

A study on blowdown of pressurized vessel containing CO₂/N₂/H₂S at cryogenic conditions

Umar Shafiq¹, Azmi M Shariff^{1*}, Muhammad Babar¹ and Abulhassan Ali²

¹CO₂ Research Centre (CO2RES), Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia

²Department of Chemical Engineering, University of Jeddah, Jeddah, Saudi Arabia

*azmish@utp.edu.my

Abstract. At times, CO₂ capture and sequestration from the gaseous mixture have to be done at high pressure and high concentration of CO₂ in vessels and pipelines. During depressurization of CO₂ mixture from high pressure vessel, the chances of solidification increase and the mixture undergo sudden complex phase behavior changes that can lead to accidental events. By avoiding solidification and controlling the complex phase transitions, the chances of accident and unscheduled breakdowns can be minimized. In this paper, a simulation study is presented for the depressurization of highly pressurized vessel containing the ternary mixture of CO₂/N₂/H₂S. The simulation is performed over different blowdown valves with orifice sizes of 4.325 mm, 6.325 mm, and 8.325 mm using BLOWDOWN software package in Aspen HYSYS[®] V9 to predict the phase behavior of mixture and changes in the temperature and pressure. The results indicate that the chances of an accident are minimized by avoiding the solidification during depressurization process using blowdown valve with an orifice diameter of 4.325 mm.

Keywords: Depressurization, Accident, CO₂ Capture, Solidification, Pressure Relief Valve, Phase Transitions

1. Introduction

In recent years, the development of technologies for the economical CO₂ capturing and sequestration (CCS) from various industrial sources such as fossil fuel-fired thermal power plants and other chemical process plants has attracted remarkable attention [1; 2]. Considering the fact that highly concentrated CO₂ is asphyxiating and highly toxic, an adult can be exposed to 5000 ppm CO₂ only up to 1 min [3]. The CCS is considered as one of the most effective method to mitigate the continuously rising CO₂ concentration in the atmosphere [4; 5]. Another application of CCS involves depressurization of CO₂ in the reservoir to enhance the oil recovery [6]. The transportation of a huge quantity of CO₂ at high pressure via several kilometers long pipelines passing through populated areas increases the chances of accidents due to very low-temperature that can lead to the solid formation. The chances of accidents can be reduced by safety assessment of pressurized pipelines or vessels [7-11].

Safety assessment of the pressurized pipelines (or vessel) transporting a massive quantity of CO₂ involves the accurate prediction of the fundamentally important data, such as outflow parameters of pipeline in the event of a rupture. The mass discharge rate, fluid phase, the temperature of the mixture,



and initial pressure within the pipeline are some of the important outflow parameters [7; 12; 13]. In case of any accident or failure event, further damage can be avoided by blowdown of the highly pressurized vessel or pipeline. The blowdown of the highly pressurized vessel containing CO₂ is very complex due to some specific challenges related to CO₂ transport. First, CO₂ has a different critical point (7.38 MPa at 31.1°C) and triple point (0.518 MPa at −56°C) as illustrated in Figure 1 which highlights that CO₂ transport is possible in the dense liquid state. Second, the transported CO₂ is generally impure [14]. Depending upon the fuel source and capturing process, CO₂ might contain oxygen, water, nitrogen, SO_x, methane, and other impurities. These two factors introduce considerable challenges in modelling and simulation studies since the presence of even small traces of impurities may significantly affect the thermodynamic and transport properties of the gaseous mixture [15; 16]. The composition of the gaseous mixture used for simulation by Aihara and Misawa [17] is presented in Table 1.

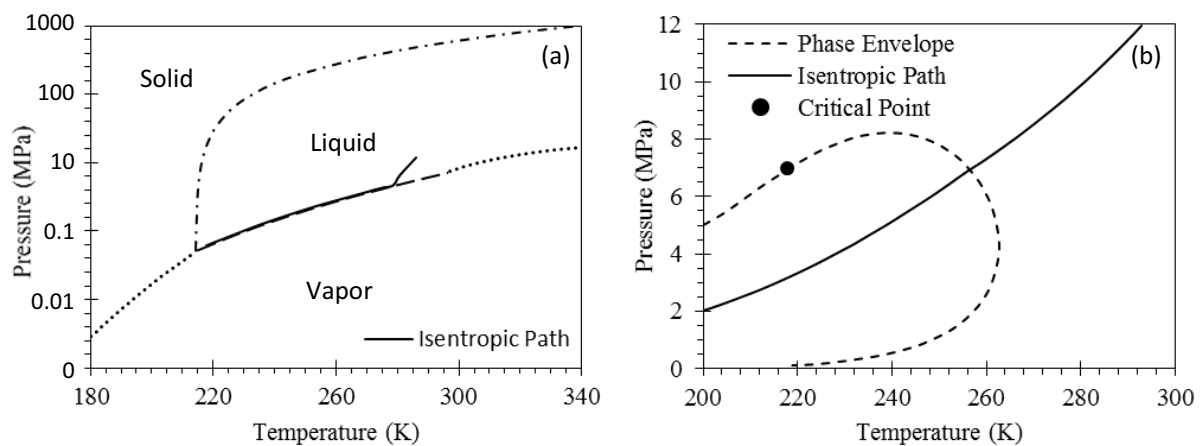


Figure 1. Isentropic depressurization of pure and impure CO₂ from 12 MPa at 293K. **(a)** CO₂ is in dense liquid state until it reaches the saturation line and then triple point, **(b)** Natural gas is in dense gaseous phase until it reaches the two-phase area

Table 1. Gaseous mixture composition [17]

Component	(Mole %)
CH ₄	88.9
C ₂ H ₆	6.2
C ₃ H ₈	2.5
<i>i</i> -C ₄ H ₁₀	0.4
<i>n</i> -C ₄ H ₁₀	0.6
<i>i</i> -C ₅ H ₁₂	0.1
<i>n</i> -C ₅ H ₁₂	0.1
<i>n</i> -C ₆ H ₁₄	0.1
N ₂	0.3
CO ₂	1.0

For dynamic simulation study, different models are developed for the study of depressurization of mixture over time for the oil and gas industry. Some of the significant models are LEKCON [18], BLOWDOWN [19], SAFIRE [13], OLGA [20], RELEASE [21], PHAST [22], and BLOWSIM [23-25]. In this study, BLOWDOWN is used because it doesn't assume the thermodynamic equilibrium and can simulate three phases. Density dependency can be modelled using the equation of state (EoS) based upon

extended corresponding state principle which is more accurate than cubic EoS, however, it requires more run-time.

Data for depressurization of CO₂ or CO₂-N₂ mixture is available in the literature. Simulation studies or experiments were conducted by researchers previously. The results unveil that even small amounts of impurities will affect the depressurization path. Therefore, the aim of this research is the simulation study of depressurization of CO₂ with added impurities of N₂-H₂S to observe the effect of orifice size on depressurization path. To conduct this study, BLOWDOWN package in Aspen HYSYS® V9 is used as a simulation tool.

2. Research Methodology

Optimum blowdown time requires a delicate balance between the maximum admissible depressurization time, minimum fluid, and wall temperatures that may be safely considered [26]. To overcome issues regarding blowdown, the accurate predictions of these parameters are crucial. The traditional approach has been to use material more than required also known as ‘overdesign’. However, this approach has become less attractive because of the rapidly decreasing profit margins of the oil and gas industry [24]. Therefore, to calculate optimum blowdown parameters, different simulations were performed to get most suitable blowdown parameters with minimum cost and hazards. In this work, three simulation-based case studies are performed to investigate the effect of orifice size and time on the temperature, pressure and phase behavior of a ternary mixture of CO₂, N₂, and H₂S.

To study the solid formation, initially the mixture is considered at the cryogenic condition. Since the mixture is already at very low temperature (cryogenic conditions), the Joule-Thomson effect with sudden depressurization causes the spontaneous drop in temperature that leads to the formation of solids. These case studies helped to observe phase behavior changes with time and orifice size. The mixture inside the vessel was at -40°C and 40 bar pressure. The cryogenic conditions helped to observe the worst-case scenario as well as planned blowdown of the CO₂ gaseous mixture. The simulation parameters and conditions used for this study are given in Table 2.

Table 2. Simulation parameters and conditions

Composition CO ₂	82.4 Mole %
N ₂	15.3 Mole %
H ₂ S	2.3 Mole %
Initial temperature	-40 °C
Initial pressure	40 bar
Vessel orientation	Vertical
Orifice diameter	4.325 mm (1 st Case) 6.325 mm (2 nd Case) 8.325 mm (3 rd Case)
Leakage direction	Top
Ambient temperature	25 °C
Back pressure	1.01325 bar

For this study, a 1.524 m long and 0.273 m wide vessel with 25 mm thickness was used as given in Table 3. The tan-to-tan length of the vessel is 1.524 m, while the thickness of walls and head of the vessel is constant. To simulate the process, the BLOWDOWN package in Aspen HYSYS® V9 is used as a simulation tool. Peng-Robinson [27] EoS is selected as a property package. After selecting Blowdown utility, blowdown valve is linked to the top of the vessel. A feed stream at -40 °C and 40 bar is connected to the vessel. Vessel conditions and dimensions are defined along with ambient temperature and pressure. First, the blowdown process is converged for 4.325 mm orifice size followed by 6.325 mm and 8.325

mm. The vessel at high pressure (40 bar) is depressurized to atmospheric pressure with different orifice sizes. Larger the orifice size, smaller the depressurization time required to reach the atmospheric pressure.

Table 3. Dimensions of the vessel

Inner diameter	0.273 m
Length	1.524 m
Wall thickness	25 mm

Pressure-time, temperature-time profiles and phase behavior of mixture during blowdown process is generated. Pressure-time profiles display the depressurization path followed by the mixture during blowdown process. Temperature-time profiles are the dynamic temperature change of vapors inside the vessel. Pressure-Temperature graphs are the phase behavior of ternary mixture during the blowdown process. These profiles are created to see the effect of orifice size on the temperature and pressure inside the vessel. To observe the chances of solid formation, frost line for the ternary mixture is generated using Aspen HYSYS®. This will indicate that the mixture inside the vessel is entering the solid region from vapor-liquid region. To avoid solidification, the mixture should not pass the frost line, otherwise the solid formation starts that may cause the blockage.

3. Results and Discussions

Figure 2 represents the pressure-time profile for depressurization path followed by the mixture for orifice sizes of 4.325 mm, 6.325 mm and 8.325 mm. Orifice with the highest size is the quickest to reach the lowest pressure while depressurization through orifice 4.325 mm took more than 250 seconds to reach minimum pressure.

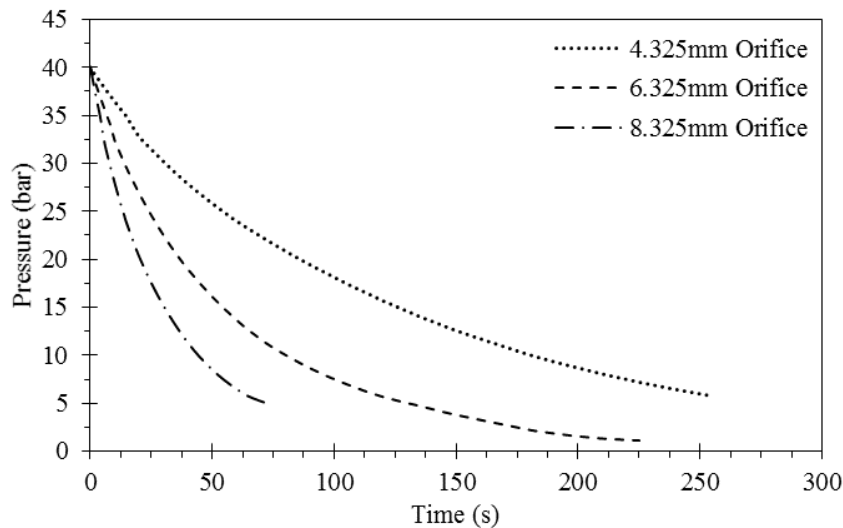


Figure 2. Main vessel pressure variations with time during depressurization

The mixture inside the vessel with an orifice size of 8.325 mm starts solidifying after 20 seconds when it reaches a pressure below 20 bar. Similarly, mixture inside the vessel with an orifice size of 6.325 mm takes 40 seconds to form solids. However, for 4.325 mm orifice size, the mixture remains in the vapor-liquid region throughout the process. During the depressurization process, the pressure suddenly decreases according to the Joule-Thomson effect that leads to changes in the phase behavior of mixture in

the trivial time interval. This abrupt change in phase behavior enhances the solidification which is interconnected with the pressure stabilization [28].

Dynamic change in temperature of vapor inside the vessel is shown in Figure 3. Temperature variations manifest a sudden fall in temperature in earlier time of depressurization process and then temperature rises with time. This is because, at the initial conditions, the vessel was full of mixture and highly pressurized but with the passage of time, the mass of the mixture inside the vessel decrease and so does the pressure. Pressure drop can be observed from 40 bar to 5 bar within 60 seconds with orifice size 8.325 mm and temperature also falls below -70°C . After 20 seconds the mixture inside the vessel with 8.325 mm orifice size enters the solidification region while at the same time, the mixture is in vapor-liquid phase for other orifice sizes. Similarly, the mixture inside vessel with orifice size 6.325 mm starts forming CO_2 solids just after 40 seconds. However, mixture inside the vessel with orifice size 4.325 mm successfully reaches the minimum pressure without entering into the solidification region. In this research, 4.325 mm orifice size is found to be compatible for a successful blowdown of the vessel. But a further brief study is required to understand the complex phase behavior changes during depressurization process in order to avoid any accident.

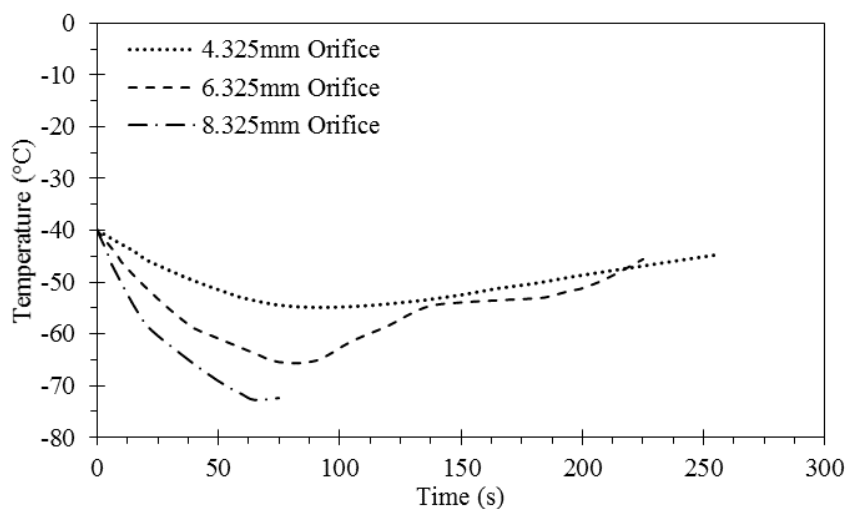


Figure 3. Temperature variations of vapor with time during depressurization

The prediction of solidification and phase behavior of ternary mixture during depressurization is illustrated in Figure 4. The vapor temperature inside the vessel is also reported along with the vapor-liquid and solidification region. Both phases are differentiated with frost line at which the formation of solid starts. At the beginning of the blowdown, the mixture is in vapor-liquid region but with the passage of time, it can enter the solidification region. Therefore, it can be observed in Figure 4 that the vapor temperature for 6.325 mm and 8.325 mm orifice diameter below 20 bar pressure falls below the freezing temperature. This can lead to the formation of solids of CO_2 because of swift decrease in temperature with an abrupt decrease in pressure. However, the orifice with diameter 4.325 mm indicates no chances of solidification because the mixture remains in the vapor-liquid region throughout the process. Although it takes more time to evacuate the mixture from the vessel with smaller orifice size but chances of accident are minimized.

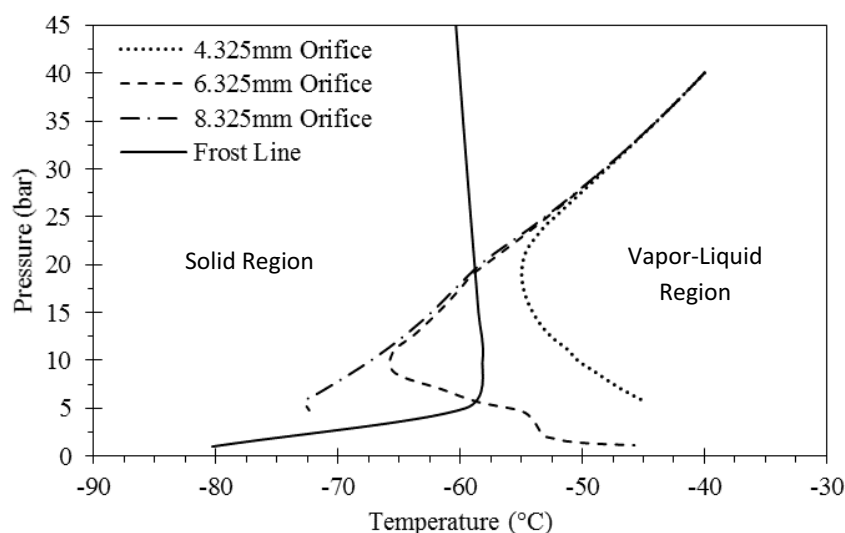


Figure 4. Phase behavior of ternary mixture during depressurization

4. Conclusions

A simulation study of depressurization of highly pressurized vessel containing ternary mixture is carried out aimed to investigate the temperature and pressure changes and phase behavior of gas mixture over three different orifice diameters i.e. for 4.325 mm, 6.325 mm, and 8.325 mm. The results show that the orifice with diameter 4.325 mm can prevent the solidification during depressurization and reduce the chances of accidents while other two orifice sizes can provoke solidification leading to the blockage or any accidental event in the pipelines. In future, blowdown process can be expanded to natural gas industry to avoid hazards in case of emergency or planned shutdown.

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