Quantitative Safety and Health Assessment Based on Fuzzy Inference and AHP at Preliminary Design Stage

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ABSTRACT: *Quantitative assessment is the most important means to identify hazard potential and manage risk for industrial process. The implement of quantitative assessment in early stage will help to develop inherently safer process, eliminating hazard and reduce the possibility of accidental chain-events and the magnitude of consequences. In this paper, after reviewing the presently available assessment method, we present the disadvantages of current technology in several aspects. Focusing on the main disadvantage of subjectivity in two aspects of index valuing and weighting, which is a serious barrier to measure the real level of process safety, we propose a quantitative assessment method integrated fuzzy inference and Analytic Hierarchy Process(AHP) to quantify safety and health hazards of chemical process route in preliminary design stage. The purpose of integrating fuzzy inference into it is to reduce the subjectivity of index valuing system. The fuzzy inference system is designed without medium variable in order to eliminate its negative effect on assessment result. Index weighting is determined by AHP more objectively based on the ordering of inherent safety guidewords. Finally, the proposed method is applied to assessment nine competing routes of acetic acid manufacture to present its improvement.*

KEYWORDS: *Safety assessment; Health assessment; Index weighting; Fuzzy inference; AHP; Inherent safety.*

INTRODUCTION

Currently, the constantly increasing scale of industrial operations has more complicated issues and greater hazard potential, which exacerbate the magnitude of accidental consequence and domino effect. Safety assessment is an useful means to reveal the probability of accident risk by quantificationally obtaining the real safety level of chemical processes [1]. There are several safety assessment principles and methods recommended to identify hazards and manage risks for chemical process. However, most of them have the disadvantage of the subjectivity in two aspects of index value and weighting, which is the main barrier to achieve the substantial safety assessment. In this work, we provide a safety assessment method integrated fuzzy inference and AHP, i.e. Inherent Preference Index(IPI), aiming to quantify the risk of chemical process in early stage. The subjectivity in index valuing system will be reduced by application of fuzzy inference, which is treated as appropriate mathematical

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approach to eliminate uncertainty of issue. In addition, the subjectivity in index weighting is reduced by application of AHP, which is a multi-objective decision-making method suitable to obtain index weighting vector objectively. In section 2, the current methods are reviewed to put forward the possible perspective of safety assessment firstly. Then the proposed method is discussed in detail in section 3. Finally, it is applied to acetic acid process routes screening to illustrate its availability.

Review of quantitative assessment method

Quantitative assessment is particularly suitable to implement inherent safety guidewords in the early stages of design. Some indexing methods are proposed for comparing alternatives of chemical process [2-4]. *Edwards & Lawrence* firstly develop a Prototype Index of Inherent Safety (PIIS) to analyze the inherent safety of process route [5]. It contains seven parameters—Inventory, Temperature, Pressure, Yield, Toxicity, Flammability, and Explosiveness. Other methods are proposed to improve the assessment in several aspects, such as the magnitude of index, the subjectivity issue, assessment mode, scoring system, intelligence and how to be integrated to process design tools etc. [6-34].

Quantitative assessment methods proposed earlier mainly extend the magnitude of index. Such as, Inherent Safety Index (ISI) is developed to classify process alternatives during preliminary process design[6,7]. Besides of the indices in PIIS, this method adds additionally the sub-indices of chemical interaction, heat of main reaction, heat of side reaction, and corrosiveness in chemical aspect and equipment safety and process structure safety in process aspect. Similarly, The I-safe is developed to distinguish alternative routes with closely inherent safety scores, which considers additionally five other supplementary indices, Hazardous Chemical Index (HCI), Hazardous Reaction Index (HRI), Total Chemical Index (TCI), Worst Chemical Index (WCI) and Worst Reaction Index (WRI)[9]. Generally, the potential hazards both in HSE (Health, Safety, Environment) properties of substances and process conditions should be considered during assessment process. The EHS and IBI method both involve safety, environment and health indices [16,18]. They treat safety assessment decision-making as a tradeoff of multiple objectives, i.e. safety, environment and health effects.

The most current methods have subjectivity in index interval and weighting, which is the main barrier to measure the actual inherent safety level. Especially for the qualitative index (such as the inherent safety index in I2SI), the scale of index interval is subjective and indefinite, which led to different evaluation results for the same chemical process possibly [13,14]. In order to obtain the objective assessment result, the subjectivity in safety assessment should be reduced as far as possible. The two aspects of subjectivity (index value and index weighting) are described separately, because the former refers to single index and the latter refers to the relationship among indices. In the first aspect, it is divided into two parts, i.e. the scaling of index interval and the determination of index value. In safety assessment, index is based on parameter (e.g. temperature, flash point, etc.), the value of which is divided into several intervals(or stage) subjectively. Because the scaling of index interval is determined based on the engineering empirical data generally, the reduction in this aspect of subjectivity is limited. However, the determination of index value, namely scoring system, can be improved to achieve objectively. An example is Inherent Benign-ness Indicator (IBI), which standardizes index value by developing mathematical function for scoring system [18]. The Fuzzy Based Inherent Safety Index applies fuzzy theory to safety assessment, which reduces the uncertainty of index value[10-12]. The guideline of it is that index can partially belong to adjacent index intervals according to its membership function, which reduce the subjectivity of index scoring. However, the application case illustrates the assessment result will deviate from the fact situation when the number of medium variables increases in multistage fuzzy system. In the second, the index weighting should be considered because index has different contribution for the end index value (the total safety level) due to its impact. This aspect is hardly concerned by far. Gupta and Edwards propose a simple graphical method which discusses that just an overall index value can not indicate the contribution of different index. The individual index should be evaluated separately. The IBI uses Principal Components Analysis (PCA) to reduce dimensionality of variables, which identify the main impact factors to indicate the difference of process routes[18]. This work proposes AHP to determinate the index weighting in safety assessment.

According to the principle of protection layers, accident is caused by a chain effect that hazards in different layer's follows a certain logical relationship. Accordingly, the index relationship should be considered during safety assessment process. Moreover, the logical relationship should conform to the practical hazardous scenario, which represent the practical hazardous behavior other than isolated index.

It contributes to develop inherently safer process that improving intelligence of safety assessment and integrating it into process research and design technology [31-34]. The process synthesis strategy considered safety factor is proposed, applying to separation sequence and reaction structure synthesis [8,9]. The strategy generates alternatives by Genetic Algorithms (GA), then evaluating them by inherent safety indices, finally selecting the best alternative according to evaluation results. An intelligent Benign Design Tool (iBDT) is developed, which generates the alternatives by heuristics based on material, reaction conditions and process unit information. Their safety and environmental impacts are analyzed, assisting to make decision in the design stage of process [14]. The framework of Inherent Safety Index Module (ISID), Integrated Consequence Estimation Tool (ICET), and Integrated Probability Estimation Module (IPEM) in HYSYS is proposed to evaluate inherent safety, accident consequence and risk probability of chemical process based on the results of simulation [32]. The development of inherently safer process demands the support of intelligent inherent safety design technology and tools.

QUANTITATIVE SAFETY AND HEALTH ASSESSMENT INTEGRATED FUZZY INFERENCE AND AHP

Aim to reduce the disadvantage of subjectivity in index value and weighting, this section proposes an indexing method integrated fuzzy inference and AHP, which is suitable for screening inherently safer alternatives in early stage. The index value is determined by the established fuzzy inference system, which normalize the index value to [0,1]. The weightings of indices are obtained based on AHP. The weighting vector is calculated by establishing hierarchical model, forming comparison matrix and consistency test in order. The detailed assessment procedure is described as follow.

Index selection

The available process information is limited in early stage, the indices in this method mainly involve physical and chemical properties of substance, operation conditions and other aspects implemented inherent safety guidewords. The guidewords of inherent safety are *minimization*, *substitution*, *moderation*, *simplification*, following the ordering of importance[35,36].

The *minimization* guideword means minimizing the hazardous substance in process. The involved index is inventory. The higher inventory of hazardous substance has greater index value, representing the lower level of minimization guideword. As the inventory information is not available in early stage, this index is not considered here.

The indices involved the *substitution* guideword are flammability, explosion, reactivity and reaction heat, toxicity. As these indices are inherent and impartible property of substance (or reaction), the alternative in which hazardous substance (highly flammable, explosive or reactive) is substituted by less hazardous one is inherently safer. Similarly, it is more inherently safe that the strict reaction is substituted by mild reaction.

The related indices of the *moderation* guideword are temperature and pressure. The hazardous substance operated in moderate condition is inherently safer than in harsh condition. The operation conditions of alternatives are evaluated to measure the level of moderation guideword.

The *simplification* guideword mainly refers to the complexity of reaction, such as multistep reaction and yield. The multistep reaction and lower yield will increase the complexity of process in the latter design stage.

Based on available information, seven indices are considered in safety aspect, namely flammability, explosion, reactivity, reaction heat, yield, temperature and pressure. Three indices are considered in health aspect, i.e. Toxicity by Oral Ingestion(TOI), Toxicity by Respiratory(TR), Toxicity by Dermal Exposure(TDE).

Determination of index value based on fuzzy inference

Process safety is an uncertainty concept because it is not possible to be defined exactly. In other words, 'safety' can not be strictly classified into the dichotomy safe or unsafe. Accordingly, process safety should not be modeled by a statistical approach since the uncertainty is not caused by randomness (described by statistical or probabilistic approach) but by fuzziness, vagueness and ambiguity. Fuzzy inference offers an alternative mathematical method where vague and imprecise concepts can be rigorously modeled where an element can belong to more than one fuzzy interval simultaneously.

Inherent safety aims to eliminate the hazards rather than to control them. If hazard is present, the accident can occur if the protective layers fail in abnormal situation. In other words, the presence of the hazard makes the accident possible; if the hazard is eliminated, the accident can not occur. This idea is equivalent to the relation between probability and possibility: if an event is to be probable, it has to be possible. While the probability and possibility aim to solve different problems, they are described by different approach. Probability is associated with statistics, while possibility is modeled by fuzzy method.

Although the fuzzy inference is a suitable method to solve uncertain problem, in practical application, the increase of the number of medium variable in multistage fuzzy system leads to that the assessment result no longer conforms to the practical scenario. Generally in a fuzzy inference system, two input variables will generate one output variable (medium variable), which is treated as input variable for the next fuzzy inference system. Since the medium variable has no physical meaning, the classification of its fuzzy intervals has no quantitative basis. Accordingly, the more medium variable means the more subjective factor during fuzzy inference process, leading to the assessment result deviating from the practice in the end.

The proposed method develops the fuzzy inference system with one input variable and one output variable. The output variable do not participate in the next fuzzy inference system, which can overcome the shortcoming.

Evaluation of index in this method is completed through three steps as follow.

(1) Fuzzy intervals of index is determined according to its hazard hierarchic classification.

Hazard hierarchic classification of index is based on ISI(Inherent Safety Index) proposed by *Heikkila* [7]. The fuzzy intervals of safety and health indices and their membership function parameters are showed in Tables 1 & 2. Such as the flammability index, its hazard hierarchy is classifed into four stages, i.e. “Low hazard”, “Moderate hazard”, “High hazard”, “Very high hazard”, based on flash point value of chemical material. Then membership function parameter can be calculated by boundary value of hierarchy classification in order to form fuzzy intervals for the index.

As showed in Table 1, the classification of explosion index is based on the difference of UEL (Upper Explosive Limit) and LEL (Lower Explosive Limit), and the reactivity index is based on the standard of NFPA (National Fire Protection Association). Similarly, hazard hierarchy of other indices are classified into several levels. In temperature index, it is treated as more hazardous when the operation temperature is lower than -30 °C. In pressure index, the operation in negative pressure is more hazardous than in atmospheric pressure.

As showed in Table 2. The TOI index is classified into five levels based on LD50 data. LD50 data is converted to logarithm so that it is convenient to build fuzzy inference system. The TR index has different classification for gas, vapor, dust and mist, which types and parameters of MF are established respectively. The levels of TDE index is presented by Threshold Limit Value(TLV), which is also converted to logarithm.

(2) Fuzzy inference system for each index is formed in Matlab.

Since hazard hierarchy and MF parameter of index are determined, fuzzy inference system can be formed in Matlab. The type and parameter of MF decide the shape of curve of fuzzy interval. Based on data in Tables 1 & 2, fuzzy inference system for each index can be established by fuzzy logic toolbox in Matlab. Such as the temperature index, five fuzzy intervals and fuzzy inference surface made in Matlab is showed in Fig. 1.

(3) Evaluation result of index is obtained by fuzzy inference system.

Information of material and chemical process is input to fuzzy inference system, evaluation result of index is determined by fuzzy inference. For example, fuzzy evaluation of temperature index is showed in Fig. 2. Assuming reaction temperature is 200℃, its evaluation result is 0.3.

Index Weighting

The proposed method calculates index weighting according to AHP, which is suitable to the complex system of interrelated and mutual restrain. It provides

Table 1: Hazard hierarchy and membership functions parameter of safety indices.

Index name	Hazard hierarchy	Hierarchy classification	Type of MF	Parameter of MF
Flammability (Flash point) (℃)	Low hazard	≥93.4	trapezoidal	[65.6 93.4 ∞ ∞]
	Moderate hazard	≥37.8	triangular	[30.3 65.6 93.4]
	High hazard	≥22.8	triangular	[11.4 30.3 65.6]
	Very high hazard	＜22.8	trapezoidal	[-40 -40 11.4 30.3]
Explosion (U-L)	Low hazard	0-20	trapezoidal	[0 0 10 32.5]
	Moderate hazard	20-45	triangular	[10 32.5 57.5]
	High hazard	45-70	triangular	[32.5 57.5 85]
	Very high Hazard	70-100	trapezoidal	[57.5 85 100 100]
Reactivity (NFPA standard)	Low hazard	0	trapezoidal	[0 0 0.5 1.5]
	Moderate hazard	1	triangular	[0.5 1.5 2.5]
	High hazard	2	triangular	[1.5 2.5 3.5]
	Very high Hazard	3	trapezoidal	[2.5 3.5 4 4]
Reaction heat (J/g)	Very Low hazard	≤200	trapezoidal	[-∞ -∞ 100 400]
	Low hazard	＜600	triangular	[100 400 900]
	Moderate hazard	＜1200	triangular	[400 900 2100]
	High hazard	＜3000	triangular	[900 2100 3000]
	Very high Hazard	≥3000	trapezoidal	[2100 3000 +∞ +∞]
Yield (%)	Very Low hazard	80-100	trapezoidal	[100 100 90 70]
	Low hazard	60-80	triangular	[90 70 50]
	Moderate hazard	40-60	triangular	[70 50 30]
	High hazard	20-40	triangular	[50 30 10]
	Very high Hazard	0-20	trapezoidal	[30 10 0 0]
Temperature (℃)	Moderate Hazard	<-30	trapezoidal	[-∞ -∞ -40 -20]
	Low hazard	-30-70	triangular	[-30 20 185]
	Moderate hazard	70-300	triangular	[20 185 450]
	High hazard	300-600	triangular	[185 450 600]
	Very high Hazard	>600	trapezoidal	[450 600 +∞ +∞]
Pressure (bar)	Low hazard	0-0.5	trapezoidal	[0 0 0.25 1]
	Very Low hazard	0.5-5	triangular	[0.25 2.75 15]
	Low hazard	5-25	triangular	[2.75 15 37.5]
	Moderate hazard	25-50	triangular	[15 37.5 125]
	High hazard	50-200	triangular	[37.5 125 600]
	Very high Hazard	200-1000	trapezoidal	[600 1000 +∞ +∞]

MF: Membership Function

Table 2: Hazard hierarchy and membership functions parameter of health indices.

Index name	Hierarchy description	Hierarchy classification	Logarithm (lg)	Type of MF	Parameter of MF
TOI (LD50) (mg/kg)	Very Low hazard	>=5000	>=3.70	trapezoidal	[3.5 3.85 4 4]
	Low hazard	2000-5000	3.30-3.70	triangular	[2.89 3.5 3.85]
	Moderate hazard	300-2000	2.48-3.30	triangular	[1.89 2.89 3.5]
	High hazard	20-300	1.30-2.48	triangular	[0.65 1.89 2.89]
	Very high hazard	0-20	0-1.30	trapezoidal	[0 0 0.65 1.89]
TR-gas (LC50) (ppm)	Very Low hazard	>5000	>3.70	trapezoidal	[3.55 4 5 5]
	Low hazard	2500-5000	3.40-3.70	triangular	[3.05 3.55 4]
	Moderate hazard	500-2500	2.70-3.40	triangular	[2.35 3.05 3.55]
	High hazard	100-500	2-2.70	triangular	[1 2.35 3.05]
	Very high hazard	0-100	0-2	trapezoidal	[0 0 1 2.35]
TR-vapor (LC50) (mg/m^3)	Very Low hazard	>20	-	trapezoidal	[15 25 30 30]
	Low hazard	10-20	-	triangular	[6 15 25]
	Moderate hazard	2-10	-	triangular	[1.25 6 15]
	High hazard	0.5-2	-	triangular	[0.25 1.25 6]
	Very high Hazard	≤0.5	-	trapezoidal	[0 0 0.25 1.25]
TR-dust and mist (LC50) (mg/kg)	Very Low hazard	>5	-	trapezoidal	[3 7.5 10 10]
	Low hazard	1-5	-	triangular	[0.75 3 7.5]
	Moderate hazard	0.5-1	-	triangular	[0.275 0.75 3]
	High hazard	0.05-0.5	-	triangular	[0.025 0.275 0.75]
	Very high Hazard	≤0.05	-	trapezoidal	[0 0 0.025 0.275]
TDE (TLV) (ppm)	Very Low hazard	>=10000	>=4	trapezoidal	[3 5 6 6]
	Low hazard	100-10000	2-4	triangular	[1.5 3 5]
	Moderate hazard	10-100	1-2	triangular	[0.55 1.5 3]
	High hazard	1-10	0.1-1	triangular	[0.055 0.55 1.5]
	Very high Hazard	<=1	0-0.1	trapezoidal	[0 0 0.055 0.55]

a modeling approach to obtain the weightings of factors for the purpose to overcome the inconsistency in decision-making. The implementation of AHP is described in the following three steps.

(1) Establishing hierarchical model. The complex issue is decomposed to the combination of interrelated elements. The elements are classified to different stages according to their properties and relationships, forming the hierarchical model including maximum layer, intermediate layer and the bottom layer generally. The element in upper layer dominates all elements in adjacent lower layer.

In proposed method, the hierarchical model is showed in Fig. 3. The objective layer has an element which is the safety index, dominating all elements in lower layer. The rule layer contains seven elements, which are the indices of flammability, explosion, reactivity, reaction heat, yield, temperature, pressure. The weightings obtained in the end represent the contributions of each element to safety index.

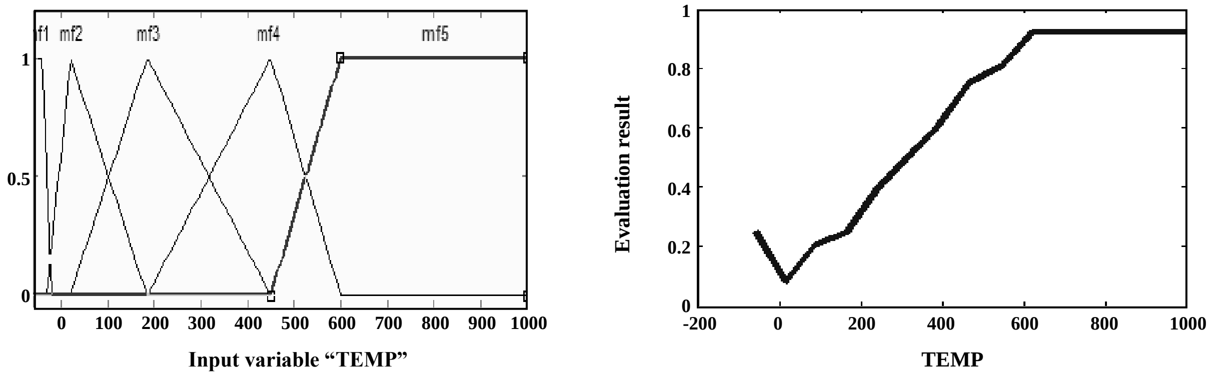

Fig. 1: Fuzzy intervals and fuzzy inference surface of temperature index.

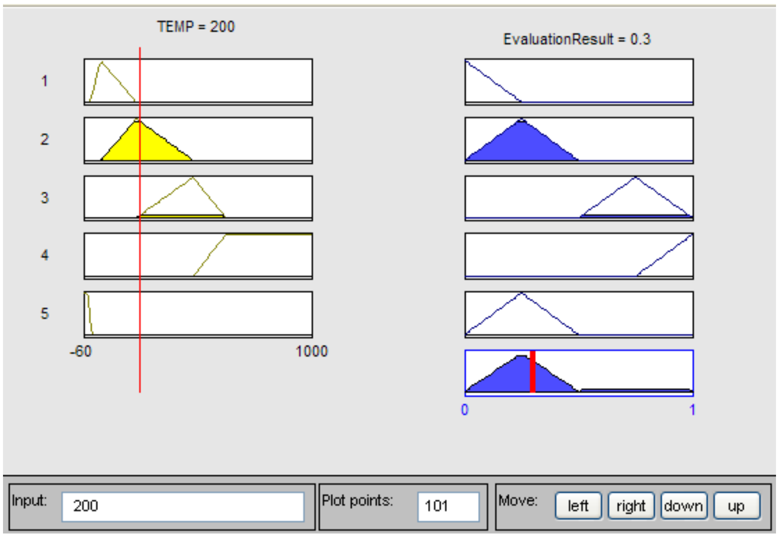

Fig. 2: Fuzzy evaluation of temperature index.

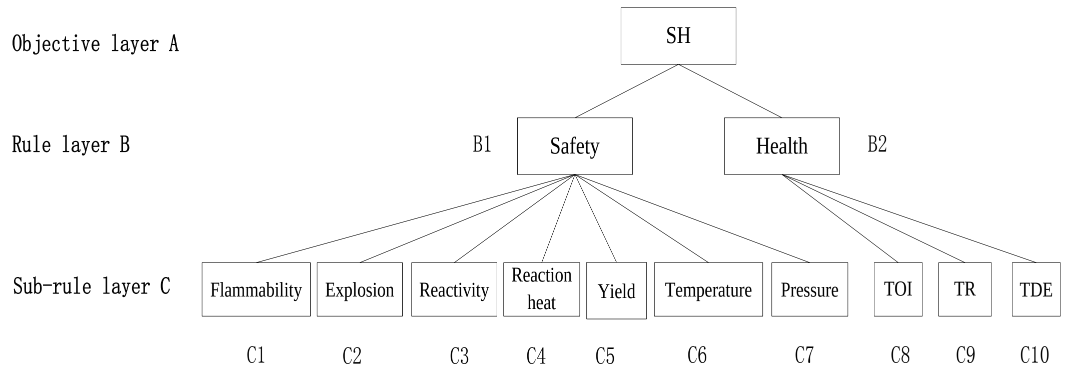

Fig. 3: Hierarchical model based on AHP.

Table 3: Judgement matrix for rule layer.

A	B1	B2
B1	1	2
B2	1/2	1

Table 4: Judgement matrix for B1 in sub-rule layer.

B1	C1	C2	C3	C4	C5	C6	C7
C1	1	1	2	2	4	3	3
C2	1	1	2	2	4	3	3
C3	1/2	1/2	1	1	3	2	2
C4	1/2	1/2	1	1	3	2	2
C5	1/4	1/4	1/3	1/3	1	1/2	1/2
C6	1/3	1/3	1/2	1/2	2	1	1
C7	1/3	1/3	1/2	1/2	2	1	1

Table 5: Judgement matrix for B2 in sub-rule layer.

B2	C8	C9	C10
C8	1	1/3	1/4
C9	3	1	1/3
C10	4	3	1

(2) Judgment matrix. Assuming to compare the impacts of n factors, expressed by X={x_1, ..., x_n}, to a factor Z, judgment matrix A=$(a_{ij})_{n\times n}$ is formed by the way of pairwise comparison. The a_{ij} called comparison factor is the comparison result between x_i and x_j. The larger of a_{ij} value represents x_i has the greater impact on Z than x_j.

According to the hierarchical model, B1,B2 represent safety and health variable in rule layer. C1～C10 represent flammability, explosion, reactivity, reaction heat, yield, temperature and pressure, TOI, TR, TDE respectively. Comparison factor is obtained by the way of pairwise comparison of above variables in the same layer. Consequently, judgment matrix of rule layer is established as showed in Table 3. Judgment matrix of for safety and health in sub rule layer is showed in Tables 4 & 5. The value of comparison factor is determined based on the priority of inherent safety principle which the index belongs to. In other words, the index in the higher stage of inherent safety principle has more contribution to inherent safety than the ones in the lower stage.

$$A=\left[B_{i,j}\right]_{2\times 2}\ ,\ B1=\left[C_{i,j}\right]_{7\times 7}\ ,\ B2=\left[C_{i,j}\right]_{3\times 3} \tag{1}$$

(3) Determination of weighting vector and consistency test. For judgment matrix, the eigenvector W can be calculated by substituting the three judgment matrixs in Equation (1) into Equation (2) respectively, which is the weighting vector for the maximum eigenvalue λ_{max} after being standardized. The weighting vector expresses the order of importance of the n factors. Consistency test aims to eliminate the inconsistency among the factors by calculating the consistency ratio. It indicates high consistency when the consistency ratio is less than 0.1.

$$AW=\lambda_{max}W \tag{2}$$

The weighting vector and consistency test result are showed in Table 6. The vector *k* is the weightings of safety and health indices in rule layer. Vector of f_1 and f_2 refer to the weightings of C1-C7 and C8-C10 indices

Table 6: Weighting vector and coincidence ratio of rule stage.

Layer	Weighting vector	Consistency ratio
Rule layer (B1,B2)	k =[0.6667,0.3333]	0
Sub-rule layer (C1-C7)	f1 =[0.2501, 0.2501, 0.1437, 0.1437, 0.0500, 0.0813, 0.0813]	0.0060
Sub-rule layer (C8-C10)	f2 =[0.1199, 0.2721, 0.6080]	0.0639

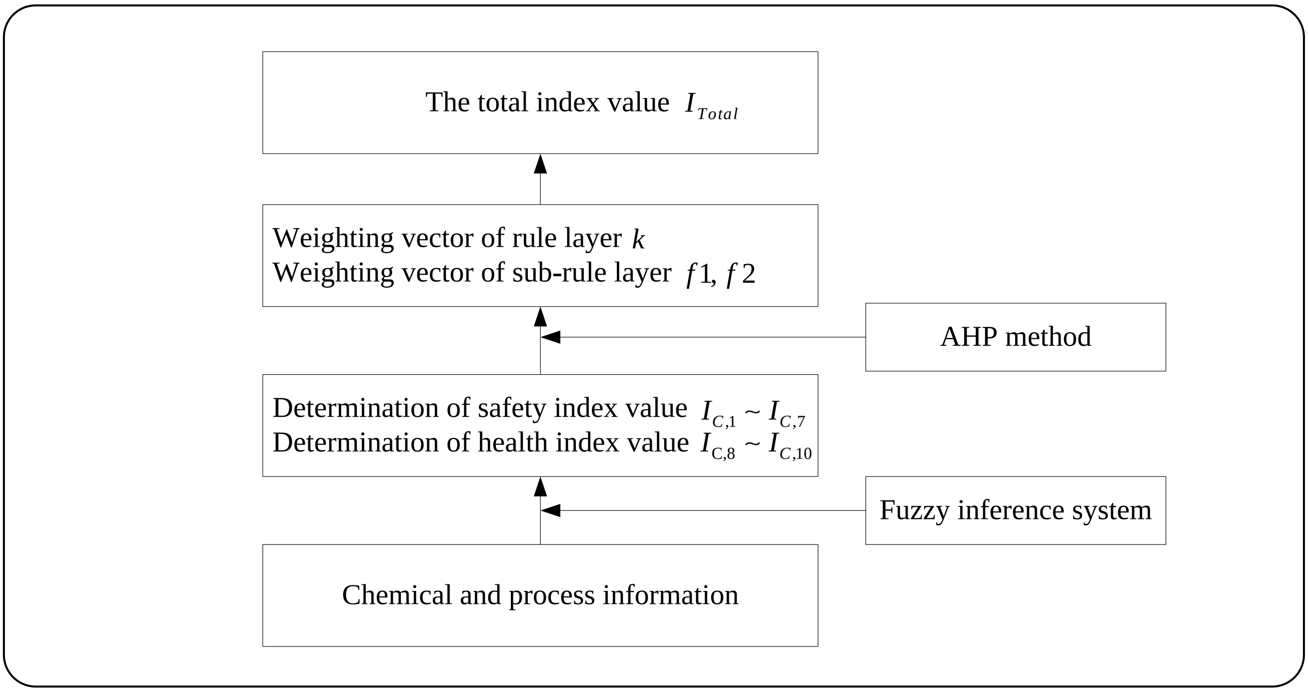

Fig. 4: Assessment procedure of proposed method.

in sub-rule layer respectively. The consistency ratio is 0,0.0060,0.0639, indicating high consistency among indices.

Assessment procedure

The assessment procedure is showed in Fig. 4. Inputing chemical and operation information, values of safety and health indices can be evaluated by fuzzy inference system. Then, safety and health indices weightings are obtained by AHP method. Finally, the total inherent safety index value can be calculated by the eqations (3)-(5). In the equations, I_{Total} means the total index value. I_S, I_H refer to safety and health index value respectively. k_1, k_2 mean elements in vector k . Similarly, $f1_i$ means elements in vector *f1* and $f2_j$ means elements in vector *f2*. $I_{C,i}$ refers to index in sub-rule layer C.

$$I_{Total} = k_1 I_S + k_2 I_H \tag{3}$$

$$I_S = \sum_{i=1}^{n=7} f1_i I_{C,i} \tag{4}$$

$$I_H = \sum_{\substack{j=1\\i=8}}^{\substack{m=3\\n=10}} f2_j I_{C,i} \tag{5}$$

APPLICATION AND DISCUSSION

The proposed IPI is applied to assess nine routes for manufacturing acetic acid as a case study. The details of the nine process routes are presented by Palaniappan [7,16], showed in Table 7.

The properties of all chemicals in above nine process routes are showed in Table 8, which are from MSDS and International Chemical Safety Cards (ICSCs) database [37]. LC50 data is converted to standard value with 2 hour exposure time by the equation (4) and (5).

For gas or vapor,

Table 7: Information of acetic acid process routes.

Number	Process route	Reactions involved	Temperature (℃)	Process Yield (%)	Reaction phase	Pressure (atm)	-ΔH (kJ/g)
1	Halcon vapor phase oxidation	Ethylene+oxygen→acetic acid	215-250	60	Vapor	10-20	6.374
2	Ethylene oxidation	Ethylene+oxygen→acetic acid	150	80	Vapor	4.5	6.374
3	Butane oxidation	Butane+oxygen→acetic acid+water	150-200	75	Liquid	56	8.185
4	Huels butene oxidation	Butene+oxygen→acetic acid + formic acid	180-240	46	Vapor	2-30	4.4
5	Acetaldehyde oxidation	Acetaldehyde+oxygen→acetic acid	60-80	95	Liquid	3-10	4.528
6	Ethane oxidation	Ethane+oxygen→acetic acid+water	150-450	25	Gas	15-30	9.809
7	Ethanol oxidation	Ethanol+oxygen→acetic acid+water	60-115	90	Liquid	1-4	7.593
8	Low-pressure carbonylation	Methanol+carbon monoxid→acetic acid	150-200	99	Liquid	4-15	1.532
9	High-pressure carbonylation	Methanol+carbon monoxid→acetic acid	250	99	Liquid	700	1.532

Table 8: Properties of chemicals in process routes.

Chemical	Molecular formula	UEL-LEL (%)	Boiling point (℃)	Flashing point (℃)	NFPA	LD50 (mg/kg)	LC50 (mg/m^3)	LC50 (2h) (mg/m^3)	TLV (ppm)
Ethylene	C_2H_4	33	-104	<-40	2	-	420000(2h)	420000	200
Butane	C_4H_{10}	6.6	-0.5	-60	0	-	658000 (4h)	465346	1000
Butylene	C_4H_8	8.4	-6	<-40	0	-	420000(2h)	420000	200
Formic acid	HCOOH	33	101	69	0	1100	15000(15min)	42430	5
Acetaldehyde	CH_3CHO	5.6	20.2	-38	2	1930	37000(0.5h)	74000	200
Ethane	C_2H_6	9.5	-89	<-40	0	-	658000(4h)	465346	1000
Ethanol	CH_3CH_2OH	15.7	79	13	0	7060	37620(10h)	16820	1000
Methanol	CH_3OH	39.5	65	12	0	5628	83776(4h)	59250	200
Carbon monoxide	CO	61.7	-191.4	<-50	0	-	2069(4h)	1460	25

$$LC50(2[h]) = LC50(x[h]) \times (x/2)^{1/2} \quad (4)$$

For mist or dust,

$$LC50(2[h]) = LC50(x[h]) \times (x/2) \quad (5)$$

The data of these chemicals are input into the developed fuzzy inference system to obtain the special index value. All chemicals in each process route are assessed respectively, the highest index value of which is treated as the end value of this route. The index I_S value is calculated by Equation (2), and the index I_H value is calculated by Equation (3). Finally, the total index value I_{Total} is obtained by Equation (1). Assessment results of the nine acetic acid process routes are showed in Table 9, which are ranked as showed in Fig. 5.

From the row of Table 9, it can be concluded that ethanol oxidation route is the inherently safer route, which has the lowest value 0.368. Huels butene oxidation route is the most hazardous one, which has the highest value 0.521. Comparing the $I_{C,1}$ value, it shows that all process routes have flammability hazard, because nearly all chemicals have very lower flashing point. Similarly, the value of $I_{C,4}$ indicates these process routes have highly reaction heat hazard, and the value of $I_{C,9}$ reveals the process route has highly respiratory toxicity hazard when hazardous vapor is leaked in processing. By comparing special single index value, process routes can be ranked

Table 9: Assessment result for acetic acid process routes.

Process route	$I_{C,1}$	$I_{C,2}$	$I_{C,3}$	$I_{C,4}$	$I_{C,5}$	$I_{C,6}$	$I_{C,7}$	$I_{C,8}$	$I_{C,9}$	$I_{C,10}$	I_S	I_H	I_{Total}
Halcon vapor phase oxidation	0.920	0.269	0.500	0.920	0.375	0.397	0.316	0	0.648	0.368	0.578	0.400	0.519
Ethylene oxidation	0.920	0.269	0.500	0.920	0.218	0.163	0.142	0	0.648	0.368	0.537	0.400	0.491
Butane oxidation	0.920	0.094	0.080	0.920	0.241	0.198	0.563	0	0.634	0.250	0.471	0.325	0.422
Huels butene oxidation	0.920	0.269	0.080	0.920	0.560	0.370	0.409	0.429	0.648	0.701	0.532	0.499	0.521
Acetaldehyde oxidation	0.920	0.094	0.500	0.920	0.080	0.233	0.228	0.343	0	0.368	0.499	0.287	0.428
Ethane oxidation	0.920	0.094	0.080	0.920	0.759	0.750	0.409	0	0.634	0.250	0.529	0.325	0.461
Ethanol oxidation	0.879	0.174	0.080	0.920	0.080	0.207	0.128	0.080	0	0.250	0.438	0.228	0.368
Low-pressure carbonylation	0.920	0.754	0.080	0.630	0	0.198	0.250	0.181	0.920	0.368	0.557	0.267	0.460
High-pressure carbonylation	0.920	0.754	0.080	0.630	0	0.397	0.892	0.181	0.920	0.368	0.625	0.267	0.506

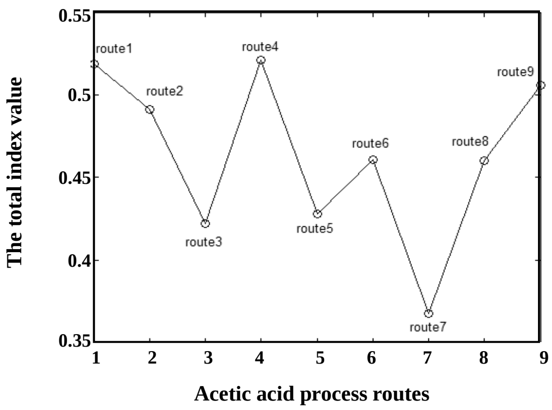

Fig. 5: Ranking of acetic acid process routes.

in the order of safety level, such as $I_{C,6}$ index, Ethane oxidation is the most hazardous one. These routes has lower hazard for Halcon vapor phase oxidation, Huels butene oxidation, High-pressure carbonylation. Others, i.e. Butane oxidation, Acetaldehyde oxidation, Ethanol oxidation, Low-pressure carbonylation have more moderate and closely reaction temperature. Finally, Ethylene oxidation has the most safety process temperature. In the same way, process routes can be ranked just by I_S or I_H value alone. Besides the comparison in sub-index is convenient to indentify hazard and take measure to develop inherently safety process, the total index value I_{Total} is relatively objective conclusion to help decision-making.

As Table 9 showed, all index values in applied assessments are normalized into [0,1], and its accuracy is 0.001, which has higher precision in assessment result. The main factors which may lead to error in assessment result is analized as follow. During evaluation process, the most important points to obtain accurate calculation result are evaluation result of fuzzy inference system and index weighting by AHP. In the fuzzy inference aspect, hierarchic classification and fuzzy intervals of index have strong effect on evaluation result. However, if they change in a small range, the effect on evaluation result can be negligible. Moreover, since the curve in Fig. 1 is continuous, small changes of input value can not cause a major change in the results, which reduce the possibility of error. In the aspect of index weighting, determination of comparison factor in judgment matrix is an important influence factor. Although it is just based on inherent safety principles, value of comparison factor gived should meet the requirement of applied assessment. The result showed in Table 6 indicates that weighting vetor obtained by AHP has higher precision.

The case studied involves similar chemicals and process condition in process routes, which challenge the discrimination ability of assessment method. The routes assessed here have different total index values, which indicates it has better discrimination in assessing similar alternatives.

CONCLUSIONS

Developing inherently safer process based on inherent safety guidewords in early stage always is better than adding on complicated and costly safety protection system in late stage. But all inherent safety guidewords are qualitative, not easy to be implemented and measured in design. Indexing method provides quantitative means to measure the level of inherent safety. The available methods have several disadvantages, especially the subjectivity in index interval and weighting. In this work, we provide a quantitative assessment approach to reveal both safety and health hazards in preliminary design Stage. The proposed method partly overcomes the shortcomings by effort in the following two aspects: (1) The uncertainty of assessment is reduced by the application of fuzzy method, which reduce the subjectivity of the determination of index value by applying fuzzy inference system. Meanwhile, the passive impact of medium variable in fuzzy inference is eliminated; (2) The index weighting is calculated by AHP considering index contribution in assessment procedure. Actually, The method has better extendibility of allowing user to add other indices according to the available information in different stage. The proposed method has been applied to acetic acid case study. The result demonstrates that it has good applicability, contributing to decision-making in early stage.

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