[Title]

Identification of accident scenarios caused by internal factors using HAZOP to assess an organic hydride hydrogen refueling station involving methylcyclohexane

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[Abstract]

Organic hydride hydrogen refueling stations have been remarked as stations that can employ a practicable method based on the organic chemical hydride system involving methylcyclohexane (MCH) for the transport of hydrogen. This station has advantages in that the storage and transportation of MCH does not require a large amount of energy compared to compressed and liquefied hydrogen, and the system can use existing infrastructure. This type of station involves some hazardous materials, and thus, scenario identifications and risk assessments have been performed by researchers. However, the sample of studies available have employed a conceptual design model, and they did not identify concrete scenarios triggered by internal factors. Therefore, the purpose of this study is to identify accidental scenarios caused by internal factors that can affect an organic hydride hydrogen refueling station. In this study, we used Hazard and Operability study (HAZOP) and examined safety measures for the scenarios. As a result of the HAZOP, 105 accidental scenarios were identified and classified into the two following groups; (i) the scenarios assumed that the substances were ignited after they were released to the atmosphere, and (ii) the scenarios assumed that the substances were ignited in the process before they were released. Significant scenarios in group (i) were MCH or toluene pool fires, hydrogen jet fires, vapor gas explosions, or flash fires. The significant scenarios classified in (ii) were newly identified in this study. The scenarios include the explosion of the explosive mixture formed by the gaseous phase of toluene and oxygen from the vent line connected to the tank due to the static electric charge in the tank. For each scenario, safety measures to prevent the progression of the accident scenario were examined with reference to the current laws and regulations in Japan.

[Key word]
Hydrogen refueling station; Organic hydride; Scenario identification; HAZOP.

1. Introduction

Hydrogen energy is a promising candidate to help in the construction of our future energy system because its usage can significantly reduce carbon dioxide emissions, and it can be produced from a variety of sources, including fossil fuels, biomass, or renewable energy. However, hydrogen has a low volumetric energy density compared to other fossil fuels. Therefore, appropriate storage and transportation methods for a large amount of hydrogen are essential to ensure the effective use of hydrogen energy. Hydrogen storage and transportation methods, such as compressed and liquid hydrogen, have already been investigated, but these methods are inefficient due to an extremely high pressure or very low temperature. Therefore, a practicable method that is based on an organic chemical hydride system that includes a way to use methylcyclohexane (MCH) has been developed (Modisha et al., 2019). This system transports hydrogen with MCH as the hydrogen carrier and produces hydrogen using a dehydrogenation chemical reaction with a catalyst developed by Okada et al. (Okada et al., 2006). It has been confirmed that MCH is produced by the hydrogenation of toluene with yields of over 99% while hydrogen can be produced from the same MCH with yields of more than 98% through the dehydrogenation process (Chiyoda Corporation, 2020). The organic chemical hydride system has two advantages: one is that the storage and transportation of MCH and toluene do not need a large amount of energy because they are in the liquid phase at ordinary temperature and pressure; the other is that the system can use existing infrastructure, such as tankers or tank trucks, because the properties of MCH and toluene are similar to the properties of conventional petrochemical products. Thus far, the organic chemical hydride system has been investigated through demonstration experiments aimed at practical application. To use the organic chemical hydride system, it is necessary to construct a hydrogen refueling station (HRS) with an on-site hydrogen production system that involves MCH.

An organic hydride HRS involving MCH has two characteristics. First, some hazardous substances, such as hydrogen, MCH, and toluene, are involved. These substances include some major hazards, such as explosiveness and flammability, and these accidents can harm people, damage properties, and hurt the environment. Therefore, it is necessary to conduct risk assessment to ensure safety in the operation of the station. Risk assessments are a useful tool to identify hazards and undesirable accident scenarios and to evaluate and control risks so that they remain at a tolerable level. Second, the station consists of existing off-site HRS and a new chemical processing plant in which dehydrogenation chemical reactions occur. Several risk assessments have already been conducted on stand-alone compressed or liquid HRS. Kikukawa et al. identified many possible accidental scenarios for compressed and liquefied HRSs using Hazard and Operability study (HAZOP) and Failure Mode and Effect Analysis (FMEA), and performed risk assessments using a risk matrix (Kikukawa et al., 2009, 2008). Zhiyong et al. conducted quantitative risk assessments (QRAs) on several kinds of compressed HRSs and discussed safety distances (Zhiyong et al., 2011, 2010). Gye et al. performed

QRA on HRS in urban areas (Gye et al., 2019). To ensure organic hydride HRS can be applied practically, various safety studies and risk assessments have been conducted. Conducting hazard and scenario identification in risk assessments is important because possible scenarios are needed to consider safety measures. Nakayama et al. analyzed thermal hazards in MCH and toluene and found no significant thermal hazards (Nakayama et al., 2018). Nakayama et al. also identified a large number of scenarios triggered by various external factors using a Hazard Identification (HAZID) study and conducted qualitative risk assessments using a risk matrix (Nakayama et al., 2016); they qualitatively analyzed security risks such as terrorist attacks or having to deal with disgruntled employees using the American Petroleum Institute Standard 780 (Nakayama et al., 2019). They also found a domino effect scenario that results from the rupturing of the hydrogen cylinders heated by the radiation heat flux from an MCH pool fire and subsequently analyzed the consequences of the scenario by using simulations before proposing safety measures for the prevention and mitigation of this scenario (Nakayama et al., 2017). Although many organic hydride HRSs scenarios have been identified, and some scenarios were analyzed as mentioned above, there have not been detailed studies on these scenarios as most studies have used a rough layout and a process flow of the conceptual design stage. Tsunemi et al. conducted screening-level QRAs on the schematic flow of organic hydride HRS in more detail than above studies and discussed safety distances from the release location (Tsunemi et al., 2018). They also estimated the consequences and damage that could result from the explosion and heat caused by MCH or toluene release (Tsunemi et al., 2017). The quantitative consequences and risks of major scenarios occurring in organic hydride HRSs have already been assessed. However, many studies only considered a portion of the scenarios after the loss of containment, and they did not focus on scenarios before the loss of containment triggered by internal factors, such as process deviations in the dehydrogenation process or human factors. The completeness of scenario identification is the most important issue in risk assessment because risks associated with unidentified scenarios have not been analyzed by any studies (Baybutt, 2018). To avoid underestimating the risk and to confirm adequate safety measures have been implemented, it is important to identify as many scenarios as possible and increase the completeness of scenarios.

Therefore, the purpose of this study is to identify accident scenarios caused by internal factors in an organic hydride HRS. There are many internal factors that may cause accidents in processing plants, but we focus on deviations in the processing parameters from normal operation (steady-state) and human factors that might affect startup and shutdown operation procedures (non-steady-state) as major internal causes. Deviations in the processing parameters should be considered, and 50% to 90% of processing accidents are generally attributed to human failure (Baybutt, 2002). In this study, we obtained scenarios from three processes that are significant to organic hydride HRSs: (i) dehydrogenation, (ii) unloading MCH, and (iii) loading toluene. Other processes were excluded because they are the same as stand-alone compressed and liquefied HRSs, and many safety studies on these processes have already been implemented. In other words, we did not consider compressors, cylinders, and dispensers in this study. To identify accident scenarios, we used the traditional method, HAZOP. In addition, we examined safety measures for scenarios that were determined to be particularly important.

2. Process description and operation procedure

2.1. Process description

Figs. 1–3 show simple flows for the three processes, which have been revised by the authors, analyzed in this study(Japan Petroleum Energy Center, 2018). Table 1 also shows a material balance sheet for the dehydrogenation process. The node number in Table 1 corresponds to the circled-number section. The processes are explained as follows (New Energy and Industrial Technology Development Organization, 2018);

Dehydrogenation process (see Fig. 1)

- Node 1: a MCH vaporization process that a multi-tube heat exchanger vaporizes MCH with a heat medium. The heating temperature is between 250 and 400 °C. MCH tank that stores MCH underground has a double shell, and its capacity is 30 kL.
- Node 2: a dehydrogenation reaction process that a reactor dehydrogenates MCH and generates toluene and hydrogen with a reaction tube filled with a dehydrogenation catalyst heated with a heat medium. The heating temperature is between 300 and 400 °C.
- Node 3: a separation process with a condenser that cools the mixture of toluene and hydrogen produced in the dehydrogenation reactor with cooling water and separates the liquefied toluene from gaseous hydrogen.
- Node 4: a recovery process that the separated toluene flows down to the underground toluene tank. The tank that stores toluene underground has a double shell and its capacity is 30 kL.
- Node 5: a compressing process that a compressor compresses and sends the separated hydrogen to a purifier (Pressure Swing Adsorption [PSA]). The toluene that remains in the gas is further separated and liquefied and flows down to the toluene underground tank. The discharge pressure of the compressor is less than 1 MPa.
- Node 6: a purification process that the PSA purifies the obtained hydrogen to achieve a quality that can be used as fuel for FCVs. The purified hydrogen suppresses pressure fluctuations in the buffer tank and is sent to the high-pressure hydrogen compressor. Operating pressure is less than 1 MPa. Off-gas is used as the fuel for in the heat source.
- Node 7: a heating process that a heater for heating and circulating the heat medium sends the heat to the vaporizer and the dehydrogenation reactor. This process is only used when start up or shut down operation.

Unloading MCH process (see Fig.2)

MCH obtained from the hydrogenation of toluene is transported to the station with a tank truck and is transferred to the underground tank by its own weight. Then, the MCH is sent to a dehydrogenation reactor. The underground MCH tank has a vent line to prevent increases in inner pressure. The vent line in the model does not have a vapor recovery function. It has a pressure balance function between the truck tank and the MCH tank or pumping with the MCH to the vaporizer.

Loading toluene process (see Fig.3)

The toluene produced by dehydrogenation is then stored in the underground tank. Then, the toluene is loaded into tank trucks by a transfer pump. The underground tank of toluene also has a vent line for the same reason.

Table 1. Material balance sheet for the dehydrogenation process

Node No.		1	2	3	4	5	6	6	6
Flow		Vaporizer inflow	Reactor inflow	Condenser inflow	Toluene tank inflow	Compressor inflow	PSA inflow	PSA outflow	PSA off-gas
State		Liquid	Vapor	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor
Temperature (°C)		Normal temperature	250–400	300–400	40	40	40	40	40
Pressure (kPaG)		50–500	50–500	50–500	Normal pressure	50–500	700–980	700–980	20–50
Maximum flow (kg/h)		1,400	1,400	1,400	1,300	192	112	54	58
Minimum flow (kg/h)		900	900	900	800	126	78	0	24
Composition	H_2	0	0	73–75	< 0.2	> 94	> 98	$\geqq$ 99.99	47–97
(mol%)	Toluene	0	0	24–25	90–99	< 5	< 1	< 0.29 ppm	3–48
	MCH	100	100	0–3	1–10	< 1	< 1		0–5

- Hydrogen production rate: 600 Nm^3/h
- Hydrogen collecting ratio of PSA: 70–99 %
- MCH conversion ratio: 90–99 %
- The parameters of the node 7 are not indicated because the node is only used when start up and shut down operation which is not steady-state.

2.2. Operational procedures

Dehydrogenation needs to start when the station opens and stop when the station closes. Fig. 4 shows the startup operational procedure for the dehydrogenation process (New Energy and Industrial Technology Development Organization, 2018). First, a power source is turned on, and all the shut-off valves in Fig.1 are opened after confirming that the cooling water is working and instrument air is being sent to the heat source. Next, the compressor and circulation pump (P02) are started after confirming the inlet pressure of the compressor. Then, the heat source raises the temperature of the reactor. After confirming the temperature and pressure of the heat medium, the MCH pump (P01) and PSA are started. Finally, hydrogen produced at the desired quality, of which is confirmed, is supplied. Fig. 5 also shows the shutdown operational procedure of the dehydrogenation process (New Energy and Industrial Technology Development Organization, 2018). This procedure is almost the exact reverse of the startup procedure, but there are a few differences. First, the MCH pump (P01) and PSA are stopped. Next, the heat source (the circulation pump (P02) for the heat medium) are also stopped, and the reactor is purged with inert gas. After confirming the temperature of the reactor, the compressor is stopped. Finally, the power source is turned off after closing all the shut-off valves.

3. Scenario identification

We conducted HAZOP to identify accident scenarios in the three processes and the two procedures described in Section 2. HAZOP is a PHA technique used worldwide and is based on a systematic approach towards assessing the safety and operability of complex processing equipment or production processes (Dunjó et al., 2010). In this study, we defined parameters and guidewords based on the CCPS guideline (CCPS, 1992).

Regarding the three processes, deviations from fluctuations in the processes' parameters were assumed. The first step was to divide the processes into some proper nodes to identify scenarios easily. Nodes separated by bold red lines and the borders of on shut-off valves, inlets, or outlets of components are shown in Figs. 1-3. The dehydrogenation process was divided into seven nodes, and the loading toluene process was divided into three nodes while the unloading MCH process was regarded as a single node because it is a simple process. The next step was to identify scenarios for each node by assuming deviations using the parameters and guidewords. To conduct scenario identification, comprehensively identifying the furthest extents in which scenarios that may occur is important. Therefore, we considered and identified all possible scenarios, even if the frequency of the occurrence of deviations were estimated to be extremely low. In addition, we assumed that safety equipment, such as shut-off valves or safety valves, would not work even if they were described in the processes.

Regarding the two procedures, we conducted HAZOP using the same guidewords but interpreted them to be able to apply to human factors. Table 2 shows the guidewords and interpretations we used to identify scenarios triggered by human factors (Aspinall, 2006).

Our study team included some process developers and experts that understood the function and operation of the processes and procedures extremely well so that there would be no difference from actual operation.

Table 2. HAZOP guidewords and their interpretations and examples related to human factors (Aspinall, 2006)

Guideword	Interpretation	Examples
No	Not done, task not completed	Operator omits step in sequence
Less	Do less of the required action	Smaller quantity handled; Not all valves opened in a step
More	Do more than or more of the required action	Larger quantity handled; Valves opened more than required
Reverse	Do the opposite of the required action	Closes valves instead of open; Needs to reverse previous action
Part of	Not all tasks in an action carried out	Actions within a step omitted
As well as	Do something in addition to the required task	Additional material handled; Open additional valve
Other than	Do something different from the required task	Acts on wrong valve; Incorrect material handled
Sooner	Carry out the action before the time specified	Changes order of steps: Takes action too quickly
Later	Carry out the action after the time specified	Changes order of steps: Takes action too slowly

4. Results and Discussion

The scenarios obtained by HAZOP describe consequences caused by deviations, but HAZOP can yield scenarios that do not result in accidents, such as causing only degradations in the quality of hydrogen produced. Therefore, we chose scenarios that could result in accidents from amongst all the scenarios, and we named them “accident scenarios.” Table 3 shows the number of identified scenarios. As a result, 105 accident scenarios were chosen from 371 scenarios identified for all processes.

Table 4 shows a portion of the significant accident scenarios identified in each process and procedure. It describes the process, node number, deviations, causes and consequences of deviations, and the final outcome for each scenario. The three processes mainly handle three substances: MCH, toluene, and hydrogen. Since MCH and toluene are associated with few thermal hazards (Nakayama et al., 2018), abnormal events that can occur as a result of these substances are not expected to occur even if some deviations, such as pressure or temperature increases, occur. Therefore, the accidental scenarios obtained in this study were classified into the following two groups; (i) the scenarios assumed that the substances were ignited after they were released to the atmosphere, and (ii) the scenarios assumed that the substances were ignited in the process before they were released.

The scenarios included in group (i) were easy to identify because it is clear that substances that can be released to the atmosphere from the three processes are MCH, toluene, and hydrogen. For example, in the dehydrogenation process, if the flow of MCH increases due to the failure of a pump transporting MCH and the MCH is released in the liquid phase from a fragile location in the process, an MCH pool fire can occur as a result of coming into contact with ignition sources. In addition, if MCH is released in the gaseous phase, a vapor cloud explosion (VCE) can occur. However, the boiling points of MCH and toluene under atmospheric pressure are 374.0 K (NIST, 2020a) and 383.8 K (NIST, 2020b), respectively, and they will quickly condense into the liquid phase under normal temperature and pressure. Therefore, in this study, we assumed that VCEs caused by MCH and toluene would not occur, and pool fires would occur as well as a release in the liquid phase. We note that MCH and toluene have some toxic effects, and they can affect people in nearby areas through leakage and diffusion even if they are not ignited. Tsunemi et al. indicated that the blast wave and acute toxicity caused by chemical leak from an organic hydride hydrogen refueling station had effects inside the station and on the surrounding residents but they were not fatal, and the effects of radiation heat flux reached to fatal level (Tsunemi et al., 2017). Since hydrogen is always handled in the gaseous phase, jet fires due to immediate ignition, vapor gas explosions, or flash fires due to delayed ignition can occur if hydrogen were to leak from a fragile location of the process due to a pressure increase.

For each scenario, safety measures to prevent the progression of the scenarios were examined. As there is currently no corresponding international regulation that regulate the process system or safety measures of an organic hydride HRS, we referred the Japanese current codes and regulations based on High Pressure Gas Safety Act (Japanese Ministry of Economy Trade and Industry, 2020) and

Fire Service Act (Japanese Ministry of Internal Affairs and Communications, 2020). For example, pressure sensors and interlocking systems that mitigate an increase in internal pressure to prevent the release of substances, safety measures to prevent the spread of dispersion after a leakage occurs, and consequences such as shut-off valves and fire walls to reduce overpressure due to vapor cloud explosions and radiation heat fluxes caused by pool and jet fires are all possible ways to respond to each scenario. Although it is desirable to validate the effectiveness of each safety measure to prevent accidents from occurring as a result of the scenarios in group (i), these measures can be considered adequate because there are more than two safety measures for each scenario.

While the scenarios in group (i) can be easily assumed, and almost all have been verified by previous studies, the scenarios in group (ii) are newly identified. The following scenarios were identified as group (ii) scenarios:

- The liquid in the condenser runs out and gas produced by dehydrogenation blows into the underground toluene tank, thereby causing equipment destruction.
- The explosive mixture of processing gas and air in the PSA is ignited and explodes.
- The explosive gas mixture configured in the gas phase in the underground toluene tank or in the tank trucks is ignited or explodes.

The third scenario is that the explosive gas mixture is formed by the gaseous mixing of toluene and oxygen from the vent line connected to the tank. Considering the vapor pressure of toluene at standard conditions, the concentration of the mixture in the tanks is higher than the lower flammable limit (1.17–1.31 vol%) (Coward and Jones, 1952). Since toluene is an electrostatically chargeable liquid that is charged in the pipes or tanks, the mixture can explode due to static electricity. However, the energy from toluene discharge is lower than the minimum ignition energy (MIE) of an explosive mixture of toluene (0.24 mJ) (Babrauskas, 2003). However, the problem is that the toluene produced in this process is characterized by the hydrogen that is dissolved. The presence of hydrogen in the mixture is known to lower their MIE (Hankinson and Lowesmith, 2009). Therefore, an explosion due to the ignition of the explosive mixture formed in the gas phase of the tanks can occur.

Since these scenarios were not identified in previous studies, no safety measures with reference to the current codes and regulations in Japan have been proposed. Therefore, we propose some safety measures that remove the ignition source and prevent the configuration of ignitable mixtures. There are some ways to prevent the configuration of the flammable mixtures, such as using a stripper located before the toluene underground tank to remove hydrogen dissolved in the toluene, or purging of nitrogen inert gas to the vapor phase of the tank.

Table 3. The number of identified scenarios

	All scenarios	Accident scenarios
Dehydrogenation process	177	47
Unloading MCH process	22	1
Loading toluene process	90	41
Startup procedure	45	10
Shutdown procedure	37	6
Total	371	105

Table 4. The significance of the accident scenarios as identified by HAZOP

Process	Node No.	Deviation	Causes	Consequences	Outcome
Dehydrogenation	1	More MCH flow to the reactor	Failure of the pump (P01)	Too high a pressure in the pipe causes MCH to leak from the most fragile location in the process.	MCH pool fire
	3	Less flow in the toluene/hydrogen mixture	Corrosion or fatigue in the materials	Leakage of the mixture and ignition due to a reason results in accidents.	Toluene pool fire; Hydrogen jet fire or explosion
	4	Less flow of toluene	Corrosion or fatigue in the materials	Leakage of toluene and ignition due to a reason results in accidents.	Toluene pool fire
	4	A greater composition (hydrogen)	Failure of separation	The hydrogen concentration in the gas phase of the toluene tank rises and configures into an explosive mixture. It explodes due to electrostatic discharge from the toluene.	Toluene-hydrogen mixture explosion
	5	More pressure in the hydrogen	Obstruction in the compressor	Too high a pressure in the compressor causes hydrogen to leak from the most fragile location in the process.	Hydrogen jet fire or explosion
Unloading MCH	8	Decreased flow in MCH	Corrosion or fatigue in the materials	Leakage of MCH and ignition due to a reason results in accidents.	MCH pool fire
Loading toluene	10	Less flow in the toluene	Corrosion or fatigue in the materials	Leakage of toluene and ignition due to a reason results in accidents.	Toluene pool fire

	11	A greater composition (hydrogen)	Failure in separation	The hydrogen concentration in the gas phase of the toluene tank rises and configures the explosive mixture. It explodes due to an electrostatic discharge from the toluene.	Toluene-hydrogen mixture explosion
Startup operational procedure		Unopened shut-off valve	Failure in a shut-off valve	Too high a pressure in the pipe due to the closing of a shut-off valve, which causes MCH to leak from the most fragile location in the process.	MCH pool fire
Shutdown operational procedure		MCH pump stopped later than appropriate	Failure of stop MCH pump	Too high a pressure in the pipe due to a failure of stop the MCH pump with a closed shut-off valve cause MCH leaked from the most fragile location in the process.	MCH pool fire

5. Conclusion

Organic hydride hydrogen refueling stations have been remarked as stations that can use liquid-phase MCH under conditions of ordinary temperature and normal pressure as a hydrogen carrier. The risks associated with HRSs have been assessed because these stations use some hazardous materials, but the sample of studies available used conceptual design models, and they did not identify concrete scenarios triggered by internal factors that can affect the processes of dehydrogenation, unloading MCH, and loading toluene. Therefore, the purpose of this study was to identify accident scenarios that can occur in an organic hydride hydrogen refueling station as a result of deviations in the processing parameters and human factors. In this study, we used HAZOP to identify accident scenarios triggered by these internal factors. As a result, 371 scenarios were identified, and 105 accident scenarios were chosen and classified into the two following groups; (i) scenarios that assumed that the substances were ignited after they were released to the atmosphere, and (ii) scenarios that assumed that the substances were ignited in the process before they were released. The significant scenarios in group (i) were easily assumed; for example, MCH or toluene pool fires can occur due to an ignition source, and hydrogen jet fires can result from immediate ignition, vapor gas explosions, or flash fires due to a delayed ignition if MCH or toluene were to leak from a fragile location in the process because of pressure increases. However, the significant scenarios in group (ii) were newly identified in this study: the explosive mixture formed by the gaseous phase of toluene and oxygen from the vent line connected to the tank can be ignited and explode due to the static electric charge in the tank. While safety measures for the scenarios in (i) have been examined with reference to the current laws and regulations in Japan, safety measures for scenarios in (ii) were newly proposed. In future works, it is necessary to perform quantitative consequences and frequency analyses for each scenario proposed in this paper to evaluate effectiveness of the examined and proposed safety measures.

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P	Pump
SV	Safety valve
ZV	Shut off valve
PI	Pressure indicator
TI	Temperature indicator

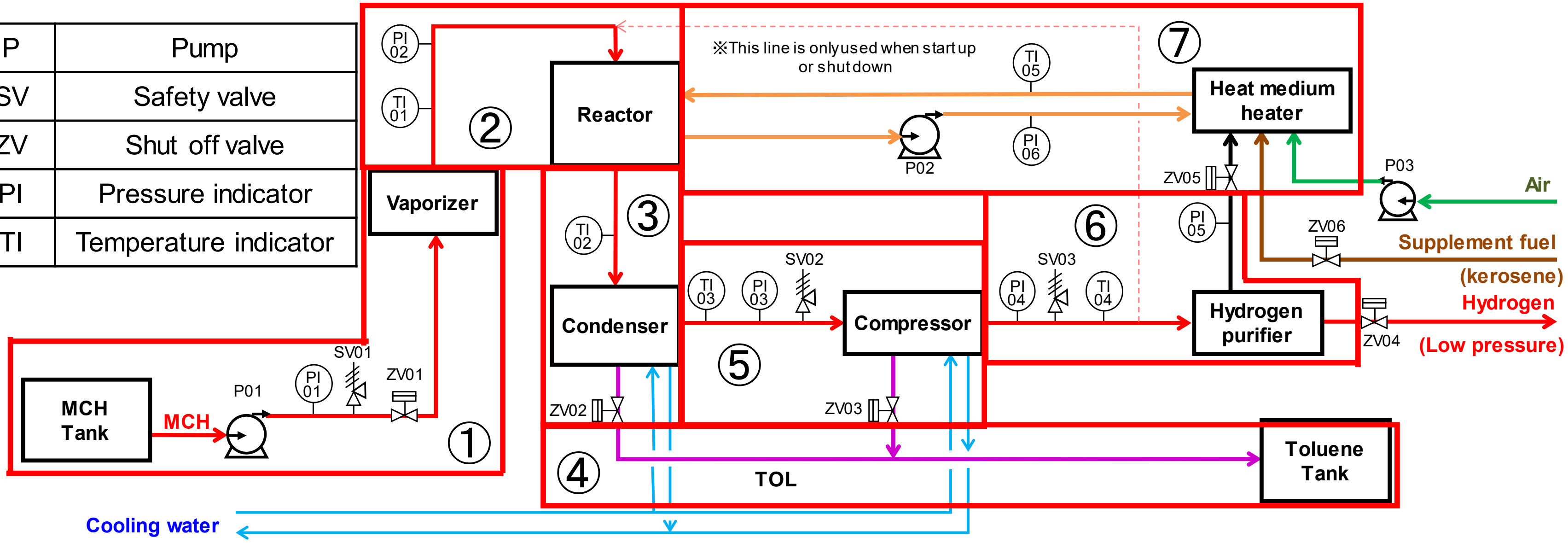


Fig. 1 Simple flow of the dehydrogenation process.

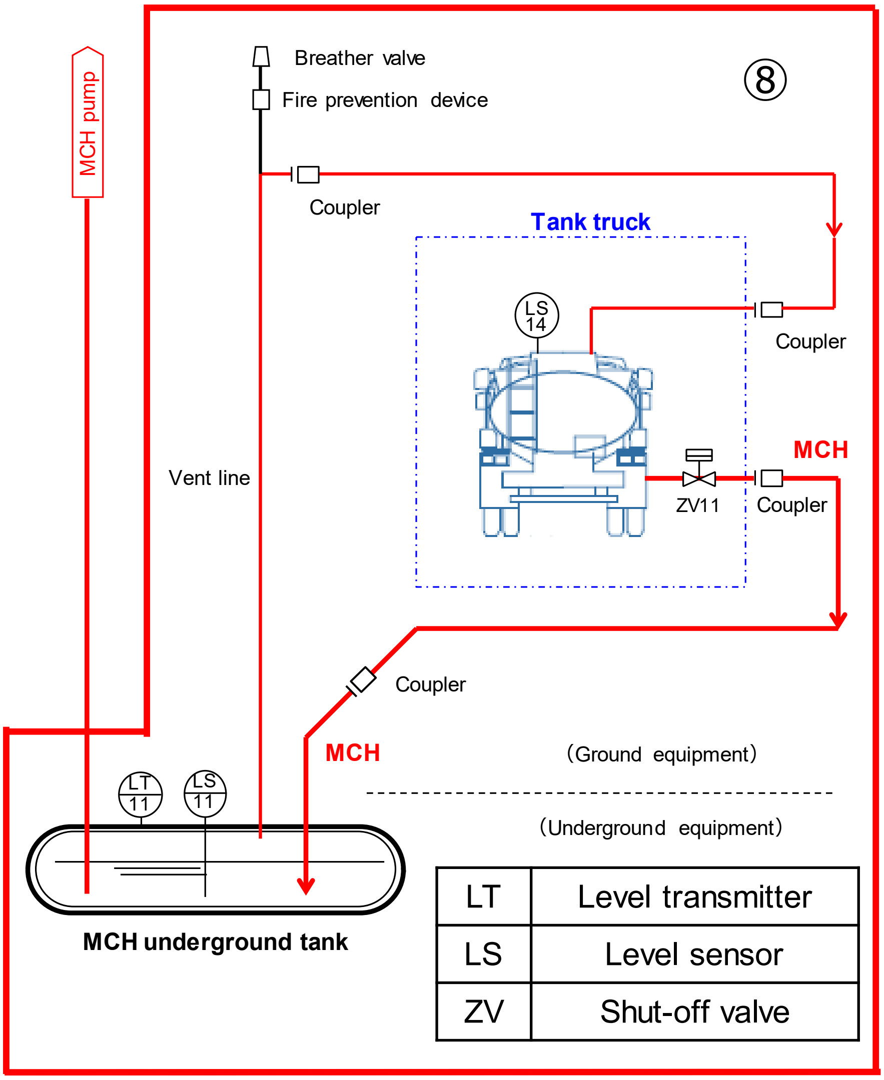
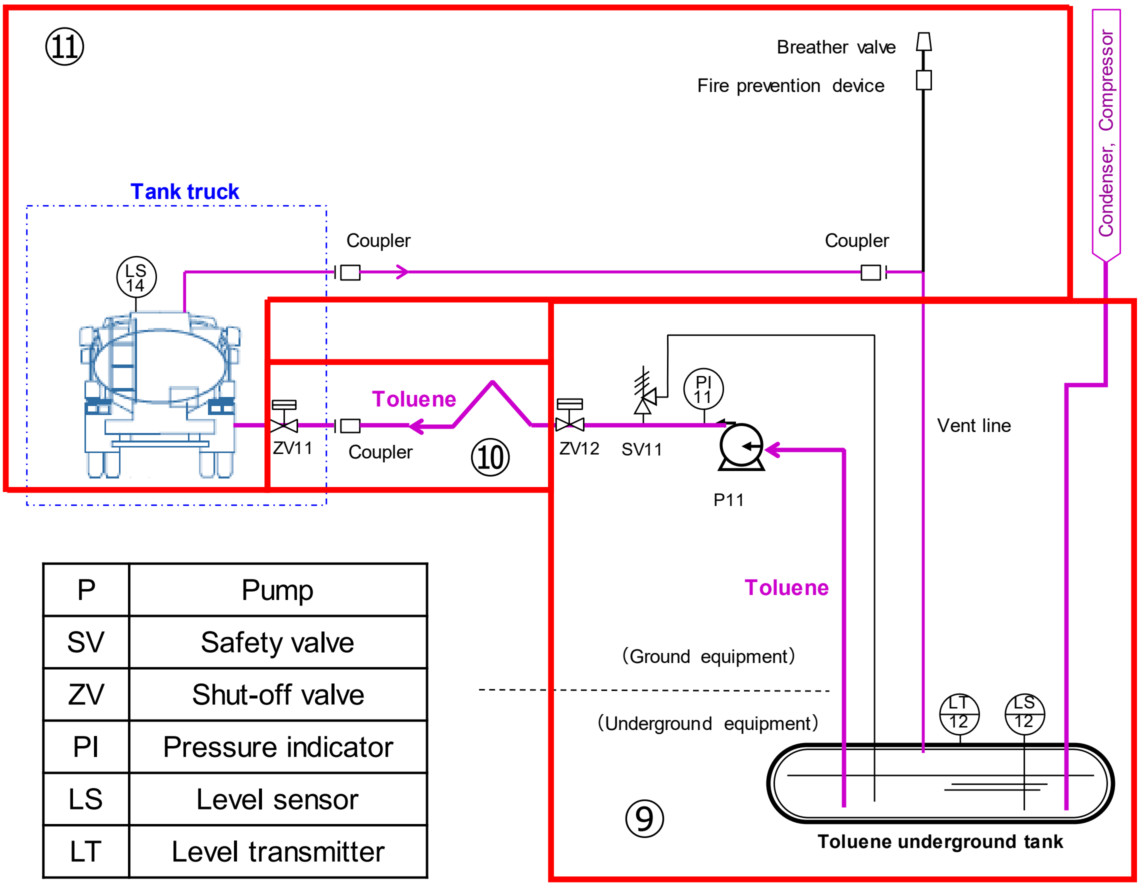


Fig. 2. Simple flow of the unloading MCH process.



P	Pump
SV	Safety valve
ZV	Shut-off valve
PI	Pressure indicator
LS	Level sensor
LT	Level transmitter

Fig. 3. Simple flow of the loading toluene process.

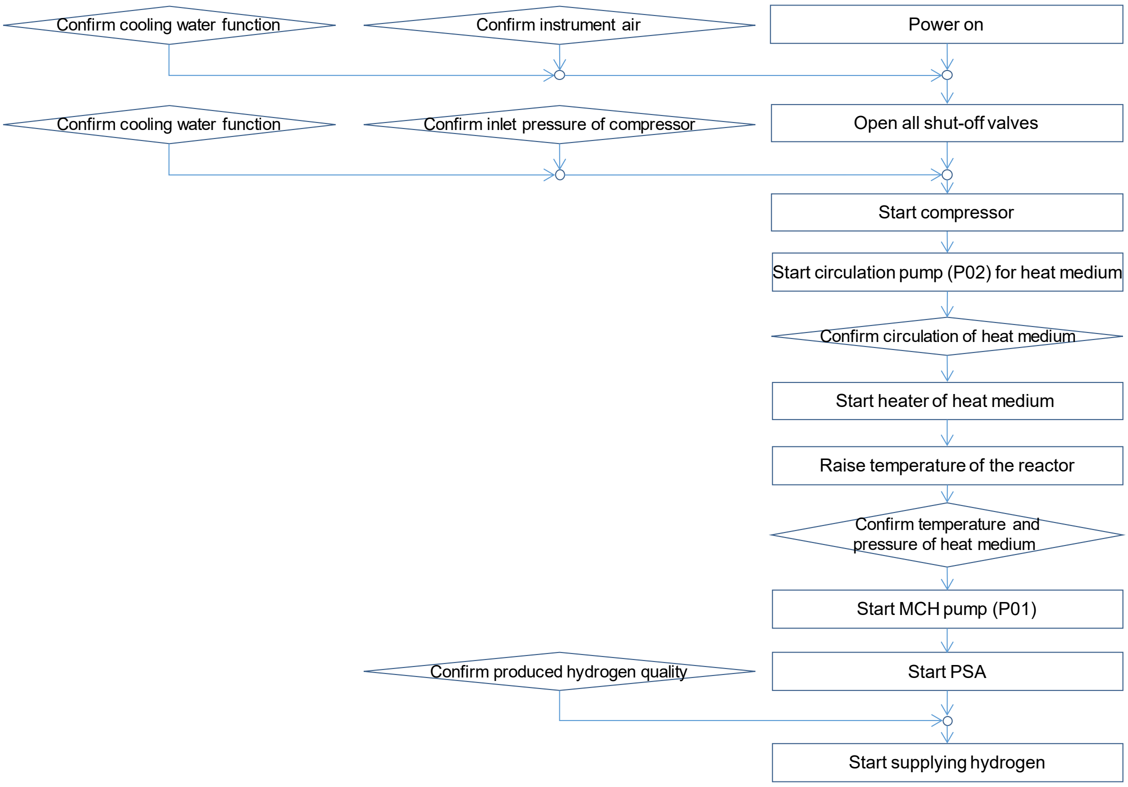


Fig. 4. Startup operational procedure of the dehydrogenation process.

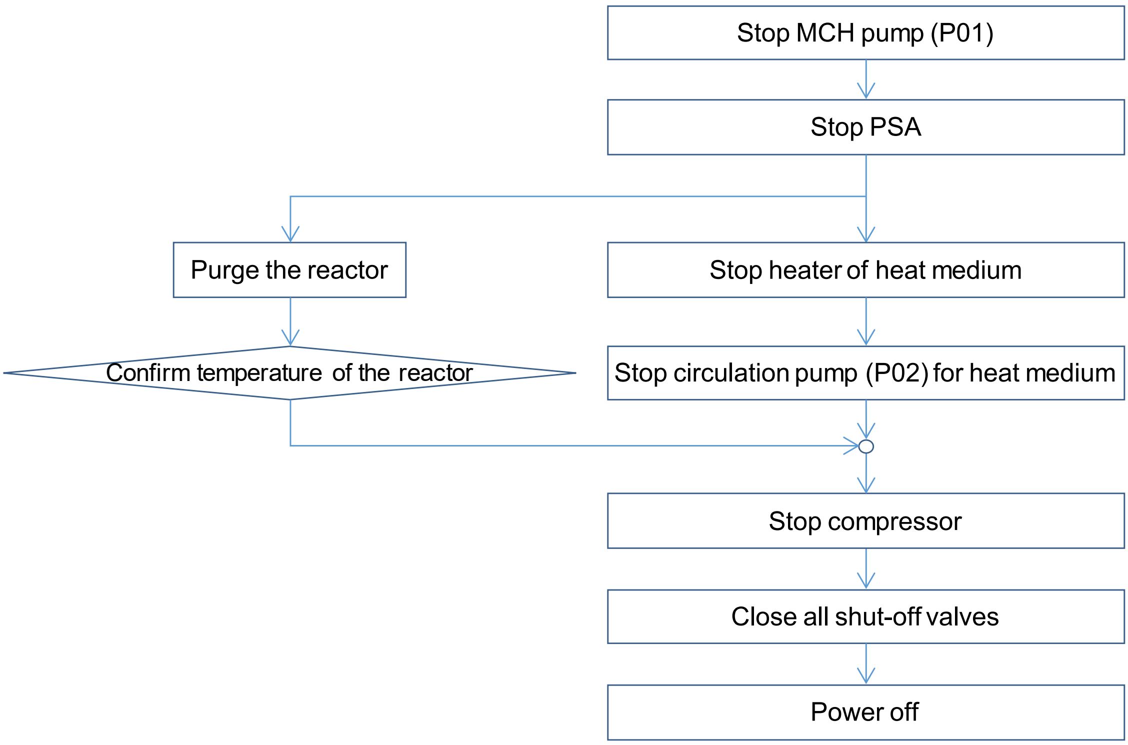


Fig .5. Shutdown operational procedure of the dehydrogenation process.