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Thermodynamic investigation and hydrate inhibition of real gas flow through orifice during depressurization

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ABSTRACT

A thermodynamic procedure has been proposed which can be used to predict the gas pressure, temperature and flow rate through orifice upon chock flow condition, using equation of state (EOS). The procedure applied for emergency depressurization operation incorporating the Peng-Robinson EOS and validated by comparing flow rates of a multi-component hydrocarbon gas mixture for thirteen experimental cases. The average absolute deviations of the predicted flow rates for orifice discharge coefficients of 0.85 and 0.9, are 7.36% and 2.03%, respectively. The corresponding error for API 520 (American Petroleum Institute Recommendation Practice 520) method is 6.91%. In this work, the hydrate formation temperature and hydrate inhibitor type and its required weight fraction for preventing the hydrate formation upon orifice and its upstream conditions are evaluated by the EZ-Thermo software using the Moshfeghian–Maddox method. The results qualitatively show that the hydrate prevention is essential for the safety of the operation due to low temperature condition.

Keywords: Depressurization; Real gas; Peng-Robinson; Chock flow; Gas hydrate; Hydrate inhibitor

1. Introduction

When emergencies arise, the rapid depressurization or blowdown of vessels and pipelines containing hydrocarbons is applied to reduce pressure and remove inventory as fast as possible. Emergency situations are due to presence of fire or having emissions in the event of a leak, or accidents if part of a vessel or line is ruptured or reaching conditions for hydrate or paraffin formation (Richardson and Saville, 1992; Erickson and Mai, 1992; Mahgerefteh and Wong, 1999). It was Haque et al. (1992) who first developed a rigorous model to simulate blowdown of a vessel containing hydrocarbons having the least simplifying assumptions.

In the case of fire, when metal is exposed to high heat flux on one side with fluid on the other, the metal temperature may reach a level at which a rupture may occur due to high thermal stress; even though the pressure within the vessel or pipeline does not exceed the allowable over-pressure, which activates pressure safety valves (Asadi Zeydabadi et al., 2006). Mahgerefteh et al. (2002) proposed a model for blowdown of vessels under fire situation. In subsea flow systems, when the pipeline is in shut down condition, the fluid temperature drops and over time, the pipeline approaches sea bed temperature and possibility of hydrate and paraffin formation increases (Erickson and Mai, 1992).

The rapid depressurization or blowdown is a hazardous operation. In the case of vessels, it leads to generate very low fluid's temperature within the vessel that leads to reach ductile-brittle temperature of the steel from which the vessel is manufactured and the steel loses its normal mechanical stress resistance. Low temperatures can also lead to the formation of hydrate, when water phase presents in the fluid (Richardson and Saville, 1992).

If the pressure reduces during the operation, condensation of gas is possible due to generation of low temperatures; since flare systems are designed for release of gas state fluid, the knockout drum should be present to separate the generated liquid (Engineering data book, 2004). In addition to the mentioned hazards, due to the large flow rate, erosion is possible in the case of pipelines during the operation (Maloney, 2008).

Gas hydrates are water solid phase compounds having entrapped gas molecules. They resemble ice but sometimes

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Nomenclature

A, B	constants
A_o	orifice area, m^2
C	parameter
c	local speed of sound, m^2/s
c_D	orifice discharge coefficient
F	degrees of freedom
H	specific enthalpy, J/kg
k	ratio of heat capacity at constant pressure to heat capacity at constant volume
k_d, k_b, k_c	correction factors
$\dot{M}$	mass flow rate, kg/s
M_w	molecular weight, kg/kmol
N	numbers of components
P	absolute pressure, kPa
R	universal gas constant, 8.3144, kPa m^3/kmol K
S	molar entropy, J/kgmol K
T	temperature, K
T_H	hydrate formation temperature, K
T_s	suppressed hydrate formation temperature, K
v	velocity of fluid, m/s
x_w	mole fraction of water in aqueous phase
z	compressibility factor

Greek letters

α_w	activity of H_2O
γ_1, γ_2, γ_3	constants

Subscripts/superscripts

o	through orifice
up	upstream of orifice
d	downstream of orifice
ig	ideal gas

are formed at temperatures much higher than water's freezing point. The temperature decrease and the pressure increase, intensify the possibility of hydrate formation (Sloan, 1998). When the system pressure and temperature are suitable for hydrate formation, water needs an induction time to form cavities to entrap gas molecules and form the hydrate solid phase. Lee and Englezos (2005) experimentally concluded that memory water (the water from decomposed hydrate) has a much shorter induction time than normal water. During depressurization, hydrate formation through restrictions such as valves, nozzles and orifices is very hazardous. Fredenhagen and Eggers (2001) experimentally demonstrated that the hydrate formation through orifice of venting pipe can totally block the releasing flow during the operation. As the presence of solid hydrate can cause great difficulties and hazards in operations, it is common to use hydrate inhibitors to prevent the hydrate formation.

The API RP 520 (2000) proposed the following equation to calculate release mass flow rate for the gas choke flow, knowing upstream conditions of the orifice:

$$\dot{M} = \frac{Ck_dP_{up}k_bk_c}{13160}A_o\sqrt{\frac{M_w}{T_{up}z_{up}}} \quad (1)$$

in which $\dot{M}$ is the mass flow rate, k_d, k_b and k_c are correction factors, A_o is the orifice area, M_w is the gas molecular weight and P_{up}, T_{up} and z_{up} are the upstream relief pressure, temperature and compressibility factor, respectively. The term C is a coefficient determined from the following expression:

$$C = 520\sqrt{k^{ig}\left(\frac{2}{k^{ig}+1}\right)^{k^{ig}+1/k^{ig}-1}} \quad (2)$$

where k^{ig} is the ratio of heat capacity at constant pressure to heat capacity at constant volume, assuming ideal gas behavior. Asadi Zeydabadi et al. (2006) investigated hydrate inhibition at upstream and downstream of the restriction during the operation using a software module based on the API RP 520. The derivation of the API method includes a number of approximations, empirical coefficients and correction factors that prevent a rigorous study of thermodynamic behavior of the fluid and in some cases, the results of the method have large deviations compared with experimental data (Raimondi, 2007; Richardson et al., 2006; Mahgerefteh and Wong, 1999).

Haque et al. (1992) and Richardson et al. (2006) proposed thermodynamic assumptions to calculate the release rate of real gas, however the fluid properties were calculated using a generalized corresponding states method, which is less applied than thermodynamic equations of states for chemical process simulations. Raimondi (2007) proposed a procedure to calculate the critical flow conditions for pressure safety devices using same thermodynamic assumptions as proposed by Haque et al. (1992) and Richardson et al. (2006), using thermodynamic equations of state and compared the results with API RP 520, however the procedure was not validated by experimental data and detailed properties calculations by equations of state were not presented.

In this paper a thermodynamic procedure presented to evaluate the release gas temperature and pressure through orifice incorporating the Peng-Robinson EOS (equation of state) for depressurization operation using same thermodynamic assumptions proposed by Haque et al. (1992) and Richardson et al. (2006) and the calculated release rate compared with the API method and experimental data. In addition, having the evaluated pressure and temperature through orifice, the hydrate formation temperature through the restriction and the required hydrate inhibitor's type and its weight percent are calculated using the "EZ-Thermo" software (Moshfeghian and Maddox, 1996) based on the "Moshfeghian–Maddox" hydrate model (Moshfeghian and Maddox, 1993).

2. Methods

2.1. *Temperature and pressure prediction through the restriction*

In most cases, the depressurization operation is performed in a condition that is usually defined "choke flow" or "critical flow" (Raimondi, 2007). If the back-pressure of the restriction is sufficiently low, the mass flow rate of gas through the orifice is a maximum and its speed in the orifice is the local speed of sound.

Eq. (3) shows the choke flow criterion (Lees, 1996):

$$\frac{P_{up}}{P_d} \geq \left(\frac{k^{ig}+1}{2}\right)^{k^{ig}/k^{ig}-1} \quad (3)$$

in which P_{up} and P_d are the absolute pressure upstream and downstream of orifice, respectively and k^{ig} denotes the ratio of