

Safety Assessment Curve (SAC) for Inherent Safety Assessment in Petrochemical Industry

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This paper highlights the development of a new numerical approach for safety assessment called Safety Assessment Curve (SAC). Most of the current methods for assessing inherent safety are index based method. Among the disadvantages of such methods is it employs scaling by dividing physical or chemical properties into subjective ranges and sudden jump in the score value at the sub-range boundary. This new technique can offer more useful features because aside from assessing the routes numerically, it could also graphically visualizes the effect of temperature, pressure, heat of reaction, process inventory, flammability, explosiveness, toxicity and reactivity in designing an inherently safer design for both, grass-root and retrofit cases in petrochemical industry without including subjective scaling and sudden jump in the score value. Due to page limitations, this paper will only discuss the development of SAC for chemical safety parameters. This novel technique can be used as an effective method to find the safer route among several number of alternatives for chemical synthesis or process retrofitting, besides highlighting the potential source of hazards in the process through numerical and graphical approach. The new SAC technique illustrated in this paper has been tested on methyl methacrylate manufacturing confirming its superiority in comparison to index-based method. Tertiary butyl alcohol (TBA) route has the lowest Chemical Safety Total Score suggesting it as the safest routes among the three routes for MMA production compared to acetone cyanohydrin (ACH) and ethylene via methyl propionate (C2/MP) based routes.

1. Introduction

Ideally, process plants should be built so that they are user-friendly and able to endure deviation from ideal performance by operators and equipment failures without serious impacts on safety, output or efficiency (Kletz and Amyotte, 2010). Thus, plants should be designed so that small amounts of hazardous materials is used so that it does not matter if it all leaks or use safer materials instead of the hazardous ones. Another approach is to use the hazardous materials at lower operating conditions in order to avoid the hazard problems rather than solving the hazard problems. This is somehow resulting to inherently safer plants. Many methods have been developed for assessing safety performance of a process during the design stage. One of the examples is the Prototype Index for Inherent Safety (PIIS) (Edwards and Lawrence, 1993) which considers seven parameters of chemical and process safety with subjective scaling for score assignments. The Inherent Safety Index (ISI) (Heikkila, 1999) also categorizes the safety assessment parameters into chemical and process safety with score assignment was done based on the available indices such as Mond Index. i-Safe (Palaniappan et al., 2002a, b) evaluates a process route based on eight parameters of chemical and process safety through an index called the Overall Safety Index (OSI). Aside from safety aspect, SHE Method (Koller et al., 2000) covers health and environmental parameters. Similarly, the Inherent Benign-ness Index (IBI) (Srinivasan and Nhan, 2008) assesses not only safety but also health and environmental aspects by using multivariate statistical analysis. Another method that integrates safety, health and environmental parameters in its evaluation is Inherent Chemical Process Properties Data (Hassim and Ali, 2009). M.I.M.O.SA. or also known as Methodology for the

implementation and Monitoring of Occupational Safety (Saracino et al., 2012) is another tool that evaluates performance of an enterprise from the perspective of health and safety in workplaces. The final score for M.I.M.O.S.A. evaluation is obtained by calculating the Index of Performance for Safety and Health (IPESHE) (Saracino, 2012).

Majority of these methods are index-based method such as the PIIS (Edwards and Lawrence, 1993), ISI (Heikkila, 1999), SHE Method (Koller et al., 2000), i-Safe (Palaniappan et al., 2002a, b) and also Inherent Chemical Process Properties Data (Hassim and Ali, 2009). As highlighted by Srinivasan and Nhan (2008), shortcomings of index-based method are subjective scaling by dividing physical or chemical properties into subjective ranges and a score based on the authors' judgment is assigned to each range making the scoring tables differ for every method on the same parameters. Another shortcoming is sudden jump in the score value at the sub-range boundary (Gupta and Edwards, 2003). A few attempts in solving these shortcomings have been done through the development of several methods e.g. the Inherent Benign-ness Index (IBI) (Srinivasan and Nhan, 2008) and the simple graphical method for inherent safety assessment by Gupta and Edwards (2003). Parameters evaluated in the IBI method are scaled to the range of 0 to 1. As a solution to shortcomings mentioned previously, this method employs frequency distribution to scale the parameters evaluated (Srinivasan and Nhan, 2008). Meanwhile Gupta and Edwards (2003) proposed a safety assessment method that can be easily done by plotting the important parameters for each step of each route on a simple graph.

The aim of this paper is to introduce a combinatorial method of numerical and graphical for safety assessment in petrochemical industry in order to address the limitation by moving the score value for the parameter evaluated in a continuous manner instead of sudden jump. Compared to methods such as Inherent Benign-ness Index (IBI) (Srinivasan and Nhan, 2008) and The Simple Graphical Method for Inherent Safety Assessment proposed by Gupta and Edwards (2003), this method adopts logistic equation for score assignment in addressing the shortcomings. Due to the limited number of pages, this paper will focus on the Safety Assessment Curve (SAC) from the perspective of chemical safety only. Details on the SAC development for process safety assessment (which consists of temperature, pressure, heat of reaction and process inventory parameters) will be discussed later in a more extended paper.

2. Methodology

2.1 Selection of Safety Parameter

There are four parameters included in this method for chemical safety evaluation which are flammability, explosiveness, toxicity and reactivity. The flammability of liquids depends on the lower flammability limit of the material and its vapour pressure in most frequent temperature (Heikkila, 1999). Thus, liquids with lower flash point exposes more hazard compared to liquids with higher flash point. The tendency of chemicals to form an explosive mixture in air or also known as explosiveness depends on the range between explosion limits (Crowl and Louvar, 2002). Under the Lower Explosion Limit (LEL), the mixture is too lean to burn while the mixture is too rich for combustion above the Upper Explosion Limit (UEL) (Crowl and Louvar, 2002). Thus, wider range between LEL and UEL indicates higher tendency for explosion. Toxicity is a property of the agent describing its effect on biological organisms (Crowl and Louvar, 2002). In this method, threshold limit values for short-term exposure limit will be used (TLV-STEL) which is more significant for acute toxicity type of event. Lower TLV-STEL value for a chemical indicates larger hazard compared to chemical with higher TLV-STEL value. NFPA reactivity rating is used to measure reactivity. NFPA rating is widely available and of the source is from Material Safety Data Sheet (MSDS) that come with the chemicals.

2.2 Development of SAC through Logistic Equation

2.2.1 Brief Introduction to Logistic Equation

The SAC is constructed through the application of logistic equation. The general equation for logistic equation is as shown in Eq(1) (Larsen and Marx, 2001). There are three main constant parameters in logistic equation which are C, B and A. C indicates the upper limit of the curve. The upper limit will give a restriction on the output value of y, this means that y value will only be equal or less than C value. This characteristic is suitable for score establishment. For example, if C value is set as 100, the maximum value for output y can only be 100 at most. B affects the slope of the logistic curve represented by Eq.(2) through m value which represent the slope inclination for the curve to be made while A affects the mid-point of the logistic curve represented by Eq.(3) through k value which is the x-axis value at $y=C/2$.

$$y = \frac{C}{1 + Ae^{-Bx}} \quad (1)$$

$$m = \frac{BC}{4} \quad (2)$$

$$A = e^{Bk}, \text{ k is the x-point at } y = C/2. \quad (3)$$

Table 1 shows both k and m values for chemical safety parameters for logistic equation development. The type of data used are flash point values for flammability parameter, UEL-LEL values for explosiveness parameter, TLV-STEL values for toxicity parameter and NFPA reactivity ratings for reactivity parameter. All of these values were analyzed using cumulative curve for each parameter. k value for each parameter is adjusted according to the mean value and median value obtained from data analysis while m value for each parameter is adjusted according to the slope of the cumulative curve constructed previously.

Table 1: k and m values for Chemical Safety Parameters

Parameters	k Value	m Value
Flammability	55.3	0.006
Explosiveness	50	0.035
Toxicity	500	0.003
Reactivity	2	0.7

2.2.2 SAC Development for Chemical Safety Parameters

Both values of m and k from Table 1 were applied into Eqs.(2), (3) and also Eq.(1) for every parameter. The logistic equation for flammability parameter is produced as Eq.(4). However, a small alteration needs to be made on the equation hence lower flash point will contribute to higher hazard. The alteration made is by subtracting the equation to the value of 1 before the whole equation is multiplied by coefficient C as shown in Eq.(5). The alteration is made in order to ensure that the curve is following the relationship of lower flash point contributed to higher hazard. With this alteration, the curve will begins at 100 score point for low flash point value that is more hazardous and ends at 0 score point for higher flash point value which is safer. This alteration was also applied in constructing SAC for reactivity parameter. Then, a curve as in Figure 1(a) is plotted. Figure 1(a) indicates that lower flash point temperature will results in higher score.

$$y = 100 \times \left(\frac{1}{1 + 3.77e^{-0.024x}} \right) \quad (4)$$

$$y = 100 \times \left(1 - \left[\frac{1}{1 + 3.77e^{-0.024x}} \right] \right) \quad (5)$$

There is one assumption in constructing SAC for explosiveness parameter. Since both UEL and LEL is expressed in percent by volume (vol%), thus the 50% range between UEL and LEL is taken as the mid-score for explosiveness SAC which indicates both not very safe and not very hazardous either. Thus, the assumption is the mid-score for explosiveness SAC is 50% range between UEL and LEL. By applying both values from Table 1 to Eqs.(1), (2) and (3) the logistic equation as shown in Eq(6) is produced. Lastly, a curve as in Figure 1(b) is plotted with higher range between UEL and LEL indicates higher hazard with high score designation.

$$y = 100 \times \left(\frac{1}{1 + 1096.63e^{-0.14x}} \right) \quad (6)$$

Threshold Limit Value (TLV) is not intended to define the "safe" and "unsafe" level. Thus, the SAC is simply made so that it starts with 0 ppm TLV-STEL with the highest score of 100. In this method, higher score represent higher hazard imposed by the chemicals. Since chemical with lower TLV-STEL value is more hazardous than chemical with higher TLV-STEL value, the equation need to be subtracted from 1

before the whole equation is multiplied by coefficient C which is 100. Eq(7) shows the logistic equation for toxicity parameter. Figure 1(c) shows the SAC plotted with higher TLV-STEL values are represented by lower score values.

$$y = 100 \times \left(1 - \left[\frac{1}{1 + 403.43e^{-0.012x}} \right] \right) \quad (7)$$

The assumption used in establishing SAC for reactivity parameter is taking NFPA rating of 2 as the mid-score in SAC due to its indication as medium level hazard. The slope for reactivity SAC is taken as 1. There are no specific reasons in taking value 1 as the slope. The value is taken so that the score values disperse widely from 0 to 100 for NFPA rating 0 to 4. The logistic equation for reactivity SAC is as shown in Eq(8) with Figure 1(d) shows the plotted curve for the equation.

$$y = 100 \times \left(\frac{1}{1 + 270.43e^{-2.8x}} \right) \quad (8)$$

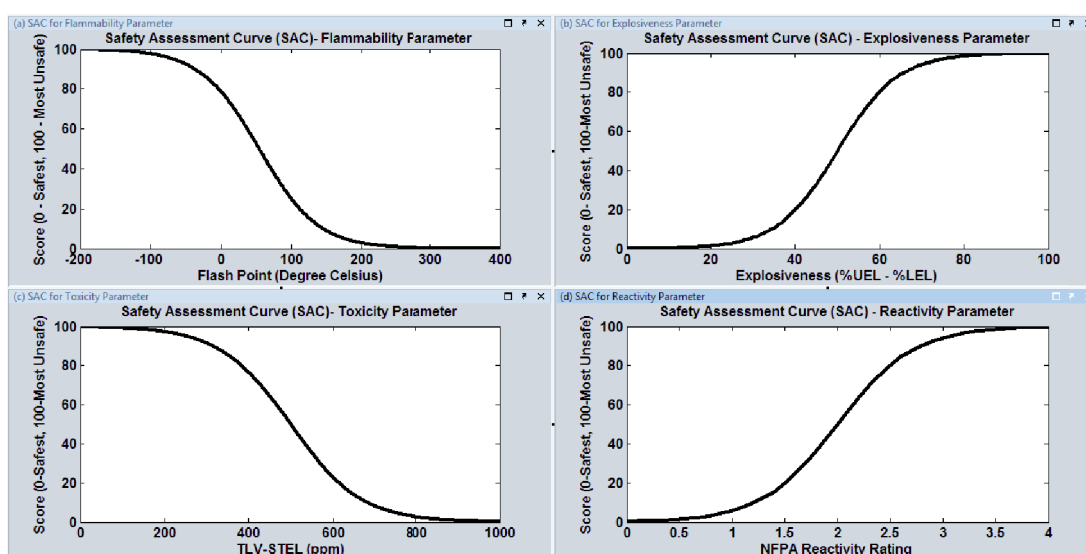


Figure 1: Safety Assessment Curve for Chemical Safety Parameter

2.2.3 Chemical Safety Total Score

The total score for Chemical Safety is calculated by adding the maximum scores evaluated from each parameters according to Eq(9). The score for each parameter is normalized from 0 to 100 through the use of logistic functions, thus enabling the scores of different parameters to be added together. The calculation of Chemical Safety Total Score is made based on the worst case situation as used in Prototype Index for Inherent Safety PIIS (Edwards and Lawrence, 1993) method and Inherent Safety Index (ISI) method by Heikkila (1999). According to Heikkila (1999), the approach of the worst case describes the most risky situation that can appear. The score for flammability, explosiveness, toxicity and reactivity are calculated separately for each chemical in the process. A higher Chemical Safety Total Score represents relatively a higher hazard level in comparison to a lower Chemical Safety Total Score.

Chemical Safety Total Score

$$= (\text{Score}_{(\text{Flammability})})_{\max} + (\text{Score}_{(\text{Explosiveness})})_{\max} + (\text{Score}_{(\text{Toxicity})})_{\max} + (\text{Score}_{(\text{Reactivity})})_{\max} \quad (9)$$

3. Application of SAC to Case Study

The method produced was applied in assessing three processing routes for methyl methacrylate (MMA) production. The three routes are;

- 1) Acetone cyanohydrin based route (ACH)
- 2) Ethylene via methyl propionate based route (C2/MP)
- 3) Tertiary butyl alcohol based route (TBA)

Table 2 shows the calculated results as well as route ranking for MMA manufacturing processes. TBA route has the lowest Chemical Safety Total Score suggesting it as the safest route among the three routes which is rank as 1. C2/MP route has the highest Chemical Safety Total Score which is 330.11 indicating it as the most hazardous route in term of chemical safety ranked as 3.

Table 2: Route Ranking for MMA Manufacturing Process

Based Route	Chemical Safety Total Score	Rank ^a
ACH	258.39	2
C2/MP	330.11	3
TBA	240.00	1

^a 1 refers to the most safest route while 3 refers to the most hazardous route

Further analysis can be done in order to identify which chemical substances influence the Chemical Safety Total Score the most by looking at the graphical representation of the case study results. This can be done by plotting the score received by each chemical on the SAC curves as shown in Figure 2. Figure 2 shows that methane used in the ACH route has the highest score for flammability parameter compared to other chemicals followed by carbon monoxide and ethylene used in the C2/MP route. As for explosiveness parameter, carbon monoxide used in the C2/MP route has the highest score followed by hydrogen cyanide in the ACH route and ethylene in the C2/MP route.

However, as for toxicity parameter, most of the chemicals in the ACH route are more toxic than the chemicals in the other two routes e.g. hydrogen cyanide, sulphuric acid, sulphur dioxide and sulphur trioxide. Analysis for reactivity parameter shows that most chemicals in all the three routes have zero (0) NFPA rating with NFPA rating 2 being the highest. Chemicals with NFPA rating 2 are ethylene and methylal in the C2/MP route, methacrylic acid in the TBA route and methacrylamide, sulphuric acid, and sulphur trioxide in the ACH route. A relatively higher Chemical Safety Total Score for the C2/MP route is greatly influenced by flammability and explosiveness parameters while the ACH route Chemical Safety Total Score is highly influenced by toxicity parameter. The TBA route has moderate scores for all parameters resulting it as the safest route among the three alternative routes.

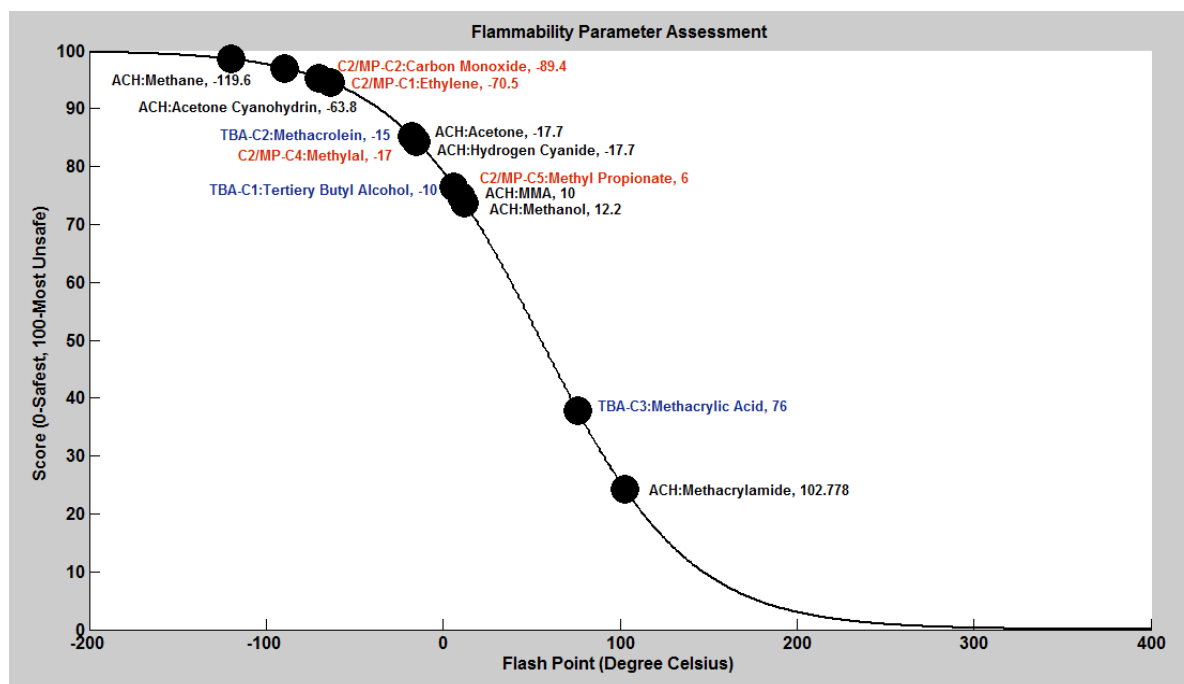


Figure 2: Case Study Results Analysis for Flammability Assessment

4. Conclusions

In conclusion, Safety Assessment Curve (SAC) proposed in this paper can be used for safety assessment during process design stage of petrochemical plant. Assessment method in a form of simple curves as well as the incorporation of worst case scenario evaluations enable users to easily identify the most hazardous route, reaction step as well as the most hazardous chemical substance even for those who are not familiar with the concept of safety. In order to produce a more detailed result, assessment on chemical safety will need to be accompanied by safety assessment on process safety aspect as well.

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References

- Crowl D. A., Louvar J. F., 2002, *Chemical Process Safety Fundamentals with Applications Second Edition*, New Jersey, USA: Prentice Hall.
- Edwards D.W., Lawrence, D., 1993, Assessing the Inherent Safety of Chemical Process Routes: Is there a Relation Between Plant Costs and Inherent Safety?, *Trans IChemE*, 71 Part B, 252-258.
- Gupta J. P., Edwards D. W., 2003, A Simple Graphical Method for Measuring Inherent Safety, *Journal of Hazardous Materials*, 104,15-30.
- Hassim M. H., Ali M. W., 2009, Screening Alternative Chemical Routes Based On Inherent Chemical Process Properties Data: Methyl Methacrylate Case Study, *J.-The Inst. of Engineers Malays*, 70,2-10.
- Heikkila A-M., 1999, *Inherent Safety in Process Plant Design An Index-Based Approach*, PhD Thesis, Helsinki University of Technology, Finland.
- Kletz T., Amyotte P., 2010, *Process Plants A Handbook for Inherently Safer Design Second Edition*, Boca Raton, Florida, USA, Taylor and Francis Group.
- Koller G., Fischer U., Hungerbuhler K., 2000, Assessing Safety, Health, and Environmental Impact Early during Process Development, *Ind. Eng. Chem. Res*, 39, 960-972.
- Larsen R. J., Marx M. L., 2001, *An Introduction to Mathematical Statistics and Its Applications*, Third Edition, New Jersey, USA: Prentice-Hall.
- Palaniappan C., Srinivasan R., Tan R., 2002a, Expert System for the Design of Inherently Safer Processes. 1. Route Selection Stages, *Ind. Eng. Chem. Res.*, 41, 6698- 6710.
- Palaniappan C., Srinivasan R., Tan R., 2002b, Expert System for the Design of Inherently Safer Processes. 2. Flowsheet Development Stage, *Ind. Eng. Chem. Res.*, 41, 6711-6722.
- Saracino A., Curcuruto M., Pacini V., Spadoni G., Guglielmi D., Sacconi C., Bocci V. M., Cimarelli M., 2012, IPESHE: An Index for Quantifying the Performance for Safety and Health in a Workplace, *Chemical Engineering Transactions*, 26, 489-494 DOI: 10.3303/CET1226082
- Saracino A., Spadoni G., Curcuruto M., Guglielmi D., Bocci V. M., Cimarelli M., Dottori E., Violante F., 2012, A New Model for Evaluating Occupational Health and Safety Management Systems (OHSMS), *Chemical Engineering Transactions*, 26, 519-524 DOI: 10.3303/CET1226087
- Srinivasan R., Nhan N. T., 2008, A Statistical Approach for Evaluating Inherent Benign-ness of Chemical Process Routes in Early Design Stages, *Process Safety and Environmental Protection*, 86, 163-174.