

Explosion of Methanol Distillation Column of Detergent Manufacturing Plant

【June 26th, 1991 Ichihara, Chiba, Japan】

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On June 26th 1991, an explosion and fire occurred during the shutdown work at the methanol rectifying column of the surfactant manufacturing plant in the Chiba factory of Lion Co., Ltd. in Ichihara, Chiba. The surfactant produced at the plant was "fatty acid methyl ester ethyl sodium sulphonate (hereinafter referred to as α -SF)", which this company had newly developed. The human damage by this explosion and fire consisted of two employees killed and thirteen employees wounded. As for the physical damage, the methanol rectifying column in which the accident occurred was destroyed, 319 spots in the factory were damaged by the blast and the fragments scattered by the explosion, and seventeen offices of nearby companies were damaged. Although according to the Fire and Disaster Management Agency investigation, the monetary damage to the factory reached 884 million yen and the monetary damage to the nearby factories totaled 129 million yen, this estimate may not have included other monetary damages such as restoration expenses and non-operation losses of the plant, so the total monetary damage is likely to be much larger.

The plant, which was changed from its original use as facilities for manufacturing alkylbenzene sulphonate, started manufacturing of α -SF from natural fat on February 11th, 1991, the year of the accident. After several operations, stops and repairs were repeated, the plant finished an operation that had started on June 19th, and the explosion and fire occurred at 10:15 on June 26th during the shutdown work for that operation. It was supposed that the scale of the explosion was equivalent to 10 to 50 kg of TNT, and the pressure of the explosion was over 16 MPa at the center of the explosion and over 11 MPa at the lower part of the explosion.

One of the main causes of this explosion and fire was the fact that organic peroxide methyl hydroperoxide (MHP) is slightly formed and then it decreases in the following neutralization process was overlooked during the research and development phase. During several hours before stopping, as pH control in the neutralization process was insufficient because of a failure of the pH sensor, the situation in which MHP cannot decompose or decrease easily was generated. Therefore, the recovered methanol that included slight larger amounts of MHP than normal was fed to the column where the

accident occurred. After stopping the methanol feed to the column, the hold operation and total reflux operation of the column were continued. The hold operation is a special name used at the factory, which means drawing-off of refined methanol from the top of the column after stopping the feed. It is assumed that during those operations, MHP accumulated at the specific trays, reached rather concentration and exploded as a result of a self-exothermic decomposition reaction. The boiling point of MHP is between the distillate methanol and the bottom products of the column (water in this case).

One of the primary causes of the accident was that the generation of the organic peroxide MHP was not found. Therefore, it was not known that MHP was decomposed in the neutralization process. As pH indications became incorrect due to a failure of the pH sensor, the flow rate of a sodium hydroxide aqueous solution for neutralization lowered extremely and the neutralization operation was carried out under acidic condition. Therefore, decomposition of MHP became difficult, and rather a large quantity of MHP remained. The MHP accumulated more than in the usual shutdown operation in the column and MHP was concentrated at a certain trays during total reflux operations and so on. pH control is a very important process for quality control in manufacturing of surfactant. If the pH control is not performed properly, MHP is not decomposed sufficiently. From matters mentioned above, it is one of the primary causes that the pH control was not performed sufficiently.

As a new analysis method for MHP was established two months after the accident, the existence of MHP was discovered. Considering the fact that the existence of MHP could not be found at the time of this accident, it seems to show the difficulties in prediction of hazards belong to the newly development technology. However, from the viewpoint of the operation, there was a problem that the pH sensor did not indicate the correct value because of an electrode failure, so that automatic pH control could not be performed sufficiently. As a result, the flow rate of an alkali solution that was used for neutralization decreased, and neutralization operation was done in an acidic condition. The problem was thought that the operation continued for several hours in the acidic condition without noticing the failure of the pH sensor. Although the stability of pH control in this process is not known, considerable fluctuation may have occurred as a result of using a strong alkali sodium hydroxide. Besides the weakness of the pH electrode against fouling was well known. If the importance of the pH sensor was realized, a doubled redundancy of the pH sensor should have been prepared.

MHP: The abbreviation of Methyl-hydroperoxide. It is organic peroxide with the structure of CH_3OOH in which one oxygen is added to an OH base of methanol. It was confirmed after the accident that MHP is formed by the reactions of methyl

sulfuric acid and hydrogen peroxide, which are by-products of the bleaching process. MHP explodes instantly when it reaches concentrations of over 25%, so it is not a desirable by-product.

1. Event

On June 26th 1991, a large explosion and fire occurred at a surfactant plant of the major toiletry company Lion Co., Ltd. at the Chiba factory in the seaside complex in Ichihara, Chiba Prefecture. The main product of the factory was surfactant manufactured by a sulfonation reaction of alkylbenzene. There were several surfactant plants in the factory. One of the plants was changed to manufacture α -SF by a sulfonation reaction of fatty acid methyl ester using a process that was developed in the company. The explosion occurred at the methanol rectifying column used for the process during the shutdown procedure.

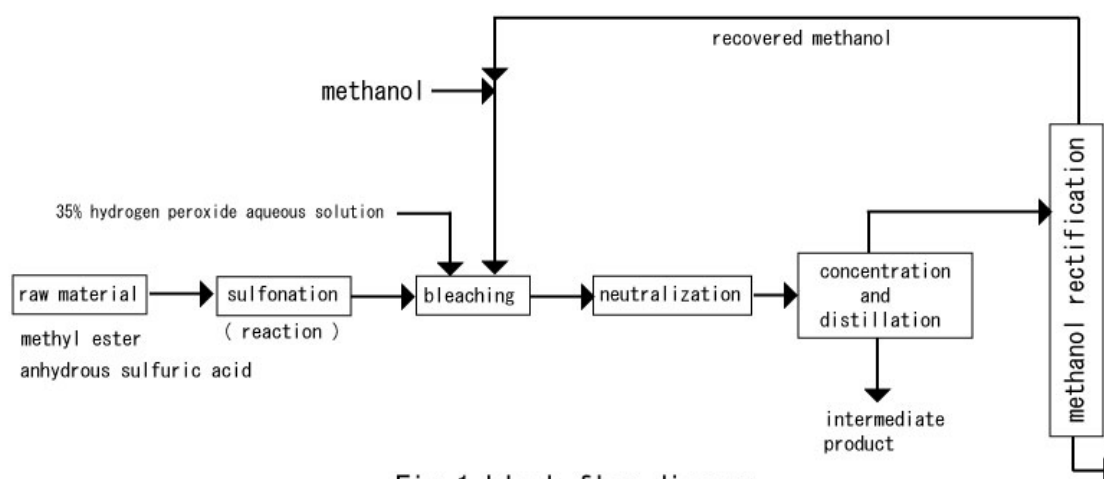


Fig.1 block flow diagram

The block flow sheet of the plant where the accident occurred is shown in Fig.1. The manufacturing process of α -SF has been divided into the following five processes: "the reaction process", "the bleaching process", "the neutralization process", "the concentration process", and "the methanol rectification process". The accident occurred at the methanol rectifying column in the methanol rectification process. In the first "reaction process", fatty acid methyl ester sulfonic acid is synthesized by sulfonation of raw material fatty acid methyl ester with sulfuric anhydride. In the next "bleaching process", oxidation bleaching is done for color improvement of the fatty acid methyl ester sulfonic acid. Next, the bleached methyl ester sulfonic acid is sent to the "neutralization process", where it is saponified by sodium hydroxide, becoming α -SF. At this point, however, the product is still in a solution of water-methanol. This solution is

sent continuously to the "concentration process", where it is separated into methanol-water vapor and product α -SF slurry, and the α -SF slurry is rundown to the product tank. The separated methanol-water vapor is sent to the "methanol rectification process" to recover methanol for reusing at the "bleaching process". Here by distillation, the feed liquid is separated into refined methanol and water and the water is sent outside of the process.

The operation was carried out entirely by the continuation method and automatic control.

The use of methanol and an aqueous solution of hydrogen peroxide together simultaneously for bleaching was a distinctive feature of this process, and it was recognized as an original technology developed by the company.

2. Course

2.1. Operation course to accident generation

On October 27th, 1990, a "water dummy run" was performed on the methanol rectifying column. A water dummy run is a confirmation operation using water instead of the actual liquid to be processed, which is performed when a plant is almost completed.

The complete survey was conducted by the fire fighting authorities, and the plant stood it on January 9th, 1991. From January 14th, a "trial liquid dummy run" was performed at the methanol rectifying column. During the trial liquid dummy run, the column was filled with a liquid that has nearly the same composition as the actual liquid to be processed, so the run conditions were almost the same as the actual operation conditions. This dummy run is conducted for checking the functioning of a rotating machine, instruments, and so on and also for training the operators.

From January 22nd to January 31st, trial runs were carried out intermittently. The first "production runs" started on February 11th, and the first shutdown was carried out on February 13th. In total, six production runs were carried out by June. A large number of operation runs were believed to be necessary for training the operators and adjusting the quantity of materials to be stored. During each operation period, the plant was shut down many times. Almost all of the causes of shutdowns seemed to be trouble at the concentration process. Although a temporary shutdown of the plant might be inevitable at the initial start-up especially at in-house developed plants, too many temporary shutdowns seems a little strange.

2.2 Operation course of just before the accident

From 21:35 on June 19th, the eighth production run started. The methanol

rectifying column was on stand-by during the total reflux operation. The “total reflux operation” means the operation where there is no supply to the column, the vapor evaporated by heating at the bottom reboiler is entirely condensed and it is all returned to the column without being drawn off and outside the process. At first, the sulfonation process started, and the processes down stream also started in order. At around 02:30 on June 20th, the feed to the methanol rectifying column in the final process started.

At around 01:20 on June 26th, the pH sensor of the neutralization process was found to be failed. Before that finding, pH control had been conducted automatically based on incorrect indication values. During this period, it is supposed that the neutralization operation was performed in acidic conditions. After finding out the failure of the pH sensor, the operation was changed to manual operation, and bleaching agents and sodium hydroxide were fed in proportion to measured of pH.

From 08:29, the shut down started from the reaction section in order to adjust the storage volume. At around 8:45, the neutralization process was shut down temporarily for repairing the pH sensor. The supply of the recovered methanol to the methanol rectifying column was stopped at around 09:15. From that point, the column was in the state of total reflux and in the so called “hold operation” in which the methanol in the reflux drum was rundown to the tank.

At around 10:15, an explosion occurred in the upper part of the methanol rectifying column. The upper part of the column and the ancillary piping fractured, and the fractured parts were scattered by the explosion. Simultaneously, a fire occurred near the column by methanol.

3. Cause

The cause of the accident was finally estimated as follows: MHP generated in the bleaching process could not be decreased during the neutralization process because of incorrect pH control caused due to a failure of the pH sensor, and as a result, methanol with a slightly higher content of MHP than normal operation conditions was fed to the column. The MHP was concentrated at specific trays during the total reflux operation and the hold operation in the shutdown procedure. This concentrated MHP caused self exothermic decomposition, which led to a thermal explosion as a result of the heat accumulation.

It seems many causes that were related to each other caused the accident. As for the operation, improper pH control, which was a basic item to maintain the products quality, was a problem. The neutralization operation continued in acidic conditions for

several hours due to a failure of the pH sensor. Methanol including high concentrated MHP which was not decreased sufficiently was fed to the column just before the shutdown operation. If the existence of MHP had not been known, and if the original operation conditions had been kept, the explosion would not have occurred. Since pH control is very important for quality control, redundancy of the pH sensor should have been prepared or the functions of the pH sensor should have been checked.

Next main problem was that the generation and decomposition of MHP was not found at the research and development stage. However, when it is considered that the existence of MHP was found two months after the investigation of the cause of the accident started by the establishment of a new analysis technology of peroxides, estimation of the formation of MHP might have been difficult. The existence of peroxide was known from before, but it was difficult to distinguish organic peroxide from the hydrogen peroxide that was used in the process. Therefore, it can be said that unknown phenomena caused the accident.

The third cause was the operation method for a shutdown of the column. The causes of a lot of chemical accidents are the related to the concentration of impurities. Distillation is one of the concentration methods, and the concentration of impurities might become high in the case of total reflux operation and hold operation. Total reflux and hold operations were not regarded as suitable shutdown methods for the first plant of the company's in-house development, since the existence of impurities is not confirmed. Though it seemed to be a general operation method at that time, it would be better to consider another shutdown operation method.

Based on the considerations above, it can be said that the accident originated from the cause of "irresistible force" or "unknown phenomena". However, an attitude of the company toward the in-house developed process was also a problem. Thoroughly verification should have been conducted. For example, there were many emergency shutdowns due to troubles at the concentration process. If many thermometers and many sampling points had been mounted in the column, might some other information about the operation have been gathered? It can be estimated that there was a maximum of 5 kg of MHP remained in the column at a normal shutdown and 40 to 50 kg of MHP remained at the accident. The estimated temperature profile during the distillation at the column is shown in Fig.4. It shows a distinct difference in temperature profiles between just before the accident and in normal operations. If this data had been available before the accident, the existence of something different from slight ester or surfactant could have been estimated.

4. Process of cause elucidation

The elucidation of the cause was difficult. At first, the facts related to the column where the accident occurred were arranged in the usual way. At this point, it was noticed that the scattered fragments had come from only the upper part of the column, from around the fourth tray to the 26th tray from the top. In addition, the time course of the entire operation was arranged.

Here, the damage to the methanol rectifying column is shown in Fig.2 and the photograph of the column after the accident is shown in Fig.3.

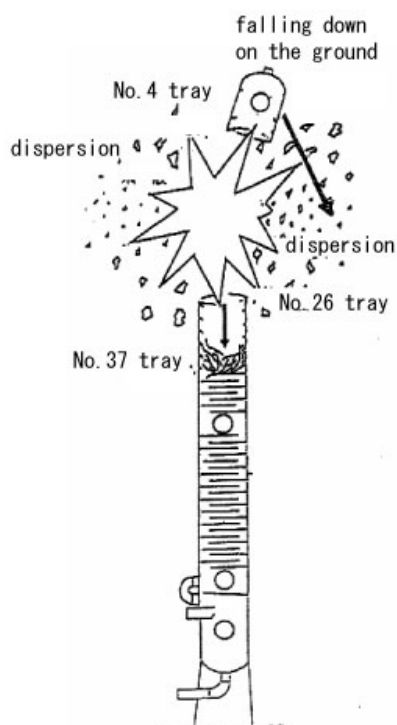


Fig.2 damage of the reactor

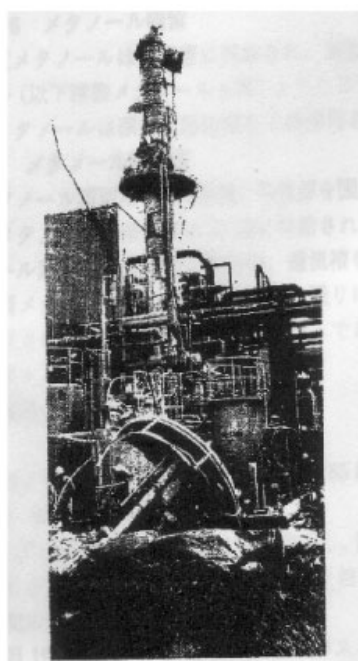


Fig.3 Rectifying column photo after explosion

In addition, the explosion pressure was estimated to be 16 MPa at the center of the explosion and 11 MPa at the lower part of the explosion, and the TNT equivalent of the explosion was judged to be 10 to 50 kg.

From the facts above, the possibilities of a vapor phase explosion, a liquid phase explosion and a solid phase explosion were examined. However, the data on the operating conditions and the experimental results denied all three kinds of explosions.

It was suggested that if explosive organic peroxide had concentrated and deposited in the column, it might explode. In order to check this idea, investigators searched inside the column thoroughly, but they could not find any trace of the deposit.

Two months after the accident, there a discovery of a new method for analyzing organic peroxide components in recovered methanol. This discovery became a trigger for reexamining the cause of the accident. The total quantity of the peroxide was measured by three kinds of analysis methods, and the results were almost equal. However, the component ratio of organic peroxide and hydrogen peroxide could not be determined. It was proven that the hydroperoxide existed in the recovered methanol as the investigation was continued with the use of various peroxide measuring methods. Simultaneously, there were peaks of both gas chromatography and NMR, the origin of which had been unclear, and it was proven that the peaks were originated from peroxide, and that the hydroperoxide was derived from peroxide having a molecular weight of 48 and that belongs to a CH_3OO - functional group. This peroxide was later identified as MHP. The object of examinations was limited to MHP after this, and the estimation of the concentration of MHP in the rectifying column, the mechanism of the generation of MHP and its explosion risk were examined.

The samples in the circumference of the methanol rectifying column were analyzed, and it was confirmed that 1700ppm MHP existed in the feed to the column, 5200 ppm MHP existed in the reflux of the column at the time of the accident, and 0 ppm MHP existed in the refined methanol during the normal operation.

When the distillation was simulated in the MHP-methanol-water system, the simulation result showed that MHP is concentrated in the column and reaches concentrations of over 10% in the total reflux operation or the high reflux ratio operation. When the rectifying column was checked, discoloration of column material was observed. The discoloration seemed to be caused by MHP, and the position of the discoloration accorded almost exactly with the place where the MHP concentration was highest in the simulation. The concept is shown in Fig.4.

The location where MHP was generated was estimated next. The MHP concentration in each place of the process was measured by analyzing the samples, which were taken at intervals during the operation and stored. The results of the analysis showed that the highest concentration was at the bleaching process outlet, and the concentration decreased to about 1/4 to 1/3 in the neutralization process, and MHP was not detected in the product -SF at the outlet of the concentration process. It was proven that almost all of the MHP entered into the recovered methanol that was supplied to the methanol rectifying column, because the methanol was the only other product of the concentration process. Regarding the generation of MHP, reproduction tests were carried out under some conditions, and it was confirmed that the possibility of MHP generation during the bleaching process was high.

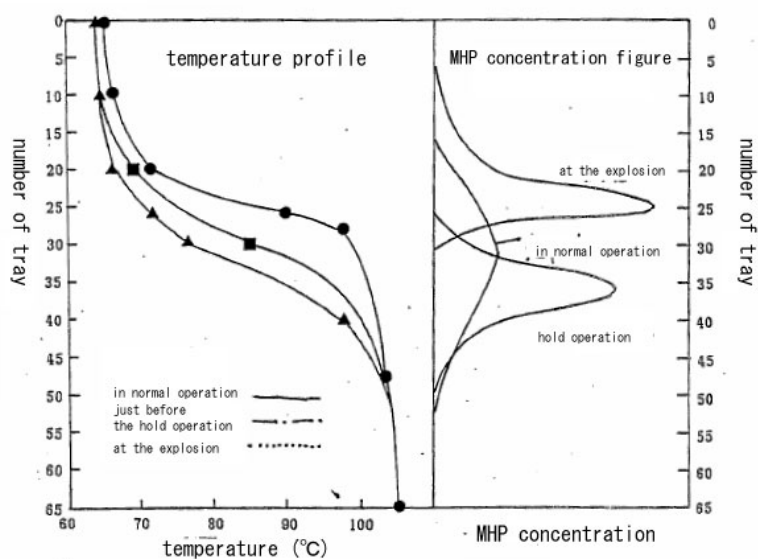


Fig.4 relation between MHP concentration and temperature profile in the column

It was a question why MHP did not cause an accident during the previous shutdowns and caused the accident on June 26th. As the operation conditions were reexamined, in the operation conducted from midnight to dawn on June 26th pH value was incorrect due to a failure of the pH sensor and the flow rate of an aqueous solution of sodium hydroxide was extremely low. According to a literature, MHP cannot be decomposed easily in acidic conditions. So it was considered that all of the MHP, which was generated in the bleaching process, did not decrease in the neutralization process and was fed to the column, then the MHP was concentrated at specific trays in the column during the total reflux operation and hold operation.

In the column, 30 to 40 kg of MHP might be accumulated during the shutdown when the accident occurred. Only a maximum of 5kg of MHP might be accumulated during previous shutdowns, so MHP might not reach the required concentration for an explosion at that time.

The danger of MHP was confirmed by various thermal analyses and simulations. The results of these studies showed that detonation of MHP may occur at concentrations of over 40%, and a decomposition reaction with a great heat occurs instantly at concentrations of over 25%. As MHP of about 23.5% concentration decomposes, rapid evaporation of methanol on the tray instantaneously could occur by an exothermic reaction of MHP, generating a pressure of about 15.5 MPa which is large enough to cause an explosion.

The explosion is considered to have progressed as follows. MHP was locally

concentrated in the column, and an exothermic decomposition reaction started. The reaction rate was increased by self-heating decomposition, and the generated large heat caused an explosion with a temperature rise (thermal explosion). Methanol on the tray instantaneously vaporized, causing a large pressure rise and detonation.

5. Immediate action

The private fire brigade turned out, and the fire was extinguished after 10 minutes.

6. Countermeasure

As countermeasures for the prevention of recurrence of the accident, the following items were indicated.

1) Improvement in the process to avoid MHP formation

The operation conditions are to be changed to avoid formation of by-products that may produce MHP and a process to decompose MHP when it is produced should be added.

2) Improvement in the operation methods

Monitoring for confirming that there is no MHP in the column feed, is to be performed. Samples are to be taken periodically for checking the existence of MHP. The pH meter is to be sufficiently maintained, and the plant should be stopped in the event a failure of the pH meter if necessary.

3) The improvement on the safety management system.

When a new product is produced by the newly constructed plant, a priori checking system that studies the safety of the plant during the development and research stage and conducts test runs beforehand is to be introduced and included in the safety management system. Furthermore, it was attempted to make the operation manual more thorough.

Items above mentioned were a matter of cause from the view point that the explosion occurred at the plant. As a general rule in the development of a new plant, particularly if it is the first plant to be constructed using new technologies created in-house, safety countermeasures, including for intermediates, should be considered, a technical follow-up should be considered for a once completed plant and/or process, and further development of the plant should be executed. As discussed before, there may be problems that cannot be foreseen before an accident occurs in a newly developed plant or process. After the accident, the money and time that are required for remodeling and improvement are very large.

7. Knowledge

- 1) In the development of a new process, the safety measures might not be sufficient even if sufficient examination and analysis is performed. Based on the issues mentioned above, it is necessary to thoroughly investigate and examine each of the reactions and physical properties involved in the process. At that the time, it is also necessary to consult with the specialists from outside of the company. Some phenomena only become known after performing continuous operation in a large-scale plant. In order to prepare for unexpected phenomena, it is desirable to mount many sampling points and measuring instruments, which may appear to be unnecessary at first.
- 2) In the distillation of a multi-component system that includes a middle fraction, the middle fraction can be concentrated to unexpectedly high concentration level as shown Fig.4 during the total reflux operation when the distillate is not rundown outside. It is necessary to sufficiently understand this fact.
- 3) It is necessary to keep the operation as decided, and it is important to prepare the facilities and operation management to maintain the decided items.

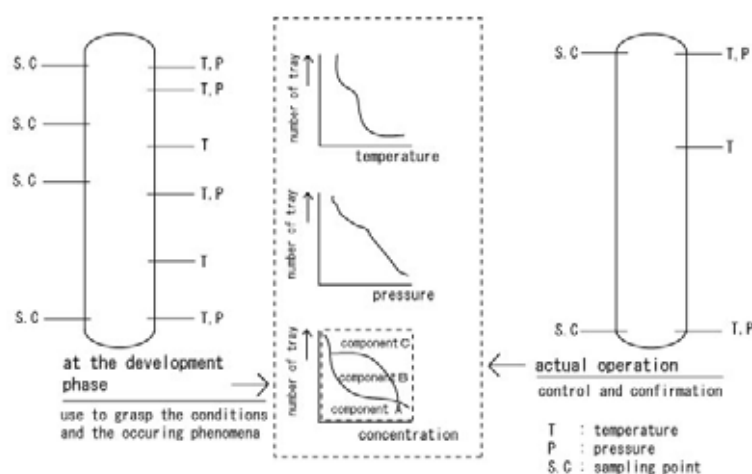


Fig.5 difference between the measuring points at the development phase of the new technology and the measuring points at commercial plant

8. Influence of failure

As for the human damage, two persons died instantly when fragments scattered by the explosion hit them on the head, and thirteen persons were injured.

The monetary damage was reported to be about 880 million yen; however, this amount may only be the direct monetary damage such as damaged buildings and damage to the plant. For the entire enterprise, the monetary damage becomes large

when other types of damage such as non-operation losses caused by the stopping of the whole factory are considered. Additionally, seventeen nearby companies in the industrial area suffered damage. The direct loss to the adjacent factories was 130 million yen. Fortunately, there was no damage to private houses because the plant was located in the seaside industrial area.

The product of this plant was a main raw material of new goods that the enterprise intended to sell in memory of 100 years anniversary of the enterprise. The accident might bring considerable large damage for the enterprise.

References

- Fire and Disaster Management Agency, “Explosion and fire of methanol rectifying column on stream”, “Accident case of the dangerous substances”, p 64-67(1991)
- Tadao Yoshida et al, “Explosion in the methanol rectifying column caused by organic hydroperoxide”, J, Japan Soc. for Safety Engineering, 35, 370-378 (1996)
- Safety Research Association on dangerous materials in Kawasaki City, “Explosion and fire of the methanol rectifying column of synthetic detergent manufacturing plant”, Accident examples of dangerous facilities with FTA immediately, p8-10(1997)