Enhancement of Inherent Safety in Chemical Industry

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The paper discusses the enhancement of inherent safety by index methods. The aim is to study, how well the safety index methods can evaluate inherent safety compared to expert evaluations and Dow Fire and Explosion index values. Studies on four levels of scope from process concept selection to equipment design were done and correlations between indices and expert values calculated. It was found that none of the selected indices is capable of assessing inherent safety on all stages. Every index has also its limitations because of differences on the parameters used and the information availability. Most problematic seems to be the sub process selection level, where the results of indices are inconsistent.

1. Introduction

The principles of inherently safer design (ISD) are an important approach to risk reduction in chemical process industry (CPI). Even the principles of inherent safety design (ISD) have been known for 30 years, the uptake of the concept is slow and major accidents keep on happening. One of the latest examples is the explosion at the Grande Paroisse plant, Toulouse in 2001, which killed 30 people and injured many hundreds more. Recent survey by Gupta and Edwards (2002) showed that the ISD concept is well accepted as a principle by CPI but still the uptake of ISD is slow and more aggressive promotion should be done to enhance the ISD application. Detail action plans for further enhancements of the inherent safety practice are discussed by Faisal and Amyotte (2003) and (Edwards, 2005). This paper discusses the application of ISD at different level of plant design by using some indices on four different scopes (levels) of process design.

2. Hazard Indices

At the moment, there are many important indices available for hazard identification, including Dow Fire and Explosion Index (F&EI), Prototype Index of Inherent Safety (PIIS) by Edwards and Lawrence (1993), Inherent Safety Index (ISI) by Heikkilä et al. (1996), í-Safe index by Palaniappan et al. (2004), Integrated Inherent Safety Index (I2SI) by Faisal and Amyotte (2005) and Inherent Safety Index Calculation (ISIC) by Abedi and Shahriari (2005). The tools may vary in goal, scope, structure and the way safety aspects are considered. In this paper, Dow F&EI, ISI, and PIIS (also i-Safe in MMA case study) will evaluated for their capability. The reasons for choosing these three indices are: Dow F&EI is the most widely used index in CPI (Faisal at.al, 2003).

PIIS is the first index published for inherent safety evaluation and required less information. ISI is an example of the later index developments.

3. Research Approach and Case Study Processes

In this paper the applicability of selected indices to provide an evaluation of inherent safety of chemical processes is studied. The analysis involves four levels of ISD application namely route and sub-route selection, unit process, and detailed equipment level. For route and sub-route selection, the correlation of indices to each other and expert values is calculated. Also their capability to determine the process ranking on safety is presented. In the next two case studies, the inherent safety level for conventional design and intensified design is estimated by three indices in two levels of process scope: unit process level and equipment level. The aim is to find out, how these indices can predict ISD aspects in the different levels of process detail.

3.1 MMA case study

Production of methyl methacrylate (MMA) has been used as a case study for comparison of inherent safety methods by many authors including Edwards and Lawrence (1993) and Rahman et al. (2005). There are 23 sub-routes from 6 routes available to manufacture MMA, namely acetone cyanohydrin (ACH) based, ethylene based via propionaldehyde, ethylene via methyl propionate, propylene based, isobutylene based, and tertiary butyl alcohol (TBA) based route (Ullmann's, 1990). The details of alternative MMA processes is given by Rahman et al. (2005).

Dow F&EI, ISI, PIIS and i-Safe index values for routes and their sub processes will be compared and compared with expert scores from Lawrence (1996). Correlation between the index as well as expert scores are also carried out by performing pair-wise linear regression. The level of correlation is indicated by the coefficient of determination (R^2). The higher the R^2 value, the stronger the correlation. Whitehead and Whitehead (1993) describe the definition of coefficient of determination R^2 as, which amount of the dependency of the one variable is explained by the other variable.

3.2 Hydrogen peroxide case study

To demonstrate the capability of indices to predict ISD aspects on different levels of process detail the process intensification of anthraquinone process for production of hydrogen peroxide is chosen as a case study (Turunen and Mustonen, 1993 and Turunen, 1997). The overall process involves hydrogenation, oxidation, extraction, regeneration and finishing to produce high quality hydrogen peroxide. In the conventional technology, the oxidation reactor is a bubble column for gas-liquid reaction, with air as the oxygen source (Liebert et al. 1975). A tubular reactor is introduced in the intensified process, where air is replaced by pure oxygen introduced via direct injection to the working fluid. Several injection points at different location are required to fulfil the reaction needs. Rapid mixing in the tubular reactor gives a very high mass transfer rate with improved selectivity. The detail of the unit processes are given in Table 1 and Figure 1.

3.3 Hydrogen peroxide case study on unit process and equipment levels

Process intensification in section 3.2 creates a new hazard in the separation of reactor effluent. The reactor outlet is a mixture of liquid and gas with high fluid velocity, thus promoting the aerosol formation in the separation vessel. The explosion risk is increased because the mist formed and unreacted oxygen present. The formation of mist can be eliminated or reduced by using a cyclone effect for separation as shown in Figure 2b.

Table 1: Hydrogen peroxide process reaction sub process alternatives

Design Criteria	**Conventional Process**	**Intensified Process**
Equipment	Bubble column	Tubular reactor
Effective Volume	160 m^3	7 m^3
Pressure	1 bar	2.39 bar
Oxygen source	Air	Pure oxygen (99%)
Oxygen utilization	76 %	93 %

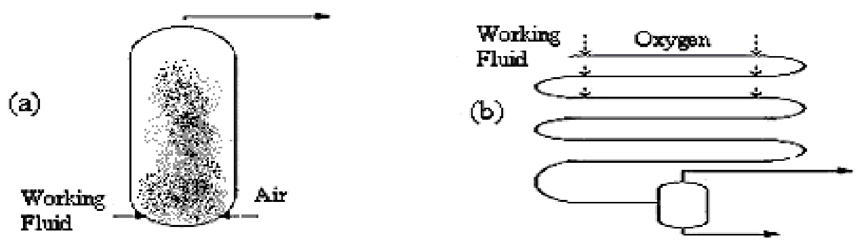

Figure 1: H_2O_2 reactor unit process (a) before and (b) after process intensification

Figure 2: H_2O_2 phase separator details with (a) high and (b) low of mist formation

4. Results

4.1 Route selection

The *index values* for the MMA routes and their sub processes are presented in Table 2. The correlation analysis was done for both the sub process as well as the total route index values of the MMA case study (see Table 4). Process route index values show good correlation between different indices. The best correlation is given by the ISI and i-Safe; average R^2 values 0.93 and 0.92, respectively. This agrees with the findings of Rahman et al. (2005). ISI has the highest correlation (0.97) to expert values.

Dow F&EI has the weakest average correlation with the other methods; average R^2 0.81. It has also significantly lower correlation (0.74) with the expert values. The conclusion is that, all inherent safety indices agree quite well with the expert values in MMA route evaluations but Dow F&EI has somewhat lowest correlation (0.74) to expert values

Table 3 gives the route *rankings* by using different indices. It can be seen that all indices agree that the ACH route is most hazardous process even the indices have somewhat different evaluation criteria. It is interesting to notice that Dow F&EI gives different ranking compared to other index methods except for the two worst routes. The safest route for Dow F&EI is C2/MP, whereas the other indices give TBA as the safest. The main difference between TBA and C2/MP route is the inventory. It is found that the penalty of Dow F&EI for TBA route is very high compared to C2/MP but other indices are less sensitive to detect the differences in inventory. Similar results were found by Faisal et al. (2003) regarding the sensitivity of the indices towards inherent safety keywords. Thus the conclusion is that the Dow F&EI is quite sensitive to the inventory of the plant and promotes inherent safety incentive through keyword ‘minimize’.

Table 2: Indices value for six MMA routes

No.	Subprocess	DOW		PIIS		ISI		i-Safe		Expert	
1	ACH 1	527		31.93		26.85		33.14		29	
2	ACH 2	324		18.25		22.56		19.33		25	
3	ACH 3	416		12.54		22.56		19.33		19.33	
4	ACH 4	428		15.96		20.41		15.19		22.33	
5	ACH 5	393		21.67		20.41		16.57		17.33	
6	ACH 6	267	***2355***	15.96	***102***	19.33	***123***	17.95	***88***	19.33	***17***
7	C2/PA 1	397		23.95		24.7		22.1		22	
8	C2/PA 2	347		27.37		24.7		22.1		23.67	
9	C2/PA 3	418		20.53		22.56		26.24		21	
10	C2/PA 4	383	***1545***	18.25	***79***	17.19	***83***	19.33	***65***	19.33	***11***
11	C2/MP 1	402		29.65		25.78		26.24		28	
12	C2/MP 2	423		19.39		22.56		22.1		19.67	
13	C2/MP 3	432	***1257***	19.39	***60***	18.26	***62***	19.33	***49***	19.33	***8***
14	C3 1	390		27.37		29		23.48		33.33	
15	C3 2	279		13.68		23.63		19.33		27	
16	C3 3	309		15.96		19.33		20.71		18	
17	C3 4	389	***1367***	18.25	***66***	17.19	***83***	19.33	***60***	19.33	***12***
18	iC4 1	437		21.67		21.48		27.62		21.67	
19	iC4 2	491		20.53		22.56		26.24		19.33	
20	iC4 3	383	***1311***	18.25	***53***	17.19	***57***	19.33	***53***	19.33	***8***
21	TBA 1	547		17.11		21.48		20.71		18.33	
22	TBA 2	473		20.53		22.56		26.24		19.33	
23	TBA 3	408	***1428***	18.25	***49***	17.19	***57***	19.33	***48***	19.33	***7***

Table 3: MMA route inherent safety rankings by different methods

RANKING	DOW	ISI	PIIS	i-SAFE	EXPERT
1	C2/MP	TBA &C4	TBA	TBA	TBA
2	C4	TBA &C4	C4	C2/MP	C4
3	C3	C2/MP	C2/MP	C4	C2/MP
4	TBA	C2/PA & C3	C3	C3	C2/PA
5	C2/PA	C2/PA & C3	C2/PA	C2/PA	C3
6	ACH	ACH	ACH	ACH	ACH

Table 4: Correlation (R^2) values between various inherent safety methods for MMA routes and sub processes

	Sub-process					Process Route				
Index	**PIIS**	**ISI**	**i-Safe**	**Expert**	***Average***	**PIIS**	**ISI**	**i-Safe**	**Expert**	***Average***
DOW	0.10	0.03	0.26	0.01	*0.10*	0.80	0.84	0.89	0.74	*0.81*
PIIS		0.41	0.47	0.36	*0.34*		0.94	0.94	0.87	*0.89*
ISI			0.34	0.62	*0.35*			0.96	0.97	*0.93*
i-Safe				0.17	*0.31*				0.90	*0.92*
Expert					*0.29*					*0.87*

4.2 Sub-process selection

Table 2 presents the index values for MMA sub processes and Table 4 the corresponding correlation values between index values. Generally, it is found that the sub-route selection gives much poorer correlation between indices and indices & expert values compared to route selection (see Table 4). The best average correlation is only 0.35. All methods also have very poor correlation with the Dow F&EI (average R^2 is 0.10). The highest R^2 value is observed with ISI vs. expert score (0.62). However even ISI suggests only a moderate level of correlation. Interestingly Dow F&I does not represent any correlation with expert values, even the expert panel included eight well known authorities such as T. Kletz and F. Lees. There are some factors contributing to these findings:

1) There are differences in calculation procedure between indices; Index values for ISI, PIIS and i-Safe were calculated based on addition of the penalty of each parameter but Dow F&EI uses multiplication between parameters. The latter gives greater impact to the index values and better sensitivity to process changes.

2) The main purpose of the indices is also different. Dow F&EI is mainly used for estimating hazards for detailed process engineering and existing plants. Inherent safety indices were developed for evaluation of routes selections at the early stages of process design.

3) Dow F&EI is mainly used for estimating the fire and explosion hazards . The toxicity point of view is less included than e.g. in ISI.

4) The indices have quite different weightings of criteria. The development of inherent safety indices was based on the personal opinions of the experts, who were mainly academics and safety consultants. In fact these experts had also differing opinions on scorings and the selection of parameters included. This shows the fundamental weakness of the inherent safety indices available today. The weighting of the penalty scales is quite subjective. Also penalty scores are discontinuous (i.e. integers). Dow F&EI uses consistent (small range) scoring values, which were developed during a long time based on industrial accident cases.

It is interesting to note that the correlation of route values were much better (0.88 on average) than sub process correlations (0.28 on average). This may be because the scoring system in inherent safety indices is somehow too rough (integers) and therefore causes 'random' variation in values. When process route index value is a summation of sub process index values for each route, the variation in sub process values is ‘compensated’ when the values are added up to represent the total route index value.

4.3 Unit process level studies

The index values of hydrogen peroxide case study described earlier are presented in Table 5. There are significant overall hazard score reduction between the original and intensified process. In general it follows the comment by Etchells (2005) on safety aspects of process intensification. The improvement of the process minimizes the volume (inventory) from 160 m^3 to 7 m^3. As a result, the final hazard score of the indices responses well to the process change. Dow F&EI gives larger reduction in index values (27%) than ISI (14%) but PIIS doesn’t response at all due to the its larger scale of inventory index.

The conclusion is that Dow F&EI is more sensitive to process change than ISI, but ISI is still applicable. Sensitivity of PIIS very poor and of no use in assessing inherent safety at this unit process design level. These case studies demonstrate that the mode of operation and equipment selection is a vital part of risk reduction strategy, which can be carried out especially in the earlier phases of process design, when changes are cheaper.

Table 5: Indices values for unit process level study on H_2O_2 reactor case

Index values	Conventional	Intensified	Differences %
ISI	14	12	14.3
PIIS	8	8	0
DOW	150	110	26.7

4.4 Equipment level studies

Table 6 shows the result of hydrogen peroxide case study on equipment level changes in phase separation equipment of the H_2O_2 process. The aim for equipment modification was to eliminate the mist or aerosol formation in the flash tank by cyclone effect. Similar to unit process level study, Dow F&EI and ISI respond to equipment modification with index reduction; 79% and 15% respectively. There is no change in PIIS values. The conclusion is that as previously Dow F&EI and ISI are able to predict in more detailed way the changes to the process. Dow F&EI clearly states that the parameter of mist has a large impact on fire and explosion safety. ISI is able to demonstrate the change but scoring is based on user experience, since there is no score for mist but only for more general 'safe process structure'.

Table 6: Indices values for equipment level study on H_2O_2 reactor case flash tank

Index values	Conventional	Modified	Differences %
ISI	13	11	15.4
PIIS	7	7	0
DOW	133	28	78.9

5. Discussion

The study on the four levels of detail (route, sub process, unit process, equipment), which also corresponds to the process design life cycle, demonstrates that the quantification of inherent safety can be carried out throughout the design lifecycle. Figure 3 illustrates the general level of the applicability of indices on different application levels. All the indices studied give very good correlation with each other and expert values in route selection level. They all have problems at the sub process selection level giving quite inconsistent values as discussed before. On equipment selection and unit process level Dow F&EI is more reliable than the other methods. It is however worse for route selection. ISI is accurate at route selection but still workable in unit process and equipment level with some limitations. PIIS only can be used at route selection.

Dow F&EI	fair	questionable	best	best
ISI	best	questionable	good	fair
PIIS	good	questionable	poor	poor
	Route level	**Sub process level**	**Unit process level**	**Equipment level**

Figure 3. Level of the applicability of indices at difference levels of detail and scope

6. Conclusion

This paper discussed applicability of the indices to assess level of inherent safety of chemical processes. Dow F&EI is preferred index for safety evaluation in unit process and equipment level because of it's sensitiveness to changes in details. However, Dow F&EI is not well applicable to route selection stage due to limited information available. Therefore inherent safety indices, such as ISI, tailored for preliminary stage are preferred. On the other hand index methods have limitations in the detailed unit process and equipment design levels because of their simplicity. Therefore none of the indices considered in this paper is best in all design stages but the indices have their optimum application areas. At the sub process selection level all the methods studied had problems and their average correlation was bad. Interestingly Dow index did not correlate with the inherent safety indices or even with expert values. Nor did inherent safety indices have good correlation with expert values, even their correlation was excellent in route selection stage. This is worth of further study.

7. References

Abedi P. and M. Shahriari, 2005, Cent. European Science J., 3(4), 756.
Edwards, D. W., 2005, Trans IChemE, 83, Part B, 90.
Edwards, D.W. and D. Lawrence, 1993, Trans IChemE, 71, Part B, 252.
Etchells J. C., 2005, Trans IChemE, 83, Part B, 85.
Faisal I .K. and P. R. Amyotte, 2005, J. of Loss Prev. Process Ind. 18, 310.
Faisal I .K, Rehan Sadiq and P. R. Amyotte, 2003, Process Safety Prog., 22(2), 83.
Faisal I .K. and P. R Amyotte, 2003, Canadian J. Chem. Eng, 81, 2.
Gupta J. P. and D. W. Edwards, 2002, Trans IChemE, 80, Part B, 115.
Heikkilä, A. M., M. Hurme, M. Järveläinen, 1996, Comp. Ehem. Eng, 20, 115.
Lawrence, D., 1996, PhD Thesis, Loughborough University, UK.
Liebert M., H. Delle and G. Kabisch, 1975, U. S. Patent 3880596
Palaniappan, C., R. Srinivasan, R. Tan, 2004, Chem. Eng. Processing. 43, 647.
Rahman, M., M. Hurme, 2005, J. of Loss Prev. Process Ind. 18, 238.
Rahman, M., A. M. Heikkilä. and M. Hurme, 2005, J. of Loss Prev. Proc. Ind. 18, 327.
Turunen I., 1997, Process Intensification in Practice, BHR Group, Cranfield, 99.
Turunen I and E. L. Mustonen, 1993, U. S. Patent 7195748
Ullmann's Encyclopedia of Industrial Chemistry, 1990, 5th Edition, VCH, Weinheim.
Whitehead P. and G. Whitehead, 1993, Statistics for Business, 2nd Ed, Pitman, London.