SCREENING ALTERNATIVE CHEMICAL ROUTES BASED ON INHERENT CHEMICAL PROCESS PROPERTIES DATA: METHYL METHACRYLATE CASE STUDY

(Date received: 7.4.2009)

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ABSTRACT

In 1988 a campaign called Responsible Care was initiated as a response to the adverse publicity of the Bhopal disaster. The initiative commits chemical industries to improve safety, health, and environmental (SHE) performance. Inherent safety concept can be incorporated at any stage of process lifecycle. However, the best results will only be achieved if it is implemented during the initial research and development (R&D) phase, when chemists and engineers are considering different choices of process alternatives, besides making fundamental and yet critical decisions such as type of raw materials and operating conditions to be used throughout the process. Process hazards assessment during conceptual stage is important since degree of freedom for making changes is still high and the associated cost is low. Besides inherent safety features can be adopted most effectively. Alternative process routes screening during the R&D stage involves the assessment of huge number of chemical routes - sometimes there can be up to hundreds of them. However, time and information available at this point are very limited; thus simple and swift approaches are highly in demand. This paper presents the methods for evaluating SHE performance of chemical processes based on inherent chemical and process properties. To ensure their practicality and applicability, the methods require data which is readily acquired from Material Safety Data Sheet (MSDS) and process reaction chemistry. The methods are applied on six methyl methacrylate (MMA) manufacturing routes. The results show that the isobutylene based route (i-C4) is the best process from inherent safety aspect and the ethylene via methyl propionate based route (C2/MP) is the best one from inherent health and environmental criteria. Finally, multi-criteria decision-making tool is applied to select a route with the optimised SHE benigness level. Based on the study, the C2/MP is regarded as the best route with the optimum performances in the SHE aspects. The case study analysis shows that the methods are capable of comparing different design concepts by their individual S, H, E criteria as well as the optimised SHE aspect altogether effectively.

Keywords: *Hazard Evaluation; Process Design; Process Development; Reaction Chemistry; Route Selection*

1.0 INTRODUCTION

Nowadays, sustainability has become the core concept when defining desired long-lasting state. Sustainability is often defined as ‘meeting the needs of the present without compromising the ability of future generations to meet their own need’ [1]. EU has adopted sustainable development as one of its central objectives. IPPC and REACH are among the EU directives that demand safety, health, and environmental (SHE) aspects to be taken into consideration in earlier phase of process development and design.

The inherent safety concept professes that potential process hazards should be identified as early as possible – ideally when the process is still ‘on paper’ [2]. Inherently safer design (ISD) is an approach that focuses on elimination or reduction of hazard from a process. Unlike extrinsic safety which depends on add-on system, procedure/management, and human intervention to control or manage hazard, intrinsic safety deals with the process property itself – thus the safer characteristic of the process is permanent and inseparable.

Generally, inherent safety property depends on the chemicals and operating conditions of a process. These two critical decisions are made at the very early stage of research and development (R&D) based on a limited amount of process information. At this stage, the feasibility of a number of chemical process routes is studied. Chemical process route can be defined as the raw material(s) and the sequence of reaction steps that converts them to the desired product(s) [3]. Economic used to be the decisive criteria in process route selection [3]. Route that is analyzed to be the most profitable during early process screening has often been chosen as the one to be considered for process development. However, the paradigm has gradually changed towards better appreciation of process performance in SHE aspects. The challenge is how to evaluate the aspects during the R&D stage when the only process-related information available is the reaction chemistry pathway.

This paper proposes a simple approach to assess chemical hazards from safety, health, and environmental perspectives at inherent level. Many engineers do not realise that inherent level study is fundamental to the industrial practice of chemical engineering and applied chemistry because it relies on the underlying chemistry and physics of the materials, chemical transformations, and molecular separations involved in chemical processing [4]. This paper aims to highlight the significance of basic knowledge on chemistry in determining the inherent hazard of a chemical process. Early process evaluation will help engineers in making sound selection of reaction chemistry pathway to be developed, which will have major impacts on later performances (*e.g.* construction, operation, decommissioning) of the process.

2.0 CHEMICAL ROUTES SCREENING BASED ON INHERENT HAZARD ASSESSMENT

Research and development is a stage where the chemical synthesis route is selected. The process designer has the greatest opportunity to incorporate inherent safety principles, since major decisions are mainly done in this stage [5]. Various methods have been developed for assessing inherent safety, health, and environmental friendliness of chemical synthesis routes. Due to time and information constraints, majority of the methods were developed as index-based. For R&D stage assessment, the index must be simple, swift, and transparent, such that it can be easily applied. Most importantly, the index must require only data which is readily available at this stage.

Since a process lifecycle starts with R&D, no data about the process is yet available. Once the target product has already been chosen, the only process information that can be obtained is reaction chemistry pathway from literature, such as encyclopedias, patents, journals, and *etc*. Reaction chemistry provides brief information about the chemicals involved in the process as well as operating conditions, typically reaction phase, temperature, pressure, and yield, which govern the development of the indexes. The earlier version of the indexes relies solely on this information; while the later version involves more detailed works and calculations - intending to produce more reliable and comprehensive assessments.

2.1 Existing Methods

Various indexes are available for inherent SHE evaluation of chemical processes throughout process development and design phase. Some were developed for the R&D stage with the aim and scope of application as previously described. Some of the methods evolve to a later stage of preliminary design, basic engineering, and detailed design, depending on their extent of research interest. Nonetheless, all of them share the same objective of assessing the inherent hazard of a process before construction phase begins. The later the assessment is performed, the cost of making changes becomes more expensive and the opportunity to integrate process with ISD features gets smaller [5].

Among safety, health, and environment criteria, methods for inherent safety assessment are the most well researched and widely available. Several of the methods that can be mentioned here are the Prototype Inherent Safety Index; PIIS [3], Inherent Safety Index; ISI [6], Hazard Identification and Ranking; HIRA [7], Rapid Risk Analysis Based Design; RRABD [8], Safety Weighted Hazard Index; SweHI [9], Simple Graphical Method [10], and *i*-Safe [11]. On top of the assorted methods, expert judgment and point of view about this subject is also available [12].

For evaluating inherent environmental hazard of chemical process, various methods have been proposed, namely the Environmental Hazard Index; EHI [13], Waste Reduction Algorithm; WAR [14], Atmospheric Hazard Index; AHI [15], Global Environmental Risk Assessment Index; GERA [16], Inherent Environmental Toxicity Hazard; IETH [17], and Environmental Consequence Index; ECI [18].

Compared to safety and environment, health is the least discussed and researched process characteristic at inherent level. Studies on the development of indexes for an exclusive inherent health assessment of chemical process routes are relatively new. Among the existing methods are the Occupational Health Hazard Index; OHHI [19], Process Route Healthiness Index; PRHI [20], Inherent Occupational Health Index; IOHI [21-22], Health Index; HI [23], and Occupational Health Index; OHI [24].

Several comparisons of the index methods have also been published [25] mainly for inherent safety methods [26-28]. Environmental and health methods were compared by Hertwich *et al*. [29] and Koller *et al*. [30]. The latest one was by Adu *et al*. [31] who made a comprehensive comparison of methods for assessing safety, health, and environmental hazards.

3.0 CHEMICAL PROCESSES SCREENING BASED ON CHEMISTRY DATA

The objective of this paper is to demonstrate how a chemical process route can be assessed in the R&D stage for its safety, health, and environmental hazard based on the chemistry data. A quick but sound approach is in need since a high number of alternative routes have to be evaluated within a limited time.

Two types of data can be acquired from reaction chemistry: 1) chemical substances and 2) process conditions. This paper focuses on the first data, which is the hazard potentially posed by chemical substances. Although for a chemical process, potential hazard is a function of both the chemical and the process, this paper aims to look at the inherent characteristics of process concepts merely from the chemical substances standpoint. Thorough understanding about chemical hazard is critical especially at the R&D stage since the upmost principle of ISD is *elimination*. Ideally, hazardous chemical should be eliminated so that the hazard and potential risk can be totally avoided. However, in most cases eliminating chemical substance from a process is not possible; therefore *substitution* should be opted as the next principle. Substituting a chemical with a less hazardous one, but posing an equivalent functional property requires adequate data on chemical hazard.

Therefore, here an approach to evaluate inherent SHE hazard of chemical process routes based on the chemical hazard data is proposed. To ensure its simplicity and wide applicability, the approach requires only those data that are readily available from Material Safety Data Sheets (MSDSs) or International Chemical Safety Cards (ICSCs) or other source of similar data. The existing inherent SHE indexes were studied in terms of their basic principles and parameters used for evaluating the process properties. In inherent safety, parameter types are relatively well established [25], but health and environmental criteria have much more uncertainty and are more pragmatic [32]. Based on the studies, common parameters that are used for assessing chemical hazard are identified. The parameters are: flammability, explosiveness, toxicity, and reactivity for safety; material state/physical appearance, volatility, chronic toxicity, and adverse impact for health; atmospheric, aquatic, and terrestrial toxicity for environment. These chemical properties are selected based on their propensity to cause exposure to hazards or their properties that may pose unwanted conditions as a result of the exposure. There are various means of expressing the parameters. This paper however, recommends the following chemical properties for each SHE aspect.

Table 1: Chemical properties for inherent SHE evaluation

Criteria	Parameter	Chemical property
Safety	Flammability	Flash point
	Explosiveness	Upper explosive limit (UEL)-Lower EL
	Acute toxicity	TLV-STEL
	Reactivity	Chemical interaction/incompatibility
Health	Material state	Form/phase
	Volatility	Boiling point
	Chronic toxicity	8-*h* exposure limit (OEL)
	Adverse impact	*R*-phrase
Environment	Atmospheric toxicity	LC50 inhalation
	Aquatic toxicity	LC50 aquatic
	Terrestrial toxicity	LD50

These chemical properties can be easily found from almost all MSDSs. Depending on user's preference, other chemical properties, classification, or labeling can also be used, *e.g.* NFPA, vapor pressure, *etc*. The significance of other parameters in influencing the level of chemical hazard is also acknowledged. However apart from those being mentioned here, the others are not included either because they require information beyond the R&D stage or they involve calculation works, *e.g.* group contribution methods, which do not fit the purpose of this paper.

4.0 INHERENT CHEMICAL SHE HAZARD EVALUATION

The approaches taken in evaluating chemical hazard are presented for safety, health, and environmental criteria.

4.1 Inherent Chemical Safety Hazard

For safety, the Inherent Safety Index, ISI [6] is selected as the basis method for performing the assessment. Other methods may also be used according to user's choice. The calculation of the ISI is based on the score assigned for each parameter (see Table 2). Each parameter is divided into sub-ranges that receive a score, which represents the contribution on the inherent safety level. The minimum score for each parameter is set to zero, while the maximum score is set in a way to represent the weighting effect on the parameter, which is based on the work done and the experts judgment [12]. It is assumed that a wider score range implies a greater impact for overall safety evaluation.

The inherent chemical safety index is calculated for each alternative process route before the results are compared for their relative safety level. The calculations of the safety index are made based on the basis of the worst situation. The approach of the worst case describes the most risky situation that can appear. Flammability, explosiveness, and toxicity scores are determined separately for each substance in the process. The scores are then totaled up and the maximum score received by a substance is taken to represent the reaction step for those particular parameters. Same goes to reactivity subindex – the maximum value of reactivity based score is used in the index calculation for each reaction step (*see Equation 1*).

$$\text{Inherent chemical safety index} = (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{INT,\, max} \quad (1)$$

The score formation and the index have been formulated in such a way that a lower index value represents an inherently safer process based on the chemical properties.

Table 2: Score assignment for chemical Inherent Safety Index [33]

Parameter	Symbol	Score formation	Score
Flammability	I_{FL}	Non-flammable	0
		Combustible (flash point > 55 °C)	1
		Flammable (flash point ≤ 55 °C)	2
		Easily flammable (flash point < 21 °C)	3
		Very flammable (flash point < 0 °C	4
		and boiling point ≤ 35 °C)	
Explosiveness (UEL-LEL, vol%)	I_{EX}	Non explosive	0
		0 - 20	1
		20 - 45	2
		45 - 70	3
		70 - 100	4
Toxic exposure (*ppm*)	I_{TOX}	TLV > 10000	0
		TLV ≤ 10000	1
		TLV ≤ 1000	2
		TLV ≤ 100	3
		TLV ≤ 10	4
		TLV ≤ 1	5
		TLV ≤ 0.1	6
Reactivity	I_{INT}	Heat formation	1-3
		Fire	4
		Formation of harmless, non-flammable gas	1
		Formation of toxic gas	2-3
		Formation of flammable gas	2-3
		Explosion	4
		Rapid polymerisation	2-3
		Soluble toxic chemicals	1

Table 3: Score assignment for chemical Inherent Occupational Health Index [21-22]

Parameter	Symbol	Score formation	Score
Material state	I_{MS}	Gas	1
		Liquid	2
		Solid	3
Volatility	I_V	*Liquid and gas*	
		Very low volatility (boiling point > 150 °C)	0
		Low (150 °C ≥ boiling point > 50 °C)	1
		Medium (50 °C ≥ boiling point > 0 °C)	2
		High (boiling point ≤ 0 °C	3
		Solid	
		Non-dusty solids	0
		Pellet-like, non-friable solids	1
		Crystalline, granular solids	2
		Fine, light powders	3

Chronic toxicity	I_{EL}	*Vapor (ppm)*	
		OEL > 1000	0
		OEL ≤ 1000	1
		OEL ≤ 100	2
		OEL ≤ 10	3
		OEL ≤ 1	4
		Solid (mg/m³)	
		OEL > 10	0
		OEL ≤ 10	1
		OEL ≤ 1	2
		OEL ≤ 0.1	3
		OEL ≤ 0.01	4
Adverse impact (*R*-phrase)	I_R	*Acute*	
		No acute toxicity effect	0
		R36, R37, R38, R67	1
		R20, R21, R22, R65	2
		R23, R24, R25, R29, R31, R41, R42, R43	3
		R26, R27, R28, R32, R34, R35	4
		Chronic	
		No chronic toxicity effect	0
		R66	1
		R33, R68/20/21/22	2
		R62, R63, R39/23/24/25, R48/20/21/22	3
		R40, R60, R61, R64, R39/26/27/28, R48/23/24/25	4
		R45, R46, R49	5

4.2 Inherent Chemical Health Hazard

The approach for inherent chemical health hazard evaluation is similar to that for safety assessment. The Inherent Occupational Health Index, IOHI [21-22] is used as a reference in score formation of the parameters and index formulation. The IOHI estimates the inherent health hazard level of a route by taking into account the exposure potential and the potential harm as a result of the exposure. Description of the parameter scoring concept, score range, and index calculation is as already explained for safety index. The scores of health parameters are summarised in Table 3 and the calculation of the index is presented in *Equation 2*.

$$\text{Inherent chemical health index} = I_{MS,max} + I_{V,max} + I_{EL,max} + I_{R,max} \quad (2)$$

Like the inherent safety index, a lower index value indicates a lower inherent health hazard level of a process.

4.3 Inherent Chemical Environmental Hazard

The evaluation of inherent environmental hazard of chemical process routes involves more complicated calculations compared to the score-based system, which is used in inherent safety and health indexes. The Environmental Hazard Index, EHI [13] is among the earliest method developed for assessing alternative process routes for environmental friendliness during the R&D stage. The EHI estimates the environmental effects of a chemical to the aquatic and terrestrial ecosystems. In the event of a loss of containment, these two ecosystems are most affected [34-35]. Gunasekera and Edwards [15] extended the research by developing the Atmospheric Hazard Index; AHI before combining the AHI with the EHI aquatic and terrestrial indexes to come out with the Inherent Environmental Toxicity Hazard, IETH [17].

The assessment of the environmental toxicity effect requires predicted environmental concentrations (PEC) to be calculated for the air, water, and soil compartments using Mackay's fugacity model [36-37]. However, the task is complex – it requires massive amount of information and it involves tedious calculations, which does not fit a criteria of a simple and swift index. Therefore, here the inherent environmental friendliness of a route will be evaluated based on the chemical toxicity data only. Since the EHI, AHI, and IETH were developed for a total loss of containment-type of event, acute toxicity data will be used: $LC50_{inhalation}$ for atmospheric toxicity, $LC50_{aquatic}$ for water toxicity, and $LD50$ for terrestrial toxicity. These data is provided by almost all chemicals' MSDSs.

The inverse of the acute toxicity limit value is a measure of toxicity potential for a chemical [38]. Thus, it is proposed here that the inherent chemical environmental index is calculated as follows:

Inherent chemical environmental index =

$$\frac{1}{LC50_{inhalation}} + \frac{1}{LC50_{aquatic}} + \frac{1}{LD50} \tag{3}$$

Since these three parameters have different units, their values need to be normalised before they can be totaled up. Similar to the previous two indexes, a lower environmental index value suggests a lower inherent environmental hazard of a process.

5.0 CASE STUDY

The inherent SHE hazard assessment approach has been tested on six potential chemical process routes to methyl methacrylate (MMA). This case study has been widely used to demonstrate various hazard assessment methods at inherent level. The six process routes considered are:

- Acetone cyanohydrin based route (ACH)
- Ethylene via propionaldehyde based route (C2/PA)
- Ethylene via methyl propionate based route (C2/MP)
- Propylene based route (C3)
- Isobutylene based route (*i*-C4)
- Tertiary butyl alcohol based route (TBA)

From the literature, the ACH based route comprises a total of six reaction steps. However, only steps 2, 3, and 4 – which are the main manufacturing steps, will be considered in the assessment to ensure consistency with the remaining five routes [10]. The process routes are discussed in more detail in Ullmann's Encyclopedia [39], Edwards and Lawrence [3], and Rahman *et al*. [40].

5.1 Results and Discussions

Table 4 summarises the results of the inherent SHE hazard index calculations for the MMA process routes. In order to ease the results presentation, the index values are normalised to the same magnitude range of 0 to 10. The routes are ranked by their SHE hazard level (*Figure 1*).

Table 4: Summary of the SHE index values of MMA process routes

Normalised						
Route	**Safety index**	**Health index**	**Environ. index**	**Safety index**	**Health index**	**Environ. index**
ACH	28	34	6.87	4.29	4	10
C2/PA	36	43	2.33	10	10	3.31
C2/MP	24	28	0.09	1.43	0	0
C3	34	40	0.52	8.57	8	0.64
i-C4	22	31	1.48	0	2	2.06
TBA	23	29	1.50	0.71	0.67	2.08

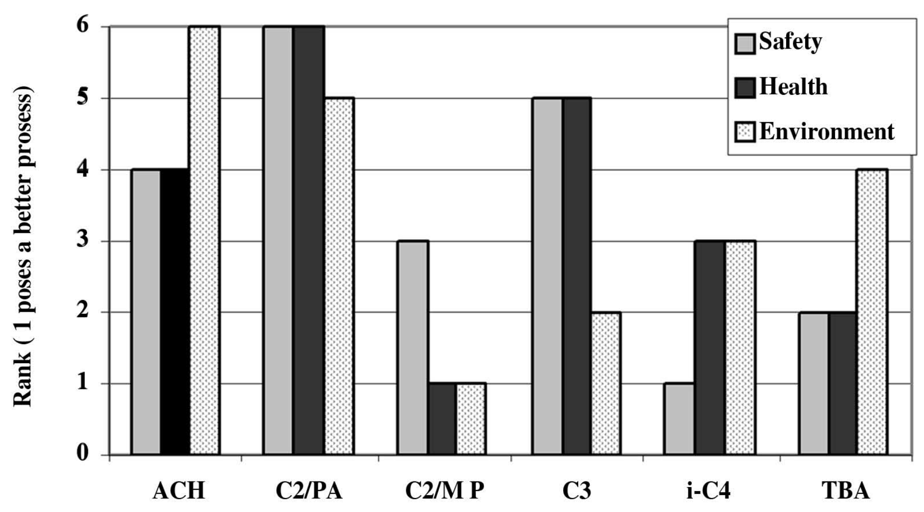

Figure 1: MMA routes rank order based on SHE index values

The index calculations indicate that the C2/PA based route has the largest potential hazard from safety and health aspects. Its impact on the environment is relatively high as well since the route is ranked as the second least environmental friendly process after the ACH. Apart from its large number of reaction steps, the C2/PA based route has several hazardous chemicals, such as carbon monoxide and formaldehyde. Carbon monoxide is a highly flammable substance, which contributes to a higher inherent chemical hazard from safety perspective. Meanwhile formaldehyde is a carcinogenic substance, which is a highly unfavorable health characteristic of a process. The presence of hydrogen cyanide and sulfuric acid in the ACH based route is among the main reasons for the process to be significantly hazardous to the environment compared to the other processes. Hydrogen cyanide for instance, is highly toxic in air, water, and terrestrial ecosystems.

On a positive note, the C2/MP is ranked as the best process option based on the health and environmental criteria. The least hazardous process from safety standpoint however is the *i*-C4. The presentation of the index values separately for the S, H, E criteria has the advantage of avoiding loss of information, which is often encountered in an integrated-type method. Here, the candidate processes can be screened based on their individual S, H, E characteristics at inherent level. In a case where users are interested to search for the most optimum process in all the SHE criteria, a multi criteria decision-making approach is recommended.

5.2 Multi Criteria Decision-making

Screening of a number of alternatives for process selection is challenging especially when more than one criteria is involved. It requires a careful evaluation of the advantages and disadvantages of different candidate processes with respect to different predetermined criteria. Various problem solving techniques are available, namely the Simple Additive Weighting (SAW), the Technique for Order Preference by similarity to the Ideal Solution (TOPSIS), and the Analytical Hierarchy Process (AHP), as well as outranking methods such as the Elimination and Choice Expressing Reality (ELECTRE) and the Preference Ranking Organisation Method for Enrichment Evaluations (PROMETHEE). The selection of the models is based on several evaluation criteria. Consistency, transparency, ease of use, realistic time and manpower resource requirements are among the deciding factors.

Here the SAW method is used to demonstrate how the optimum MMA process from the safety, health, and environmental criteria can be determined. According to the SAW method, the overall score of each process option is calculated by multiplying the value of the criteria for the process with the importance of the criteria (weight). Depending on the score formulation, the alternative with the highest or lowest score is selected as the preferred choice. In this case, a process with the lowest total score is the one with the most optimum SHE characteristics. Since usually various criteria are measured in different units or basis, the scores of the criteria have to be transformed to a normalised scale. This has already been approached in the previous section.

Criteria weighting is a vital component of the SAW method. The best way of assigning weight to predetermined criteria is based on some legislations, company policies or expert judgments. Upon none of these is available, a simple ranking method can be employed. The criteria are ranked in perceived order of importance: $c1>c2>\ldots>ci$. The weights are non-negative and sum to one. In this paper, for the purpose of demonstration it is assumed that safety criteria is slightly more important, with the other two criteria are assumed to be equally important. The calculations of the overall score for MMA candidate processes based on the SAW method and their ranking order are summarized in Table 5.

Table 5: Determination of an optimum MMA process based on SHE multi criteria

Weight:	***0.4***	***0.3***	***0.3***		
	Safety	**Health**	**Environment**	**Total score**	**Rank**
ACH	4.29	4	10	5.9	4-5
C2/PA	10	10	3.31	8.0	6
C2/MP	1.43	0	0	0.6	1
C3	8.57	8	0.64	6.0	4-5
i-C4	0	2	2.06	1.2	2
TBA	0.71	0.67	2.08	1.1	3

A lower score/rank 1 indicates a better process with an optimum performance based on S, H, E criteria

Based on the results, it is now becoming easier and more obvious to select the process with an optimum safety, health, and environmental performance for MMA production.

6.0 CONCLUSIONS

The development of a chemical plant starts with a simple chemical process routes screening during the R&D stage. The evaluation needs to be performed with extra care since any decision made at this point will affect the later stages of the process lifecycle. Besides process, chemical substance is one of the contributors to the hazard and risk profile for chemical plant facilities. Assessing the chemical hazard of a process at inherent level is very important so that a top-ranked inherent safety principle of elimination or substitution can be applied with the greatest opportunity.

In this paper, a simple and swift approach is proposed for evaluating the inherent safety, health, and environmental hazard of process routes based on chemical data. This index-based approach requires only those chemical-related information which can be easily found from MSDSs or other similar type of data sources. The parameters commonly used to describe chemical safety, health, and environmental hazards are identified and those that fit the scope of the approach are selected.

The results of the assessment allow alternative processes to be ranked by their relative inherent hazard level. Multi criteria decision-making tool can be applied to determine the process with an optimum performance in all the S, H and E aspects. The findings from such analysis can be further exploited to incorporate inherently safer design features when developing a chemical process based on the process concept.

For future research opportunities, uncertainties inherent in the process can be analysed and dealt with using methods such as Monte Carlo, rough sets or fuzzy sets to enhance the application of multi criteria or multiple attribute decision-making tools. ■

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