Explosion of Acetylene Hydrogenation Section in Ethylene Plant

【July 7th, 1973 Tokuyama, Yamaguchi, Japan】

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1973 may have been a special year for the chemical industry of Japan. Major accidents happened successively from the west to the east from the spring till the autumn of that year. The accident shown in this article was the first accident of the series.

At around 22:13 on July 7th, 1973, a large explosion and fire accident occurred at the second ethylene manufacturing plant of the Idemitsu Petrochemicals Co., Ltd. in Tokuyama, Yamaguchi. The plant started an emergency shutdown procedure as a result of an instrument air (IA) failure. When the supply of IA was restarted, preparatory work for the re-startup was carried out at the plant after a few minutes of an emergency shutdown. At that time, a runaway reaction occurred at the acetylene hydrogenation reactor, gas leaked from the outlet piping, and an explosion and fire occurred. Acetylene is a trace impurity in the product of ethylene. The fire was initially extinguished at around 12:00 the next day, but the complete extinguishing of the fire was not achieved until 10 pm on July 11th, 3.5 days after the occurrence of the fire, because the propylene used in the process began to spout out as a result of the fire, and it took many hours to stop the spouting.

The human damage of this accident consisted of the death of one person. The physical damage was the burning of about one tenth of the enormous ethylene plant, and the direct monetary damage was calculated to be 25 hundred million yen in the currency value at the time. However, the damage was much larger when the restoration expense and profit loss from the long-term no-operation period were added. In addition, the ethylene plant supplied each company in the industrial complex with raw material through the piping, and so the plants of eight companies were forced to shutdown or at least decrease their production rate as an effect of the shutdown of the ethylene plant.

The direct cause of the accident is as follows: 1) at the re-start of the acetylene hydrogenation reactor after the emergency shutdown, excess hydrogen was supplied, 2) the ethylene that had accumulated in the reactor was hydrogenated, while originally only a small amount of acetylene was hydrogenated, 3) excess heat was generated by the ethylene hydrogenation. However, it is more important why the IA failure occurred, and why the acetylene hydrogenation reaction was restarted just after the re-supply of IA started. In this series of events, it is shown that facility management and education are fundamentally important for operating a chemical plant.

Hydrogenation : One of additional reactions; hydrogen atoms are added to atoms at the both ends of unsaturated bond such as C= C double bond, C ≡C triple bond, C=O double bond (from the “essential chemistry dictionary”). The hydrogenation process used in the ethylene plant is described in the Event section.

1. Event

At ethylene manufacturing plants in Japan , naphtha is a main feedstock, and it is cracked thermally at a high temperature of around 800 ℃ with steam in a tubular cracking reactor. Products such as ethylene and propylene are obtained through more complicated refining passes. The ethylene plant block flow sheet is shown in Fig.1.

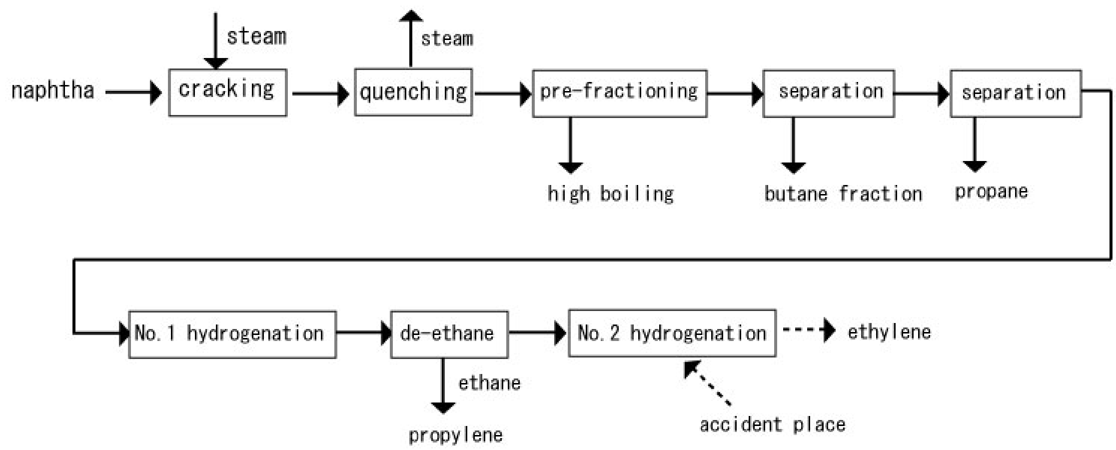

Fig.1 block flow diagram of ethylene manufacturing plant

Many isomers coexist in the product material because of the thermal cracking of naphtha. Ethane and acetylene are contained in ethylene, and propane, propadiene, and propyne are contained in propylene. Although the paraffin ingredient such as ethane and propane can be separated from ethylene and propylene by distillation using a slight boiling point difference, acetylenes and diene are removed by conversion to mono-olefin through hydrogenation. The section that carries out this hydrogenation for C2 fraction, mainly composed of ethylene, is called "acetylene hydrogenation". This hydrogenation is a large exothermic reaction, and coexisting materials of C2 fraction consists of mainly ethylene and a slight amount of acetylene. If the hydrogenation conditions are not ideal, ethylene is hydrogenated and may generate a large amount of heat. In the worst case, it might cause an exothermic decomposition reaction of ethylene. Therefore, this hydrogenation process is the most problematic section of the ethylene manufacturing process, as well as the high-temperature cracking furnace in the ethylene plant. The important points in the control of hydrogenation are to supply only a necessary amount of hydrogen for acetylene hydrogenation and to raise the selectivity of acetylene hydrogenation. The temperature range permitted to maintain the best selectivity is very narrow, so careful attention is required for temperature control, and so on.

On the night of July 7th, suddenly IA supply stopped. IA is used as a driving force for adjusting controllers such as a flow controller and adjusting an automatic control valve (CV). Therefore, the IA failure caused an immediate emergency shutdown, and all of the CVs took the failure position. At that moment, the flare stack for burning the excess gas began to kindle a large flame.

Flare stack: the equipment for burning the unnecessary gas that is discharged from a plant. In Japan, a chimney-shaped flare stack is most often used. It is a necessary piece of safety equipment for an ethylene plant because a large amount of gas is discharged during an emergency shutdown, etc.

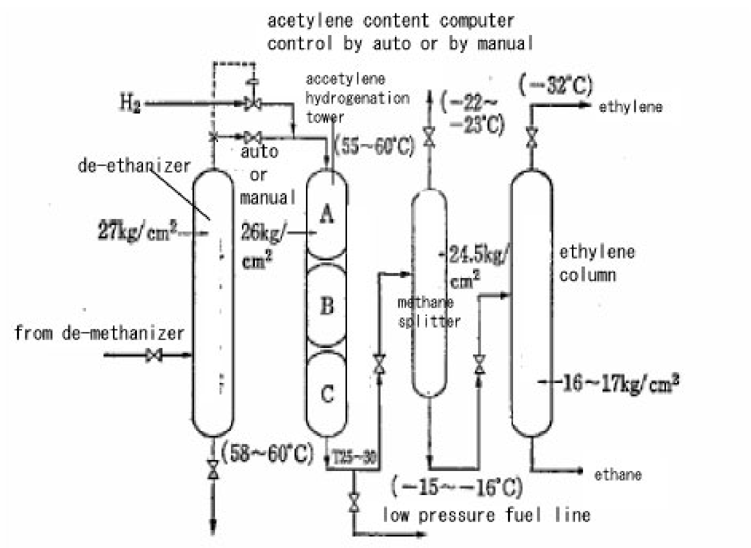

Fig.2 simplified flow sheet around the hydrogenation section

After a few minutes, the supply of IA was restarted. Preparations for restarting the operation started while the cause of the IA failure was investigated. A few minutes after the instruments returned to normal, the ethylene flow rate and hydrogen flow rate were observed to have decreased, so a control operator changed the flow rate control from automatic to manual, and closed the ethylene feed CV. Then he also closed the hydrogen CV. As the temperature at the upper part of the middle section of the reactor was rising, the control operator introduced ethylene into the reactor from a different ethylene plant for lowering the temperature. Then the temperature rose rapidly, so the block valve of the hydrogen CV was perfectly closed. The temperature indicator exceeded the scale limit – it was later found to be 970 ℃ when it was confirmed by the computer – and afterwards the temperature dropped back to 750 ℃. Meanwhile, the outlet piping of the acetylene hydrogenation reactor B division became red-hot, and the gas that leaked from the valve flange caught fire. Moreover, the piping ruptured as a result of the high temperature, and a large explosion and fire occurred. This fire destroyed a large amount of equipment, including some distillation columns and heat exchangers. A large fireball with a 60m diameter arose at this time.

The fire was got under control at 6:00 am the next morning, but spouting and combustion of the propylene refrigerant continued, and the fire was extinguished at last on July 11th.

2. Course

At around 18:50, instruments of the control room all failed simultaneously. The control operators who came in for the emergency shutdown work could not find the cause. Few minutes before the incident, a field operator opened the six inch valve of the work air piping (YA) and closed the four inch IA valve near the six inch valve by mistake, instead of closing the two inch YA valve for de-coking the cracking furnace. Therefore, the control instruments took the failure position, the plant entered an emergency shutdown, and black smoke rose from the flare stack. The operator was surprised at the black smoke, and returned the IA valve to the open position.

De-coking: coke is formed inside the cracking tubes of the cracking furnace, and it adheres to the tube wall. The coke lowers the cracking efficiency and brings about a rise in differential pressure. The work for removing the adherent coke is called de-coking. The decoking work is not only done for cracking furnaces but also for heating furnaces in general. Generally decoking work is executed in steam-air or nitrogen-air condition.

Failure position: the failure position is the position of the CV – full open, full close, or stay – which is set beforehand so that when the IA supply is cut off, the plant will be placed in a safe condition.

At around 18:58, the instruments returned to normal, and the control operators began adjusting the instruments for re-starting the plant. The supply of ethylene and hydrogen to the acetylene hydrogenation reactor had been started, but the ethylene supply stopped due to the pressure balance of the ethylene system. At 19:02, a control operator switched the controller of the ethylene feed to the reactor to manual and closed the CV. Then he noticed that the hydrogen supply was still continuing. At 20:08, he closed the hydrogen CV.

At 21:00, although the normal operating temperature was 60℃ at the middle section of the hydrogenation reactor B, it had risen to 90℃, but the control operator seemed not to be aware of it. At 21:30, the thermometer at the hydrogenation reactor B middle section showed a temperature of 120 ℃. The control operator, who discovered the abnormally high temperature, introduced ethylene gas from another plant into the hydrogenation reactor for cooling. Simultaneously, the required amount of hydrogen for the hydrogenation process was supplied by the automatic control. At 21:38, the control operator noticed the rapid temperature rise, and he stopped the supply of the hydrogen manually.

When the supply of ethylene started, the temperature indicated by the thermometer started to increase rapidly. The temperature recorder was scaled out over a maximum temperature of 200℃. At the operator's console, a temperature of 970℃ was observed at the middle section thermometer at 21:45. The middle section thermometer lowered to 750℃ at 22:00, but the thermometer of the lower section showed a temperature of 896℃.

After 22:00, the temperature at the lower section of hydrogenation reactor B exceeded 1000℃, the outlet piping became red-hot, and the gas leaked from the valve flange and ignited. At around 22:15, the hydrogenation rector B outlet pipe was destroyed by the high temperature, the gas that leaked from the pipe exploded, and a large-scale fire occurred.

After that, the fire spread and was extinguished at last – it is omitted here.

3. Cause

The cause of the explosion was determined to be the mistaken closing of the LA valve. During the restart-up operation, a control operator mistakenly closed the valve by mistake, ethylene was hydrogenated in the acetylene hydrogenation reactor, and then the temperature of the reactor became high. As a result of the high temperature, an exothermic decomposition of ethylene occurred. The outlet piping was broken by the high temperature, and a large amount of hot gas leaked from the piping. The gas ignited spontaneously by the high temperature of the piping.

Although, only a slight amount of acetylene was to be hydrogenated selectively in the reactor, excess hydrogen was supplied when the crude ethylene supply was stopped. So nearly the entire ethylene in the reactor was hydrogenated. Furthermore, although some metal based catalysts are used for this hydrogenation, it is known that a hydrogenation catalyst of palladium, which was used, causes an exothermic decomposition reaction of ethylene at temperatures over 400℃.

The true cause is considered below. The accident was regarded to have been caused by the combination of the human error of the field operator who mistook the valve operation, the judgment error of the control operator who allowed only hydrogen to be supplied at the re-startup of the hydrogenation reactor, and the judgment error of the control operator who introduced ethylene from another plant. However, actually the true cause of the accident seems to have been the following: insufficient consideration in the mechanical design phase and defects in the operation management, together with a shortage of education and training that led to a lack of understanding of the essence of the plant and the importance of reconfirming the plant condition prior to the re-startup after the emergency shutdown.

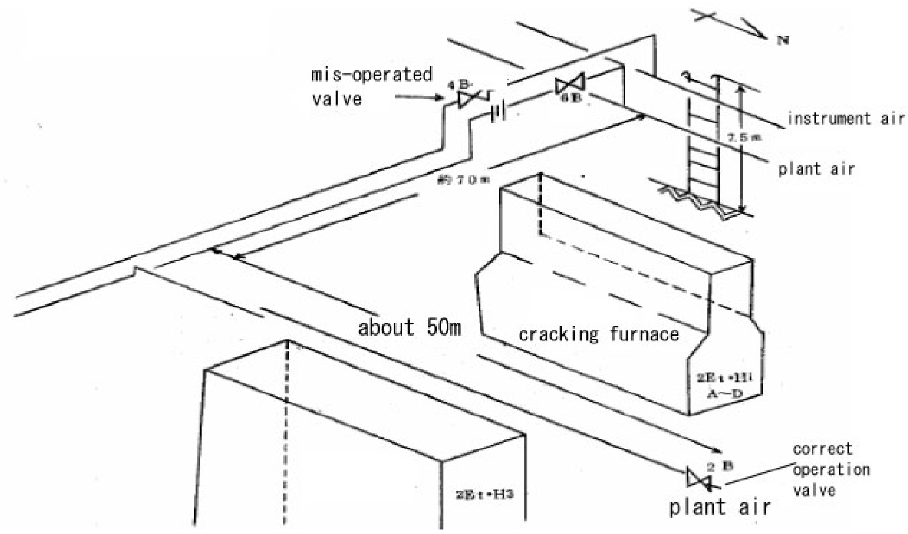

Fig. 3 location of the air piping valve

The accident was triggered when the IA was stopped by closing the IA valve by mistake instead of the YA valve. Therefore, it is also possible to consider the accident to be caused by typical human error. However, what must be considered here is why the human error was caused, and whether or not the human error could have been prevented. The piping and valves concerning the accident are shown in Fig.4. Although the reason for mistaking the valve, which was mounted at interval of 100 m cannot be known for certain, some problems can be pointed out regarding the design of the facilities and the condition of the management.

To begin with, all of the valves were mounted on racks, under the floor or in the ceiling. As the de-coking of the cracking furnace is executed several times per year, the YA valve is an often used. Therefore the valve should have been placed where operation and confirmation could be performed easily.

Next, "why the IA valve was closed" is a problem in the operation control aspect. Closing the IA valve is absolutely forbidden when the plant is on stream. For a valve that is absolutely forbidden to be turned on and off during normal operation, the person responsible for the operation must take measures to prohibit the turning of the valve. At least, color coding or hanging cards on the valve must be conducted for capture the attention of the workers. Ideally, the valve should be sealed in the presence of a manager or supervisor after the valve was set in the correct position. Valves that are absolutely forbidden to be turned are the valves that may cause damage to the safety or control of the plant if turned from the specified position, including the IA valve and the block valve of the pressure safety valve. When the author joined a certain petrochemical company in 1966, the mark “CSO(C)” was put near some of the valves in the Piping and Instrument Diagram (P&ID), which is one of the basic design drawings for a chemical plant. The author was taught that this mark means “Car Seal Open (Closed)”, indicating that the marked valves had to be sealed because they are forbidden to be turned.

It can be guessed that there were some problems in the work instruction. The person in charge of the valve operation had to instruct the correct valve clearly, and make the field operator of the valve repeat it. It is supposed that if the person, who indicated the valve had warned of the position of the two inch valve, the accident would not have occurred.

It is more important to examine why the plant operators hurried to re-start the plant. When the IA failure occurs, the plant shutdown occurs automatically at all refineries and chemical plants, not only at ethylene plants. At that time, all of the control valves are switched to their failure positions that had been set beforehand, such as full open, full closed or stay as it was. At an ethylene plant, in the event of an emergency shutdown, gas is discharged from many pressure control valves (PCV) to the flare stack, because the safety of the plant is the first priority. Therefore, the condition of the entire plant is completely different from that during the normal operation. The pressure balance cannot be maintained, and all temperatures gradually approach to ambient temperature. In such a plant, even if the IA failure time is only a few minutes, the plant must not be restarted without a detailed confirmation and checking of the situation. Moreover, the hydrogenation section must not be restarted without checking carefully, because a runaway reaction can be caused if excess hydrogenation happens.

It is supposed that managers and operators wanted to restart the plant as soon as possible because it takes a few days to restart an ethylene plant and the non-operation loss is several tens of millions of yen per day. However, the careless restart with insufficient knowledge about the plant caused the accident.

4. Immediate action

All manufacturing plants except the boiler were stopped immediately. At the plant where the accident occurred, water spraying from a stationary fireplug, separating of the burning section from the other sections, discharge of the combustible gas to the flare stack, and various other measures including introduction of nitrogen gas to the plant and extraction of the liquefied gas were conducted.

The operation of the other plants was also stopped for preventing dangerous materials from catching fire. Furthermore, shipping through the pipe line to other facilities of the companies of the complex was stopped.

During the fire fighting, the evacuation of the neighborhood inhabitants was considered because the plant was rather near the private houses, but in the end, the evacuation was judged not to be necessary.

5. Countermeasure

The report lately made by the company was describing the countermeasures ranging over six pages. At the headquarters, the safety countermeasure center and the environment and protection room was established, and strengthening and improvement of the environment and peace section of the factory were conducted.

In the subject of the facilities, many kinds of alarms at the reactors were improved and the vessels that contained large amounts of liquefied gas were remodeled so that de-pressure or discharge could be carried out rapidly. Labeling and other measures to distinguish the piping and valves were done more thoroughly in order to prevent mistakes in operation. Finally, the water sprinkling system and other systems for fire prevention were improved.

The personnel allocation was made proper, and the personnel were given complete education and training. In addition, the operating standards were drastically revised. In short, the safety conditions were totally reviewed, and it was improved in all fields.

6. Knowledge

1) It was reconfirmed that the safety of a chemical plant fundamentally depends on education and training.

2) It is important to design plants so that the possibility of human error would decrease, and it is also important that the management which can support the design is carried out. In this example, the accident would not have happened if the valve that must not be turned on or off was controlled so that the valve could not be turned, and if the plant had been designed so that mistakes in operation would not occur.

3) If a plant stops once, the situation is different from that of the plant before it stops. It is necessary to conduct the re-startup of a plant only after careful investigation and confirmation of the cause of the shutdown as well as confirmation of the situation of the entire plant.

7. Influence of failure

1) As for the human damage, one person was injured.

2) As for the physical damage, a total of 94 pieces of equipment, including twelve distillation and reaction columns and seven heat exchangers, were damaged. The direct monetary damage was estimated at 25 hundred million yen (in the value of the yen at that time). However, considering the restoration expenses, non-operation losses, and so on, the monetary damage was enormous. In addition, there were some non-operation losses resulting from the stopping of other equipment in the factory.

3) Among the neighboring facilities, twelve plants in eight companies were forced to stop or to reduce operation because the supply of ethylene and other raw materials was stopped.

8. Sequel

Multiple accidents related to petrochemical plants and a large fuel oil leakage to the Seto Inland Sea that occurred in the next year, 1974, triggered a major revision of the fire protection law and the high pressure gas law in the second half of the 1970's, which led to the establishment of present safety regulations.

9. By the side

Among the accidents of chemical plants, there are many examples where a "runaway reaction" caused the accident, includ ing this accident. A runaway reaction is caused by insufficient c ontrol of th e h eat g eneration by an ex othermic r eaction, and there are some typical cases. Some of those are introduced here. To begin with, there is a case where the cooling function is lost. The loss of cooling function can originate from blockage in the heat exchanger for cooling, a temperature rise of cooling water, stops of the cooling water, agitation, and so on. Sometimes a runaway reaction is caused by the restart of th e agitation, although there was no problem in the stop of agitation. This runaway reaction is th e result of the separation of the contents into two phases whi le agitation stops. It led to a rapid exothermic reaction when mixing is restarted quickly. In a selective reaction where a small p art of the feed material is reacted using a slight condition d ifference, someti mes t he entire contents of the feed material r eact completely when the conditions of composition, temperature, and flow rate are changed, resulting in a runaway reaction.

The accident at the ethylene plant introduced here is an example where a selective reaction changed to a runaway reaction. Another example of a selective reaction is as follows; a selective hydrogenation reaction of a pyrolysis gasoline fraction using a sulfurized metal catalyst changed to a runa way reaction by the removal of sulfur . In the composition of the feedstock, some runaway reacti ons occurred when an oxidizing agent was i njected over the regulated rate. In short, there are many possibilities in which a runaway reaction can be caused, if temperature control is insufficient.

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