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A deployable barrier preventing liquid oxygen accumulation and safety risks during liquid hydrogen transfers

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Abstract. Insulated and uninsulated surfaces exposed to cryogenic temperatures can result in the formation of liquid air, an oxygen-rich mixture. The National Fire Protection Agency NFPA 2-2023 code specifies a non-combustible material must be underneath the transfer line to prevent liquid air from dripping onto combustible materials. Concrete is a non-combustible material commonly used in infrastructure that is heavy and generally immobile. Another common material used in infrastructure is asphalt which is considered a combustible material due to the tar content. Literature has discussed asphalt combustibility with pure liquid oxygen. This work describes experimental attempts to combust asphalt and other common ground surfaces in the presence of liquid air formation. A deployable barrier was designed to comply with the NFPA 2 standard while not requiring expensive materials like concrete. This barrier enables the safe transfer of liquid hydrogen in conditions where concrete pads are unavailable, particularly in off-road applications.

1. Introduction

Hydrogen is an alternative fuel that has a high potential for decarbonizing heavy duty sectors. The low volumetric density of hydrogen gas at ambient pressure leads to large volume requirements for storing usable quantities of hydrogen. Compressing or liquefying hydrogen decreases the volume requirement with compression increasing the density of hydrogen up to 450x while liquefaction increases the density up to 850x. Liquid hydrogen (LH2) has been previously found to be the most likely form of hydrogen transport with demands less than 60 tonnes per day [1]. Unique safety designs, to mitigate risks such as the liquefaction of air or static discharge, must be implemented due to the flammable and cryogenic nature of liquid hydrogen.

Cryogenic transfer lines can reach temperatures around 20 K (-420 °F) during LH2 distribution. These conditions promote the liquefaction off air in the proximity of the transfer line and connections at both delivery and receiving vehicles. While transfer lines with compromised insulation pose a serious risk, even well insulated lines can liquefy air under the right conditions. As air liquefies the oxygen content enriches to ~50% as shown in the composition diagram (Figure 1).

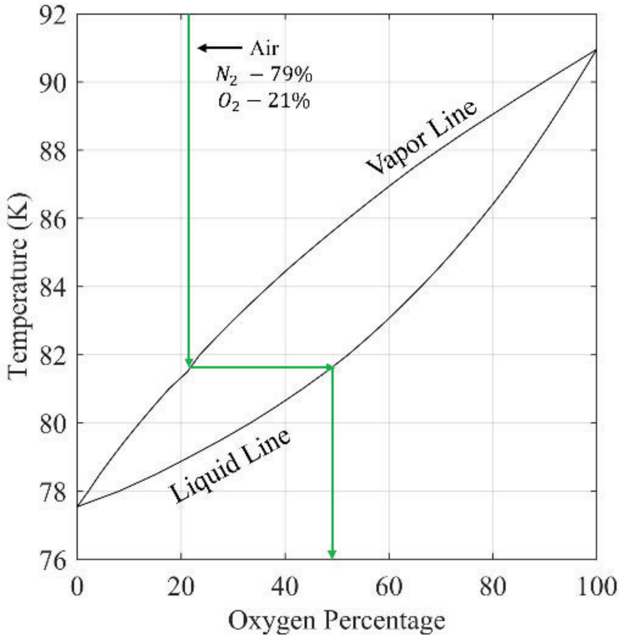

Figure 1. Oxygen-nitrogen phase diagram. Recreated from Baly et al. [2].

The National Fire Protection Agency NFPA 2-2023 [3] codes state that for outdoor locations all surfaces located below LH2 piping, which include tank and vehicle connections, "shall be constructed of non-combustible materials" [3] ensuring no flammable mixtures in an oxygen rich environment. Common surfaces including asphalt and bitumastic paving do not adhere to the NFPA 2 codes for transfers as asphalt is composed of aggregates and bitumen (a byproduct of petroleum) and combusts in the presence of liquid oxygen igniting at low impact pressures [4].

Concrete is another material commonly used for infrastructure but is considered non-combustible making it compatible with the NFPA 2 Hydrogen codes. However, the use of concrete is costly and permanent after installation. For example, a concrete refuelling pad must be 12 feet by 12 feet in area to comply with NFPA 2 codes and at least 8.5 inches thick with 6 inches of an aggregate base for an industrial application using a front loader with a gross vehicle weight of 130,000 lbs [5]. This concrete pad requires at least 3.78 cubic yards of concrete weighing approximately 15,000 lbs costing ~$630 not including labour using the national average cost for concrete per yard [6]. While the material cost is relatively low for a concrete slab, having slabs in many remote locations for refuelling is impractical while also creating permanent infrastructure.

In addition to the condensation of liquid air, another example of a safety risk present during LH2 transfers is the low minimum ignition energy of hydrogen-air mixtures, which is 0.019 mJ [7]. A common static discharge from ungrounded humans can release up to 0.5 mJ of energy [8], which is more than enough to ignite a hydrogen-air mixture. Currently, the NFPA 2 codes do not discuss the implications of static electricity during transfers.

The commercialization of LH2 as a fuel requires lightweight deployable safety barriers for transfers that occur in remote locations with sectors like agriculture, construction, forestry or mining mitigating environmental or user risks when transferring LH2. In this work a novel deployable barrier is described which is composed of non-combustible materials to be used during LH2 transfers. This solution adheres to

NFPA 2 hydrogen codes for mobile LH2 transfers and is conveniently stowed during transport. Section 2 discusses the development of the barrier and section 3 discusses the initial prototype. The next steps for commercialization are discussed in section 4.

2. Barrier Development

Complying with the NFPA-2 Hydrogen codes is of utmost importance to create a usable barrier to protect from LOx induced combustion below a LH2 transfer line. A deployable barrier configuration with lightweight, non-combustible materials which adheres to the NFPA-2 Hydrogen code can be utilized for LH2 transfers. The proposed barrier must be at least 12'x12' and cover the ground directly beneath the LH2 delivery vessel, transfer line, and receiving vessel to comply as discussed above. The proposed design of this barrier is composed of three primary layers. The base layer, closest to the ground uses Nomex® fiber fabric by DuPont™. Nomex® is composed of incredibly durable, inherently flame and chemical-resistant meta-aramid fibers [9]. Using Nomex® as the base layer prevents damage to the barrier that could be caused by sharp protrusions underneath during the movement of vehicles at the beginning or end of fill. The thick fibers of Nomex® make it difficult to compress any LOx that may enter the fibers, but accumulation is possible due to the wicking nature of Nomex®. In addition, Nomex® is known as an electrical insulator requiring the grounding of the barrier to eliminate the risk of static buildup. The potential accumulation of LOx due to wicking and the insulative properties of Nomex® necessitate the need for the second layer which will be fixed to the first layer as shown in Figure 2.

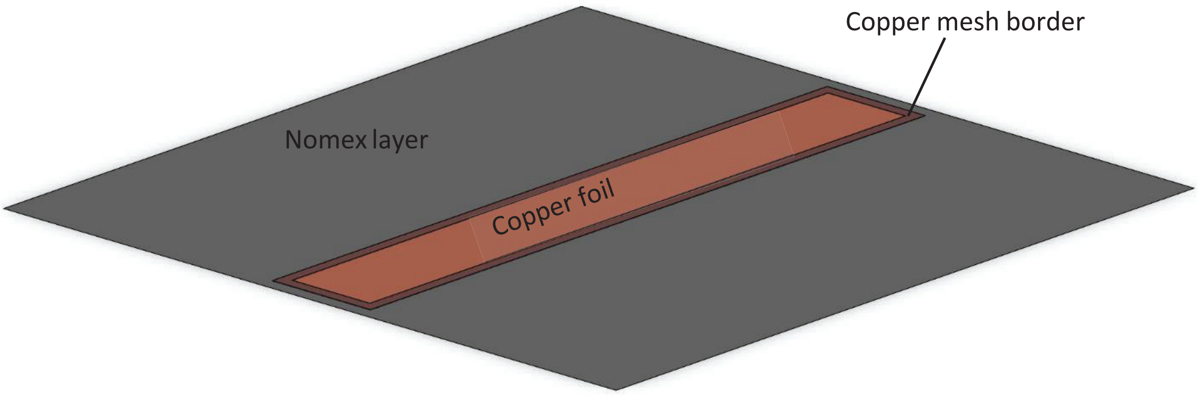

Figure 2. CAD model of the LH2 refuelling barrier showing a copper mesh bordering a copper sheet centered on the Nomex® base layer.

This second layer must be constructed out of a non-combustible and anti-wicking material without reducing the compactness of the foldable Nomex®. To satisfy this constraint, thin copper sheeting 0.127 mm thick is selected to be installed directly under the transfer line. Based on mechanical impact tests with LOx and high gaseous oxygen environments, copper resists ignition below pressures of 68.95 MPa (10,000 psi) [10] and is non-wicking due to the metallic nature. The purpose of this second layer creates a non-wicking barrier before the Nomex® which would wick the liquid air into its fibers. Instead, as the liquid air droplets impact the non-wicking copper material it is dispersed due to the impact allowing for faster evaporation, and no chance of concentrated oxygen within the fibers of the Nomex®. Copper is also a good electrical conductor, so the copper can be grounded to discharge any static electricity build-up of the barrier. The thin copper sheeting remains very pliable and easily folded while being resistant to ripping. Fold lines are built into the entire barrier to reduce the likelihood of tears propagating through the copper foil.

Depending on the environment, as liquid air drops from the transfer line to the copper layer of the barrier pooling, splashing and runoff of the liquid can occur. To prevent the concentrated amounts of liquid air from reaching the Nomex® layer, a border of copper mesh is added around the copper layer. The border will be constructed of a 50.8 mm wide copper mesh of size 16. Previous studies have been conducted exploring the flammability of copper mesh in the presence of pressurized pure oxygen gas [11] which found that size 60x60 copper mesh with a pore diameter of 0.19 mm is only flammable in the presence of an oil promoter and pure oxygen at a pressure of 12.17 MPa (1,700 psi). Increasing the diameter of the pores to 0.89 mm and 1.59 mm, the mesh was not flammable at the highest testing pressure of 34.58 MPa (5,000 psi) [11].

3. Experimental Verification

A small demonstrator is constructed as show proof of concept for the design. Spare materials from around the lab were utilized to create the small barrier, shown in Figure 3. All materials were available except the copper foil, which is substituted for a thin sheet of copper due. The thickness of the copper sheet used in the demonstrator prohibits the bonding of materials together. As such the demonstrator is used to show performance against liquid air droplet combustions and not scaling of weight and storage space requirement.

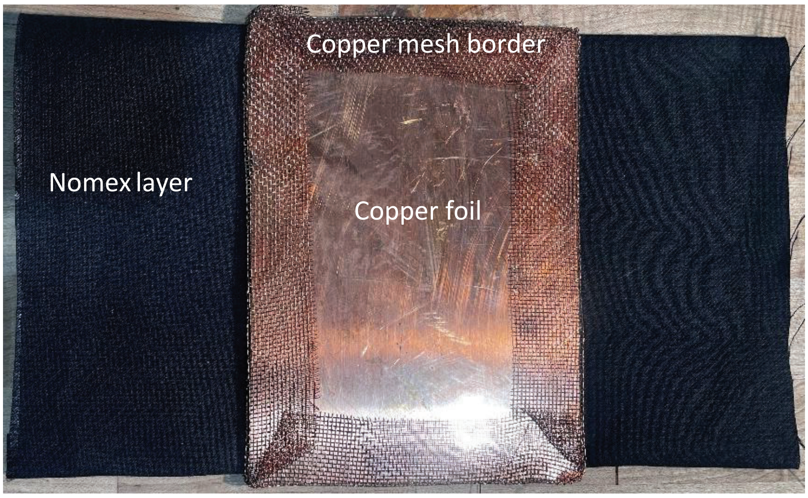

Figure 3. Liquid hydrogen refuelling barrier prototype mock-up with Nomex® base layer, copper plate, and copper mesh border.

Experimental verification using liquid nitrogen is shown in Figure 4. Liquid nitrogen (77 K) is inserted into a non-insulated kettle allowing the outside surface to condense liquid air. The liquid air drips from the kettle onto the surface of the barrier falling the distance of approximately one foot. The droplets fall from the kettle to the copper where it begins to evaporate, as well as dispersing upon contact with the copper. Droplets can move freely around the copper sheet until the copper mesh border where they are trapped and evaporate. The shorter drop results in less impact forces on the droplet which aid in flash evaporation and dispersion of liquid air. Testing through this method creates a worst-case scenario where liquid air droplets can accumulate on the copper sheet. An enlarged picture of the liquid air dripping on the copper portion of the demonstrator is shown in Figure 5. The droplets of liquid air become entrapped by the copper mesh on the border allowing evaporation to occur before wicking into the Nomex®.

Figure 4. Experimental verification setup of mock-up liquid hydrogen refuelling barrier using liquid nitrogen in a teakettle to create liquid air.

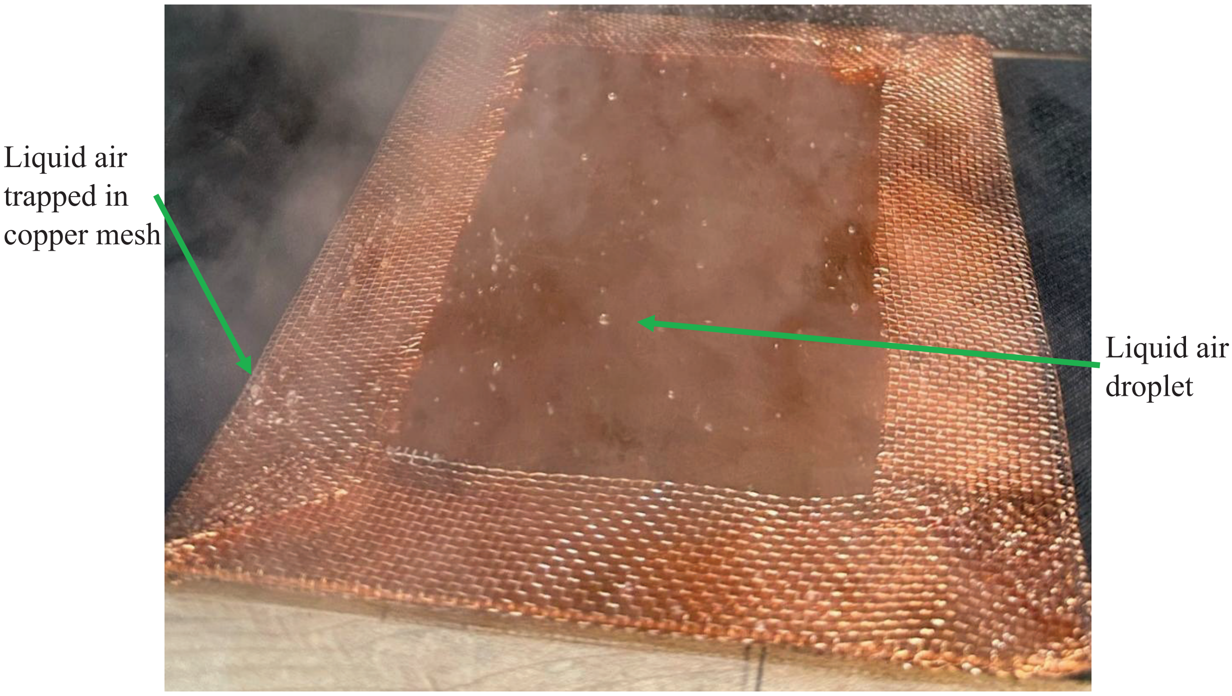

Figure 5. Testing of the mock-up LH2 refuelling barrier with condensed liquid air dripping from a tea kettle filled with liquid nitrogen. Liquid air droplets can be seen on the copper surface and trapped in the copper mesh.

In addition to evaluating the capacity of the demonstrator to collect and disperse liquid air droplets the combustion properties in the presence of liquid air were also evaluated. With the accumulated liquid aid on the copper sheet and trapped in the copper mesh an ignition source was used to attempt to promote ignition of the copper materials. No combustion of copper was noted throughout testing. The Nomex® layer was also evaluated with liquid air to ensure no combustion events occurred. No combustion was noted by the Nomex® when an ignition source was presented both above and below the material with liquid air droplets falling directly on the Nomex®.

4. Future Studies

Barrier verification will continue with a full-size prototype constructed and tested at HYPER's outdoor research facility. Sources for Nomex® fabric, copper sheeting, and copper mesh have already been identified. Testing will be conducted to provide experimental measurements on the effectiveness and durability of the refueling barrier in different refueling environments. These tests include different concentrations of liquid air, impact testing, and intentional ignition on the barrier following ASTM standards to characterize the flammability characteristics and effectiveness of these barriers. In parallel to these experiments, WHA International oxygen compatibility testing will be pursued to provide further data on the safety of the barrier in a LOx environment. Additional testing includes the evaluation of static accumulation and wear on the materials. The prototype will be evaluated using a coulombmeter to quantify and eliminate static discharge from the barrier. Durability testing of the barrier will include many cycles folding and unfolding of the barrier material to ensure no significant breakdown occurs. Puncture and wear testing will also be conducted to ensure longevity of the product to harsh working conditions. Testing under harsh environmental factors like rain and snow on the barrier may also be evaluated. Finally, optimization of this design will be parameterized for different industrial sectors for ease to the user. All data will be compiled and provided to the NFPA as validation for the barrier as a certified refueling risk mitigation mechanism in commercial applications.

5. Conclusions

In this work a deployable LH2 transfer barrier is described for use during refueling preventing the combustion of materials below the transfer line with liquid air droplets. The barrier is deployable for refueling in remote locations, utilizing low cost and low weight materials conveniently folded for storage between fills. The barrier is composed of a base layer of Nomex® fabric with copper mesh bordered copper sheet for the prevention of the accumulation of liquid air. The barrier will be sent to WHA International for validation of oxygen compatibility along with in-house testing at the Hydrogen Properties for Energy Research Center exploring durability and static discharge potential. This refueling barrier mitigates safety risks associated with LH2 transfers and expands the availability of LH2 to different markets safely.

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