Defence Science Journal, Vol 47, No 2, April 1997, pp. 197-205

Quantitative Risk Assessment in a Process Plant

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ABSTRACT

This paper outlines quantitative assessment of a critical event in the sub-section of a process plant wherein a key ingredient required for the manufacture of propellants is produced. This sub-section is identified as possessing a fire hazard by qualitative HAZAN techniques. Fault tree and safety tree analyses have been used to identify basic equipment and the operational failures which could lead to top event occurrence and to calculate its probability. Consequence analysis of one of the probable scenarios has lead to an estimation of risk in terms of fatality and injury. These results form basic inputs for risk management decisions.

NOMENCLATURE

m'' Rate of evaporation ($kg/m^2.s$)

L_f Length of flame (m)

d Diameter of liquid pool (m)

E Average intensity of radiation (Wm^{-2})

VP Vapour pressure (Pa)

τ Atmospheric coefficient of transmission

r Distance to the fire (m)

q_r Heat flow density at distance r.(Wm^{-2})

A $(1+Y)^2 + X^2$

B $(1-Y)^2 + X^2$

F_{max} Maximum view factor

a Height of flame (m)

b Radius of flame (m)

1. INTRODUCTION

Risk assessment of chemical process plants has received world-wide attention[1-5]. On the other hand, process plants dealing with explosives, propellants and similar hazardous materials, both in terms of intrinsic nature of materials handled as well as in the manner of their processing, have paradoxically attracted little attention.

The process of production of key ingredients of propellants is divided into a number of separate sections, each section handling one step in the overall process. This is in contrast to most modern continuous chemical process plants having single stream operation. Many sub-sections of such plants pose a major hazard in themselves and require detailed hazard analysis and risk assessment.

Technological developments in the design of chemical plants have taken a quantum leap in the recent past. The pressure to keep pace, however, offers little opportunity for plant designers to learn by gradual evolution and experience. It also tends to make the designs somewhat vulnerable to failure. This is especially true in case of plants handling explosives, propellants and such materials under extremes of operating conditions. It is therefore necessary to reduce the probability of failure and to evolve safe design and operating

Received 07 February 1996, revised 30 July 1996

practices by identifying potential hazards and gaining some 'synthetic' experience of running the plant. This paper aims at quantifying these hazards and their consequences by using well-known techniques of fault tree analysis, safety tree analysis, and consequence analysis.

2. THE PROCESS

In the propellant manufacture process, the key ingredients are: Oxidizer, fuel, binder, bonding agent, plasticizer, catalysts, etc. Raw materials undergo various stages of preparation before they are termed key ingredients. The key ingredients are then processed by mixing, casting, etc. to get the end product.

2.1 Hazard Identification

Fire explosion and toxicity index (FETI) analysis and the hazard and operability (HAZOP) studies have pinpointed certain sections of the plant as more hazardous. In particular, the preparation of the bonding agent involves handling and processing of toxic and flammable chemicals under hazardous operating conditions. This section has been identified as a moderate fire and toxic hazard on the basis of FETI analysis. The HAZOP study has revealed that, in case of fire, there is a possibility of exposure due to skin contact and inhalation of toxic fumes. On the basis of this study, the preparation of the bonding agent has been taken up for detailed qualitative and quantitative hazard assessment using various well-established techniques.

2.2 Bonding Agent Preparation

Preparation of the bonding agent involves distillation of methyl aziridinyl phosphine oxide (MAPO) with two dicarboxylic acids—tartaric acid and adipic acid—in the presence of methanol under total reflux. Methanol, used as a solvent in this process, is recovered by differential vacuum distillation.

3. FAULT TREE ANALYSIS

Based on FETI analysis and HAZOP studies, fault tree analysis for the critical event 'fire in bonding agent preparation room' has been carried out. Fault tree analysis gives all possible minimum combinations of basic human, instrument or equipment failures, called minimal cut-sets, which could lead to the occurrence of the critical event, also called 'top event'. In other words, the solution of the fault tree yields a number of sets of events, with each set comprising of one or more basic events, whose simultaneous occurrence would lead to the unwanted top event. A number of events constituting each set determine the order of the set. Cut-sets are ranked in an increasing order, with single order cut-sets being ranked first, followed by cut-sets of order two, three and so on. A quantitative estimation of the probability of occurrence of top event is made by assigning appropriate failure rates to each of the basic failures.

3.1 Fault Tree Construction

A fault tree has been constructed for the top event. The completed tree is shown in Figs 1(a) and 1(b). A study of this tree shows that the top event can occur only if spill of MAPO occurs simultaneously with occurrence of fire in the preparation room. Each of the events has been broken down into its basic causes. MAPO is brought into the process room in SS containers. The required quantity of MAPO is then transferred into a beaker. Using a ladder, an operator pours the ingredient down the reaction flask. The MAPO spill could take place either during this transfer operation, or due to cracks in the beaker or flask.

Sub-tree for 'fire in the room' is more complex as the fire could result due to various interacting causes. It could result from either a fire within the flask or due to an external source. The presence of fuel (methanol in this case), oxidizer (atmospheric oxygen), and a source of ignition is essential to

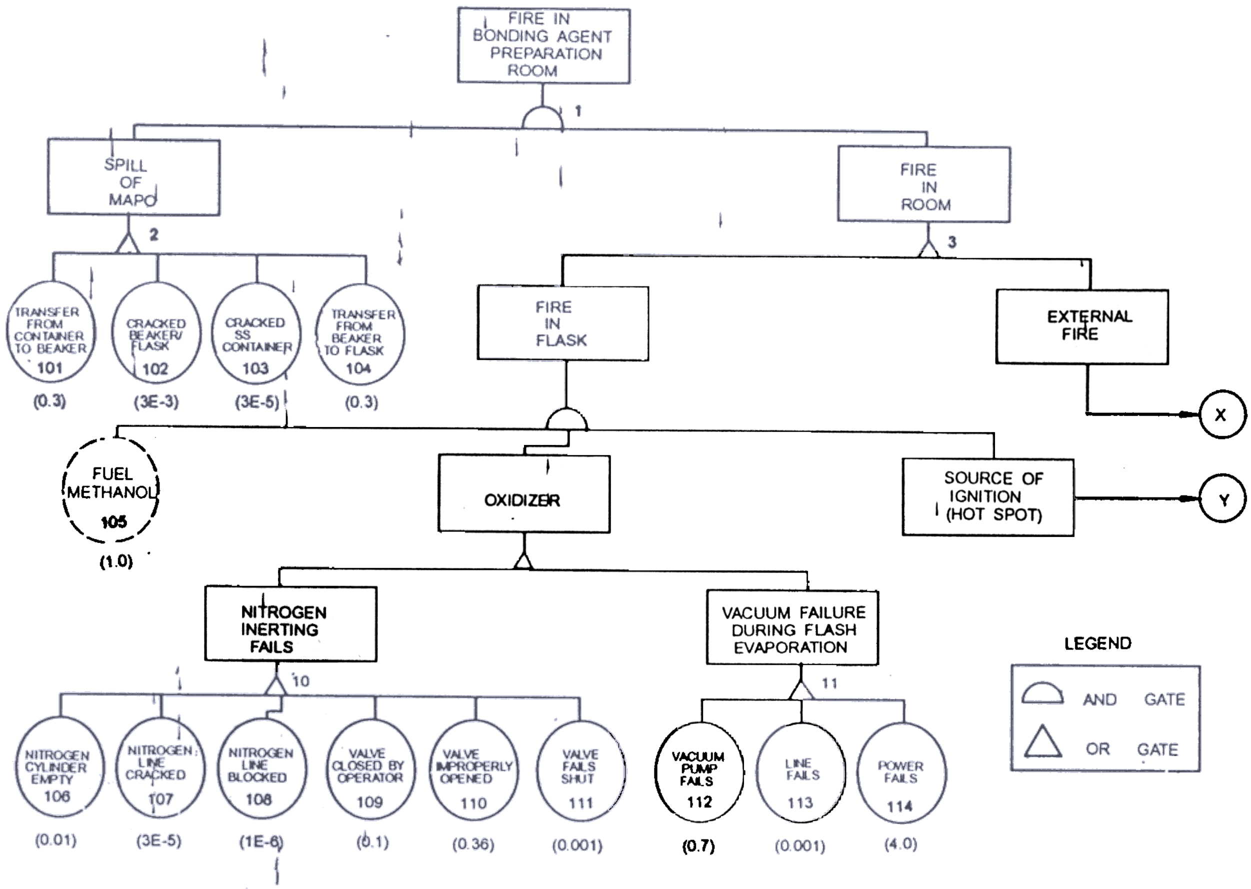

Figure 1(a). Fault tree for fire in bonding agent preparation room

cause this fire. Taking up 'fire in the flask', oxygen could be present due to one of the two possibilities – failure of nitrogen inerting or a vacuum failure during flash evaporation. Considering only one of these events, 'vacuum failure' could occur as a result of any one of the basic failures, namely, vacuum pump failure, vacuum line failure, or power failure.

Similarly, each of the intermediate events is broken up into its contributory basic failures resulting in various branches of the fault tree as shown in Figs 1(a) & 1(b). A computer programme developed for the analysis of fault tree has been used to calculate the minimal cut-sets. The data to this program is input through values in a sequence of main node number, type of gate connecting it to next event (AND, OR), number of sub-nodes in that branch, numbers of sub-nodes, and probability of occurrence of each node. The outputs of cut-sets are sorted and arranged in the order of decreasing frequency of occurrence. The failure rates of events are based on data from several sources[5,6] suitably modified, where necessary, to account for Indian conditions.

3.2 Fault Tree Analysis

The total number of minimal cut-sets for this tree has been computed to be 312, of which there are no single, double, or triple point cut-sets. In other words, the minimum number of events whose simultaneous failure will cause the top event to occur, is four. The minimal cut-sets in the order of decreasing probability of occurrence of top event or increasing number of years between each fault are listed in Table 1. Probability of occurrence of

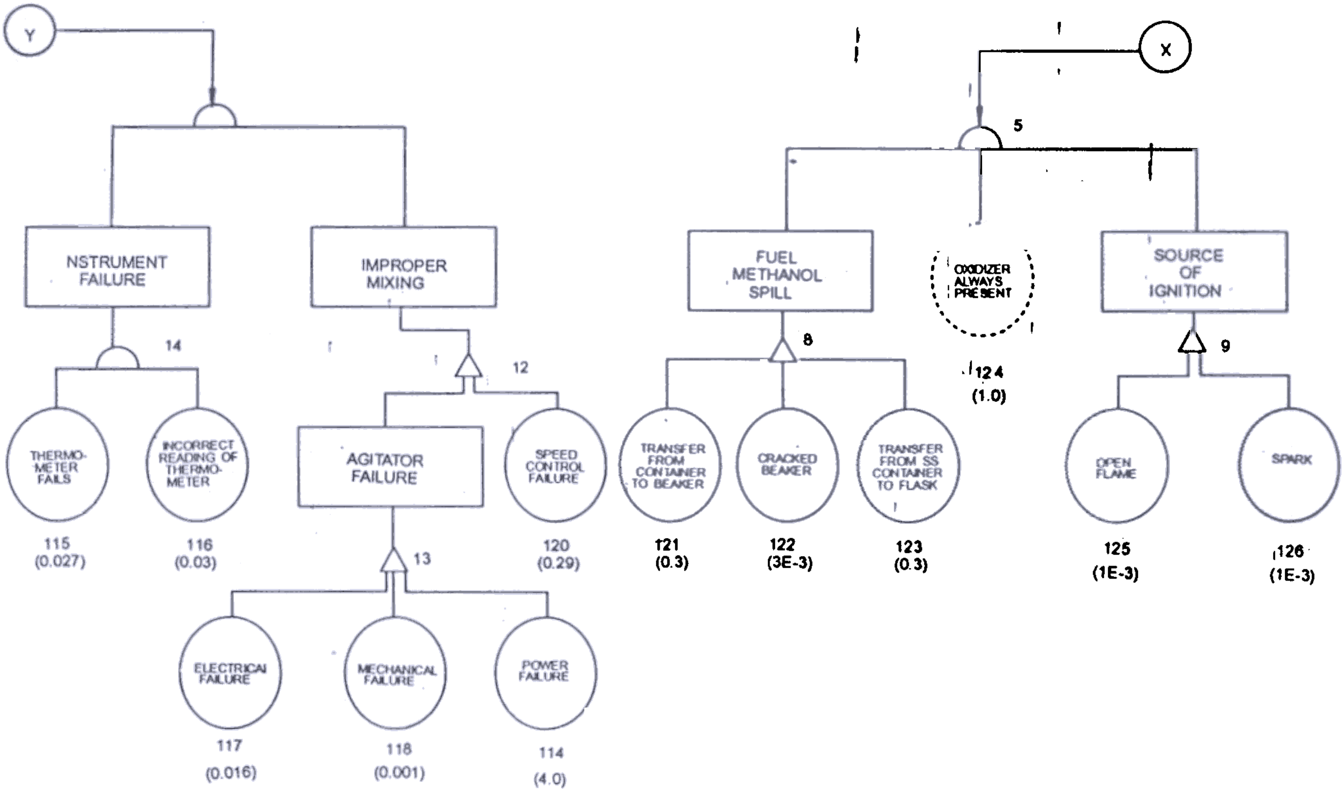

Figure 1(b). Fault tree for fire in bonding agent preparation room

this critical event, 'fire in bonding agent preparation room', works out to be 0.036 times a year or about 28 years between each occurrence.

Table 1. Fault tree analysis: Criticality ranking of occurrenc of top event in bonding agent preparation room

Minimal cut-sets	Years/faults

The key basic failures which lead to the high frequency of top event occurrence are:

(a) Supply failures: Power supply failure,

(b) Equipment & instrumental failures: Vacuum pump failure, temperature gauge failure, and

(c) Operator errors: Transfer operations involving MAPO, incomplete opening of valve in nitrogen line.

Power supply failure is a common mode failure, occurring in two branches of the tree, which meet at an AND gate. This makes it imperative that an alternate source of power supply should be provided. Operator-related failure rates are generally higher as compared to the instrument failure rates and are often unpredictable[1]. These can be minimised by proper training and adherence to laid down norms.

3.3 Safety Analysis

The safety analysis of 'fire in bonding agent preparation room' is carried out to find all possible ways of reducing probability of occurrence of the critical event. Safety tree is basically the logical reverse of a fault tree and is constructed by interchanging all AND and OR gates in the original fault tree. The analysis of this tree gives the minimum combination of events for the avoidance of top event.

Table 2. Minimal cut-sets for safety tree for bonding agent preparation room

Cut-sets						
	(124)					
	(125)	(126)				
	(116)	(124)				
	(116)	(125)	(126)			
(105)	(121)	(122)	(123)			
(101)	(102)	(103)	(104)			
(115)	(116)	(121)	(122)	(123)		
(114)	(117)	(118)	(120)	(124)		
(114)	(117)	(118)	(120)	(125)	(126)	
(114)	(117)	(118)	(120)	(121)	(122)	(123

Table 2. lists ten minimal cut-sets ranging from 2 to 7 point cut-sets in the order of increasing number of basic events per cut-set. For the safety analysis, only the first four cut-sets are being considered. Cut-sets with five or more events are being ignored as being impracticable.

It is evident from Table 2, that strict adherence to safety norms and extreme care by workers both during material transfer operations and temperature monitoring are essential for improving the safety of this section. Some of the points requiring specific attention are:

(a) Avoidance of methanol and MAPO spills during transfer operations and checking of containers for cracks, and

(b) Avoidance of open flames, sparks, and any other source of ignition in the room.

3.4 Results of Fault Tree & Safety Analyses

The fault tree and safety analyses have brought out specific instruments, operations and equipment whose proper functioning is critical to the system safety. On the basis of these observations, several recommendations regarding design/maintenance have been made. Sensitivity analysis further highlights the effects of incorporating these recommendations on system safety.

3.5 Sensitivity Analysis

An analysis of the effects of various suggested modifications on the top event probability is presented in Table 3. As seen from this table, effects of various suggested improvements in the design/operations result in an improvement of several orders of magnitude in the system safety.

Table 3. Sensitivity analysis: Effect of recommendations on system safety

Basic failure	Suggested recommendations	Top event occurrence (years between each fault) Modifications	
		Before	After
Power failure	Auto-start generator		
Spillage of MAPO	a) Reduce no. of transfer operations b) Transfer over shallow pans/tubs		
Vacuum pump failure	Standby pump	1150	2012
Incomplete opening of valve in nitrogen line	Alarm fitted to pressure gauge in nitrogen line	2012	3621
Incorrect reading of thermometer	Adequately lighted digital display	3621	10863
Presence of methanol spill	Water deluge system to dilute methanol spill	10863	32589

4. CONSEQUENCE ANALYSIS

Consequence analysis for the event 'fire in bonding agent preparation room' brings out the physical effects of a pool fire caused by a methanol spill on the ground and estimates the damage caused to human beings due to such effects.

4.1 Physical Effects

A heat radiation model[5] has been used to calculate the effects of methanol fire in terms of heat fluxes at various distances from the fire. The heat load, q_r, is given as

$$q_r = \tau_1 \times F \times E$$

where

τ_1 = Atmospheric coefficient of transmission

F = Geometric view factor

E = Average intensity of radiation ($W\,m^{-2}$)

The following assumptions are made in this model:

(a) Surface area of the pool caused by the spill is constant, and

(b) The pool is round.

Only the stationary fire phase is described. The initial ignition and fire development are not considered. Both assumptions (a) and (b) are valid in the present case. In case of (a), it is expected that the spread of the pool will take place immediately after the outflow when the fire is still not well developed. In case of (b), there being no restriction to the flow of liquid, the liquid methanol would tend to assume a circular shape (Fig. 2).

The values of relevant parameters assumed in obtaining these results are:

(a) Ambient temperature ~ 38 °C

(b) All the methanol is spilled (about 20 l)

Table 4. Radiation loads at various distances from fire

m" = 0.0206			L/d = 1.335		E - 9860 Wm^{-2}		VP = 3 352 Pa	
r (m)	X=a/b	Y=r/b	A	B	E_{max}	r^*VP (m.Pa)	τ	qr (Wm^{-2})
0.1	1.335	0.090	2.970	2.611				
0.5	1.335	0.448	3.880	2.086				
1	1.335	0.897	5.380	1.793	0.578	3 352	0.91	5 186.162
2	1.335	1.794	9.587	2.412	0.228	6 704	0.86	1 933.348
5	1.335	4.484	31.860	13.923	0.037	16 760	0.81	295.504

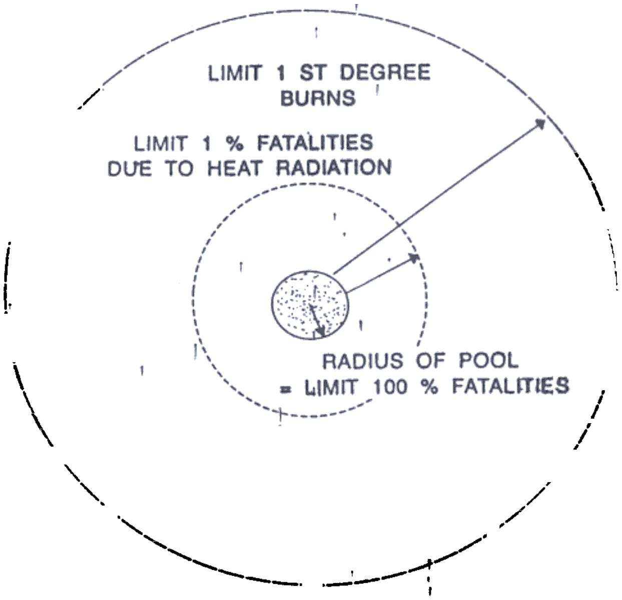

Figure 2. Model for methanol pool fire

(c) E, the average intensity of radiation (calculated) is 9.86 kW m^{-2}.

The thermal load q has been calculated at various distances (r) from the fire and the results are presented in Table 4.

4.2 Damage Model for Heat Radiation

Injuries caused by heat radiation at various thermal loads (at various distances from the fire) and at various exposure times have been calculated using this model. It is assumed that everyone inside the area covered by the burning pool will be asphyxiated or burnt to death. Probit equations [Eqns (2) and (3)] are used to calculate respectively the percentage of lethality and first degree burns that will occur at a particular thermal load and period of exposure to an unprotected body.

$$Pr = -36.38 + 2.56\ ln\ (t.q^{4/3}) \quad (2)$$

$$Pr = -39.83 + 3.0186\ ln\ (t.q^{4/3}) \quad (3)$$

where

t is the exposure time in seconds

q is the thermal load in W m^{-2}

Pr is the probit which can be converted to a percentage of exposed persons who will suffer the above symptoms.

The calculated values of *q* match well with the results of small scale experiments with methanol as reported in TNO by Hoftijzer[7]. For each value of *q* calculated as shown in Table 4, *Pr* can be calculated at various time intervals and for various types of exposures (lethality, first degree burns).

It is assumed that injuries will be reduced by a factor of seven if people are wearing protective clothing. Tables 5 and 6 give the results both in terms of probits and percentages (in brackets) of the persons who suffer from the symptoms due to exposure.

Table 5. Probit values for various radiation loads (lethal)

r (m)	*t*(s) q_r(Wm^{-2})	20	25	30	40	50	100	200	500	1000	2000
1	5186.10	0.486	1.057	1.521	2.26	2.83 (1.7 %)	4.606 (35 %)	6.307 (90 %)	8.653 (100 %)	10.428	12.202
2	1933.30						1.173	2.948 (2 %)	5.294 (62 %)	7.068 (98 %)	8.842 (100 %)
5	295.50									0.673	2.447 (0.9 %)

Table 6. Probit values for various radiation loads (first degree burns)

r (m)	*t*(s) q_r(Wm^{-2})	20	25	30	40	50	100	200	500	1000	2000
		3.554 (7 %)	4.228 (22 %)	4.778 (41 %)	5.646 (74 %)	6.320 (91 %)	8.412 (100 %)	10.505	13.270	15.363	17.455
2	1933.30						4.451 (29 %)	6.543 (94 %)	9.309 (100 %)	11.401	13.494
5	295.50									3.860 (13 %)	5.953 (83 %)

4.3 Consequence Analysis Calculations

In the event of fire, workers would sustain first degree burns within 3 min if they are within 2 m but not within the radius of fire but will sustain a fatal injury if they are within the radius of fire. Assuming that the total response time for the persons to move out of the room is 30 s, the fatality rate would be about 0.5 per cent. For two persons in the room it works out to 0.01 deaths per event. Also 41 per cent of the people exposed would suffer first degree burns, which is 0.82 injuries per event (Table 6).

5. RISK ASSESSMENT

5.1 Calculation of Risk

In the fault tree for 'file in bonding agent preparation room', the probability of occurrence of a methanol fire due to spills has been calculated to be 3 x 10^{-4} per year (Fig. 1A). Since both the probability of occurrence and the consequences are known, the risk can be calculated as:

Risk = Probability × Consequences

$= 3 \times 10^{-4}$ events per year × 0.01 death per event

$= 3 \times 10^{-6}$ deaths per year

5.2 Acceptable Risk

For chemical industries, the accepted figure for fatal accident frequency rates (FAFR) per 10^8 working hours is 4. The total working hours in the bonding agent preparation being about 1600 per year, the FAFR for methanol fire in this room works out to 0.2. This value of FAFR is well within acceptable limits. However, if there is any delay in escaping from the room due to injury or mishap, the FAFR for a response time of 60 s will be 1.7, which is still within the acceptable limits.

6. CONCLUSION

The quantitative assessment of one of the critical events in a process plant making a key ingredient for the manufacture of propellant and similar materials, and identified as a fire hazard, has been taken up in this paper. Fault tree and safety analyses techniques have been used to identify key failures leading to top event occurrence and to calculate the probability of occurrence of this event. Risk assessment of one of the critical events identified has led to the estimation of risk in terms of fatality and injury. Results of such assessments provide basic inputs for risk management decisions regarding the acceptability of a process and modifications to the existing design or operating procedures for improving the process safety.

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