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Safe Oxidation Reactions. Development of an Explosion Protection System from Process Development Lab to Large Scale Production Plant

Myriam Kuppinger[a]*, Iris Obermüller[b], and Bruno Peterhans[a]
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Abstract: The systematic development of an explosion protection system for an oxidation reaction in pure oxygen following a thorough risk analysis is described. By evaluating both probability and consequences of all risks identified it could be shown that an explosion in the investigated system cannot be prevented completely. Therefore the emphasis of the system was to protect humans and the environment from the consequences of this residual risk. Several design alternatives were considered. Only an explosion decoupling system, consisting of a combination of a flame interrupter and a fast-acting valve can fulfill this task. The successful start-up and running production process up to now confirm the chosen path.

Keywords: Explosion protection · Oxidation reaction · Safety concept

1. Introduction

In 2004 DSM Nutritional Products inaugurated a new production plant in Sisseln, Switzerland built to produce 25'000 t/a vitamin E [1]. It replaced two old plants, each running for more than twenty years. One of the reaction steps is an oxidation. The reaction is carried out in a semibatch reaction vessel using pure oxygen. The block-flow diagram for the whole step can be seen in Fig. 1. Although the reaction itself is only a small part of this step compared to the catalyst recovery and work-up, it is nonetheless very important.

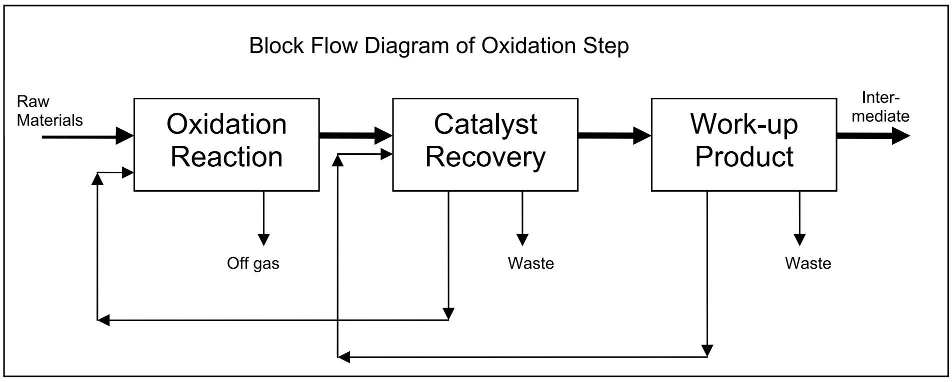

Fig. 1. Block flow diagram oxidation

During the course of the project several risk assessments were undertaken. Starting from a design study done by Lischick and Riekert [2] in 1999 the identified risks helped to improve the design step by step. With the additional information gathered over the duration of the project the design was finalized and executed.

A more general overview about the safety concept itself can be found in the article by Obermüller [3].

2. Process Development

The main task of chemical development is to find technical reaction conditions (temperature, pressure, raw material quality, concentrations …), running scheme (batch; continuous) and size or material of construction. In a very early phase of development the safety aspects must also be considered. The focus has to be set on the future production plant. A ***process safety analysis*** will show the critical points. Problems can arise from the physical properties of involved substances as well as their compatibilities. Also the safety parameters like maximum explosion pressure, ignition temperature or toxicity are a good basis for the safety study. An oxidation reaction with pure oxygen is obviously a very reactive system with a high risk potential.

**Correspondence*: Myriam Kuppinger[a]
Tel.: +41 61 688 8447
Fax: +41 61 688 1546
E-Mail: myriam.kuppinger@dsm.com
[a]DSM Nutritional Products Ltd.
VTC 241/643
PO Box 3255
CH-4002 Basel
[b]Novartis Pharma AG
WSJ-330.2.24
CH-4056 Basel

The extensive development work began with a very robust system from the old plant. This step showed potential for improvement. The focus was set mainly on the integration into the whole production process and on producing information necessary for the design and scale-up. The process safety analysis showed very early the high risk of an explosion for an oxidation in an organic solvent. Several alternatives were tested. One eliminated the organic solvent but unfortunately the conversion rate was unacceptably low. In the very early design phase we already decided on the basic safety strategy. This was to go for an explosion-resistant reactor system.

3. Basic Design

3.1. *Risk Assessment*

After the project moved from the miniplant to the basic design another risk assessment took place. Several risks were identified and solutions were developed which established the safety components relevant to the construction. Fig. 2 shows one possible explosion scenario developed during the risk assessment. The numbers correspond to the estimated probability.

Oxygen could not be left out as a reaction component in the process. The presence of a flammable organic solvent and by-products in quantities close to the lower explosion limit requires a sound safety concept. Several possible scenarios describe how an ignition source (the third factor necessary for an explosion, with oxygen and flammable liquid already present) can be effectively excluded. Despite all measures to avoid an explosion the risk is rated as not acceptable.

3.1.1. *Explosion Pressure*

As stated earlier it was clear that the design for the reaction vessel had to be explosion proof. Since safety lab explosion measurements in pure oxygen were not totally conclusive the design pressure was extrapolated using data measured in air; the proposed operating pressure was determined in the pilot plant trials with an additional safety margin. It was decided to use the maximum explosion pressure as design pressure. If an explosion occurs then the vessel will not be deformed and can be reused after thorough testing. The second main parameter for the vessel was the construction material. Because of the solvents and catalysts used in this reaction a highly corrosion resistant material was needed. Since it is not practical to design a thick vessel wall with an expensive material the final reactor was designed with a corrosion-resistant titanium layer explosion-clad on a thick carbon steel plate.

3.1.2. *Runaway Reaction*

Tests in the safety lab showed that the reaction mixture has a potential for a runaway reaction. The maximum temperature during such a reaction would be sufficiently high to cause an ignition in the gas phase. The pressure increase of a runaway reaction is rather slow compared to that of an explosion. Since the reactor design is already explosion proof it was decided that a runaway reaction can be best handled inside the reactor vessel itself. Therefore a safety valve with connection to a blow-down tank was eliminated from the design. The design conditions now take both maximum pressure and elevated temperature into account. To decrease the probability of a runaway reaction the vessel conditions (pressure, temperature, …) are very well monitored. A very moderate temperature increase will already stop the feed to the reaction and start the emergency cooling system. It is already very efficient because the heat of reaction for the oxidation is rather high.

3.1.3. *Titanium*

By choosing titanium as the construction material because of the corrosion issues, additional ignition sources had to be considered. Titanium metal can burn in an oxygen atmosphere when the oxidizing layer is removed. Possible reasons can be friction between two pieces of metal, for example the cooling coils inside the vessel rub against the piping support when the agitator turns. Also high oxygen velocities along a metal surface can ignite titanium. These hazards were translated into the design. The piping support was for example always coated with a thick PTFE layer. The oxygen inlet pipe also has a 5 mm thick PTFE inliner. This can be seen in Fig. 3 which shows the bottom section of a reaction vessel during construction. Another area where a metal-to-metal contact is still possible is the double mechanical seal on the agitator shaft. Here it is important that lubricating liquid is always available. This is why the lubricant container has a low level alarm installed.

3.1.4. *Oxygen*

Leakage of oxygen into the surroundings must also be avoided. The chosen piping standard therefore calls for an oil and fat-free installation. Also the time during which there is an oxygen atmosphere inside the vessel during a batch is limited. It was decided at a very early stage of the project that oxygen should be present only during the actual reaction. While catalyst is being charged or finished product is waiting to be pumped to the next step an inert atmosphere is used. This also reduces the risk of carryover of oxygen into the next production step. In order to achieve a fast changeover between oxygen and nitrogen the vessel can be evacuated using a liquid ring vacuum pump. A special inlet pipe was designed which sparges the gas below the agitator. This pipe is used for both oxygen and nitrogen. The inlet nitrogen pressure is set well above that of the oxygen. In addition to a non-return valve both control system alarms and safety valves make sure that no oxygen can contaminate the nitrogen pipeline.

3.1.5. *Purge*

It is obvious that the mixture in the gas phase can exceed the lower explosion limit. By introducing a purge the risk can be reduced but not eliminated. Since the connection to the downstream equipment is open during the whole reaction time, decoupling measures are necessary.

What happens with the explosion when it propagates into this pipeline and is there an additional risk because all three reactors are linked together *via* the exhaust scrubber? A propagating explosion has to be prevented by decoupling those connections. The overall aim was still to protect the personnel and environment and the equipment from effects of a propagating detonation.

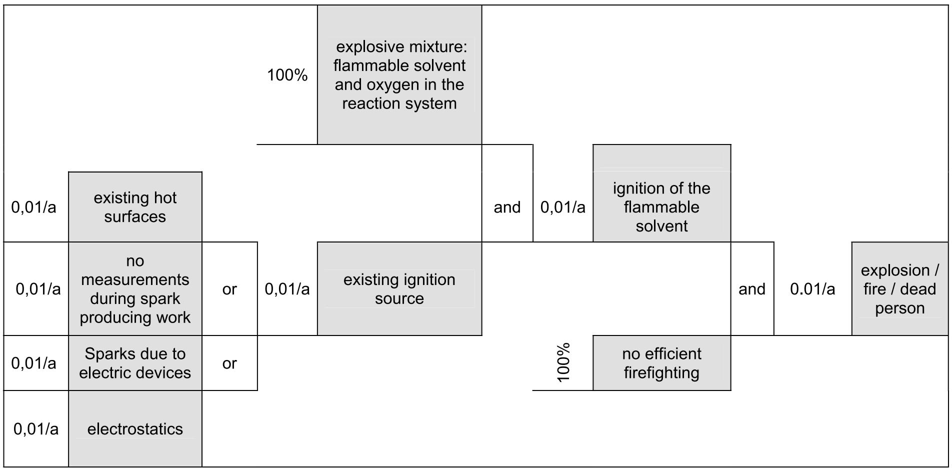

Fig. 2. Explosion scenario

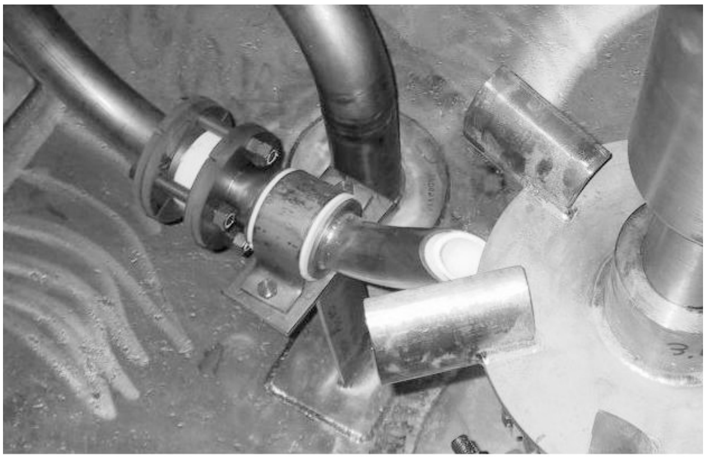

Fig. 3. Reactor internals

Safety lab experiments do not represent the potential explosion pressure since they did not cover the dynamics taking place in long pipelines. From the literature it was known that explosions can turn into detonations. Calculation of the explosion venting area using the measured pressure rise coefficient showed that the use of relief valves or rupture disks would not be suitable.

3.2. *Explosion Trials*

Considering all the risks identified during the risk assessment it was decided that additional data were needed. We approached several companies who provide safety support. We were especially interested in answering three questions: how can we detect an explosion, what happens after an explosion in the attached piping network and is there a method to isolate the event? Experiments at Fike Coorperation in Kansas, Missouri were carried out which simulated the exhaust piping geometry (the preliminary equipment layout placed the reaction vessel at different elevations inside the building). The results confirmed that a detonation in those pipes can occur. Flame propagation velocities exceeded 1000 m/s; detonation pressures over 30 bar were observed.

Looking for commercially available safety equipment was not an easy task. Most devices are only tested and certified in air. No information is available on their usefulness in pure oxygen. Another problem was to find a detection device for the chemistry we were using. Most devices work with a fast pressure indicator that can differentiate between explosions and normal pressure increases. It is important to detect the explosion as early as possible to have time to start the isolation. In our case we were not able to use pressure indicators since at the time of the project execution these instruments were not available (and certified) in a corrosion proof material. The project schedule did not allow us to wait for the new design of such a device. Therefore another objective of the experiments was to test a different detection method. At the end of a pipeline a rupture indicator will act as an explosion detector. It is attached on top of a flame interrupter. This device will at least delay flame propagation long enough for an explosion isolation valve to close in time. More details about the experiments can both be found in the article from Obermüller [3] as well as in the AIChE presentation by Snoeys and Going [4].

4. Detail Design

4.1. *Risk Analysis*

At the detail design phase of the project, when both the mechanical details of the piping system with all the dimensions, materials, and instruments were specified and also the process automation was ready for programming a detailed risk analysis was carried out. The risk analysis forced us to describe the specific hazards and systematically classify the probability and the consequences of each evaluated risk. The probability of a possible ignition was controlled by primary and secondary explosion protection measures. The consequences of a fatal detonation for personnel, environment and equipment could be excluded by the implementation of the combined system of a flame interrupter with a fast acting valve. This system works as an explosion decoupling system. It prevents the propagation of the explosion and limits the destruction of the further parts of the plant as much as possible. With the decoupling system we could reduce the consequences of the explosion risks to an acceptable range. A single oxidation reactor could withstand the explosion but we had to make sure that such an explosion could not propagate through the connecting network into another reactor or downstream equipment. Therefore an explosion isolation design was introduced.

In the unlikely event of an explosion some damage to the equipment will result, but there will be no loss of containment or risk to persons in the vicinity of the vessel. It is expected that for example the functionality of the mechanical sealing or the instrumentation will be affected but the shut down period after an event will be limited. We were convinced that we could fulfill the company goals as well as the authority regulations in terms of remaining risk.

Regulations for restarting operation have been worked out in order to take the right measures after an interruption as a consequence of a hazardous event. This is necessary to ensure the correct and safe operation steps of the process. It is a part of the operating instructions.

4.2. *Connections*

During the risk analysis each connection from the reactor to other equipment was thoroughly looked at. We needed a clear definition of where the explosion will stop in each case. There were roughly three major categories of connections. Some connections are usually closed during the reaction. For safety reasons it was only necessary to check the status of each connecting valve on the PLC. If the status is wrong (open instead of closed), the reaction cannot be started. The liquid catalyst for example was still charged and heated to reaction temperature before the atmosphere change started. A later addition of catalyst was impossible. A second category was the feed lines to the vessel. They definitely have to stay open during the reaction. Both feeds (liquid raw product as well as the oxygen itself) are fed into the vessel through submerged lines. If an explosion occurs it will take place in the gas phase above the liquid. The pressure propagation in the liquid will be stopped by a check valve designed for this pressure. Since the oxygen line is also submerged, the liquid will also close the check valve. The only connection that cannot be treated this way is the off gas line vented from the vessel. It was clear that to solve this problem both explosion detection as well as a device acting fast enough to close this connection would be needed. All auxiliary equipment (valves, pipes, instruments) was chosen using standardized pressure ratings to keep costs reasonable.

4.3. *Explosion Protection System*

Based on the explosion tests the venting pipes of the reactors are equipped with a flame interrupter which will prevent or delay flame propagation. At the same time a rupture indicator will break upon opening of the vent and provide a signal to the designated explosion protection controller (EPC). This signal will instantaneously activate the explosion isolation valve installed far enough downstream from the flame interrupter to allow the valve to be closed before the flame front can reach it. The closed valve provides a physical barrier to guarantee pressure and flame isolation. A cross firing signal from the controller to the other two systems will close those valves as well. A relay contact in the controller is used to communicate with the process control unit of the plant. It will cause an emergency shutdown (closing all feed lines, fully opening the cooling water valve *etc.*) While the internal communication of the explosion protection system is in milliseconds, the response time of the process controller is in seconds.

A schematic drawing of the system can be seen in Fig. 4. Fig. 5 shows the flame interrupter during construction on the roof of the building. The pipes were heated electrically. In Fig. 6 the whole setup with both fast-acting valve and flame interrupter can be seen.

5. Production

5.1. *System Testing*

The official dry run of the explosion protection system was limited to measuring spikes and noise in cables from the rupture indicator and to the fast-acting valves. The interface between the explosion protection controllers and the PLC was also tested. It consists of both a trouble relay and an alarm relay which is used to force an emergency shut-down.

After the first couple of batches with real chemistry, one night the explosion protection system activated, all valves closed and the process was stopped. First checks on the roof of the building could not find any broken rupture disks or faulty indicators (Fig. 6). Close examination of the process data records showed that the 'detection' occurred while an empty reactor was being evacuated. Although we had determined the lifetime of the rupture disks in advance by a cycle test representing the pressures in the plant the rupture indicator was causing the problems encountered. After some evaluation and several changes in the design of the rupture disc the error was located in mechanical stress caused by the frequent pressure changes during the gas phase change. Although these interruptions were very stressful we could show that the explosion system itself works exactly as it is designed to do. When one rupture indicator reported a failure to the EPC all three fast acting valves were closed immediately (in milliseconds). At the same time this failure was reported to the PLC which switched this unit operation from production into a failsafe status. All feed valves closed, and the cooling water switched to emergency level. One reaction vessel was at the oxidizing step when the alarm occurred. The temperature in the vessel was cooled down to ambient temperatures, which slows down any reaction; also no additional oxygen could enter the system since the rupture disk was not broken. Since the agitator was still running (to allow for improved cooling) the oxygen still inside the system was used up by the feed. After about 10 to 15 min the vacuum inside the vessel was almost at 100 mbar abs.

This 'live' test started just short of an explosion without all the damage such a test would have caused, but with all the useful information about the correct programming of the system. We are now even more confident that it would work as well during a real emergency.

5.2. *Know How Transfer*

A lot of detailed knowledge was accumulated during the design and construction phase. Also much practical experience was gained in the start-up and during the first batches. It was very helpful that the project team included members from development, engineering, and the future production crew which meant that the interfaces between the project phases did not cause a loss of information. Different organizational measures were implemented to ensure that safety know how for the ongoing process would be maintained. First of all any changes have to be checked for consequences in the current detailed process description and in a risk analysis. As a consequence of that the standard operation procedures have to be updated. Influences on the evaluated hazards have to be discussed again in order to

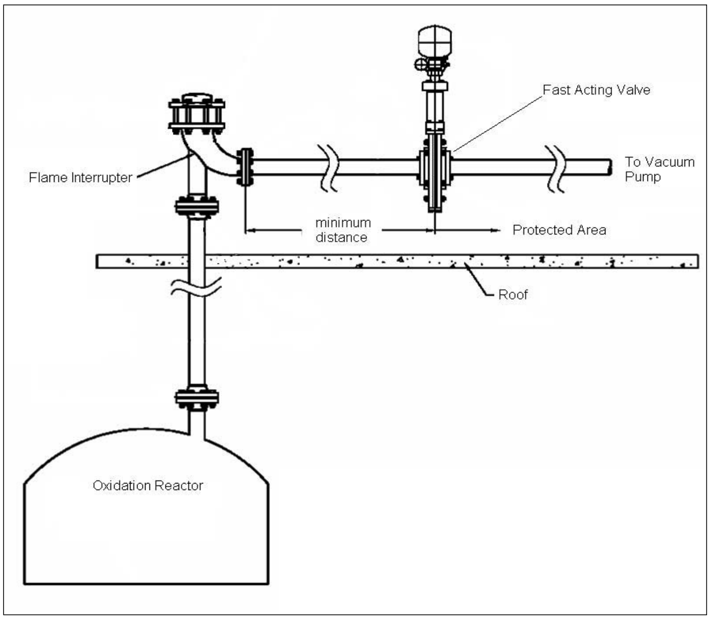

Fig. 4. Schematics of the explosion protection system

Fig. 5. Flame interrupter

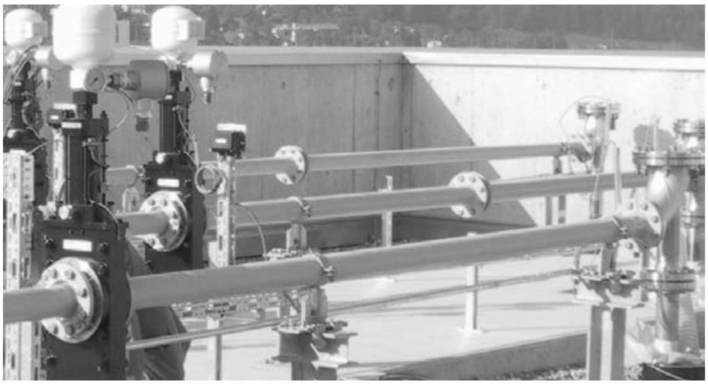

Fig. 6. Roof setup with fast-acting valves and flame interrupters

keep the same safety standard. All operators and new ones have to be trained in this. The process manager is responsible for controlling, documentation and observance of these procedures. This is a 'must' and has to be seen as a component of daily work.

6. Conclusion

This article described the development of a safety concept for a reaction in pure oxygen starting in the development lab and finishing with the successful implementation in a large scale production plant. We wanted to show how during the whole project from the first steps in the development lab to production a couple of years later safety aspects needed to be systematically considered. Most ideas can be transferred to different systems as well and are not restricted to oxidation reactions.

Acknowledgements

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