



MODIFICATION OF KATZ DIAGRAMS IN ALLOWABLE PRESSURE DROP ACROSS A THROTTLE VALVE FOR AVOIDING GAS HYDRATE FORMATION

Mohamadmostafa Owji¹, Jafar Javanmardi¹, Aliakbar Roosta^{1*}, Bahman Tohidi²

¹Department of Chemical, Oil and Gas Engineering, Shiraz University of Technology, Shiraz, Iran

²Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH 14 4AS, United Kingdom

Abstract - One of the first and easiest ways to determine the equilibrium conditions of hydrate formation for gas mixtures is gas gravity method presented by Katz. In addition, based on this fact that pressure depression in a throttle valve is a constant enthalpy process and so the temperature decreases when the pressure of the natural gas decreases, Katz presented a series of curves to estimate the maximum allowable pressure drop before gas hydrate formation. In this communication, the van der Waals and Platteeuw solid solution theory has been used for predicting of hydrate formation conditions. Moreover, using the Peng Robinson equation of state to predict the enthalpy of natural gas in the inlet and outlet streams of throttling valve, the maximum allowable pressure drop curves, have been reproduced. Finally, results of this work have been compared with the Katz curves for maximum allowable pressure drop.

1. Introduction

Gas hydrates are solid crystalline compounds which created from combination of suitable size hydrate former and water. Gas molecules, or guests, trapped into the cages of the water molecules, or hosts, network through hydrogen bonds between water molecules. Usually, it has been assumed that there is no interaction between guest-guest molecules and the guest-host molecules only held together by van der Waals force. Typical of the gas molecules are compounds smaller than pentane such as methane, ethane, propane, or carbon dioxide. Clathrate hydrates were first discovered in 1810 by sir Humphry Davy [1]. He observed that when an aqueous solution of chlorine is cooled to a temperature below than 9 °C, solid material obtained. Then, Faraday [1] in 1823 confirmed the existence of such solid materials and stated that the solid content created from 11 parts water and one part chlorine. Since Hammerschmidt [2] found that the formation of hydrates causes the blockage of gas pipelines, began wide researches to prevent hydrate formation. One of the first and easiest way to determine the equilibrium temperature or pressure of hydrate formation for gas mixtures, is the gas gravity method presented by Katz et al. [3], Fig. 1.

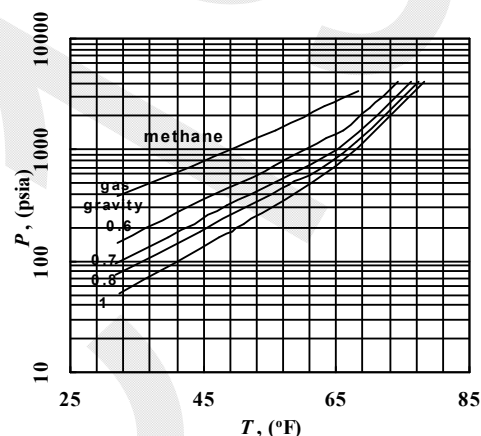


Fig. 1. The gas gravity chart to predict the equilibrium conditions of natural gas presented by Katz et al. [3]

Expansion process is the key process in refrigeration cycles which happen in throttling valve. This process occurs almost at constant enthalpy condition, this process is also called the Joule-Thomson expansion. In this process, gas enters to the valve at a specific temperature and pressure, T_1 and P_1 . After that, the gas pressure reduces to P_2 . The temperature of outlet stream, T_2 , should be specified such the inlet and outlet enthalpies be equal by passing the valve, Fig. 2.

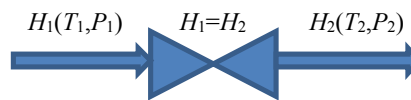


Fig. 2. Schematics of a throttle valve.

The constant enthalpy charts described by Brown [4,5], provide the relationship of temperature versus pressure for gases of various gravities for free expansion. From the cross of the constant enthalpy curves along with Katz gravity charts, the curves of allowable pressure drop to prevent hydrate formation have been obtained [6].

2. Method

Usually, for natural gases, the temperature of the outlet stream will reduce in passing through a throttle valve due to pressure drop and Joule-Thomson effect.

* Corresponding author Email: aa.roosta@sutec.ac.ir

To estimate the maximum pressure drop in a throttle valve before locating in hydrate formation region, two relations should be satisfied simultaneously:

1- Pressure and temperature of the outlet streams, i.e., T_2 and P_2 , should locate on the hydrate phase boundary of the gas.

2- The enthalpy of the outlet stream should be equal to the inlet stream. Enthalpy of natural gas is a function of pressure, temperature and composition.

In this work, the van der Waals and Platteeuw solid solution theory [7] and method presented by Holder et al. [8] have been used to estimate the phase boundary of the natural gas. The governing equation is as follows:

$$\frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{\beta-1}}{RT} dT + \int_{P_0}^P \frac{\Delta v_w^{\beta-1}}{RT} dP - \sum_{m=1}^{no.of.cavity} v_m \ln \left(1 + \sum_{i=1}^{nc} C_{mi} f_i \right) - \ln(a_w) = 0 \quad (1)$$

Also, the Peng Robinson EoS has been used to calculate of enthalpy departures of the streams at the inlet and outlet of the throttle valve. Also, ideal gas state specific heat capacity is considered as function of temperature as given by Kyle [9].

3. Results and Discussion

Katz diagrams in allowable pressure drop in a throttle valve to prevent gas hydrate formation as a function of gas gravity are compared with the results obtained in this work in Figures 3 through 6.

As is clear from these figures, the difference between Katz diagrams and this work increases at high initial pressures. To justify this, the following reasons may be said:

1- In this work, the Peng Robinson equation of state was used to estimate streams enthalpies, while Katz curves have been obtained by constant enthalpy charts developed by Brown [4,5]. According to ref. [7], constant enthalpy diagrams developed by Brown at initial pressures higher than that 3000 psia have errors.

2- The van der Waals and Platteeuw method for hydrate phase boundary calculations is expected to be more accurate than Katz gravity charts. One major weak point of gas gravity chart is that it does not distinguish between hydrate characteristics of various isomers, for example, i-butane and n-butane, or pentane, i-pentane, and new pentane.

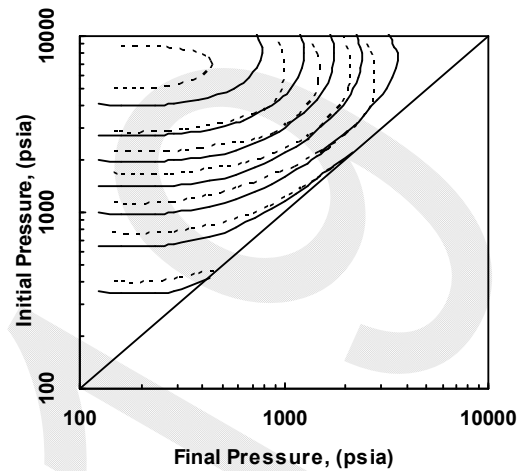


Fig. 3. Katz diagrams, dashed lines, for allowable pressure drop in a throttle valve in comparison with this work, solid lines, for 0.6 gas gravity, Temperatures are respectively from top to bottom: 170, 150, 130, 110, 90, 70, 50 °F. and Gas compositions are: $y_{c1}=0.9267$, $y_{c2}=0.0529$, $y_{c3}=0.0138$, $y_{i1c4}=0.00338$, $y_{nc4}=0.00182$, $y_{nc5}=0.0014$.

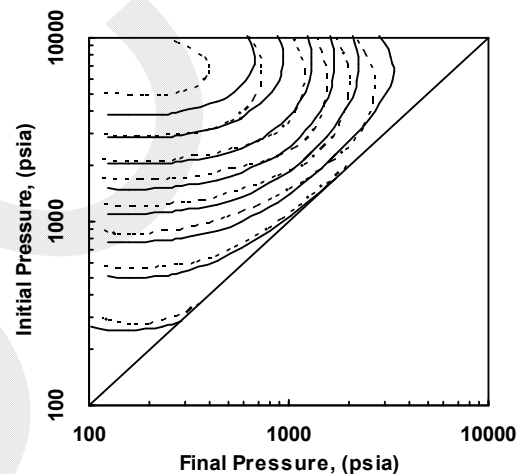


Fig. 4. Katz diagrams, dashed lines, for allowable pressure drop in a throttle valve in comparison with this work, solid lines, for 0.7 gas gravity, Temperatures are respectively from top to bottom: 184, 170, 150, 130, 110, 90, 70, 50 °F. Gas compositions are: $y_{c1}=0.8605$, $y_{c2}=0.0606$, $y_{c3}=0.0339$, $y_{i1c4}=0.0084$, $y_{nc4}=0.0136$, $y_{nc5}=0.023$.

4. Nomenclature

- D number of water molecule to the number of cavity
- μ the chemical potential
- a activity
- C Langmuir constant
- f fugacity
- h enthalpy
- P system pressure
- R gas constant
- T system temperature
- v specific volume

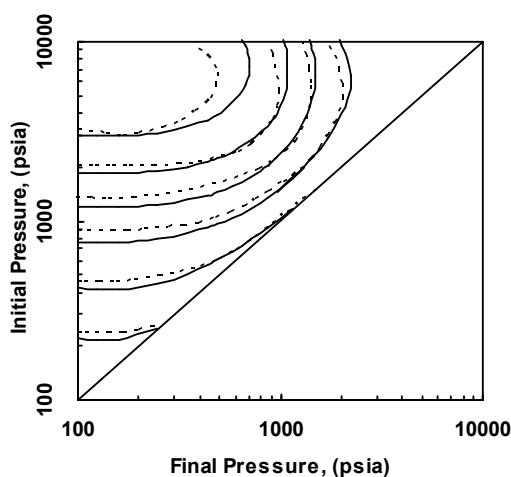


Fig. 5. Katz diagrams, dashed lines, for allowable pressure drop in a throttle valve in comparison with this work, solid lines, for 0.8 gas gravity. Temperatures are respectively from top to bottom: 190, 160, 130, 100, 70, 50 °F. Gas compositions are: $y_{c1}=.735$, $y_{c2}=.134$, $y_{c3}=.069$, $y_{i4}=.008$, $y_{nc4}=.024$, $y_{nc5}=.03$

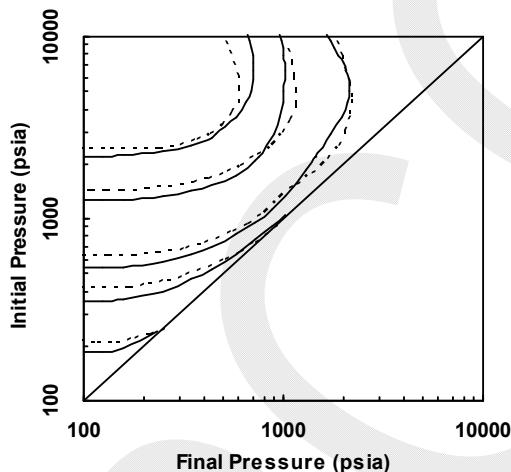


Fig. 6. Katz diagrams, dashed lines, for allowable pressure drop in a throttle valve in comparison with this work, solid lines, for 0.9 gas gravity. Temperatures are respectively from top to bottom: 190, 150, 90, 70, 50 °F. Gas compositions are: $y_{c1}=.6198$, $y_{c2}=.1777$, $y_{c3}=.1118$, $y_{i4}=.015$, $y_{nc4}=.0414$, $y_{nc5}=.0343$

5. Acknowledgment

The authors acknowledge gratefully the financial support of Shiraz University of Technology.

6. Conclusions

Using the Peng Robinson EoS for calculating enthalpies of natural gas streams at the inlet and outlet of a throttle valve, a method for reproduction of Katz diagrams in allowable pressure drop before hydrate formation in throttle valve has been developed. The van der Waals and Platteeuw theory has been used for predicting the hydrate phase boundary of the gas

stream. The predictions of the model developed in this work are compared with those of Katz diagram. Some deviations are observed at high pressure conditions, however, it is believed the results of the model developed in this work are more accurate than Katz diagram. This is due to the fact that Katz diagram has used constant enthalpy curves developed by Brown and there are uncertainties in these values. In the light of successful modelling, it is planned to extend this approach to acid gases.

7. References

- [1] E.D. Sloan, C., Koh, Clathrate Hydrates of Natural Gases, third edition, CRC press, Taylor & Francis Group, (2008).
- [2] E. Hammerschmidt, Formation of gas hydrates in natural gas transmission lines, *Industrial & Engineering Chemistry*, 26 (1934) 851-855.
- [3] D. Katz, Carson, D., Wilcox, W., Natural gas hydrates, *Trans. AIME*, 146 (1942) 150-158.
- [4] G.G. Brown, *Proc. Nat. Gasoline Assn. of Amer. 19th Annual Convention*, 54 (1940).
- [5] G.G. Brown, A Series of Enthalpy-Entropy Charts for Natural Gases. (1944), 65-76.
- [6] D.L. Katz, Prediction of Conditions for Hydrate Formation in Natural Gases, *Trans. AIME*, 160 (1945) 140-149.
- [7] J.H. van der Waals, and Platteeuw, J. C., Clathrate solution, *Adv. Chem. Phys.* 2 (1959) 1-57.
- [8] G.D. Holder, G. Gorbin and K.D. Papadopoulos, Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon, and Krypton, *Ind. Eng. Chem. Fundamen*, 19 (1980) 282-286.
- [9] B.G. Kyle, *Chemical and Process Thermodynamics*, Englewood Cliffs, NJ: Prentice-Hall, (1984).