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Explosion free in fire self-venting (TPRD-less) composite tanks: Performance during fire intervention

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HIGHLIGHTS
- Performance of self-venting (TPRD-less) tanks during fire intervention is studied.
- Examined fire intervention scenarios: removal from fire, fire extinction by water.
- Microleaks-no-burst carbon-carbon and carbon-basalt tanks tested in fire.
- Self-venting tanks allow standard fire intervention strategies and tactics.

ABSTRACT
This paper describes the performance of explosion free in fire self-venting (TPRD-less) composite tanks in fires of realistic specific heat release rate (HRR/A), i.e., total fire HRR over the source area, A, of HRR/A = 1 MW/m², during fire intervention. This breakthrough safety technology does not require thermally activated pressure relief devices (TPRD). It provides microleaks-no-burst (μLNB) performance of hydrogen storage tanks in fire. The study investigated two fire intervention strategies, i.e., removal of vehicle with μLNB tank from the fire, and extinction of fire by water. One carbon-carbon and one carbon-basalt double-composite wall tanks were assessed in the removal from fire scenario. Four carbon-basalt prototypes were studied in fire extinction scenarios. All six prototypes of 7.5 L and nominal working pressure of 70 MPa have demonstrated safe release of hydrogen through microchannels of the wall after the liner melting. The μLNB technology allows to apply standard intervention strategies and tactics.

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Introduction
Rupture of high-pressure hydrogen storage tanks must be excluded in any fire scenario to eliminate hazards from blast wave, fireball, projectiles. The tank rupture consequences are different in the open [1−3] and confined spaces, like tunnels, where the blast wave decay is weaker [4,5], and thus drastically affects hazard distances.

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The use of conceived at Ulster University the breakthrough safety technology of explosion free in a fire self-venting tank [6,7] will provide an unprecedented level of life safety and property protection. This would reduce hazards and associated risks of hydrogen-powered vehicles to the level equal to or below that for fossil fuel vehicles. The technology does not require thermally activated pressure relief device (TPRD) which can be unreliable in localised fires. For example, the FireComp project suggests 50% TPRD failure probability in which can be unreliable in localised fires. For example, the FireComp project suggests 50% TPRD failure probability in

localised fires. The Fire in-...
The situation changes drastically if the same tank is in a fire of a higher intensity, e.g., gasoline/diesel spill fire of HRR/A = 1 MW/m² after a traffic incident. Fig. 2 shows that in such a fire intensity the tank could rupture in 5–6 min, i.e., before the TPRD is affected by the engulfing fire (see the insert at the bottom right corner of Fig. 2). This can create unacceptable hazards and associated risks for life and property in fires of higher intensity. It is thus understandable, that the fire test protocol suggested in GTR#13 could have serious life safety implications in real life, especially for the first responders, and must be amended to include fires of higher intensity.

The analysis presented in this section demonstrates that the fire test protocol of GTR#13 should be changed to include fire intensity of HRR/A = 1 MW/m² 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 element, are beyond the scope of this study yet must be addressed by GTR#13 fire test protocol too.

**Overview of microleaks-no-burst (µLNB) safety technology**

Fig. 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, in addition, a 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 standard and µLNB tanks include the heat propagation into the wall and the degradation of resin in the composite (“Resin decomposition” line), as well as the moving outwards load-bearing wall thickness fraction (“Load bearing fraction” line). In the case of standard tank, when these two fronts, i.e., the resin decomposition front and the load-bearing wall thickness fraction...
location, meet each other the tank is not anymore able to bear the load of increasing in fire hydrogen pressure and ruptures. This happens for the standard tank because the hydrogen-tight liner does not melt before the rupture conditions are met.

The LNB tank has two composites in the wall, one over another, of different thickness and properties, including thermal conductivity, heat of decomposition, etc. The self-venting performance of the tank is provided by a proper design using the intellectual property of Ulster University [6–7] and in-house proprietary models and tools [32,37] accounting for all important thermophysical and geometrical parameters of the liner, two composite layers, the safety factor that is the ratio of the tank initial burst pressure to the nominal working pressure, etc. The design of LNB tank provides melting of the liner before the tank loses its load-bearing ability. The melting of liner initiates microleaks of hydrogen through structure of FRP and TPL layers which are not hydrogen-tight. Despite further propagation of the decomposition front into the tank wall (see Fig. 3, right), the load-bearing wall thickness fraction reduces drastically due to the tank depressurisation through the “natural” microchannels in the composites. This eliminates conditions for tank rupture in a fire and thus devastating blast wave, large fireball, and projectiles, including a vehicle itself.

The design of LNB tank strongly depends on the choice of liner material and thickness. For example, higher melting temperature of Nylon, i.e. polyamide (PA), liner, e.g., 219 °C [39], compared to that of high density polyethylene (HDPE) liner, 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 takes much less amount of heat to melt it, than it would to melt the PA liner. There is another substantial safety advantage of HDPE compared to PA liner. Numerical experiments performed at Ulster University [7] have explained the interesting observation in the previous experimental campaigns [20,21], where Type IV composite tanks with HDPE liner leaked in a fire without rupture if they were charged with pressures below of about the half of the nominal working pressure (NWP). This would not be possible for PA liner. In addition, PA mechanical properties are less favourable compared to HDPE liner at temperatures below −40 °C, which may be important for use of hydrogen storage, e.g., for high altitude aviation applications, etc.

The experimental studies by Ruban et al. [21], and Blanc-Vannet et al. [20], demonstrated the leakages of Type IV hydrogen tanks in fires at lower states of charge (SoC) due to the melted liner. This phenomenon was reproduced in simulations by the authors [25] and explained. The fires in experiments were continuous. No research was found on the interrupted fire test with hydrogen tank where the burner would be terminated, and/or with flame extinction. Therefore, there is a knowledge gap on the Type IV hydrogen tanks behaviour in such conditions that should be investigated and closed.

The significant not related to the safety benefit of the LNB technology is the reduction of amount of shortage in supply of carbon fibre [40,41] and substitution of at least a part of it by cheaper (in some cases the prices differ by the order of magnitude) fibres like glass, basalt, etc. This, along with the increase of public confidence in safety of hydrogen systems and infrastructure, will accelerate the transition to the economy based on the use of renewable electricity and green hydrogen.

The approach applied by HySAFER to design and manufacture LNB tank prototypes is based on the use of a standard tank design as a starting point. This allows tank manufacturers in most cases to use their usual design of liner and bosses as well as the way of filament winding. This facilitates manufacturing of inherently safer hydrogen storage tanks by the collaborators around the globe using their facilities, established procedures and acquire a strong competitive advantage on the market due to unprecedented safety features of LNB tanks.

**Characteristics of tank prototypes and testing procedure**

Hydrogen storage tank rupture during a fire incident is a critical concern for the responders at an incident scene. In this study we expand the validation domain for this innovative safety technology of explosion free in fire self-venting (TPRD-less) tanks from scenarios of continuous fire [6] to scenarios of intervention at the fire scene. This is relevant to intervention of responders not only to fires involving hydrogen vehicles on roads, but equally to fires in storage rooms on hydrogen-powered trains, maritime vessels in harbours, planes at

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airports, etc. To address the safety concerns of firefighters, all fire tests were performed following regulations UN GTR#13 and EC R134 [31,42]. The localised and engulfing sections of the burners provided the specific heat release rate of HRR/\(A\) \(\equiv 1\) MW/m\(^2\) characteristic for realistic gasoline/diesel spill fires rather than fires with decreased HRR/\(A\) as per the GTR#13 (Phase 2) fire test protocol of 0.3 MW/m\(^2\) and 0.7 MW/m\(^2\) respectively [26,28].

Table 1 shows the parameters of six \(\mu\)LNB tank prototypes tested in two different fire intervention scenarios within the research programme of the HyTunnel-CS (https://hytunnel.net/) project coordinated by Ulster University. The HySAFER Centre of Ulster University designed all \(\mu\)LNB tanks using in-house heat and mass transfer models with phase transitions (degradation and melting) [32,37]. Our USA collaborator manufactured the tank prototypes. The designs of the prototypes were based on the original 7.5 L and \(\text{NWP} = 70\) MPa Type IV tanks, with HDPE liners and of sizes 186 × 520 mm (\(L/D = 2.8\)). The HyTunnel-CS project partner French Alternative Energies and Atomic Energy Commission (CEA) performed fire tests analysed in this study for the scenario with tank removal from the fire (two first tank prototypes COPV#CC and COPV#CB-1, Table 1). The HyTunnel-CS project partner University of South-Eastern Norway (USN) conducted tests for the scenario of fire extinction by water spray (test with tank COPV#CB-5), and the fire testing laboratory in the USA investigated the same scenario in tests with three tanks (COPV#CB-2 to COPV#CB-4).

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 to design and manufacture the tank prototypes. The first two tanks in Table 1 were tested in the scenario of removal of the tank from a fire. The behaviours of other four tanks were evaluated in fire tests with extinction conditions using water sprays. Both scenarios were imitating intervention by firefighters at the fire incident scene involving hydrogen vehicle. The first two and the fifth \(\mu\)LNB tank had outside diameter slightly increased compared to the original standard tank diameter by 2%. Other three \(\mu\)LNB prototypes had external diameter exactly as in the original standard tank (requires protection by TPRD with all mentioned above drawbacks). The \(\mu\)LNB tanks generally have a diameter equal or with minimum deviation from the original tank diameter, and the portion of the original carbon fibre composite wall is substituted by a composite with different, a cheaper fibre. This means that \(\mu\)LNB tanks will have equivalent and, in some cases, provide savings in material costs, compared to the standard Type IV tank (which do explode in a localised fire or in engulfing fire, in case a TPRD is not triggered, triggered with unacceptably long delay or is faulty).

### Results and discussion: removal from a fire and fire Re-ignition

Fig. 4 (left) shows the pressure and temperature dynamics in the \(\mu\)LNB tank made of carbon-carbon double-composite wall (COPV#CC) during the fire test. Fig. 4 (right) presents the pressure and temperature transients for carbon-basalt double-composite wall tank (COPV#CB-1) during the fire test of the same intensity of realistic fire of \(\text{HRR}/\text{A} = 1\) MW/m\(^2\). Both tanks undergone the same testing procedure. Pressure and temperature transients inside the tanks demonstrated similar

<table>
<thead>
<tr>
<th>Prototype</th>
<th>Liner</th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Outside D increase*</th>
<th>Fire scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>COPV#CC</td>
<td>L1</td>
<td>CFRP#1</td>
<td>CFRP#2</td>
<td>2%</td>
<td>Removal from a fire</td>
</tr>
<tr>
<td>COPV#CB-1</td>
<td>L1</td>
<td>CFRP#1</td>
<td>BFRP</td>
<td>2%</td>
<td>Removal from a fire</td>
</tr>
<tr>
<td>COPV#CB-2</td>
<td>L2</td>
<td>CFRP#1</td>
<td>BFRP</td>
<td>0%</td>
<td>Water supply to fire</td>
</tr>
<tr>
<td>COPV#CB-3</td>
<td>L1</td>
<td>CFRP#1</td>
<td>BFRP</td>
<td>0%</td>
<td>Water supply to fire</td>
</tr>
<tr>
<td>COPV#CB-4</td>
<td>L2</td>
<td>CFRP#1</td>
<td>BFRP</td>
<td>2%</td>
<td>Water supply to fire</td>
</tr>
<tr>
<td>COPV#CB-5</td>
<td>L2</td>
<td>CFRP#1</td>
<td>BFRP</td>
<td>0%</td>
<td>Water supply to fire</td>
</tr>
</tbody>
</table>

Note: * - increase of diameter compared to the original standard tank.
tendencies with few differences. The initial pressure in both tests of CEA in real tunnel was 54–55 MPa, i.e., below the NWP = 70 MPa. In the fire, pressure and temperature inside the tank grow due to heat transfer through the wall from the external fire. In the case of carbon-carbon (COPV#CC) μLN 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 later at 6 min 40 s. The microleaks are manifested by a sharp pressure drop from 56 to 57 MPa to about 15 MPa in just a minute. During this short time of pressure drop, the hydrogen temperature inside the tank decreased from about 80 °C to 24 °C for the COPV#CC tank and to 29 °C for the COPV#CB tank due to gas expansion. To imitate the removal of vehicle located over a spill fire, the burner was switched off (left vertical dashed line on the graphs) when the hydrogen release started (following the melting of liner in the μLN tank).

Because combustion of the resin of the composite continues after the burner was switched off, hydrogen temperature in tanks was growing further. Hydrogen temperature continued to grow even after the visible flames disappeared on the tank surface (middle vertical dashed line) at 10 min for the COPV#CC prototype and 12 m 40 s for the COPV#CB-1 tank (invisible microflames could still be present [43]). 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 the pressure in both tanks stabilised at 3.5–4.3 MPa pressure plateau. Such residual pressure of 4.3 MPa 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 pressure. Therefore, a requirement of safe pressure for scenario with water jets supply to the tank from the above. The order of actions in the tests was as follows. The burner was ignited when pressure in tanks was equal to NWP = 70 MPa. Tank COPV#CB-2 started to leak after melting of liner L2 after 4 min 45 s when pressure inside the tank increased to 78 MPa, while liner L1 in COPV#CB-3 melted 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 °C), while the smaller rate of pressure decrease in tank COPV#CB-3 resulted in temperature decrease from 62 °C to minimum of 26 °C (decrease by 36 °C).

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 two tests proceeded differently. While in the test with tank COPV#CB-2 the water supply continued to the test end, in the test with tank COPV#CB-3 the water supply

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**Results and discussion: fire extinction**

Fig. 6 shows comparison of pressure and temperature dynamics for tank COPV#CB-2 (left) and tank COPV#CB-3 (right) for scenario with water jets supply to the tank from the above.
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. The visible flames on the tank surface disappeared in both of these tests.

Fig. 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 than in the original standard tank and other prototypes.

Fig. 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/m² (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 melted at 5 min 30 s (not shown in Fig. 8). The burner was switched off shortly after the microleaks began. 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 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 to resolve weak flames (see snapshot “13 min 30 s”) beneath the tank. The pressure of hydrogen in the tank dropped to atmospheric at 16 min.

The analysis of temperature transient in Fig. 7 (right) shows that the initial hydrogen temperature in the tank was 43 °C (probably above the ambient due to insufficient time for cooling 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 °C) due to the gas expansion during pressure relief through microleaks. Then temperature started to grow again even in the presence of 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 57 °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 temperature decrease after 12 min 30 s of the test.

Hydrogen temperature in the test with tank COPV#CB-4 (Fig. 7, left) grows after the pressure in the tank drops to atmospheric. Like for tests with COPV#CC and COPV#CB-1, it could be explained by the contact of the thermocouple in the tank with melted and deformed liner or resin, or penetration of hot fire products through the matrix of fibres with degraded resin.

Tests with COPV#CB-4 and COPV#CB-5 (both with HDPE liner of grade L2) support the observation made from the test with COPV#CB-2 analysis that the use of grade L2 liner can eliminate the existence of the pressure plateau at all, and provide 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 it takes more than 43 min for tank COPV#CB-3 with liner L1. However, it is worth noting that faster release of hydrogen could require large vent area for mitigation of the pressure peaking phenomenon [45–49] in confined space of hydrogen storage rooms 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 conditions of fire intensity of HRR/A = 1 MW/m² characteristic for gasoline/diesel spill fires, with imitation of different intervention strategies of responders to extinguish the fire. The scenario of a hydrogen vehicle with onboard storage tank removal from the fire scene with re-ignition, and scenarios of continuous and temporary extinction of the fire by water supply on the tank were investigated. 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 a fire, including conditions of intervention of responders at a fire scene. The use of μLNB tanks reduces hazards and associated risks for first responders when dealing with fires of hydrogen-powered vehicles.
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 fire fighting in confined spaces like tunnels, underground parking, etc. The design of explosion free in a fire TPRD-less tank usually reduces the use of carbon fibres, as being seen in high demand and with almost doubled costs during last years, by cheaper ones. It is found that for the scenario of hydrogen storage tank removal from the fire, the microleaks through the composite wall could cease due to contraction of the wall or solidification of liner. This occurs after the reduction of pressure in the tank by the order of magnitude and accompanied by solidification of previously melted liner 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 lose structural integrity. 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 in the form of microleaks and pressure drop in the tank to atmospheric. 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 standard firefighting procedures could be followed 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 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 in conditions of fire intervention. The μLNB tanks are tested at realistic fire intensity of HRR/A = 1 MW/m², which is above those dangerously 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 jets 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 the acceptable level of life safety and property protection, including 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 responders at the fire incident scene with involvement of hydrogen-fuelled vehicle. However, some proprietary information is not disclosed being the intellectual property of Ulster University.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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