

# Simulation of Pipeline Depressurization in the Transportation of Oil&Gas with High CO<sub>2</sub> and H<sub>2</sub>S Content

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The problem of a reliable simulation of relief condition of a fluid (flow rate, pressure and temperature) is a preliminary and fundamental step to the calculation of dispersion effects. The evaluation of the mass discharged from pipelines in cases of leaks or abnormal operating conditions is largely based on the use of commercial simulators for safety analysis like PHAST or more specialized codes developed for oil&gas transportation such as OLGA and Ledaflow. However all these codes use a simplified thermodynamic approach since physical and transport properties are calculated on the basis of fixed fluid compositions and stored in tables. To avoid these limitations vapour-liquid equilibrium and fluid dynamics equations should be coupled and solved at the same time. This paper presents the implementation of two-fluid model fluid dynamics equations in a process simulator (XPSIM) providing an integrated tool which allows the simulation of vapour-liquid flows taking into account also the changes in the chemical composition. Since in this field experimental data are almost not available the validation of simulations is very difficult and different results are to be expected with different codes. The first case considered is the fast discharge of a rich CO<sub>2</sub> mixture obtained in a small experimental flow-loop: the simulated results are described and compared with experimental values. The second case presents the results of the depressurization of a pipeline used to transport a hydrocarbon fluid with high hydrogen sulfide content in the case of an emergency through a control valve.

## 1. Introduction

In the complex field of flow assurance the transportation of hydrocarbon fluids containing high amounts of acid gases is considered a critical topic. This paper is dealing with simulation aspects in two cases: the first is related to CO<sub>2</sub> transportation as usually required by "Carbon dioxide capture and storage" (CCS) projects, i.e. where carbon dioxide emitted from industrial or energy-related sources before entering the atmosphere, is recovered, compressed, transported and injected in geological formations with the scope of mitigation of greenhouse effects and the reduction of related global warming and climate changes. The second examines the importance of the evaluation of hydrogen sulphide content in the vapour phase discharged when either a leak or abnormal conditions are met. Simulation required for both engineering design and operating analyses are usually carried out by means of commercially available process simulators (HYSYS, AspenPlus, ChemCad, etc.) and fluid-dynamics simulators (OLGA, LedaFlow, etc.). The results obtained using these tools are not always reliable, in particular the fluid dynamic codes are based on the use of property tables calculated using a fixed initial composition. The simulation of the transport of almost pure carbon dioxide streams is very sensitive with respect to thermodynamic methods and equations of state used: the selection of reliable calculation methods for vapour-liquid equilibrium, enthalpy, entropy, density and viscosity play a key role in the fluid-dynamic calculations required by for safe and cost-effective pipeline design. This general problem has been described by the author in a previous event series (Raimondi, 2014) where some examples taken from industry projects have been discussed. The fluid-dynamic implementation considers most important two-phase flow patterns: stratified, annular, slug and bubble flows are considered even in cases of fast depressurization where most published papers apply a homogeneous no-slip flow model.

## 2. Fluid Dynamic Model

The equations required for the description of single phase and multiphase flows are well known and their derivation can be found in many text-books and publications related to multi-phase flow dynamic. Among available documentation we can quote the text of Ishii and Hibiki (2006), so, conservation equations for mass, momentum and energy are only summarized. A fluid system formed by  $N$  chemical components (e.g. methane, ethane, nitrogen, etc.) whose relative amount is defined by the number of moles or mass units. The composition is described by a vector  $\mathbf{z}$  of dimension  $N$  and each individual chemical component is identified by an upper index. Two possible approaches are currently used to describe a two-phase system: (1) the drift-flux model or (2) the two-fluid model. In the first case momentum balance equations of the vapour and liquid phases are coupled together and the phase different velocities are described by drift relations. Separate equations are instead used in the two-fluid model. In this study the two-fluid model is used. The conservation of mass is given by the differential equation:

$$\frac{\partial \alpha_k \rho_k}{\partial t} + \nabla(\alpha_k \rho_k u_k) = m_k \quad (1)$$

where  $\alpha$  is the volume fraction,  $\rho$  the density,  $u$  the phase velocity and  $m$  the mass exchanged between phases (e.g. by evaporation or condensation). The subscript  $k$  is used to indicate the vapour or the liquid phase: usually the index 1 is used for the vapour phase V and the index 2 indicates the liquid phase L. In the case of a fluid mixture, volumetric and thermodynamic properties, which are usually considered functions of the pressure and temperature only, are dependent on the phase compositions as well. The phase composition is denoted by the vector  $\mathbf{z}$  whose components  $z_i$  denote the molar or weight fraction of the  $i$ -th chemical component. In some cases the symbol  $y$  is used to identify the vapour composition vector and the symbol  $x$  is used for the liquid phase. So in general, we can write the phase density as:

$$\rho_k = \rho(T, P, \mathbf{z}_k) \quad (2)$$

Similar equations can be written for internal energy, enthalpy, entropy, viscosity and thermal conductivity for the vapour and liquid phases. For a two-phase system, the vapour and liquid volume fractions  $\alpha_k$  sum to 1.

$$\alpha_V + \alpha_L = 1 \quad (3)$$

The momentum balance equation of phase  $k$  can be written as:

$$\frac{\partial \alpha_k \rho_k u_k}{\partial t} + \nabla(\alpha_k \rho_k u_k u_k + \alpha_k P) = P_k \nabla \alpha_k + \alpha_k \rho_k g \sin \vartheta + M_k^i \quad (4)$$

where  $P$  is the pressure,  $g$  the gravitational acceleration,  $\vartheta$  the inclination angle and  $M_k^i$  the sum of momentum transfer of phase  $k$  with pipe wall and the other flowing phase phase.

By introduction of the phase enthalpy, the conservation of energy takes the form:

$$\frac{\partial \rho_k H_k}{\partial t} + \nabla(\rho_k H_k u_k) = -\nabla q_k + \frac{DP_k}{Dt} + \dot{q} \quad (5)$$

When a compositional approach is used the mass balance of the chemical component contained in the vapour and liquid phases must be considered. Taking into account a control volume, the mass balance of the  $i$ -th component of the mixture (e.g. methane) can be written as:

$$\frac{\partial m_k^i}{\partial t} + \nabla(m_k^i u_k) = 0 \quad (6)$$

where the index  $i$  applies to all chemical components existing in the fluid system (from 1 to NC).

The complete set of the Navier-Stokes equations are then solved using a mixed implicit-explicit integration scheme. The material and momentum balance equations are integrated using an implicit scheme. The energy balance equations are combined and solved using an explicit Euler integration. Details of the applied integration method are not given and a valuable reference is the text of Ferziger and Peric [3]. The component balance equation (6) is integrated based on the new phase velocities and densities obtained in the previous steps.

### 3. Carbon-dioxide depressurization

In the simulation of carbon-dioxide and CO<sub>2</sub>-rich mixtures the selection of thermodynamic models represents a very important aspect; as the simulation of pure components using temperature and pressure as independent variables (TP surface) presents a discontinuous phase change from vapour to liquid. At constant pressure below the critical point and across the vapour pressure line, a change of temperature small at will can produce a complete shift from the vapour to the liquid phase or vice-versa. Some key chemical-physical parameters important for the next discussion are collected in Table 1.

*Table 1: Pure carbon-dioxide thermodynamic parameters*

Property	Value
Critical temperature	30.97 °C
Critical pressure	73.773 bar
Triple point temperature	-56.6 °C
Triple point pressure	5.18 bar
Acentric factor	0.22394

A remarkable characteristic of carbon dioxide is that a normal-boiling point does not exist since no liquid phase can exist at 1 atmosphere and a solid phase is obtained when the vapour is cooled down below approximately -78.5 °C. It means that below triple point pressure, a reduction of temperature of the vapour phase (as often happens during depressurization) produces the direct formation of solid without the transient formation of an intermediate liquid phase. For the simulation of pure CO<sub>2</sub> transport, one of the leading fluid-dynamics simulation software (OLGA) has recently introduced the use of the Wagner equation (Span and Wagner, 1996) however classical cubic equations of state such as the Soave-Redlich-Kwong SRK (Soave, 1974) and Peng-Robinson PR (Peng and Robinson, 1978) give sufficiently reliable values. With respect to the Span-Wagner equation which applies only to pure CO<sub>2</sub>, the GERG model (Kunz et al., 2007) can be applied also to CO<sub>2</sub> mixtures containing light hydrocarbons (C1, C2, C3 etc.) and inert gases (N<sub>2</sub> and O<sub>2</sub>). This simulation will try to reproduce the results obtained in the experiment described by Ruden (Ruden et al. 2014) carried at the CO<sub>2</sub> test loop at the Institute for Energy Technology (IFE, Norway). The experiment consists in the fast depressurization of a fluid whose composition is reported in Table 2. Some details (e.g. pipe material and thickness) required to set-up a reliable simulation cannot be found in the paper and are estimated.

*Table 2: CO<sub>2</sub> stream with impurities composition*

No	Component	Molar fraction %
1	CO <sub>2</sub>	89.9
2	CH <sub>4</sub>	5.3
3	N <sub>2</sub>	4.8

The fluid is contained in a 2" stainless steel pipe (internal diameter 44.35 mm, wall roughness 1.3 micron) with a length equal to 13 m. The fluid is pressurized at about 90 bar and 20 °C. At these conditions the fluid is a supercritical liquid since the critical temperature is about 31 °C and the critical pressure 80 bar. The depressurization is obtained by a sudden open of a relief valve defined by a nominal diameter of 6 mm with a C<sub>v</sub> value equal to 0.37. The fluid is discharged into a receiving vessel kept at about 15 bar so the depressurization is completed at this pressure value with a final temperature of -34 °C. The fluid is let to flow for 10 s when the valves are closed at both ends of the pipe, the discharge valve is opened the next second so the depressurization of the system starts at 11 s. The latter is very fast and is completed in about 80 s. Figure 1 shows how the temperature and pressure of the outlet fluid change during the depressurization. Since the external temperature is kept at 20 °C, when the depressurization is almost completed, the final pipe end temperature rapidly reach the external value. In Figure 2 the temperature-pressure path is compared with experimental values reported by the quoted paper. The two curves are drawn over the calculated phase envelope of the mixture. The agreement between calculated and experimental data is quite acceptable especially when compared with calculated results obtained using other simulation codes. (Ruden, 2014).

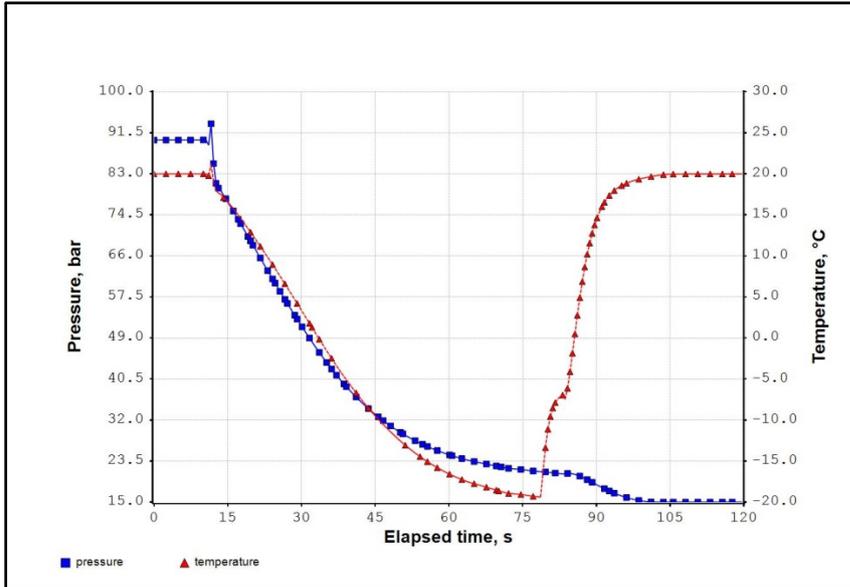


Figure 1: Carbon dioxide depressurization. Outlet temperature and pressure vs time.

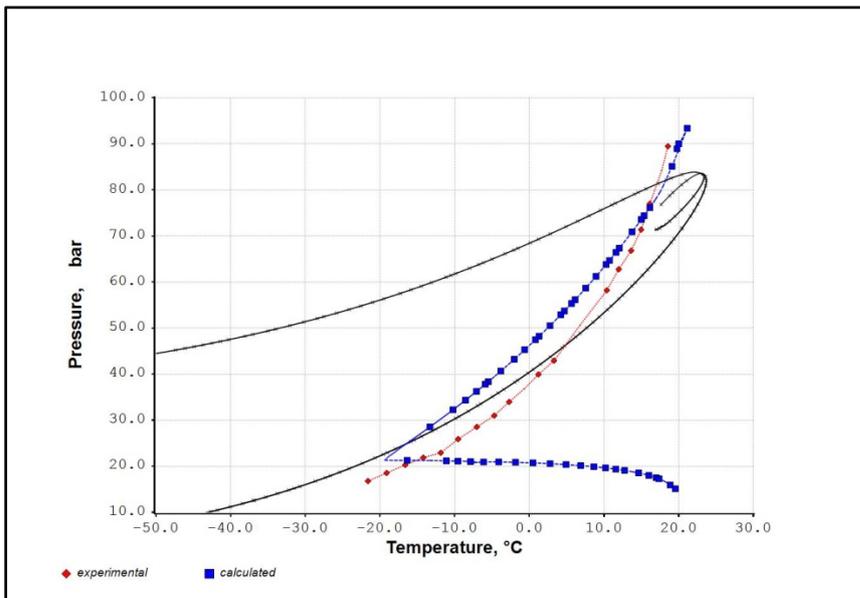


Figure 2: Carbon dioxide depressurization. Pressure-temperature curves over phase envelope.

#### 4. H<sub>2</sub>S transportation and depressurization

The second case is the transport of a hydrocarbon mixture containing a large amount of hydrogen sulphide; this fluid composition can be representative of some oil fields in the Caspian Sea area. For this study, the mixture is only slightly simplified and up to 14 chemical components are considered as shown by Table 3. The pipeline considered has a diameter of 0.676 m and its length is around 100 km but for this study we consider only a segment about 10 km long. The pipeline profile is almost horizontal with the exception of the initial 100 m where an elevation change of -3 m is located. The fluid enter the pipeline at 50 bar and 75 °C, the outlet pressure is about 45 bar for an initial flowrate of 360000 kg/h.

Table 3: H<sub>2</sub>S rich fluid composition

No	Component	Mole fraction	No	Component	Mole fraction
1	NITROGEN	0.01	8	ISOPENTANE	0.01
2	HYDROGEN SULPHIDE	0.22	9	PENTANE	0.01
3	METHANE	0.50	10	HEXANE	0.02
4	ETHANE	0.10	11	HEPTANE	0.01
5	PROPANE	0.05	12	OCTANE	0.01
6	ISOBUTANE	0.02	13	NONANE	0.005
7	BUTANE	0.03	14	DECANE	0.005

The ambient temperature is about 0 °C. For the assessment of risks associated to the depressurization of this fluid one can be interested in the concentration of the hydrogen sulphide in the discharged phase. It is a common engineering practice, by using steady state process calculation, to try to evaluate the hydrogen sulphide fraction at the initial conditions and estimate final conditions. These are defined by a final pressure equal to the atmospheric value and a temperature near 0 °C. This procedure computes hydrogen sulphide vapour composition values not very different from the feed molar composition as defined by Table 4.

Table 4. Hydrogen sulphide vapour composition from steady state simulation.

Pressure, bar	Temperature, °C	Molar fraction %
50	75.0	0.224
40	1.0	0.171
1	0.0	0.228

Scope of the simulation is to monitor the change of the H<sub>2</sub>S content in the discharged fluid. We will show that very different values are obtained from the compositional simulation showing that either steady state equilibrium approximations or the use of table properties are not able to described real changes.

Assuming an initial flow rate of 360000 kg/h, inlet pressure of 50 bar and inlet temperature at 75°C, the transport of the fluid is simulated for 30 minutes when the pipeline is shut-down by closing the valves at both ends. At this stage the liquid volume fraction in the pipe is about 0.5 and this value is almost constant since the profile is horizontal. After 60 minutes the depressurization is started at the final end by opening a relief valve of 7 inches diameter. The flowrate of the fluid discharged from the relief valve is shown by Figure 3. The pressure behaviour at both pipeline ends during the preliminary shut-down and the subsequent depressurization are also presented by the same Figure 3.

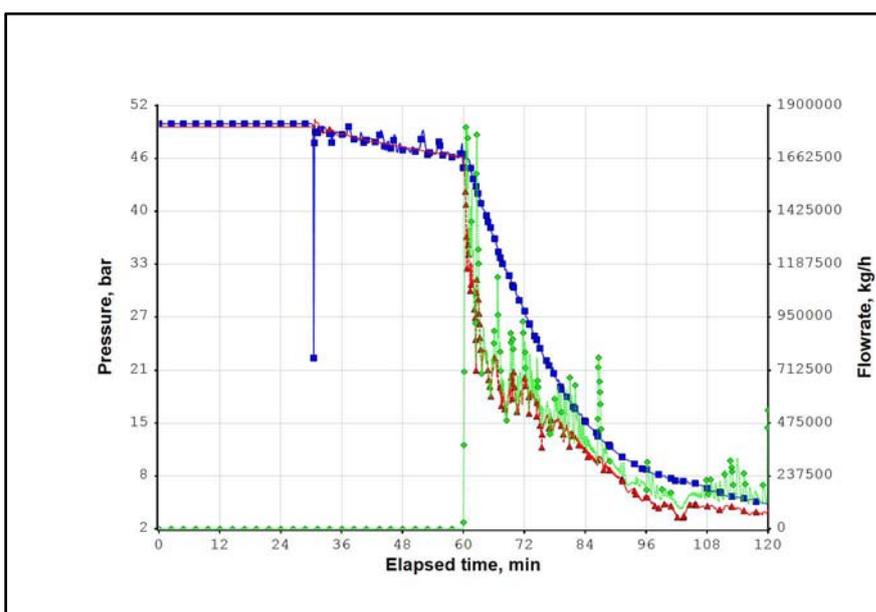


Figure 3: H<sub>2</sub>S rich fluid depressurization. Pipeline pressure at initial end ■, at final end ▲; discharge flowrate ◆ from relief valve.

Finally the hydrogen sulphide content in the vapour phase, as obtained by the simulation, is presented in the next Figure 4. The hydrogen sulphide final molar fraction becomes near 0.450 that is completely different from what is derived by using the initial fluid composition.

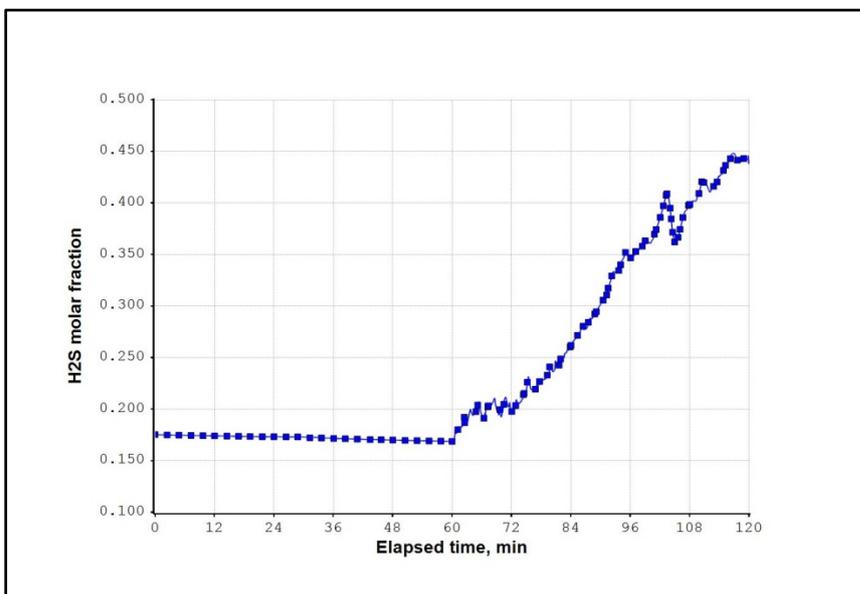


Figure 4: H<sub>2</sub>S rich fluid depressurization. Hydrogen sulphide molar fraction in the discharged vapour.

## 5. Conclusions

The development of the integration of vapour-liquid equilibrium simulation with a general fluid dynamic framework in a process simulation code provides a greater insight into the effects associated to the simulation of vapour-liquid fluid transport in pipelines. The code is applied to the simulation of two cases, industrially relevant, involving the transportation of fluids containing high amounts of carbon dioxide and hydrogen sulphide. The results obtained in the simulation of two pipeline depressurizations are presented and discussed. For the second case, where hydrogen sulphide is involved, it is shown that integration of the compositional approach with fluid dynamics can provide more exact and reliable results.

## References

- Ferziger J.H, Peric M., 2002, Computational Methods for Fluid Dynamics, 3rd Edition, Springer
- Ishii M., Hibiki T., 2006, Thermo-Fluid Dynamics of Two-Phase Flow, Springer, Berlin
- Kunz O., Klimeck R., Wagner W., Jaeschke, M., The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures, Groupe Européen de Recherches Gazières, 2007
- Peng D.Y., Robinson D.B., 1976, A new two-constant equation of state, Ind. Eng. Chem. Fund. 15, 59–64.
- Soave G., 1972, Equilibrium constants from a modified Redlich-Kwong equation of state, Chem.Eng.Sci. 27, 1197-1203.
- Span R., Wagner W., 1996, A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple Point Temperature to 1100 K at Pressures up to 800 MPa, J. Phys. Chem. Ref. Data, Vol 25, no 6, 1509-1596.
- Raimondi L., 2014, CO<sub>2</sub> Transportation with Pipelines - Model Analysis for Steady, Dynamic and Relief Simulation, Chemical Engineering Transactions, Vol. 36,
- Ruden A.T. et al., 2014, Simulating flow of CO<sub>2</sub> with impurities in OLGA; dealing with narrow phase-envelopes and the critical point, Energy Procedia, 51, 344-352.
- XPSIM (eXtended Process SIMulator), 2015, Reference Manual, Version 2.02., Process Simulation Services, [www.xpsimworld.com](http://www.xpsimworld.com).