

Prevention of the explosion of acetylene cylinders involved in fire: experiments and simulations

F. Ferrero*, M. Beckmann-Kluge, M. Kreißig, U. Schmidtchen, K. Holtappels
BAM Federal Institute for Materials Research and Testing
Division 2.1 "Gases, Gas Plants"
Unter den Eichen 87, D-12205 Berlin, Germany

1 Introduction

Pressurized cylinders for the storage of acetylene may explode with generation of a fireball if they come in contact with a strong heat source, for example a fire. Since acetylene (chemical formula: C_2H_2) is capable of decomposing explosively into carbon black and hydrogen without the presence of oxygen -provided its temperature and/or pressure are sufficiently high-, such cylinders are extremely dangerous. In fact, once the decomposition reaction is initiated by the fire exposure, it may proceed even after the heat source is removed, i.e. the flames are extinguished, since the decomposition reaction is self-sustained by the heat it releases. This may eventually lead to the cylinder rupture.

One way to prevent the burst of heated acetylene cylinders involved in fire is to cool them with water. Nevertheless, as reported by Kurth (1999) [1], this method may be ineffective if critical conditions in the cylinder are reached, i.e. if the reaction rate of decomposition has reached a point beyond that the related heat production exceeds the heat removed by the water cooling.

In order to assess the effectiveness of the water cooling as a safety measure to prevent the burst of acetylene cylinders involved in fire, a total of 13 fire exposure experiments (bonfire tests) have been performed with fully loaded cylinders of 8.9, 10 and 50 l in volume. During the tests, temperatures at different spots inside and on the outer surface of the cylinder as well as the head pressure were recorded. In some of the experiments a cooling system was activated some seconds before the expected burst. Thus, the fire was extinguished, the cylinder was cooled and it was observed whether an explosion could be prevented.

Together with the information acquired from lab-scale tests, the data recorded during the experimental campaign were used for the development and validation of a mathematical model to predict the heat transfer in acetylene cylinders during the fire exposure and the subsequent cooling with water.

The current paper presents a short summary of the work performed and may provide help for improving the handling of acetylene cylinders involved in fire.

2 Experimental

Figure 1 shows a 50-l-cylinder prepared for the bonfire test (left picture), where the locations for the pressure and temperature measurements in the cylinder are shown. Up to seven thermocouples were located inside the cylinder. As a safety measure, acetylene cylinders are usually filled with a porous material, which can prevent the propagation of the decomposition reaction under normal operating conditions, i.e. if the porous material is not appreciably heated or damaged at the moment the decomposition is initiated. Moreover, a solvent -typically acetone (chemical formula: C_3H_6O) or DMF (chemical formula: C_2H_7NO)- is used, in order to increase the stored amount of acetylene. Due to the construction process, a small gap between the cylinder shell and the porous material is present, leaving space for free gas to gather. Since this space might constitute a spot, where acetylene decomposition is likely to be initiated, one of the thermocouples inside the cylinder was always set at its head for measuring the temperature of the gas phase. Furthermore, during the experiments the flame temperature was recorded at two representative locations. A detail of the cooling system, which consisted of five shower heads, is shown in Figure 1 (right picture).



Figure 1. Acetylene cylinder prepared for the bonfire test (left) and detail of the cooling system (right).

In most of the experiments performed a peak in the temperature at the top was observed shortly after the bonfire started (3 to 11 minutes after the pile ignition), indicating the occurrence of a decomposition, as shown in Figure 2. After the on-set of the decomposition the slope of the pressure curve normally increased and the cylinder burst within 2 minutes, if no cooling was applied. Without cooling cylinders burst within 15 minutes after the test was started and at the moment of the explosion the pressure recorded was between 46 and 126 bara. These values lay clearly under the burst pressure of such cylinders, since the steel constituting the shell was weakened by the thermal load. In fact at the moment of burst shell temperatures between 340 and 570 °C were registered. At such temperatures the steel loses more than a half of the strength it has at ambient temperature. Overall, 8 burst tests were performed, in order to determine the time to explosion for cylinders with different inner volumes with sufficient reproducibility.

Moreover, a total of 5 extinction experiments were performed. Here, shortly before the expected burst, a water shower was activated, in order to extinguish the bonfire and to apply a cooling to the cylinder. Only in 2 experiments an explosion could be prevented. The pressure, the shell temperature and the temperature at the top clearance for these tests are presented in Figure 2.

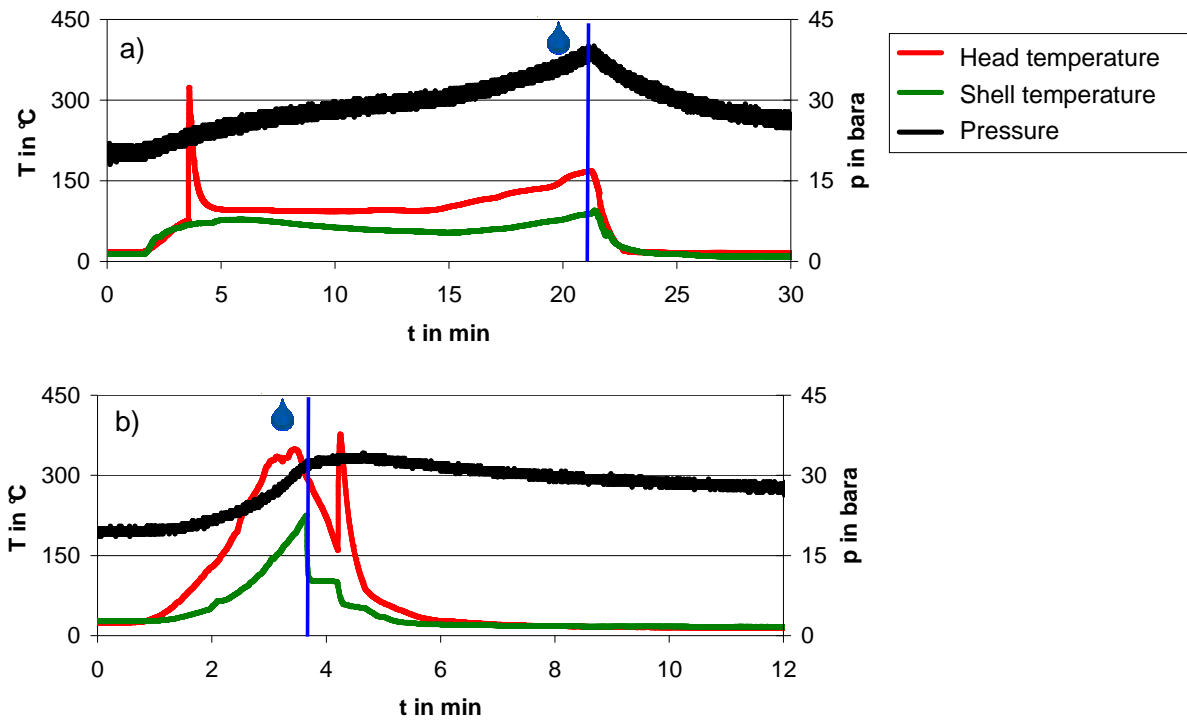


Figure 2. Extinction tests, where the cylinder burst could be prevented (a: 8.9-l-cylinder; b: 10-l-cylinder).

Apparently, in the successful extinction test with a 8.9-l-cylinder (Figure 2 a) a decomposition in the top clearance had already been initiated, before the cooling was started. This means, the decomposition may be stopped by cooling with water if it did not advance too far. From the results of the current experimental campaign and from previous data with 40-l-cylinders [1], it seems that cooling might be effective to bring back the system to non-critical conditions only if the cylinder pressure does not exceed about 40-45 bara. This is valid for single acetylene cylinders exposed to fire, but might not be adequate for bundles.

3 Model

A model to predict the heat transfer in the acetylene cylinder was developed and solved numerically using the software COMSOL Multiphysics®, which uses the finite element method (FEM). Due to the complexity of the system, the following assumptions were made:

- inside the cylinder and through the walls of the cylinder only heat conduction was considered. Because of the presence of porous material, convection is strongly limited. Therefore only conductive heat transfer equations were considered;
- it was assumed that, in the top clearance without porous material only acetylene was present. Due to the small disposable space, no convection was taken into account here as well;

- acetone was considered as solvent. Due to its higher vapor pressure it was considered to be more dangerous than DMF, the other common solvent for acetylene. Moreover, acetone is more frequently employed than DMF, especially for single acetylene cylinders;
- the boundary conditions were defined on the cylinder shell, considering two main contributions for the heat transfer from the flame to the cylinder: a heat transfer by convection, which is generated by the hot gases arising from the fire source and a heat transfer by radiation from the flame. The flame temperature for these calculations was assumed to be 850 °C;
- for the calculation of the heat release by the decomposition reaction, formal kinetics proposed by Greene et al. (1958) [2] was considered. Parallel to the decomposition reaction, polymerization of acetylene takes place. The main product of the reaction has been supposed to be vinylacetylene, according to the works of Silcocks (1957) [3] and Bradley and Kistiakowsky (1961) [4]. In order to avoid divergence problems a maximum rate for both decomposition and dimerization reactions was set.
- the pressure inside the cylinder was calculated from the experimental data on vapor-liquid pressure equilibrium data for acetylene-acetone mixtures found in literature (Voronkov et al., 1975 [5]);
- the material properties were considered as temperature dependent and taken from Yaws (2003) [6].

In order to validate and eventually adjust the boundary conditions for the simulations of the exposure to fire and cooling of real acetylene cylinders, a test with a dummy was performed. This was basically an acetylene cylinder with a radius of 0.115 m, where the upper part was cut and the porous material was removed and substituted by mineral wool. The height of the cut cylinder was 1.06 m. Here the temperature at the outer and inner shell was measured during the fire exposure and the afterward cooling. Figure 3 compares the experimental temperatures of the inner shell at 0.50 m from the cylinder top (T1 and T2) with the results of the computations.

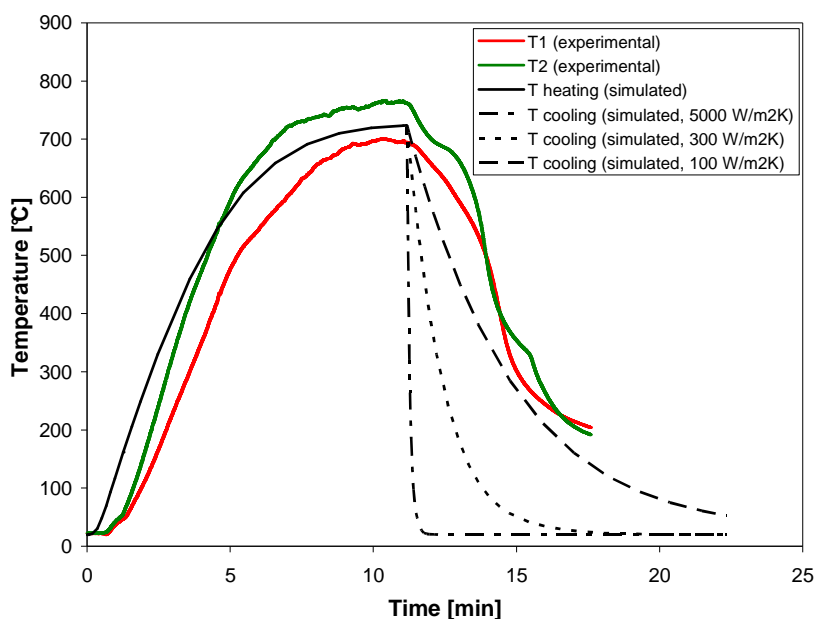


Figure 3. Comparison between experimental and simulated temperatures of the inner shell during the fire exposure of a dummy acetylene cylinder (radius = 0.115 m, height = 1.06 m).

Obviously the chosen set of boundary conditions for the fire exposure is satisfactory. In the simulations of the cooling the initial guess for heat transfer coefficient cylinder-water was adjusted to 100 W/(m²·K).

After the validation of the boundary conditions, the model was applied to real acetylene cylinders. The pressure calculation method revealed some limitations, if the pressure exceeds 45 bara. However, in the experiments performed, it was observed that if a fully charged acetylene cylinder completely involved in fire reaches a pressure of 45 bara, it will burst within a short time (less than 1 minute up to 5 minutes). Otherwise, if a pressure release happens at lower pressures, a jet flame is likely to occur but no fireball will be detected. Under this consideration, the experimental and predicted times to reach 45 bara during a fire exposure for 10- and 50-l-cylinders, are summarized in Table 1, showing a good agreement. The predicted burst times were calculated by adding 1 minute to the time where 45 bara are reached in the simulations and are shown in the same table.

Table 1: Comparison between the experimentally determined and predicted times required to reach a pressure of 45 bara during the heating of acetylene cylinders fully involved in fire

Volume [l]	Time to pressure = 45 bara [s]		Time to burst [s]	
	Experiments	Simulations	Experiments	Simulations
10	220 (Worst Case)	180-240	275 (Worst Case)	240-300
50	250 (Worst Case)	240-260	290 (Worst Case)	300-320

For further information, the calculated shell temperatures at the time, where 45 bara are predicted by the model are compared with the measured values in Table 2. The agreement is good for the 10-l-cylinders, but temperatures are overestimated for the 50-l-cylinders. It has to be noted, that in the simulation, the flame has been supposed to have a constant temperature, but in reality variations along the fire axes are present. In fact, the hottest part of the flame is found near the fuel source, in this case the wood pile. For a 50-l-cylinder the thermocouple on the cylinder was placed not directly in this zone, but above it and this might lead to the observed discrepancies.

Table 2: Predicted and measured shell temperatures at the time the pressure reaches 45 bara during the heating of acetylene cylinders fully involved in fire

Volume [l]	Shell temperature at pressure = 45 bara [°C]	
	Experiments	Simulations
10	462 (Worst Case)	470
50	420 (Worst Case)	540

The output from these calculations was taken as the input temperature distribution for the simulation of the heat transfer during cooling with water. It has been experimentally observed that the water cooling is only effective, if it is started before a certain no-return-point, after which the heat production inside the cylinder will be higher than the heat removed by the cooling. In order to use the model to predict the mentioned effectiveness, various calculations of fire exposure with afterward cooling were performed. The start of the cooling was varied, as to find the time up to which the reaction still may be stopped. The results are reported in Table 3, under the assumption that a homogeneous cooling is applied. According to the simulations, water cooling is only effective, if it is started within 3 to 4 minutes after the start of the fire, if the cylinder is completely involved in it. In the experiments performed, burst of the 10-l-cylinder could be prevented if the cooling system was activated 3 minutes after the pile ignition. The water started running about 3 minutes and 40 seconds after the ignition. Thus, the model results seem promising. Table 3 also shows that the pressure should not exceed 40-45 bara for the cylinder to be saved, which is in agreement with the experimental results.

Table 3: Predicted maximum allowed time for the cooling to be started, if an acetylene cylinder is directly involved in fire and corresponding pressure (homogeneous cooling)

Volume [l]	Predicted latest start of cooling [s]	Predicted pressure at cooling [bara]
10	170	44
50	210	40

The simulations also showed that, if cooling is effective, a one hour water supply is sufficient to bring the cylinders back to non-critical conditions, since thereafter the temperature will not further rise.

Conclusions / Summary

In order to assess the effectiveness of water cooling of acetylene cylinders involved in fire, a total of 13 bonfire tests with 8.9-, 10- and 50-l-cylinders were performed. During the experiments the pressure in the cylinder and the temperature at different locations within the porous material and on the shell surface as well as the flame temperature were measured. Overall 8 burst tests were performed, in order to determine the times to explosion for the cylinders. Cylinders failed not later than 15 minutes from the ignition of the bonfire, often with generation of a fireball. During the other 5 tests, the fire was extinguished before the expected burst and the cylinder was cooled with water. In 2 of the 5 extinction experiments, the explosion of the cylinder could be prevented. Noticeably, in one case the on-set of the decomposition of acetylene had already been observed, before the cooling was started. In spite of that, the cooling was still effective. The interpretation of the current results and of the data from previous tests with 40-l-cylinder suggests that single acetylene cylinders involved in fire might be saved by cooling, if their pressure does not exceed a value of about 45 bara. The recorded values of pressure and temperature were used to develop and validate a mathematical model for the prediction of the heat transfer in acetylene cylinders during the exposure to fire and the afterward cooling. The predictions agreed well with the experimental results.

References

- [1] Kurth L. (1999). Explosionsgefahren durch Acetylenflaschen bei einem Brand. Techn. Überwach. 40(1): 33 (in German).
- [2] Greene EF, Taylor RL, Patterson Jr. WL. (1958) Pyrolysis of simple hydrocarbons in shock waves. J. Phys. Chem. 62(2):238.
- [3] Silcocks CG. (1957) The kinetics of the thermal polymerization of acetylene. Proc. R. Soc. Lond. A 242:411.
- [4] Bradley JN, Kistiakowsky GB. (1961) Shock wave studies by mass spectrometry. II. Polymerization and oxidation of acetylene. J. Chem. Phys. 35: 264.
- [5] Voronkov AP, Mislavskaya VS, Mushii RYa, Khodeeva SM. (1975) Phase Equilibria in the acetone - acetylene system. Russ. J. Phys. Ch. 49(12):3128.
- [6] Yaws CL. Yaws' handbook of thermodynamic and physical properties of chemical compounds. Knovel (ISBN / ASIN: 1591244447, Electronic ISBN).

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