

Reaction Path Synthesis Based on Fuzzy Evaluation in Safety, Environment and Health Impact

Xiaoyan Sun^a, Yao Fang^a, Wei Jiao^{b,*}, Shuguang Xiang^a

^aInstitute of Process System Engineering, Qingdao University of Science and Technology, China

^bDepartment of Chemistry and Chemical Engineering, Qingdao University, China
sun_xyan@163.com

To eliminate hazards during early phase of chemical process and obtain chemical reaction path with benign safety, the strategy is proposed by considering safety factors during reaction path synthesis. Material screening rules, safety constraints and inherent safety evaluation were integrated during reaction path synthesis. Safety factors were considered in this process. The implement of the strategy was divided into three steps. Based on inherent safety principles and indices, and reaction path including fire, explosion, toxicity hazards, material screening rules that considered safety were formed. According to material screening rules, the substance with extreme hazardous characteristics can be eliminated from materials. Focus on reaction hazards and substantial hazards, the NLP (non linear programming) model involving safety constraints was established. The result was shown that it was a more benign chemical reaction path. By inherent safety evaluation, the best relatively benign reaction path was obtained. Finally, by analyzing the application of reaction path synthesis for carbaryl production, the results were indicated that safety factors were considered during the early phase of process, and stoichiometric equations of chemical reaction path with benign safety were acquired. In conclusion, the strategy is useful in process decision-making.

1. Introduction

In recent decades, the disastrous consequences that caused by chemical process accidents attracted widespread concern about process safety. As one of the main fields of process synthesis, reaction path synthesis has become a crucial preliminary tool in identifying the most desirable reaction routes (Li et al., 2016). It can provide the opportunity to implement inherent safety in the conceptual design stage. If the Safety Environment and Health impacts are considered in reaction path synthesis, the inherent benign reaction path can be obtained early. The aim of inherent safety is to eliminate hazards by selecting un Hazardous materials or process operation conditions. Therefore, the possibility of accident can be minimized. It is a proactive approach for risk management. While inherent safety was implemented during the whole chemical process life cycle, it is advisable to apply it as early as possible.

Reaction path synthesis is a large and complex problem. The methods are divided into two categories - logic-based systems — the roots in mathematics and information-based systems, and the roots in chemistry. Rotstein et al. emphasized the path synthesis on the thermodynamic properties of reactions (Rotstein et al., 1982). Reaction schemes with two degrees of freedom were proposed (Fornari et al, 1989) and the factors were taken into consideration, such as economics and processing safety, when the reaction path is synthesized (Fornari and Stephanopoulos, 1994). Pistikopoulos et al. proposed an integrating methodology for the environmental impact minimization (MEIM) to reaction path synthesis for the environmental evaluation of alternatives (Pistikopoulos et al., 1994). Buxton et al. (1997) proposed a hierarchical strategy for the reaction path synthesis. By evaluating the alternatives by MEIM, several optimal reaction paths with benign economics and environment are screened out. Heikkila et al. (1996) proposed the process synthesis strategy considering safety factor for the application of separation sequence and reaction structure synthesis. The alternatives were generated by the genetic algorithm (GA) of the strategy, and were evaluated by inherent safety indices, and then the best alternative was selected according to the evaluating results (Heikkila, 1996). Toshio et al. (2018) proposed an efficient fast path optimisation (FPO) method to optimize the reaction paths on energy surfaces by using chains

of conformations. The optimisation of reaction paths with this method can drastically reduce the number of optimisation cycles for both potentials. Based on an algebraic analysis procedure, the possible reaction paths are explored. Zhou et al. (2020) constructed information flow diagram (IFD) to illustrate the reaction network. By simplifying, the transformation relations between a reactant and other molecules are identified, and the reactor parameters were analyzed and optimized to increase the yield of desired product and to reduce the production of byproduct.

Reaction path synthesis is treated as an issue of multi-objective optimisation. The objective function involves economy, thermodynamic, environment, safety, and so on. However, all of the influence factors of SEH (safety, environment and health) should be considered during reaction path synthesis. Meanwhile, the advanced evaluating means is used to evaluate the alternatives. The fuzzy evaluation was integrated with the reaction path synthesis in this study. The Inherent Preference Index based on Fuzzy Logic was used to assess safety, health and environmental impacts of materials for the desired product. The optimisation model including SEH index constraints was established, and the optimal reaction paths were obtained. Finally, the strategy was applied to the synthesis of production routes for carbaryl, and was illustrated its availability.

2. Strategy of reaction path synthesis based on fuzzy evaluation in SEH

The proposed strategy was divided to two main steps. The first step is to generate the SEH index of the raw material of the target product by the fuzzy evaluation using IPI (inherent preference index) method. The second step is the development of the optimisation model containing SEH index constraints. The framework of the strategy was described as following and was shown in Figure 1.

All substances involved in the desired product are evaluated by the Inherent Preference Index based on fuzzy logic. In the preliminary design stage, less process information was considered. The substances are the main evaluation object. The evaluation index includes flammability, explosion, toxicity and reactivity, especially the hazards of fire, explosion, environment, and toxicity. The fuzzy logic method is applied during the evaluation process. The evaluative results quantitatively indicated the hazardous extent of each substance.

The benign reaction paths were obtained by means of optimisation. The atom balance equation between the raw materials and the desired product is formed. Its solutions are all the possible stoichiometric equations. Meanwhile, the factors of SEH, thermodynamics, and economics are considered for screening reaction paths. The NLP model involving several constraints is formed, which was set the value of SEH index as the objective function. The results are the prospective reaction paths with benign SEH characteristics.

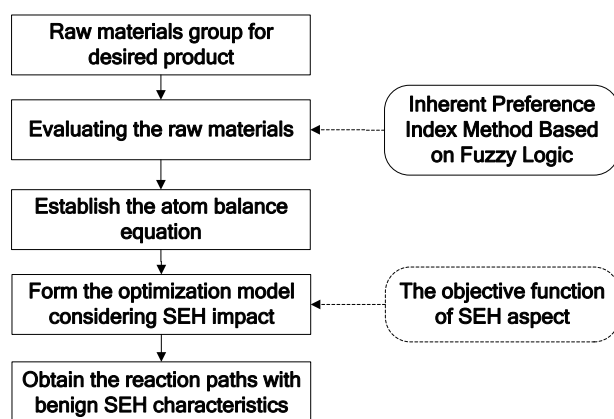


Figure 1: Strategy of reaction path synthesis considered SEH impact

3. Implementation of strategy of reaction path synthesis considered SEH

According to the proposed strategy, the implementation of each step was elaborated in the following sections.

3.1 Fuzzy evaluation

Fuzzy evaluation is a kind of uncertain reasoning method, which is based on fuzzy logic. On the premise of fuzzy judgment, using fuzzy language rules, some new approximate methods of fuzzy judgment is proposed. Gentile et al. developed an Fuzzy Based Inherent Safety Index by fuzzy logic tool. In their opinion, safety is traditionally considered as a subjective issue because of the high uncertainty associated with its significant descriptors and parameters. The use of fuzzy logic is helpful to model uncertainty and subjectivities

implied in the evaluation of certain variables and is helpful for the combination of quantitative data with qualitative information. Fuzzy logic can contribute to model numerical and heuristic expert knowledge by using fuzzy IF-THEN rules (Gentile et al., 2003).

However, fuzzy based on inherent safety index is relatively complicated, and is difficult to be used. The weights of variables are not reasonably considered (Gentile et al., 2003). When the number of medium variables increases, the value of final index is unreasonable, especially for extremely hazardous data. Meanwhile, the safety, environment and health impacts are not separately considered. The IPI method based on fuzzy logic and ESH (IPI-FLESH, IPI for short) is proposed to avoid the disadvantages mentioned above. In IPI, the multistage of fuzzy inference model is developed, which was showed in Figure 2. The detailed step-by-step method shown in Figure 2 is the “inherent preference index method based on fuzzy logic” mentioned in Figure 1. Because process information was not acquired in the early stage, some indices that contained temperature, pressure, inventory, reaction heat were not considered in the fuzzy evaluation in the reaction path synthesis.

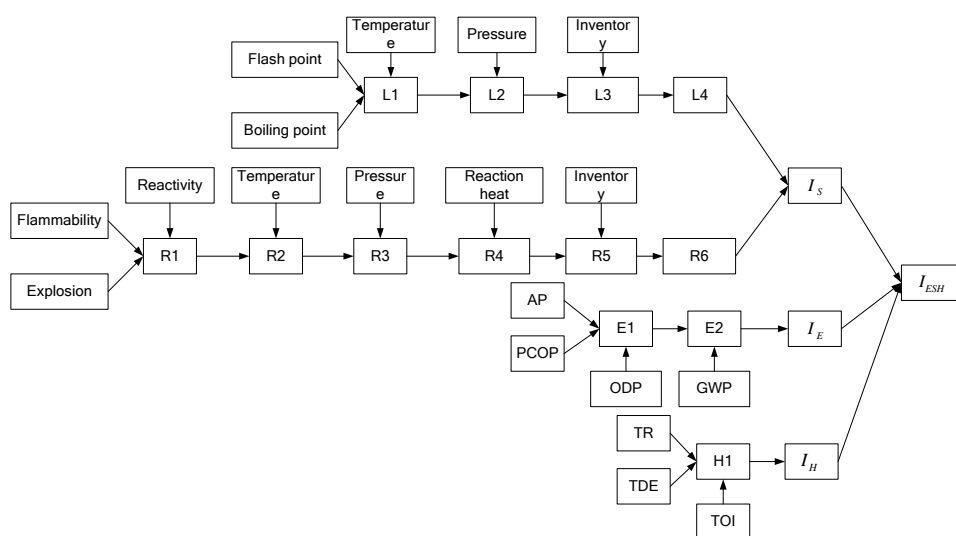


Figure 2: The fuzzy inference model of IPI method. Notation: TOI, toxicity by oral ingestion; TR, toxicity by respiratory; TDE, toxicity by dermal exposure; PCOP, photochemical oxidation; ODP, ozone depletion preference; GWP, global warming potential; AP, acidification preference

As shown in Figure 2, the value of final index in IPI was obtained through multistage fuzzy inference process. Each stage of fuzzy inference system contains two input variables and one output variable. To illustrate the evaluation procedure of IPI, the design of a fuzzy inference system is described as an example. In this system, the medium variables, such as R1 and R2, are the output variables for the previous fuzzy inference system, and are also the input variables for the next fuzzy inference system at the same time. According to R1 and R2, I_{SEH} is obtained, and then get the optimisation target I_j according to I_{SEH} of each substance.

Among them, Mamdani reasoning is a commonly used method in fuzzy control, which is still a synthetic reasoning method in essence, but takes different forms for fuzzy implication relations (Mamdani, 1977). According to the indice rating, the membership function of each variable is established. Meanwhile, the fuzzy rules of variables are formed. According to the parameters of variables, the fuzzy inference system was formed by the fuzzy logical tool by Matlab mathematical programming software. The output surface was presented in Figure 3, which indicated the relationship between the input and output variables. Similarly, other fuzzy inference systems are designed for all stages including in the IPI. Through multistage fuzzy inference, all variables are considered in the evaluation procedure. The values of all output variables were scaled between 0 and 1.

3.2 The optimisation model for screening the benign reaction paths

Reaction path synthesis can be treated as an optimisation problem. The optimisation model in this study takes the value of SEH index of the reaction path as an objective function. The atom balance equation is the basic equation in optimisation model, and it must be satisfied for all possible reaction paths. Other factors are set as the constraints. The optimisation model is presented as following.

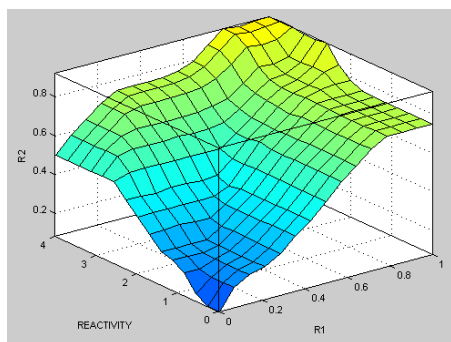


Figure 3: The output surface of fuzzy inference system

The SEH factor of all reactants and resultants involving reaction path are included in the objective function. Because the value of SEH index of each substance is acquired, the sum of index value of the substances involving reaction path is taken as an objective function. The weights of each substance are adopted to avoid the situation that a reaction path with lower sum value but containing hazardous substance with high value. The objective function has the following expression, where $\mu'_{i,j}$ is [0,1] integer decided by the stoichiometric coefficient $\mu_{i,j}$ of the substance i in the reaction path j . The $\alpha_{SEH,i}$ is the weights, and $I_{SEH,i}$ is the value of SEH index of the substance i .

$$\min I_j = \sum_i \mu'_{i,j} \alpha_{SEH,i} I_{SEH,i} \quad (1)$$

$$\alpha_{SEH,i} = \frac{I_{SEH,i}}{\sum \mu'_{i,j} I_{SEH,i}} \quad (2)$$

Other factors, such as thermodynamics, economics, the number of substances in reaction path are set as the constraints. The following expressions are presented. Each reaction path should satisfy the atom balance equation,

$$A_{\varepsilon \times (s+1)} \mu_{s+1} = 0 \quad (3)$$

Where $A_{\varepsilon \times (s+1)}$ is the atom matrix of reaction system, the row represents the type of element, the column represents the type of substance, and the value in the matrix represents the type of element in the substance. The μ_{s+1} is the stoichiometric coefficient vector, which has same dimension with the row of $A_{\varepsilon \times (s+1)}$. The final element in μ_{s+1} is the stoichiometric coefficient of desired product, whose value is 1 in each reaction path.

Considering the feasibility of the obtained reaction path, the Gibbs free energy change should be lower than a given value. The expression of the constraint is

$$\Delta G_j = \sum_{i=1}^s \mu_{i,j} \Delta G_i^f(T) < 41.8 \text{ kJ/mol} \quad (4)$$

Where ΔG_j is the Gibbs free energy change calculated from the Gibbs energy formation $\Delta G_i^f(T)$ of each substance in reaction path. It is generally agreed that if a reaction is to be commercially feasible, the Gibbs free energy difference must be less than a value about 41.8 kJ/mol (May and Rudd, 1976).

The maximum number of substances in each reaction should be limited, where n is the given maximum number. In the early stage, the considering economics factor is merely the prices of reactants and products, where V_i is the price of substance i .

$$\sum_{i=1}^{s+1} |\mu_{i,j}| \leq n \quad (5)$$

$$\sum_{i=1}^{s+1} V_i \mu_{i,j} > 0 \quad (6)$$

Minimising the SEH impact and using the constraints (Eq(2) - (6)), the problem of reaction path synthesis can be treated as a mixed-integer nonlinear optimisation program. Nevertheless, not all the obtained reactions can meet the need of reaction rate and selectivity. However, in most cases, the mechanism of a reaction can only be explored in the laboratory investigation. Whether a solution is desirable can only be proved through experiments.

4. Case study

The proposed strategy is applied to the case of the production of vinyl chloride. Possible materials were chosen for the production of carbaryl include naphthalene, chloronaphthalene, naphthol, hydrogen chloride, chlorine, methyl chloride, methanol, phosgene, methyl formamide, water, hydrogen, methylamine, oxygen, and methyl isocyanate.

Table 1: The results of fuzzy evaluation of all constituents, (1)

No.	substance	R1	R2	I_S	H1	H2	I_H	I_{SEH}
1	naphthalene	0.22	0.248	0.235	—	0.63	0.63	0.523
2	chloronaphthalene	0.08	0.188	0.156	0.377	0.377	0.377	0.312
3	naphthol	0.08	0.188	0.156	0.31	0.31	0.31	0.258
4	hydrogen chloride	0	0.218	0.218	0.92	0.812	0.869	0.686
5	chlorine	0	0.08	0.08	0.92	0.92	0.92	0.853
6	methyl chloride	0.919	0.811	0.868	0.79	0.75	0.771	0.814
7	methanol	0.916	0.808	0.865	0.752	0.75	0.751	0.812
8	phosgene	0	0.218	0.218	0.92	0.92	0.92	0.786
9	methyl formamide	0.08	0.188	0.156	0.239	0.239	0.239	0.206
10	water	0	0	0	—	0	0	0
11	hydrogen	0.907	0.75	0.836	—	0.836	0.836	0.836
12	methylamine	0.175	0.238	0.211	—	0.701	0.701	0.588
13	oxygen	0	0	0	—	0	0	0
14	methyl isocyanate	0.907	0.79	0.853	—	0.92	0.92	0.888

—: no data

The materials are separately evaluated by the Inherent Preference Index based on Fuzzy Logic. The results of fuzzy evaluation of all materials were shown in Table 1. The value of I_{SEH} quantitatively indicated the SEH impact of each material. The hazardous material, namely methyl isocyanate, has the highest value of SEH index (Table 1). Other more hazardous substances are chlorine, hydrogen, phosgene. According to the inherent safety principle of minimization, the most hazardous materials should not be used as reactants and products.

The atomic matrix of this problem is

$$\begin{matrix}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 \\
 \begin{matrix} C \\ H \\ O \\ N \\ Cl \\ X \end{matrix} & \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 2 & 0 & 0 & 1 & 0 & 2 & 2 \\ 1 & 0 & 1 & 1 & 0 & 3 & 4 & 1 & 5 & 2 & 2 & 5 & 0 & 3 & 4 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 & 2 & 1 & 2 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 & 2 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \times \mu_{ij} = 0
 \end{matrix} \quad (7)$$

where X means the group of benzene ring. According to the optimisation model, all reaction paths satisfying the constraints can be obtained through solving the problem by Matlab mathematical programming software. The stoichiometries and objective function I_j are shown in Table 2.

Table 2: The results of stoichiometries and objective function I_j of each reaction path, (1)

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	I_j
1	0	0	-1	2	-1	0	0	0	-1	0	0	0	0	0	1	0.653
2	-1	0	0	0	0	1	0	-1	-1	0	0	0	0	0	1	0.685
3	0	0	-1	1	0	0	0	-1	0	0	1	-1	0	0	1	0.697
4	0	-1	0	0	0	1	-1	0	-1	0	1	0	0	0	1	0.725
5	-2	0	1	0	0	0	0	0	0	0	0	0	-1	-1	1	0.676
6	1	-1	-1	1	0	0	0	0	-1	0	0	0	0	0	1	0.479
7	0	0	-1	0	0	0	0	0	-1	0	1	0	0	0	1	0.622
8	1	0	-2	0	0	0	0	0	-1	1	0	0	0	0	1	0.388

In Table 2, the notation includes: 1. naphthalene, 2. chloronaphthalene, 3. naphthol, 4. hydrogen chloride, 5. chlorine, 6. methyl chloride, 7. methanol, 8. phosgene, 9. methyl formamide, 10. water, 11. hydrogen, 12. methylamine, 13. oxygen, 14. methyl isocyanate, 15 carbaryl.

As shown in Table 2, the path of reaction No.8 has the lowest I_j value of 0.388, which indicated that this reaction path has the minimum SEH influence in theory. The reaction path should be preferred in the experiment development stage. However, others are also good alternatives with benign SEH characteristics.

5. Conclusions

The key idea of inherent safety is that inherent safety process should be developed in the early stage but by adding on complicated and costly safety protection system in the late stage. Inherent safety evaluation is an important way to quantitatively measure the level of the inherent safety of the process. It benefits to develop an inherently safer process by integrating the inherent safety evaluation with process research and design. In this study, a strategy was proposed by combining the fuzzy evaluation with a reaction path synthesis, and an optimal reaction paths with lower SEH impact was obtained.

According to minimization and substitution principle, based on considering safety index, environment and health index were selected to form HSE index structure. Membership function of index was set up and fuzzy inference system is established. Weight of index was determined by AHP (analytic hierarchy process) according to the index structure, thus a fuzzy HSE evaluation method was established. The fuzzy HSE evaluation method was applied to the reaction path synthesis, and the multi-objective NLP model was established with the HSE property of the reaction path as an objective function, and the reaction path with excellent HSE comprehensive index was obtained. This method was applied to the comprehensive case analysis of reaction paths of carbaryl and vinyl chloride, the value of each reaction path and its HSE objective function value are acquired. The method provided quantitative data for the optimisation of reaction paths in the early stage of the process.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 21476119) and Major Science and Technology Innovation Projects of Shandong Province (No. 2018CXGC1102).

References

- Buxton A., Livingston A.G., Pistikopoulos E.N., 1997. Reaction Path Synthesis for Environmental Impact Minimization. *Computers & Chemical Engineering.*, 21, 959–964.
- Fornari T., Rotstein E., Stephanopoulos G., 1989. Studies on the Synthesis of Chemical Reaction Paths- II. Reaction Schemes with Two Degrees of Freedom. *Chemical Engineering Science*, 44, 1569–1579.
- Fornari T., Stephanopoulos, G., 1994. Synthesis of Chemical Reaction Path Synthesis: Economic and Specification Constraint. *Chemical Engineering Communications.*, 129, 159–182.
- Gentile M., Rogers W.J., Mannan M.S., 2003. Development of A Fuzzy Logic-Based Inherent Safety Index. *Process Safety and Environmental Protection*, 81(6), 444–456.
- Heikkila A.M., 1996. Safety Considerations in Process Synthesis. *Computers and Chemical Engineering*, 20, 115–120.
- May D., Rudd D.F., 1976. Development of Solvay Clusters of chemical Reaction. *Chem. Eng. Sci.*, 31, 59–69.
- Mamdani E.H., 1977. Application of Fuzzy Logic to Approximate Reasoning using Linguistic Systems. *IEEE Transactions on Computers*, 26, 1182–1191.
- Li M.H., Hu S.Y., Li Y.R., Shen J.Z., 2013. A Hierarchical Optimisation Method for Reaction Path Synthesis. *Industrial & Engineering Chemistry*, 39, 4315–4319.
- Pistikopoulos E.N., Stefanis S.K., Livingston A.G., 1994. A Methodology for Minimum Environmental Impact Analysis. *AIChE Symposium Series*, 90, 139–151.
- Rotstein E., Resasco D., Stephanopoulos G., 1982. Studies on the Synthesis of Chemical Reaction Paths-I. Reaction Characteristics in the $(\Delta G, T)$ Space and a Primitive Synthesis Procedure. *Chemical Engineering Science*, 37, 1337–1352.
- Zhou L.H., Liu G.L., Hang P., Li K.Y., 2020. Analysis and Optimisation of Reaction Network based on the Information Flow Diagram. *Journal of Cleaner Production*, 258, 120653.
- Toshio A., Nozomi S., Takuya N., Shiro K., 2018. An Improved Reaction Path Optimisation Method using a Chain of Conformations. *Chemical Physics Letters*, 699, 255 – 260.