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Process Hazard Analysis of Hydrogen Generation System with Electrolysis Process

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Abstract.
The research and development of hydrogen as one of the renewable energy sources were conducted in many countries. In this study, the production of hydrogen is focused on electrolysis process. The technology development of electrolysis cannot be separated from the study about risks in its processes. A qualitative risk analysis using Hazard and Operability (HAZOP) study is conducted in order to identify the risk level of a small scale hydrogen generation system with Alkaline Electrolyser (AEL) Process. The initial risk rank of the hydrogen generation system result is from medium to very high risk (40% medium risk, 50% high risk, and 10% very high risk). After safeguard implementation, the final risk rank result is from low to medium risk (90% low risk and 10% medium risk).

Keywords: Hydrogen, Electrolysis, Risk, HAZOP

Introduction
One of the new and renewable energy sources that currently going through a great number of research and development as well as implementation on pilot projects is hydrogen. Hydrogen is not an energy source in itself and has to be produced from e.g. natural gas using steam reforming or water using large-scale electrolyser [1]. Nowadays the preferred pathway of hydrogen production is through water electrolysis and the core component of the electrolysis process is the electrolyser where the electrolysis reaction takes place. Ishaq et. al in 2015 mentioned that the significant electrolyser types utilized for electrolysis process are proton exchange membrane (PEM) electrolyser, solid oxide (SO) electrolyser and alkaline (ALK) electrolyser [2]. Hydrogen is vastly utilized in industrial sector. Although hydrogen is already widely used in the industry for several processes such as ammonia production for fertilizers, it is associated with crucial safety criticalities due to the specific substance properties [3]. The primary hazards associated with hydrogen are the following: combustion, pressure, low temperature, hydrogen embrittlement and exposure [4]. A good understanding of the safety aspects of hydrogen is required, including the ability to efficiently and accurately estimate possible risks and give recommendations for risk reduction measures [5]. Safety Planning should be an integral part of the design and operation of any system, requiring one to (1) identify hazards, (2) evaluate risks by considering the likelihoods and consequences of incidents associated with the hazards, and (3) minimize those risks [6]. This study will focus on analysis of hazard and risk in order to identify the risk level and adequacy of safeguard in hydrogen generation system with Alkaline Electrolyser (ALK) process, since alkaline electrolysers are the dominant type of units in commercial operation today [10].

Materials and Methods
The scope of process safety risk analysis will be focused on small scale hydrogen generation system with Alkaline Electrolyser (AEL) process which produce 5.6 Nm^3/hour of Hydrogen and 2.8 Nm^3/hour of Oxygen. The electrolysis process occurred in the electrolyser module using Kalium Hydroxide (KOH) electrolyte. The hydrogen will be compressed and stored in the storage cylinders while the oxygen is vented to the atmosphere. The specific Process Hazard Analysis (PHA) method used for hazard and risk analysis in the hydrogen generation system is Hazard and Operability (HAZOP) study. Risk matrix is generated prior to HAZOP study in order to determine risk rank based on the likelihood and severity of each process deviation scenario. The basic concept of the HAZOP study is to take a full description of the process and to question every part of it to discover what deviations from the intention of the design can occur and what the causes and consequences of these deviations may be systematically

by applying suitable guidewords [7]. The guidewords in this study are based on British Petroleum guidance with document number GP 48-02 [8]. The overall system will be divided into smaller study boundaries based on Process Flow Diagram (PFD) and Piping and Instrumentation Diagram (P&ID) called nodes. Every node will have specific process deviation scenario developed based on guidewords. The scope of node in this study based on PFD can be seen in Fig. 1 where the blue box represents Node 1, the red box represents Node 2, and the green box represents Node 3.

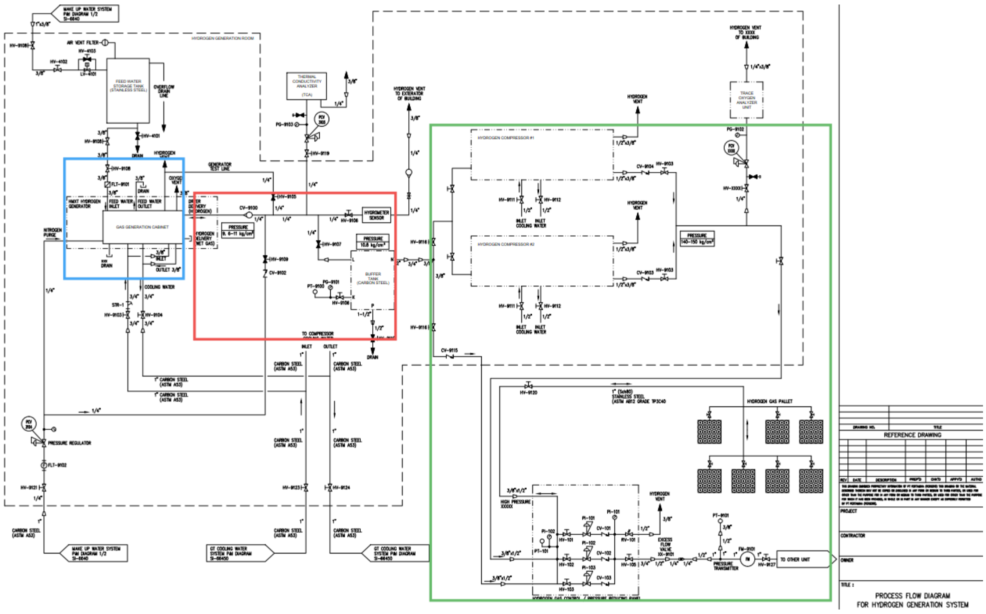


Fig. 1: Process Flow Diagram and Node Breakdown of Hydrogen Production System

Each deviation scenario will consist of guidewords, cause, consequence, initial risk rank, available safeguards, final risk rank, and available recommendations. The risk criteria and risk matrix used for the study is shown in Table 1 and Fig. 2. The result of HAZOP study from each deviation on all nodes will be in form of risk rank. The final purpose of this study is to evaluate the risk by analysing the adequacy of safeguards and also the impact of safeguards in reducing risk in hydrogen generation system.

Table 1: Risk Criteria for the Basis of Risk Matrix Development [9]

Parameter	Code	Category	Remarks
Likelihood	1	Improbable	Not occurred within the last 5 years
	2	Remote	Occurred within the last 36 months
	3	Occasional	Occurred within the last 24 months
	4	Probable	Occurred once within 12 months
	5	Frequent	Occurred more than once within last 12 months
Severity	A	Negligible	Non-treatment incidents
	B	Marginal	Recordable incidents
	C	Critical	Disabling injury or illness
	D	Catastrophic	One or more fatalities
Risk Rank	L	Low Risk	No action need
	M	Moderate Risk	Recommendation with suggestive level
	H	High Risk	Action required with high priority
	C	Very High Risk	Immediate action required

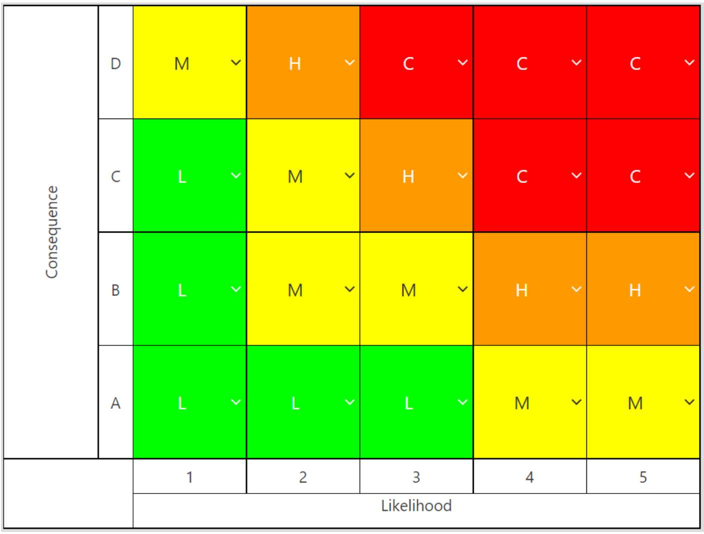


Fig. 2: Risk Matrix for HAZOP study developed with OpenPHA Software

Results and Discussion

HAZOP study result

HAZOP study is done by dividing major system into smaller nodes. There are three nodes being used in this study namely electrolyser module, hydrogen buffer storage, and hydrogen compression and storage which specified as Node 1, Node 2, and Node 3 respectively. The scenarios in this study developed with identifications of process deviations cause and consequence which may have impact on safety, asset, people and environment. Guidewords that are applicable for this study are the ones that related to fluid flow, fluid pressure, fluid temperature, wrong percentage of specific operation parameter, impurities in hydrogen, events of equipment leak or rupture and also the maintenance factor. The safeguard categories identified from HAZOP study are operation procedures, operator inspections, process instrumentations i.e. pressure gauge, pressure transmitter, gas detector and alarm, and also safety instrumentations i.e. pressure switch, temperature switch, and pressure relief valves. The example of HAZOP worksheet of each node is shown in Fig. 3. Further discussion from the result of HAZOP study will focus on the deviations that possess initial risk rank on the range of medium to high on each node. The deviation from Node 1 is taken from KOH pump where there is risk of corrosion on pump piping that will cause KOH spill to surrounding process area or to other equipment and the availability of safeguards in form of operator inspection, operating procedure, and also the application of stainless steel material for piping installation the risk rank can be reduced from high risk to low risk. Other deviation that identified in Node 1 is over current of electric supply to electrolyser module which may cause fire and explosion due to spark that ignite hydrogen or oxygen and the availability of safeguard in form of overload protection system which consist of fuse, temperature switch and also circuit breaker thus the risk rank can be reduced from very high risk to low risk.

The process deviation from Node 2 is taken from buffer tank where the lack of inspection of buffer tank that built with carbon steel material may cause tank damage due to hydrogen embrittlement phenomenon that may affect 2 aspects namely asset aspect and safety aspect. The impact regarding asset aspect is the lifetime of tank will be reduced and the impact from safety aspect is the probability of hydrogen release from tank which may trigger fire and explosion. Hydrogen embrittlement hazard could always be present in hydrogen operations due to the fact that hydrogen is a special fluid that diffuses very easily (diffusion coefficient in NTP air is 0.61 cm^2/s) even in metallic materials [4]. The deviation from safety aspect possess safeguard in form of combustible gas detector complete with interlock system thus operator may have time to mitigate the loss of containment event, but for the deviation from asset aspect there are no available safeguard. Lack of safeguard bring out a recommendation to replace buffer tank with stainless steel material instead of carbon steel. The risk rank from safety aspect is able to be reduced from medium risk to low risk, but from the asset aspect still remain the same in medium risk.

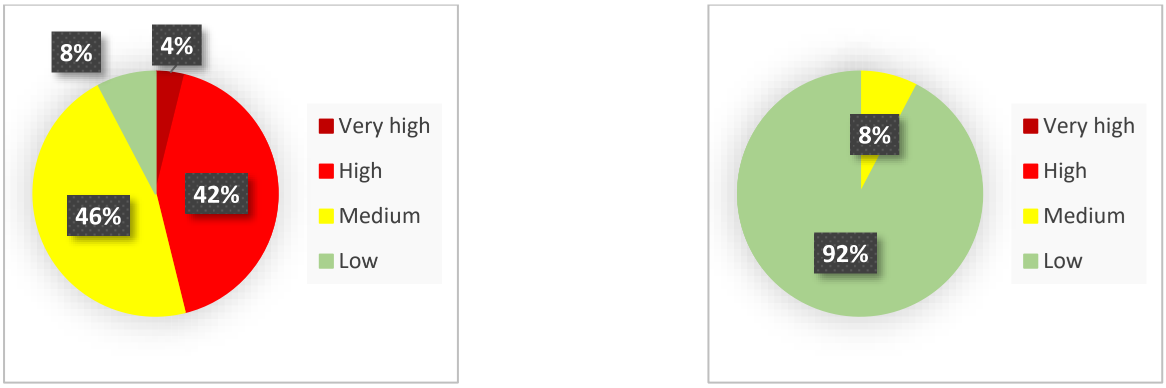
Node	Deviation	Causes	Consequences	CAT	Initial S	Initial L	Initial RR	Safeguards	S	L	RR	PHA Recommendation
1	2.21 Leak/rupture	2.21.1 Corrossion on KOH transfer piping (pump suction and discharge line, Heat Exchanger Inlet and Outlet line)	2.21.1.1 KOH exposure outside process system which may cause other equipment damage	A	C	3	H	20 SOP for maintenance 21 Operator routine inspection 30 Stainless steel piping	B	1	L	-
			2.21.1.2 KOH exposure outside process system which may cause harm for operator	C	C	3	H	20 SOP for maintenance 21 Operator routine inspection 30 Stainless steel piping	B	1	L	-
			2.21.1.3 KOH exposure outside process system which may have corrosive impact for nearby area	E	C	3	H	20 SOP for maintenance 21 Operator routine inspection 30 Stainless steel piping	B	1	L	-
	3.5 Wrong percentage/part of	3.5.1 Over Current from electric power supply to Alkaline Electrolyzer Unit	3.5.1.1 Explosion due to spark to make contact with previously formed Hydrogen and Oxygen inside Electrolyzer Unit leading to fire and explosion	S	D	4	C	8 Overload protection system (fuse for SCR, temperature switch, circuit breaker)	A	2	L	-
2	6.22 Maintenance	6.22.1 Hydrogen embrittlement phenomenon	6.22.1.1 Reduced lifetime of tank which may cause damage	A	B	3	M		B	3	M	7 Replace tank material with stainless steel
			6.22.1.2 Hydrogen Leakage to process area leading to fire or explosion	S	B	3	M	19 Combustible gas detector 33 Venting system installation	B	1	L	-
3	7.8 Higher Pressure	7.8.1 Higher Hydrogen Pressure delivered from Hydrogen Compressor	7.8.1.1 Loss of containment from Hydrogen Storage Cylinder	S	C	4	C	16 Pressure Gauge and Pressure Switch on Hydrogen Compressor #1 and #2 17 Pressure Indicator on discharge line (PI-102) 18 Pressure Relieve Valve on Hydrogen Compressor #1 (PRV-9101 and PRV-9103) and Compressor #2 (PRV-9102 and PRV-9104) 19 Combustible gas detector 32 Pressure switch to shutdown the compressor	A	2	L	-

Fig. 3: Example of HAZOP Result for Hydrogen Generation System of Node 1, 2, and 3

The deviation from Node 3 is taken from hydrogen compressor where there is a possibility of hydrogen delivery at higher pressure to the hydrogen storage cylinder. The intended condition for hydrogen delivery to storage is in the range of 140-160 kg/cm^2.g based on process condition in Fig. 1. The consequence of this deviation is hydrogen loss of containment in storage cylinder area. Releases from storage bottle connections, could give major jet fires, flashfires or explosions [5]. There are two safeguards available to reduce the risk on higher pressure deviation from compressor. The first safeguard is pressure relief valve on compressor no.1 with the tag number of PRV-9101 and PRV-9103 and also on compressor no. 2 with the tag number of PRV-9102 and PRV-9104. The second safeguard is the installation of combustible gas detector complete with interlock function which will trigger the action to shut down the compressor during the indication of 50% Lower Explosive Limit (LEL). The implemented safeguards are able to reduce the risk from high risk to low risk.

Risk Evaluation

The evaluation of overall risk is done based on risk rank data. There are total of 26 HAZOP scenarios. The early development of scenarios before considering available safeguards results in 1 scenario or 4% of overall scenarios with very high risk, 11 scenarios or 42% of overall scenarios with high risk, and 12 scenarios or 46% of overall scenarios with medium risk, and also 2 scenarios or 8% of overall scenarios with low risk. The risk range from initial risk rank is from low to very high risk. The repercussion of process deviation scenarios after safeguards are identified results in 2 scenarios or 8% of overall scenarios with medium risk and 24 scenarios or 90% of overall scenarios with low risk. Graphical representations regarding comparison of risk level of hydrogen plant either for the result of overall risk level before and after identifying safeguards are shown in Fig. 4. The HAZOP study conclude that the hydrogen generation system with AEL Process is operable with the level of low to medium risk which means the final level of risk is in category of As Low As Reasonably Practical (ALARP).



(a) (b)

Fig. 4: Hydrogen Generation System Risk Rank of each deviation scenario from HAZOP study (a) Risk Rank before safeguard identification (b) Risk Rank Risk Rank after safeguard identification

Conclusions

The result of the HAZOP study shown that there are various identified process safety risks with low, medium, and high risk for the operation of small hydrogen generation system and the study also found out that implementation of safeguards is important to keep the risk as low as possible. The final risk of the hydrogen generation system is ranging from very low to medium risk. Further studies regarding consequence analysis need to be done in order to verify the result of the study since HAZOP is limited to define risk in qualitative method.

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