Int J Ind Chem (2014) 5:13
DOI 10.1007/s40090-014-0013-9

RESEARCH

Phenol–formaldehyde runaway reaction: a case study

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Received: 2 November 2012 / Accepted: 28 March 2014 / Published online: 17 April 2014

Abstract
Introduction The paper deals with a workspace accident in a phenol–formaldehyde resin plant.
Methodology Detail accident investigation has been reported. Error identification and safety-related issues are also discussed. Job hazard analysis and SWOT analysis are used to identify the potential hazards in the workplace. Lesson learnt and management practice is also discussed to prevent similar incident in future.
Conclusion Job hazard analysis and SWOT analysis identified the probable causes and remedial action.

Keywords Phenol · Formaldehyde · Run away reaction · Job hazard analysis

Introduction

In chemical process industry workplace accident is common despite the regulations, technical protections, campaigns, training, etc. So identifying and assessing the hazards and their risks are the essential steps for safety management [1–5]. Major releases, that is heat, toxic materials, fire, etc. resulting from the uncontrolled developments in the course of an industrial activity, are very common [6]. Different hazard analysis techniques are used to predict the errors or wrong operation which might cause accidents in the process industry. So learning from workplace accidents or incidents is very important. Investigation of accidents and learning from accidents are important research topics, and different methodologies and their approaches have been developed and used [7–10]. This paper deals with job hazard analysis (JHA) and SWOT analysis based on an accident that occurred in phenol formaldehyde resin manufacturing unit.

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Methodology

Job hazard analysis

Job hazard analysis (JHA) is a valuable technique used for hazard identification and risk assessment in industrial processes [11]. It focuses on the relationship between the worker, the task, the tools and the work environment. JHA identified the proper job procedure after carefully studying and recording each step of the job and then identifying the existing or potential job hazards to determine the best way to perform the job to reduce or completely eliminate the hazards potential. This method has also proven to be effective for planning the safest way to perform a task [3]. The benefit of this analysis is to reduce injuries and illnesses of the workers. It identifies the more effective and safer work methodologies which lead to increased productivity and also reduce workers compensation costs. It is also a valuable tool for training new employees. The management must also demonstrate their commitment towards the safety and health of their employees by taking the corrective measure as identified by the JHA. The JHA is effective for the management to gain their credibility and employees' confidence even under dangerous situation (US

Department of Labor, OSHA 3071 [12, 13]). The JHA consists of three main steps [11]:

1. Identification—choose a specific job, break down the job into a sequence of stages and identify the possible incident that might occur during the work.
2. Assessment—evaluate the risk that might occur during the work.
3. Action—measure to reduce or eliminate the risk.

It also describes the formal job so that both the employee and the supervisor understand the job completely and perform according to the procedure [14, 15].

SWOT analysis

The SWOT analysis (strengths, weakness, opportunities and threats) is an effective and useful tool to identify the strengths and weaknesses and also to examine the opportunities and threats of an industry. Strength and weakness analysis focuses on the past performance, present strength, resources and capabilities. The opportunity analysis focuses on the improvement of working procedures and working environment and threats indicate the obstacles in job and problems which affect productivity.

The SWOT method is used to identify a solution of a problem or developing a plan which analyses the strengths and weakness within the organization and the opportunities and threats outside the organization. The internal and external factors highlight the positive points, that are strengths and opportunities, and negative points, that are weakness and threats, of the organization. It gives a clear idea about the job and the working environment to the management and workers. Hence it minimizes the accident/near misses situations and also raises safety awareness.

Runaway reaction

A runaway reaction is a chemical reaction which accelerates because the heat produced exceeds the vessel's cooling capacity [16]. The uncontrolled, or runaway reaction, occurs as a result of various situations such as mischarged raw materials, the presence of contaminants, failure of a reactor's cooling system, etc. If the heat generation exceeds the reactor's ability to remove it, the reaction can accelerate, that is runaway and cause increase in temperature and in some cases also pressure to increase. A large increase in pressure may lead to an explosion which has the potential risk for injuries to workers, even death in on-site or offsite of the plant and affects the environment. Barton and Nolan [17] reported the incidents and causes of 189 runaway reactions in the UK during the period 1962–1987, of which 64 were related to polymerization reactions and 13 to the phenol and formaldehyde reaction alone. British Plastic Federation [18] published a booklet on phenol–formaldehyde reaction which helps to minimize and control the runaway reaction. On September 10, 1997, the Georgia Pacific Resins Plant in Columbus experienced a large explosion in a phenol–formaldehyde resin reactor no 2 due to runaway reaction. The explosion caused a release of liquid resin and other chemicals. This accident caused the death of one operator, injury to four other employees and chemical burns to three fire fighters. The blast was felt at least two miles from the plant. The residents within a ¾ mile radius of the plant were evacuated. According to the City of Columbus's Incident Report [19], nine people including eight residents and one safety officer complained of symptoms at the time of the incident; symptoms included burning of skin, rashes, sore throat, headaches, breathing problems due to bronchitis, burning of throat and nausea. A number of residents reported burning eyes and irritation of their nose and throat.

Phenol–formaldehyde reaction

The phenolic resin is prepared by the reaction of phenol or substituted phenol with an aldehyde such as formaldehyde, in the presence of an acidic or basic catalyst. Phenolic resins are used as adhesives for binding wood-particle boards, fibre boards, plywood, nonwoven textiles and insulation materials, coatings, adhesives for papers and moulding compounds and water-based paints, as well as the manufacture of high-tech high-temperature resistant composite materials. Acid-catalysed phenol formaldehyde resins are known as novolacs and base-catalysed resins are called resols.

The resols have three stages of polymerization reactions: addition, condensation and curing. The first step is addition of formaldehyde to phenol to form methylophenols (2 hydroxymethylphenol, 4-hydroxymethylphenol, 2,6-dihydroxymethylphenol, 2,4-dihydroxymethylphenol and 2,4,6-trihydroxymethylphenol). This methylophenols condense to form low-molecular-weight prepolymers. On heating the prepolymers transform to various molecular weight polymers with a rigid cross-linked network [20]. Whereas in the acid-catalysed reaction the first step is the addition reaction—formaldehyde and phenol form methylophenols (2-hydroxymethylphenol, 4-hydroxymethylphenol), the methylophenols condense to form dihydroxydiphenyl methane and on heating they finally condense together to form a linear polymer called novolacs [21].

Debing et al. [22] studied the kinetics of resol formation using ammonia as catalyst and showed that the rate was first order. Goldblum [23] reported that the ammonia and acid-catalysed phenol–formaldehyde reactions are similar in nature but the molecular weight of ammonia-catalysed resins were 2–3 times higher than those resin obtained using sulphuric acid as catalyst. Megson [24] reported that under the acidic conditions the reaction is bimolecular, but Jones [25] reported that at low temperatures the reaction is mono-molecular. In alkaline condition both mono and bi-molecular reactions are observed, but in general ammonia leads to mono-molecular reaction.

Phenol formaldehyde reactions are exothermic and probability of accident is higher than that for any other kind of chemical reaction. Once the reaction is initiated, heat generated by the reaction increases the reaction rate and generates more heat, thus accelerating the reaction. According to the British Plastic Federation [18] the heat of reaction is

$$\begin{aligned} \Delta HR &= -17.2\ \mathrm{kJ/mol\ of\ HCHO\ reacting\ to\ a} \\ &\quad -\mathrm{CH_2OH\ methylol\ group} \\ \Delta HR &= -90\ \mathrm{kJ/mol\ of\ HCHO\ reacting\ to\ a} \\ &\quad -\mathrm{CH_2}-\ \mathrm{methylene\ bridge} \end{aligned}$$

and the heat of reaction for ammonia catalysed resins would be between $\Delta HR = -66$ and -71.5 kJ/mol.

Manufacturing process

In a batch the ratio of phenol to formaldehyde was approximately 1:1.1 and catalyst ammonia was about 1/40 times of the total mass of the batch. In the manufacturing process the raw phenol was taken as water solution having 87 % concentration and formalin concentration was about 37 %. A batch of 6,000 L was used to prepare the resin.

After charging phenol and formaldehyde in the reactor, normally ammonia was added from overhead tank. There was also heating coil and cooling coil arrangement in jacket outside the reactor for heating or cooling purpose. The reactor mass was continuously stirred by using electric motor. One drain line was provided at the bottom of the reactor. There was temperature indicator and pressure gauge attached to the reactor for measuring temperature and pressure, respectively.

At the top of the reactor there was a vertical condenser connected to the reactor and with a receiver. Vapour from the reactor condensed in the condenser and again back to the reactor until desired quality of distillate was reached, which was then transferred to the receiver. A rupture disk was installed between the reactor and condenser vapour pipeline. In case of high pressure the ruptured disk will open thus saving the reactor. Temperature was maintained in the reactor by increasing or decreasing the supply of steam in the reactor jacket at around 100 °C. If temperature became higher in the reactor then cold water was applied to the jacket to maintain the temperature.

The incident

The incident occurred on 26 Aug. 2001 at around 2:45 p.m. in Kalyani, Nadia District, West Bengal, India. On the day of incident the trial run was started using ammonia as catalyst. The earlier operation was based on caustic soda as catalyst and safe operating procedure was available. So there is no safe operational procedure for the reaction using ammonia as catalyst and hence the entire operation was started using manual control under the supervision of an expert. The phenol, formaldehyde and liquid ammonia were stored in the storage.

Initially phenol in water solution having concentration of 87 % was taken in the reactor, and then the formalin having 37 % concentration was transferred to the reactor. The stirring arrangement in the reactor was started slowly. Then the liquid ammonia as catalyst was added manually to the reactor. During the catalyst addition, liquid catalyst spilled on the hand of the operator and the operator felt some burning sensation. The temperature of the reaction mass was already raised by steam heating to nearly 100 °C and after few minutes it was observed that the temperature was increasing abnormally. The supervisor present nearby the reactor felt some abnormality in the reactor and he instructed to drain the reaction mass from the reactor in several 100/200 L drums available in the plant. After filling the drums the operators closed the lids of some drums which were taken away to the open space at a distance from the reaction zone. There were still some reactants in the reactor. After a few minutes the closed drums exploded one after another and pieces of drums flying at a height of 30–40 ft struck the wall and roof of the shed of the nearby areas. The residual mass in the reactor was drained to the other empty drums and those drums were not closed. These drums did not explode.

Probable causes of the accident

After examination it was found that the liquid used as catalyst was not liquid ammonia but it was concentrated nitric acid. It causes vigorous reaction of the reactants inside the reactor. Concentrated nitric acid helps to lead the reaction as runaway reaction, which increased temperature of the reactor mass. So the abnormal temperature rise was observed in the reactor and cooling arrangement was not adequate to control the reactor temperature. Due to vigorous reaction at high temperature (as rate of reaction doubled roughly with increase of every 10 °C) and production

Table 1 Job hazard analysis based on standard process

Basic job steps 1	Potential hazards or injuries 2	Cause 3	Required safe job procedures 4
This process is based on ammonia catalyst	Wrong catalysts make the reaction runaway	Wrong catalyst concentration nitric acid used	Proper catalyst should be added
Adequate cooling arrangement should be provided	Inadequate cooling increases temperature	As the temperature increases in the reactor the reaction rate also increases and in general the reaction rate is doubled for an approximate increase of 10 °C. As the reaction rate increases the generation of water vapour (reaction product) also increases which increases the pressure in the reactor	Adequate vent arrangement (proper sized vent) in the extreme condition should be provided; otherwise, there is possibility of explosion due to over pressure; it causes complete destruction of the reactor vessel and there are possibilities of flying of metal pieces in and around the plant which is dangerous for the human in site and off site and also release of hazardous materials
In store material should be kept in proper order. Display of MSDS in working areas and checking of delivery order etc. are required to avoid mixing the wrong chemical in the process	Proper reactants or catalyst should be identified and used for the reaction and also used in proper sequence	Wrong reactants or catalysts or wrong sequences in the input to the reactor can also make the reaction runaway	Chemicals should be labelled and the use of personal protective equipments insisted upon (PPEs) for carrying the chemicals
The runaway reaction is exothermic in nature and therefore increases temperature, so the reaction mass is transferred or drained away from the reactor zone in case of emergency	The reaction mass transferred to a container with closed lid leads to the explosion of the container	Create high temperature (as rate of reaction doubled roughly at increases of every 10 °C) inside the container and also release of steam–pressure rises	Always transfer the reaction mass in a container with open lid. This does not create high pressure inside the container
Any kind of operating negligence	Accident, blast, or explosion occurs	Reaction is highly exothermic, so any negligence can make the situation accident prone	Implement various protective measures: arrange operator training, gain knowledge about chemical reactions, show them past accident histories

of steam, the closed drums experienced high pressure. The high pressure led to the explosion of the drums. The drums without lids did not explode. Draining of the reaction mass saved the reactor. So, it was clear that the operator added the wrong catalyst, that is concentrated nitric acid instead of liquid ammonia, to the process and that too at a high rate. Investigation shows that the accident occurred due to human and maintenance error.

Errors and the accident analysis

Job hazard analysis (JHA) and SWOT analysis have been carried out to investigate the accident. Table 1 shows the basic step of JHA. It explains all the possible factors behind the incident in a simple step-by-step manner. After the analysis it was shown that operating error and maintenance error were the main causes of this accident. The maintenance error occurred because the catalyst jar was not labelled, so the worker added the wrong catalyst. This analysis also suggests the preventive measures shown in Table 1. Table 2 shows SWOT analysis which represents the strengths, weaknesses, opportunities and threats of this manufacturing plant which identified the reasons of this accident and also found out the solution to prevent this type of accident in future. This analysis concluded that the supervisor of the plant had knowledge and experience about the process but faulty management was the main cause for accident.

Remediation

All the reactants should be labelled properly and kept in proper place in the storage. The reactants are to be added in the reactor in a measured quantity, maintaining a precise sequence as prescribed in the operating manual.

Lessons learnt

1. Based on job hazard analysis and SWOT analysis
   (a) All chemicals in the storage are to be labelled.

Table 2 SWOT analysis

	Positive	Negative
Internal	*Strengths*	*Weaknesses*
	Standard process	The chemicals are not labelled in the storage
	Experience in the process technologies by the engineers, also the knowledge and experience in runaway reaction	Inadequate knowledge of the workers
	Due to sufficient knowledge and experience dangerous situation is avoided; otherwise, reactor may burst, leading to more adverse situation	Faulty management system
	Management is committed for the new product using ammonia as catalyst	Management is not confident enough in the new process
		No emergency planning for in-site and off-site
		Lower level staff are mostly illiterate and do not have much knowledge of the process due to lack of training
		Lack of communication skill of the workers
		Lack of knowledge of the released chemicals and their amounts in the accident scenario
External	*Opportunities*	*Threats*
	Proper training—to impart knowledge about the process and the runaway condition of the process	Uncontrolled exothermic runaway reaction
	Showing MSDS of the chemicals in the proper place	Human error/maintenance error
	Adequate cooling arrangement in the reactor	Accident or explosion
	Chemical should be added in the reactor in proper sequence	Loss of life and productivity
	Proper storage facilities	
	Separate racks for separate chemicals in the storage with proper labelling	
	Profit margin is rising due to high market demand, particularly in local and export market	

   (b) Proper storage facilities for chemicals to be arranged.
   (c) Proper catalyst should be added to the reactor in proper sequence.
   (d) Adequate cooling arrangement is to be provided to the reactor to avoid uncontrolled raise in temperature.
   (e) Display of the material safety data sheet (MSDS) in the working area is to be made mandatory.
   (f) Personal protective equipment (PPEs) is to be used for carrying the chemicals.
   (g) Training for the operators is to be provided at regular intervals of time, like once a year, to avoid error in operation.

2. Administrative controls
   (a) Management is to prepare the standard operating procedures (SOPs) of the process.
   (b) Emergency preparedness programmes are to be prepared for onsite and offsite.
   (c) SOPs are to be followed.
3. Proper sized emergency relief valve must be provided in the reactor.
4. Learning from accident history and near misses are to be recorded to provide necessary information and to guide to control accident.

Steps to be taken to reduce hazards (EPA 2011)

1. SOPs for the new ammonia-catalysed process are to be developed to improve the inherent process safety.
2. Various protective measures like temperature control, instrumentation and interlocks to eliminate the opportunities for human failures are to be implemented.
3. The chemical and process hazards are to be understood by the operators and their consequences are to be evaluated for the process hazards assessment.
4. Operators are to follow SOPs.
5. Lessons learned from the incident, root causes and all recommendations are to be incorporated to prevent recurrence.
6. Management is to provide training for the operators at regular time intervals to improve work-place safety.

Conclusion

An accident case study has been reported on the process of manufacturing of phenol–formaldehyde resin using ammonia as catalyst in the new trial run process. Due to operator's mistake concentrated nitric acid was used in the reactor instead of ammonia as catalyst and run away reaction was started. The job hazard analysis (JHA) and

SWOT analysis identified the probable causes and remedial action.

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