THE INFLUENCE OF SAFETY CONSIDERATIONS ON THE DESIGN OF AN ACETIC ACID PLANT

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SYNOPSIS

The way in which safety considerations can influence the development and design of a new chemical process is illustrated with particular reference to the Distillers Chemicals and Plastics Limited process for the direct oxidation of light hydrocarbons to acetic acid. The major risks on this process are discussed under the headings of explosions, effect of high pressures, danger from process materials, and fire. An assessment of each particular safety problem is made, and possible remedial actions are discussed. Finally, an indication is given of the factors that influenced the decisions taken on the desirability of following any particular course of action.

Introduction

During the development of a new chemical process from the original idea to a fully commercial plant many differing problems must be solved. In addition to studies of chemical feasibility, engineering design, and process operability, various aspects of safety have often to be considered. This paper sets out to demonstrate the ways in which safety considerations may influence the development and design of a particular chemical process, in this case the Distillers Chemicals and Plastics Ltd. [now BP Chemicals (U.K.) Ltd.] acetic acid process. It does not attempt to claim that the problems related to this process are in any way unique but merely indicates in how many different ways the requirements of safety must be borne in mind.

The D.C.P.L. Acetic Acid Process

The D.C.P.L. acetic acid process is a single-stage, liquid-phase oxidation of a paraffinic hydrocarbon feedstock to acetic acid and its homologues. The feedstock is generally a light naphtha containing mainly C_5 to C_7 aliphatic paraffins. This material, in a solution of the reaction products, is subjected to oxidation by air at temperatures of up to 200°C and at a suitably elevated pressure. The liquid reaction product consists of a complex mixture of unreacted hydrocarbons, ketones, esters, formic, acetic, propionic and higher acids, water, and various complex high-boiling residues. The gas phase leaving the reaction vessel contains, in addition to nitrogen from the feed air, any unreacted oxygen, carbon monoxide, carbon dioxide, and condensible material comprising the whole range of constituents of the liquid product. This condensible material is recovered from the inert gases by condensation at reaction pressure in a series of heat exchangers. The last stage of cooling is provided by submitting the residual off-gas to a work expansion allowing the recovery of a useful amount of the pressure energy of the gas as electric power and at the same time providing very cold low-pressure gas that can be used as refrigerant in the final heat exchangers of the train.

The liquid product leaving the reactor is fed to a series of distillation columns. The first columns of the series are used to remove the majority of unreacted hydrocarbons and intermediate reaction products such as ketones and esters. Water formed in the reaction stage is removed by an azeotropic distillation and formic acid is then recovered as a pure, dry product. Pure acetic and propionic acid are then separated by conventional distillation procedures and after some further treatment are produced in an extremely pure form.

Safety Problems

The safety problems of this process can be grouped into four main categories:

(1). Explosion risks.

(2). Danger from the use of high pressure.

(3). Danger from process fluids.

(4). Fire risks.

To some extent these categories, of course, overlap, but it is convenient to examine some of the more interesting safety considerations under this general classification.

Explosion risks

Considerable thought was given from the time when the initial concept of the process was being examined on a laboratory scale, through the pilot-plant stage, and on to the commercial design stage to the possibility of suffering explosions at various points in the process.

AIR COMPRESSION

The first part of the process is the air compression stage. Both on the pilot plant and on the first commercial plant, electrically-driven reciprocating compressors were used to provide air at reaction pressure. The advice of various experts in the compression field on the danger of explosions caused by oil mists or films in the presence of high-pressure air was sought. Consideration was given to the provision of special devices to protect against crank-case explosions, but finally it was decided that proper design of the machines, coupled with adequate regular maintenance, reduced this danger to a very low level. The provision of interstage oil–water separators reduced to some extent the danger from oil mists both in the cylinders themselves and in the associated pipework and by limiting the interstage temperatures to about 150°C it was considered that there was little possibility of oil-mist explosions occurring. The siting of the air intakes was studied in some detail. On the factory site at which the first commercial plant was to be installed it was possible that occasional discharges of small quantities of acetylene to the atmosphere could occur and the air intakes were so positioned that there was no chance that the acetylene concentration in

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the air drawn into the compressors could reach the lower explosive limit. Experimental checks both of acetylene concentration and of the concentrations of other contaminants were taken at the proposed site.

During certain stages of the plant start-up and shutdown procedure the reaction vessels are held under pressure when the compressors are shut down. Consequently, a leakage of process material back into the air line is possible and could result in the high-pressure air contacting organic material on the resumption of normal operation. There could then be the possibility of propagating fires in these air lines. To guard against this eventuality the discharge temperature of the air from the final stage of the compressor was limited to 130°C, a catchpot was provided close to the reactor to limit the possible area contaminated, and high-temperature alarms were installed on the air lines to indicate any abnormal conditions.

REACTION SYSTEM

The main reaction risk in the process undoubtedly lies in the reaction stage itself where the hydrocarbons and intermediates react in a fairly strong exothermic manner. Laboratory and pilot-plant work indicated that the most suitable reaction vessel should take the form of a well-mixed tower reactor containing heat transfer surface which could be used to control the course of the reaction by generating steam at a variable pressure.

Studies of available literature indicated that the limits of flammability of the pure components present in the reaction mixture widened as the pressure increased and that their spontaneous ignition temperature dropped markedly as soon as pressures much above atmospheric were considered. Furthermore, " cool flames " were possible with hydrocarbons at concentrations above the normally quoted upper limit of flammability and these had unusually low spontaneous ignition temperatures. Experts in the field were consulted; they indicated that the spontaneous ignition temperature of the complex mixture leaving the head of the reactor could well be as low as 230°C. The concentration of flammable materials at the reactor head was probably above the upper limit but would undoubtedly pass into the explosive range as this concentration fell throughout the condenser train. Cool flames could be formed at the reactor head and could well result in the formation of normal flames once they had propagated and caused either a pressure rise that would result in conditions suitable for normal flames or passed through to a part of the condenser system where concentrations lay within the flammable range. Only by limiting the oxygen concentration to values below the level at which combustion is possible could the danger of ignition in some form be reasonably avoided.

The safe control of the reaction for the laboratory and pilot plant studies was therefore designed around this limit on oxygen concentration. The oxygen concentration of the gas leaving the reactor was measured by a D.C.L./Servomex oxygen analyser which was set to alarm a condition when an oxygen concentration well below the danger level occurred in the off-gas at the reactor head and to cut off the air supply to the reactor when a somewhat higher concentration, still considerably below the danger level, was reached. It proved impossible, however, to design a sampling system for this meter with a delay time from the head of the reactor to the meter of less than about one minute so that an abnormally high rate of rise in oxygen concentration could cause an approach to the danger level. Secondary shutdown alarms were therefore installed on the commercial plant to cut off the air supply when hazardous conditions that would finally lead to a high oxygen concentration occur. Procedures were also adopted to avoid temperatures in excess of 200°C so that the danger of spontaneous ignition and cool flames would be minimised. During the whole of the extensive programme of laboratory and pilot-plant work, during which conditions outside those recommended for a commercial plant were investigated, there were only two occasions when any evidence of some form of vapour phase oxidation was apparent. In neither case was there an appreciable pressure rise. The actual process conditions existing at these times were studied in detail and the design conditions and procedures for operating the commercial plant were modified accordingly.

Massive breakthrough of oxygen—which could result in explosive mixtures at the reactor head—could occur in several ways. For example, a sudden reduction in the efficiency of mixing the reactor contents could cause the generation of a " hot-spot " rising through the reactor followed by a flow of unreacted air. Failure of the heat transfer control system resulting in a fall in temperature could cause a breakthrough because insufficient oxidation could occur at the lower temperature. Abnormal values of the parameters controlling the degree of mixing and reaction temperature have therefore been arranged to shut down the reactor system. A high-temperature shutdown system guards against an approach to spontaneous ignition temperatures and various other alarms avoid other conditions that could damage items of equipment or personnel. After consideration it was decided that these various alarms should not be duplicated to guard against failure of the alarm components since all were secondary alarms, failure of which would result only in a rather delayed operation of the primary high oxygen concentration shutdown alarm. A second, completely independent, sampling system and alarm was, however, installed to safeguard failure of this primary alarm.

Although the design of the instrumentation on the reaction system was developed to an extent where it was felt that all major hazards could be avoided a detailed study was also made of the effect of an explosion in the reactor system and of other ways of avoiding or minimising the resulting damage. Experts consulted indicated that the explosive force to be expected would be of medium energy and they felt that a considerable proportion of this energy would be absorbed in rupturing the high-pressure equipment. A fairly small number of large missiles could be expected to be projected from the shattered reactor. The economics of shielding the reactors by blast walls were considered but it was finally decided not to install such walls since the risk of explosion did not seem to justify the high cost involved in constructing walls to an adequate height. Similarly, the development of an explosion suppressant system was studied but it became apparent that no existing system was adequate for the purpose and the costs of the considerable development programme required seemed scarcely justified. The mechanical design of the reactor equipment was developed to minimise the vapour volume involved. It was felt that the major danger of explosions lay in ignition—either spontaneous or from, say, a catalytic source—of abnormal vapour mixtures, whilst the risk of an explosion in the liquid phase or in bubbles rising through a liquid phase was very slight. The total energy from any explosion would therefore be kept at the lowest possible value if the free vapour volume was kept small. For the first commercial plant the reactors were sited at the end of a long process structure rather than in the midst of other equipment so that damage to equipment or to personnel working on it would be minimised. Since the plant was fully automated the major concentration of personnel was to be in the control room and associated buildings and these were designed with reinforced roofs to provide protection from missiles and with no windows facing the plant: in this way the danger from blast would be reduced. The design of the compressor house, which it was felt would be affected by the blast from any explosion, was such that the relatively light covering sheeting attached to a strong steel framework would become detached from the framework rather than resisting the blast and causing major distortion to the building.

OTHER EXPLOSION RISKS

Other areas of the process plant where explosions were possible were identified. The naphtha feedstock for the commercial plant was to be received in bulk from sea tankers and was likely, therefore, to be contaminated with small amounts of water. Pumping of this material, as essentially a hydrocarbon phase containing water droplets, has been shown to cause a considerable build-up of static electricity which can cause a discharge sufficient to ignite any flammable vapour existing above a liquid surface, for example, in a storage tank. This danger has been shown to be minimised by the use of pumping velocities below 3 ft/s and, of course, by avoiding the formation of vapour within the explosive limits by the use of inert gas cover. The latter solution was employed on the bulk storage of raw materials for the first commercial plant and, for extra safety, the velocity limitation was also imposed on the transfer line. Process conditions did not allow the use of inert cover on the plant feed tanks but the velocity limit was again imposed on the feed lines from bulk storage to these tanks. Furthermore, conductivity checks were carried out on other plant streams containing hydrocarbons, particularly those recycling unreacted and partially reacted material to the reactor, to ascertain whether there was any danger from static generation at these points. It was established, however, that sufficient quantities of the various organic acids were soluble in the hydrocarbon phases to raise the conductivity to safe values.

Dangers from high pressure

The pressures involved in the reaction system of the acetic acid plant do not in themselves cause major design difficulties but the highly corrosive nature of the process fluids has meant that specific attention has been necessary to aspects of the engineering design that could cause increased corrosion and consequent possible rupture of vessels and ancillaries due to local thinning. Extensive use has been made of non-destructive testing procedures—particularly of ultrasonic methods—both during initial fabrication and afterwards during plant operation. The introduction of vessels fabricated in carbon steel clad with a relatively thin layer of stainless steel on the latest plant extension has increased the risk of large-scale failures—possibly including rupture—following a minor local corrosive attack which could penetrate the stainless steel and then attack the carbon steel extensively. Elaborate checking and testing programmes have therefore been developed to monitor the state of the reactors.

Pilot-plant experience indicated that the combined effects of pressure and corrosion called for rather special gasketting requirements and fully restrained gaskets of a modified design for both piping and equipment were developed in conjunction with the manufacturers.

During the design stages of the various plants particular attention was paid to the danger of overpressurising low-pressure equipment connected to the high-pressure system and adequate protection devices were installed, particularly where the loss of liquid levels in high-pressure vessels would result in vapour, rather than liquids, passing into the low-pressure equipment.

Throughout the plant relief valves were provided wherever there was a danger that pressures higher than the design limits could be generated in systems not freely and adequately vented to atmosphere. Wherever possible, the relief valves were sited in positions where the process materials passing through them were neither flammable nor dangerous to personnel though this could rarely be achieved absolutely.

The whole of the high-pressure reaction system is purged and pressurised with inert gas prior to start-up. At this time a detailed check of all high-pressure joints is made, so that the chance of a major leak of flammable materials following, for example, maintenance work, is avoided.

Danger from process fluids

Consideration was given throughout the development of the process to the risks that personnel could run in handling or otherwise contacting the process fluids contained in the plant. Prior experience in handling acetic acid had already resulted in knowledge about its toxicity and corrosive effects to the human body and the homologous acids were found to have similar properties, formic acid being rather more corrosive than acetic. However, prior experience, in particular with respect to toxicity, was not available for various of the intermediate streams and a number of these, including the residues stream, were tested for their effect on skin and eyes; lethal doses, maximum allowable concentrations, and any systemic effects on animal tissue were also established. The results of these tests indicated that there were no severe toxicity problems involved. The safety of personnel was covered by providing safety showers and sodium bicarbonate solution at convenient positions to allow rapid removal and treatment of acidic material splashed or spilt on individuals and also by insisting upon the wearing of adequate protective clothing—including goggles—while in the plant area.

To limit the chances of personnel contacting accidental discharges from relief valves throughout the plant all such valves on process streams were arranged to blow into a header system which separated liquid from vapour and discharged both to safe areas.

The reactor off-gas is discharged to atmosphere after the economic recovery of useful materials. Studies of the stack height and size required to disperse this under the most unfavourable weather conditions were made and the final height was selected to ensure that ground level concentrations of carbon monoxide and hydrocarbons were well below the minimum allowable concentration.

Finally, the detailed plant layout was developed to allow personnel to run quickly from any dangerous area and also to maintain necessary items of equipment without exposing themselves to danger. On the second D.C.P.L. plant the provision of a permanent crane on the top of the structure was made largely to assist in a number of awkward maintenance jobs whilst on the first plant permanent lifting beams at vital positions were provided to allow safe and easy maintenance.

Fire risks

Fire is, of course, almost inevitable following any explosion on a plant of this nature. In addition, however, the ignition of spillages of flammable material could result in a fire without an initial explosion. Studies of how either type of fire could best be dealt with were carried out. All electrical equipment used on the process plant was specified as intrinsically safe, flameproof to Division I standards, or sparkproof to Division II standards. To reduce the magnitude of any fire the flooring beneath the plant was divided into sections by drainage gullies which can carry a fairly large quantity of liquid out of the plant area thus reducing the floor area over which the fire could spread. The possible installation of a water-spray system to protect the steelwork and major items of equipment was investigated but proved to be economically impractical because of the complex nature of the plant structure. The facilities of the factory fire brigade were, however, reviewed and implemented to enable an adequate service to be provided. To avoid the possibility of starting fires by impingement, equipment such as thermopockets on the high-pressure section of the plant were arranged as far as possible to point outwards from the plant so that any major leaks at these points would fall to a safe place. Fire extinguishers capable of handling small fires were provided at convenient positions throughout the plant. After considerable deliberation it was decided not to fireproof the steelwork because it was felt that the risk of unseen attack on the proofed steelwork by acid leakage outweighed the risk of experiencing a major fire.

Conclusion

The foregoing discussion has described briefly some of the areas in which considerations of safety have influenced the process and plant design of a particular plant. Whilst the risk of explosion is probably the greatest hazard in this particular process it has been shown that a large number of other possible sources of danger have had to be considered. The solution to any particular problem is often governed by economics; this is as true in the field of safety as in any other with the added difficulty that the decision is usually a balance between the expenditure of extra money to provide the safety features and the often imponderable risks involved in not installing them. In the study described above it has been shown that a number of possible safety devices or schemes have been considered but not installed; time alone will show whether all these decisions were as wise as they might be. It is clear, however, that only by a searching and rigorous appraisal of new processes from the earliest stages in their development can a satisfactory balance between economics and safety be achieved. The danger of omitting features essential for the safe operation of a plant is greatly increased if such considerations are left to a late stage since pressures both of cost and time will favour their omission. The safety problems peculiar to a new process can often be outside the scope of previous experience and in such cases we have not hesitated to enlist the help of outside experts in the relevant fields. In the development of this particular process we have attempted to cover the whole spectrum of plant design, operation, and maintenance and hope, at least, to have placed most possible dangers under the harsh light of criticism.

Up to the present time the process has been operated on a commercial scale for a total of over ten operating years during which time there have been no major explosions, no major fires, and no serious accidents involving personnel. Two or three minor fires, not particularly related to more dangerous areas of the plant, have occurred and been dealt with without any escalation to serious proportions. In a plant that has a number of potentially serious hazards this record is reasonable and we hope indicates that the approach we have taken to safety is a sound one.

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DISCUSSION

Mr. A. V. Bailey said that he was interested in the statement about ultrasonic checking. Was the checking carried out continually? It appeared that the corrosion was expected to be perfectly even. If pitting took place a 100% coverage would be necessary. That must be very inconvenient to do at all frequently, implying free access to all parts of the vessel and necessitating the removal of lagging.

Mr. Claydon replied that the use of clad vessels in highly corrosive conditions was a new venture to his company; initially ultrasonic checking would be carried out continuously while the vessel was in operation. The insulation was designed to be removable in sections so that it could be done. Prior experience on solid vessels under the same operating conditions had shown that pitting corrosion was not extensive; serious effects were generally localised at or near welds. An attempt had been made in the design of the vessels to keep the welding in an accessible position so that the ultrasonic checking of vessels on shutdown could be carried out specifically along welds in addition to covering the general areas of plate.

Mr. A. D. Craven commented that Claydon had said in his presentation that there had been a changeover to centrifugal compressors from reciprocating compressors. That was normally done on purely economic grounds but it might be that it could be done purely on hazards grounds. Centrifugal compressors were much safer than reciprocating compressors.

He asked if the use of detergent oils or mineral oil mixed with a small amount of detergent oil had been considered for use in reciprocating compressors. Had the placing of bursting discs on the main reactor been considered? Finally, was there any method of fireproofing steelwork and at the same time giving acid resistance because he understood that the fire authorities were recently getting tougher about that?

Mr. Claydon replied that detergent oils were used on the machines in question.

As far as bursting discs were concerned, their use had been considered; a bursting disc had been fitted on the pilot-plant reaction vessel. Corrosion was serious in this reaction system and the thin bursting discs involved presented a severe problem. It had not been possible to find any material for the discs that was sufficiently resistant to corrosion to be satisfactory on a commercial plant. It was felt that bursting discs which were likely to fail every three or four months would produce more hazards than were otherwise likely to occur on the system.

With regard to fireproofing, he knew of no genuinely acid-resistant fireproofing system and would welcome any suggestions. One of the big problems was maintaining the seal of the fireproofing to the steel work so that there was no penetration at the top.

Mr. P. L. Klaassen asked about the allowable velocity of low conducting oils and hydrocarbons. He thought it was 3 ft/s or 1m/s for normal hydrocarbons. He did not think that that velocity was applicable if water was present.

He asked if the sheeting of the compressor house was steel sheeting or thicker sheeting, or asbestos-cement sheeting, which was very unpleasant when there was an explosion.

Had Claydon a formula for the dispersion carbon monoxide in the atmosphere which was convincing to the authorities?

Mr. Claydon said that he was of the opinion that 3 ft/s was a safe velocity for hydrocarbons containing small quantities of water. Velocities of up to 20 ft/s were acceptable if the material was absolutely water free. On the plant in question, the material into which the hydrocarbon stream was pumped had an adequately high conductivity so that by pumping it in below the liquid surface there was not too much risk of static causing a spark.

The sheeting of the compressor house used was thin steel sheet with an asbestos/bitumen covering.

The author did not know of a method for calculating carbon monoxide dispersion in the atmosphere that was satisfactory under all conditions. The Alkali Inspectorate appeared to accept the standard formulae quoted in text books on the subject.

Mr. R. J. HULSE asked if Claydon could give some idea of the safety precautions taken during start-up and whether there were safety devices on the plant to assist up to steady conditions.

Mr. CLAYDON indicated that a number of the safety shutdown relays had to be isolated during start-up as the relevant interlocks would have otherwise prevented air feed from being introduced to the reactor. The exact start-up procedure had been carefully developed to avoid dangerous occurrences and closer supervision was provided during start-up periods. Potentially dangerous conditions had occurred on a few occasions when the procedure had not been followed carefully. Blanketing nitrogen could be introduced rapidly to the top of the reactor if dangerous conditions occurred during start-up but basically the oxygen meter system, which was not isolated during that period, was still the main automatic protection system.

Mr. B. Y. WALKER said that great reliance was obviously placed on the instrumentation. Was it the practice of Claydon's company to accept what instrumentation companies offered to them without question or to prove it themselves? He asked because, some years ago, he had an unpleasant experience of having to distil a highly toxic material and had found that an instrument purchased from a highly respected firm was completely unreliable. The cold junction compensation specified as 0·3% accuracy, proved in fact to be 15% when there was a draught of hot air on the case. If that had not been noticed it could have been extremely serious. As a results of that he doubted everything the instrumentation company told him until he had proved for himself that it was in fact right.

Mr. CLAYDON said that his company tended to use instruments on new plants that they had proved very adequately on existing plants. Instruments were generally checked completely in the company instrument shops before installation.

Instruments for specialised duties, such as the oxygen meter used on this plant, had been developed within the company when no adequately proven commercial instrument was available.

Mr. F. J. OWEN said that a matter not covered in the paper concerned the possible dangers arising from layouts of plants, accessibility of valves for the operators, and maintenance, *etc.* At what stage were layout drawings shown to production, safety, or maintenance people and what say did they have in the final layout produced?

Mr. CLAYDON replied that such relevant personnel were consulted from early on in the design and construction of the commercial plant. A plant of the size and complexity described in the paper was generally engineered and constructed by an outside contractor but the company demanded a considerable say in the way that the plant layout was developed. Comments from production, maintenance, and safety personnel were collated and discussed by the company project personnel in the first few weeks of the design work and passed to the contractor as quickly as possible so that unnecessary delays were avoided.