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A Study about Explosion Hazards in Presence of a Uncontrolled Anaerobic Digestive Process

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In general, the risk associated at presence of biogas, generated in controlled conditions, is low. However, a recent case teaches that incidents with gaseous mixture like this to occur. The example of a serious incident with gaseous hydrogen, methane, in presence of ammonium ions, is explosion occur in a pharmaceutical industry in Italy.

Biogas is considered as a valuable source for its energy potential. Knowledge of its safety characteristics is a very important practical issue. This explosion was a typical example of a low knowledge of chemistry reactions that, if uncontrolled, can produce hazard consequences.

Produced biogas during an anaerobic digestion process was investigated to determine relationship between gaseous hydrogen, methane (present in biogas) and substances, like ammonium ions (present in growing medium to production of active principle).

In the present study was analysed a case study about a tank explosion occurred in a pharmaceutical company.

1. Introduction

The present case-study aims to identify and to analyse the danger and risk factors associated with an incident occurred in a pharmaceutical plant located in Italy. The accident was the explosion occurred in a process exhausted broths (water from process) storage tank located in a wastewater treatment plant (WWTP).

Objective of this study was to analyse the design, operational and technical-management aspects that led to loss of control of plant with particular reference to analysis and accident risk evaluation in connection with substantial modification carried out in the plant.

1.1 Description of accidental event

In reference at accident event occurred at a storage tank in WWTP of a pharmaceutical company, analysis and evaluation have been carried out to define explosion root causes. The analytical approach has been conducted following different aspects in order to identify the nature of flammable gas/vapours generated inside the storage tank (about 170 m^3), in space above free surface of liquid, which was ignite by sparks produced by firing of a power tool used to perform therein a planned maintenance. In fact, at time of the accident an extraordinary maintenance was being carried out consisting in replacement of final section (4” diameter and 0.6 m long) of tank inlet pipe, by cutting it with an electrical saw.

The storage facility appeared to be a waste fluids equalization atmospheric reservoir of an active pharmaceutical substance.

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The aforementioned works were motivated by need of the Plant Manager to use the same tank for the storage of waste fluids from production process of a second active substance under test.
In fact, according to analysis of trials reports relative to aforementioned experimental activities, as well as to the statements of the Plant Manager, it was noted that in few days preceding the accident event trial tests were concluded. However, the above is confirmed by documents examined in relation to the plant modifications taking place. In fact, it has been noted that the Manager intended to send waste fluids of experimental tests for production of new active substance to the equalization tank. This management option was, probably, considered favourably since final connection was made to adapt system to equalization plant with outlet pipe for disposal of trial waste fluids. The above was also confirmed from evaluation of 'work permits' issued by the Manager in the few days prior to the accident event.

2. Analysis of production process

2.1 Summary of production process

The active ingredient production process starts from preparation of culture medium, consisting of adequate nutrients (sugars, flours, etc..), in which specific organisms inoculated are able to activate the synthesis process.
At the end of fermentation, the fluid is sent to a storage facility where it is heated to 105 - 110 °C by injecting steam and subjected to a stripping with separation of chloroform. The waste fluid is stripped, then cooled to a temperature of about 60 °C and sent in an equalization tank of WWTP, where the pH is adjusted to a value of about 8.0 - 8.5 through the injection of 30 % sodium hydroxide.
In reference to this case, flow entering the tank was found to be approximately 2-3 m^3/h and the maximum fill level of the tank amounted to about 50 % of its height. The amount of stored waste stripped fluid in the tank was of approximately 150 – 160 m^3. The volume between the free surface of the liquid in the tank and the roof of the tank appeared to be approximately 170 m^3.

2.2 Description of the production process of biogas

The anaerobic digestion process occurs in a sequence of biochemical reactions catalysed by several different strains of bacteria which act some sequentially in series in symbiotic form and others in competitive parallel ways.
The results of these processes lead to production of biochemical terminal compounds according to energies provided by environmental conditions established. Therefore, in function of environmental conditions, the type of substrate present at the time of accident event and species of microorganisms eventually selected, this complex of reactions may have been completed or ended at intermediate stages.
In particular, Blonda et al. (1991) reported that the occurrence of these uncontrolled anaerobic conditions seems to favour production of hydrogen gas through the valve mechanism called H_2 (formic-hydrogen-lyase enzyme complex) ubiquitous in terms of bacterial species involved .
In terms of optimum temperature for occurrence of biological activities, it appears that very low temperatures imply reduced activity whilst high temperatures, above 65 °C, causes the death of the bacteria. Therefore, for most microorganisms, particularly methanogenic, the optimal temperature range is 35 to 55 °C. The bacteria, whatever their nature, are divided into three main categories, depending on temperature, such as psychrophilic (10 - 25 °C), mesophilic (30 to 38 °C), thermophilic (49 to 60 °C).
Therefore, the process temperature affects directly on Hydraulic Retention Time (HRT), defined as the permanence time of organic mass in the tank. At the increase of process temperature correspond, proportionally, a decrease of time required to decompose organic matter.
Vasquez et al. (2004) has shown that good efficiencies in reduced time of treatment have highlighted for mesophilic and thermophilic processes. Gas production follows a typical bell-shaped pattern (Figure 1). The composition of the biogas produced during the digestion process appears to be, in general, equal to methane (CH_4) for 50 to 80 %, carbon dioxide (CO_2) for 15 to 45 % and other gases (mainly H_2 and N_2) for 5 %.

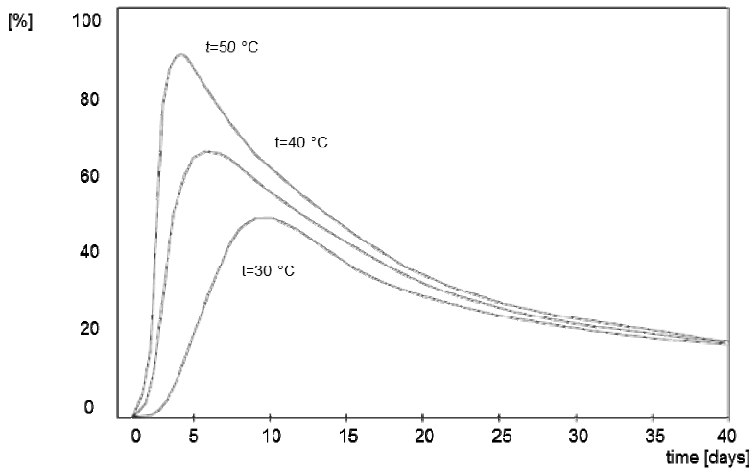

Figure 1: Graph of the production of biogas depending on HRT and the process temperature.

3. Analysis of hypothetical accident scenarios

On the basis of analysis of technical and managerial aspects related to execution of works in progress, and the study of dynamics, is possible to assume the following accident scenarios.
In the first analysis, we consider that in the tank were stored waste fluids from a single production process (Scenario A). Next, we proceed to analyse the potential factors which increased the level of risk, with particular reference to hypothesis that waste fluids from experimental process of production of new active substance were sent to the storage tank of waste fluids of a single production process (Scenario B).

3.1 Scenario A

The development of an explosive atmosphere has potentially originated from developed biological activities, compatible with the time of permanence of waste fluids inside tank and presence of suitable substrates. In fact, the atmospheric tank was used as closed system, under anaerobic conditions. An analysis of P&ID WWTP shows that in the tank was expected the installation of a blowing oxygen system in order to ensure the absence of anoxia conditions. Therefore, it should be noted that establishment of biological anaerobic activities in tank was considered probable already in design phase of storage facility, considering the behaviour of bacteria used for active ingredient production in anaerobic conditions .
The chemical analysis results carried out about stripped waste fluids stored in tank showed presence of organic matter, also confirmed by high value of COD, potentially subject to decay with production of biogas.
The measured temperature inside tank, of about 40 - 60 °C (initial temperature is of 60 °C, adjusted to thermal gradient of 20 °C with wash water addition), has encouraged thermophilic activities, if not the mesophyll one. It should be noted that waste fluid (containing about 5 % of chloroform) is subjected to a stripping with steam injection at 4.5×10^5 Pa, reaching a temperature of 105-110 °C, and then recovered from bottom of stripper and after pre-cooling to about 60 °C sent to equalization tank. It should also be noted that although ‘heat treatment’, carried out at temperatures of 105-110 °C, may have stopped microbial activities, it may have reactivated in view of permanence time of stripped waste fluid in unit upstream of the equalization tank and of subsequent addition of washing water, whose biological characteristics are not known, apart from the permanence of whole mixture in the same tank for about 2-3 days.
Therefore, it should be noted that described ‘heat treatment’ cannot be considered as an efficient sterilization process for matrix. Taking further into account that tank does not appear to have been subjected to systematic cleaning, it’s possible to assert that this condition has allowed accumulation of stripped waste fluid to a depth of about 0.4 m (height of the point of installation of the exhaust valve),

thus promoting the reactivation of microbial charge in more comfortable time, but also recontamination of fluid.
Moreover, it should be noted that Sung et al. all (2003) reported that biokinetic studies have shown presence of bacterial activity, by hydrogenbacteria, with permanence times of organic matter less than 6 hours due to specific rate of growth of hydrogenon bacteria. In particular, this occurs in conditions of permanence of organic matter for time significantly higher, such as 2-3 day permanence of stripped waste fluid in the storage tank.
Finally, the presence of an alkaline environment, of course, favours the production of hydrogen (H_2).
The methane formation is believed to be negligible since, as demonstrated by Thiel (1969) and confirmed by Ueki et al. (1998), it is inhibited by presence of chloroform ($CHCl_3$). The latter if on one side is a specific suppressor of methanogenesis reactions, on the other favours hydrogen H_2 accumulation, making even more probable its presence on free surface of liquid in the tank.
Therefore, operating conditions analysis of accumulation of stripped waste fluid in the equalization tank, in terms of temperature (40-60 °C), of permanence time of organic matter (2-3 days), of pH operation (alkaline), it is plausible to believe that a significant concentration of hydrogen gas was produced inside it. Hydrogen is a highly flammable gas with flammable range between 4 % and 75 % in air at atmospheric pressure. Its presence has certainly facilitated formation of an explosive environment. In fact, considering H_2 presence, of even in a minimum concentration of 4 %, it is plausible to assume that there was a quantity of about 500 g of H_2 inside the tank that would consistently develop about $8x10^7$ J of energy in the event of ignition. This energy is compatible with the deformation and consequent detachment of the roof of the tank and technician working on it being projected at about 20 m south-southwest from original position.
Therefore, in view of this, it is possible to consider more significant the rates of hydrogen formation and risks associated with H_2 presence to ignition point, although the chloroform presence in significant quantity in stripped waste fluid, as well as in groundwater used in washing step of production cycle, has been established from analysis carried out by the company.
However, it is appropriate to highlight importance of chloroform hazardous properties, especially in relation to improper use of it. In fact, although chloroform is not classified as flammable, it reacts violently with sodium (Na^+) or sodium Medil (CH_3ONa) in presence of methyl alcohol.
In addition, there is negligible capacity to convert it into phosgene ($COCl_2$), an aggressive and highly toxic gas if exposed to light and left in contact with atmospheric oxygen.

3.2 Scenario B
As evidenced by the Plant Manager, to continue in next step of active ingredient fermentation process, as an experiment, we evaluated various scenarios including transfer of fluid into a filtration unit and then bioreactor. In this case a critical situation might have arisen in relation to the lack of an equalization tank between the two units. Problem avoidable by sending the waste mycelia to the equalization tank. Therefore, the Company had started adaptation works to the equalization tank in order to make permanent a temporary modification presumably activated in order to verify efficiency of the entire system.
Evidences of this are found in the ‘Work Permits' signed by the WWTP Manager. The analysis of quantities of raw materials used in charge of fermentation system show that those of ammonia (in form of ammonium sulphate) appear to be much lower, less than one third, compared to those found in analysis carried out by ARPA Apulia after the accident event.
Therefore, this consideration suggests that stripped waste fluids from production process of another active ingredient arrived in the tank at the time of accident event.
In reference to this hypothesis, in the analysis of documentation, you may find that culture medium prepared for the active ingredient synthesis being tested was made up of various compounds and nutrients such as ammonium sulphate, present in large quantities, amounting to $477x10^3$ g, and ferrous sulfate, prepared in solution for correct running of the fermenter at a rate of 766 g.
Accident event occurred six days after of experimental testing conclusion of new active ingredient fermentation process. Most likely during this period, the biological process continued but we have no evidence of where waste fluid has been sent, sent and/or stored waiting to proceed with the activity of disposal to WWTP.

In company's documentation, it is noted that the ammonia nitrogen concentration in final stage of new active ingredient fermentation process was equal to 6.5 g/L.
The outcome of analysis carried out by ARPA Apulia on sample taken from inside the tank, about 3 hours and 30 min after the explosion, shows the presence of chloroform (2.9 g/L), methanol (0.14 g/L), alcohol isopropyl alcohol (0.47 g/L) and ammonia nitrogen at concentrations equal to 0.85 g/L, likely values compared to input quantities and considering that part of them were used up during the explosive process, and subsequently in evaporating fumes.
Ammonia (NH_3) is a gaseous compound lighter than air and with strong basic features, it tends to be present in free form in a basic environment which is considered (from 8.5 to 10 even 14), thus contributing to formation of explosive mixtures.
Kersten et al. (2004), as part of its studies, has highlighted the highly ammonia explosive nature, as confirmed by D'Errico (2006), with values of concentrations in atmospheric conditions between 15 % (lower limit of explosive) and 28 % by volume (upper limit of explosiveness, historically used as a cut-off) in presence of adequate ignition.
Sparks arising from static electricity are one of ignition sources of fires and explosions more frequently in industrial areas, cause of one accident a week in the UK and one a day in Europe.
Finally, it is believed that hydrogen gas (H_2), methane (CH_4) and ammonia gas (NH_3) produced by anaerobic digestion could be responsible for the accident.
However, analysis of data shows that hydrogen gas (H_2) has a lower density than air and other two compounds (CH_4 and NH_3), this enables it to occupy the top empty space of the tank, close to the pipe, and be considered the most critical substance.
Therefore, the explosive atmosphere can mainly be due to hydrogen gas (H_2) presence and methane (CH_4), potentially originated from biochemical processes. In fact, during the permanence time of complex matrix of waste cultured (consisting of both waste fluids which were added to wash water and sent to the equalization tank), can be created favourable conditions for biological activity with biogas formation or, therefore, hydrogen and methane formation. They can have increased the explosive gas mixture nature already present in the tank.

4. Conclusions

We feel obliged to point out that despite the Company to date has not provided information on actual production process, in progress at time of accident event. However, it can be argued that the mixture explosive nature, formed inside the equalization tank, is due to intrinsic characteristics of mixture with particular reference to hydrogen and methane present in both scenarios. In fact, presence of hydrogen would be due to activation of biological processes and/or chemical affinities determined by intrinsic characteristics of waste fluids, while presence of ammonia (Scenario B) is related to chemical characteristics of waste fluids from active ingredients production and washing water introduced into the process.
In the event that explosive mixture formed in the tank would be due to the high presence of hydrogen gas (Scenario A), developed by biological activities facilitated by favourable conditions in terms of lack of oxygen, temperature, pH, HRT of waste fluids in the tank, just a minimum concentration of 4 % by volume (equal to an amount of about 500 g) is sufficient to develop an energy of about $8x10^7$ J, compatible with the deformation and consequent detachment of tank roof.
Moreover, in the case of coexistence of both waste fluids, it is possible the onset of effects whose results have not been evaluated, tested, and thus prevented by the Company through appropriate security management systems adoption.
Condition exacerbated by lack of systematic planning of draining operation of the tank to prevent occurrence of certain biochemical reactions from uncontrolled accumulation of waste fluids in the tank from bottom up to height of exhaust valve of the tank, by failure to drain the tank during works as reported at time of accident event, by the lack of description of fluids from production of both active substances and of washing water.
In particular, the analytical controls absence aimed to determine biochemical description of waste fluids to be sent to the tank and failure to implement the provisions of operating procedure (for example: emptying and cleaning operations of the tank, the interruption of pipe before start of hot works) appear

to be non-negligible contributory factors to development of uncontrolled reactions of incompatible substances.

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