Publication 8

Mimi H. Hassim, Miina Grönlund, and Markku Hurme. 2008. Inherent EHS considerations in process development. In: Simberto Senni Buratti (editor). Proceedings of the 3rd International Conference on Safety & Environment in Process Industry (CISAP-3). 1st edition. Rome, Italy. 11-14 May 2008. Associazione Italiana Di Ingegneria Chimica. Chemical Engineering Transactions, volume 13, pages 295-302. ISBN 978-88-95608-07-5.

Inherent EHS Considerations in Process Development

Mimi H. Hassim, Miina Grönlund, and Markku Hurme
Helsinki University of Technology
Plant Design, P. O. Box 6100, FIN-02015 TKK, Finland
mimi@cc.hut.fi, markku.hurme@tkk.fi

A correlation analysis between index based environment, health and safety (EHS) assessment techniques was done. The aim was to study, if any interdependency exists between EHS characteristics in inherent level. For the purpose values of 12 EHS index methods were correlated pair wisely by linear regression in a methyl methacrylate process route case study. It was found that safety & environmental and safety & health factors show the strongest binary correlation (R^2 = 0.78). Health vs. environment was less correlated. The results suppose also that only one index method can be used for evaluating all EHS properties in this case.

1. Introduction

Sustainability is often defined as 'meeting the needs of the present without compromising the ability of future generations to meet their own need' (Anon, 1987). Many chemical companies have nowadays committed to sustainability by joining programs such as Responsible Care. Also EU directives, such as IPPC and REACH, have affected process development and design so that EHS aspects have to be taken into consideration in earlier phase.

Inherently better designs were first introduced as a principle of designing chemical processes by focusing on hazard minimization (inherent safety) or waste reduction (clean technology). The aim was to remove or reduce unsafe or waste generating process features by using less hazardous materials & process conditions or reducing waste generation at source. Later the ideology was extended to inherent occupational health (Hassim and Edwards, 2006).

Inherent design evaluation methods are needed to identify and rate hazardous, waste producing or unhealthy process concepts, which would require later extensive add-on systems to fix the problems. The early EHS assessment allows inherently better designs to be developed before conceptual changes become too costly. Therefore the best results are achieved, when the approach is implemented during the early stages of process design.

A number of index methods have been presented in literature for evaluating the inherent characteristics of process concepts. Also some comparisons of the index methods have been published. For example, comparisons of inherent safety methods were done by Rahman et al. (2005), Koller et al. (2001) and Khan et al. (2003). Health and environmental methods were compared by Hertwich et al. (1998) and Koller et al. (2000).

An interesting question arising is, whether the inherent EHS properties have anything in common? That is; is e.g. an inherently safer process also cleaner or occupationally healthier? Interestingly no comparison has been published to authors' knowledge on this aspect. Such information would be useful to identify and enhance factors contributing to good inherent properties of process from *several* EHS point of views at the same time. Therefore the aim of this paper is to study, if the inherent safety, health and environmental properties are correlated. The study is done by comparing the different process concepts for methyl methacrylate (MMA) manufacturing.

2. Methodology

2.1 Index methods used

In this paper, 12 inherent assessment approaches were selected for comparison:
For *inherent safety* three index based methods; Inherent Safety Index; ISI (Heikkilä et al., 1996), Prototype Inherent Safety Index; PIIS (Edwards and Lawrence, 1993) and *i*-Safe (Palaniappan et al., 2004) were chosen. The methods evaluate the level of process inherent safety based on the chemical properties, chemical inventory and operating conditions. Also expert scoring for MMA case study was included in the evaluation to give an expert point of view (Lawrence, 1996).

For *occupational health* evaluations Process Route Healthiness Index; PRHI (Hassim and Edwards, 2006), Inherent Occupational Health Index; IOHI (Hassim et al., 2006), Health Index; HI (Hassim and Hurme, 2008) and Fugitive Emissions; FE (Hassim and Hurme, 2008) were chosen. Like inherent safety indexes, these methods attempt to foresee the inherent occupational healthiness of a process. The PRHI and IOHI utilize properties of the chemicals used and data on process conditions, whereas the HI and FE are purely fugitive emission based indices for inhalation based exposures. HI has the reference to occupational exposure limits, whereas FE includes only the fugitive emission rate. PRHI has also a leak and fugitive emission variable.

The inherent *environmental* evaluation methods used are Environmental Hazard Index; EHI (Cave and Edwards, 1997), Atmospheric Hazard Index; AHI (Gunasekera and Edwards, 2003), Inherent Environmental Toxicity Hazard; IETH (Gunasekera and Edwards, 2006) and Waste Reduction Algorithm; WAR (Young and Cabezas, 1999). The first three are total loss of containment type of indices for evaluating short-term impacts of catastrophic incidents on environment. EHI is for water and terrestrial environment and AHI for atmosphere. IETH is the combination of EHI and AHI. WAR is a normal operation type of index calculated by balance principle for process input and output streams, typically including feedstocks, products and emissions. It describes, how the process increases or reduces environmental load as a whole.

2.2 Principles of the methods

In order to understand the causes responsible for correlations between the methods, it is important to discuss the basic elements of the methods. In general, each index uses various types of parameters for evaluating the process properties (Table 1). In inherent safety, parameter types are relatively well-established, but as discussed by Crawley and Ashton (2002) health and environmental criteria have much more uncertainty and are more pragmatic.

Also the type of index calculation, scenario and time scale considered differs (Table 2). *Type of index calculation* can be an additive way, in which the process is divided into sub processes, which are evaluated separately. Finally scores are totaled up to give the route index value. Therefore the index value is the larger the more sub processes there are. Another way is to calculate the index without division into sub processes. Then the index value does not directly depend on the number of sub processes in the route. Most methods are formulated based on the additive principle except HI and WAR.

Operating scenario considered in evaluation can be either on catastrophic or normal operation. All safety and many environmental methods assume a worst-case scenario, i.e. total loss of containment. Health methods and WAR are normal operation based.

Time scale refers to the length of timescale during which the influences are considered. All safety methods discuss short-term events. Most occupational health methods consider both short and long-term effects, as well as the environmental methods except EHI and IETH, which considers only short-term events.

Table 1: Parameter types used in the index methods

Criteria	ISI	PIIS	i-Safe	PRHI	IOHI	HI	FE	EHI	AHI	IETH	WAR
Reaction chemistry	X	X	X								
Inventory	X	X	X					X	X	X	
Material state				X	X	X	X	X	X	X	X
Material toxicity	X	X	X	X	X	X		X	X	X	X
Process temp & pres	X	X	X	X	X						
Proc. equipment	X			X	(X)	X	X				X
Fugitive emissions				X		X	X				
Water&soil toxicity								X		X	X
Air toxicity									X	X	X

Table 2: Characteristics of assessment methods

	ISI	PIIS	iSafe	PRHI	IOHI	HI	FE	EHI	AHI	IETH	WAR
Calculation	A	A	A	A	A	E	A	A	A	A	A/E
Scenario	C	C	C	O/C	O/C	O	O	C	C	C	O
Time scale	S	S	S	L/S	S/L	L	L	S	S/L	S	S/L

A, additive; E, average; C, catastrophic event; O, normal operation; S, short-term; L, long-term

2.3 The case study process

The evaluation was done by using the six process routes for manufacturing methyl methacrylate (MMA) as a case study. The routes 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), and tertiary butyl alcohol based route (TBA). For more details see Rahman et al. (2005).

2.4 Correlation method

For finding out the correlation between the EHS evaluation methods pair-wise linear regression was done between MMA process route index values. This technique allows two methods with different scales to be compared through correlation. Linear regression was considered appropriate, since the index-based methods are mathematically linear. Also preliminary evaluations showed linear relationship being satisfactory.

The coefficient of determination (R^2) acts as an indicator of the correlation between the methods compared; the higher the R^2 value, the stronger the correlation. The coefficient of determination describes, which amount of the dependency of the one variable is explained by the other variable (Whitehead and Whitehead, 1993).

Each method was paired with other method (e.g. ISI vs. PRHI). The R^2 value of each pair was calculated (Table 3). Finally, the average R^2 values were also calculated between EHS criteria (e.g. safety vs. health, etc.) as shown in Table 5.

3. Results and discussion

Table 3 presents the coefficients of determination calculated between individual indices by pair-wise linear regression.

Table 3: Correlation (R^2) of MMA route index values by pair-wise linear regression

	Safety			**Health**					**Environment**				
Index	PIIS	i-Safe	Expert	PRHI	IOHI	HI	FE	*Avrg*	EHI	AHI	IETH	WAR	*Avrg*
ISI	0.94	0.96	0.97	0.71	0.97	0.30	0.23	*0.55*	0.88	0.55	0.92	0.63	*0.74*
PIIS		0.94	0.87	0.54	0.87	0.22	0.36	*0.50*	0.95	0.58	0.87	0.66	*0.76*
i-Safe			0.90	0.59	0.97	0.22	0.26	*0.51*	0.93	0.65	0.91	0.79	*0.82*
Expert				0.82	0.92	0.37	0.17	*0.57*	0.76	0.40	0.85	0.54	*0.64*
Average				*0.67*	*0.93*	*0.28*	*0.26*		*0.88*	*0.54*	*0.88*	*0.65*	
PRHI					0.66	0.72	0.15		0.43	0.11	0.48	0.23	*0.31*
IOHI						0.24	0.18		0.87	0.64	0.93	0.71	*0.79*
HI							0.36		0.17	0.00	0.09	0.02	*0.07*
FE									0.41	0.16	0.11	0.12	*0.20*
EHI										0.76	0.86	0.72	
AHI											0.73	0.67	
IETH												0.69	
Average									*0.47*	*0.23*	*0.40*	*0.27*	

3.1 Intra criteria correlations

Before comparisons between methods for different criteria are discussed, it is worth seeing, how the methods in each criterion (intra-criteria) correlate (see Table 3).

All *safety* index methods have an excellent correlation with each other ($R^2 \approx 0.95$) for the process routes. The methods also have a very good correlation with expert values. ISI has the best correlation with expert values. This is consistent with the findings of Rahman et al. (2005). The reason for excellent correlations between safety indices is that they have much the same parameters and characteristics as shown in Table 1 and 2. However it is known that the sub process index values have lower correlation than the route values (Hurme and Rahman, 2005).

The *occupational health* methods don't show correlation, except PRHI vs. IOHI or HI. Interestingly IOHI and HI don't have much correlation. This is because they represent different sides of occupational health; IOHI has number of general health variables but lacks fugitive emission calculation. HI considers fugitive emissions and exposure limits but lacks the other variables. The conclusion is that neither fugitive emissions nor the other variables alone are able to predict occupational health level as a whole but both approaches are needed.

PRHI is a rough compromise between these aspects (e.g. it includes a fugitive emission and leak term), therefore it correlates with both IOHI and HI.

FE index is only the rate of fugitive emissions without reference to exposure limits, therefore it does not correlate with the other health methods. The conclusion from this is that exposure limits combined with fugitive emissions are essential data for health evaluations.

Comparison between *environmental* methods gives R^2 average value 0.74. The best correlation is between the EHI and IETH. This is quite obvious, since EHI is the main part of IETH.

The three indices give somewhat worse correlation with WAR (0.69 on average). This is not surprising since WAR is operational based and others are catastrophe based. The relatively good correlation is explained by inclusion of partly the same type of environmental impact parameters.

3.2 Safety vs. health

In Table 3 all safety methods show excellent correlation with the health method IOHI (R^2 on average 0.93). Some indices even have nearly a full correlation (*i*-Safe and ISI 0.97). This is because of similar type of parameters in indices (Table 1) and the same calculation basis; loss of containment. Correlation with HI and FE is bad, because these methods are fugitive emission based and don't have common parameters with inherent safety methods.

All safety methods give a moderate correlation with the PRHI (R^2 on average 0.67), because of the same reasons as with IOHI. The difference is probably because PRHI includes fugitive emission and a leak factor, which make the correlation worse.

3.3 Safety vs. environment

All safety methods have good correlation with environmental methods EHI and IETH (average R^2 values 0.88 both). The reason is, even though the criteria assessed are different, their formulation is similar. They all are additive-type methods and the assessments are based on catastrophic events within mostly short-term duration. We can conclude that the inventory aspect strongly binds together the inherent safety and environmental indices with catastrophic scenario background.

The correlation with AHI is worse (0.54), probably since the parameters are different (i.e. airborne, partly long term) from those considered in inherent safety indices. For WAR the average R^2 is not bad (0.65), even though WAR has different basis than the safety methods (operation based vs. catastrophic).

3.4 Health vs. environment

Health method IOHI correlates reasonably well with most environmental methods (average R^2 = 0.79), especially with IETH and EHI (R^2 = 0.93 and 0.87). This is somewhat unanticipated and not easy to explain, because IETH and EHI are indices with catastrophe scenario. Still all the three methods include considerable amount of general toxicity data but for different purposes. This may be of fundamental interest and a topic for a further study.

Health method PRHI has poor correlation with all the environmental methods (0.31 on average). PRHI includes a fugitive and leak element, which may disturb the correlation, since other methods (HI, FE) with strong fugitive background, also correlate badly with environmental methods in general (R^2 = 0.07 and 0.2). It is worth mentioning that HI (i.e. fugitive emissions with occupational exposure limits) has no correlation whatsoever with AHI (environmental atmospheric hazard index with catastrophe scenario) even both include also toxicity data. In fact fugitive emission based indices HI and FE correlate very badly with any other EHS indices. Therefore the conclusion is, that the effect of fugitive emissions cannot be estimated by any other means (e.g. from properties of chemicals involved) but only calculating the fugitive rates.

The WAR method has correlation (average $R^2 \approx 0.7$) with all loss of containment type of safety and environmental methods even though the background of WAR is normal operation based. It has also a similar size of correlation with IOHI.

3.5 Search for one index for EHS

If the aim is to simplify index based EHS evaluations, it would be ideal to have only one or two indices need for the whole EHS evaluation. By looking at the correlation in Table 3, it can be seen that there are some methods, which have high correlation in all

Table 4: Correlations if only one index is used for all criteria in MMA route evaluations

Index 1	instead of:	Average R^2
IOHI	ISI and IETH	0.95
ISI	IOHI and IETH	0.94
IETH	ISI and IETH	0.92

Table 5: Average correlation between EHS criteria

Criterion 1	Criterion 2	Average R^2
Safety	Health	0.78
Safety	Environment	0.78
Health	Environment	0.55

EHS categories. Such methods are ISI, *i*-Safe, IOHI and IETH (also EHI but it is a subindex of IETH). *i*-Safe can be used instead of ISI with similar results but it has lower correlation with inherent safety expert values, so ISI was selected.

By using only one index method for evaluating all EHS aspects, the correlations (R^2) found are presented in Table 4. For example the first line shows that, if IOHI is used for estimating also inherent safety and inherent environmental toxicity hazard for MMA routes, the coefficient of determination (R^2) is 0.95.

The conclusion is that IOHI or ISI method alone can be used as a single index method for estimating all the EHS properties at least in the MMA case study for route selection. One should remember however that health aspects do not in this case include the inhalation based fugitive sources, since those did not correlate with the other health indices. They should be evaluated separately. Also it is known that the correlation is worse for single sub process comparisons as discussed by Hurme and Rahman (2005).

3.6 Average correlation between EHS criteria

As shown before in Table 4 the correlation of the best EHS indices in the case study is very good. Table 5 presents average correlation between *all* EHS criteria, when HI and FE indices and expert values are excluded. This exclusion was done, since HI and FE values did not have any correlation with any other EHS methods and expert values were only reference data.

From Table 5 it can be seen that the average correlation between EHS indices is strongest between safety & health and safety & environmental criteria (0.78). The correlation is less between health & environment (0.55).

4. Conclusions

A correlation between methods for assessing different hazard criteria of chemical processes was investigated by subjecting EHS index methods to pair-wise comparison. It was found out that the index methods have different basic characteristics in the type of calculation (additive vs. average), operating scenario (normal operation vs. catastrophic event) and time scale considered (long vs. short) as shown in Table 2. In addition the methods have different sets of parameters included (Table 1). Understanding this background is essential when comparing the methods and their correlations. It was found that the average correlation between EHS indices is strongest between safety & health and safety & environmental criteria (0.78). The average correlation between health & environment is worse (0.55) in the case study done.

The aim to simplify index-based EHS evaluations by using only one index for the whole EHS evaluation looks feasible, since the correlation of the best EHS indices is very good (0.95). The conclusion is that IOHI or ISI method alone can be used as a single index method for estimating all the EHS properties for route selection in this case study. It is however known that the correlation is less for sub process evaluations.

By studying the index correlations, it was found also that neither fugitive emission estimation with exposure limit values nor the properties of chemicals involved in the process are able to predict total occupational health level but both approaches are needed. The estimation of inherent fugitive emission rates is essential for both the health and environmental evaluations.

The findings from this correlation analysis can be further exploited accordingly to optimize the overall EHS performance of a chemical process, since most EHS properties go together.

5. References

Anon, 1987, Our Common Future, Oxford University Press, Oxford.
Cave S. R. and D. W. Edwards, 1997, Comp. Chem. Eng. 21, S965.
Crawley F. K. and D. Ashton, 2002, J. Hazardous Mat. 93, 17.
Edwards D. W. and C. Lawrence, 1993, Process Saf. Environ. Prot. 71(B4), 252.
Gunasekera M. Y. and D. W. Edwards, 2003, Process Saf. Environ. Prot. 81, 463.
Gunasekera M. Y. and D. W. Edwards, 2006, J. of Loss Prev. Process Ind. 19(1), 60.
Hassim M. H. and D. W. Edwards, 2006, Process Saf. Environ. Prot. 84(B5), 378.
Hassim M. H., D. W. Edwards and M. Hurme, 2006, Chem. Eng. Trans. 9, 119.
Hassim M. H. and M. Hurme, 2008, Manuscript.
Heikkilä A.-M., M. Hurme and M. Järveläinen, 1996, Comp. Chem. Eng. 20, S115.
Hertwich E. G., W. S. Pease and T. E. McKone, 1998, J. Env. Sci. Tech. 32(5), 138A.
Hurme M. and M. Rahman, 2005, J. of Loss Prev. Process Ind. 18, 238.
Khan F. I., R. Sadiq and P. R. Amyotte, 2003, Process Safety Prog. 22(2), 83.
Koller G., U. Fischer and K. Hungerbühler, 2000, ESCAPE-10, Elsevier, 931.
Koller G., U. Fischer and K. Hungerbühler, 2001, Process Saf. Environ. Prot. 79, 157.
Lawrence, D., 1996, PhD Thesis, Loughborough University, UK.
Palaniappan C., R. Srinivasan and R. Tan, 2004, Chem. Eng. Process. 43, 647.
Rahman M., A.-M. Heikkilä and M. Hurme, 2005, J. of Loss Prev. Process Ind. 18, 327.
Whitehead P. and G. Whitehead, 1993, Statistics for Business, 2nd Ed, Pitman, London.
Young D.M. and H. Cabezas, 1999, Comp. Chem. Eng. 23, 1477.