



5th Annual Symposium, Mary Kay O'Connor Process Safety Center
"Beyond Regulatory Compliance: Making Safety Second Nature"
Reed Arena, Texas A&M University, College Station, Texas
October 29-30, 2002

Some Thoughts on Measuring Inherent Safety

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Abstract:

Inherently Safer Design (ISD) concepts have been with us for over two decades since their elaboration by Trevor Kletz [1]. Interest has really taken off globally since the early nineties after several major mishaps occurred during the eighties (Bhopal, Mexico city, Piper-alfa, Philips Petroleum, to name a few). Academic and industrial research personnel have been actively involved into devising inherently safer ways of production. The regulatory bodies have also shown deep interest since ISD makes the production safer and hence their tasks easier. Research funding has also been forthcoming for new developments as well as for demonstration projects.

A natural question that arises is as to how to measure ISD characteristics of a process? Several researchers have worked on this [2 - 4]. Many of the proposed methods are very elegant, yet too involved for easy adoption by the industry which is scared of yet another safety analysis regime. In a recent survey [5], companies desired a rather simple method to measure ISD. Simplification is also an important characteristic of ISD. It is therefore desirable to have a simple ISD measurement procedure.

The proposed ISD measurement procedure can be used to differentiate between two or more processes for the same end product. The salient steps are: Consider each of the important parameters affecting the safety (e.g.: temperature, pressure, toxicity, flammability, etc.) and the range of possible values these parameters can have for all the processes under consideration for an end product. Plot these values for each step in each route and compare. No addition of values is being suggested to derive an overall ISD index value since that conceals the effects of different parameters. Further, addition of numbers with different units (C for temperature, atm./bars for pressure, tonnes for inventory, etc.) is inappropriate in scientific sense. These need to be made dimensionless before addition. The proposed approach has a major advantage of expanding consideration in future to incorporate economic, regulatory, pollution control and worker health aspects, as well as factors such as the experience one has or 'the comfort level' one feels with each of the processes under

consideration. Further, this would also guide the designers and decision makers into affecting specific changes in the processes to reduce some of the discomforting features.

We demonstrate our simple approach by using the example of 6 routes to making methyl methacrylate as documented by Edwards and Lawrence [2, 6] and show that the decision could well have been different if addition of disparate hazards had not been done.

Introduction:

The concepts of Inherently Safer Design (ISD) have been with us for over two decades since their elaboration by Trevor Kletz [1]. These simple words convey a powerful meaning that has, since the early nineties, generated a lot of interest in the process industry. For those uninitiated, ISD means avoidance of hazards by design rather than controlling them by add-on measures. Apart from managers in industries, researchers in academics, the regulatory bodies have also shown interest in this.

There are as yet no definitive hard and fast rules as to how to make a process inherently safer. This is just as well since it leaves one to apply one's experience and keep in mind the ground realities based on his geographical location and business environment. It is however agreed that the best time to apply ISD concepts is at the initial R&D stage when the research chemists and engineers work hard to decide what reactants to use and under what operating conditions to produce the desired products. After a lot of investment has been made at the R&D stage, it becomes difficult to make fundamental changes, like altering the reactants or operating conditions, since that would mean loss of all the efforts, money and time invested thus far and, probably also missing the window of opportunities to come out with the desired product in time. However, ISD concepts can be applied in an operating plant as well.

Current status:

As is known to researchers, there are many ways to skin a cat. One could, in many cases, use any of the possible multiple approaches (reactants, catalysts, operating conditions, etc.) towards producing the desired product. Thus far, the technical feasibility and economics have guided the choice; the process safety has grudgingly been added as a criterion since the Bhopal tragedy. A natural question that arises is as to how to decide which of the various choices available is the best as far the application of the ISD concepts is concerned. Several researchers have worked on this [2 - 4]. Many of the proposed methods are very elegant, yet too involved for easy adoption by the industry which is scared of yet another safety analysis regime, not yet mandated by law. Further, for ISD to make a real impact, research chemists, who thus far have generally remained oblivious of the safety issues and hazard analysis, etc., will need to use it. They would not be too pleased with any involved methodology imposing upon their time. In a recent survey [5], companies desired a rather simple method to measure ISD. Simplification is also an important characteristic of ISD. Actually, simplicity and inherent safety are complementary [5a]. It is therefore desirable to have a simple ISD measurement procedure. It should be stated at the outset that what is proposed is a first step designed to induce the concerned people to use the simple approach and make their processes

inherently safer. It may not be the most inherently safer design possible but a significant step in that direction. With widespread use of the proposed method, will come modifications and a final method will evolve by consensus. It is of course difficult to predict the way the future will unfold in this regard. [Consider PCs. If the early ones in 1980s were as sophisticated as the present ones, their adoption would have been slower. The earlier ones were simple, people went for them, the industry put in more and more money and efforts into R&D, thus leading to the global IT boom and the present increasingly sophisticated PCs readily accepted by the users.]

In all our discussions, it is assumed that the process equipment as designed, fabricated and erected, is as per the approved codes and standards and is suited for the intended duty under the prescribed operating conditions. It is the unintended deviations from the desired operating conditions, reactants' purity, good maintenance practices, recommended operator training, and the impact of natural or man-made disasters that can lead to significant and sudden changes, increasing the risks of hazards materializing. If a unit is not well designed to handle its intended duty, no amount of precautions will stop risks from materializing even during the normal operating conditions.

Our proposed method uses Edwards and Lawrence [2] index extensively as a background. Hence, it is appropriate to discuss that index and point out the proposed differences.

Edwards and Lawrence Index:

We present our proposed method by means of an example. A splendid one has been provided by Edwards and Lawrence [2] with all the details being in Lawrence's thesis [6]. They listed 17 parameters that they thought might affect inherent safety (IS) of a process (Table 1). Of these, they chose to work with 7 parameters in the first application of their proposed IS index (Table 1). They looked at the total ranges that each of these parameters could possibly take in the process industry, divided each into several sub-ranges and assigned numerical scores to each sub-range. These subdivisions were based on some existing indices [Dow Index (7), Mond Index (8)] or on their own thoughts at that moment. Tables for temperature, pressure, inventory, and explosiveness are given in Tables 2 to 5 for our discussion purposes. The original reference has tables for yield, toxicity and flammability also. In this elaborate exercise, they considered 6 routes to manufacture methyl methacrylate (MMA, Table 6). They looked at length at each of the steps involved in the six routes. They noted down the operating pressure and temperature, yield, as well as flammability, toxicity and explosiveness of all the chemicals and intermediates involved. For inventory, they took a one-hour residence time, and stoichiometric relationship into account for a 50,000 tonnes per year production of the final product, MMA. For each step, they considered the worst chemical for flammability, toxicity and explosiveness. Flammability score was based on the flash point and boiling point of a chemical (adapted from the Dow Index), explosiveness was based on the range of explosive mixture (the difference between the upper and lower explosive limits, UEL-LEL), while toxicity was based on the threshold limit value (TLV) that a worker can be exposed to for 8 hours a day, 5 days a week throughout his working life without developing any adverse effects.

The scores for each step in a given process route for pressure, temperature and yield were added together and called the 'process score', while those for inventory, toxicity, flammability, explosiveness were added together and called the 'chemical score'. The scores thus obtained for each step in a route were then added to get a score for each route. These final scores were taken as a measure of the inherently safer (actually, inherently riskier) nature of different routes and the one with the highest numerical value was taken to be the worst route (Tables 7, 8). Based upon this exercise, it was concluded that the ACH route was the most inherently unsafe one. Note that this is the only route in use in major manufacturing facilities worldwide for several decades (unless some local laws prohibit the use of hazardous chemicals like HCN, HF, etc., thus forcing the choice of a different route).

Another path-breaking approach that Edwards and Lawrence took was to invite 8 renowned process safety experts to comment on their work (List of Experts in Table 9). These experts first looked at each of the routes *in toto*, then at each of the steps (without referring as to which route the specific step belonged to) and finally at the proposed index. Their ranking of the different routes matched to a large extent the ranking obtained by Edwards and Lawrence using the proposed index. That is not surprising since, **whether with or without an index**, a process route with high pressure, high temperature, high values of toxicity, flammability and explosiveness, and high inventory is more dangerous (and hence more inherently unsafe) than routes that are otherwise.

This pioneering work by Edwards and Lawrence caught the attention of several researchers and has resulted in modifications of the proposed index. Heikkila [3] added a few more parameters (type of equipment, safety of process structure, chemical interaction) to the list of Edwards and Lawrence, altered some of the scoring tables and went on to propose a modified index. She included the equipment layout as well. Both the Edwards and Lawrence index and the Heikkila index have a sudden jump in the score value at the sub-range boundary; e.g., looking at Table 2 for temperature, while the score remains 2 for a variation from 100 C to 199 C, it changes to 3 for a 1 C change, from 199 to 200. Similar discontinuities exist in other parameters' scoring tables as well. Gentile, et al. [4] have proposed an ingenious way of getting around this by the use of fuzzy logic which moves index values in a, sort of, continuous manner instead of sudden jumps. Palaniappan [9] has proposed an expert system, called *iSafe*, for the design of inherently safer processes.

All of the above developments were influenced by the pioneering work of Edwards and Lawrence. In Lawrence's thesis [6], there were comments by the invited experts. These comments seem to have either been ignored by other developers or they did not know of them. We will summarize some of them hereunder while referring the interested readers to the thesis for the details. We have added our comments within square brackets. The experts' comments follow:

- Addition of disparate hazards destroys dimensionality. How can one add temperature (C), pressure (atm.), inventory (tonne), toxicity (ppm), etc., and compare the summed values for different process routes? To add, all the terms should have the same dimensions or be made dimensionless to start with. [This is the very crux of chemical engineering, rather all engineering and science disciplines. Mix-up in units or just

errors in conversions have led to terrible designs or shortening the range of test missiles. Making dimensionless would mean that the numbers should mean the same in each table. Thus, a numerical value of 3 for the range 200 C to 299 C in the temperature table (Table 2) would mean the same level of hazard as a pressure of 141 psi to 250 psi (Table 3), an inventory of 2501 to 7000 tonnes of inventory (Table 4), a toxicity offered by a TLV of 10 to 99 ppm (Table 5), and so on for the other parameters. Establishing this kind of equivalency [matrices of equal hazards] is a mammoth task, costing huge amounts and one has to decide whether it is really worth doing this. Such kinds of expenditure to evaluate the inherently safer nature of a plant will discourage potential users.]

- Adding together different steps in a route gives the same weightage to each route. A route with 2 steps may not be twice as bad as a single step route; it could be better or worse than that. A multi-step process could be better than a single-step, high-hazard process. The index does not account for such situations. [Since individual steps do not differ too much from each other, the number of steps became the deciding criterion, which is not the intention in any process development, though one does try to keep the number of steps low.]
- The experts' assessment of individual steps differed significantly from that done by using the scoring tables of the index [6, page 82]. [This shows that the scoring tables probably have a limited value in assessing the inherently safer nature of a reaction step. This comment would also apply to the overall route assessment procedure wherein the scores for each of the steps are summed up.]
- Small inventories of several chemicals could be worse than large inventory of a single chemical.
- Instead of using UEL – LEL as the criterion, use LEL since that is more important. Looking at ammonia, ethane and pentane, one finds the explosive ranges as

Ammonia: $27 - 16 = 11$, score 2 [Table 5]

Ethane: $12.5 - 3 = 9.5$, score 1

Pentane: $7.8 - 1.4 = 6.4$, score 1

Ammonia having a significantly greater LEL requires a richer mixture in air before it will ignite. It will ignite after ethane and pentane and is therefore safer while a score of 2 above would imply it to be less safe than ethane and pentane. Hence, the score based on the range is not as good.

Some experts even said that knowing whether a chemical is flammable/ explosive or not is sufficient [and there is no need to consider the range or the LEL].

- Yield is irrelevant since it affects inventory, which is accounted for separately.

- Low temperature (cryogenic) effects are known from the process conditions and hence can be accounted for in the selection of material of construction. Even water-common salt mixtures can reach -25 C for which a penalty of 3 has been proposed, same as for the 200 C to 299 C range. [At the extremes of the two ranges, i.e., -25 C and 299 C , the temperature difference is 324. If the thumb rule of reaction rate doubling for a 10 C rise in temperature were to hold all through, the rate at 299 C would be 2^{32} times than that at -25 C , a very high rate to control for heat release! Yet the score assigned is the same at -25 C and 299 C]. Leakages at low temperatures result in minimal evaporation and hence are not as hazardous as are the leaks at high temperatures. Possibility of leakages and massive flash also exist at high temperature. Hence, high temperature, and not low temperature, needs to be considered as an operational hazard.
- The pressure score from the pressure table would be 16 at the pressures used for high-density polyethylene manufacture (HDPE). This will override other considerations and make the plant appear to be excessively dangerous, while the experience shows that HDPE plants are safe to operate.
- Inventory sub-range of 0.1 to 250 tonnes is rather wide. Most process industry inventories will fall in this range. Anything above it would usually be bulk storage, not a process inventory.
- While the U.K. Health and Safety Executive (HSE) says that hazard is proportional to the square of inventory, the table gives more like proportional to the square root of inventory, thus downgrading it by an exponent of 4. While a 20-T propane disaster in Spain had resulted in over a hundred deaths, the suggested score in the inventory table would be 1 only, i.e., the safest of all.

There are comments on other parameters as well as suggestion of new parameters to be added, need for separation process inventories, etc. For these, Lawrence's thesis should be consulted. We have mentioned only the comments that affect our proposed methodology.

Our proposed method:

The above comments of the experts on additive index are self-explanatory. Primarily, there are two concerns:

- Addition of different types of hazards
- Arbitrary assignment of scores to different parameters (P, T, Inventory, ...) without establishing equality of hazard for the same numerical value (Does a number 3 in the table for pressure present the same hazard as 3 in table for inventory or flammability, etc.)

The experts, when they looked at the reaction steps, were not looking at the tables of scores but at each step individually as to how it measured up vis. a vis. the hazard potential. Actually, they did not know of those scoring tables till late. This confirms our view that

consideration of each step is important instead of the tables of scores and their subsequent addition that will get biased by the number of steps, like in the ACH route to MMA or one major number, like the pressure in the HDPE process.

Hence, we propose that the parameters of interest be plotted individually for each step in a process route without carrying out any mathematical operation and then be compared with each other.

When we first proposed the above and forwarded for comments to some experts, we got the following comments from Trevor Kletz [10] "... 'Instead of an absolute index we could compare a proposed new design (or designs) with ... an existing design, using a number of headings. This benchmarking approach would give a comparison of alternatives rather than a position on a scale. This should be satisfactory as users want to know how different methods of making X compare, not if a plant for making X is safer than a plant for making Y...'. He further wrote [11] "... Your comments support my gut feeling that displaying a series of measurements will be more useful than trying to find a single number that measures inherent safety".

As a demonstration of our proposed method to measure inherent safety (or inherent risk), we will consider the 6 routes for ACH, data for which is in Lawrence's thesis [6]. We have plotted the values of temperature, pressure and a combined value for flammability, explosiveness and toxicity (FET) for each step in Fig. 1. FET values have been taken from the tables in Lawrence's thesis [6]. This has been done for two reasons: all the numbers in this are dimensionless: flammability based on flash point and boiling point; explosiveness based on volume percent and toxicity based on parts per million. Further, we did not wish to clutter the plot with too many points while introducing our idea of measuring inherent safety; it is as well conveyed with 3 points (for T, P, FET) as with 5 points (for T, P, F, E, T, if FET were plotted as 3 separate points).

In Lawrence's work [6], the FET values have been taken for the worst chemical in any reaction step. However, it is likely that while one chemical has the highest score for flammability, another may have for explosiveness and yet another may have the highest score for toxicity. In such a case, if there is a fire/explosion and the chemicals are released, it would be the chemical with the highest toxicity that will affect the exposed population the most. Thus, the FET value that we have plotted is the sum of the highest values for flammability, explosiveness and toxicity in that route. In many cases though, it was the same chemical that had the highest values for all the three.

We have not used the yield since, as an expert's comment noted above, it affects the inventory. Inventory too has been left out since it is difficult to calculate for each step at the preliminary stage and the values used in Lawrence's thesis were based on an arbitrary figure of one-hour residence time, without any reaction rate data being used to evaluate it. Reaction rate data is an essential parameter in evaluating inventory in any reactor to obtain the desired production rate.

Coming to Fig. 1, we will compare temperatures, pressures and FET values in one route with the respective temperatures, pressures and FET values in the other routes. We find, looking at the 6 steps in the ACH route, that the maximum pressure is 7 bars, while the next three routes have a maximum pressure of 49 to 100 bars. The maximum pressure in the remaining 2 routes is 7.5 bars, about the same as in the ACH route (7 bars). Further, 3 of the steps in the ACH route operate at atmospheric pressure, which would result in no flashing, if leaks were to occur. Summing up, the ACH route has a significant advantage over all the other routes as far the pressure is concerned.

Considering temperature, two of the steps in the ACH route have a higher temperature than any other route has. However, we feel that a higher pressure is more of a hazard than a higher temperature in as far leakage, flashing of a liquid or rupture of vessel and formation of energetic missiles and/or BLEVE with a possible domino effect, are concerned. This matches with the number of times (41) the experts in Lawrence's thesis used pressure as the key feature in describing their assessment of hazards in the MMA routes compared to the number of times (9) they used temperature as an important parameter (Fig. 2). Only one expert treated temperature on its own as an important parameter.

The experts gave the number of steps involved in a route a low importance. Two of the experts downgraded the hazards of the ACH route because of the experience they had had on this process and had found it to be very safe.

Looking at the FET values (Flammability, Explosiveness and Toxicity), the ACH route, in general has values similar to those in most other routes. On the other hand, the values of one or more steps in the next three routes are way high compared to the values in most other steps in all the routes. Following the experts' evaluation of key factors (Fig. 2), after pressure, the next important factors are flammability, toxicity, partial oxidation (not considered here) and explosiveness. When one takes these into account, the ACH route is really not all that unsafe. A larger number of moderate steps are probably better than a smaller number of steps with significantly higher pressure and FET values. As Fig. 1 shows, the ACH route appears to be better than at least the next three routes. We are unfamiliar with the figures on the number of major facilities using routes other than the ACH one, worldwide. They are unlikely to be many since the ACH route has proved successful over several decades.

The discussion above is not to favor one route for MMA production over the others, or to show that the conclusions drawn earlier need to be re-evaluated. It is to point out that the measurement of relative inherent safety between several routes for the manufacture of a product can be done by putting the important parameters for each step of each route on a simple plot and assessing the various values, especially in light of Fig. 2. Also, since the ISD can be applied to operating plants, one can look at the options in a similar way.

The advantage of this simple method of comparing inherently safer approaches is that one can expand consideration to incorporate economic, regulatory, pollution control and worker health aspects, as well as factors such as the experience one has or the 'comfort level' one feels with each of the processes under consideration. Results from accident databases can

be included as a parameter (e.g., frequency of accidents, loss per accident, etc.) As it expands, one can bring into consideration important aspects like of process intensification, where if the volume is reduced by, say a thousand fold, one can work at higher pressures, closer to runaway temperatures and with more toxic reactants since the total release in case of an accident would be rather limited due to the very small amounts involved. It can be argued that if each of the parameter has to be looked at individually, there is no need to plot them; instead a table of values would do as well. And that is so, except that a 'figure is worth a thousand words', and it does not make the procedure any more complex than having a table of values to compare.

The simple proposal above is to encourage the research chemists and process development personnel to consider inherently safer aspects right from the beginning. Actually, getting them to learn about ISD and use it are amongst the important aims of the ISD community, not so much the way one approaches ISD since many are common sense approaches. Once the R&D chemists start, they as well as the process safety personnel and researchers in academics and industry will gain more experience, leading to improvements in the inherent safety measurement procedures around which consensus would evolve.

The suggested procedure meets the desires of the process safety personnel surveyed recently from all over the world about the use of ISD [5]. The response was that they realized the importance and advantages of ISD; that they would like to use it if the procedures were simple and did not require too much time since they already had several mandated safety protocols to follow and file periodic reports on them with the regulatory bodies. [They also desired to know successful case studies of ISD applications.] They would not want to have to spend a lot of time and expertise in looking at the inherently safer aspects. Our feeling is that once the company personnel starting from research chemists, process engineers and the rest start using ISD, they would actually see the advantages and want to use it more and more. With process plants thus becoming significantly safer, the regulators are likely to gradually relax on process safety protocols for the plants whose management has gone through the ISD aspects thoroughly. This would be one way for the regulators to encourage the use of ISD without mandating it. It will be a win-win situation for all.

Once ISD is successfully applied to process industries, it can be extended to other accident prone industries such as mining, construction, transportation, etc. The Health and Safety Executive (HSE) of U.K. is planning to issue a Guideline on it [12].

In a somewhat related issue, accident investigations reveal problems with one or more of the following: company management, plant design, operation, maintenance, operator training and civic authorities, amongst others. It is difficult to assign any numbers to these and measure them. Yet, flaws in them can undo the best of process safety. To take an example of Bhopal tragedy, there were numerous items found wrong with it during subsequent investigations. Several of them are listed in Table 10. A related list could be made for the TMI or Chernobyl or Piper Alfa, etc. While it is difficult to measure the various items and give them numerical values, this does point to the need for using inherently safer designs in plants since the risks are greatly reduced.

References:

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Table 1: Parameters listed by Lawrence [6]

1. Inventory (volume or mass)*
2. Temperature*
3. Pressure *
4. Conversion
5. Yield*
6. Toxicity*
7. Flammability*
8. Explosiveness*
9. Corrosiveness
10. Side reactions
11. Waste and co-products
12. Reaction rate
13. Catalytic action
14. Heat of reaction
15. Phase
16. Phase change
17. Viscosity
18. Number of steps
19. Uniformity of steps

* Parameters considered in the MMA example.

Table 2: Temperature scoring table [6]

Temperature (°C)			Score
	T <	-25	10
-25	≤ T <	-10	3
-10	≤ T <	10	1
10	≤ T <	30	0
30	≤ T <	100	1
100	≤ T <	200	2
200	≤ T <	300	3
300	≤ T <	400	4
400	≤ T <	500	5
500	≤ T <	600	6
600	≤ T <	700	7
700	≤ T <	800	8
800	≤ T <	900	9
900	≤ T		10

Table 3 – Pressure scoring table [6]

Pressure (psi)	Score
0 - 90	1
91 - 140	2
141 - 250	3
251 - 420	4
421 - 700	5
701 - 1400	6
1401 - 3400	7
3401 - 4800	8
4801 - 6000	9
6001 - 8000	10
+1 point per 2500 psi	

Table 4 – Inventory scoring table [6]

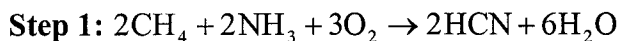
Inventory (Tonnes)	Score
0.1 - 250	1
251 - 2500	2
2501 - 7000	3
7001 - 16000	4
16001 - 26000	5
26001 - 38000	6
38001 - 50000	7
50001 - 65000	8
65001 - 80000	9
80001 - 100000	10

Table 5 – Explosiveness scoring table [6]

Explosiveness		Score
$S = (UEL - LEL)\%$		
0	$\leq S < 10$	1
10	$\leq S < 20$	2
20	$\leq S < 30$	3
30	$\leq S < 40$	4
40	$\leq S < 50$	5
50	$\leq S < 60$	6
60	$\leq S < 70$	7
70	$\leq S < 80$	8
80	$\leq S < 90$	9
90	$\leq S < 100$	10

Table 6 – DETAILS of 6 MMA ROUTES [6]

Route 1: Acetone Cyanohydrin based route (ACH)



Methane + Ammonia + Oxygen → Hydrogen Cyanide + Water

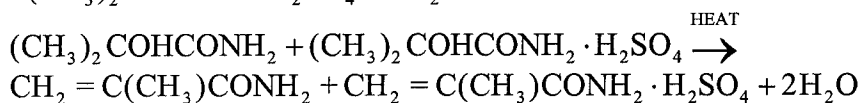
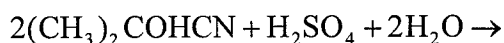
Gas Phase; Pressure: 3.4 Atm; Temperature: 1200° C; Yield: 64%



Acetone + Hydrogen Cyanide → Acetone Cyanohydrin

Liquid Phase; Pressure : Atmospheric; Temperature : 29-38° C; Yield : 91%

Step 3:



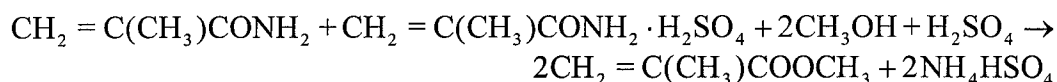
Acetone Cyanohydrin + Sulphuric Acid + Water →

2-Hydroxyl-2-Methyl Propionamide + 2-Hydroxyl-2-Methyl Propionamide Sulphate →

Methacrylamide + Methacrylamide Sulphate + Water

Liquid Phase; Pressure : 7 Atm; Temperature : 130-150 ° C; Yield : 98%

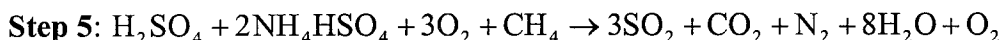
Step 4:



Methacrylamide + Methacrylamide Sulphate + Methanol + Sulphuric Acid →

Methyl Methacrylate + Ammonium Bisulphate

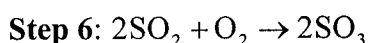
Liquid Phase; Pressure : 7 Atm; Temperature : 110-130 ° C; Yield : 100%



Sulphuric acid + Ammonium bisulphate + Oxygen + Methane →

Sulphur dioxide + Carbon dioxide + Nitrogen + Water + Oxygen

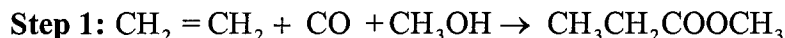
Gas phase; Pressure : Atmospheric; Temperature : 980-1200 ° C; Yield : 100



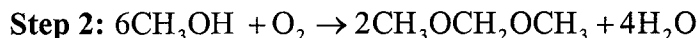
Sulphur dioxide + Oxygen → Sulphur trioxide

Gas phase; Pressure : Atmospheric; Temperature : 405-440° C; Yield : 99.7%

Route 2: Ethylene (via Methyl Propionate) based route (C2/MP)



Ethylene + Carbon Monoxide + Methanol \rightarrow Methyl Propionate
Liquid Phase; Pressure : 100 Atm; Temperature : 100 ° C; Yield : 89%



Methanol + Oxygen \rightarrow Methylal + Water
Vapour Phase; Pressure : ? ; Temperature: ?; Yield: ?

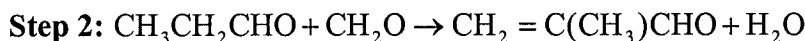


Methyl Propionate + Methylal \rightarrow Methyl Methacrylate + Methanol
Liquid Phase; Pressure : ? ; Temperature : 350 ° C; Yield : 87.4%

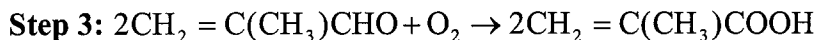
Route 3: Ethylene (via Propionaldehyde) based route (C2/PA)



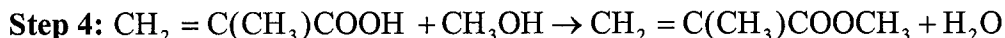
Ethylene + Carbon Monoxide + Hydrogen \rightarrow Propionaldehyde
Gas Phase; Pressure : 15 Atm; Temperature : 30 ° C; Yield : 90.7%



Propionaldehyde + Formaldehyde \rightarrow Methacrolein + Water
Liquid Phase; Pressure : 49 Atm; Temperature : 160-185 ° C; Yield : 98.2%



Methacrolein + Oxygen \rightarrow Methacrylic Acid
Gas Phase; Pressure : 350 Atm; Temperature : ?; Yield : 57.75%

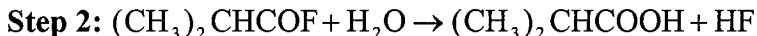


Methacrylic Acid + Methanol \rightarrow Methyl Methacrylate + Water
Liquid Phase; Pressure : 6.8-7.5 Atm; Temperature : 70-100 ° C; Yield : 75%

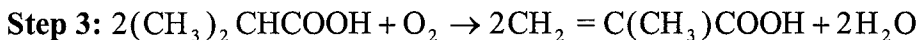
Route 4: Propylene based route (C3)



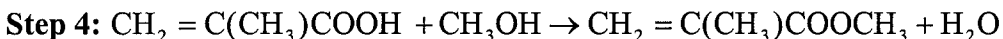
Propylene + Carbon Monoxide + Hydrogen Fluoride \rightarrow Isobutryl Fluoride
Liquid Phase; Pressure : 90-100 Atm; Temperature : 70 ° C; Yield : 94.5%



Isobutryl Fluoride + Water \rightarrow Isobutyric Acid + Hydrogen Fluoride
Liquid Phase; Pressure : 10 Atm; Temperature : 40-90 ° C; Yield : 96.2%

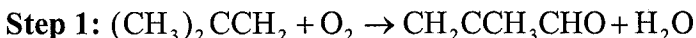


Isobutyric Acid + Oxygen \rightarrow Methacrylic Acid + Water
Vapour Phase; Pressure : 2.5-3 Atm; Temperature : 320-354 ° C; Yield : 70.5%

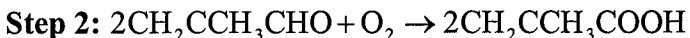


Methacrylic Acid + Methanol \rightarrow Methyl Methacrylate + Water
Liquid Phase; Pressure : 6.8-7.5 Atm; Temperature : 70-100 ° C; Yield : 75%

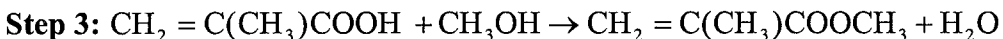
Route 5: Isobutylene based Route (i-C4)



Isobutylene + Oxygen \rightarrow Methacrolein + Water
Vapour Phase; Pressure : ?; Temperature : 395 ° C; Yield : 41.8%

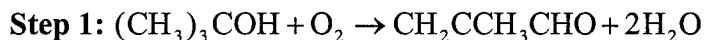


Methacrolein + Oxygen \rightarrow Methacrylic Acid
Vapour Phase; Pressure : 3.7 Atm; Temperature : 350 ° C; Yield : 57.75%



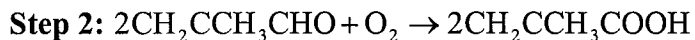
Methacrylic Acid + Methanol \rightarrow Methyl Methacrylate + Water
Liquid Phase; Pressure : 6.8-7.5 Atm; Temperature : 70-100 ° C; Yield : 75%

Route 6: Tertiary Butyl Alcohol based Route (TBA)



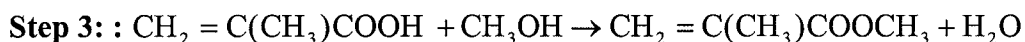
Tertiary Butyl Alcohol + Oxygen \rightarrow Methacrolein + Water

Vapour phase; Pressure : 4.8 Atm; Temperature : 350 ° C; Yield : 83%



Methacrolein + Oxygen \rightarrow Methacrylic Acid

Vapour Phase; Pressure : 3.7 Atm; Temperature : 350 ° C; Yield : 57.75%



Methacrylic Acid + Methanol \rightarrow Methyl Methacrylate + Water

Liquid Phase; Pressure : 6.8-7.5 Atm; Temperature : 70-100 ° C;

End of Table 6

Tables 7 to 10 are on the following pages

Table 7 - Breakdown of scores for each step in MMA routes [6]

ROUTE	STEP NO.	CHEMICAL WITH HIGHEST SCORE	CHEMICAL SCORE	PROCESS SCORE	STEP SCORE
ACH	1	HCN	13	15	28
	2	HCN	13	3	16
	3	ACH	6	5	11
	4	Methanol	10	4	14
	5	Methane	8	11	19
	6	Sulphur trioxide	8	7	15
C2/MP	1	CO	15	11	26
	2	Methanol	10	-	10
	3	Methanol	10	6	16
C2/PA	1	CO	15	6	21
	2	Formaldehyde	17	9	26
	3	Methacrolein	7	9	16
	4	Methanol	10	6	16
C3	1	CO	15	9	24
	2	Isobutyric acid	7	5	12
	3	Isobutyric acid	7	8	15
	4	Methanol	10	6	16
i-C4	1	Methacrolein	7	10	17
	2	Methacrolein	7	10	17
	3	Methanol	10	5	15
TBA	1	TBA	8	7	15
	2	Methacrolein	7	10	17
	3	Methanol	10	5	15

Table 8 - scores for MMA routes from trial index [6]

Route	Chemical score	Process score	Index score
ACH	58	45	103
C2/PA	49	30	79
C3	39	28	67
C2/MP	35	17	52
i-C4	24	25	49
TBA	25	22	47

Table 9: Process Safety Experts invited to comment on IS Index [6]

Prof. F.P.Lees -	Loughborough University
Mr. M.Kneale -	Independent consultant
Prof. H.A.Duxbury -	Independent consultant/Loughborough University
Dr. T.A.Kletz -	Independent consultant/Loughborough University
Mr. C.C.Pinder -	BP Chemicals Ltd/Loughborough University
Mr. W.H.Orrell -	Independent consultant
Mr. M.L.Preston -	ICI Engineering
Dr. A.G.Rushton -	Loughborough University

Table 10: Some items found wrong during Bhopal investigations

- Disproportionately large plant. It produced a decreasing fraction of its capacity, ran into increasing losses and hence severe economic measures applied that affected process safety
- Scrubber and flare not designed to handle the worst credible scenario
- Water spray as designed unable to reach the MIC discharge point
- Earlier accidents not fully investigated
- Recommendations of a HQ team in 1982 not fully implemented
- Severe manpower reduction in all shifts and in maintenance
- Untrained people posted at hazardous operations, including the plant superintendent who had come from the battery unit
- Excessive MIC produced and stored significantly in advance (approx. 5 weeks) of the actual production of the pesticide
- Very poor maintenance which made the operators lose confidence in the readings of the various gauges and instruments
- Lax maintenance wherein important work not done for several days/weeks
- Refrigeration turned off to save approx. \$20 per day on power though it resulted in MIC storage tank temperature becoming 20 C instead of the mandated 0 C in the company manuals
- The civic authorities not told about the hazards of MIC and its antidote
- Allowing housing or shanties to be built within the vulnerable zone
- People living nearby not told of the hazard and what to do in case of a leak
- Company chose the MIC route though until 1973 they had used a less hazardous route
- A continuous process was available but the company chose a batch process. The continuous process would have required no storage of MIC.
- The company used different standards of safety at its plant in the US and in India

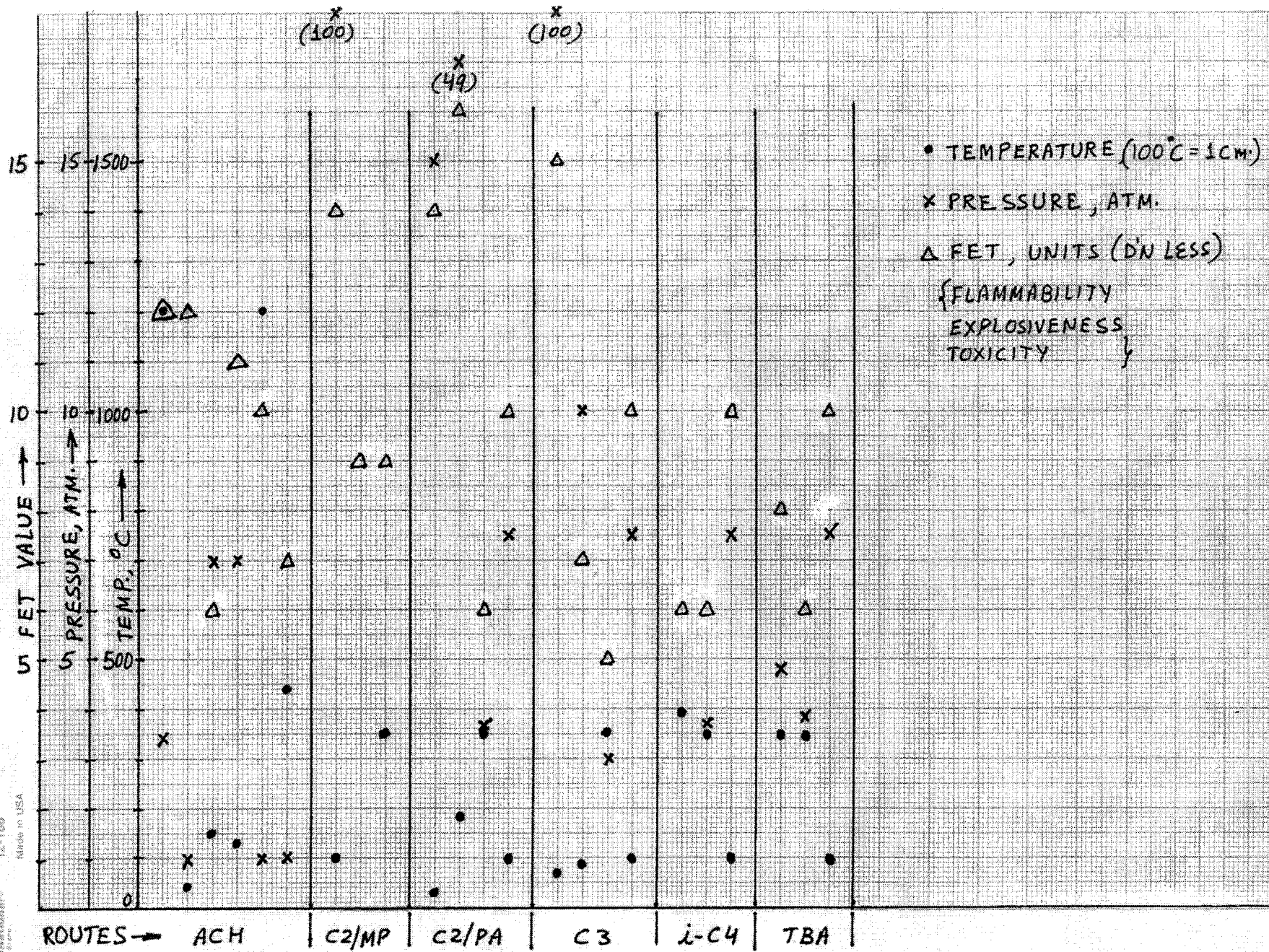


FIG. 1 MMA ROUTES

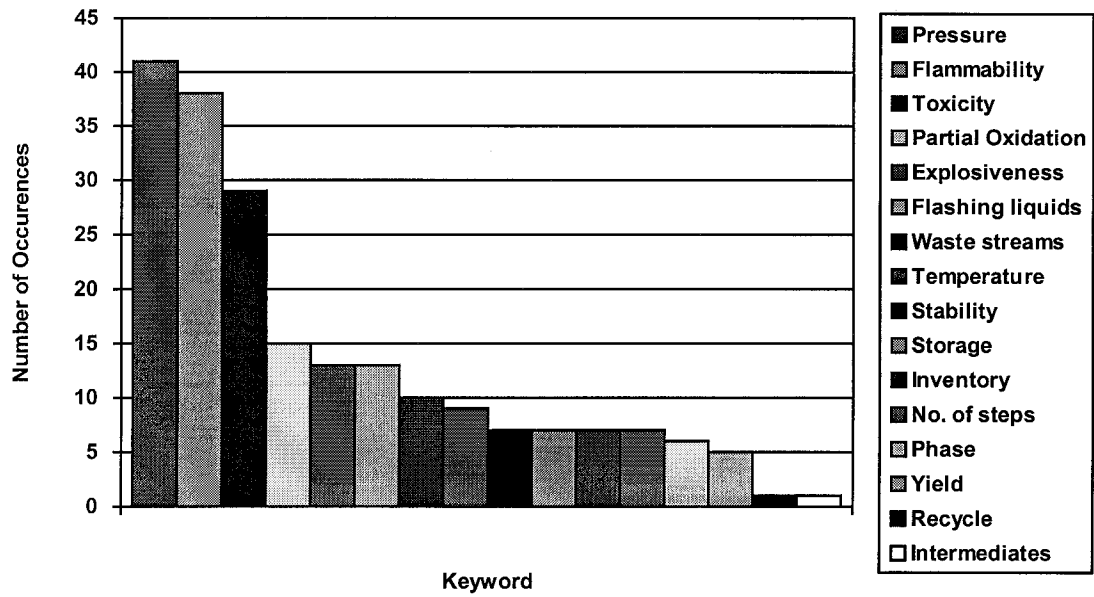


Figure 2 - Number of occurrences of keywords [6]