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# Preliminary hazard identification for qualitative risk assessment on a hybrid gasoline-hydrogen fueling station with an on-site hydrogen production system using organic chemical 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 study). As a result of the HAZID study, 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.

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## 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. Moreover, 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 [4–9]. 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 [10–12]. 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 have investigated safety issues of a hybrid gasoline-hydrogen fueling station with a liquefied hydrogen storage tank [13,14]. In this study, 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 uniquely hybrid accident

scenarios and risks in the station of preliminary design stage with qualitative risk assessment. Furthermore, we suggested improvement safety measures to eliminate or reduce risks for inherently safer station design.

## 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 study) 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 study [9]. We carried out HAZID study 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 study on accident scenarios involving compressed hydrogen and gasoline systems were not considered because the previous study has already identified such scenarios [13,14]. Therefore, we conducted HAZID study on the coexistence between gasoline and organic chemical hydride systems.

## 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 frequency levels [13]. We relatively evaluated hybrid fueling station risks based on the criteria by comparing the risks to other risks identified using HAZID study.

## Station model

The station model in Fig. 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

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