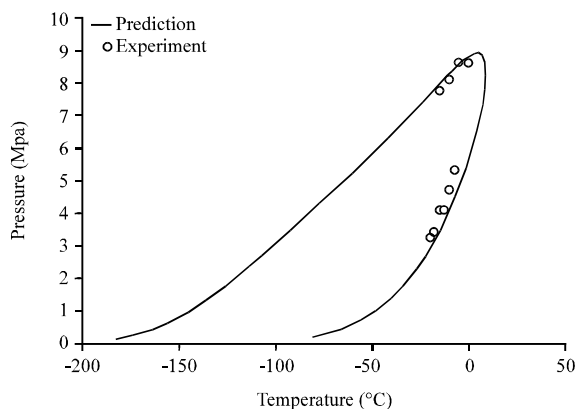

Fig. 4: Comparison between model prediction and experimental data point, (-) PR-EOS, experimental results of SNG-B

point is measured with dew point experiment using Hydreval, and few bubble points were measured with fluid Eval PVT. Similarly, SNG-B and SNG-C data points measured is shown in Fig. 4 and 5. Due to equipment temperature limitation, we cannot gather data point below -20°C and only able to measure some bubble point nears the critical point. Due of complex nature and instability of the compounds at their critical point (Gamba *et al.*, 2009), experimental data is difficult to obtained. Also at critical point the equilibrium phase becomes identical and it is very difficult to differentiate between gas and liquid phases (Kolar and Kojima, 1996). Percentage average absolute deviation for pressure (%AADP) obtained for bubble point and dew point gas mixture is shown in Table 3.

Table 3: %AADP, ADP Results obtained for dew point and bubble point

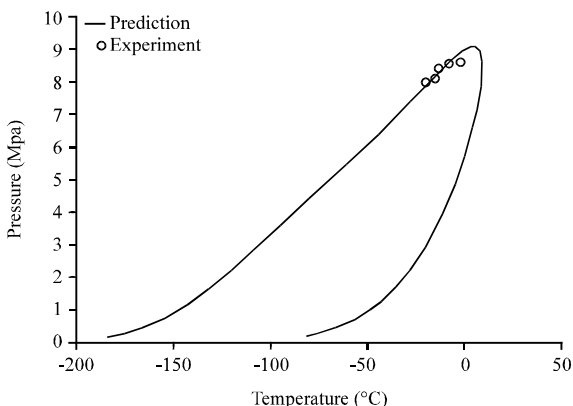| No.	Dew point AAD$_P$ (%)	Bubble point AAD$_P$ (%)
SNG-A	3.48	2.75
SNG-B	11.51	2.99
SNG-C	-	1.52

Fig. 5: Comparison between model prediction and experimental data point, (-) PR-EOS, (™) Experimental results of SNG-C

CONCLUSION

Pressure-temperature (P-T) phase diagram is valuable and can provide information for the design of recovery and processing operations of natural gases at high pressure. The point of interest in this study is focus on dew-point and bubble point measurement together with model based on Peng-Robinson EoS. The EoS is effectively tested and predicated with experimental data points for rich CO_2 gas mixture, prediction results shows close match with experimental data point with minimum AAD$_P$ (%). The term used to calculate AAD$_P$ (%) is given as below (Morch *et al.*, 2006):

$$\% AAD_P = \frac{1}{np} \sum_i^{np} |\%DEV_P|$$

where, %DEV$_P$ is stated as:

$$\%DEV_P = \frac{100\,(P_{cal} - P_{exp})}{P_{exp}}$$

where, n_p is number of data point.

ACKNOWLEDGEMENTS

REFERENCES

Alonso, T.V., 2010. High efficiency on co_2 removal in natural gas with ucarsol solvents. Proceedings of the International Conference on Rio Oil and Gas Expo it is the Largest Tradeshow in Latin America, September 13-16, 2010, Rio de Janeiro, Brazil.

AspenTech, 2013. Experience the new aspen HYSYS®. Aspen Technology Inc., Burlington, MA., USA. http://www.aspentech.com/hysys/.

Avila, S., S.T. Blanco, I. Velasco, E. Rauzy and S. Otin, 2002. Thermodynamic properties of synthetic natural gases: Part 4. Dew point curves of synthetic natural gases and their mixtures with water: Measurement and correlation. Fluid Phase Equilib., 202: 399-412.

EIA, 2008. Qatar holds the world's third largest natural gas reserves and is the single largest supplier of liquefied natural gas. U.S. Energy Information Administration (EIA), Qatar.

Fong, W.S., S.I. Sandler and A.S. Emanuel, 1996. A simple predictive calculation for the viscosity of liquid phase reservoir fluids with high accuracy for co_2 mixtures. SPE J., 1: 243-249.

Gamba, S., G.S. Soave and L.A. Pellegrini, 2009. Use of normal boiling point correlations for predicting critical parameters of paraffins for vapour-liquid equilibrium calculations with the SRK equation of state. Fluid Phase Equilibria, 276: 133-141.

Kariznovi, M., H. Nourozieh and J. Abedi, 2011. Experimental apparatus for phase behavior study of solvent-bitumen systems: A critical review and design of a new apparatus. Fuel, 90: 536-546.

Kolar, P. and K. Kojima, 1996. Prediction of critical points in multicomponent systems using the psrk group contribution equation of state. Fluid Phase Equilibria, 118: 175-200.

Morch, O., K. Nasrifar, O. Bolland, E. Solbraa, A.O. Fredheim and L.H. Gjertsen, 2006. Measurement and modeling of hydrocarbon dew points for five synthetic natural gas mixtures. Fluid Phase Equilibria, 239: 138-145.

Ndefo, E.O., P. Geng, S. Laskar, L. Tawofaing and M.J. Economides, 2007. Russia: A critical evaluation of its natural gas resources. Energy Tribune, February 13, 2007.

Omidvar, H., 2007. Iran's aggressive natural gas expansion plans. Energy Tribune, September 17, 2007.

PETRONAS, 2012. International energy mix shifting to natural gas. http://www.petronas.com.my/our-business/gas-power/wgc/Pages/International-Energy-Mix-Shifting-to-Natural-Gas-.aspx.

Peng, D.Y. and D.B. Robinson, 1976. A new two-constant equation of state. Ind. Eng. Chem. Fundam., 15: 59-64.

UnionGas, 2013. Chemical composition of natural gas. http://www.uniongas.com/about-us/about-natural-gas/Chemical-Composition-of-Natural-Gas.

Vinci Technologies, 2013a. Fluid eval for PVT studies. Vinci Technologies, Rue du Port, Nanterre, France. http://www.vinci-technologies.com/products-explo.aspx?IDM=717433&IDR=113221&IDR2=88545.

Vinci Technologies, 2013b. Hydrates. Vinci Technologies, Rue du Port, Nanterre, France. http://www.vinci-technologies.com/products-explo.aspx?IDR=113221&idr2=88545&IDM=717433%5b.