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EXPLOSION FREE IN FIRE SELF-VENTING (TPRD-LESS) COMPOSITE TANKS: PERFORMANCE UNDER FIRE INTERVENTION CONDITIONS

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ABSTRACT

This paper describes the performance of explosion free in fire self-venting (TPRD-less) composite tanks of Type IV in fires of realistic intensity HRR/A=1 MW/m^2 in conditions of first responders' intervention. This breakthrough safety technology does not require the use of thermally activated pressure relief devices (TPRD). It provides microleaks-no-burst (μLNB) performance of high-pressure hydrogen storage tanks in a fire. Two fire intervention strategies are investigated, one is the removal of a vehicle with μLNB tank from the fire, and another is the extinction of the fire. The removal from the fire scenario is investigated for one carbon-carbon and one carbon-basalt double-composite wall tank prototype. The fire extinction scenario is studied for four carbon-basalt prototypes. All six prototypes of 7.5 L volume and nominal working pressure of 70 MPa demonstrated safe release of hydrogen through microchannels of the composite wall after melting a liner. The technology allows fire brigades to apply standard intervention strategies and tactics at the fire scene with hydrogen vehicles if μLNB tanks are used in the vehicle.

1.0 INTRODUCTION

One of the goals of safety engineering is to exclude hydrogen storage tank rupture in any fire. This would eliminate hazards from blast waves, fireballs and projectiles, and thus exclude catastrophic consequences of tank rupture in a fire. Ultimately, the hazards and associated risks for hydrogen-powered vehicles would be reduced to a level equal to or below that for fossil fuel vehicles and an unprecedented level of life safety and property protection will be achieved. The goal can be realised by application of the conceived at HySAFER Centre of Ulster University the breakthrough safety technology of explosion free in any fire self-venting tank. The technology does not require a thermally activated pressure relief device (TPRD), whose reliability in localised fire or fires of low intensity is questionable. This innovative safety technology provides the microleaks-no-burst (μLNB) performance of Type IV tanks in a fire [1] which is explained below. The detailed concept description and initial experimental validations of the technology for several carbon-carbon and carbon-glass double-composite wall μLNB tank prototypes are published elsewhere [2].

1.1 Incident fire scenarios and fire intensity

There is a wide range of real fire scenarios which could have different intensity. These are ranging from comparatively low temperature smouldering fires [3–5] through the vehicle tyre fire and liquids fuel spill fires [6–8] to extreme scenarios of impinging hydrogen jet fires [9], which could be a scenario, e.g., a jet erupting from nearby storage tank. The fire intensity is characterised by the specific heat release rate, HRR/A, which is the ratio of the fire heat release rate, HRR, to the fire area, A. The fire resistance rating (FRR) is defined as a time to rupture in a fire for a storage tank or compressed hydrogen storage system (CHSS) with failed to be activated, e.g., by smouldering fire or a localised fire, or blocked from a fire during incident TPRD. There is a number of numerical and experimental studies on the tank performance in a fire, where ruptures of standard tanks were the prominent outcomes [9–18].

Figures 1 and 2 shows the results of the experimental and numerical studies on the dependence of FRR on value of HRR/A (blue strip). At first, the FRR decreases with HRR/A, but then stabilises and does not practically change for HRR/A≥1-2 MW/m^2. Hydrogen regulations and standards, e.g., GTR#13 [19], require fire testing of CHSS. Prescribed currently by the regulation fire test conditions require lower HRR/A values compared to real fires of higher intensity.

Figure 1 explains how this lower HRR/A value can allow for passing the fire test but would create hazards in real fires of higher intensity. Fire of intensity HRR/A=0.2 MW/m^2 will result in FRR=24 min. This time is longer than the duration of the localised fire stage of 10 min (see bottom right insert in Figure 1). During the localised fire stage, the tank is exposed to the fire by its end without TPRD and which should be maintained before commencing the engulfing fire stage. Thus, after 10 min of the fire, the engulfing fire will begin to thermally affect the entire tank including TPRD which is required to be on the side of the tank opposite to the localised fire. The TPRD with a delay equal to its response time will start hydrogen release from the tank and, if sized properly, will prevent tank rupture (on such low-intensity fire only!).

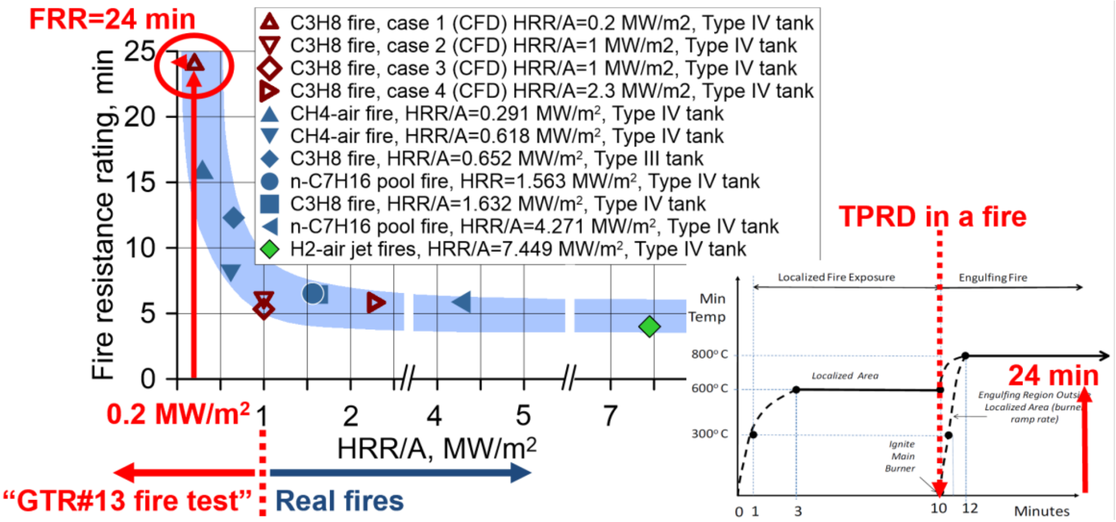

Figure 1. Dependence of FRR on HRR/A demonstrates that in the fire of low-intensity HRR/A=0.2 MW/m^2 the FRR=24 min, i.e., longer than the localised fire (see the insert in the right bottom corner) [9,11,18–25].

However, the situation changes drastically if the same tank is in fire of higher intensity, e.g., gasoline/diesel spill fire of HRR/A=1 MW/m^2. Figure 2 shows that in such intensity fire the tank will rupture in only 5-6 min, i.e., before the TPRD is affected by the engulfing fire (see the insert in bottom right corner of Figure 2). Understandably, the fire test protocol suggested by GTR#13 could have serious safety implications in real life, especially for first responders.

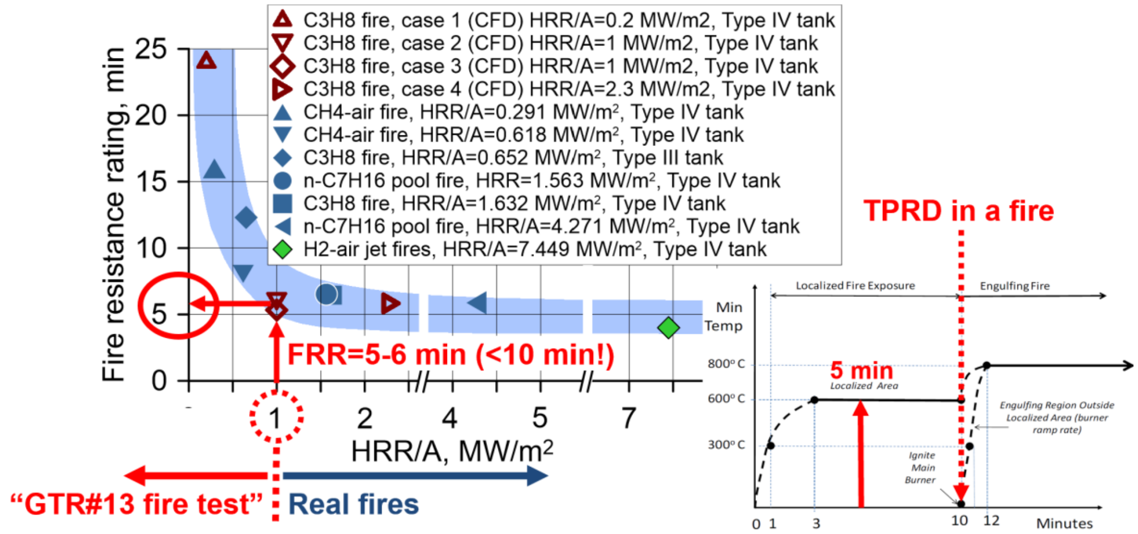

Figure 2. Dependence of FRR on HRR/A demonstrates that in the fire of typical gasoline spill fire intensity HRR/A=1 MW/m^2 the FRR=5-6 min, i.e., shorter than the localised fire stage (see the insert in the right bottom corner) [9,11,18–25].

The analysis presented in this section demonstrates that the fire test protocol of GTR#13 should be changed to fire intensity of HRR/A=1 MW/m^2 to underpin the safety of hydrogen storage tanks in real life conditions such as spill fires of fossil fuel during a traffic incident. Low-intensity fires, e.g., smouldering fires, which can hardly trigger TPRD sensing elements, are beyond the scope of this study and will be investigated in due course in forthcoming research at HySAFER.

1.2 Microleaks-no-burst (μLNB) safety technology concept

Figure 3 schematically explains the performance of a standard (left) and a μLNB tank (right) in a fire. The standard tank has a liner and a fibre-reinforced polymer (FRP). The μLNB tank has an additional thermal protection layer (TPL) that can be load-bearing as well. Heat flux from a fire is applied to the external tank surface. The common features for both types of tanks include heat propagation into the wall and degradation of the composite resin ("Resin decomposition" line) and the moving outwards load-bearing wall thickness fraction ("Load bearing fraction" line). In the case of the standard tank, when two fronts, i.e., resin decomposition front and load-bearing wall thickness fraction location, meet each other the tank is not anymore able to bear the load of increasing hydrogen pressure and, thus, ruptures. This happens for the standard tank if the hydrogen-tight liner in the tank is intact, i.e., did not melt. The μLNB tank has two composites of different thermal conductivity, the heat of decomposition, etc. The self-venting performance of the tank is provided by a proper design using the intellectual property (IP) of Ulster University [1,2] and HySAFER in-house proprietary models and tools accounting for thermophysical and geometrical parameters of the liner, two composite layers, safety factor, etc [24,25]. The design of μLNB tank provides melting of the liner before the tank loses its load-bearing ability. The melting of the liner initiates microleaks of hydrogen through the structure of FRP and TPL layers. Despite further propagation of the decomposition front into the tank wall (see Figure 3, right), the load bearing wall thickness fraction reduces drastically due to the tank depressurisation. This eliminates conditions for tank rupture in a fire.

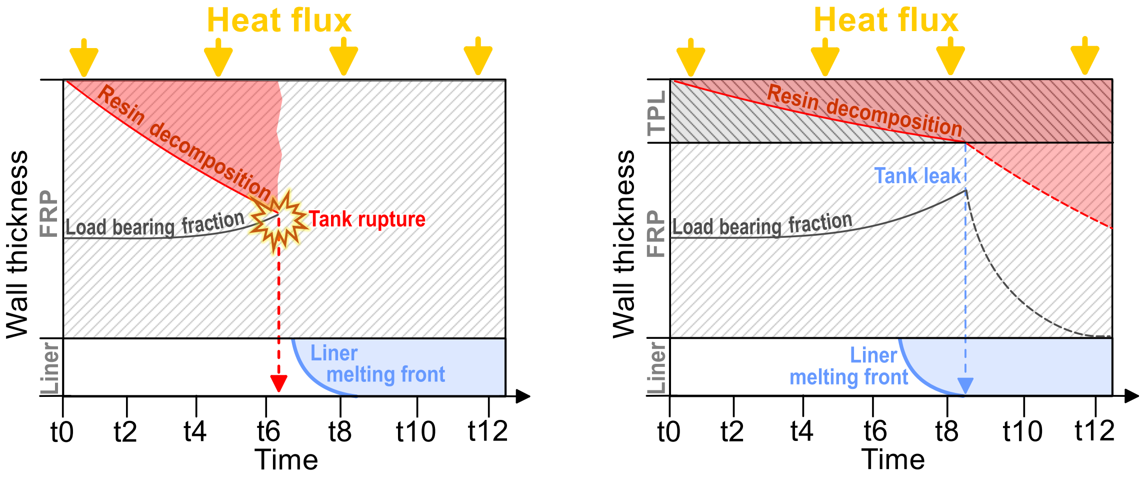

Figure 3. Schematic explanation of μLNB safety technology [2] for Type IV tanks: original (left) and μLNB (right) tank performance in a fire

The design of μLNB tank strongly depends on the choice of liner. For example, a higher melting temperature of Nylon, i.e. polyamide (PA), liner, e.g. 219°C [26], compared to that of high density polyethylene (HDPE), e.g. 118-134°C [5, 6] would result in a design with a thicker double-composite wall for a tank with PA liner. The HDPE liner requires a much less amount of heat to be transferred through the composite and to melt it than a PA liner. There is another advantage of HDPE compared to PA liner. Numerical experiments [7] explained the observations in the previous experimental campaigns [9,11], where Type IV composite tanks with HDPE liner leaked in a fire without rupture if they were charged with pressures below about half of normal working pressure (NWP). This wouldn't be possible for PA liners. In addition, PA mechanical properties are less favourable compared to HDPE liners at temperatures below -40°C, which may be important for use of hydrogen storage, e.g., for high altitude aviation applications.

The significant, but not directly related to the safety benefit of the μLNB technology, is the reduction of the amount of short-in-supply carbon fibre and substitution of at least a part of it by cheaper fibres like glass, basalt, etc. This, along with the increase of public confidence in the safety of hydrogen systems and infrastructure, will accelerate the transition to an economy based on the use of electricity and hydrogen from renewable sources.

The approach applied by HySAFER to design and manufacture μLNB tank prototypes is the use of a standard tank as a starting point. This allows tank manufacturers in most cases to use their usual design of liner and bosses and the way of filament winding. This facilitates our collaborators around the globe to manufacture inherently safer hydrogen storage tanks using their facilities and established experience and ultimately get a competitive advantage of the market due to the unprecedented safety features of μLNB tanks.

2.0 TECHNOLOGY VALIDATION FOR FIRE INTERVENTION SCENARIOS

Hydrogen storage tank rupture in a fire incident is a serious concern of first and second responders to an incident. In this study, we expand the validation domain of this innovative safety technology of explosion free in fire self-venting tanks from continuous fires [2] to conditions of fire intervention at the fire scene. This is equally relevant to scenarios of intervention of first responders to fires involving hydrogen vehicles on roads, on hydrogen trains, on ships in harbours, on planes at airports, etc. To address the safety concerns of firemen, all fire tests were performed using burners with the specific heat release rate of HRR/A=1 MW/m^2 characteristic for realistic gasoline/diesel spill fires [25].

Table 1 shows the parameters of six μLNB tank prototypes that were tested in two different fire intervention scenarios within the research programme of the HyTunnel-CS (https://hytunnel.net/) project coordinated by Ulster University. The safety designs of all 7.5 L, NPW=70 MPa μLNB tanks were done by HySAFER Centre. The tanks were manufactured by a collaborator in the USA. Fire tests analysed in this study were performed by HyTunnel-CS partner CEA for the scenario with tank removal from the fire (two first prototypes COPV#CC and COPV#CB-1, Table 1), and for the scenario of fire extinction by water spray by HyTunnel-CS partner USN (test with tank COPV#CB-5), and by a fire testing laboratory in the USA (tests with tanks COPV#CB-2 to COPV#CB-4).

Table 1. Parameters of the six μLNB tank prototypes of 7.5 L and NWP=70 MPa.

Prototype	Liner	Layer 1	Layer 2	Outside D increase	Fire scenario
COPV#CC	L1	CFRP#1	CFRP#2	2%	Removal from a fire
COPV#CB-1	L1	CFRP#1	BFRP	2%	Removal from a fire
COPV#CB-2	L2	CFRP#1	BFRP	0%	Water supply to fire
COPV#CB-3	L1	CFRP#1	BFRP	0%	Water supply to fire
COPV#CB-4	L2	CFRP#1	BFRP	2%	Water supply to fire
COPV#CB-5	L2	CFRP#1	BFRP	0%	Water supply to fire

Two grades of HDPE liner (L1, L2), two carbon fibre reinforced polymers (CFRP#1, CFRP#2), and one basalt fibre reinforced polymer (BFRP) as a thermal protection layer (TPL) were used in tank prototypes. The first two tanks in Table 1 were tested in the scenario of removal of the tank from a fire. The rest of four tanks were tested in fire extinction conditions. Both scenarios were imitating possible intervention by fire brigade at the fire incident scene involving a hydrogen vehicle. The first two and the fifth tanks had outside diameter slightly increased compared to the original standard tank diameter by 2%. Other three μLNB prototypes had diameter exactly as in the original tank (requires protection by TPRD).

2.1 Removal from the fire and fire re-ignition scenario

Figure 4 (left) shows the pressure and temperature dynamics in the μLNB tank made of carbon-carbon double-composite wall (COPV#CC) during the fire test. Figure 4 (right) shows the pressure and temperature transients for carbon-basalt double-composite wall tank (COPV#CB-1) during the fire test of the same intensity of the realistic fire of HRR/A=1 MW/m^2. Both tanks were undergone the same testing procedure. Pressure and temperature transients inside the tanks demonstrated similar tendencies with some differences. The initial pressure in both tests was 54-55 MPa, i.e., somewhat below the NWP=70 MPa. In the fire, pressure and temperature inside the tank grow due to heat transfer through the wall from outside. In the case of the carbon-carbon (COPV#CC) μLNB tank, hydrogen release through the microchannels of the composite wall started at about 4 min 40 s, and for the carbon-basalt (COPV#CB) tank a bit later at 6 min 40 s. The microleaks are manifested by a sharp pressure drop from 56-57 MPa to about 15 MPa in just a minute. During the same period of pressure drop hydrogen temperature decreased from about 80˚C to 24˚C for the COPV#CC tank and to 29ºC for the COPV#CB tank due to gas expansion. To imitate the removal of a vehicle located over a spill fire, the fire test burner was switched off (left vertical dashed line on the graphs) when the hydrogen release started following the melting of liner in the μLNB tank.

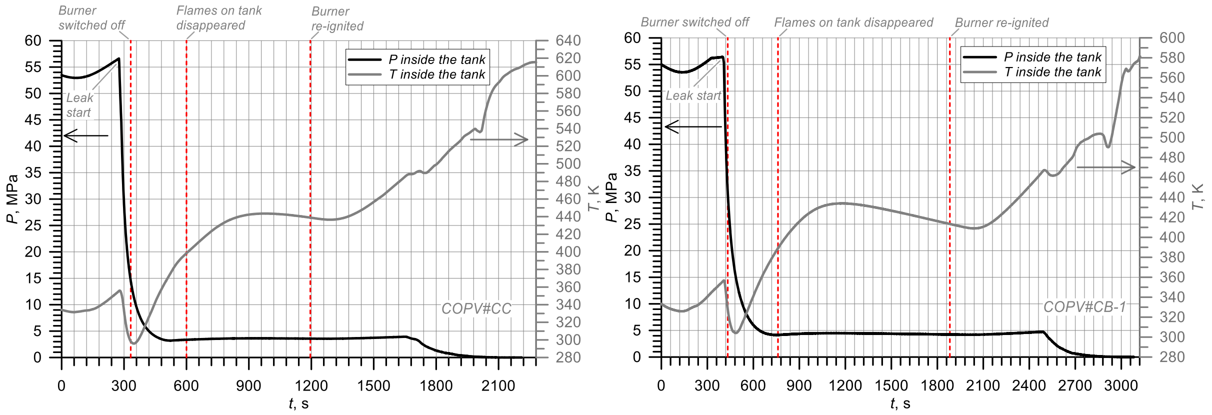

Figure 4. Pressure and temperature transients in µLNB tanks with liner of grade L1 during the fire test. Left: carbon-carbon double-composite wall tank COPV#CC. Right: carbon-basalt double-composite wall tank COPV#CB-1

Due to continuous combustion of the resin of the composite, hydrogen temperature in tanks was growing further after the burner was switched off. Hydrogen temperature continued to grow even after the visible flames disappeared on the tank surface (middle vertical dashed line) at 10 min for the CC prototype and 12 m 40 s for the COPV#CB-1 tank. Because of heat accumulated in the wall and its higher temperature, hydrogen temperature continued to raise for about 6 more minutes for both tanks. Only then hydrogen temperature began to decrease. The pressure decrease stopped at about 8 min for the COPV#CC tank and 12 min for the COPV#CB-1 tank when pressure in both tanks dropped to and stabilised at 3.5-4.3 MPa pressure plateau. Such residual pressure would require more than 33 times (NWP=70 MPa multiplied by safety factor 2.25 and divided by 4.3 MPa) thinner wall compared to the initial wall thickness to bear the load 4.3 MPa. This could be equivalent of one composite ply, if tanks original wall thickness would be 33 mm.

To complicate the intervention scenario, it was assumed that the fire re-ignites. To imitate this, the burner was re-ignited in the experiment (right vertical dashed line on the graphs of Figure 4). The COPV#CC tank started to leak again after 7 min 30 s from re-ignition, and the microleaks in the COPV#CB-1 tank began with 10 min 30 s delay after re-ignition. Hydrogen temperature reached at the time of the second leak about 120˚C in the COPV#CC tank and just under 100˚C in the COPV#CB-1 tank. The temperature of the HDPE liner for such hydrogen temperature is of the order of its melting temperature and is higher than hydrogen temperature inside the tank. This is thought to be the reason for microleaks to begin again. Finally, the pressure drops to atmospheric in 5 min after the start of the secondary leak for both tanks. Yet, the hydrogen temperature continues to grow due to heat from the fire even there is no overpressure in the tank. Thermocouple readings reach about 335ºC for the COPV#CC tank and 295˚C for the COPV#CB-1 tank at the end of the measurements. This is close to epoxy resin decomposition temperature of about 280-375˚C in composite, e.g. [11], but significantly below of decomposition temperature of carbon fibres of about 700-750˚C for carbon fibres [33].

The increase of temperature after the pressure in the tank dropped to atmospheric could be explained, e.g., by the contact of thermocouple with melted liner or resin, or by penetration of hot combustion products inside the tank. The last is less probable reason.

Figure 5 shows a series of snapshots of fire test with COPV#CB-1. The test starts when the burner is ignited (snapshot "0 s"). Microleaks are started after the liner melts at 6 min 40 s (snapshot "6 min 40 s"). The flame size around the tank is practically the same with an insignificant increase at the moment of leak start. Snapshot "7 min 20 s" shows combustion around the tank when the burner flame is switched off. What is seen in this snapshot is the combustion of composite resin assisted by hydrogen released through the microchannels in the wall. Few residual flames are seen in snapshot "11 min 40 s" which corresponds to the time when the pressure decrease stops due to the contraction of the composite wall at significantly decreased pressure and formation of the pressure plateau at a level of 4.3 MPa. No flame was observed in the snapshot “13 min 20 s”.

Figure 1. Snapshots of the µLNB tank fire test with COPV#CB-1

2.2 Fire extinction scenario tests

Figure 6 shows the comparison of pressure and temperature dynamics for tank COPV#CB-2 (left) and tank COPV#CB-3 (right). The only difference in tanks’ design is the grade of liner. The order of actions in the tests was as follows. The burner was ignited when the pressure in tanks was practically equal to NWP=70 MPa. Tank COPV#CB-2 started to leak after melting of liner L2 after 4 min 45 s when pressure increased to 78 MPa, while liner L1 melted somewhat faster at 3 min 50 s when pressure raised to only 74.5 MPa. The rate of pressure growth was the same in both tanks but in test COPV#CB-3 liner L1 melted earlier. The drop of pressure in the test with tank COPV#CB-2 is responsible for the decrease of hydrogen temperature from 45°C down to -38°C (decrease by 83 degree), while the smaller rate of pressure decrease in tank COPV#CB-3 resulted in temperature decrease from 58°C (indicating that liner L1 could have higher thermal conductivity) to the minimum of 25°C (decrease by 33 degrees only).

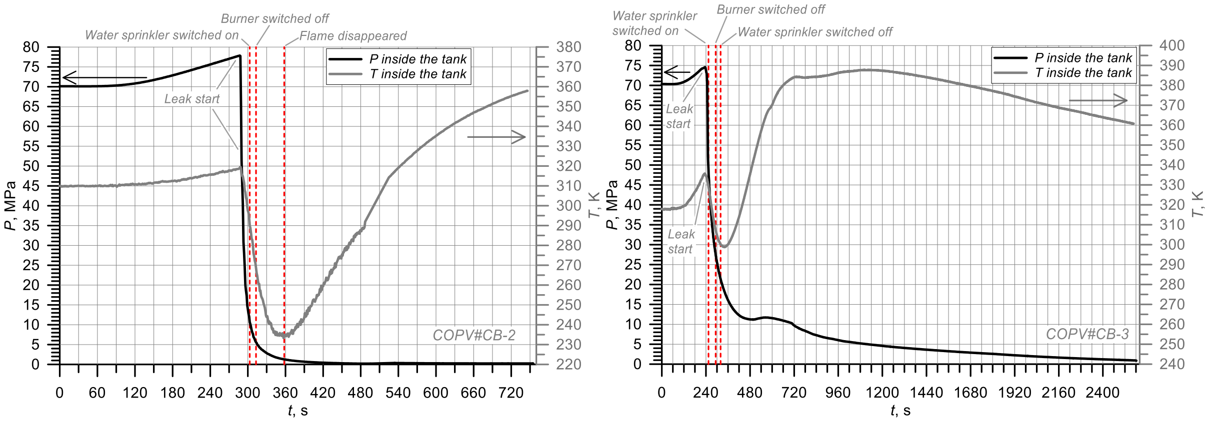

Figure 2. Pressure and temperature transients measured inside µLNB tank prototypes during the fire tests: COPV#CB-2 with liner L2 (left), COPV#CB-3 with liner L1 (right)

In about 10 s after the start of microleaks, the sprinkler was switched on and water sprays were applied to the top to the burning tank surface. Then in 10-20 s the burner was switched off. Then the tests proceeded differently. While in the test with tank COPV#CB-2 the water supply continued to the end of test, in test with tank COPV#CB-3 water was switched off in 20 s after the burner was switched off. This is thought to be a reason of larger temperature drop in test with COPV#CB-2.

Figure 7 shows the pressure and temperature dynamics inside μLNB tank prototypes COPV#CB-4 (left) and COPV#CB-5 (right) during the fire tests performed in different laboratories. Both tanks had liner L2 and the external diameter of tank COPV#CB-4 was slightly (2%) larger.

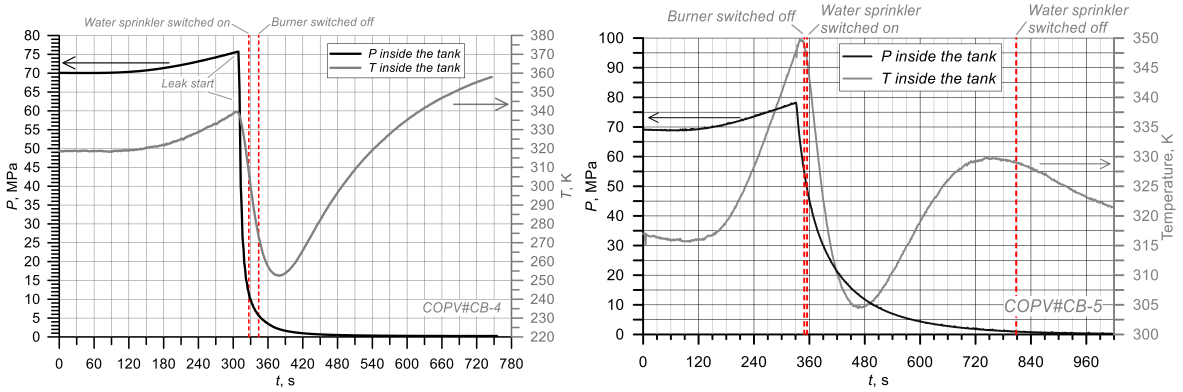

Figure 7. Pressure and temperature transients inside μLNB tank prototypes during the fire tests: COPV#CB-4 (left) and COPV#CB-5 (right) both with liner L2

Figure 8 presents snapshots explaining the development of the fire test with μLNB tank prototype COPV#CB-5. The test begins from the localised fire stage of intensity HRR/A=1 MW/m^2 (snapshot "0 s"). Resin combustion is seen in snapshot "1 min 19 s". The hydrogen starts to leak through microchannels in the wall after the liner is melted at 5 min 30 sec (not shown in Figure 8). The burner was switched off shortly after the microleaks begin. The epoxy resin of the composite continues to burn afterwards (see snapshot "5 min 49 s"). Then, the sprinkler is switched on to supply water jets on the top of the tank (snapshot "5 min 55 s"). The direction and moderate intensity of the water supply is not sufficient to fully terminate combustion, which is seen on the bottom surface of the tank (snapshot "6 min 30 s"). When the sprinkler was stopped the video allows for resolving weak flames (see snapshot "13 min 30 s"). The pressure of hydrogen in the tank dropped to atmospheric at 16 min.

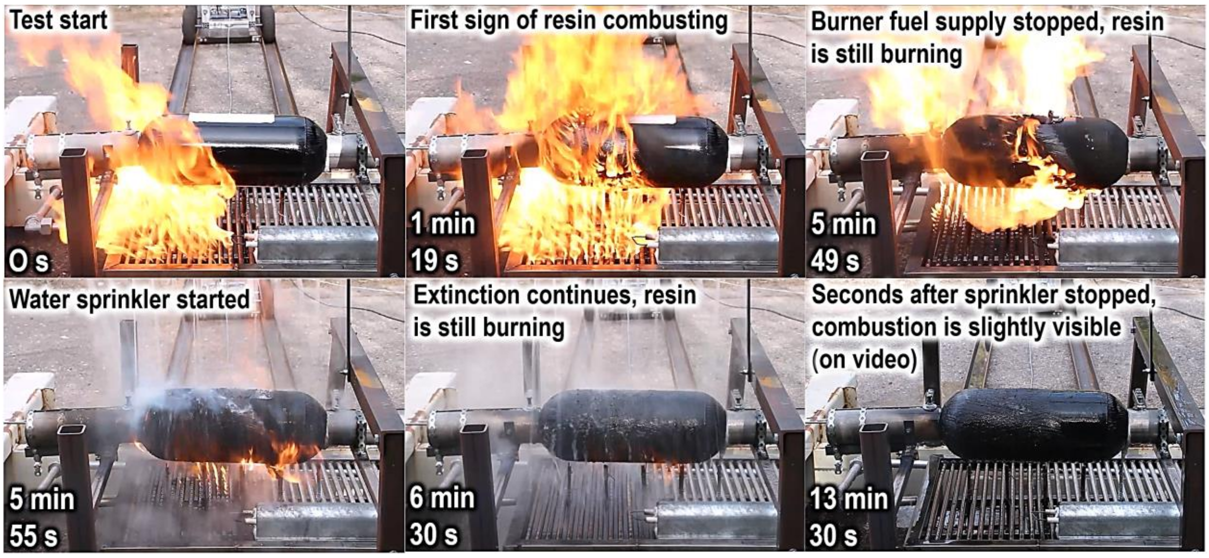

Figure 8. Snapshots of the μLNB tank prototype COPV#CB-5 behaviour in the fire test

The analysis of temperature transient in Figure 7 (right) shows that the initial hydrogen temperature in the tank was 43ºC (probably above the ambient due to insufficient time for colling after filling the tank by hydrogen), and then went up to 76°C before the microleaks started, then dropped to the minimum of 32°C (by 44 degree) due to gas expansion during pressure relief through microleaks. Then, the temperature started to grow again even in the presence of a water supply on the tank top. However, the residual combustion at the bottom of the tank visible in the video seems was sufficient to provide temperature increase from 32°C up to the maximum of about 56°C at time 12 min 30 s. The combustion at the tank bottom could be hydrogen-assisted resin combustion that ceases when the pressure at the tank tends to atmospheric. This explains the temperature decrease after 12 min 30 s of the test.

The temperature in the test with tank COPV#CB-4 (Figure 7, left) grows after the hydrogen pressure drops to atmospheric. As for tests with COPV#CC and COPV#CB-1, it could be explained by the contact of the thermocouple in the tank with a melted and deformed liner.

Tests with COPV#CB-4 and COPV#CB-5 (both with HDPE liner of grade L2) strongly support the observation made from the test with COPV#CB-2 analysis that the use of grade L2 liner can probably eliminate the existence of the pressure plateau at all, and provide a faster release of hydrogen (pressure drop in the tank to atmospheric took in tanks with liner L2 from 8 min (COPV#CB-2, COPV#CB-4) to maximum 16 min (COPV#CB-5) and more than 43 min for tank COPV#CB-3 with liner L1. However, it is worth noting that faster release of hydrogen could require a large vent area for mitigation of the pressure peaking phenomenon [34–36] and adequate natural ventilation.

CONCLUSIONS

The *originality* of this study is in the investigation of explosion free in fire self-venting (TPRD-less) tank performance beyond the fire test protocol of GTR#13 (Phase 2), i.e., in realistic fire conditions imitating different intervention strategies of first responders to extinguish the fire with characteristic for gasoline/diesel spill fires intensity of HRR/A=1 MW/m^2. The scenario of a hydrogen vehicle with an onboard storage tank removed from the fire scene with re-ignition and scenarios of continuous and temporary extinction of the fire, were investigated. Testing of µLNB tanks in these scenarios confirmed that the fire extinction does not interrupt hydrogen release through microleaks, i.e., firefighters can conduct their interventions at an incident scene following current strategies and tactics. The study revealed that the proper choice of HDPE liner grade could further improve the performance of the technology and eliminate the low-pressure plateau.

The *significance* of this work is in the demonstration that self-venting µLNB tanks could have the same size as original tanks but exclude rupture in fire, including conditions of intervention of first responders at the fire scene. The use of µLNB tanks reduces hazards and associated risks for first responders when dealing with fires of hydrogen-powered transport and fires in storage enclosures onboard of road vehicles, trains, marine vessels, planes at airports and hydrogen storage infrastructure at hydrogen refuelling stations. The same is valid for the firefighting in confined spaces like tunnels, underground parking, etc. Standard procedures to attack a fire could be followed by firemen as the use of µLNB self-venting tanks eliminates hazards of blast waves, fireballs, projectiles, long flames from TPRD, formation of flammable cloud and hot products under the ceiling of underground parking, mitigates the pressure peaking phenomenon in enclosures, reduces property loss, and protects life from adverse effects of incidents involving hydrogen. The design of explosion free in a fire TPRD-less tank usually reduces the use of carbon fibres, as seen in high demand and with almost doubled costs during last years, by cheaper ones. It is found that for scenario of hydrogen storage tank removal from the fire, the microleaks through the composite wall could cease due to the contraction of the wall or solidification of a liner. This occurs after the reduction of pressure in the tank by the order of magnitude, and possible liner solidification during temperature drop as the result of gas expansion. The tank does not rupture with the residual plateaued pressure inside, because, despite the resin decomposition to the wall depth, the decomposition of fibres does not happen due to the higher decomposition temperature. Thus, hydrogen will rather leak than the tank shell with degraded resin will rupture. This is proved by the extension of the removal scenario to re-ignition of fire under the tank that resulted in the safe secondary release of hydrogen and pressure drop in the tank to atmospheric.

The *rigour* of this study is confirmed by experimental validations of the μLNB technology efficiency for 6 tank prototypes of 7.5 L volume and NWP=70 MPa made of carbon-carbon (1 tank) and carbon-basalt (5 tanks) double-composite walls prototypes. The μLNB tanks are tested at realistic fire intensity of HRR/A=1 MW/m^2, which is above those misleadingly reduced by the GTR#13 (Phase 2) fire test protocol, and conditions imitating different scenarios of first responders' intervention at the fire scene. All tank prototypes successfully passed fire testing in scenarios with intervention by tank removal and water supply on the tank surface.

The breakthrough safety technology of explosion free in fire self-venting (TPRD-less) tank opens the way for tank and vehicle manufacturers to drastically reduce the hazards and associated risk of hydrogen-powered vehicles to an acceptable level of life safety and property protection, including the safety of first responders. The paper described in detail the performance of μLNB tank prototypes and the technology validations in conditions imitating the intervention of first responders at the fire incident scene with the involvement of a hydrogen-fuelled vehicle. However, some proprietary information is not disclosed, being the intellectual property of Ulster University.

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