Study on Risk Evaluation of Acetochlor Production Process

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Abstract. To scientifically evaluate the danger of acetochlor production process, this article identifies and analyzes dangerous and harmful factors in a company's factory from dangerous and hazardous substances, equipment, and places, etc. Fire, leakage, and explosion are the main risk factors of the plant. Taking the ethanol storage tank leakage in the storage area as an example, the FLUENT software was used to simulate the leakage of ethanol, and it was found that the leakage outlet emitted a concentration of more than 8% and migrated to the windward side, which was extremely prone to vapor cloud explosion. Then, the TNT equivalent explosion model was used to calculate that the vapor cloud explosion may cause the death radius, severe injury radius, and minor injury radius to reach 57.27m, 138.39m, and 252.21m. At the same time, the radius of explosion damage under other overpressures was calculated. Based on this, suggestions for targeted safety countermeasures can be provided, which can provide a reference for accident prevention and emergency treatment.

1. Introduction
With the continuous improvement of the level of agricultural mechanization in China, the manual labor force in rural areas has gradually decreased, the demand for chemical herbicides has continued to increase, and the market has expanded accordingly. Acetochlor is currently one of the most popular herbicide products in the domestic agricultural market [1], and its manufacturing raw materials, as well as the transportation and storage methods of the products, are very dangerous [2]. It is easy to cause security accidents, which will not only have a negative impact on economic development, but also cause a lot of economic losses and even casualties. Therefore, it is particularly important to identify dangerous and harmful factors in the production process of acetochlor and analyze the dangers of the production process.

2. Engineering background and research scope
The acetochlor production area of the company is divided into two areas: north and south. The north area is from east to west with ammonium chloride recovery unit and alcohol recovery unit; the south area is from east to west with class a tank farm, acetochlor production workshop and its auxiliary facilities. Among them, the control room, power distribution room, and nitrogen generator room are adjacent to each other on the west side of the acetochlor workshop.

In this paper, hazard source identification and analysis were carried out in the production process of acetochlor. The identification scope is shown below.

(1) Production facility: one acetochlor production facility, one alcohol recovery device and one ammonium chloride recovery device;
(2) Storage facilities: two 20m$^3$ and two 130m$^3$ vertical acetochlor tanks, one 50m$^3$ and three 130m$^3$ vertical ethanol tank, two 130m$^3$ 2,6-methylethylaniline vertical tanks;
(3) Public works and auxiliary facilities: nitrogen generator room, control room, power distribution room and its auxiliary facilities, etc.

3. Identification and analysis of dangerous and harmful factors

3.1. Identification purpose and method
The purpose of hazard and harmful factor identification is to identify the potential hazard of the system, determine its hazard level, and put forward corresponding countermeasures according to the hazard level, so as to ensure the safety of operators.

Dangerous and harmful factors mainly refer to objectively existing dangerous, harmful substances or equipment and places beyond the control of people [3]. Hazard source is the source or basic condition that may cause injury, property loss, work environment damage or combination of these conditions, including the energy, energy carrier or toxic, harmful and dangerous substances [4]. It is the process of identifying hazard sources and determining their characteristics, which is the basis of hazard control.

3.2. Risk analysis of transportation and storage of hazardous materials
1. Hazard analysis of main hazardous materials
From the aspects of hazardous substances, equipment and places, the hazardous and harmful factors in the plant are identified, involving 15 kinds of main hazardous materials, as shown in Table 1.

Table 1. Distribution of major hazardous substances.

| Project area                      | Name of main hazardous substances                                                                 | Fire hazard classification | Classification of occupational exposure to toxic substances |
|-----------------------------------|--------------------------------------------------------------------------------------------------|---------------------------|----------------------------------------------------------|
| Acetochlor workshop               | Raw materials: 2,6-methylethylaniline, paraformaldehyde, triethylamine, chloroacetyl chloride, ethanol, ammonia, toluene, hydrochloric acid, sodium hydroxide; intermediate products : Spermine, acylate ; Product: acetochlor; By products: ammonium chloride, ethyl chloroacetate; others: nitrogen, compressed air, formaldehyde solution, etc. | A                         | II                                                      |
| alcohol recovery device           | Ethanol, nitrogen, compressed air, etc.                                                           | A                         | IV                                                      |
| Ammonium chloride recovery device | Ammonium chloride, nitrogen, compressed air, etc.                                                   | E                         | III                                                     |
| Tank farm                         | Acetochlor, ethanol, MEA(2,6-methylethylaniline)                                                   | A                         | III                                                     |
| Public and auxiliary facilities system | Nitrogen, compressed air                                                                            | E                         | IV                                                      |
2. Risk analysis during transportation and storage

Dangerous materials should be handled lightly during transportation to prevent damage to the packaging and leakage, which could cause fire, explosion, poisoning. In the transportation of materials with severe drugs, they should be kept away from crowds, water sources, etc. To prevent leakage, cause poisoning and environmental pollution. Avoid poisoning caused by spontaneous combustion, explosion or volatilization of dangerous materials caused by high temperature.

The materials in the storage tank may be leaked if the packaging or tank body is impacted, cut, or scratched; If the strength of the tank and its pipelines is not enough, quality defects, improper anti-corrosion measures, external damage, pipelines and other seals are not tight, there is a possibility of leakage; The liquid level gauge malfunctions or blocks, or the control valve fails. After the material is overfilled, the pressure in the tank rises, causing rupture and causing the material to overflow.

3.3. Analysis of dangerous, harmful factors and their degrees

Identify the main dangerous and hazardous substances in each relevant device and process in the production of acetochlor, and in accordance with the GB50016-2014 "code for fire protection design of buildings" [5] fire risk of each project area is divided into grades, according to the GBZ 230-2010 "occupational exposure poison damage degree classification"[6] divide each project area of management of occupational contact poison damage level, the results are shown in table 1.

Further analysis of the dangerous and harmful factors in each device and process is shown in Table 2.

**Table 2. Major dangerous and harmful factors.**

| Distribution of hazardous and harmful factors | Acetochlor workshop | Alcohol recovery device | Ammonium chloride recovery device | Storage facilities | Public and auxiliary facilities |
|---------------------------------------------|---------------------|------------------------|----------------------------------|--------------------|-------------------------------|
| Fire and chemical explosion                 | √                   | √                      | √                                | √                  | √                             |
| Poisoning and suffocation                   | √                   | √                      | √                                | √                  | √                             |
| Physical explosion                          | √                   | √                      | √                                | √                  | √                             |
| Scald                                        | √                   | √                      | √                                | √                  | √                             |
| Get an electric shock                       | √                   | √                      | √                                | √                  | √                             |
| Mechanical injury                           | √                   | √                      | √                                | √                  | √                             |
| Falling high                                | √                   | √                      | √                                | √                  | √                             |
| Object strike                               | √                   | √                      | √                                | √                  | √                             |
| Lifting injury                              | √                   | √                      | √                                | √                  | √                             |
| Collapse                                    | √                   | √                      | √                                | √                  | √                             |
| Vibration and noise hazards                 | √                   | √                      | √                                | √                  | √                             |
| Vehicle injury                              | √                   | √                      | √                                | √                  | √                             |

As can be seen from the above analysis, the main dangerous and harmful factors are fire and chemical Sexual explosion, poisoning and suffocation, physical explosion and burning. Among them, most of the accidents such as explosions and poisoning are caused by the leakage of flammable, toxic, corrosive and other harmful substances, so fire, leakage and explosion are the main dangerous factors. Therefore, the analysis of the consequences of an accident begins with a leak analysis.
4. Simulation analysis and evaluation of accident consequences
The accident consequence simulation analysis method is a method that uses a quantitative calculation to accurately determine the degree of damage to the equipment, facilities and personnel. Equipment damage or operation errors can easily cause leakage accidents, leading to the large-scale release of flammable, explosive, and toxic substances. If effective disaster prevention measures are not taken, major accidents such as fire, explosion, and poisoning will eventually occur.

4.1. Numerical simulation of leaking ethanol concentration
Ethanol is a flammable and volatile liquid at normal temperature and pressure. Its vapor can form an explosive mixture with air. It is easy to expand when heated and easy to accumulate static charges [7]. In order to explore the law of ethanol leakage and diffusion, the company's three 130m³ ethanol storage tanks were simulated, and the turbulence model in fluent software was used to describe the air flow and the multi-component transport model was used to describe the ethanol gas flow. The boundary type of the air flow inlet is set as VELOCITY_INLET, the speed is 1.5m/s, and the outlet boundary is set as pressure outlet. As for the parameters of ethanol gas, a multi-component transport model is set up, the energy equation is opened, and the ethanol injection speed is set to 20 m/s.

In order to analyze the law of ethanol gas escape, the ethanol concentration map near the leakage height (z = 0.5m) and the breathing zone height (z = 1.8m) is intercepted, as shown in Figure 1.

![Airflow velocity cloud diagram](image)

Figure 1. Airflow velocity cloud diagram

At the leakage port of the ethanol storage tank, the leaked ethanol evaporates and emits higher concentration ethanol gas than 8%. Under the action of air flow, ethanol gas diffuses to the road space and moves down the wind side (northwest side), resulting in a relatively reduced concentration. But due to the excessive concentration of the leak and the rapid airflow velocity, the ethanol concentration in the road space is still higher than 6%. Then, due to the blocking effect of each workshop, ethanol gas accumulated at the corners, and the concentration increased to more than 8%. With the two obviously deviated flows continuing to spread down the wind side, the concentration gradually decreased. In the longitudinal direction, the concentration of ethanol decreased with the increase of the height, but the concentration of ethanol still exceeded the limit at the height of the breathing zone.

4.2. TNT equivalent explosion model
The main accident consequences of ethanol leakage are pool fire, vapor cloud explosion, boiling liquid expansion vapor explosion [8]. After the leakage of ethanol, its vapor premixes with the surrounding air, which will cause combustion and explosion in case of open fire and high heat energy. After the explosion
of vapor cloud, its destructive effects mainly include blast wave, thermal radiation of explosion fireball, damage and destruction to surrounding personnel, buildings, tanks and other equipment \[^9\]. At present, the prediction models of the shock wave of vapor cloud explosion mainly include TNT equivalent model, TNO multi-energy model, ME model, etc \[^10\]. In this paper, TNT equivalent explosion model is used to simulate and analyze the consequences of a 130m\(^3\) ethanol storage tank leakage explosion in the storage tank area.

1. **NT equivalent calculation**

   \[ W_{TNT} = aW/Q_{TNT} \]  

   Among them: \( W_{TNT} \), the quality of explosive chemicals and the quality of TNT, kg; \( a \) is the equivalent coefficient of LPG vapor cloud (statistical average value is 0.04, value is 0.04); \( W \) is the mass of combustible gas in vapor cloud, kg; \( W = 1.027 \times 10^5 \) kg; \( Q \) is the combustion heat of combustible gas, J/kg; \( Q = 2.9639 \times 10^4 \) kJ/kg; \( Q_{TNT} \) is the explosion heat of TNT, J/kg (4230-4836 kJ/kg, generally 4500 kJ/kg on average). Calculated \( W_{TNT, ethanol} = 4.8703 \times 10^4 \) kg

2. **Calculation of explosion damage radius**

   (1) Damage radius at atmospheric pressure

   - Death radius: \( R_1 = 13.6 \times (W_{TNT}/1000)W_{TNT}^{0.37} = 57.27 \) m
   - Serious injury radius: \( R_2 = 1.07 \times (1000 \times W_{TNT} \times Q_{TNT}/P_0)^{1/3} = 138.39 \) m
   - Minor injury radius: \( R_3 = 1.95 \times (1000 \times W_{TNT} \times Q_{TNT}/P_0)^{1/3} = 252.21 \)

   (2) Damage radius formula of overpressure explosion:

   \[ R = 0.3967W_{TNT}^{1/3}\exp[3.5031 - 0.7241\ln \Delta p + 0.0398 (\ln \Delta p)^2] \]  

In case of explosion of the ethanol tank, overpressure damage effect, accident consequence and explosion damage radius are shown in Table 3:

| Serial number | Overpressure /kPa | Accident consequence | Explosion damage radius (m) |
|---------------|-------------------|----------------------|-----------------------------|
| 1             | 1.035             | Typical pressure for glass damage | 478.61                      |
| 2             | 2.07              | 10% glass broken     | 265.99                      |
| 3             | 3.45              | Damage to windows, minor damage to building structure | 176.80                      |
| 4             | 4.83              | Upper limit of reversible impact on personnel | 136.64                      |
| 5             | 6.90              | The house is partially damaged, the metal plate is twisted, and the glass pieces are scratched. | 105.01                      |
| 6             | 13.8              | Partial collapse of walls and roofs | 64.80                       |
| 7             | 16.56             | Rupture of eardrum in exposed persons | 57.43                       |
| 8             | 17.25             | Critical mass of human death | 55.92                       |
| 9             | 20.7              | Distortion and foundation displacement of steel structure building | 49.73                       |
| 10            | 34.5              | Fracture of wood structure | 36.30                       |
| 11            | 69.0              | Almost all buildings collapsed and people's lungs bleed | 24.48                       |
| 12            | 138               | 100% death due to direct shock wave | 17.15                       |
4.3. Disaster prevention measures

Based on the above simulation and analysis results, the following disaster prevention measures are recommended:

1. Leak-proof materials should be provided near the storage tank area so that measures can be taken immediately to prevent leaks in the event of an accident in order to reduce the scope of influence and minimize personnel casualties and economic losses caused by the accident.

2. The places of public works and auxiliary facilities shall be equipped with protective equipment (respirators, etc.). When a leak occurs, it can ensure the safe evacuation of on-site personnel.

3. Strengthen the maintenance of fragile equipment in storage tanks. Vulnerable equipment should be regularly maintained and repaired to reduce the possibility of leakage accidents.

4. Improve accident emergency plans, strengthen emergency drills and safety rescue education and training, improve employees' safety awareness and emergency protection capabilities, and minimize casualties caused by accidents.

5. Establish an emergency evaluation system in line with the actual situation of the enterprise, strengthen the inspection and supervision of major dangerous sources, and improve the level of safety management.

5. Conclusion

1. According to the hazardous characteristics and process parameters of materials in the production process, the classification of hazardous devices is as follows: The fire risk of acetochlor production workshop, alcohol recovery device and storage tank area belongs to class A, and that of ammonium chloride recovery device belongs to class E; The degree of occupational exposure in acetochlor production workshop is class II, and that in class a tank farm is class III.

Leakage, fire and explosion are the main risk factors of the plant. Discovered through ethanol leak simulation, at the leak, road space, acetochlor production workshop, the intersection of ammonium chloride recovery device and alcohol recovery device, the ethanol gas concentration reaches 3% or even 8% or more, which is extremely prone to vapor cloud explosion.

Calculations show that when a 130m³ ethanol storage tank leaks and explodes under normal pressure, within a range of 138.39m ~ 252.21m, 57.27m ~ 138.39m and 0 ~ 57.27m, the shock wave caused minor injuries, severe injuries and deaths to personnel. And the damage caused by the overpressure explosion seriously affects most of the company's plant areas, and may also affect the roads outside the neighboring companies.

References

[1] Zhang Jianhua. Synthetic process and precautions of herbicide acetochlor [J]. Science and Technology Wind, 2011 (15): 100.

[2] Zhao Lianchi, Zhang Guiying, Meng Yuanyuan, Wei Liang, Li Qitai, Zhu Mengmeng. Analysis of Dangerous and Harmful Factors in the Storage Process of Solvent Oil Enterprises [J]. Shandong Chemical Industry, 2019, 48 (18): 259-260.

[3] Liu Zhongbo. Identification and Analysis of Hazardous and Harmful Factors in the Process of Cooperative Disposal of Hazardous Waste in a Cement Kiln [J]. Cement Engineering, 2019 (02): 80-83.

[4] Cao Qinggui, Qu Nannan. Theoretical and Conceptual Analysis of Causes of Accidents Related to Dangerous Sources [J]. Safety, 2019, 40 (09): 5-10 + 25 + 5.

[5] GB50016-2014, Code for fire protection of building design [S]. Beijing: China Planning Press, 2014.

[6] GBZ230-2010, Classification of hazards of occupational exposure to toxicants [S]. Beijing: China Standard Press, 2010.

[7] Xu Jianjun. Explosion caused by indoor installation of ethanol vapor vent tube [J]. Labor Protection, 2019 (03): 62-63.

[8] Miao Jinming, Liu Qianqian, Zhang Xianjin. Quantitative simulation analysis of the
consequences of accidents in ethanol storage tank area [J]. Journal of Beijing Institute of Labor and Social Security, 2012, 6 (01): 36-39 + 60.

[9] Li Jingjing. Explosion Hazard of Gas Cloud Leaked from Natural Gas Pipeline [D]. China University of Petroleum, 2010.

[10] Wang Tianyu, Lu Chen, Hu Xinsheng, Liang Yueqiang. Simulation study on the consequences of vapor cloud explosion accidents in natural gas pipelines [J]. Coal Technology, 2017, 36 (07): 295-297.