CHEMICAL ENGINEERING TRANSACTIONS
VOL. 106, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216
DOI: 10.3303/CET23106140

Inherent Safety and Health Assessment of Hydrogen Storage Process

Syaza I. Ahmad[a,b,*], Naim Hisham[a], Mardhati Zainal Abidin[a,b]

[a]Chemical Engineering Department, Universiti Teknologi PETRONAS 32610 Seri Iskandar, Perak, Malaysia
[b]Centre of Advanced Process Safety, Universiti Teknologi PETRONAS 32610 Seri Iskandar, Perak, Malaysia
syaza.ahmad@utp.edu.my

The consumption of fossil fuel as the main energy sources results in the production of a large amount of greenhouse gases, such as carbon dioxide and methane, which are one of the main causes of climate change. Research and development as well as implementation of clean energy has been put as high priority in various countries to combat this issue. Hydrogen is one of the most promoted energy sources of clean energy due to its environmental benefits and high energy production. Major development can be seen in the field of hydrogen energy in the past few years from the stage of hydrogen production until the stage of hydrogen storage. This further enhanced the importance of hydrogen safety considerations. Safety considerations usually begins with hazard identification which can be done using various inherent safety assessment tools. Even though there a lot of inherent safety assessment methods that are available, the method that can be used to specifically assess the safety and health level of hydrogen storage is lacking. The aim of this paper is to introduce the development of an inherent safety and health assessment method specifically for hydrogen storage processes. This research begins with the identification of safety and health hazard parameters that existed in hydrogen storage process. Then, a hazard scoring index for safety and health parameters focusing on hydrogen storage is developed. At the current phase, this research will only focus on material-based chemisorption in stationary hydrogen storage technique. The scoring development for inherent safety and health assessment will be done quantitatively using logistic function. The inherent safety and health assessment methods developed will rank the chemicals involved according to their hazard level.

1. Introduction

The world's primary sources of energy today are petroleum-based. This primary energy sources consumption releases an abundance of unwanted greenhouse gases such as carbon dioxide and methane which can lead to climate change. To solve the issue of climate change, various researchers have been working harder to identify the best alternative to petroleum-based fuel. One attractive alternative to fossil fuel is hydrogen energy due to its cleaner, sustainable, and efficient generation, consumption, distribution, and storage processes. It is expected by 2030, various developed countries will implement hydrogen energy in numerous industries for example, ammonia manufacturing and transportation technology (Mitsubishi, 2022). Fuel cells, which are applied in automobiles and use hydrogen as a fuel source to create electricity with water as a by-product, are another example of technological innovations that utilise hydrogen (Usman, 2022).
The utilization of hydrogen in an increasing number of modern technologies over the past decades has increased the importance of hydrogen safety issues (Ustolin et al., 2020). Hydrogen has been known to leak easily, has low minimum ignition temperature, large flammable and explosion range, and embrittlement effects (Li et al., 2022). This makes the utilization of hydrogen as the source of energy has certain limitations in terms of safety. Landucci et al. (2008) estimate several inherent safety key performance indicators (KPIs) involving hydrogen storage. The focus of the KPIs is mainly on consequence assessment of possible loss of containment events involving hydrogen storage. Aside from assessing the inherent safety from the hydrogen loss of containment point-of-view, it is also important to identify the inherent safety and health level of materials that are being used in storing hydrogen. A comprehensive inherent safety and health assessment is needed as an initial measure to reduce the safety issues involving the materials used in hydrogen storage. Even though there

Paper Received: 29 May 2023; Revised: 29 October 2023; Accepted: 5 November 2023
Please cite this article as: Ahmad S.I., Hisham N., Abidin M.Z., 2023, Inherent Safety and Health Assessment of Hydrogen Storage Process, Chemical Engineering Transactions, 106, 835-840 DOI:10.3303/CET23106140

a lot of safety assessment methods that are available, the method that can be used to assess the safety and health level of material used in hydrogen storage is lacking. Current inherent safety and health consideration focuses on specific industry for example petrochemical or oil and gas. For example, the Inherent Safety Index (ISI) (Heikkila, 1999) which focuses on inherent safety assessment for general processes, the Numerical Descriptive Inherent Safety Technique (Ahmad et al., 2014) which focuses on inherent safety assessment for petrochemical processes, Inherent Occupational Health Index (IOHI) (Hassim and Hurme, 2010), Inherent Occupational Health Assessment Index for Research and Development Stage of Process Design (So et al., 2021) which also focuses on petrochemical processes, inherent safety assessment of solvent alternatives for palm oil recovery (Aahmad et al 2019), and safety and health assessment for waste-to-energy technologies (Ahmad et al 2019).

The main objective of this paper is to introduce an inherent safety and health assessment method for chemicals utilized in the hydrogen storage processes. The outcome of this work is in terms of inherent safety and health scoring related to the chemical properties of the chemicals involved in hydrogen storage specifically the chemisorption process of material-based hydrogen storage comprises of few types of chemicals such as ammonia, metal hydrides, formic acid, carbohydrate, and liquid organic hydrogen carriers (LOHC). This method can be used in evaluating the inherent safety and health parameters of the stationary hydrogen storage systems comprises of on-site storage at point of use, on-site storage at point of production and stationary power generators. Discussion on the scoring method produced in this paper will focus on two parameters that have been identified for chemical safety which are flammability and toxicity.

2. Methodology

2.1 Parameter Involved

2.1.1 Flammability

The ability of a material to burn in air is known as flammability (King, 1990). It is applicable to solids, liquids, and gases. Knowing flammability is crucial, especially in situations involving leaks. A liquid that can produce a combustible combination and has a flash point below the processing or storage temperature is generally regarded as hazardous. The lower flammability limit of the substance and its vapour pressure at the ambient temperature determine a liquid's flammability. The flash point is the lowest temperature at which a liquid release an amount of flammable vapour at or near its surface that causes it to catch fire when in close proximity to air and a spark or flame. As a result, the primary factor in determining how hazardous liquids is their flash point, and government laws are based on this (Lees, 1996). The boiling point can be used to determine a material's volatility. The boiling point of a flammable liquid can also be used as a direct indicator of the risk associated with using it (Sax, 1979). Comparable methodologies were employed by Edwards and Lawrence (1993) and the Dow Fire and Explosion Index (1987).

2.1.2 Toxicity

Chemical effects that are unpleasant or harmful are measured by their toxicity. Toxicology endpoints are specific categories of these harmful effects, such as genotoxicity or carcinogenicity, and it can be measured quantitatively or qualitatively, such as binary or ordinary. Toxicology tests seek to determine whether a material has hazardous effects on people, animals, plants, or the environment after acute exposure by single dose or multiple exposure by multiple doses (Raies and Bajic, 2016). A measurement of the likelihood that such damage may occur is the toxic hazard. The frequency, length, and chemical concentration of the exposure all have a role in determining it. A substance's toxicity is determined by its physical and biological properties, the route of entry, in an industrial culture, this would be through the skin, inhaling, or ingesting, and the dosage.

Regular exposure of workers to a variety of industrial toxins at relatively low levels can result in chronic illnesses that can cause severe disability or even early death (King, 1990). Process materials pose serious health risks due to their carcinogenicity, teratology, and mutagenicity. The Time Weighted Averages (TWA), which must not be exceeded during any 8-h work shift during a 40-h work week, is the employee's average airborne exposure. The maximum level of exposure to which an employee can be subjected without running the risk of experiencing negative health consequences is the 8-hour. TWA are based on a variety of impacts, ranging from irritability to physiological harm. TWA are the most practical toxicity values, particularly in industrial settings where they are intended to safeguard workers. In this work, the health effects are assessed for the chemicals that are being used in storing hydrogen specifically the chemisorption process of material-based hydrogen storage comprises of few types of chemicals such as ammonia, metal hydrides, formic acid, carbohydrate, and liquid organic hydrogen carriers (LOHC).

2.2 Brief Introduction to Logistic Function

In data analysis, logistic function for each parameter will be developed to be used for all materials that have been identified based on basic logistic function equation (Ahmad et al., 2014). Eq(1), Eq(2), and Eq(3) show the general logistic function equation used in the scoring development:

$$y = \frac{C}{1 + Ae^{-Bx}} \quad (1)$$

$$B = \frac{4m}{C} \quad (2)$$

$$A = e^{Bk} \quad (3)$$

In Eq(1), y refers to the scores for each parameter value, x refers to the parameter value, and C is the maximum limit of the scores. m in Eq(2). is the slope inclination for the curve which will be adjusted later to produce a smooth curve line while k in Eq(3). is a value that will produce the mid score of the assessment which will give the half of the fixed maximum score when x value is equal to k.

2.3 Development of Inherent Safety and Health Scoring

The development of inherent safety and health scoring for flammability and toxicity parameters was conducted according to the methodology shown in Figure 1.

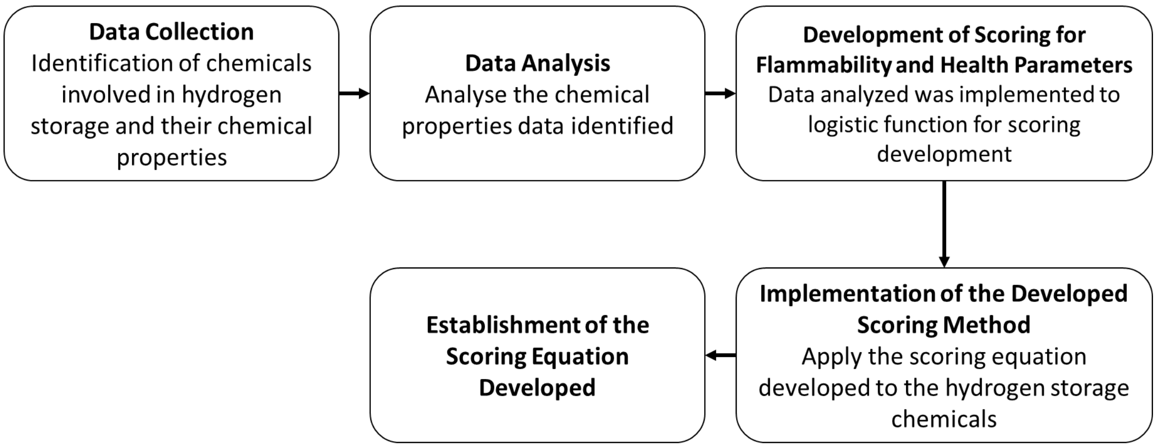

Figure 1: Methodology Flowchart

The first step of the methodology is data collection. In this step, chemicals that are involved in hydrogen storage as well as their flash point and TLV values are identified from the literature. Table 1 listed the chemicals identified in hydrogen storage.

Table 1: Chemicals Utilized in Hydrogen Storage

Classification	Formula	Name
Ammonia	NH_3	Ammonia
Metal Hydrides	$NaAlH_4$	Sodium Aluminium Hydride
	AlH_3	Aluminium Hydride
	$LiBH_4$	Lithium Borohydride
Formic Acid	CH_2O_2	Methanoic Acid
Carbohydrate	$C_6H_{10}O_5$	Cellulose
Liquid Organic	CH_3OH	Methanol
Hydrogen Carriers (LOHC)	C_6H_{12}	Benzene
	$C_6H_5CH_3$	Toluene

The flash point and TLV values were then identified for each chemical was analyzed for minimum and maximum values as well as the median values. These identified values were then adapted into the logistic function as in Eq(1), Eq(2), and Eq(3). in the third step for the development of flammability and toxicity scoring. In the logistic function developed for each parameter, lower score indicates that the chemicals have lower hazard than chemicals with higher score. The flammability and toxicity scoring equation developed was implemented to a case study to illustrate its usage.

3. Results and Discussion

3.1 Logistic Scoring Produced for Flammability and Toxicity Parameters

3.1.1 Flammability

Eq(4) shows the scoring equation produced for flammability parameter. The value of the flash point is ranged between -100 °C to 300 °C as the range of the common materials in hydrogen storage process that have been identified from the data collection step is between -21 °C to 286.7 °C. As for flammability, the k value is the mid-score of the assessment and this value will be the separator between the lesser hazardous score and the more hazardous score. The value for k that has been decided is 38 as the Occupational Safety and Health Administration (OSHA) has categorized 38 ºC as the flash point value that could potentially be hazardous at workplace. The m value for the function is negative as the lesser the flash point, the more hazardous the material it will be. The flammability score function that has been developed is shown in the logistic equation above and it can be used in determining the flammability hazard score of a material by simply substituting the value x with the flash point of the material.

$$Score_{Flammability} = \frac{100}{1 + 0.3198e^{0.03x}} \tag{4}$$

3.1.2 Toxicity

Based on the toxicity logistic curve, the value of the TWA ranges between 0 ppm to 400 ppm as the range of TWA value based on the chemicals used in storing the hydrogen that have been identified from database is between 0.00737 ppm to 400 ppm. As for toxicity, the k value is the mid-score of the assessment and this value will be the separator between the lesser hazardous score and the more hazardous score. The value for k that has been decided is 200 ppm because it is the middle point of the range as TWA is ranged between 0 ppm to 400 ppm. The m value for the function is negative as the lesser the TWA value, the more hazardous the material it will be. The toxicity score function that has been developed is shown in Eq(5). and it can be used in determining the toxicity hazard score of a material by simply substituting the value x with TWA value of the material.

$$Score_{Toxicity} = \frac{100}{1 + 0.002479e^{0.03x}} \tag{5}$$

3.2 Implementation of Flammability and Toxicity Parameters Scoring

The scoring method developed was implemented to several chemicals used in hydrogen storage system. The flash point and TWA values identified as listed in Table 2 were inserted into Eq(4). and Eq(5). to produce flammability and toxicity scores for each chemical. Table 2 shows the scores produced for each chemical for flammability and toxicity parameters. In Table 2, Rank 1 indicates the least hazardous chemical while Rank 10 indicates the most hazardous chemical.

Table 2: Flammability and Toxicity Scores Produced for Several Chemicals used to Store Hydrogen

Chemical	Flammability			Toxicity		
	Flash Point Value (°C)	Score	Rank*	TWA Value (ppm)	Score	Rank*
Lithium Borohydride	-21	97.42	10	200	50.00	3
Sodium Aluminium Hydride	-10	96.44	9	2.26	99.74	9
Ammonia	8.85	93.90	8	25	99.48	6
Methanoic Acid	50	81.76	6	5	99.71	8
Methanol	11.11	69.14	2	200	50.00	3
Benzene	-11	81.31	5	0.1	99.75	10
Toluene	4.4	73.26	3	100	95.26	5
Naphthalene	78.5	22.88	1	10	99.67	7
Methylcyclohexane	-3	77.38	4	400	0.25	1
Cyclohexane	-20	85.07	7	300	4.74	2

* Rank 1 indicates the least hazardous chemicals while Rank 10 indicates the most hazardous chemicals

In terms of flammability parameter, lithium borohydride is the most hazardous with a score of 97.42 due to its lowest flash point value of 21 °C while naphthalene is the least hazardous in terms flammability with a flash point value of 78.5 °C. Lithium Borohydride, sodium aluminium hydride, and ammonia have almost similar flammability scores indicating them as the three most hazardous in terms of flammability parameters as shown in Table 2. Benzene is deemed as the most hazardous in terms of toxicity parameter with a score of 99.75 due to its lowest TWA value of 0.1 ppm while methyl cyclohexane is indicated as the least hazardous in terms of toxicity parameter with a TWA value of 400 ppm resulting in a toxicity score of 0.25. Based on the results shown in Table 2, most attention needs to be given to benzene, sodium aluminium hydride, and methanoic acid as these chemicals as the three most hazardous chemicals in terms of toxicity with TWA values of 0.1 ppm, 2.26 ppm, and 5 ppm, respectively. This information can be used to assist users in planning for suitable accident prevention and mitigation strategies.

4. Comparison with other Scoring Method

Comparison was made between the logistic scoring produced in this work with the flammability and toxicity scoring in Inherent Safety Index (ISI) (Heikkila, 1999). The ISI method was chosen for comparison due to its similarity in terms of the parameter values used which is flash point and TWA values for flammability and toxicity parameters. Table 3 shows the comparison made.

Table 3: Result Comparison with the ISI Method

Chemical	Flammability					Toxicity				
	Flash Point (°C)	Logistic Scoring		ISI Method		TWA (ppm)	Logistic Scoring		ISI Method	
		Score	Rank*	Score	Rank*		Score	Rank*	Score	Rank*
Lithium Borohydride	-21	97.42	10	4	6	200	50.00	3	2	1
Sodium Aluminium Hydride	-10	96.44	9	4	6	2.26	99.74	9	4	7
Ammonia	8.85	93.90	8	3	3	25	99.48	6	3	5
Methanoic Acid	50	81.76	6	2	1	5	99.71	8	4	7
Methanol	11.11	69.14	2	3	3	200	50.00	3	2	1
Benzene	-11	81.31	5	4	6	0.1	99.75	10	6	10
Toluene	4.4	73.26	3	3	3	100	95.26	5	3	5
Naphthalene	78.5	22.88	1	2	1	10	99.67	7	4	7
Methylcyclohexane	-3	77.38	4	4	6	400	0.25	1	2	1
Cyclohexane	-20	85.07	7	4	6	300	4.74	2	2	1

* Rank 1 indicates the least hazardous while Rank 10 indicates the most hazardous

According to Table 3, both methods agree on the least hazardous and most hazardous chemicals as both methods indicates naphthalene and lithium borohydride as the least hazardous and most hazardous chemicals in terms of flammability parameter, respectively. This is also similar to toxicity parameter in which both methods indicate methylcyclohexane and benzene as the least hazardous and most hazardous chemicals, respectively. This similarity indicates that the logistic equation scoring produced by analysing the flash point and toxicity data agrees with the general assumption of hazard level as in the ISI Method. Differences can be seen in terms of the chemical hazard ranking. The logistic scoring produced in this work shows the ability of unique ranking to every chemical evaluated compared to the ISI method. In ISI method, several chemicals can be seen to have the same score with different parameter values. This further highlights the advantage of logistic scoring compared to the existing inherent safety assessment index.

5. Conclusions

In conclusion, this paper introduces an inherent safety and health assessment method based on logistic scoring. This method utilizes information obtained from the flammability and toxicity data involving hydrogen storage chemicals and implements them in the general logistic function producing a logistic scoring indicating this method to be specific for hydrogen storage chemicals with unique assessment ranking. Comparison with the ISI method shows that this method also agrees with the general assumption of hazard level as in the existing method. However, in order to have a more comprehensive inherent safety and health assessment, the method introduced in this work needs to be accompanied with other inherent safety and health parameters such as explosiveness and reactivity. Inclusion of other aspects of hydrogen storage such as operating temperature and pressure can also contributes to a more specific and comprehensive inherent safety and health evaluation.

Acknowledgments

Special thanks to Universiti Teknologi PETRONAS for the support received in completing this manuscript through the YUTP-FRG research grant (vot: 015LC0-469).

References

Ahmad S.I., Hashim H., Hassim M.H., 2014, Numerical descriptive inherent safety technique (NuDIST) for inherent safety assessment in petrochemical industry, Process Safety and Environmental Protection, 92(5), 379-389.

Ahmad S.I., Ho W.S., Hassim M.H., Elagroudy S., Bong C.P.C., 2019, Development of quantitative index for waste to energy technology selection: Safety and health parameters, Chemical Engineering Transactions, 72, 43-48.

Ahmad S.I., Yunus, N.A., Hashim, H., Rashid, R., 2019, Inherent safety assessment of solvent alternatives for palm oil recovery, Chemical Engineering Transactions, 72, 49-54.

Dow Chemical Company, (6th Ed), 1987, DOW's Fire & Explosion Index Hazard Classification Guide, American Institute of Chemical Engineers, New York.

Edwards D.W., Lawrence D., 1993, Assessing the Inherent Safety of Chemical Process Routes: Is There a Relation Between Plant Costs and Inherent Safety? Trans IChemE, 71, Part B, 252–258.

Heikkilä A.M., 1999, Inherent safety in process plant design: An index-based approach, PhD Thesis, VTT Technical Research Centre of Finland.

Hassim M.H., Hurme M., 2010, Inherent occupational health assessment during process research and development stage, Journal of Loss Prevention in the Process Industries, 23(1), 127-138.

King R., 1990, Safety in the Process Industries, Butterworth-Heinemann, London.

Landucci G., Tugnoli A., Cozzani V., 2008, Inherent safety key performance indicators for hydrogen storage systems, Journal of Hazardous Materials, 159, 554-566.

Lees F.P., (2nd Ed), 1996, Loss Prevention in the Process Industries, Butterworth-Heinemann, Oxford.

Li H., Cao X., Liu Y., Shao Y., Nan Z., Teng L., Peng W., Bian J., 2022, Safety of hydrogen storage and transportation: Aan overview on mechanisms, techniques, and challenges, Energy Reports, 8, 6258-6269.

Mitsubishi, 2022, Mitsubishi Power Asia Pacific Pte. Ltd. <https://power.mhi.com/regions/apac/> accessed 02.11.2022.

Raies A.B., Bajic V.B., 2016, In silico toxicology: computational methods for the prediction of chemical toxicity. Wiley Interdisciplinary Reviews: Computational Molecular Science, 6(2), 147-172.

Sax N.I., (5th Ed), 1979, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold Company, New York.

So Y.S., Hassim, M.H., Ahmad, S.I., Rashid, R., 2021. Inherent occupational health assessment index for research and development stage of process design, Process Safety and Environmental Protection, 147, 103-114.

Usman M.R., 2022. Hydrogen storage methods: Review and current status, Renewable and Sustainable Energy Reviews, 167, 112743.

Ustolin F., Paltrinieri N., Berto F., 2020, Loss of integrity of hydrogen technologies: A critical review, International Journal of Hydrogen Energy, 45(43), 23809-23840.