DYNAMIC SIMULATION BASED SAFETY CONSEQUENCE ANALYSIS OF CHEMICAL PROCESSES

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***Abstract*— Consequence analysis can timely predict the occurrence of potential chemical safety accidents, but is time-consuming and inaccurate when using a manual and qualitative mode. A safety con-sequence analysis method based on dynamic simulation is proposed for chemical processes in this paper. The dynamic simulation system of chemical process is composed of complete thermodynamic model and general unit model to quantitatively descrybe the dynamic change of chemical process parameters. Combined with fault tree analysis, the accident model is designed prior to forecasting safety consequences by computational fluid dynamics. This method was applied to acetylene production process. A dynamic simulation system was designed to calculate the pressure and concentration of acetylene leakage gas and analyze the parameters affecting the diffusion of acetylene gas. The results show that this method can obtain the quantitative change of acetylene concentration with time at different locations around acetylene generator, which is convenient for accurate and dynamic analysis of process safety consequence.**

***Keywords*— Chemical process safety, Dynamic simulation, Consequence analysis, Mechanism model.**

I. INTRODUCTION

Chemical production is characterized by inflammable, explosive, toxic, high temperature, high pressure and corrosion, so is more dangerous than other industrial sectors. Losses caused by large-scale production accidents to enterprises, society and the environment are even more incalculable (Zhao and Wang, 2017; Agarwal *et al.*, 2022). For example, on March 23, 2005, the isomerization unit of BP oil refinery in Texas of the United States suffered a serious fire and explosion. The accident killed 15 and injured more than 170 employees. The smoke from the explosion caused varying degrees of damage to people working and living nearby. There-fore, the problem of chemical safety production has aroused widespread concern. How to control the accident and reduce the accident rate has become a hot spot of chemical safety research.

On the basis of a detailed understanding of the system, the accident consequence analysis assumes the situation of the accident and its consequences caused by the major hazard source, and then chooses the appropriate mathematical model to calculate the relevant parameters of the accident consequence (Llanos *et al.*, 2019). The analysis conclusion is discussed after it compares these parameters with their allowable corresponding parameter values. The analysis of consequences provides decision-makers with information about the con-sequences of major accidents and facilitates targeted protective measures. In recent years, the mode of safety work in the chemical industry is approaching to the commonly adopted mode – "major hazard source, accident hidden danger identification, monitoring, early warning, emergency plan system construction, new technology application" (Yet-Pole and Fu, 2021). The systematisms has been its prominent characteristics and advantages. Its operation mode can be summarized as "process safety management, risk identification, consequence analysis, risk analysis, training, emergency plan", which changes the inevitable isolated, scattered characteristics and limitations in the potential accidents contingency plans. The emergency plan established on the basis of the identification, analysis and control of accident risk is more systematic, practical and reliable. Consequence analysis methods are divided into qualitative analysis method, semi-quantitative analysis method and quantitative analysis method (Luo *et al.*, 2017; Nascu *et al.*, 2022). Among them, the quantitative analysis of consequences is the advanced stage of consequence analysis, but sometimes its calculation is very complicated and the requirement for the calculator is high. The consequence analysis method can also be divided into the accident consequence analysis method based on experiment and the accident consequence analysis method based on numerical simulation of computational fluid dynamics (CFD).

Chemical simulation system, also known as process simulation system, receives input information about chemical process and carries out systematic analysis and calculation useful for process development, design or operation (Casavant and Cote, 2004; Hu and Tian, 2021; Pandit *et al.*, 2022). The dynamic simulation introduces the time variable into the system model, and obtains the functional relationship between the description variable and the state variable and the output variable through analyzing the physical and chemical mechanism of the process. Dynamic simulation involves material balance equation, mass transfer equation, heat transfer equation and fluid mechanics equation, etc. The mathematical model thus established by mechanism has very clear physical meaning. The application of dynamic simulation in safety analysis of actual chemical production has also been rapidly developed and achieved good results. For example, Luyben (2010) developed a plantwide control structure for the butyl acetate process, and demonstrated its effectiveness in the face of very large disturbances by dynamic simulation. Schafer *et al*. (2019) presented a reduced dynamic model by combining compartmentalization to reduce the number of differential equations with artificial neural networks to express the nonlinear input-output relations within compartments, and applied the model to the optimal control of an air separation unit. Chisalita and Cormos (2018) developed a dynamic mathematical model to simulate interconnected fluidized bed reactors of a syngas-based chemical looping combustion process with iron based oxygen carrier for a full understanding of the dynamic behavior of reactors. Ko *et al*. (2020) integrated quantitative risk assessment (QRA) with dynamic simulation and accident simulation to discover inherent risks that are undetectable by conventional risk analysis methods based on steady-state conditions. Tian and Sun (2018) performed a lot of research on fault diagnosis of chemical process on the basis of dynamic simulation, and proposed a new on-1ine dynamic model correction based method for building fault diagnosis system of distillation tower. Wang *et al*. (2016) presented a systematic methodology based on plant-wide dynamic simulation for safety-oriented chemical process industry (CPI) flare minimization (FM) under abnormal operating conditions. Two case studies on FMs for start-up and shut-down operations of an ethylene plant have been employed to demonstrate the efficacy of the method.

On the platform of chemical dynamic simulation system, the chemical production process can be well simulated and monitored by controlling various important parameters in chemical production process. So in this paper, combined with the actual production process and fault tree analysis, the most common fault models are established on the chemical dynamic simulation system, and the initial fault parameters are calculated by the dynamic simulation system. On the basis of the initial parameters, the consequence analysis method is used to simulate the severity of the accident consequence. This method is applied in acetylene production by calcium carbide, where the consequences of acetylene leakage are predicted and analyzed by simulating the accident situation of acetylene leakage by means of CFD.

The novelties and main contributions of this paper are listed below.

- One dynamic simulation based consequence analysis method is proposed, aiming to quantitatively discover potential risks in the process that may be ignored by traditional qualitative consequence analysis methods.
- The initial parameters of fault are calculated by dynamic simulation system combined with fault tree analysis, effectively alleviating the challenge to obtain abnormal working condition data with label.

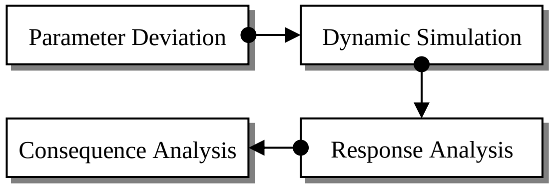

Figure 1: Framework for safety analysis of chemical process.

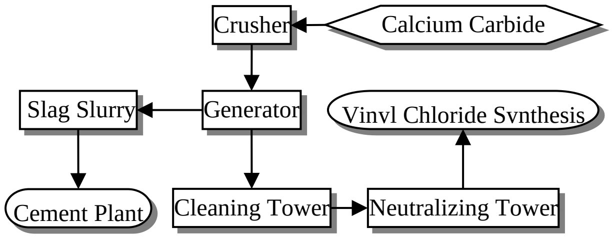

Figure 2: Flowsheet of acetylene production process.

- Through dynamic simulation technology, this method pays attention to the severity of various accident risks and their real-time changes, which not only provides references for chemical safety design and emergency response, but also greatly reduces labor costs.

II. CONSEQUENCE ANALYSIS FRAMEWORK BASED ON DYNAMIC SIMULATION

The dynamic simulation based consequence analysis method is shown in Fig. 1. The dynamic simulation based on the dynamic mechanism model composed of balance calculation relation and thermodynamic relation is the core of this method. It can accurately reflect the relationship between the failure cause and the quantitative mechanism of the consequences, and effectively overcome the problems of weak mechanism and insufficient quantification caused by manual experience analysis.

A. Dynamic Simulation

A chemical process is composed of serveral reactors and unit operations, which are connected with complex pipe network. For example, the flowsheet of acetylene production as the case process in this paper is shown in Fig. 2. This process uses wet generation, spray cooling, secondary sodium cleaning, alkali neutralization to produce qualified acetylene gas for vinyl chloride conversion process, where the slag slurry is transported for outer usage after pressure filter. The core equipment in this process include generator and heat exchangers, in which material balance and heat balance should be specifically modeled during dynamic simulation.

The basis of establishing chemical production model is material balance. The material balance of component i can be expressed by Eq. (1).

$$
\begin{aligned}
d\left(mz_i\right)/dt = & \sum_j \left(F_{\text{in},j} x_{\text{in},j,i}\right) - \sum_j \left(q_{\text{g},j} y_i\right) \\
& - \sum_j \left(q_{L,j} x_i\right) + V_{\text{L}} \sum_k r_i
\end{aligned} \qquad (1)
$$

where q_{L}, q_{g} and F_{in} represent the flow rate of liquid, gas and feed respectively; x, y and z represent the molar concentration of liquid phase, gas phase and total material respectively; t is time; m is the holding amount; r is the reaction rate; V is volume; subscripts i, j, L, g and in represent component number, material number, liquid phase, gas phase and feed respectively. As reaction usually takes place in liquid phase for a gas-liquid reactor, such as the liquid reaction of calcium carbide with water in generator in Fig. 2, Equation (1) only includes reactions occurring in the liquid phase.

At the same time, there exists heat transfer process in the heat exchanger, which can be expressed by the heat balance equation, as shown in Eq. (2). It can be used to calculate the variation trend of each temperature parameter T.

$$\begin{aligned} d(mH)/dt = \sum_j F_{\mathrm{in},j} H_{\mathrm{in},j} - \sum_j F_{\mathrm{g},j} H_{\mathrm{g},j} \\ - \sum_j F_{\mathrm{L},j} H_{\mathrm{L},j} + KS(T_0 - T) \end{aligned} \tag{2}$$

where H is enthalpy; K is the total heat transfer coefficient; T_0 is the temperature of heating/cooling medium; S is heat transfer area. Other symbols in Eq. (2) are the same as Eq. (1).

With the elemental substance under standard conditions as the enthalpy reference here, the heat of reaction is not clearly given in Eq. (2) as the change in enthalpy due to the change in substance has already been included in the enthalpy balance.

The dynamic simulation in this paper is constructed based on the dynamic simulation & analysis system (DSAS), which was independently developed by Qingdao University of Science and Technology. DSAS inherits the data structure and important algorithm of the classical steady-state process simulation system, and develops the mechanism model by using "tracking approximation method," receiving the fast and accurate effect of dynamic simulation. The structure of DSAS is shown in Fig. 3, in which background simulation system DSAS can correspond to multiple internal operation interface VDCS and external operation interface 3DField with an independent safety analysis module OGS. DSAS adopts a unified strict mechanism model to achieve dynamic switching of different process conditions. That is, it can simulate abnormal conditions at any time when simulating normal operation process with data consistency. DSAS has been successfully applied in the development of dynamic simulation system of more than 30 sets of chemical plants, involving the synthesis of ammonia, polyformaldehyde, acetic acid, caprolactam, vinyl chloride, methanol, etc.

B. Failure Consequence Analysis

By means of fault tree analysis, the causes of fire and explosion in production equipment are analyzed, and various basic events leading to production accidents are obtained. Using the principle of fault tree analysis, the importance of the minimum cut set based on the fault tree is calculated and compared in terms of magnitude, providing an effective way for fault source search (Karen and John, 2002; Wang *et al*., 2002; Shi *et al*., 2014). Finally, an accident model is established on the plat-form of chemical dynamic simulation system, and the initial accident parameters are obtained.

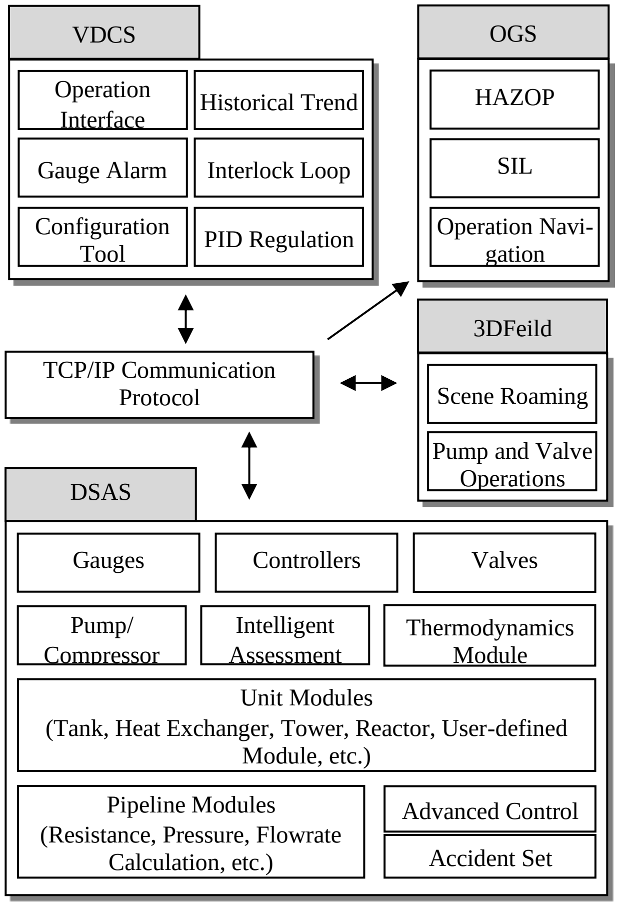

Figure 3: The architecture of DSAS.

Gaussian model is the most commonly used model to simulate gas diffusion (Whittles *et al*., 2006; Xu *et al*., 2021), as shown in Eq. (3).

$$\begin{aligned} \frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z} = \\ \frac{\partial}{\partial x}\left(k_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial c}{\partial z}\right) + \sum_{p-1}^{N} S_p \end{aligned} \tag{3}$$

where c is the gas concentration; x, y and z are coordinates of three directions; u, v and w are velocity components in three directions; k_x, k_y and k_z are diffusion coefficients in three directions; t is diffusion time; S_p is the intensity of leakage source.

According to the mass conservation principle, the equation is integrated according to the element volume and solved with boundary conditions. Let $x=ut$, $\sigma_y^2=2k_yt$, $\sigma_z^2=2k_zt$, the standard form of Gaussian diffusion model can be obtained, as shown in Eq. (4).

$$c(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y{}^2} + \frac{z^2}{\sigma_z{}^2}\right)\right] \tag{4}$$

III. CASE STUDY

In this paper, the above method is applied to the safety analysis of acetylene production process by calcium carbide, and the dynamic simulation and safety consequence analysis results are given and discussed.

A. Analysis of simulation results

With the acetylene station in the process of polyvinyl

Table 1. The mass and heat balance result of acetylene generator.

Stream		Calcium carbide feeding	Water feeding	Acetylene discharging	Slurry discharge
Temperature/K		315.00	340.26	358.15	358.15
Pressure/kPag		75.15	76.06	72.07	144.81
Flowrate/kmol/h		10.33	344.36	41.34	305.56
Phase		solid	liquid	gas	liquid
Mole fraction	CaC_2	0.76369	0	0	0
	CaO	0.20024	0	0	0
	MgO	0.02857	0	0	0
	CaS	0.00512	0	0	0
	Ca_3P_2	0.00143	0	0	0
	Ca_2Si	0.00095	0	0	0
	H_2O	0	1.00	0.80	0.96
	C_2H_2	0	0	0.20	0
	$Ca(OH)_2$	0	0	0	0.04

Table 2. The simulation results of acetylene process.

Parameter	3# Generator		5# Generator		Product	
	Simulation	Design	Simulation	Design	Simulation	Design
Temperature/K	357.2	353.1-363.1	354.2	353.1-363.1	286.2	287.9
Pressure/kPa	8.13	2.00-12.00	8.47	2.00-12.00	64.4	64.4
Molarity/%	-	-	-	-	98.15	≥95.00

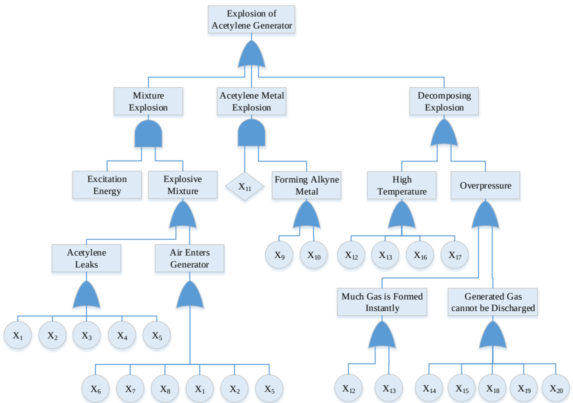

Figure 4: Fault tree for fire or explosion of acetylene generator.

chloride (PVC) of a chemical enterprise in China as an example, the dynamic simulation of acetylene process was per-formed with feed data (temperature, flow, concentration) and unit operation data (operating temperature, pressure, heat load) from DCS to determine initial model parameters. The data provided by the enterprise is used as the design value of stream or control point, which is also the target value and reference value of simulation results. The Euler method is chosen as the dynamic simulation algorithm in this paper because the operation is possible at any time interval in chemical production. Using DSAS as the simulation platform, the program is developed based on Visual C + + 2005 environment. It runs on a PC con-figured with PIII 650, 128 M memory, and 40 G hard disk.

Acetylene gas is not only the final product of acetylene production process but also the raw material gas of PVC production, so acetylene generator is the most important and fundamental section of acetylene production process. In this section, acetylene generators are hence simulated for consequence analysis. Besides the primary reaction of calcium carbide with water for acetylene, five secondary reactions also take place together in these generators, as shown in Eq. (5). These reaction are assumed as fast irreversible reaction for simplicity. The diameter and height of each acetylene generator are set as 3.2 and 10.0 meter respectively according to the size data provided by plant.

$$\begin{cases} CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \\ CaO + H_2O \rightarrow Ca(OH)_2 \\ MgO + H_2O \rightarrow Mg(OH)_2 \\ CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S \\ Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2H_3P \\ Ca_2Si + 4H_2O \rightarrow 2Ca(OH)_2 + SiH_4 \end{cases} \quad (5)$$

The mass and heat balance results of acetylene generator based on simulation are listed in Table 1. The concentration of acetylene gas produced is the key factor to determine the success or failure of production. In this paper, the pressure and temperature of No.3 and No.5 acetylene generators and the pressure, temperature and molarity of acetylene products are taken as examples to compare and analyze the simulation values and design values. The results are shown in Table 2.

By analyzing the data in Table 2, it can be seen that the range of deviation between the simulated pressure and temperature of acetylene generator and their designed value is relatively small. At the same time, the mole fraction, pressure and temperature of acetylene product also meet the requirements of production.

B. Fault tree analysis

The acetylene production device can be divided into generation, purification, compression, filling and other units, with the generation unit as the core. This paper takes fire explosion accident from acetylene generator as an example to introduce the accident tree, as shown in Fig. 4, where X_1~X_{20} denote safe water seal failure, operation error, slag discharge, emptying, equipment failure, replacement failure, negative pressure formed in slag discharge, too low liquid level within generator, gauges containing copper and mercury, tool containing copper and mercury, excitation energy, small particle size of calcium carbide, discharge pipe blockage, fast charging, scrubber in packing agglomerate, thermometer failure, cooling water stop, bell jar stuck of gas holder, without safety relief devices, lack of acetylene pipe water, respectively.

Boolean algebra was used to simplify the accident tree and 50 minimum cut sets were obtained at last. Then the order of structural importance for each minimum cut set was obtained. The electrostatic spark, electric spark, impact spark, lightning spark and other factors are the most important, followed by the air into the acetylene reactor through various ways or acetylene leakage through various ways and other factors. With the qualitative

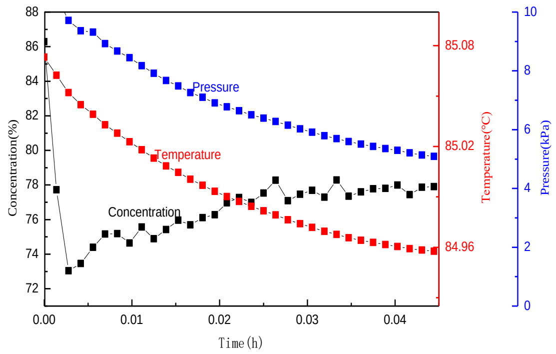

Figure 5: Change of fault parameters.

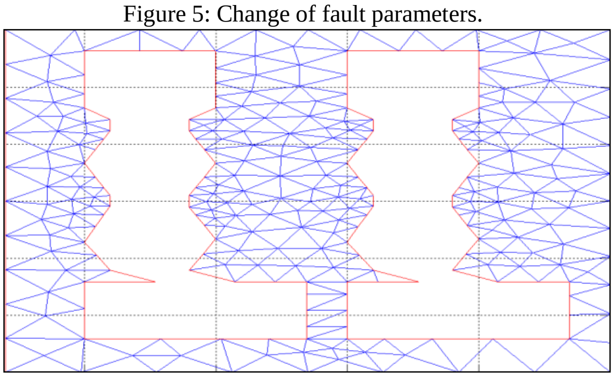

Figure 6: Front view of mesh for two acetylene generators.

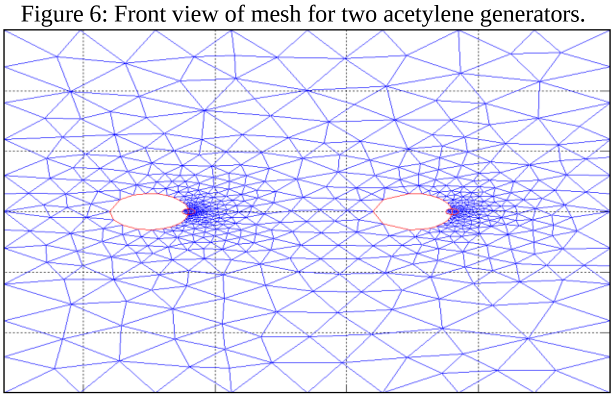

Figure 7: Top view of mesh for two acetylene generators.

results of fault tree analysis of acetylene generator above and the common accidents of acetylene production in reality, the leakage fault of calcium carbide feed valve in storage bucket of acetylene generator was selected as the research object in the following dynamic simulation.

After the acetylene leakage model was established in the dynamic simulation system of acetylene, the initial parameters of acetylene gas leakage were obtained. The change of accident parameters including the acetylene concentration, temperature and pressure in the storage bucket of acetylene generator over time under the leak fault is shown in Fig. 5. It can be seen that the pressure, temperature and concentration of acetylene gas decrease to some extent after leakage, but the concentration of acetylene gas tends to rise again after a short period of decline. This is mainly because with the production of acetylene in acetylene generator, the decline trend of acetylene gas concentration will pick up and finally reach a dynamic balance, stable at about 77%.

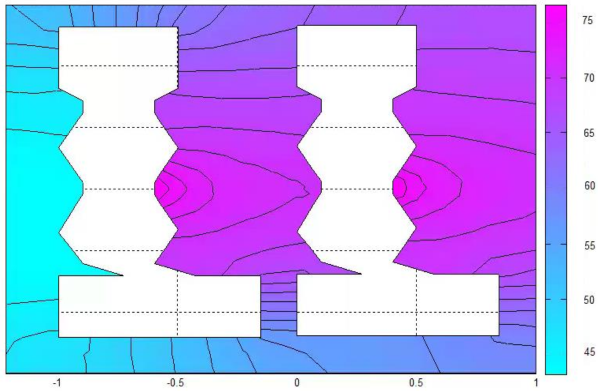

Figure 8: Front view of contour at 10 seconds.

C. Consequence analysis based on CFD

On the basis of the initial parameters of acetylene gas leakage obtained in section 3.2, the acetylene gas leakage situation was simulated with CFD, and the consequences of acetylene gas leakage accident were analyzed. One sub-stream from storage bucket of acetylene generator to environment is added to simulate the leakage fault. The flow rate of acetylene leak is 0.385kmol/h, with a diameter of hole as 8 mm. In this paper, two acetylene generators are selected as the research object, in which the three-dimensional acetylene generators are simplified into two-dimensional graphics. Acetylene gas diffusion is studied from the front and the top of the acetylene generators respectively. In the actual acetylene production process, acetylene generation section generally includes multiple acetylene generators. Acetylene generator as an obstacle will affect the diffusion of acetylene gas, so a single generator study for acetylene gas leakage diffusion is not a comprehensive demonstration of the acetylene gas leakage diffusion situations.

The drawing function in PDETOOL toolbox of Matlab was used to establish the solving domain model of two acetylene generators, and grid division and grid encryption were carried out for solving domain model. The solving domain after grid division was shown in Figs. 6 and 7.

The parabolic equation was chosen to solve the domain model of two acetylene generators after setting the boundary conditions. The "Solve PDE" command in the "Solve" menu is used to solve the partial differential equation and display the graphic solution. The contour maps of the concentration distribution after the leaking acetylene gas is spread for 10 seconds are shown in Figs. 8 and 9. The contour maps of the concentration distribution after 1000 seconds diffusion are shown in Figs. 10 and 11.

According to the calculation results, the concentration of acetylene gas at the leakage point of two acetylene generators is the highest, same as the concentration of acetylene gas in the storage bucket of acetylene generator, up to 77%. Due to acetylene generator itself as a barrier to acetylene gas diffusion, the acetylene gas concentration on the leakage mouth side of two generators is higher than the acetylene gas concentration on the other side of the left generator. The situation of leaking 10 sec-

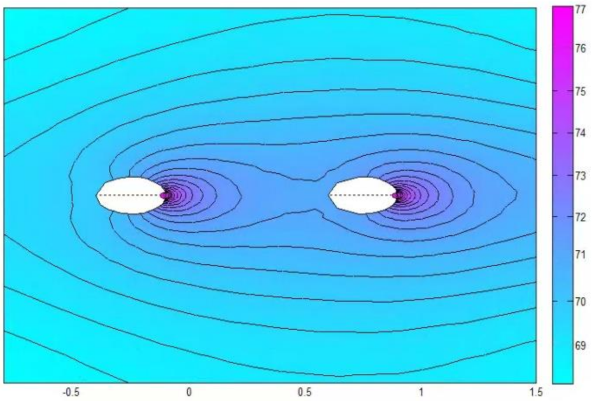

Figure 9: Top view of contour at 10 seconds.

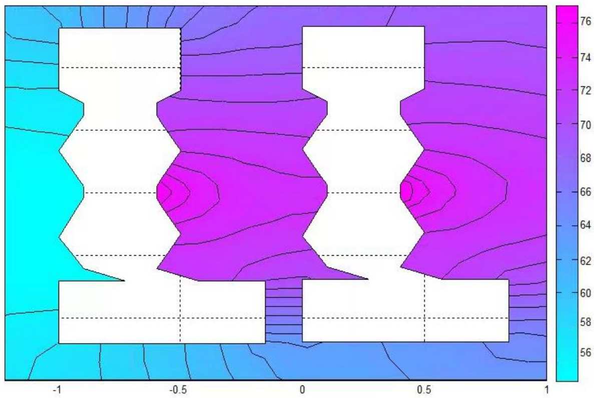

Figure 10: Front view of contour at 1000 seconds.

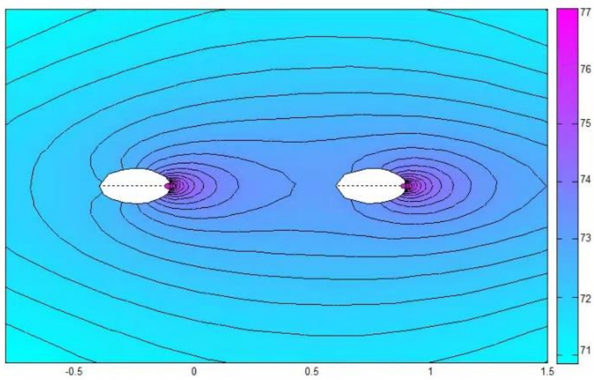

Figure 11: Top view of contour at 1000 seconds.

onds shows that the acetylene concentration of 0.5 meters away from the leakage point on the same side of the leakage point is more than 70%. The concentration of acetylene gas of 0.5 meters away from the other side of the leakage point of the left generator is about 45%. The comparison of acetylene gas diffusion at 10 seconds and 1000 seconds shows that the acetylene gas concentration near the leakage point does not change much. But because of the diffusion effect, the acetylene gas concentration at the far position from the leakage point decreases. The diffusion of acetylene gas makes the difference of acetylene gas concentration at each position in the calculation area smaller.

The calculation results of the two acetylene generators show that the presence of an-other acetylene generator increases the obstruction effect of the leakage of acetylene gas to the other side of the leakage point. Therefore, the leakage of acetylene gas after a long time will gather near the leakage point. This increases the difference of acetylene gas concentration on both sides of the generator, thus making acetylene poisoning accidents more likely occur.

IV. CONCLUSIONS

This paper designed a dynamic simulation system for the acetylene production process, and diagnosed the most common fault causes in the process. The acetylene gas leakage fault was selected as the research object, and the change of acetylene concentration with time in the acetylene generator plant after acetylene gas leakage was analyzed. The research conclusions of this paper are as follows:

(1) The establishment of acetylene dynamic simulation system provides data guarantee for acetylene safety production.

(2) The fault tree analysis method was used to analyze the fault of acetylene production process. Combined with the results obtained from the fault tree analysis of acetylene generator and the common accidents in acetylene production in reality, the leakage fault of calcium carbide feed valve under the storage bucket of acetylene generator was selected as the research object. Based on the dynamic simulation system of acetylene production, the leakage fault of calcium carbide feed valve in storage bucket of acetylene generator was simulated and the initial parameters of acetylene gas leakage were obtained.

(3) The numerical solution of partial differential equation simulating gas diffusion is calculated using CFD numerical algorithm. By visual processing of the numerical solution, the dynamic situation of acetylene leakage and diffusion of two acetylene generators was demonstrated, and the variation of acetylene concentration with time at different positions in the acetylene generator building was predicted.

The conclusion observed in this research suggests the potential application of this method to more real production systems, which can be modeled with mechanism principles. The simplification of CFD based consequence analysis will be the focus of future re-search.

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