HAZARD IDENTIFICATION STUDY FOR RISK ASSESSMENT OF A HYBRID GASOLINE-HYDROGEN FUELING STATION WITH AN ON-SITE HYDROGEN PRODUCTION SYSTEM USING ORGANIC HYDRIDE

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ABSTRACT

Hydrogen infrastructures are important for the commercialization of fuel cell vehicles. Hydrogen storage and transportation are significant topics because it is difficult to safely and effectively treat large amounts of hydrogen because of hydrogen hazards. An organic chemical hydride method keeps and provides hydrogen using hydrogenation and dehydrogenation chemical reactions with aromatic compounds. This method has advantages in that the conventional petrochemical products are used as a hydrogen carrier, and petrochemicals are more easily treated than hydrogen because of low hazards. Hydrogen fueling stations are also crucial infrastructures for hydrogen supply. In Japan, hybrid gasoline-hydrogen fueling stations are needed for effective space utilization in urban areas. It is essential to address the safety issues of hybrid fueling stations for inherently safer station construction. We focused on a hybrid gasoline-hydrogen fueling station with an on-site hydrogen production system using methylcyclohexane as an organic chemical hydride. The purpose of this study is to reveal unique hybrid risks in the station with a hazard identification study (HAZID). As a result of the HAZID, we identified 314 accident scenarios involving gasoline and organic chemical hydride systems. In addition, we suggested improvement safety measures for uniquely worst-case accident scenarios to prevent and mitigate the scenarios.

1.0 INTRODUCTION

Hydrogen is a promising automobile fuel toward a more sustainable society because of the significantly reduced carbon dioxide emissions from its use. In the near future, it is important to prepare hydrogen infrastructures for the commercialization of fuel cell vehicles. Hydrogen has characteristic hazards, such as hydrogen embrittlement and detonation [1, 2]. Therefore, hydrogen storage and transportation are important topics because it is difficult to safely and effectively use large amounts of hydrogen. Some methods for hydrogen storage and transportation have already been investigated, for example, compressed hydrogen, liquid hydrogen, ammonia, and metal hydride. Although these methods have advantages and disadvantages, one practicable method is to use organic chemical hydrides. The organic chemical hydride method can keep and provide hydrogen using hydrogenation and dehydrogenation chemical reactions with aromatic compounds at a relatively mild condition. This method has advantages in that the conventional petrochemical products, such as methylcyclohexane (MCH) and decaline, are used as a hydrogen carrier, and these chemicals are safer than hydrogen. Therefore, the existing equipment is used for the safe storage and transportation of large amounts of hydrogen under ambient temperature and pressure. A disadvantage of this method is that there has been no dehydrogenation catalyst having a sufficient stability performance. However, Okada Y. et al. recently developed a new dehydrogenation catalyst for MCH, cyclohexane, and decaline [3]. This is a breakthrough development for the practical use of the organic chemical hydride method. The development led to the concept of an on-site hydrogen production system at a hydrogen fueling station.

Hydrogen fueling stations are also crucial infrastructures for hydrogen supply. In Japan, hybrid gasoline-hydrogen fueling stations are needed for effective space utilization in urban areas. It is essential to address the safety issues of hybrid fueling stations for safe station construction and stable hydrogen supply. Risk assessment is a useful tool to identify hazards and undesirable accident scenarios and to evaluate and control risks under a tolerable level. Risk assessment has already been implemented in stand-alone compressed hydrogen and liquid hydrogen fueling stations [4, 5]. Recently, hydrogen dispersion and explosion behavior analyses using computational fluid dynamics (CFD) have been carried out on stand-alone stations for more detailed risk assessments [6-8]. Therefore, safety investigations on a stand-alone hydrogen fueling station have been conducted with qualitative and quantitative analyses. On the other hand, qualitative and quantitative risk assessments for hybrid gasoline-hydrogen fueling stations have scarcely been conducted. For hybrid fueling station construction, it is important to reveal unique hybrid risks involving gasoline and hydrogen systems. We focused on a hybrid gasoline-hydrogen fueling station with an on-site hydrogen production system using MCH as an organic chemical hydride. The purpose of this study is to reveal unique hybrid accident scenarios and risks in the station with qualitative risk assessment. Furthermore, we suggested improvement safety measures to eliminate or reduce risks for inherently safer station design.

2.0 RISK ASSESSMENT PROCEDURE

The first step in the risk assessment was to define station risk criteria. The second step was to define a hybrid fueling station model based on Japanese regulations, expected hydrogen demand, and space restrictions. Hazard identification was the significant third step in risk assessment. There are some qualitative and quantitative methods such as hazard and operability study (HAZOP), failure mode and effect analysis (FMEA), and fault tree analysis (FTA). For risk reduction, a qualitative risk analysis is first carried out on a new chemical plant to roughly identify accident scenarios and risks in general. A quantitative risk analysis is then needed for estimating consequences and probabilities of accident scenarios in detail. Risk assessment using combined qualitative and quantitative methods leads to better risk management. Hazard identification study (HAZID) is one of the qualitative methods for identifying hazards and undesirable accident scenarios from a comprehensive point of view. A previous study presented detailed information about the advantages and procedures of HAZID [9]. We carried out HAZID in this study for worst-case scenario identification. The last step was to identify hybrid risks and scenarios due to the coexistence among gasoline, hydrogen, and organic chemical hydride systems based on risk matrixes. HAZID on accident scenarios involving compressed hydrogen and gasoline systems were not considered because the previous study has already identified such scenarios [9]. Therefore, we conducted HAZID on the coexistence between gasoline and organic chemical hydride systems.

2.1 Risk criteria

The risk criteria for risk evaluation were set as low, middle, and high. The previous study defined the risk criteria with a risk matrix in Table 1, risk levels, consequence severity levels, and probability levels [9]. We relatively evaluated hybrid fueling station risks based on the criteria by comparing the risks to other risks identified using HAZID.

Table 1. Risk Matrix

		Probability			
		1	2	3	4
Consequence severity		Improbable	Remote	Occasional	Probable
5	Catastrophic	High (3)	High (3)	High (3)	High (3)
4	Severe loss	Middle (2)	High (3)	High (3)	High (3)
3	Major damage	Middle (2)	Middle (2)	High (3)	High (3)
2	Damage	Low (1)	Low (1)	Middle (2)	High (3)
1	Minor damage	Low (1)	Low (1)	Low (1)	Middle (2)

2.2 Station model

The station model in Figure 1 is defined for Japanese regulations, anticipated demand, and space restrictions. Gasoline and kerosene supply systems consist of underground tanks and dispensers. The hydrogen supply system mainly consists of an organic chemical hydride system, a hydrogen compressor, pressurized hydrogen tanks, a pre-cooling system, and dispensers. The organic chemical hydride system is divided into a dehydrogenation reactor, a heat exchanger, a gas-liquid separator, and a hydrogen refinery; the pressure condition of the system is below 1 MPa. Hydrogen and toluene are produced by MCH dehydrogenation reactions in the presence of a catalyst at 300-400 °C, and then separated in a gas-liquid separator. Toluene is then transported to an underground tank for recovery and resupply to a hydrogenation plant. Hydrogen is refined to eliminate impurities and transported to the hydrogen compressor. Compressed hydrogen is then stored in the pressurized hydrogen tanks at 82 MPa. Kikukawa et al. [10] summarized various safety measures incorporated into a station based on Japanese regulations, for example, shutdown systems, material selection against corrosion and fatigue, hydrogen detector, water drain, collision guard, and a concrete safety barrier and fire protection wall height of 2 m. MCH, toluene, gasoline, and kerosene lorries are placed and operated at the same position.

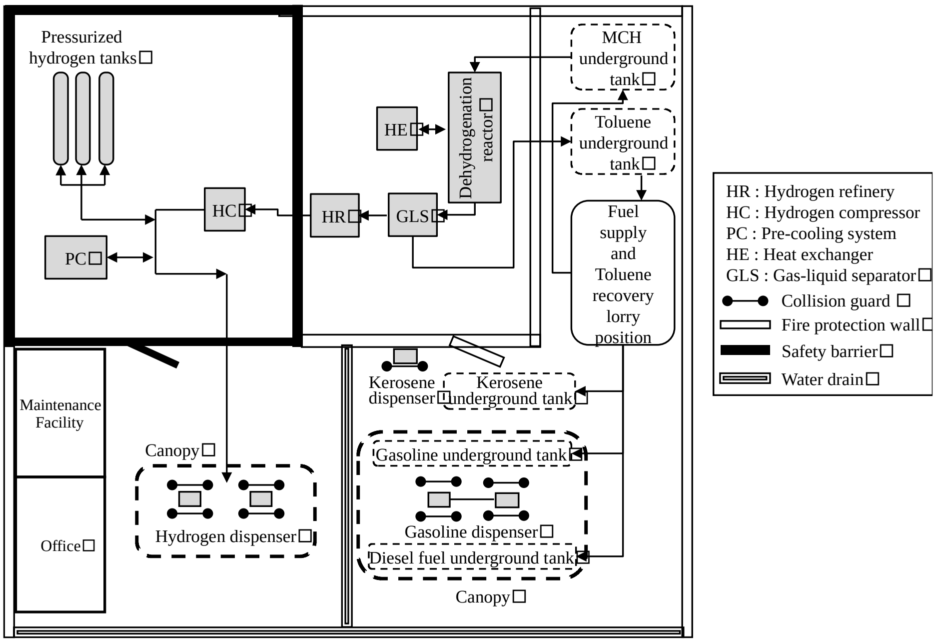

Figure 1. Hybrid gasoline-hydrogen fueling station model

2.3 Hazard identification study (HAZID)

Expert members performed a HAZID to imagine and present every hazard and undesirable scenario during brainstorming sessions. They referred to accident databases [10-12] to investigate and understand equipment vulnerabilities in the station for qualitative analysis and consulted the HAZID for hydrogen infrastructures [13]. For better objectivity and logicality, the team associated accident scenarios with guidewords in Tables 2 and 3. Hybrid fueling station hazards consist of natural hazards, external event hazards, chemical hazards, and process hazards. Many types of natural hazards and external event hazards were incorporated into guidewords so as to not overlook hidden scenarios and to roughly identify station risks. The HAZID used station layout hazards to discover problems in the station design. Hybrid event hazards were set up to search for unique scenarios with coexistent gasoline and hydrogen, which stand-alone hydrogen or gasoline stations do not have. In this study, we identified only hybrid risks due to the coexistence between gasoline and organic chemical hydride systems, as these risks have not yet been identified, while hybrid risks involving gasoline and compressed hydrogen systems have already investigated in the previous study [9].

Table 2. HAZID guideword sheet

Applicable guideword for a station			
1. Natural hazard		2. External event hazard	
1.1	Earthquake	2.1	Airplane crash
1.2	Tsunami	2.2	Automobile collision
1.3	Tidal wave	2.3	Arson
1.4	Flood	2.4	Terrorism
1.5	Thunderbolt	2.5	Crane collapse
1.6	Falling rock	2.6	Helicopter crash
1.7	Ground deformation	2.7	Explosion outside station area
1.8	Snow	2.8	Fire outside station area
1.9	Rain	2.9	Chemical release from a neighboring facility
1.10	Hail	2.10	Neighboring building collapse
1.11	Wind	2.11	Attack by animal or insect
1.12	Debris flow	2.12	Cyber-terrorism
1.13	Mudslide	2.13	Car fire on a nearby road
1.14	Meteor	2.14	Tension cable
1.15	Avalanche	2.15	Interference
1.16	Tornado	3. Station layout hazard	
1.17	Yellow dust	3.1	Isolation
1.18	Liquefied ground	3.2	Approach
1.19	Ash deposits	3.3	Evacuation
1.20	Lava flow	4. Hybrid event hazard	
1.21	Pyroclastic flow	4.1	Station fire
1.22	Ash flow	4.2	Gasoline leakage
1.23	Air temperature	4.3	Kerosene leakage
1.24	Typhoon	4.4	MCH leakage
		4.5	Toluene leakage
		4.6	Incorrect operation
		4.7	Gasoline vehicle collision
		4.8	Fire fighting

Table 3. HAZID guideword sheet (Continued)

Applicable guideword for a system				
5. Process hazard				Organic chemical hydride
5.1	Toxic material	5.12	Power blackout	Organic chemical hydride equipment analysis
5.2	Combustible material	5.13	Water outage	
5.3	Explosive material	5.14	Fuel gas outage	
5.4	Oxidative material	5.15	Fuel oil outage	
5.5	Spontaneous ignition material	5.16	Electric communication shutoff	
5.6	Carcinogenic material	5.17	Steam outage	
5.7	Storage	5.18	Instrumentation air outage	
5.8	Fire	5.19	Inert gas outage	
5.9	Explosion	5.20	Nitrogen outage	
5.10	Toxicity	5.21	Chemical outage	
5.11	Exothermic reaction			

Figure 2 shows a bow-tie diagram that clearly describes an accidental scenario from a hazard to a consequence. The diagram also indicates a correspondence relation between a scenario and safety measures. Lack of safety measures corresponding to a scenario can be clearly seen with the diagram. Furthermore, the diagram can calculate the probability of an accidental event by inputting accurate failure probabilities of various safety measures into each scenario. Therefore, risks can be quantitatively analyzed with the diagram. According to concept of the diagram, we conducted a HAZID as a qualitative analysis from two perspectives. The first perspective is that prevention, control, and mitigation measures are sufficient. This perspective simulates realistic situations and identifies safety measures implemented in the station to prevent loss of containment and mitigate consequences. In contrast, the second perspective is that only mitigation measures are effective and that prevention and control measures are not considered. This perspective imagines incident scenarios after loss of containment, which discusses whether mitigation measures are sufficient. These perspectives can reveal safety measures implemented in a station for risk reduction.

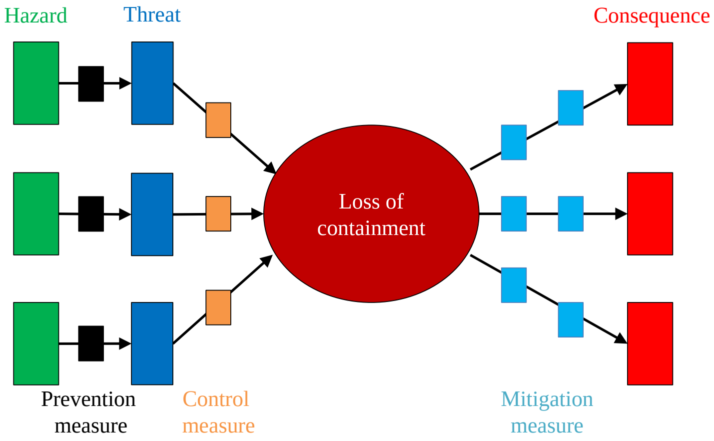

Figure 2. Bow-tie diagram

Table 4 presents a HAZID sheet including the following contents:

- “No.” is the accident scenario number.
- “Guideword” shows the guidewords.
- “Cause” describes causes of an accident scenario associated with the guideword.
- “Effect” is a list of events caused by content from “Cause”.
- “Risk level without safety measures” is a qualitative estimation of consequences, probabilities, and risks without safety measures implemented.
- “Safety measures” are current safety measures based on Japanese regulations that prevent, control, and mitigate station events.
- “Risk level with safety measures” is a qualitative estimation of consequences, probabilities, and risks with safety measures implemented.
- “Additional actions” describes additional safety measures if the risk level with present safety measures is high or new safety measures are necessary.

Accident scenarios and risks are summarized in Table 3, which describes one example scenario due to length constraints. The HAZID sheet visualizes hazard, scenario, risk, and safety measures, through which risk analysis and assessment processes can be objectively pursued. The safety measures column is divided into design, construction, operation, and maintenance to further clarify the various safety measures. In addition, safety measures such as the safety barrier and fire protection wall were underlined. These indicate passive safety measures operating without an electrical power supply, which deals with reducing the consequence level. Other safety measures without an underline reduce the level of probability in this study. There were two methods to reduce consequence and probability levels using safety measures. For an accident scenario causing a fatal event having effects outside the station, consequences and probability levels are reduced by two by using more than three safety measures, while a scenario leading to a medium event has its consequences and probability levels reduced by two by using only two safety measures. In this study, we did not associate the guidewords with devastating and simultaneous multiple scenarios to prevent divergence of discussion. We identified a scenario from a hazard to a consequence with a guideword in consideration of an escalation scenario.

The HAZID identified an example in Table 4 in the following steps:

1) Combustible material as a guideword is selected from Table 3.
2) At a gas-liquid separator, toluene is leaked from a pipe failure caused by corrosion, fatigue, or hydrogen embrittlement.
3) The toluene pool is gradually spread, and toluene gas is dispersed in the atmosphere due to vaporization. A vapor cloud explosion of toluene occurs if it is ignited. The explosion will affect people and equipment outside the station.
4) If there are no safety measures in the system, the risk is high (3) because the consequence causing catastrophic damage outside the station is 5 and the probability of this occurring once in the lifetime of one hydrogen station is 3.
5) Various safety measures have already been implemented in the system in the safety measures column.
6) The levels of the explosion consequence and probability are respectively reduced to 3 and 1 because of three passive and active safety measures. Therefore, the explosion risk level is reduced to medium.
7) There are no additional actions because the risk level is medium and the accident scenario is effectively prevented, controlled, and mitigated by safety measures.

Table 4. HAZID sheet

No.	Guideword	Cause	Effect	Risk level *without* safety measures			Safety measures	Risk level *with* safety measures			Additional actions
				Consequence	Probability	Risk		Consequence	Probability	Risk	
1	Combustible material	Toluene leakage from pipe failure caused by corrosion, fatigue or hydrogen embrittlement	(1) Toluene leakage (2) Dispersion (3) Ignition (4) Explosion (5) Loss of people and equipment	5	3	3	[1] Design (1) <u>Material selection</u> (2) Flame detector (3) Shutdown system (4) <u>Fire protection wall</u> (5) <u>Safety barrier</u> [2] Construction NA [3] Operation NA [4] Maintenance (1) Inspection	3	1	2	

3.0 RESULTS AND DISCUSSION

Tables 5 and 6 give risk matrixes without and with safety measures, respectively. The risk matrixes indicate the risk distributions, which can clearly visualize where risks are. The HAZID identified 314 accident scenarios for the coexistence of gasoline and organic chemical hydride systems. For example:

1. MCH leaks due to a pipework fracture by fatigue or corrosion in an organic chemical hydride system. MCH then flows to the gasoline dispenser, and is ignited, causing a MCH pool fire.
2. An earthquake affects the dehydrogenation reactor, and MCH, toluene, and hydrogen leak though a damaged area. MCH and toluene pool fires or a hydrogen explosion occurs if they are ignited.
3. A massive amount of gasoline leaks from an operating gasoline lorry. A gasoline pool fire affects an organic chemical hydride system, and MCH, toluene, and/or hydrogen eventually leak due to damage by thermal radiation of the pool fire.

Almost all of the risks including the above examples are reduced to medium or low risks by various prevention and mitigation measures, such as shutdown valves with seismometers, a seismic design, hydrogen detectors, and fire protection walls. In particular, safety measures for natural hazards that frequently occur in Japan, such as earthquakes and typhoons, are adequately implemented in the station and equipment design. Safety measures can also be added for safer stations; for example, the risk level in the third scenario was reduced to a medium risk level using current safety measures, but a safety distance as an additional effective safety measure is needed to further reduce the risk. Thermal radiation depends on the distance from a fire. Therefore, the station layout should be rearranged to extend the distance from an organic chemical hydride system to a lorry position for a consequence reduction in pool fires.

Table 5. Risk matrix without safety measures

		Probability			
		1	2	3	4
Consequence severity	5	0	71	98	0
	4	0	63	82	0
	3	0	0	0	0
	2	0	0	0	0
	1	0	0	0	0

Table 6. Risk matrix with safety measures

		Probability			
		1	2	3	4
Consequence severity	5	19	0	0	0
	4	95	27	0	0
	3	126	19	0	0
	2	26	2	0	0
	1	0	0	0	0

The HAZID identified 46 high risk scenarios categorized into four types: (a) partial station destruction caused by helicopter clash or neighboring building collapse, (b) automobile collision, (c) massive combustible material leakage, and (d) firefighting. The partial station destruction would be treated as a residual risk because there are no practicable safety measures and these events are very rare. Representative example scenarios of the other three types were as follows:

(b) A gasoline car crashes into an operating MCH or toluene lorry. Large amounts of MCH or toluene then leak from the lorry and disperse into the atmosphere. Eventually, a major MCH or toluene vapor explosion occurs if it is ignited.

(c) A massive amount of gasoline leaks from an operating gasoline lorry. A gasoline vapor cloud explosion affects an organic chemical hydride system, and MCH, toluene, and/or hydrogen eventually leak. As a result, an escalation event such as an MCH pool fire or hydrogen explosion may occur.

(d) MCH and toluene disperse into the atmosphere because firefighters are extinguishing a fire occurring at an organic chemical hydride system and MCH and toluene leak from damaged areas. Subsequently, a major MCH or toluene vapor explosion occurs if they are ignited.

For the (b) scenario, a collision guard at the lorry position can prevent the gasoline car from crashing into the lorry. A water drain around the lorry position can also mitigate the event. The (c) scenario, which is loss of containment, indicates that effective mitigation measures are insufficient. The improvement measures are a safety distance from the lorry position to the organic chemical hydride and a water drain around the lorry position to mitigate the spreading of gasoline pool. These additional measures can mitigate the event, although the measures cannot prevent the event. For the (d) scenario, directly pouring a fire-extinguishing agent into the pool fire during firefighting may cause the escalation event because of the flammable gas dispersion. Therefore, different firefighting tactics need to be developed for consequence mitigation. For example, a water deluge system can effectively mitigate a gas explosion consequence [14], but it is difficult to install the system in a practical way because of expensive equipment. Additionally, firefighting mitigates damage from a pool fire by using cooling equipment around the pool fire, and waiting for the fuel to run out. The last scenario is a major problem to resolve for an emergency response.

The risk reduction measures can be effectively implemented into more preliminary process lifecycle stages [15]. In a process lifecycle, research and process development are important stages for hazard elimination or reduction, but the development of new chemicals and processes requires long periods of time. Regarding the hybrid station in this study, it is difficult to develop new chemicals and process systems, although the effectiveness of elimination or reduction is significantly high. The next stage in process lifecycle is basic design, which contains process condition, rough station layout, and fundamental safety systems. From the results of the HAZID, the lorry position needs to be rearranged to maintain a safety distance, and a water drain and a collision guard should be additionally installed around the lorry position for the mitigation of flammable liquid spread. These safety measures are categorized as inherent and passive safety measures. Inherent and passive safety measures can effectively eliminate or reduce hazards and risks than active and operational safety measures [16]. Hybrid fueling stations should implement inherent and passive safety measures in the basic design stage of the process lifecycle for the reduction or elimination of hazards and risks because implementing inherent and passive safety measures is more difficult at later stages of process lifecycle. In addition, hydrogen station stakeholders have to preliminarily define firefighting tactics as an emergency response plan for accident mitigation at the station.

For the construction of hybrid fueling stations, accident scenario identifications using HAZOP and FMEA and a concrete emergency response plan at the detailed design stage are needed because HAZID is an effective but rough scenario identification method at the basic design stage. In particular, a detailed hazard identification analysis is crucial for organic chemical hydride processes because of the dehydrogenation reaction that may potentially cause runaway reactions or rapid pressure release reactions. A quantitative risk assessment using CFD and FTA is also important for consequence and probability analyses. For inherently safer hydrogen fueling stations, it is critical to investigate and develop prevention and mitigation safety measures by effectively conducting qualitative and quantitative risk analyses through the process lifecycle.

4.0 CONCLUSIONS

We conducted a HAZID for scenario identification and qualitative risk assessment of a hybrid gasoline-hydrogen fueling station with an on-site hydrogen production system using organic chemical hydride. From the accident scenario identification using the HAZID, 314 hybrid scenarios involving gasoline and organic chemical hydride systems were identified. In particular, we could identify critical scenarios, which included massive combustible material leakage, automobile collision, and firefighting. Furthermore, additional prevention and mitigation safety measures were suggested for the representative unique scenarios. Inherent and passive safety measures should be incorporated into the hybrid station for safer station construction, and emergency response plans should be prepared for accident mitigation.

5.0 ACKNOWLEDGEMENTS

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