

An Experimental Investigation of Rapid Boiling of CO₂

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1 Introduction

Accidental explosions involving rapid boiling of liquified gases are a great concern in process safety. Such events are commonly referred to as Boiling Liquid Expanding Vapour Explosions (BLEVEs). They can occur in storage and transportation of high pressure liquified gases like LPG or CO₂. To prevent and mitigate BLEVE accidents, detailed knowledge about the boiling process is needed. In the present study, experiments with rapid depressurization of liquid CO₂ are carried out in a transparent shock tube to allow the observation of boiling waves and other structures. The thermodynamical mechanisms that are governing the boiling process are not unique for CO₂, and the same principles can be applied for any liquid gas.

Evaporation waves in a superheated liquid was observed by Simoes-Moreira and Shepherd [1], who did a series of experiments with superheated dodecane. Pinhasi et al. [2] have developed a one dimensional numerical model, where several of the structures observed in the present work are predicted. Bjerketvedt et al. [3] did a series of small scale experiments with CO₂ BLEVEs.

The present experiments were photographed by a high-speed camera. Boiling waves propagating into the liquid was observed, traveling at near constant velocity in the order of 20 m/s. A contact surface between the vapour and the liquid-vapour mixture was also observed, accelerating out of the tube. Pressure readings in the tube suggests that the boiling wave could be close to a spinodal decomposition wave, but further experiments are needed to warrant any conclusions.

The scope of the experimental work is to provide a basic reference for the development of a numerical model capable of describing the boiling mechanisms in a CO₂ BLEVE. Validation of such a model will require more detailed experimental work, particularly with pressure readings in several points in the tube (only two pressure readings are used presently). The present study will also serve as a reference if a new experimental rig is to be constructed.

2 Experimental setup

A shock tube filled partly with liquid CO₂ was used. The tube was made of lexane, which is transparent. A schematic illustration of the tube is found in fig. 1. The distance between the two pressure transducers was 43.5 cm, and the transparent part of the tube was 32 cm. The inner diameter of the tube was 9 mm, and the outer diameter was 12 mm. During experiments, the tube was in a vertical position. One end

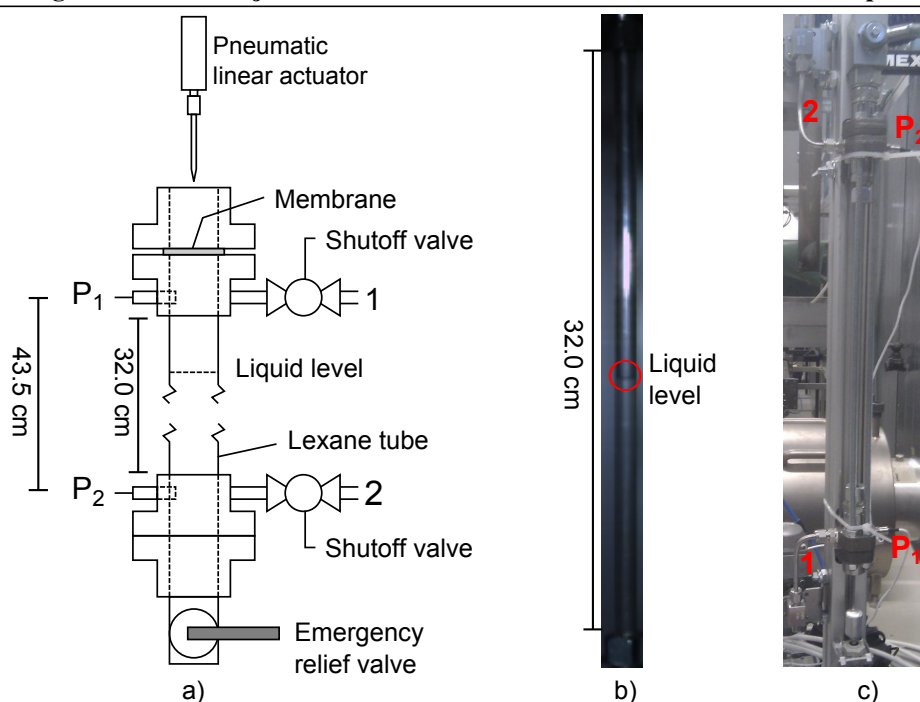


Figure 1: (a) Schematic illustration of the shock tube with vapour side penetration (not to scale). The tube is filled at the inlet (2), while (1) is used for controlled pressure relief to allow liquid CO₂ to fill the tube. P₁ and P₂ are pressure transducers. The distance from P₁ to P₂ is 43.5 cm, and the visible part of the tube is 32.0 cm; (b) High speed shot of the tube filled with liquid CO₂; (c) Photo of the tube with the vertical orientation switched (liquid side membrane penetration). In this case, the tube is filled at (1).

of the tube was a membrane which was punctured by a needle. Two layers of Mylar sheet was used as membrane material. The experiment was photographed by a high-speed camera of type Photron APX-RS at 16 000 frames per second, to allow visual tracking of front propagation and boiling. In addition, two pressure transducers (P₁ and P₂ in fig. 1) of type Kulite XT-190 were used to monitor the pressure inside the tube. The first series of experiments were carried out with the membrane placed at the top of the tube. In the second series, the vertical orientation of the tube was switched, so that the membrane was placed at the bottom.

The tube was filled at an inlet valve at the bottom of the tube using liquid CO₂ from a gas bottle with a riser tube. Careful pressure relief at the top of the tube allowed the liquid CO₂ to fill up to the desired level. When the fill and relief valves ((1) and (2) in fig. 1) were closed, the state inside the tube was assumed to be saturated liquid conditions at the given pressure.

3 Experimental results and discussion

The experimental results are split into two sections. In the first section, the membrane was placed at the top of the shock tube, so that the tube was filled with vapour at the membrane side. In the second section, the vertical orientation of the tube was switched, so that the membrane was penetrated at the liquid side. The results of the high speed images are displayed as series of isochronously spaced images. This way, fronts are easily tracked. Front velocities are found by polynomial curve fitting of front position vs. time and derivation. All images are cropped to show only the transparent part of the tube, with a height

of 32.0 cm. Visual tracking of fronts is possible, but the resulting calculations should be regarded as preliminary results, as the front position is not always clear. The idea behind these experiments is to provide an overview as to what processes are at work in as liquid CO₂ boils due to a rapid drop in pressure. Due to the curvature of the tube, it was difficult to observe any fine structures.

3.1 Vapour side membrane penetration

Fig. 2 shows the experimental results with the shock tube filled with liquid CO₂ up to 45% of the height between P₁ and P₂. The pressure measurements in fig. 2 show a 1.9 ms delay between the upper and the lower pressure transducer in the first pressure drop (A). This corresponds to a mean speed of sound of 228 m/s. As a reference, the Span-Wagner equation of state [4] at 5.5 MPa saturated conditions and a liquid fill level of 45% gives a mean speed of sound of 248 m/s (198.0 m/s in the vapour and 356.8 m/s in the liquid phase). Note that this speed of sound is only a reference for the first rarefaction wave that passes through the shock tube.

From the pressure drop of P₁, there is a time delay of 0.8 ms (B) until any visual changes in the tube. Some of this delay can be explained with the 5.75 cm gap between the pressure transducer and the upper end of the visual tube, but it is possible that the pressure in the tube drops some time before visual changes appear. The white front that is propagating into the vapour from $t = 72$ ms is most likely CO₂ droplets or solid crystals (depending on the local thermodynamical state) that is generated because of the temperature drop in the vapour.

1.4 ms after the initial pressure drop of P₁ (C), the liquid starts to boil at the interface. The boiling propagates as a front into the liquid, at a rate of 23.5 m/s (D). At the same time, a front is seen accelerating upward in the vapour phase (E). This is most likely the front of the liquid-vapour mixture that is the result of boiling liquid. The velocity of the return wave is in the order of 100 m/s as it leaves the visible part of the tube. The acceleration seems to decrease at this point. The rarefaction wave(D) and the contact surface (E) are plotted in fig. 3. These fronts are well known phenomena in the context of supercritical evaporation waves, and are mentioned among others by Pinhasi et al. [2]. The pressure at the top of the tube increases slightly after the contact surface passes, and then stabilizes at 2.6 MPa. With isentropic expansion from 5.5 MPa at saturated conditions, the Span-Wagner spinodal lies at 3.1 MPa. While it is hard to find the exact pressure at the liquid vapour interface with the current experimental setup, it is possible that it is in the same order as the top pressure after the contact surface passes. If this is the case, the boiling wave could be close to a spinodal decomposition wave.

After $t = 74$ ms, the liquid appears to be boiling at the bottom of the tube (F). At this point, P₂ is stabilizing at roughly 4.6 MPa. The pressure is most likely stabilized because of the boiling process in the liquid.

3.2 Liquid side membrane penetration

In these experiments, the membrane was placed at the bottom of the tube. Fig. 4 shows the experimental results with the shock tube filled with liquid CO₂ up to the top of the visible part of the tube. A 1.5 ms gap is observed between the first drops of P₁ and P₂. This corresponds to a mean speed of sound of 281 m/s, which is a bit lower than what could be expected with such high liquid fill rate. However, the measurements from P₂ are not clear as to when the first pressure drop appears. There are some small perturbations at A₁, and a drop of 0.1 MPa at A₂, so these measurements does not necessarily provide sufficient data to determine the speed of sound. 2.0 ms after the first drop in P₁ (B), the first signs of boiling appear. It is interesting to note that the boiling appear to happen at the liquid/vapour interface

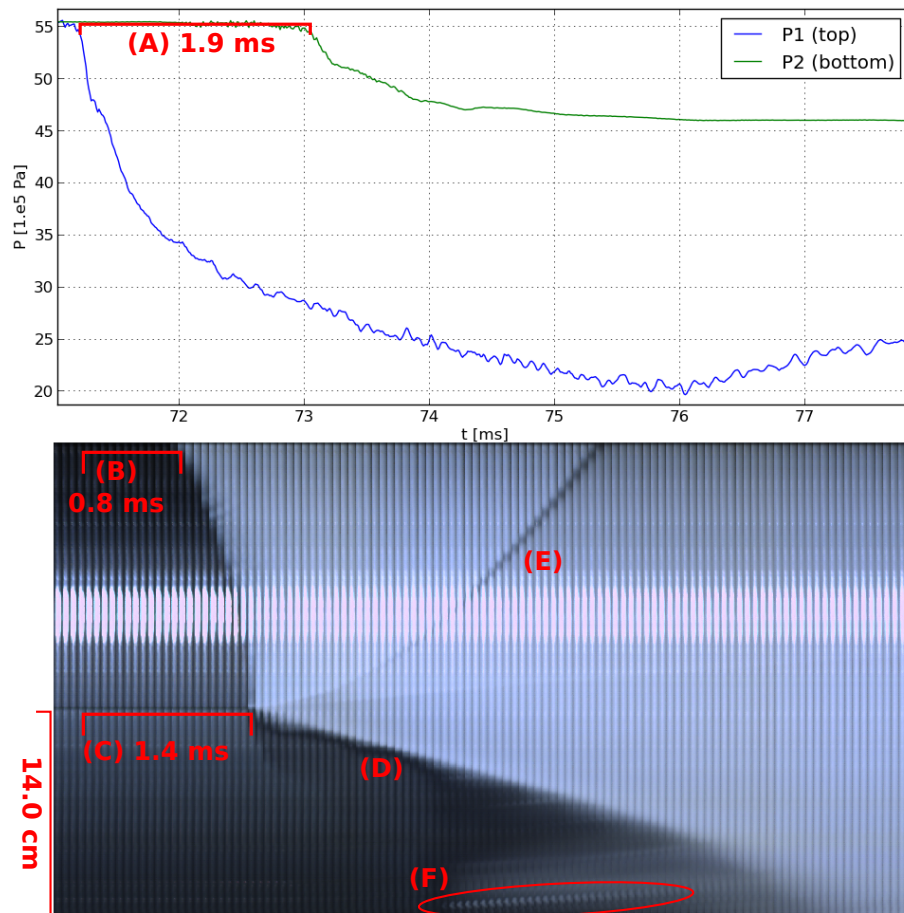


Figure 2: Experimental results with vapour side membrane penetration. P_1 and P_2 refers to fig. 1 (a). The time-scale is relative to the trigger mechanism of the membrane penetration device

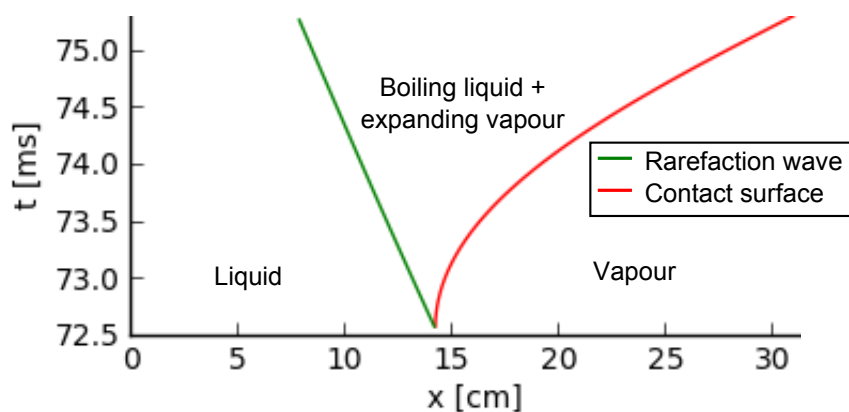


Figure 3: Diagram of front positions from fig. 2 plotted with time.

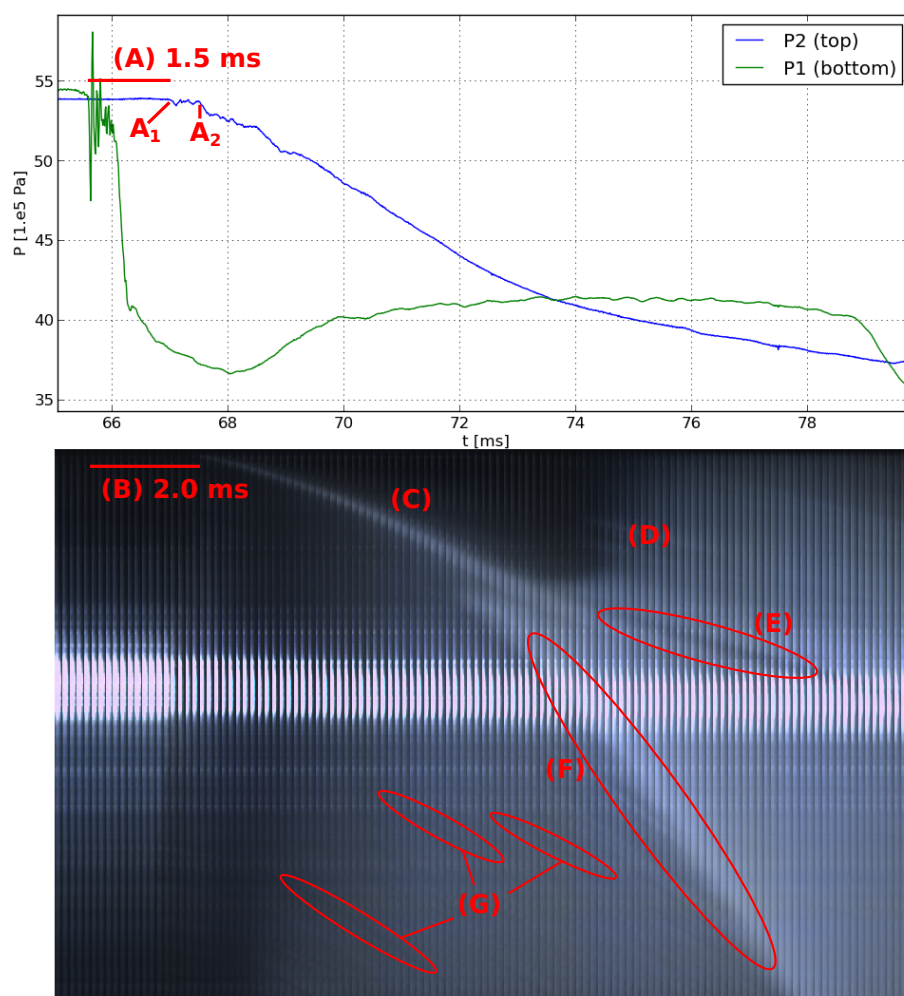


Figure 4: Experimental results with liquid side membrane penetration. P_1 and P_2 refers to fig. 1 (a). The time-scale is relative to the trigger mechanism of the membrane penetration device

at the top even if the membrane is placed at the bottom of the tube. The liquid will also boil at the membrane side, but the flow velocity seems to be greater than that of the boiling front. The assumed liquid/vapour interface is traveling downwards at a velocity of 13.5 m/s (C), most likely due to the expansion of the vapour phase. At $t = 75.5$ ms the vapour phase becomes opaque (D). The liquid/vapour interphase continues downwards, but appears to be decelerating (E). Around $t = 72$ ms, a new front appears (F), accelerating from 28 m/s at $t = 72$ ms to 50 m/s at $t = 77$ ms.

The accelerating front (F) may be a rarefaction wave similar to the one observed in the first series of experiments. (C) and (E) is then possibly a mixture/vapour interface. The difference is that in the first series, the liquid phase was stagnant, allowing observation of the wave velocity. Here, the liquid phase is flowing out of the tube at an unknown, possibly increasing flow velocity. By careful consideration of fig. 4, one can observe some lines in the liquid phase (G), corresponding to a velocity in the order of 12 m/s. Note that these lines are barely visible. They may be small structures (bubbles) in the liquid indicating flow velocity, but may also just be artificial disturbances. If the flow rate is in fact in the order of 12 m/s, the rarefaction wave (F) has a much greater velocity than the one observed in the first series of experiments.

4 Conclusion

- High speed photography of a shock tube with liquid CO₂ is capable of capturing some structures in the boiling process.
- The small diameter of the tube makes it difficult to observe detailed structures, especially in the cross-sectional direction.
- When the membrane was penetrated at the vapour (top) side, a boiling wave was observed, traveling into the liquid with a velocity in the range of 20 m/s. Another front, assumed to be the contact surface between the vapour and the liquid/vapour mixture, was also observed, accelerating out of the tube.
- When the membrane was penetrated at the liquid (bottom) side, a rarefaction wave and mixture/vapour interface still appeared at the top of the tube, but further experiments are needed to determine front velocities.

Due to the lack of pressure measurements inside the tube, it is hard to say anything about the thermodynamical states in the observed structures. Knowledge about such states is critical in understanding the governing mechanisms in a BLEVE. A new experimental setup is needed to provide pressure and temperature readings in several places in the tube. Such setup should also have a square tube profile or much larger tube diameter, in order to capture detailed structures in the boiling front.

References

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