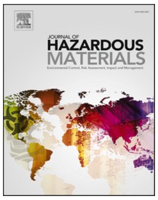
Journal of Hazardous Materials 421 (2022) 126590

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Research Paper

Development of an inherent system safety index (ISSI) for ranking of chemical processes at the concept development stage

Sharmin Sultana [a,b,*], Stein Haugen [a]

[a] *Department of Marine Technology, Norwegian University of Science & Technology, NTNU, Norway*
[b] *Department of Research and Innovation, DynSoL AS, Norway*

ARTICLE INFO

Editor: Dr. R Teresa

Keywords:
Inherent safety
System safety
Chemical industry
Process industry
Risk management

ABSTRACT

Inherently safer design is the most proactive approach to manage risk, as referred by scientists and experts. Researchers have adopted various methods in evaluating inherent safety indices like parameter-based indexing, risk-based indexing, consequence-based indexing, etc. However, the existing approaches have their limitations. The present paper focuses on establishing an inherent system safety index (ISSI) to evaluate inherently safer design during the concept development stage. The analysis starts by identifying a non-harmful system's inherent safety characteristics and related parameters. Four subindexes, determined from the non-harmful system's characteristics, are established using their relevant parameters. The safety of the chemical process system, the health of workers, and the environment's safety can be assured by selecting relevant parameters. Parameters are scored based on their deviation from the non-harmful condition. The sum of the deviations of the parameters gives the value of the inherent safety index. The case study looks at various routes of Methyl Methacrylate (MMA). According to the present case study, MMA production followed by Tertiary butyl alcohol is the safest route given health, safety, and environmental perspective. This approach helps overcome the limitation of parameter-based indexing, which arises from selecting predefined fixed parameters that become invalid in case of system variation or significant modification of the system. Besides, it considers the complexity and vulnerability that arises from the interaction of various factors|, which increase predetermined risk calculated at the design stage when the system is in operation. The subindices can be used individually if a focus is needed in *a* definite section of *a* system with *a* particular application or a smaller portion. This method is helpful for the industry in designing *a* safer plant considering the health, safety, and environmental perspective at the concept development stage.

1. Introduction

Inherently safer design (ISD) is a proactive approach to risk reduction (Amyotte and Khan, 2002). Risk reduction strategies fall into four types, inherent, passive, active, and procedural (CCPS, 2009). Inherently safer design strategy focuses on reducing hazard from the root, e.g., hazardous material or operations, rather than installing controlling systems (Heikkilä, 1999). This concept's application should start from the early design stage, unlike other strategies, which begin at the detailed design or commissioning stage (Shariff and Leong, 2009b). Along with its proactivity, this approach minimizes the cost of additional maintenance, energy, waste management, and pollution management and reduces the system's probability of failure (Abedi and Shahriari, 2005; Gupta and Edwards, 2002). Trevor Kletz, the pioneer of inherently safer design, proposed four main principles to achieve inherent safety (Kletz, 1978). These are intensification, modification, substitution, and simplification. Kletz, in his later works, introduced the concept of the friendly plant and included several other principles such as limitation of effects, making incorrect assembly impossible, tolerance, ease of control to make a plant more user-friendly (Kletz, 1988, 1989, 1990). Later several other researchers have worked on applying inherently safer design principles (Gowland, 1996; Ohashi et al., 2012; Theis and Askonas, 2013; Turney, 2001; Windhorst, 1995), establishing inherent safety guidelines (CCPS, 2009), finding conflicts in applying IS principles (Abidin et al., 2016; Hendershot, 1995; Rusli et al., 2013), etc.

With the expanded innovation of new technology and tools, achieving inherent safety by applying these principles in the chemical or process industry has become complex and complicated (Mannan et al.,

---

* Corresponding author at: Department of Marine Technology, Norwegian University of Science & Technology, NTNU, Norway.
E-mail address: sharmin.sultana@ntnu.no (S. Sultana).

https://doi.org/10.1016/j.jhazmat.2021.126590
Received 22 March 2021; Received in revised form 2 July 2021; Accepted 4 July 2021
Available online 10 July 2021

2015). Some recent accidents are the Richmond refinery accident of 2012, the BP (British Petroleum) Deepwater Horizon accident (Bly, 2011), and the BP Texas City refinery accident (Holmstrom et al., 2006). The casualties direct the attention that lack of proper application of inherent safety measures still exists. The design did not include enough Well integrity, which caused BP Deepwater Horizon Accident (Ingersoll et al., 2012). The Richmond Refinery accident could have been avoided by taking inherent safety measures at the plant design and operation stage, such as corrosion prevention of piping in an inherently safer way, ignition prevention, and avoiding hazardous activity (Grim et al., 2015). Adequate disposal equipment and inherent safety alternatives of disposal system such as flare could have prevented the BP Texas City refinery accident (Kaszniak, 2009). Kletz, in his latest literature (Vaughen and Kletz, 2012), expressed the opinion that the introduction of complex systems and digitization in the industry has introduced a gap in safety management that should be reduced. Industrial automation has introduced new challenges in process safety management (Kletz, 2009, 2012).

Researchers have been used various inherent safety evaluation methods to check the safety prospect of a design for a long time (Marchaterre et al., 1984, 1986; Tzanos et al., 1976; Waltar et al., 1985; Zobel, 1985). Established methods can be classified into six categories: consequence-based evaluation(Shariff and Zaini, 2010; Tugnoli et al., 2007), parameter-based indexing procedures, graphical assessment, risk-based evaluation, evaluation based on both safety and environmental prospects, and approaches based on optimization. In the consequence-based indexing approach, the potential of inherent safety is evaluated based on the estimated consequences for the system's specific design. Examples of such works are Dow's index (Murphy, 1995; AICHE, 1998), Mond index (Tyler, 1985; Lewis, 1979), I2SI (Khan and Amyotte, 2004), TORCAT (Shariff and Zaini, 2010), and the works of Etowa et al. (2002), Suardin (2006), Tugnoli et al. (2007), etc. Dow's and Mond's indexes have been used most widely in the industry for inherent safety evaluation. However, they are not usable in the early stage of process design, and the results are difficult to interpret (Rahman et al., 2005). These approaches cannot consider all aspects of inherently safer design, e.g., layout, the complex interaction, and require greater rigor, accuracy, and precision in quantifying the impact of safety measures on the values of hazard indices (Khan et al., 2001). The knowledge of I2SI can give the risk analyst confidence that the process is comparatively safer, considering the inherent safety perspective. The drawback of it is that it takes enormous effort and time to calculate all the steps. I2SI is not flexible enough when applied to different process design life cycles (Abedi and Shahriari, 2005). TORCAT can support the reduction of the severity of consequence by using inherent safety principles during the preliminary design stage. Modifying design is easy since TORCAT directly links process design simulation and the consequence model (Sharmin Sultana et al., 2020).

In parameter-based indexing methods, researchers select parameters that are relevant for specific applications. The final evaluation is done based on the condition of the parameters. This type of indexing method provides a direct relationship between various parameters and the occurrence of an accident (Athar et al., 2019). Prototype inherent safety index (PIIS) (Edwards and Lawrence, 1995) is the first work of parameter-based indexing. Heikkilä (1999) presents a simple weight-based inherent safety index (ISI) consisting of two sub-indices for chemical and process. The chemical sub-index considers chemical reactivity, the heat of reaction, chemical interaction, flammability, explosiveness, toxicity, and corrosiveness. Inventory, temperature, pressure, equipment safety, and safe process structure are considered in the process subindex. In the expert system (*i*Safe) method developed by Palaniappan et al. (2002), process routes are ranked based on selected parameters, and a graphical approach is designed for analyzing reaction networks. PIIS, ISI, and *i*Safe treat chemicals as individual components, not as a mixture. They cannot reflect the contribution of different elements in the mix (Shariff et al., 2012).

Leong and Shariff (2008) developed an inherent safety index module to determine the inherent safety level. The classification approach of Heikkilä (1999) is adopted for the ranking process. Based on the obtained indices, streams with unfavorable inherent safety levels are identified. In the process route index (PRI) developed by Leong and Shariff (2009), the level of explosiveness is considered a quantitative measure of the inherent safety level for selecting the process route. The level of explosiveness depends on fluid density, pressure, combustibility, mass heating value, and flammability. PRI can prioritize the inherently safest option among several process routes producing the same products. It considers chemicals in the processing system as a mixture. Changes in temperature and pressure on upper and lower flammability limits are also considered. The process stream index (PSI) (Shariff et al., 2012) is developed to compare and prioritize the level of individual stream's inherent safety level against overall streams. The method takes the particular parameter ratio for the selected stream against the simulation's average parameter values.

The ratio of parameters includes the ratio of heating value, pressure, density, and flammability limit. Using PSI, designers can prioritize the streams based on explosion potential and quickly identify the critical streams for improvement to avoid or minimize explosion hazards. Athar et al. (2018) established a chemical reactor inherent safety index. The index consists of three sub-indices: chemical, process, and reaction. The chemical sub-score is comprised of the scores for autoignition temperature, flammability, and explosiveness. The pressure and temperature of the process are considered in the process sub score. Three parameters are considered in the reaction sub-index — reaction parameter, reaction heat, and yield. A reaction parameter score is used to estimate the tendency to get a runaway reaction in a chemical reaction. Parameter-based methods have been widely used due to the early design stage's flexibility with less information available for process route selection (Srinivasan and Nhan, 2008). However, it has some shortcomings, such as subjective scaling and weighting factors. Parameters make a sudden jump in the score value at the sub-range boundaries, and it does not consider the interaction between different factors (Gupta and Edwards, 2003). Models are not flexible enough to incorporate additional available data. Parameters established for a specific type of industry may not be relevant for another sector. The parameter index-based approach does not help the user fully understand the hazards evolved in each process route as it does not discuss the exact cause of hazards.

Another problem is the dimensionality problem (Gupta and Edwards, 2003). Adding parameters of different dimensions like temperature (C), pressure (atm), inventory (t), toxicity (ppm), and comparing the summed value may become unacceptable scientifically from the chemical engineering point of view. Making the terms dimensionless and scoring parameters based on their hazard rating is time-consuming (Gupta and Edwards, 2003). It has been possible to overcome the shortcomings of the parameter-based indexing method, such as the dimensionality problem of adding parameters of different dimensions by applying graphical techniques as done in Gupta and Edwards' work. The graphic technique uses root cause analysis of accidents and compares selected parameters for inherent safety assessment. Gupta and Edwards (2003) work on a graphical approach for root cause analysis and comparison of selected parameters for inherent safety assessment. Ahmad et al. (2013) presented a visual procedure in designing an inherently safer design for both grass-root and retrofit cases in the petrochemical industry without including subjective scaling and a sudden jump in the score value. Graphical procedure visualizes the effect of parameters such as temperature, pressure, heat of reaction, process inventory, flammability, explosiveness, toxicity, and reactivity in the system using graphical way. The flexibility in parameter selection and subjective scaling has been removed in this work. In Tugnoli et al. (2012), accident scenarios are developed for the system. Relevant parameters are identified, which gives flexibility in parameter selection and establishes the logical relationship of parameters with accidents.

Index based on safety and environmental prospects consider parameters that may impact health, safety, and environment (Hendershot, 1997). The inherent chemical process route index, proposed by Warnasooriya and Gunasekera (2017), considers potential toxicological impacts on the environment, the occupational health potential, and chemical process safety impact. The toxicological impact is selected as an environmental hazard. Chemical exposure due to fugitive emission is chosen as an occupational health hazard. Seven parameters are selected as chemical process safety impact, and subjective scaling is used for inherent safety evaluation. Seven parameters are inventory, chemical stability, temperature, pressure, flammability, and explosiveness. Inherent Benignness Indicator (Srinivasan and Nhan, 2008) is based on a multivariate approach using principal component analyses to compare process routes. Fifteen factors are considered related to health, safety, and environmental aspects. Various routes from health, safety, and environmental performances are also evaluated in Mimi Haryani and Wijayanuddin (2009). They considered flammability, explosiveness, toxic exposure, and reactivity for safety scoring. Material state, volitivity, and chronic toxicity are considered for the health index. For the environmental index, they regarded atmospheric toxicity, aquatic toxicity, and terrestrial toxicity.

Risk-based assessment techniques evaluate the risk inherent to a process owing to the chemical it uses and the process conditions (Eljack et al., 2019; Rathnayaka et al., 2014; Shariff and Leong, 2009a; Shariff and Zaini, 2013). However, the detailed procedures in finding probabilistic data and consequence determination take time and resources. The use of risk control measures, i.e., in RISI (Rathnayaka et al., 2014), may divert attention to more additional measures than inherent safety measures. The multi-objective optimization approach is adopted to overcome the conflicting objectives, e.g., increasing safety considering the cost (Eini et al., 2015; Lee et al., 2019; Suardin, 2006; Sugiyama et al., 2008; Vázquez et al., 2018).

The present paper establishes an inherent safety index for inherent safety evaluation at the chemical process's route and concept selection stage. To find a logical relationship between the selected parameters and predicted accidents, a non-harmful, inherently safer system is imagined. Relevant characteristics of such a non-harmful system are sought. Possible parameters are set which may affect the system to deviate from the non-harmful situation. This approach gives flexibility in the model to apply in a different kind of industry. Other types of hazards may become dominant for different applications. Searching characteristics of a non-harmful, inherently safer system will give flexibility in searching relevant parameters in IS evaluation model. Various scores are assigned based on the deviation of multiple parameters in the actual case from the non-harmful situation. Finding a deviation ratio removes the problem of dimensionality in determining the inherent safety index. Various parameters are also considered in the model, and penalty factors are assigned for various interactions. This consideration gives the logical reason that most of the accident occurs due to dangerous interaction of multiple parameters instead from the effect of a single parameter.

The present research only considers hazards related to the hazardous chemicals and processes used in the chemical industry, and the indices are proposed based on the identified hazards. Other types of hazards, e.g., geological or biological, are not considered here but can be included when considering another kind of plant. Section 2 of the paper discusses earlier work on various inherent safety index methods. Section 3 describes the detailed procedure of the proposed method for determining the inherent system safety index. The application of the index in a case study is described in Section 4. The case study evaluates the inherent safety of various routes for methyl methacrylate production and determines the best route. Section 5 presents the results obtained by applying the present method and compares them with previous works. This section also discusses the benefits and drawbacks of the present method. Section 6 presents a conclusion and describes possible future outcomes for extending the method.

2. Development of ISSI

2.1. Inherent risk and hazard factors

The establishment of the ISSI is based on the concept of inherent risk and hazard factors. The inherent safety characteristics are determined based on the system's possible hazards and risk factors. Hazard is the existence of factors that has the potential to cause harm to people, environment, or asset. Hazard factors are the properties, conditions, or causes that may cause harm. Hazard factors can be of two types: triggering hazard factors and impacting hazard factors. Triggering hazard factors are those factors which can directly contribute to a hazardous event. The presence of motion implies kinetic energy that can cause a hazardous event. Motion is, therefore, a triggering inherent hazard factor. Impacting hazard factors do not contribute to creating a hazardous event directly but affect the severity or probability of a hazardous event indirectly. The object's geometry affects the amount of kinetic energy and affects the related hazardous event's severity.

An inherent risk factor is the quantitative expression of the two types of hazard factors, triggering inherent hazards factors and impacting inherent hazard factors. Triggering inherent risk factors contribute to creating a hazardous event directly. In contrast, impacting inherent risk factors do not contribute to creating a hazardous event directly but may affect triggering inherent hazard factors or risk level in the system, thus changing the probability or severity of the hazardous event. The conceptualization of inherent risk factors assumes that the risk level (in terms of a quantitative measure) can be controlled by changing/ managing/ controlling the inherent risk factors.(Fig. 1).

2.2. Inherently safer system and real system

Fig. 2 shows an imaginary non-harmful, inherently safer system and a real system. An inherently safer system consists of four criteria — safe inflow, safe production, invulnerable, and simple. Design engineers always try to achieve these criteria as much as they can. Details of these four criteria are described in the next section.

2.3. Characteristics of an inherently safer system

Various types of risk factors evolved from various triggering and impacting hazard factors in the industry. Risk factors can be harmful physical or chemical properties of the material, for example, flammability, chemical instability, harmful reaction chemistry, harmful emission, or complexity. Complexity-related risk factors can be congestion, incomprehensibility. Moreover, the interaction of these various types of risk factors creates additional risks. The system should have such characteristics built-in to avoid all these risk factors or reduce these as little as possible to make an inherently safer system. The present method tries to identify the characteristics of a chemical process to avoid potential risk factors in the chemical process system. Various risk factors are identified from various earlier literature (Barbour et al., 1998; Brock, 1986; Greenberg et al., 1991; Keller and Associates, 2013; OSHA, 1983). The Present method tries to identify required inherent safety characteristics from system engineering concepts. After analyzing the inherent risk factors of a chemical process system, the authors determined that a chemical process system should have four characteristics to make an inherently safer system. The characteristics are safe inflow to the system, safe production in the system, less vulnerability, simplicity. The criteria are described in the following and summarized in Table 1.

2.3.1. Safe inflow to the system

To ensure safe material inflow, we need to select such raw material that is less hazardous. Inflow does not mean only the raw material of a reaction but refers to any material used for the whole system. So, inflow to the reactor system or any mechanical production system should be considered. If a process uses less hazardous material storage, the

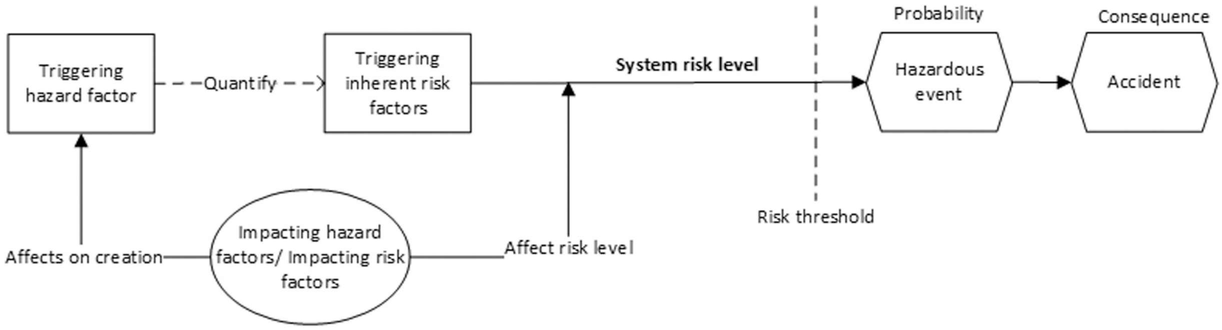


Fig. 1. Relationship between inherent hazard factors, risk factors, and hazardous event.

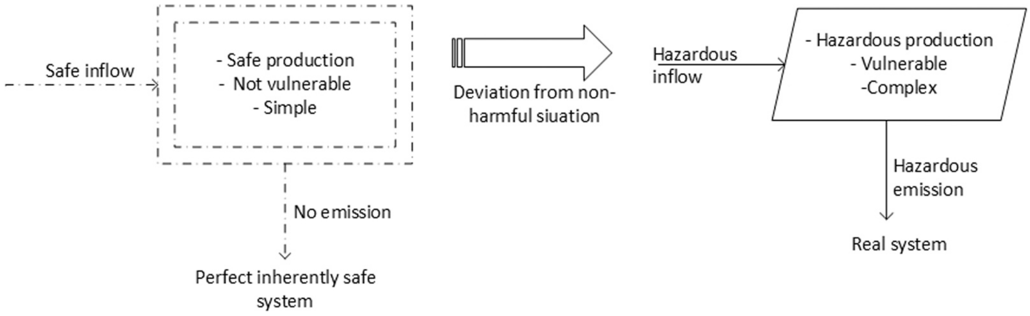


Fig. 2. Deviation from a non-harmful inherently safer system to the actual system.

Table 1
Overview characteristics, condition, and parameters of an inherently safer system.

Characteristics of the inherently safer system	Conditions related to the inherent safety	Inherent safety parameters
1. Safe inflow to the system	Safer material inflow	Chemical, physical, and external properties of the material (Flammability, chemical instability, corrosivity, viscosity, phase, quantity, or mass)
	Less energy consumption by the process and equipment	Energy consumptions by the process Energy consumption of the equipment
	Higher efficiency of the processes or equipment	Efficiency of equipment
2. Safe production of the system	Safer intermediate product or by-product	Chemical, physical, and external properties of the by-product and intermediate products
	Safer energy production	Heat of reaction
	Less production of waste material	Amount of waste material
	Less production of emission	Amount of greenhouse gas emission Amount in the form of CO_2, CO, steam, SO_2, etc.
3. Simple	Simpler processes and individual components and procedures	Process complexity parameters
4. Non-vulnerable	Safer process	Presence of unique hazardous process
	Compatible	Hazardous interaction between various parameters
	Safer process condition	Extreme hazardous condition

probability of leak or emission of hazardous material or the severity of the unwanted incident's consequence will be lower. Material's physical and chemical properties determine whether it will be hazardous or not. Physical properties are quantity, mass viscosity, toxicity, corrosivity. Flammability, instability, explosiveness, etc., are chemical properties (Brar, 2011). High energy consumption will create demand for a high level of electricity or other forms of energy. Since control of high energy will be difficult and hazardous (Klugmann-Radziemska, 2014), low energy consumption is an inherent safety characteristic. Energy requirements by the process and by individual pieces of equipment should be considered. Equipment with high efficiency will demand less energy, fuel, and material consumption. So if the equipment uses any hazardous material, high-efficiency equipment will consume less hazardous material in the long run (Clinton, 1994).

2.3.2. *Safe production in the system*

To ensure safe production in the system, we need to provide safer intermediate products and by-products and safer energy production. We need to select a reaction that does not produce any hazardous material or produces a meager amount of hazardous material as intermediate material or by-product. A machine that is crushing solids may create lots of dust material which is not desirable. Whether a product or intermediate material will be hazardous or not is determined by its properties, as have mentioned in Section 2.3.1. Dangerous energy evolution is the most common hazard in any industry. A reaction with a high heat of reaction needs extra control equipment to prevent other equipment and human from damage due to high heat (Crowl and Elwell, 2004). We have to select a process and reaction that produces less energy and has lower heat of reaction. If a process creates a higher amount of waste, it needs more control equipment to disburse the trash (Cheremisinoff and Cheremisinoff, 1995). Similarly, a process producing a higher amount of emission will need many redundant processes or equipment, which will increase the process risk (Xue et al., 2017). The amount of waste production and amount of emission is two inherent safety parameters that need to be considered in design selection.

2.3.3. Simple

This characteristic is applicable both at the components level and facility level. The characteristics include avoiding complexities of product, equipment, or information loading, simplifying the design by reducing operation steps, connections, congestion, and user-friendly processes. Some issues are thought to increase the complexity of a chemical process system. Examples of such matters are number of inputs and output streams, mixing steps, stages, critical changes in a route, changes of condition, state of process materials in the stream, the criticality of operations, number of equipment, type of equipment, number of unstable intermediates in a route (Song et al., 2018).

2.3.4. Less vulnerable

Vulnerability in a process system is created by the presence of a particular chemical process or extremeness of any hazardous properties of material or process. Vulnerability can also be created by the incompatibility of various process or system conditions evolved from the system's activity. Such incompatibility should be adequately identified. This inclusion is an essential condition as it is seen that despite having safer inflow in the system or relatively safer production in the system, these incompatibilities or conditions may increase the risk of a system to a large extent. There can evolve many such incompatibilities in a chemical process. The present research tries to identify some critical conditions possible to consider at the conceptual design stage. Conditions are as below:

- Presence of any unique hazardous process or chemical interaction; such as oxidation, hydrogenation, alkylation, etc. (Abedi and Shahriari, 2005)
- Incompatibility includes the presence of two hazardous conditions at the same time, such as highly toxic material at high pressure, highly toxic material with high vaporization, Highly volatile material at high pressure and temperature, etc. (Pohanish, 2017)
- The extremeness of any hazardous properties of the material or process, e.g., presence of highly flammable or toxic material in the system (Abedi and Shahriari, 2005)

2.4. Determination of ISSI

The ISSI comprises four subindexes: the inflow safety index, production safety index, complexity sub-index, and vulnerability sub-index.

$$ISSI = IFSSI + PSSI + CSI + VSI \tag{i}$$

Where IFSSI is the inflow safety subindex, PSSI is the production safety subindex, CSI is the complexity subindex, VSI is the vulnerability subindex.(i).

2.4.1. Inflow safety subindex (IFSSI)

For a chemical process, inflow safety refers to the safety of material that the system is taking per day or per hour. Along with the flow rate of material per hour or per day, storage inventory is also important. In the present method, inflow risk determines a property's deviation from a non-harmful situation. The inflow safety subindex is given as,

$$IFSSI = Dev_{IM} + Dev_{EC_{pr}} + Dev_{EQ} \tag{ii}$$

Where, Dev_{IM} is the deviation due to materials used in the inlet. $Dev_{EC_{pr}}$ is the deviation due to the energy consumption of the process. Dev_{EQ} is the deviation due to the energy consumption of the equipment. In the present paper, five material properties are considered to be most important for a chemical process. They are flammability, chemical instability, corrosiveness, toxicity, and quantity. There can be many other hazardous material properties. However, these properties can give quite a good indication of material safety (NFPA, 2017). Toxicity indicates a health hazard. Flammability and instability refer to chemical hazard which may become dangerous at high temperature and pressure. Corrosion is chosen as many minor- and large-scale accidents arise due to industrial corrosion in a chemical process.

$$Dev_{IM} = \frac{\sum_{i=1}^{m}\left(\left(Dev_{fl_i} + Dev_{CI_i} + Dev_{cor_i} + Dev_{tox_i}\right)/4\right)Dev_{Q_i}}{m} \tag{iii}$$

Here, Dev_{fl_i} is the deviation due to flammability of material' i' in a process, Dev_{CI_i} is deviation due to chemical instability of material' i' in a process, Dev_{cor_i} is deviation due to corrosiveness of material' i' a process, $Dev(TX)_i$ is deviation due to toxicity of material' i' in a process, Dev_{Q_i} is deviation due to the quantity of the material' i'. m is the total number of materials in the inlet. Values of properties are determined, considering each component as individual components. The following equation should be used to evaluate the property of a mixture:

$$M = \sum y_i M_i \tag{v}$$

Where M_i is the property of individual component i, y_i is the mole percentage of a component in a stream (Perrot, 1998). Dev_{EQ} is determined by the following equation:

$$Dev_{EQ} = \frac{Dev_{EC_{eq}}.Dev_{eff_{eq}}}{N} \tag{iv}$$

EC_{eq} is energy consumption by individual equipment, eff_{eq} is the efficiency of individual equipment.

2.4.1.1. Determination of energy consumption of process.

The following energy balance equation can be used to determine the energy requirement of a steady-state process:

$$\left\{\begin{matrix}\text{Energy input}\\ \text{with}\\ \text{input streams}\end{matrix}\right\} - \left\{\begin{matrix}\text{Energy output}\\ \text{with}\\ \text{output streams}\end{matrix}\right\} + \left\{\begin{matrix}\text{Energy}\\ \text{generation}\\ \text{within streams}\end{matrix}\right\} \pm \left\{\begin{matrix}\text{Energy}\\ \text{leaving or}\\ \text{added to system}\end{matrix}\right\} = 0 \tag{vi}$$

Mathematically,

$$\left(-\Delta H_{T_r}\right) + \sum_i n_i\left(H_T - H_{T_r}\right)_i = \sum_j n_j\left(H_T - H_{T_r}\right)_j + Q_{loss} + Q_{rec} \tag{vii}$$

Where n_i and n_j denote the number of reactants i and products j, respectively. $(-\Delta H_{T_r})$ represents the total reaction enthalpy occurring in the system at the reference temperature (T_r) (Sohn and Olivas-Martinez, 2014). For an exothermic reaction, this term is positive (i.e., energy input to the system). For overall endothermic reactions, it is negative. $(H_T - H_{T_r})_i$ is the addition of energy to the system in the form of the sensible heat of the reactants. $(H_T - H_{T_r})_j$ represents the energy removed from the system as sensible heat in the products. Q_{loss} is heat removed from the system to surroundings. Q_{rec} is the recoverable heat from the process. The energy requirement is found from the following equation (Sohn and Olivas-Martinez, 2014):

$$\text{Energy requirement} = \left(-\Delta H_{T_r}\right) + \sum_j n_j\left(H_T - H_{T_r}\right)_j + Q_{loss} \tag{viii}$$

A chemical reaction's enthalpy change that occurs at constant pressure is called the heat of reaction. Standard enthalpy of reaction is calculated using standard enthalpy of formation of both reactants and products by using the below formula (Petrucci et al., 2010):

$$\left(-\Delta H_{T_r}\right) = \sum \vartheta_p \Delta H_f(\text{products}) - \sum \vartheta_r \Delta H_f(\text{reactants}) \tag{ix}$$

Where, ϑ_p is the stoichiometric coefficient of the product from the balanced reaction, ϑ_r is the stoichiometric coefficient of the reactants from the balanced reaction, ΔH_f is the enthalpy of formation for the reactants or products in kJ/mol at the reaction temperature.

For a component which is solid at 25 °C, if the reaction temperature is above its boiling point, change of enthalpy is calculated by the following equation (Perrot, 1998):

$$\Delta \mathrm{H_f} = \int_{298}^{\mathrm{T_m}} \mathrm{C_p dT} + \Delta \mathrm{H_{fus}} + \int_{\mathrm{T_m}}^{\mathrm{T_b}} \mathrm{C_p dT} + \Delta \mathrm{H_{vap}} + \int_{\mathrm{T_b}}^{\mathrm{T_r}} \mathrm{C_p dT} \tag{x}$$

$$C_p(T) = A + BT + CT^2 + DT^3 + ET^4 \tag{xi}$$

Where T_m is the melting point of a material, °C, T_b is the boiling point of the material, °C, T_r is reaction temperature, °C, ΔH_{fus} is the heat of fusion of material in kJ/mol, ΔH_{vap} is the heat of vaporization of material in kJ/mol, C_p is heat capacity in j/mol.K, a function of temperature, *A, B, C, D, E* are experimentally determined constants of a particular material and in a specific temperature range.

2.4.2. *Production safety subindex (PSSI)*

The following equation determines the production safety sub-index,

$$PSSI = \sum_{j=1}^{n} Dev_{PM_j} + Dev_{HR_j} + Dev_{w_j} + Dev_{em_j} \tag{xii}$$

$$Dev_{PM} = \frac{\sum_{i=1}^{m} \left(\left(Dev_{fl_i} + Dev_{CI_i} + Dev_{cor_i} + Dev_{tox_i} \right) / 4 \right) Dev_{Q_i}}{m} \tag{xiii}$$

Here, Dev_{PM} is a deviation due to material properties used in the process j. Dev_{HR_j} is deviation due to heat of reaction evolved in process j, Dev_{em_j} is deviation due to emission in the form of steam, vapor in process j, Dev_{w_j} is deviation due to the amount of waste material in process j. Deviations of material properties of chemicals are determined due to their four properties and inventory, as discussed in the earlier section. The flow rate is considered here to find the deviation of inventory. Feed and product rate for route steps are calculated using stochiometric factors, molecular weights of the chemicals present, and reaction step yields. The feed flow rate is calculated using the formula: Mass of reactant = Mass of desired product out /yield of reaction (Lawrence, 1996).

$$F_A = \frac{F_P * \vartheta_A * MW_A}{\vartheta_p * yr} \tag{xiv}$$

Here, F_A *is flowrate of a feed material A.* F_P *is the flowrate of product P.* ϑ_A *is stoichiometric coefficient of material A, found from the material balance equation.* ϑ_p *stoichiometric coefficient of product P.* MW_A *is the molecular weight of feed A.*

2.4.2.1. *Determination of deviation of waste material.*

Previously there have been many kinds of research on the ranking of industries by their effluent in general (Ahmad et al., 2020; Pennington and Bare, 2001) or as a part of the inherently safer design (French et al., 1995, 1996; Mansfield et al., 1997). In the present method, to simplify the calculation, effluent ranking is done from the following equation:

$$Dev_{w_j} = \sum_{i=1}^{n} q_i DS_i \tag{xv}$$

Where, q_i is the quantity of chemical i in the effluent stream, n = total number of chemicals in the effluent stream, DS_i is the score of chemical i, in effluent stream, DSi of a chemical is determined based on its waste code which considers the following four properties: ignitable, corrosive, reactive, toxic (Baker et al., 1992; Rosenfeld and Feng, 2011). Deviation due to these four properties is determined using relevant tables and is averaged.

2.4.2.2. *Determination of vapor emission.*

The amount of flammable vapor that will be produced immediately from a liquid at a temperature above its atmospheric boiling point can be calculated by the following equation (King, 2016):

$$Q_v = \frac{2 Q_L C_P (T_1 - T_2)}{H_v} \tag{xvi}$$

Where, Q_v = mass of flammable vapour released (kg), Q_L = mass of liquid (kg), C_p = specific heat at $(T_1 + T_2)/2$ of liquid (kJ/kg.°C), T_1 = liquid temperature (°C), T_2 = atmospheric boiling point of liquid (°C), H_v = heat of vaporisation of liquid at T_2 (kJ/kg).

2.4.3. *Complexity subindex (CSI)*

One of the critical principles of inherent safety design is process simplification. If process configuration becomes complex, operators' and maintenance crews' control and prevention of errors also become more complex. The complexity of a process is ranked by selecting parameters that affect the control requirement of the process. This paper adopts the method proposed by Song et al. (2018) with several modifications to rank complexity. In the present method, the modified complexity index considers equipment complexity, the number of stages, the difficulty of processes, and the parameters specified by Song et al. (2018).

Parameters for process complexity considered fourteen parameters. Parameters are the total number of input streams, total number of the output stream, number of changes of condition, number of mixing steps, the total number of changes in the state of process materials, the total number of Flashing liquid, the total number of flashing inventory at ambient, number of time-critical operations, number of sequence-critical operation, number of critical changes of operations, equipment ranking, number of recycling of the process, number of stages, number of unstable intermediates. Number of the input stream, output stream, number of changes, mixing steps, changes in the state- this information can be obtained from the process flow diagram and the process description of each route. For equipment ranking following procedure is followed.

2.4.3.1. *Ranking of equipment.*

This classification of equipment is done based on their hazard rating without considering their failure rate. Furnaces and flares are considered most hazardous as they are the most common ignition sources for any leaks (Instone, 1989; Planas-Cuchi et al., 1997) and more hazardous than reactors (AIChE and Dow, 1987). Compressors, high-pressure storage tanks are considered very unsafe as they contain moving parts (Marshall, 1987), they are subject to vibration, can release flammable gas in a case of failure (Heikkilä, 1999). Process drums, towers, heat exchangers, pumps containing flammable liquid are lower scores as they give lower loss statistics (Heikkilä, 1999; Instone, 1989; Mahoney, 1990). The safest equipment is equipment handling nontoxic and non-flammable material. Reactors pump above autoignition are more hazardous than process drum. A high-hazard reactor is more hazardous than a typical reactor (Heikkilä, 1999). (Table 2).

Table 2
Score for various types of equipment.

Equipment items	Hazard rating	Score
Equipment handling non-flammable and nontoxic material	Safest	0
Heat exchangers, pumps, towers, drums, atmospheric storage tank	Less hazardous	3
Air coolers, reactors, high hazard pumps	Moderately hazardous	5
Cooling tower, compressors, high hazard reactors, high-pressure tank, refrigerated storage tanks	Highly hazardous	7
Boilers, Furnaces, fired heaters, flares	Most hazardous (Instone, 1989)	10

2.4.4. Vulnerability subindex (VSI)

Chemical process systems may become vulnerable due to particular processes, the interaction of parameters, or extreme values of any specific parameters (Lawrence, 1996). Because in addition to stepwise deviation in risk level, extremism or interaction may vastly increase the risk level. Highly flammable or highly toxic material needs extra precaution and regular safety structure (Kletz, 1995; Lawrence, 1996). Yield is not a sensitive factor in system risk level. However, lower yield may lead to large recycles and large separation sections. Additional scores are assigned to consider these risk level changes, which are termed penalties. Vulnerability sub-index, $VSI = \sum penalties$. To assign penalty, a vulnerability scale is created (shown in Fig. 3), which is based on additional risk increment due to presence vulnerability factors. Risk increment can be increase in the probability of accident or increase in the severity of consequence if mishap happens.

Penalty and interpretation:

- 5: Very high-risk increment - the possibility of catastrophe if not controlled properly
- 4: High-risk increment - the potential of significant consequence if cannot be controlled
- 3: Elevated risk - need special attention to avoid mishap
- 2: Moderate risk increment - can be controlled with particular attention
- 1: Low-risk increment - can be controlled with ease

Following types of penalties are identified due to:

I. Special processes, which are especially vulnerable, need special control features, such as oxygen, hydrogenation, vice versa

Various penalty factors are assigned for unique processes as they need special control features. Examples of special operations are hydro-generation, hydrolysis, isomerization, and alkylations. They require special attention to handle the process (Heinemann, 1979). Processes that have a high toxic effect that is very harmful to the living creatures, such as halogenation (Safe, 1982), are given a score of 10. Moderately exothermic processes, such as alkylation, esterification (King, 2016), are assigned a penalty of 5. Mildly exothermic processes, e.g., hydrogenation, isomerization (King, 2016), are given a penalty of three.

II. Chemical interaction

Here, chemical interaction considers the unwanted reactions of process substances or the formation of intermediate products in the plant. They are also considered to introduce additional risk in the plant-based on reaction or intermediate products. Penalties for chemical interaction are assigned based on the EPA matrix (Hatayama, 1980) and hazard classification of chemical interaction (Heikkilä, 1999). The formation of highly toxic or flammable gas is given the highest penalty as they may cause the most hazardous accident, fire, and explosion. Formation of harmless, non-flammable gas is less harmful than other categories, hence given a penalty 1.

III. Interaction between various parameters that increases the risk level of a system

Penalty factors for interaction are determined based on possible interactions among various factors in the system. The risk level cannot be determined by simply summing up the risk score of parameters individually. If this was the case, we were lucky enough not to have a massive accident. In reality, the interaction between factors plays a significant role in the determination of risk level. Due to the interaction of various parameters, aggregated risk of a system may become huge, and accidents occur with high severity in that case (Lawrence, 1996). For example, among chemical properties, flammability, toxicity, and explosion are not internally correlated. Whereas for phase change, the value of these properties changes. The state of material plays a vital role in increasing risk due to these properties. In the presence of these properties, external properties such as quantity play significant value in the system. For a reaction, energy risk is controlled by the heat of the reaction. For lower yield and low reaction rate, residence time will be higher, and the system will be more exposed to high heat. Process parameters follow a similar trend in risk increment. If pressure increases, temperature also increases while the flow rate decreases. So, all the risk scores increase simultaneously. If the heat of the reaction increases, the temperature will increase in the system, thereby increasing the risk.

Any material which has hazardous intrinsic properties need special equipment and structure. Equipment or facility becomes unsafe if it handles hazardous material instead of a relatively safer material like water. A combination of chemical properties of material and energy sources is very hazardous. A small amount of energy source may create a severe accident in the presence of high chemical properties of the material's material and external physical properties. Flammability, chemical instability; these issues are dependent on temperature and pressure. If a system runs at a temperature in the material's flammability limit, care should reduce the interaction risk. Different scale of penalties is assigned based on assumed risk contribution in the system. Various types of interaction can be toxic material at high pressure with the possibility of flash off, high temperature with the possibility of flash off, and vice versa. Penalties are assigned based on the qualitative assessment of hazards from accident databases and case studies (Lawrence, 1996; Macdonald, 2004; Mannan and Lees, 2012; Stephanopoulos, 1984). If process temp is above a material's autoignition temp, it is most hazardous; hence the penalty score is 5. Process temp above flash point is less dangerous than earlier, therefore scored as 3.

IV. The extreme value of any specific parameter that increases the risk level of a system to a large extent

Extreme conditions of parameters include high flammability, high toxicity, high chemical instability, and vice versa. The extreme value of these parameters can increase the risk level to a vast amount. Penalty factors are assigned for extreme values of these parameters to consider the additional increase of risk level. Penalty score one per material is given when the deviation of the parameter is above 6. Operating temperature going above autoignition temp or boiling temp or flash point temp. Three types of penalty factors are assigned based on these three conditions. For lower yield, residence time will be higher; penalties are set for lower yields.

2.5. Determination of deviation from the imaginary non-harmful situation

The inherently safer design potential is determined by estimating the system's deviation of various parameters from the imaginary non-

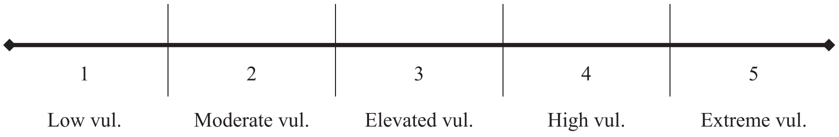


Fig. 3. Penalty score for vulnerability.

harmful situation. The deviation of each parameter is selected from predicted tables of deviations. Different deviational scores are given for multiple conditions. A minimum deviation is assigned as zero, and the highest deviation is set as 10. Various deviation scores are assigned according to their possibility of harm. For example, when giving a deviation score for the material property, flammability, zero is set for non-flammable material. Ten is assigned for highly flammable materials with a flashpoint below 0 °C. In the heat of reaction, a score of one is given for a neutrally thermal reaction, and a score of ten is assigned for a highly exothermic reaction, of which heat of reaction is more than 3000 kJ/kg. Various types of process equipment are also scored. Equipment handling non-flammable material is scored as 1, while fired heaters and flares are 10 (Instone, 1989; Planas-Cuchi et al., 1997). The deviation table for flammability is presented in Table 3. Deviational tables for other properties are shown in the Supporting Material.

2.5.1. *Flammability*

Flammability is how easily a material or a compound will burn or ignite, resulting in fire and combustion (ChemSafetyPro, 2021). The flammability of various materials is defined here by their flash point and boiling point. The flashpoint and boiling point of the mixture is calculated in the process simulator. The deviation score is assigned from the insight of GHS (global harmonization system) classification criteria (UN, 2003) and NFPA rating of hazardous materials (NFPA, 2017).

Other assumptions are as following:

- Materials, which has a flashpoint below 0 °C rapidly vaporize at atmospheric pressure and average temperatures, readily disperse in the air, and burn readily, are very flammable and most hazardous
- Liquid and solid, which has a flashpoint below 23 °C and initial boiling point below 35 °C, can easily ignite under normal temperature conditions, easily flammable, and secondly hazardous
- Materials, which has flashpoint which has below 23 °C and an initial boiling point above 35 °C, can ignite under normal temperature conditions, are less hazardous than the earlier category
- Materials which has a flash point above 23 °C and below 60 °C need to be lightly heated or to relatively high ambient temperatures to ignite them and are less flammable
- Materials which has a flash point above 60 °C and below 90 °C must be preheated before they ignite, are termed combustible
- Material with a flash point above 93 degrees Celsius is not be regarded as a flammable liquid or a hazardous chemical according to GHS classification criteria; hence here, the deviation is very close to the safest material
- Materials that do not burn are the safest in terms of flammability, such as water

2.6. *Execution of procedures*

Fig. 4 shows the work steps to determine the ISSI. It starts with the identification of the inherent safety characteristics of a relevant system.

Table 3
Various types of flammable material and related deviational score.

Flammability	Deviation score
Non-flammable	0
Less combustible (Flashpoint above 93 °C)	2
Combustible (Flashpoint at or above 60 °C, but below 93 °C)	3
Less flammable (flashpoint at or above 38 °C but below 60 °C)	5
Moderately flammable (flashpoint at or above 23 °C but below 38 °C)	6
Flammable (flash point below 23 °C and the boiling point at or above 38 °C)	7
Easily flammable (flash point below 23 °C and boiling point below 38 °C)	8
Very flammable (flash point below 0 °C)	10

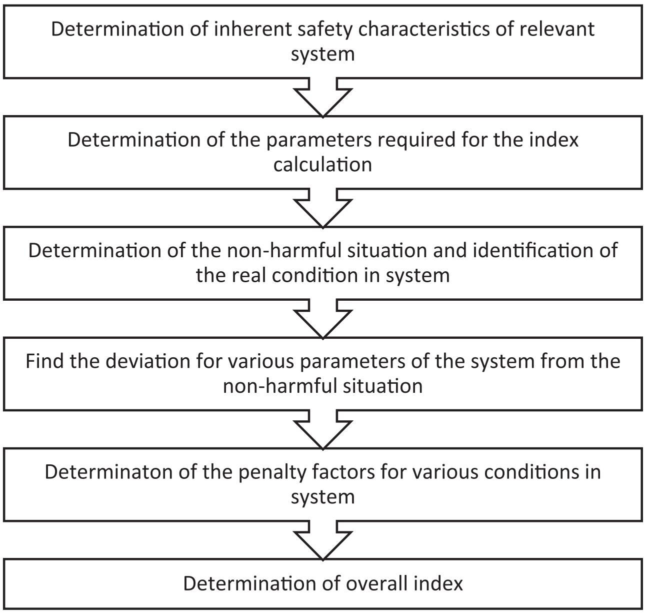


Fig. 4. Work steps to determine the ISSI.

At first, the inherent safety characteristic of a related system is identified for a non-harmful situation. Relevant parameters related to each characteristic are identified. The next task is to determine the values of each parameter in a non-harmful situation and an actual situation. The deviation of each parameter in an existing system is determined by finding its deviation from a non-harmful state. In addition to the deviation, various complexity factors are identified and scored. Various penalty factors are assigned after the evaluation of various interactions of parameters in the system. The overall index is calculated by using the equations earlier.

Fig. 5 shows the procedure of determining ISSI when comparing various design alternatives. Various alternatives are thought of at the beginning of the analysis. One needs to find inflow risk, production risk, complexity, and vulnerability index for each design alternative considering all process streams. Chemical properties and physical properties of material and reaction are collected from the chemical database. Energy consumption of equipment can be collected from the vendors. The streams involved in an alternative are distinguished to avoid repetitions of calculation. For each stream, material properties in the inlet stream and energy consumption by individual equipment are evaluated. Deviation due to each property is determined using deviation tables presented in Supplementary Material, and the inflow safety index is calculated using Eq. (ii). Properties of each material in the outlet stream of each equipment, emission, and amount of waste are evaluated. Production safety subindex is calculated using equation (xii). In the next step, various complexity factors that increase the system's complexity are sought, and the complexity subindex is calculated using factors described in Section 3.4.3. The vulnerability subindex is calculated from penalties due to various interactions present in the system. It is checked whether all the stream in a route is evaluated. When ISSI is calculated for an alternative, the analyst goes for another alternative and repeats the same process. Evaluation of all the alternatives indicates the completeness of the analysis.

3. Case study

3.1. *Development of alternative routes*

The present case study assesses various routes of the production process of Methyl Methacrylate (MMA). The assessed routes are the production of MMA by using Acetone Cyanohydrin (ACH); Ethylene via

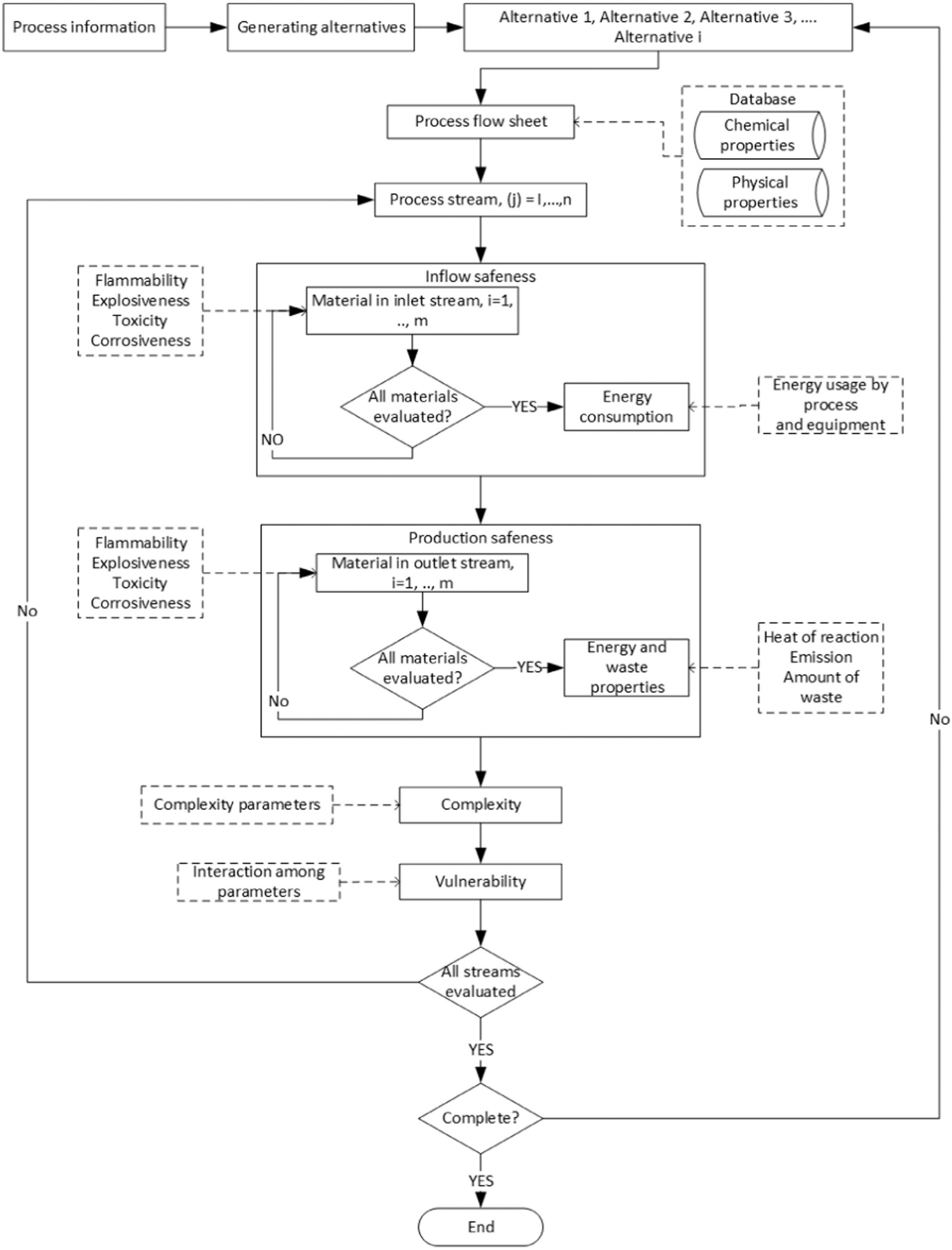


Fig. 5. Proposed framework for evaluating ISSI.

Propionaldehyde (C2/PA); Ethylene via Methyl-Propionate (C2/MP); Propylene (C3); Tertiary butyl alcohol (TBA), and Isobutene (iC4). Due to page limitation, ISSI calculation for only the ACH production route is shown here. An evaluation of ISSI for other routes is presented in the Supplementary Material.

3.2. *Calculation of the indices for the ACH route*

The acetone cyanohydrin process is the conventional process for MMA manufacture. Process flow of the route along with involved equipment and materials are identified in the process. The state of each parameter, reaction temperature, pressure, process changes, and any recycling is also investigated. Hydrogen cyanide is reacted with acetone to give acetone cyanohydrin (ACH). ACH is treated with sulfuric acid and heated to provide Methyl Acrylamide. The final step is the reaction of methyl acrylamide with methanol to produce MMA. The sulfuric acid is recovered from the Ammonium Bi-Sulphate by-product. A simplified process flow diagram is illustrated in Fig. 6.

3.3. *Calculation of inflow safety subindex*

Material flow in the storage and reactors is only considered to calculate the inflow safety subindex to simplify the calculation. First, it is identified which materials need to be stored. Materials that are supplied continuously pose some risk in their pipeline transportation. Pipeline transportation risk is not considered in the present case. Methane, ammonia, oxygen, acetone, and H2SO4 are stored temporarily for the ACH route. The chemical and physical properties of each involved material are collected from the relevant database. These properties often vary with the change of pressure and temperature. Due to the simplicity of the calculation, constant values of material are assumed irrespective of pressure and temperature change. The deviation of each parameter from the non-harmful condition is determined from the predefined tables shown in the Supporting Material. Inflow safety subindex is calculated using equation (ii). Supplementary Material contains detailed calculation processes. Deviation of material properties of these chemicals is determined due to their material properties and inventory. Inventory is calculated by using the following equation:

$$\text{Storage inventory } (kg) = 14 \text{ days} * \text{daily flow rate } (kg/day) \qquad \text{(xvii)}$$

It is assumed that chemicals are stored for 14 days. Energy consumption by individual equipment, the efficiency of equipment, energy consumption by the process, calculation of waste materials is not considered in the case study due to lack of sufficient data and information.

3.4. *Calculation of production safety subindex*

In the present case study, the material production of the reactor is considered only to calculate the production safety subindex. The liquid will vaporize both from the reactor and storage. Deviation for vapor formation and heat production is determined. The heat of reaction is calculated using equation (*ix*). The vapor release rate is calculated using Eq. (xvi). While calculating feed and product flow rate for each step, yearly output from the plant is assumed as 50,000 t/yr, and the average operating hour of the plant is considered as 7500 h/yr. The actual recycling stream and recycle rate are not known. For simplicity, the feed and recycle stream is assumed as the feed stream. The flowrate of feed is calculated using equation (*xiv*).

3.5. *Calculation of complexity and vulnerability subindex*

Complexity parameters are found out from the PFD diagram (Fig. 6). ACH route has ten input streams, seven output streams, and three mixing steps. Seven reactors, two separators, two purifiers, and five storage tanks are used in the route. Overall equipment ranking is found out by considering the ranking of each equipment and number of equipment. Other complexity parameters are also found out from PFD and the information database. To calculate the vulnerability index after investing presence of special processes like oxidation or hydrogenation are investigated. Interactions of various parameters are sought for reactor and storage. Four interactions are found for the reactor. They are toxic material at high pressure, high toxicity with the possible flash off, high pressure with the possible flash off, and high temperature. One

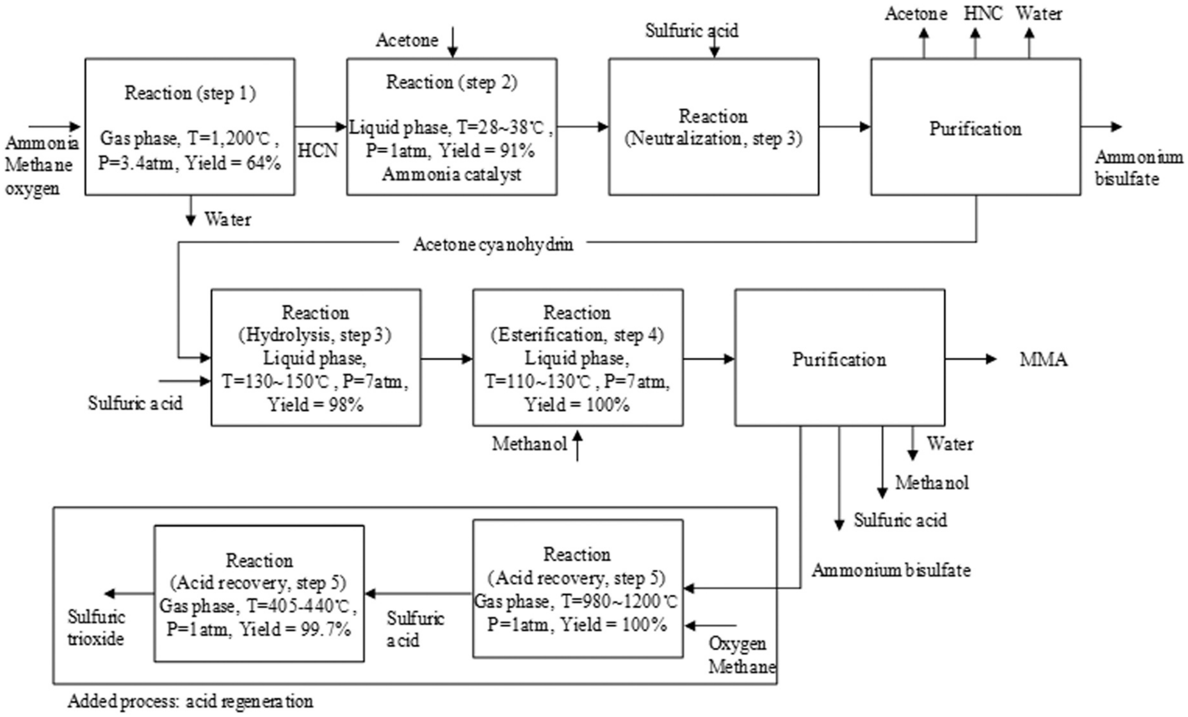


Fig. 6. MMA production by ACH route (Song et al., 2018).

interaction is found in storage which is high toxicity with the possible flash off. Four extreme parameters are investigated for storage and the reactor. They are very high flammability, very high instability, high toxicity, very high corrosiveness. Finally, the penalty is assigned for process temperature greater than autoignition temp or boiling point or flashpoint. All the penalties are summed to get the value of the vulnerability subindex.

3.6. Results

The calculated sub-indices and overall index by the present method are presented in Table 4.

4. Discussions

ACH route is most inherently unsafe, which is logical as it has the most significant number of stages, equipment, and streams, which increases its complexity and vulnerability. ACH route is worst considering its complexity and vulnerability, which is also apparent, as it has many unstable intermediates and many steps. C2-PA has the highest hazardous inflow to the route.

4.1. Comparison with earlier works

Various other researchers (Andraos, 2016; Anuradha et al., 2020; Gupta and Edwards, 2003; Mimi Haryani and Wijayanuddin, 2009; Song et al., 2018; Sugiyama et al., 2008) evaluated MMA production routes given inherent safety perspectives. The evaluation result is presented in Table 5. All of the methods show that TBA and iC4 are the most inherently safest methods among all others. The result varies because of different perspectives and selecting various parameters for those perspectives' s method. On a comparative analysis with PIIS, ISI, and iSafe, the authors evaluated the total index by adding scores for various parameters related to material and process. The complexity of the process and interaction of multiple parameters were not considered in those methods. Inherent benignness index uses principle component analysis to compare the routes.

The green metric method considers material consumption, energy consumption, material, and environmental impact. Each consumption and effect are determined quantitatively, and overall ranking is done based on the quantitative result of the assessment. In PRI, parameters which affect explosion accidents are considered only. In the work of Song et al. (2018), parameters are added without considering the difference in magnitude of hazard, the complexity of the procedure, or expert opinion. Fuzzy logic is used for chemical properties, process data, and chemical accident databases. The index considers the type of reaction and equipment parameter, process safety, complexity, operability, and the chemical characteristics index and sub-indexes process characteristics. In the extended process route index (Athar et al., 2020), parameters for all equipment to reflect equipment characteristics are averaged for a process route compared with others. The Process Route Healthiness Index (PRHI) quantifies the health hazards that might arise from chemical processes. The PRHI is influenced by potential chemical releases and the concentration of airborne chemicals inhaled by workers that may impact their health.

Table 4
Determination of inherent system index (ISSI) and ranking by using the present method for various routes of MMA production.

Inherent safety sub-Indices	ACH route	C2-PA route	C2-MP route	C3 route	TBA route	iC4 route
Inflow safety sub index (IFSSI)	73.38	68.42	60.15	71.52	63.75	70.63
Production safety subindex (PSSI)	93.22	112.25	106.00	69.88	58.25	65.25
Complexity Sub index (CSI)	8.33	5.27	6.47	5.80	4.00	4.47
Vulnerability sub index (VSI)	132.56	104	130.25	110.25	46.5	60.75
ISSI index	307.48	289.93	302.86	257.45	172.50	201.09
Ranking	6	4	5	3	1	2

Table 5
Ranking of various routes of Methyl Methacrylate production by different inherent safety assessment methods.

Methods	Ranking					
	ACH route	C2-PA route	C2-MP route	C3 route	TBA route	iC4 route
Inherent safety performance index (Song et al., 2018)	5	3	4	6	1	2
PIIS (Song et al., 2018)	6	3	5	4	2	1
ISI (Song et al., 2018)	6	3	4	4	1	1
*i*Safe (Song et al., 2018)	6	2	5	4	3	1
Inherent benignness index (Srinivasan and Nhan, 2008)	6	2	3	5	1	4
Extended process route index (Athar et al., 2020)	–	3	4	–	1	2
PRI (Athar et al., 2020)	–	3	4	–	1	2
Green matric (Andraos, 2016)	5	3	4	6	2	1
SHE performance based (Mimi Haryani and Wijayanuddin, 2009)	4	6	1	5	3	2
Process route healthiness index (Hassim and Edwards, 2006)	5	3	4	6	1	2

The present method falls under the fifth category of the inherent safety evaluation methods described in the introduction, which considers health, safety, and environmental perspective. The method considers the chemical properties of material like flammability, chemical instability, and corrosiveness. Essential environmental aspects, toxicity, type of waste materials, and quantity of waste material are also considered. It also considers energy consumption and emission. Inherent safety methods are often subjected to having the limitation of considering a limited set of aspects. While considering inherent safety parameters developed from inherent safety characteristics, various relevant factors that should be given focus based on the system's type, nature, or location can be considered. This method considers materials as streams instead of individual material where it is relevant, unlike most hazardous material considered in other methods (Heikkilä, 1999). If only the most hazardous material is considered, the scope of opportunity to improve the design by substitution of hazardous materials becomes shorter.

4.2. Improvement in the calculation process

Adding parameters of different dimensions like temperature (°C), pressure (atm), inventory (t), toxicity (ppm), and comparing the summed value is unacceptable from the engineering point of view. Either we need to make the terms dimensionless or need the score parameters based on their hazard rating. Various deviation scores are assigned to parameters considering their hazard level to remove this dimensionality problem. Scored are assigned chiefly based on earlier guidelines (NFPA, 2017). Rest are given based on the qualitative judgment of possible hazard scenarios. Many accidents occur due to the complexity of the process, as the crew members and operators cannot handle it. The lack of incomprehensibility of the system is considered by determining fourteen parameters related to it. Parameters consider the number of equipment, equipment complexity, the difficulty of the process, changes of state of the material, etc., which may induce additional risk.

4.3. The implication in overall risk consideration

Interaction of various parameters increases predetermined risk calculated at the design stage when the system is in operation, e.g., hazardous material in a reactor. Again, the extreme value of any parameter adds additional risk in the system, e.g., volatile material. The incapability to capture these interactions and considerations are often seen as the limitation of subjective scaling in parameter based indexing method (Gupta and Edwards, 2003). The reflection of vulnerability ensures that possible interactions between various risk factors are considered in the model. The selection of alternatives among many conflicting parameters is always challenging. This method can identify multiple, incompatible interactions of numerous parameters, which is crucial for any chemical process. Various penalties are assigned for temperature above autoignition temperature, boiling point temperature, or flashpoint temperature. Because the hazard of a subcooled liquid working at 350 °C is not the same as an overheated stream working at 400 °C, the risk is reflected by this penalizing. The unjustified measurement of the various parameters is balanced by assigning multiple penalties such as high pressure, high temperature, or high toxicity. Penalties are given due to high temperature and special vulnerable equipment.

4.4. Analysis with a specific focus

The subindices can be used individually if a focus in a particular section is needed, e.g., the production subindex can be calculated for various alternative designs to find the inherent safety perspective of a smaller portion of a plant such as a reactor. This method is flexible enough to analyze multiple systems, as it starts from identifying the inherent safety characteristics of the system and parameters related to those characteristics. This approach helps overcome the limitation of parameter-based indexing, which arises from selecting predefined fixed parameters that become invalid in case of system variation or significant modification of the system. This analysis will be helpful for the industry when designing a safer plant at the concept development stage.

Consideration of vulnerability and complexity has considered many factors, making it easier for engineers to modify the process accordingly. Modification is a crucial inherent safety principle. Although in practical cases, the application of this principle becomes very challenging. The detailed analysis of the present method will modify the system, reducing the pressure where material toxicity is high. If the parameter modification is not possible, the evaluated score will give design engineers caution in which factors should prioritize the detailed design stage. The method is easy to apply, not very time-consuming.

4.5. Limitation in scope

Although the present method reduces some of the limitations of earlier approaches, it still has some practical limitations. Hazards related to the chemical industry are only considered, and indices formulas are proposed based on that. There can be many other types of hazards, i.e., geological, biological depending on the application variability, which are not considered here. Material properties are affected by temperature and pressure. The value may also change due to other operations parameters in the system. A constant value of operating temperature is considered in the model. Considered operating temperature is the maximum average temperature that is obtained from field data of a similar factory. Some parameters are excluded from the established subindex, e.g., the scale of recycling fuel gas used, etc., to keep the method more straightforward due to the limitation of the scope of work. Although it has considered many interactions in any chemical process, many other interactions are not considered, e.g., ambient vapor pressure vs. threshold limit value and threshold limit value change for phase change. Risk level change due to many conflicting interactions of parameters are not considered, e.g., with the increase of the boiling point, the volatility decreases, thereby reduces the risk level. Again, if operating temperature increases, the risk level due to dispersion also increase. These effects are not considered here.

At the development process's route choice stage, it is impossible to say where intermediate storage will be placed or how much will be needed. Decisions about intermediate storage are made at the detailed design stage when the process flowsheet is available. In any case, provision for intermediate storage goes counter to the principle of an inherently safer design. Therefore, for the index, intermediate storage is left out of the inventory estimation. The distinction between long-time stored and transient chemicals is not considered. Five properties of materials are considered hazardous properties. Many other properties are considered, e.g., viscosity. While considering the complexity of equipment, ranking is performed based on numbers and type of equipment. The deviation score for various equipment is assigned based on their hazard rating in general, considering their type, type of material they handle, the maximum average temperature etc. Modern automated systems are equipped with many safety features. The features may reduce the complexity of the system, such as separate input/output module, devices with direct measurement possibility/failure on the specified state, simple graphical display, user-friendly human-machine interface, standard operating limit, enough margin in the alarm system, and distinguishable safety alarm from other alarms (Summers, 2018). Consideration of these features may give a different hazard rating from the established one here. The main focus in the present research is to identify parameters and their interaction that may affect risk level considerably at the concept development stage. Many aftereffects such as atmospheric stability and wind velocity on the leaked material's dispersion are not considered.

4.6. Possible future work

The present model can be used at different stages of process design. When detailed data such as equipment sizing, auxiliary equipment, etc., are available in the detailed design stage, the inherent safety level can be checked. The tool can be modified to consider all the relevant parameters. Other issues like layout, structural integrity are not included in the present model as it is developed focusing availability of parameters and data available at the concept development stage. The model can be modified to include these issues and to be used at later design stages. Future work can be done to increase the sophistication of the method and to remove the existing limitations. If the model can be linked with a process simulator, the processing options and safety evaluation can be accomplished simultaneously to detect unsafe conditions derived from changes in another unit. Future work should be directed toward applying the method in other chemical industries and other industrial applications.

5. Conclusion

A novel method to determine an inherent system safety index is presented in the paper. A case study is conducted to check the inherent safety perspective of various alternative Methyl Methacrylate production routes. After evaluating ISSI for various routes of MMA production, TBA is the safest route found from the analysis per the present method. The result shows variation with similar earlier approaches like SHE performance-based evaluation, Benignness index. The difference in perspective, the procedure of assessment, and selected parameters in those approaches are the causes for the variation.

Identification of the inherent safety characteristics of the system and identification of parameters related to those characteristics are the basis of the calculation of the present method. So, various types of systems can be analyzed by using this single method. Evaluating inherent safety parameters derived from the inherent safety system's characteristics makes it possible to further extend the method in other industrial applications in the future. Deviation scores are assigned for various parameters based on the hazard rating of each parameter. This approach removes dimensionality in calculating various subindices, which was a limitation of the earlier parameter-based indexing methods. Interactions between various process parameters relevant to the chemical process industry are considered. The present research considers the interaction between different process parameters pertinent to the chemical process industry. The risk level of a system increases at the operational stage due to the interaction of various parameters. Various interactions are considered as 'vulnerability' parameters, and penalties are assigned for various vulnerabilities. Different complexity parameters are identified, which may decrease the comprehensibility of the system, thereby increasing the risk level, e.g., type of equipment, number of streams, etc. The approach will help the design engineers modify the process to make it inherently safer by identifying the specific factors more easily. However, these indices share general limitations, i.e., manual data extraction of process parameters. Hazards related to the chemical industry are only considered, and indices formulas are proposed based on that. Chemical instability is chosen to represent explosion and chemical reactivity hazards. Special cases like condensed phase runaway reactions are kept out of the scope of the present paper and can be included in the elaboration of the method in the future.

Various interactions and conflicting interactions are not considered. Future work can be done to increase the sophistication of the method. In the present work, the focus is given to technical issues only. Consideration of cost can be work on also in the future. If the model can be linked with a process simulator, the processing options and safety evaluation can be accomplished simultaneously to detect unsafe conditions derived from changes in another unit. Future work should be directed toward applying the method in other chemical industries and other industrial applications. The technique can be extended to use at later stages of process design. Layout, structural integrity, sizing of equipment, and other issues can be included in the model by including relevant parameters to assess inherent safety in the later stages.

CRediT authorship contribution statement

Sharmin Sultana: Conceptualization, Methodology, Software, Writing – original draft preparation, Visualization. **Stein Haugen:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors gratefully acknowledge the financial supports from Research Council, Norway and DynSoL AS Norway through grant number 283861. We express our cordial gratitude toward the Engineering design team of DynSoL AS for their continuous support in executing the research's case study. The contribution of project leader Kamrul Islam and project administrator Gisle Obrestad is also acknowledged. The authors like to acknowledge their gratitude to anonymous reviewers for their valuable comments and advice.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126590.

References

Abedi, P., Shahriari, M., 2005. Inherent safety evaluation in process plants—A comparison of methodologies. Open Chem. 3, 756–779.

Abidin, M.Z., Rusli, R., Buang, A., Shariff, A.M., Khan, F.I., 2016. Resolving inherent safety conflict using quantitative and qualitative technique. J. Loss Prev. Process Ind. 44, 95–111.

Ahmad, S.I., Hashim, H., Hassim, M.H., Srinivasan, R. 2013. Safety Assessment Curve (SAC) for Inherent Safety Assessment in Petrochemical Industry. In: Proceedings of teh 16th International Conference on Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction *(Pres'13),* 35**,** 1267–1272.

Ahmad, S.I., Ho, W.S., Hassim, M.H., Elagroudy, S., Kohar, R.A.A., Bong, C.P.C., Hashim, H., Rashid, R., 2020. Development of quantitative SHE index for waste to energy technology selection. Energy 191, 116534.

AIChE, Dow, 1987. Fire & Explosion Index: Hazard Classification Guide. Amer Inst of Chemical Engineers.

AICHE, D.A., 1998. Dow's Chemical Exposure Index Guide. AIChE. Google Scholar, New York, USA.

Amyotte, P.R., Khan, F.I., 2002. An inherent safety framework for dust explosion prevention and mitigation. J. De Phys. Iv 12, 189–196.

Andraos, J., 2016. Complete green metrics evaluation of various routes to methyl methacrylate according to material and energy consumptions and environmental and safety impacts: test case from the chemical industry. ACS Sustain. Chem. Eng. 4, 312–323.

Anuradha, H., Gunasekera, M., Gunapala, O., 2020. Comparison of chemical routes based on inherent safety, health and environmental impacts of accidental and daily operational releases. Process Saf. Environ. Prot. 133, 358–368.

Athar, M., Shariff, A.M., Buang, A., Hermansyah, H., 2020. Equipment-based route index of inherent safety. Process Saf. Prog. 39.

Athar, M., Shariff, A.M., Buang, A., Shaikh, M.S., See, T.L., 2019. Inherent safety for sustainable process design of process piping at the preliminary design stage. J. Clean. Prod. 209, 1307–1318.

Athar, M., Zaidi, N.A.B., Shariff, A.M., Buang, A., Khan, M.I., 2018. Chemical reactor inherent safety index at preliminary design stage. IOP Conf. Ser.: Mater. Sci. Eng. 458, 012048.

Baker, R.D., Warren, J.L., Behmanesh, N., Allen, D.T., 1992. Management of hazardous waste in the United States. Hazard. Waste Hazard. Mater. 9, 37–59.

Barbour, A.K., Houghton, J.T., King, N.J., Matsui, S., Slater, D.H., Spiro, T.G., Taylor, D., Warner, F., Williams, D.R., Petts, J., 1998. Risk Assessment and Risk Management. Royal Society of Chemistry, Cambridge, Cambridge.

Bly, M., 2011. Deepwater Horizon Accident Investigation Report. Diane Publishing.

Brar, S.K., 2011. Hazardous Materials: Types, Risks and Control. Nova Science Publishers, Hauppauge, Hauppauge (Incorporated).

Brock, W.E., 1986. Safety & Health Guide for the Chemical Industry. Department of labor Washington DC occupational safety and health administration.

CCPS, 2009. Inherently Safer Chemical Processes: A Life Cycle Approach. John Wiley & Sons.

ChemSafetyPro. 2021. What is flammability? [Online]. Available: 〈https://www.liquisearch.com/what_is_flammability〉 [Accessed 2021].

Cheremisinoff, N.P., Cheremisinoff, P.N., 1995. Hazardous Materials and Waste Management: A Guide for the Professional Hazards Manager. Noyes Publications, Park Ridge, N.J.

Clinton, B., 1994. Technology for a Sustainable Future: A Framework for Action. US Government Printing Office, Washington, DC.

Crowl, D.A., Elwell, T.I., 2004. Identifying criteria to classify chemical mixtures as "highly hazardous" due to chemical reactivity. J. Loss Prev. Process Ind. 17, 279–289.

Edwards, Lawrence, 1995. Assessing the inherent safety of chemical process routes. Loss Prevention and Safety Promotion in the Process Industries, 1 and 2, B473–B482. WOS:A1995BE41U00097.

Eini, S., Abdolhamidzadeh, B., Reniers, G., Rashtchian, D., 2015. Optimization procedure to select an inherently safer design scheme. Process Saf. Environ. Prot. 93, 89–98.

Eljack, F., Kazi, M.K., Kazantzi, V., 2019. Inherently safer design tool (i-SDT): a property-based risk quantification metric for inherently safer design during the early stage of process synthesis. J. Loss Prev. Process Ind. 57, 280–290.

Etowa, C.B., Amyotte, P.R., Pegg, M.J., Khan, F.I., 2002. Quantification of inherent safety aspects of the Dow indices. J. Loss Prev. Process Ind. 15, 477–487.

French, R.W., Williams, D.D., Wixom, E.D. 1995. Inherent safety, health and environmental (SHE) reviews. *Lps 1995.* In: Proceedings of the 29th Annual Loss Prevention Symposium, 27–34.

French, R.W., Williams, D.D., Wixom, E.D., 1996. Inherent safety, health, and environmental (SHE) reviews. Process Saf. Prog. 15, 48–51.

Gowland, R., 1996. Applying inherently safer concepts to a phosgene plant acquisition. Process Saf. Prog. 15, 52–57.

Greenberg, H.R., Cramer, J.J., Stone, Webster Engineering, C., 1991. Risk Assessment and Risk Management for the Chemical Process Industry. Van Nostrand Reinhold, New York.

Grim, L., Tillema, D., Cutchen, S., Wingard, M., Johnson, A., 2015. CSB investigation of Chevron Richmond refinery pipe rupture and fire. Process Saf. Prog. 34, 355–359.

Gupta, J., Edwards, D.W., 2003. A simple graphical method for measuring inherent safety. J. Hazard. Mater. 104, 15–30.

Gupta, J.P., Edwards, D.W., 2002. Inherently safer design - present and future. Process Saf. Environ. Prot. 80, 115–125.

Hassim, M., Edwards, D., 2006. Development of a methodology for assessing inherent occupational health hazards. Process Saf. Environ. Prot. 84, 378–390.

Hatayama, H., 1980. A Method for Determining the Compatibility of Hazardous Wastes. Environmental Protection Agency, Office of Research and Development.

Heikkilä, A.-M., 1999. Inherent Safety in Process Plant Design: An Index-based Approach. VTT Technical Research Centre of Finland.

Heinemann, H. 1979. A Brief History of Industrial Catalysis.

Hendershot, D.C., 1995. Conflicts and decisions in the search for inherently safer process options. Process Saf. Prog. 14, 52–56.

Hendershot, D.C., 1997. Measuring inherent safety, health and environmental characteristics early in process development. Process Saf. Prog. 16, 78–79.

Holmstrom, D., Altamirano, F., Banks, J., Joseph, G., Kaszniak, M., Mackenzie, C., Shroff, R., Cohen, H., Wallace, S., 2006. CSB investigation of the explosions and fire at the BP Texas City refinery on March 23, 2005. Process Saf. Prog. 25, 345–349.

Ingersoll, C., Locke, R.M., Reavis, C., 2012. BP and the Deepwater Horizon Disaster of 2010. MIT Sloan School of Management (Case Study).

Instone, B., 1989. Losses in the hydrocarbon process industries. In: Proceedings of 6th International Symposium Loss Prevention and Safety Promotion in the Chemical Industries, Oslo, pp. 118–119.

Kaszniak, M. 2009. Examining Organizational and Safety Culture Causes of the BP Texas Cty Refinery Explosion.

Keller, J.J., Associates, I., 2013. OSHA Compliance Manual. J. J. Keller & Associates, Inc, Neenah, Neenah.

Khan, F.I., Amyotte, P.R., 2004. Integrated inherent safety index (I2SI): a tool for inherent safety evaluation. Process Saf. Prog. 23, 136–148.

Khan, Husain, Abbasi, 2001. Safety weighted hazard index (SWeHI): a new, user-friendly tool for swift yet comprehensive hazard identification and safety evaluation in chemical process industrie. Process Safety and Environmental Protection 79 (2), 65–80.

King, R., 2016. Safety in the Process Industries. Elsevier.

Kletz, T., 1978. What you dont have, cant leak - jubilee lecture. Chem. Ind. 287–292.

Kletz, T., 1988. Plants should be friendly. Chem. Eng. 35-35.

Kletz, T., 2012. The history of process safety. J. Loss Prev. Process Ind. 25, 763–765.

Kletz, T.A., 1989. Friendly plants. Chem. Eng. Prog. 85, 18–26.

Kletz, T.A., 1990. The need for friendly plants. J. Occup. Accid. 13, 3–13.

Kletz, T.A. 1995. Inherently safer design - The growth of an idea. *Lps 1995. In:* Proceedings of the 29th Annual Loss Prevention Symposium, 1–11.

Kletz, T.A., 2009. Don't just pass the parcel: accidents that would not have occurred if those involved had talked together. J. Loss Prev. Process Ind. 22, 667–671.

Klugmann-Radziemska, E., 2014. Environmental Impacts of Renewable Energy Technologies. Int Conf Environ Sci Technol. IPCBEE, Singapore, pp. 104–109.

Lawrence, D., 1996. Quantifying Inherent Safety of Chemical Process Routes (©). Duncan Lawrence.

Lee, Y., Kim, J., Ahmed, U., Kim, C., Lee, Y.W., 2019. Multi-objective optimization of organic rankine cycle (ORC) design considering exergy efficiency and inherent safety for LNG cold energy utilization. J. Loss Prev. Process Ind. 58, 90–101.

Leong, C.T., Shariff, A.M., 2008. Inherent safety index module (ISIM) to assess inherent safety level during preliminary design stage. Process Saf. Environ. Prot. 86, 113–119.

Leong, C.T., Shariff, A.M., 2009. Process route index (PRI) to assess level of explosiveness for inherent safety quantification. J. Loss Prev. Process Ind. 22, 216–221.

Lewis, D. The Mond Fire, Explosion and Toxicity Index-a Development of the Dow Index. In: Proceedings of the AIChE on Loss Prevention Symposium, New York, 1979.

Macdonald, D., 2004. Practical Industrial Safety, Risk Assessment and Shutdown Systems for Industry. Newnes, Amsterdam, Oxford.

Mahoney, D., 1990. Large Property Damage Losses in the Hydrocarbon-chemical Industries: A Thirty-year Review. M & M Protection Consultants.

Mannan, M.S., Sachdeva, S., Chen, H., Reyes Valdes, O., Liu, Y., Laboureur, D., 2015. Trends and challenges in process safety. AIChE J. 61, 3558–3569.

Mannan, S., Lees, F.P., 2012. Lee's loss prevention in the process industries: hazard identification, assessment, and control (ed). In: Mannan, Sam (Ed.), Loss Prevention in the Process Industries, fourth ed. Butterworth-Heinemann; Elsevier, Boston, Amsterdam.

Mansfield, D., Clark, J., Malmén, Y., Schabel, J., Rogers, R., Suokas, E., Turney, R., Ellis, G., Van Steen, J. & Verwoerd, M. 1997. The INSET Toolkit—Inherent SHE Evaluation Tool. AEA Technology/Eutech Engineering Solutions/INBUREX/Kemira Agro/TNO/VTT Manufacturing Technology, Risley (UK)/Winnington (UK)/Hamm (Germany)/Espoo (Finland)/Apeldoorn (Netherlands)/Tampere (Finland), version, 1.

Marchaterre, J., Sevy, R., Cahalan, J. 1986. Integral Fast Reactor Concept Inherent Safety Features.

Marchaterre, J., Sevy, R., Lancet, R., Mills, J., 1984. Key Asset-inherent Safety of LMFBR Pool Plant. Argonne National Lab.

Marshall, V.C. 1987. Major Chemical Hazards.

Mimi Haryani, H., Wijayanuddin, M. 2009. Screening Alternative Chemical Routes Based on Inherent Chemical Process Properties Data: Methyl Methacrylate Case Study.

Murphy, J. 1995. Dow's fire and explosion index - A risk reduction tool. 7th Ethylene Producers' Conference, Proceedings, 4, 252–270.

NFPA, 2017. NFPA 704, Standard System for the Identification of the Hazards of Materials for Emergency Response. National Fire Protection Association.

Ohashi, H., Sato, H., Tachibana, Y., Kunitomi, K. & Ogawa, M. 2012. Concept of an Inherently-safe High Temperature Gas-cooled Reactor. In: Proceedings of the 3rd International Conference on Advances in Nuclear Science and Engineering 2011 (Icanse 2011), 1448, pp. 50–58.

OSHA, 1983. General Industry: OSHA Safety and Health Standards (29 CFR 1910). OSHA, Washington, DC.

Palaniappan, C., Srinivasan, R., Tan, R., 2002. Expert system for the design of inherently safer processes. 1. Route selection stage. Ind. Eng. Chem. Res. 41, 6698–6710.

Pennington, D.W., Bare, J.C., 2001. Comparison of chemical screening and ranking approaches: The waste minimization prioritization tool versus toxic equivalency potentials. Risk Anal.: Off. Publ. Soc. Risk Anal. 21, 897–912, 897-897.

Perrot, P., 1998. A to Z of Thermodynamics. Oxford University Press on Demand.

Petrucci, R.H., Herring, F.G., Madura, J.D., 2010. General Chemistry: Principles and Modern Applications. Pearson Prentice Hall.

Planas-Cuchi, E., Montiel, H., Casal, J., 1997. A survey of the origin, type and consequences of fire accidents in process plants and in the transportation of hazardous materials. Process Saf. Environ. Prot. 75, 3–8.

Pohanish, R.P., 2017. Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens. William Andrew.

Rahman, M., Heikkila, A.M., Hurme, M., 2005. Comparison of inherent safety indices in process concept evaluation. J. Loss Prev. Process Ind. 18, 327–334.

Rathnayaka, S., Khan, F., Amyotte, P., 2014. Risk-based process plant design considering inherent safety. Saf. Sci. 70, 438–464.

Rosenfeld, P.E., Feng, L., 2011. Risks of Hazardous Wastes. William Andrew.

Rusli, R., Shariff, A.M., Khan, F., 2013. Evaluating hazard conflicts using inherently safer design concept. Saf. Sci. 53, 61–72.

Safe, S., 1982. Halogenated hydrocarbons and aryl hydrocarbons identified in human tissues. Toxicol. Environ. Chem. 5, 153–165.

Shariff, A.M., Leong, C.T., 2009a. Inherent risk assessment-a new concept to evaluate risk in preliminary design stage. Process Saf. Environ. Prot. 87, 371–376.

Shariff, A.M., Leong, C.T., 2009b. Inherent risk assessment—A new concept to evaluate risk in preliminary design stage. Process Saf. Environ. Prot. 87, 371–376.

Shariff, A.M., Leong, C.T., Zaini, D., 2012. Using process stream index (PSI) to assess inherent safety level during preliminary design stage. Saf. Sci. 50, 1098–1103.

Shariff, A.M., Zaini, D., 2010. Toxic release consequence analysis tool (TORCAT) for inherently safer design plant. J. Hazard. Mater. 182, 394–402.

Shariff, A.M., Zaini, D., 2013. Inherent risk assessment methodology in preliminary design stage: a case study for toxic release. J. Loss Prev. Process Ind. 26, 605–613.

Sharmin Sultana, J.E. V., Jan Dahlsveen, Stein Haugen, 2020. Inherent safety assessment: current state of the art and why is still not effectively adopted by industry. 30th European Safety and Reliability Conference and the 15th Probabilistic Safety Assessment and Management Conference, Italy. Research Publishing, Singapore.

Sohn, H., Olivas-Martinez, M., 2014. Methods for calculating energy requirements for processes in which a reactant is also a fuel: need for standardization. JOM 66, 1557–1564.

Song, D., Yoon, E.S., Jang, N., 2018. A framework and method for the assessment of inherent safety to enhance sustainability in conceptual chemical process design. J. Loss Prev. Process Ind. 54, 10–17.

Srinivasan, R., Nhan, N.T., 2008. A statistical approach for evaluating inherent benignness of chemical process routes in early design stages. Process Saf. Environ. Prot. 86, 163–174.

Stephanopoulos, G., 1984. Chemical Process Control. Prentice Hall, Englewood Cliffs, NJ.

Suardin, J.A., 2006. The Integration of Dow's Fire and Explosion Index into Process Design and Optimization to Achieve an Inherently Safer Design. Texas A&M University.

Sugiyama, H., Fischer, U., Hungerbühler, K., Hirao, M., 2008. Decision framework for chemical process design including different stages of environmental, health, and safety assessment. AIChE J. 54, 1037–1053.

Summers, A., 2018. Inherently safer automation. Process Saf. Prog. 37, 31–36.

Theis, A.E., Askonas, C.F., 2013. Inherently safer design concepts applied to laboratories. Process Saf. Prog. 32, 142–145.

Tugnoli, A., Cozzani, V., Landucci, G., 2007. A consequence based approach to the quantitative assessment of inherent safety. AIChE J. 53, 3171–3182.

Tugnoli, A., Landucci, G., Salzano, E., Cozzani, V., 2012. Supporting the selection of process and plant design options by inherent safety KPIs. J. Loss Prev. Process Ind. 25, 830–842.

Turney, R.D., 2001. Inherent Safety: What can be done to increase the use of the concept. HJ Pasman: Loss Prevention and Safety Promotion in the Process Industries-10th International Symposium, pp. 519–528.

Tyler, B., 1985. Using the Mond Index to measure inherent hazards. Process Saf. Prog. 4, 172–175.

Tzanos, C., Barthold, W., Bowers, C., Ferguson, D., Prohammer, F., Van Erp, J., 1976. Design-Related Inherent Safety Characteristics in large LMFBR Power Plants. Argonne National Lab., IL (USA).

UN, 2003. Globally Harmonized System of Classification and Labelling of Chemicals (GHS). United Nations, New York.

Vaughen, B.K., Kletz, T.A., 2012. Continuing our process safety management journey. Process Saf. Prog. 31, 337–342.

Vázquez, D., Ruiz-Femenia, R.N., Jiménez, L., Caballero, J.A., 2018. Multi-objective early design of complex distillation sequences considering economic and inherent safety criteria. Ind. Eng. Chem. Res. 57, 6992–7007.

Waltar, A.E., Padilla, A., Odell, L.D., Nguyen, D.H., Smith, D.E., Omberg, R.P., 1985. A perspective on the inherent safety of liquid-metal reactors. Trans. Am. Nucl. Soc. 49, 273–274.

Warnasooriya, S., Gunasekera, M.Y., 2017. Assessing inherent environmental, health and safety hazards in chemical process route selection. Process Saf. Environ. Prot. 105, 224–236.

Windhorst, J.C.A., 1995. Application of inherently safe design concepts, fitness for use and risk driven design process safety standards to an LPG project. Loss Prev. Saf. Promot. Process Ind. 1/2, B543–B554.

Xue, Y., Nie, L., Zhou, Z., Tian, H., Yan, J., Wu, X., Cheng, L., 2017. Historical and future emission of hazardous air pollutants (HAPs) from gas-fired combustion in Beijing, China. Environ. Sci. Pollut. Res. 24, 16946–16957.

Zobel, R. 1985. Computer Aided Compliance-A Tool to Increase the Inherent Safety of Vehicles. SAE Technical Paper.