

HIGH PRESSURE BEHAVIOR OF HYDROCARBONS

JOULE-THOMSON EXPANSION OF GAS CONDENSATES

**W. G. KORTEKAAS, C. J. PETERS
and J. de SWAAN ARONS**

Delft University of Technology¹

COMPORTEMENT DES HYDROCARBURES À HAUTE PRESSION

DÉTENTE DE JOULE-THOMSON DE GAZ À CONDENSATS

Cet article présente des calculs de l'effet d'inversion de Joule-Thomson pour des gaz à condensats à haute température et haute pression. La détente isenthalpique a été modélisée pour plusieurs compositions de gaz à condensats trouvées dans la littérature, en utilisant les équations d'état de Soave-Redlich-Kwong et de Peng-Robinson. Ces calculs confirment qualitativement le réchauffement des gaz à condensat lors de la détente. Bien que les températures de gisement se trouvent dans la région où un refroidissement s'observe, c'est-à-dire à l'intérieur de la courbe d'inversion, on a montré que les pressions de gisement correspondent à l'extérieur de cette région, de sorte que la température augmente jusqu'à ce que la courbe d'inversion soit atteinte. Le réchauffement calculé n'est pas très important. Il est typiquement de 10 à 30°C pour des pressions de gisement de 1000 bar, la valeur exacte dépendant de la composition du fluide, des conditions de gisement et de la diminution de pression. Une étude de sensibilité a montré que la pression du gisement et la composition du fluide exercent une influence particulière sur le réchauffement. Si la pression du gaz à condensat ou sa teneur en constituants lourds sont élevées, l'effet thermique possible est accru. Malheureusement, ces résultats de calcul n'ont pas pu être validés par manque de données expérimentales.

HIGH PRESSURE BEHAVIOR OF HYDROCARBONS

JOULE-THOMSON EXPANSION OF GAS CONDENSATES

This paper presents calculations of Joule-Thomson inversion effects in high-pressure-high-temperature gas condensates. Isenthalpic expansions were modeled for several gas condensate mixtures reported in literature using the Soave-Redlich-Kwong and the Peng-Robinson equations of state. The calculations confirmed qualitatively the heating of gas condensates at expansion. Although reservoir temperatures are in the region where cooling occurs, i.e., inside the inversion curve, it was shown that reservoir pressures lie outside this region, and that the temperature will increase until the inversion curve is reached. The calculated temperature increases are not very large. Although exact values depend on fluid composition, reservoir conditions, and pressure drop, typical calculated temperature increases are in the range of 10-30°C for reservoir pressures of 1000 bar. A sensitivity study showed that both reservoir pressure and fluid composition greatly affect the temperature increase. With increasing pressures and increasing amounts of heavy constituents present in gas

(1) Faculty of Chemical Technology and Materials Science,
Laboratory of Applied Thermodynamics and Phase Equilibria,
Julianalaan 136, 2628 BL Delft - The Netherlands

condensate mixtures, the maximum possible temperature effect will also increase. Unfortunately, due to lack of experimental information, the reliability of the calculated results could not be verified.

COMPORTAMIENTO DE LOS HIDROCARBUROS SOMETIDOS A ALTA PRESIÓN

EXPANSIÓN DE JOULE-THOMSON DE GASES DE CONDENSADOS

Se presentan en este artículo los cálculos del efecto de inversión de Joule-Thomson para los gases de condensados sometidos a alta temperatura y alta presión. Se ha modelizado la expansión isentálpica para varias composiciones de gases de condensados procedentes de la literatura técnica, utilizando las ecuaciones de estado de Soave-Redlich-Kwong et de Peng-Robinson. Estos cálculos vienen a confirmar cualitativamente, el calentamiento de los gases de condensados en el momento de la expansión. A pesar de que las temperaturas de yacimiento se encuentran en la región en que observa un enfriamiento, o sea, en el interior de la curva de inversión, se ha demostrado que las presiones de yacimiento corresponden al exterior de esta región, de tal modo que la temperatura aumenta hasta el momento en que se alcanza la curva de inversión. El calentamiento calculado no es sumamente importante. Típicamente, es de 10 a 30°C para presiones de yacimiento de 1000 bares, pero su valor exacto depende de la composición del fluido, de las condiciones de yacimiento y la disminución de la presión. Un estudio de sensibilidad ha permitido demostrar que la presión del yacimiento y la composición del fluido ejercen una influencia particular, con respecto al calentamiento. Si la presión de gas de condensados o su concentración en componentes pesados son elevadas, se habrá de incrementar el efecto térmico posible. Desdichadamente, estos resultados de cálculo no se han podido validar por carecer de datos experimentales.

INTRODUCTION

With improving technology, it has become possible to drill for oil at considerable depth, i.e., at depths where high pressures and high temperatures are encountered. Drilling into these high-pressure-high-temperature (HPHT) oil reservoirs can give rise to additional problems which are not met in more conventional reservoirs. During production of a North Sea HPHT gas condensate reservoir, a temperature increase of the produced condensate at pressure relief was observed. Although theoretically not impossible, the phenomenon was rather surprising because a temperature decrease was expected to be more likely. It is suspected that due to the high pressures and high temperatures in this gas condensate reservoir, i.e., temperatures in the range of 100-200°C and pressures over 1000 bar, the temperature may increase at expansion due to the Joule-Thomson inversion effect.

Little is reported in the literature regarding temperature increases in HPHT reservoirs. Jones (1988) reported that, due to the Joule-Thomson inversion effect, bottomhole temperatures increased while flowing, and as a result the wellbore was heated to above the normal static reservoir temperature during production. Temperature increases were typically in the order of between 2 and 7°C for reservoir pressures of 230 bar. Baker and Price (1990) reported temperature increases of some 8 to 11°C during a series of production tests for a UK Central North Sea HPHT well. Typical reservoir conditions encountered were in the range of 1100 bar and 200 °C. Unfortunately, due to confidentiality requirements, fluid composition and reservoir modeling results could not be published.

The main objective of the present work is to investigate the possibility that heating could occur at expansion of HPHT gas condensates, due to the Joule-Thomson inversion effect. In addition, the manner in which reservoir conditions and fluid composition influence this heating effect is examined. Therefore, several gas condensates reported in the literature (Pedersen *et al.*, 1988, 1989, and Aasberg-Petersen and Stenby, 1991) are used to perform isenthalpic expansion calculations. The Soave-Redlich-Kwong and the Peng-Robinson equations of state are used to model the isenthalpic expansion of gas condensates.

1 MODELING

In this section the various modeling aspects are briefly summarized. For details, see Kortekaas *et al.* (1997).

1.1 Equations of State

Cubic equations of state (EoS) are often used for oil and gas PVT and phase equilibrium calculations. These equations give relatively simple expressions for the thermodynamic properties and phase equilibrium relationships, and little computer time is needed to perform calculations. In this work the Soave-Redlich-Kwong (1972) and the Peng-Robinson (1976) equations of state, along with quadratic mixing rules for both the a - and b - parameters, are used.

Values of the binary interaction parameter k_{ij} are considered to be equal to zero for hydrocarbon-hydrocarbon interactions, and non-zero for interactions between a hydrocarbon and a non-hydrocarbon or pairs of unlike hydrocarbons, whereas values of the binary interaction parameter l_{ij} are all considered to be zero. Non-zero values for k_{ij} for use with the SRK and PR equations of some lighter constituents of petroleum mixtures are taken from Reid *et al.* (1987).

1.2 Heavy-End Characterization

Gas condensate mixtures may consist of many components or fractions of pseudocomponents. This number can easily exceed values of thirty or more, and it is obvious that for extensive calculation purposes this number must be reduced. For that purpose, it was necessary to apply lumping and characterization techniques. These methods have already been described in the literature, and for the details see Pedersen *et al.* (1984, 1985, 1988), Cavett (1964), Kesler and Lee (1976), Katz and Firoozabadi (1978) and Aasberg-Petersen and Stenby (1991). A more extended paper on this topic (Kortekaas *et al.*, 1997) also provides additional information.

1.3 Calculation of the Inversion Curve

Several studies have been published on predicting the Joule-Thomson inversion curve. Corner (1939) was one of the first to calculate inversion curves using equations of state. Many years later, calculations were continued by Miller (1970), Juris and Wenzel (1972), Dilay and Heidemann (1986), Geneã and Feroiu (1992), and Najjar *et al.* (1993). Gunn *et al.* (1966) derived a general correlation by a curve fit to experimental data. Because only components with acentric factors close to zero were used, the correlation is limited to simple fluids. Heyes and Llaguno (1992) proposed a new

molecular dynamics procedure for determining the inversion curve of simulated model fluids.

The inversion curve can be calculated from any equation of state by satisfying the following condition, for which the Joule-Thomson coefficient is equal to zero:

$$T \left(\frac{\partial P}{\partial T} \right)_V + V \left(\frac{\partial P}{\partial V} \right)_T = 0 \quad (1)$$

Solving Eq. (1) simultaneously with either the SRK or the PR EoS provides the locus of the inversion curve. Dilay and Heidemann (1986) obtained analytical expressions for both the SRK and the PR EoS expressed in terms of the temperature T and the volume V . However, contrary to Dilay and Heidemann, this study deals with multi-component mixtures which makes the extraction of the temperature T from the a -parameter somewhat more difficult.

1.4 Isenthalpic Expansion

To model the isenthalpic expansion of multi-component mixtures, a computational scheme presented by Nagy (1991) is applied. This scheme differs from traditional computational schemes, e.g. Asselineau *et al.* (1979) for isenthalpic problems in the two-phase region, where the key point is the calculation of the system enthalpy at saturation conditions, i.e., bubble and dewpoint temperatures at a certain final pressure P . The main disadvantage of this scheme is that it is incapable of verifying the existence of the two-phase region. To verify the presence of two (or more) phases, Nagy (1991) applied the Gibbs tangent plane criterion to check for phase stability, as described by Michelsen (1982).

2 RESULTS AND DISCUSSION

The Joule-Thomson effect for six gas condensates (GC1-GC6), a volatile oil (OIL1) and a North Sea Black oil (OIL2) were examined by performing isenthalpic calculations as discussed in the previous sections. The initial state was 400 K and 1000 bar for all cases and the SRK and the Aasberg-Petersen-Stenby characterization procedure was applied for their characterization. Calculations for methane (C1) are included for comparison. The difference in composition of the various reservoir fluids is expressed as a difference in the average molecular weight of the mixture. Figure 1 shows that the temperature change as

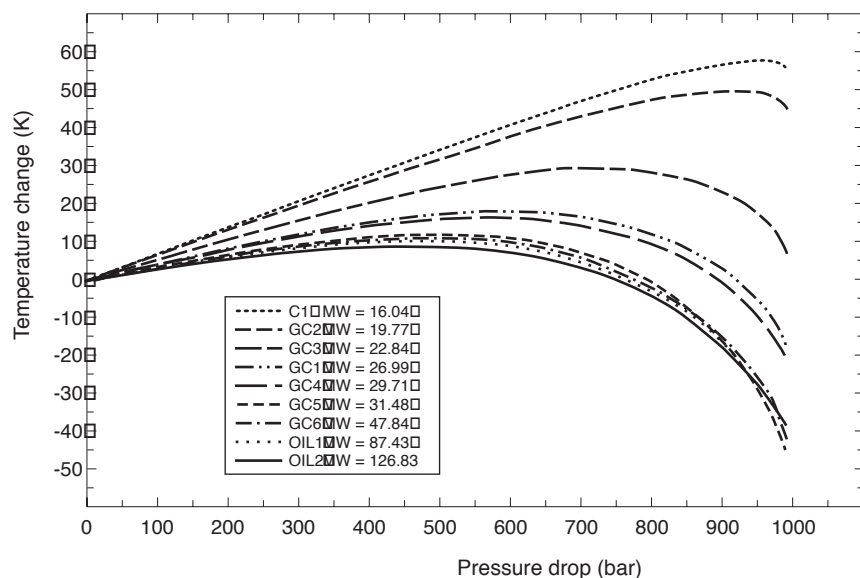


Figure 1

Isenthalpic expansion of gas-condensates (influence of composition on temperature effect).

a function of the pressure drop can be positive, i.e., increase of the temperature at pressure relief certainly is possible. From Figure 1 it also becomes apparent that with increasing molecular weight the temperature increase is larger. This finding suggests that (positive) temperature changes increase for systems with increasing amounts of heavy constituents. It also confirms that for the most common gas condensate reservoirs ($MW = \pm 20\text{-}30$ g/mole) the maximum temperature increase does not exceed 20 K for the initial state as defined above.

CONCLUSIONS

This investigation has shown that temperatures of gas condensates obtained from high-pressure-high-temperature gas condensate reservoirs may increase at expansion due to the Joule-Thomson inversion effect. It was also shown that both reservoir pressure and fluid composition greatly affect the temperature increase. Due to lack of any experimental information, the reliability of model predictions could not be verified, i.e., isenthalpic data for high-pressure-high-temperature gas condensate systems are lacking.

REFERENCES

Asselineau, L., Bogdanic, G. and Vidal J. (1979) A versatile algorithm for calculating vapor-liquid equilibria. *Fluid Phase Equilibria*, 3, 273-290.

Aasberg-Petersen K. and Stenby E. (1991) Prediction of thermodynamic properties of oil and gas condensate mixtures. *Ind. Eng. Chem. Res.*, 30, 248-254.

Baker A.C., Price M. (1990) Modeling the performance of high-pressure high-temperature wells. *SPE European Petroleum Conference*, 21-24 October 1990, 217-230.

Cavett R.H. (1964) Physical data for distillation calculation, vapor-liquid equilibria. *27th Midyear Meeting, API Division of Refining*, San Francisco, CA, May 15, 1964.

Corner J. (1939) The Joule-Thomson inversion curves of recent equations of state. *Trans. Farad. Soc.*, 35, 784.

Dilay G.W. and Heidemann R.A. (1986) Calculation of Joule-Thomson inversion curves from equations of state. *Ind. Eng. Chem. Fundam.*, 25, 152-158.

Edminster W.C. (1988) *Applied Hydrocarbon Thermodynamics*, 2, Houston, Gulf Publishing Company.

Geneã D. and Feroiu V. (1992) Calculation of Joule-Thomson inversion curves from a general cubic equation of state. *Fluid Phase Equilibria*, 77, 121-132.

Gunn R.D., Chueh P.L. and Prausnitz J.M. (1966) Inversion temperatures and pressures for cryogenic cases and their mixtures. *Cryogenics*, 6, 324-329.

Heyes D.M. and Llaguno C.T. (1992) Computer simulation and equation of state study of the Boyle and inversion temperature of simple fluids. *Chemical Physics*, 168, 61-68.

Jones C. (1988) The use of bottomhole temperature variations in production testing. *SPE European Petroleum Conference*, 16-19 October 1988, 423-431.

Juris K. and Wenzel L.A. (1972) A study of inversion curves. *AIChE Journal*, 18, 4, July 1972, 684-688.

Katz D.L. and Firoozabadi A. (1978) Predicting phase behavior of condensate/crude-oil systems using methane interaction coefficients. *J. Pet. Technol.*, 20, 1649-1655.

Kortekaas W.G., Peters C.J. and de Swaan Arons J. (1997) Johnson-Thomson expansion of high-pressure-high-temperature gas condensates. *Fluid Phase Equilibria*, 139, 205-218.

Kesler M.G. and Lee B.I. (1976) Improved prediction of enthalpy of fractions. *Hydrocarbon Processing*, 55, 153-158.

- Michelsen M.L. (1982) The isothermal flash problem. Part I. Stability. *Fluid Phase Equilibria*, 9, 1-19.
- Miller D.G. (1970) Joule-Thomson inversion curve, corresponding states, and simpler equations of state. *Ind. Eng. Chem. Fundam.*, 9, 4, 585-589.
- Nagy S. (1991) The influence of hydrocarbon condensation on natural gas throttling temperature. *Archiwum Termodynamiki*, 12, 1-4, 101-115.
- Najjar Y.S.H., Al-Beiruty M.H., Ismail M.S. (1993) Two-constant equation of state for accurate prediction of the Joule-Thomson inversion curve for air in cryogenic applications. *Cryogenics*, 33, 2, 169-174.
- Pedersen K.S., Thomassen P. and Fredenslund Aa. (1983) SRK-EoS Calculation for crude oils. *Fluid Phase Equilibria*, 14, 209-218.
- Pedersen K.S., Thomassen P. and Fredenslund, Aa. (1984) Thermodynamics of petroleum containing heavy hydrocarbons. 1. Phase envelope calculations by use of the Soave-Redlich-Kwong equation of state. *Ind. Eng. Chem. Process Des. Dev.*, 23, 163-170.
- Pedersen K.S., Thomassen P. and Fredenslund Aa. (1984) Thermodynamics of petroleum containing heavy hydrocarbons. 2. Flash and PVT calculations with the SRK equation of state. *Ind. Eng. Chem. Process Des. Dev.*, 23, 566-573.
- Pedersen K.S., Thomassen P., Fredenslund Aa. (1985) Thermodynamics of petroleum containing heavy hydrocarbons. 3. Efficient flash calculation procedures using the SRK equation of state. *Ind. Eng. Chem. Process Des. Dev.*, 24, 948-954.
- Pedersen K.S., Thomassen P. and Fredenslund Aa. (1988) Characterization of gas condensate mixtures. Paper presented at the 1988 AIChE Spring National Meeting New Orleans, Louisiana, March 6-10, 1988.
- Pedersen K.S., Thomassen P. and Fredenslund Aa. (1989) *Properties of Oils and Natural Gases*, Gulf Publishing Company, Houston, USA.
- Peng D.Y. and Robinson D.B. (1976) *Ind. Eng. Chem. Fundam.*, 15, 59.
- Reid R.C., Prausnitz J.M. and Sherwood T.K. (1987) *The Properties of Gases and Liquids*, McGraw-Hill, New York.
- Soave G. (1972) *Chem. Eng. Sci.*, 27, 1197.

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