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Fuzzy Optimization for Screening of Sustainable Chemical Reaction Pathways

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Screening of chemical reaction pathway appears to be one of the most critical tasks in new chemical process development. Various methods for synthesis of chemical reaction pathway such as logic-centered, direct associative methods and optimization–based approaches have been proposed. However, majority of the previous works are focusing on economic and environmental performance; while very few have taken inherent safety and health into consideration. In order to develop a sustainable chemical reaction pathway, all inherent SHE aspects and economic should be considered. The application of inherent approach during early design stage allows the reduction and elimination of hazards intrinsically and avoids costly modification or add-on system. In this work, fuzzy optimization is adapted for screening of sustainable chemical reaction pathway by minimizing the impacts of inherent safety, health and environment whilst maximizing the economic performance. To illustrate the proposed approach, a case study on synthesis of methyl methacrylate (MMA) is presented.

1. Introduction

Screening of chemical reaction pathway is recognized as one of the most critical tasks in new process development. The most common mean of selection is based on the ranking of chemical reaction pathway for the pre-determined criteria. The ranking could be derived according to individual or multiple objectives which greatly affect the performance of chemical plants (Srinivasan and Nhan, 2007; Mansfield and Hawksley, 1998). Besides, various methods for synthesis of reaction pathway have also been proposed since early 1980's, which include logic-centered (Ugi and Gillespie, 1971; Hendrickson, 1971) and direct associative methods (May and Rudd, 1976). These methods recognize the fact that a number of structural subunits are available; in case where the molecules can be brought together using some standard reactions, the target molecule can be synthesized. Later, economic and environmental objectives (Crabtree and El-Halwagi, 1994) and life cycle analysis (Buxton et al., 1997) were introduced for reaction pathway synthesis. It is noted that majority of the previous works are focusing on economic and environmental performance; while very few take inherent safety and health into consideration. However, all these factors should be considered simultaneously in order to generate the highest benefit.
According to inherent safety concept (Kletz, 1984), the earlier hazards in a process are identified, the greater are the benefits. Earlier assessment allows potential hazards to be reduced or eliminated rather than controlled or managed by external add-on system. In particular, inherent concept introduces intrinsic analysis and countermeasures at early design stage so that to avoid the costly and extra

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efforts in engineering modifications. Apart from safety aspects, Kletz (1984) also proposed the inherent concept to be applied to environment and industrial hygiene as comprehensive protection to the people and the environment. This issue has become crucial after the establishment of several voluntary and legal requirements related to sustainability (Hook, 1996). Therefore, safety, health and environment (SHE) need to be taken into consideration towards achieving sustainable development. As shown in the literature (Gentile et al., 2003; Hassim and Hurme, 2010a; Iriarte et al., 2011), it is important to evaluate the inherent safety, healthiness and environmentally friendliness properties of a process in preliminary design stage.

For inherent safety, the earliest method proposed by Edwards and Lawrence (1993) is known as Prototype Index of Inherent Safety (PIIS). PIIS is the simplest method for ranking alternative reaction pathway based on inherent safety performance. However, the method poses some shortfalls such as dimensionality for overall index calculation, arbitrary assignment of score and weightage of each parameter. Later, Heikkila (1999) developed a more comprehensive and accurate method known as Inherent Safety Index (ISI). ISI involves reaction hazard in details by considering heat of reaction and reactivity. Besides, ISI also considers additional aspect of process equipment and layout in the assessment. Subsequently, numerous improved methods have been proposed, e.g. i-Safe (Palaniappan et al., 2002), fuzzy logic-based inherent safety index (Gentile et al., 2003) and Process Route Index (PRI) (Chan and Shariff, 2009).

For early inherent health analysis, the methods like Occupational Health Hazard Index (OHHI) (Johnson, 2001) and Process Route Healthiness Index (PRHI) (Hassim and Edwards, 2006) had been proposed to rank alternative chemistry pathways by their inherent healthiness properties. Nonetheless, those methods are not highly applicable because they require large amount of process data which are not easily obtained or are uncertain during the early stage. As improvement, Hassim and Hurme (2010a, b and c) had proposed suitable method dedicated for each stage. These include Inherent Occupational Health Index (IOHI) in process research and development, Health Quotient Index (HQI) in preliminary design and Occupational Health Index (OHI) in basic engineering stage. These three methods require only those data available in each design stage they are intended for.

Among the earlier methods for inherent environmental evaluation are Environmental Hazard Index (EHI) (Cave and Edwards, 1997) and Atmospheric Hazard Index (AHI) (Gunasekera and Edwards, 2003). Later, a combination method of the EHI and AHI was derived, which is known as Inherent Environmental Toxicity Hazard (IETH) (Gunasekera and Edwards, 2006). In general EHI, AHI and IETH focus on the environmental impacts in terms of aquatic, terrestrial and atmospheric hazard. Those methods consider catastrophic scenario where the total loss of containment to environment is assumed, whilst the hazard level of the chemical is evaluated based on its properties and quantity present in the plant. Apart from that, another method called Potential Environmental Index (PEI) was also proposed by Cabezas et al. (1997). PEI was derived from Waste Reduction Algorithm (WAR) by Hilaly and Sikdar (1994) which uses mass balance to identify and calculate the pollutant streams within the whole process.

The economy performance (EP) data could be expressed as cost of production (COP) or return of investment (ROI). COP denotes the operating cost based on unit mass of product, while ROI refers to the net profit from the investment. From the early analysis, the COP is further categorized into non-capital, variable and 20 % ROI COP (Edwards and Lawrence, 1993). 20 % ROI COP refers to the cost of production per unit mass which inclusive of 20 % of the total fixed investment (or capital cost). However, despite the advantages of inherent approach for effective hazard reduction, the question arises on the cost-effectiveness and operability of the concept in real industries (Gupta and Edwards, 2002). Edwards and Lawrence (1993) conducted inherent safety analysis on methyl methacrylate (MMA) production processes and revealed significant findings that the chemical and process scores as well as the total PIIS index values are highly correlated to the number of process steps. Therefore, simplification of process is able to engender inherently safer features in a plant. Kim et al. (2006) has conducted optimization based on safety and cost consideration for styrene monomer plant using Goal Performance (GP) and modified Summation of Weighted Objective Function (mSWOF). However with the conducted analysis by researches, it is noted that considering only safety without environment, economy performance and other parameters does not able to synthesize a holistic and sustainable chemical reaction pathway.

To promote sustainable process development, screening of alternative reaction pathways with the consideration of SHE and EP simultaneously is needed. To enable this, the suitable assessment and design decision methodologies are major determinant for synthesis of sustainable pathway (Jayswal et al., 2011). In this work, fuzzy optimization is adapted for the screening of sustainable chemical reaction pathway based on multi-criteria which minimize SHE whilst maximize EP. Fuzzy optimization determines the most desired alternative(s) in decision-making process (Tan and Cruz, 2004). A case study is solved to illustrate the proposed approach.

2. Case Study

To illustrate the proposed approach, a case study on methyl methacrylate synthesis (MMA) is presented. In a typical MMA production process, there are six commonly cited alternative pathways, which include (1) ACH – acetone cyanohydrin based route, (2) C2/PA – ethylene via propionaldehyde based route, (3) C2/MP – ethylene via methyl propionate based route, (4) C3 – propylene based route, (5) i-C4 – isobutylene based route, and (6) TBA – tertiary butyl alcohol based route. The choice of reaction pathway at early design stage is the key design decision that allows the adoption of inherently more benign features into the process (Edwards and Lawrence, 1993). Therefore, this evaluation is focused on early chemical design stage of process chemistry research and development (R&D) using the appropriate hazards and cost assessment indexes that have been developed for this particular stage.

Based on the literature (Edwards and Lawrence, 1993; Hassim and Hurme, 2010a; Gunasekera and Edwards, 2006; Garrett, 1989), the indexes of economy performance (EP), inherent safety (S), health (H) and environment (E) are summarized in Table 1. Note that EP index is measured based on 20% ROI COP (Edwards and Lawrence, 1993). Meanwhile, PIIS is used as the measurement of inherent safety. In this work, PIIS is selected because it is the earliest and simplest analysis on inherent safety. It sums up all process scores covering pressure, temperature and yield; and chemical score which involves inventory, toxicity, flammability and explosiveness (Edwards and Lawrence, 1993). On the other hand, IOHI (Hassim and Hurme, 2010a) is taken as inherent health index. IOHI systematically considers the physical and process hazards i.e. process mode, pressure, temperature, material phase, volatility, corosiveness; and health hazards based on exposure limit data and R-phase. This health index evaluates both long and short-term effects of chemical to health, which are the main element of any health hazard evaluation. As for environmental perspective, IETH (Gunasekera and Edwards, 2006) is used as inherent environmental index in this work. This index introduces comprehensive coverage of aquatic, atmospheric and terrestrial environmental impacts.

The aim of the analysis is to screen the chemical reaction pathway with maximum EP, while minimum negative impacts of SHE. In this work, as EP is measured in term of 20% ROI COP, therefore minimum 20 % ROI COP gives the maximum EP. Hence, the term of minimization of COP will be used at the latter part. Based on fuzzy optimization approach, a degree of satisfaction (λ) is introduced to trade off the difference of satisfaction amongst each parameter. To determine the λ of S, H, E and EP simultaneously, Eq (1) is included in the model. It is noted that the upper (S^U, H^U, E^U and EP^U) and lower (S^L, H^L, E^L and EP^L) fuzzy limits need to be pre-defined. For simplicity, linear relationship between the upper-lower bound and the limit of λ (0 to 1) is used. In here, the EP is expressed as COP and hence the target of minimizing EP is more applicable in this case. For minimization of COP, S, H and E, the lower index value which denotes less impacts or cost would desirably come closer to λ = 1. When the index value equals or lower than lower bound value, the λ = 1 and this shows the highest satisfaction.

$$\lambda_i \le \frac{X_i^U - X_i}{X_i^U - X_i^L} \tag{1}$$

where,

X = Parameters of consideration, X ∈ EP, S, H and E.

i = Process route, i ∈ ACH, C2/PA, C2/MP, C3, i-C4, TBA

Superscript U = Upper value of parameter X
Superscript L = Lower value of parameter X

To achieve the maximum λ, the optimization objective is shown as below:

$$\text{Maximize } \lambda \tag{2}$$

3. Results and Discussions

Compared to single objective, multiple optimization approach uses λ to represent the trade-off value over all the objectives, with the optimized reaction pathway portrays the highest λ values across all alternative pathways. By doing this, the impacts of more than one parameter could be considered simultaneously and the approach will suggest for the pathway that exhibits the best performance in all chosen criteria. Solving the fuzzy optimization model, TBA route is found with the highest λ value of 0.83. This indicates that TBA is the most desirable pathway amongst the other reaction pathways.

For more detailed analysis, all the parameters of the six reaction pathways are solved individually. The index values of each reaction pathway are compiled in Table 1. From economics point of view, C2/MP shows the lowest COP in terms of 20 % ROI while C2/PA incurs the highest COP. Meanwhile, the ACH route appears to be the second highest in COP criteria.

Table 1: EP, S, H and E Index Values for Six MMA Reaction Pathway

Category	Index	Reaction Pathway					
		ACH	C2/PA	C2/MP	C3	i-C4	TBA
Economics	COP	1591	1690	1290	1405	1420	1320
Safety	PIIS	41	79	52	67	49	47
Health	IOHI	44	58	39	58	43	42
Environment	IETH	43.1	24.7	16.3	21.4	10.1	15.7

For safety ranking, C2/PA route shows the highest impact (most hazardous) while ACH route appears as the safest route to produce MMA. It is also noted that C2/PA and C3 route may cause the highest impact to workers' health due to occupational exposures. Based on Table 1, C2/MP is evaluated as the healthiest route with less hazardous chemicals used and milder operating conditions. When the environmental impacts are considered, ACH route is found to cause the highest impact (most hazardous) which is resulted from the use of hydrogen cyanide (HCN). Meanwhile, i-C4 route is identified as the most environmental-friendly route for MMA production. Based on the single objective assessment, different results are generated with different assessment objective or target. The effects of other parameters might be overlooked when they are not being considered in evaluation. Overall, the single objective analysis portrays inconsistent and less reliable result in the screening of chemical reaction pathways. In addition, the index values for each parameter are disparate and therefore direct comparison is not possible.

Therefore, with the introduction of λ in fuzzy optimization, all four parameters can be assessed simultaneously. This approach also enables the optimization model to analyse all reaction pathways. It is noted that λ converts the original index values into dimensionless values in order to make them comparable. Note that with the definition of lower and upper value, the value of λ would become zero if the impact is the highest. Therefore, that reaction pathway will be phased out if one or more parameters are showing high impacts. Unlike the calculation of average value for ranking purpose, the result would be misleading whereby the synthesis pathway with lowest rating in one or more parameters may be ranked at high level in overall. The application of fuzzy optimization in multi-objective screening enables rapid and easy computation even if the involved parameters are linked to sub-input values or functions. The function for the parameter could be generated by combining individual variable such as operating condition in mathematical equation. Based on the pre-calculated index data, the fuzzy optimization model can be used to determine the pathway with the maximum degree of satisfaction for all parameters.

4. Conclusion

In this work, fuzzy optimization is adapted to screen and synthesize the sustainable chemical reaction pathways based on multiple selection criteria which include economic performance, safety, health and environment perspectives. The feature of sustainability is adopted from inherent approach which focuses on early chemical design stage for the greatest merit in application. MMA production is used to illustrate the proposed approach. Based on the optimized result, TBA process route is found to be the most desirable pathway. Fuzzy optimization enables more representative and reliable screening of reaction pathways for the determination of the most sustainable chemical reaction pathway which is beneficial to human, property and the environment.

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