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Safety evaluation of rectisol process based on quantitative hazard and operability analysis

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ABSTRACT

In order to break through the limitations of the traditional hazard and operability (HAZOP) analysis, this study established a gray evaluation model based on gray theory for the riskiness ranking of deviations and semi-quantitative analysis of risk levels. A quantitative HAZOP analysis combining HAZOP with Aspen Plus, Aspen Dynamics, Fault Tree Analysis (FTA), Risk Matrix and Layer of Protection Analysis (LOPA) was performed for high risk deviations. The dynamic model of the methanol washing unit in the rectisol process was established by Aspen Dynamics and the effects of different deviations on the risk indicators and operability indicators were investigated. Then, the risk of deviations was ranked according to the simulation results and the high-risk deviations were identified. Subsequently, the sensitivity analysis module of Aspen Plus software was used to calculate the fluctuation range of high-risk deviations, whose results were imported into Aspen Dynamics to simulate and analyze the risk level of accidents, and then FTA was used to quantify the probability of accidents. Synchronizing the two to the risk matrix determined the deviations to have initial risk ratings of 10 and 15, both of which are high-risk deviations. The HAZOP quantitative analysis report is finalized after reducing the residual risk level of the deviation to 9 (low risk) through LOPA analysis. The results of the case study showed that the method can verify the accuracy of the gray evaluation model to a certain extent, and the quantitative HAZOP analysis report is of guiding significance for actual production.

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1. Introduction

The progress of society and the development of industrial technology have increased the scale and complexity of chemical plants. The consequences and impacts of accidents have become more and more serious [1], and therefore, the necessity of research on industrial production safety has been greatly increased, especially for high-risk process in the industries such as coal chemical industry [2]. As a core element of Process Safety Management (PSM) [3], Process

Hazard Analysis (PHA) [4] ensures process safety by simulating the chemical production process, identifying and evaluating potential hazards and eliminating or controlling them, preventing and mitigating accidents that may occur in the process [5–7].

Hazard and operability (HAZOP) analysis is one of the most common PHA approaches [6–8], which is generally used by a team of experienced cross-disciplinary experts to discuss the hazards and the causes in the production units or processes, for systematically and comprehensively evaluating the risk of the units based on deviations [9]. However, the traditional HAZOP analysis essentially divides the complete process into multiple nodes that can be easily analysis according to the operating procedures, qualitatively analyzing the reasons and the possible consequences for the deviation of each node based on the parameters and the

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guide words, as well as further suggesting additional safety measures [10]. However, the process is highly dependent on the subjective experience of the analyzers [11], and does not incorporate the concept of ‘quantity’, which makes it difficult to identify potential hazards in complex chemical production processes [12]. Therefore, it is necessary to include other risk evaluation methods to complete the quantitative HAZOP analysis [13].

In order to improve the accuracy of HAZOP analysis, many scholars have carried out research on HAZOP quantification. For instances, Chiappetta *et al.* [14] combined the steady-state process simulation with HAZOP to analyze the intrinsic safety of the membrane reactor under different working conditions. Shi *et al.* [15] took the stripper extraction process as an example and combined HAZOP analysis with HYSYS software to conduct dynamic simulation of the screened high-risk deviations, which achieved good results. Zhou *et al.* [16] combined LOPA analysis with HAZOP analysis to achieve a quantitative assessment of the reliability of protection measures. Chen *et al.* [17] quantitatively analyzed the potential hazards in the process by combining the HAZOP analysis method with the FTA method, which provided a reliable basis for the enterprise to carry out targeted protection measures. Chen *et al.* [18] conducted a quantitative HAZOP risk analysis of the nitrification section process of nitrobenzene production using Aspen Plus sensitivity analysis module. Eizenberg *et al.* [19], Labovsky *et al.* [20], Ramzan *et al.* [21], and Komulainen *et al.* [22] introduced dynamic process simulation technology into HAZOP analysis to carry out quantitative HAZOP analysis, however, it is not in-depth study on the effectiveness of existing protection measures and adjustment means of the process. These quantitative HAZOP analysis methods which do not rank the riskiness of deviations, rely on the subjectivity of the analysts and cannot accurately select higher-risk deviations for detailed quantitative analysis. Meanwhile, the researchers have not established a quantitative relationship between the range of fluctuation of deviations, the consequences of accidents, the probability of occurrence, and the level of risk. Thus, it could not provide guidance for the safe operation of the plant and the rectification of potential hazards, which may lead to a large degree of manpower and property consumption, and the final HAZOP analysis report would be less readable and less instructive.

The safety evaluation index system of chemical process needs to fully consider the safety status data of chemical process, which involves a large number of evaluation indexes. The contribution rate of each evaluation index to the safety status has the problem of being difficult to be quantified. Therefore, it is necessary to find the key factors which affecting the safety status of chemical process with the help of certain methods, so as to improve the safety of chemical process [23]. Gray theory [24] was firstly proposed that the core content is to take the uncertain system with ‘partly known information and partly unknown information’ as the research object. The theory achieves the analysis and prediction of the operating rules through the study of known information. At present, the rectisol process in the domestic coal gasification field has been widely applied due to its advantages of high efficiency and low cost. However, there are relatively few studies on the safety evaluation of this process. Jiang [25] only conducted a qualitative HAZOP analysis of the low-temperature methanol washing process and did not carry out a quantitative safety evaluation. Li *et al.* [26] conducted a systematic analysis of the wastewater treatment system (WWT) for the low-temperature methanol washing process. Through sensitivity analysis, the effects of theoretical series and desalinated water flow rate on tail gas were studied. Meanwhile, the rapid response of the wastewater treatment system to disturbances was dynamically simulated, confirming the reasonable design of the wastewater treatment system. However, it has not been combined with the safety assessment methods of the system, and its guiding role in actual industrial production is limited. Based on this, in the study, we established a gray evaluation model (GM) for the methanol washing unit in the rectisol process as an example, to perform riskiness ranking and semi-quantitative risk classification of simulatable deviations. Subsequently, we proposed a security evaluation method that combined the traditional HAZOP with the Aspen Plus, Aspen Dynamics, Fault Tree Analysis (FTA) [27], Risk Matrix and Layer of Protection Analysis (LOPA) [28], by which we tried to establish a quantitative relationship among the range of deviation fluctuation, the occurrence probability of accident, the risk class and the increased protection measures. This new method is expected to improve the traditional HAZOP analysis

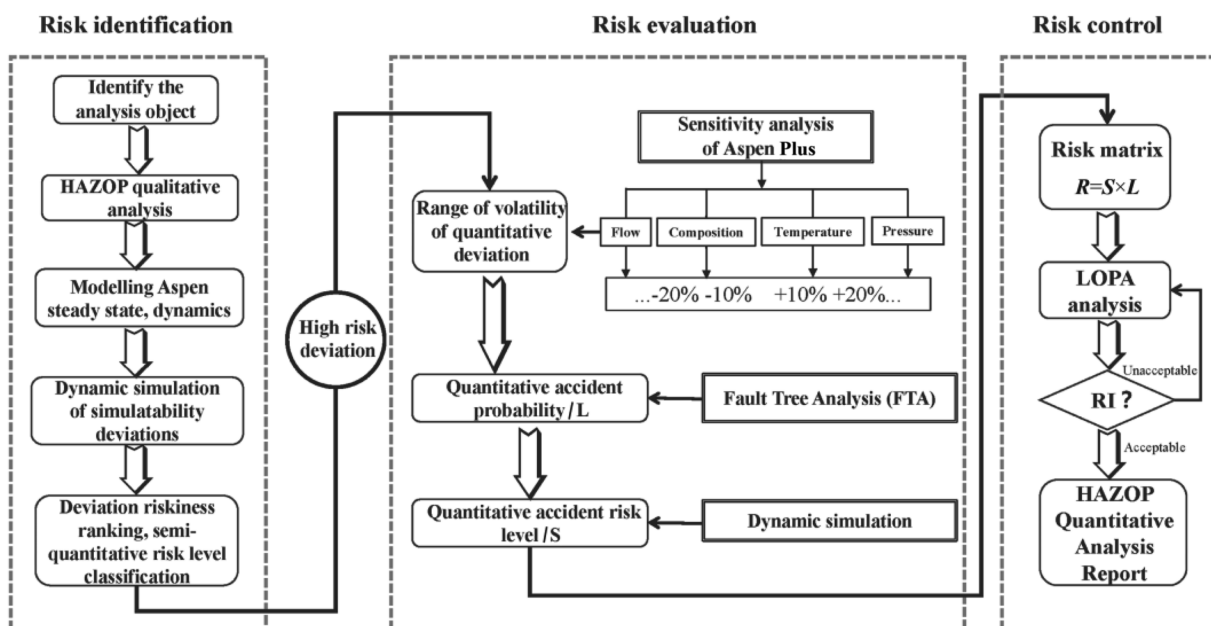


Fig. 1. The quantitative HAZOP analysis flowchart.

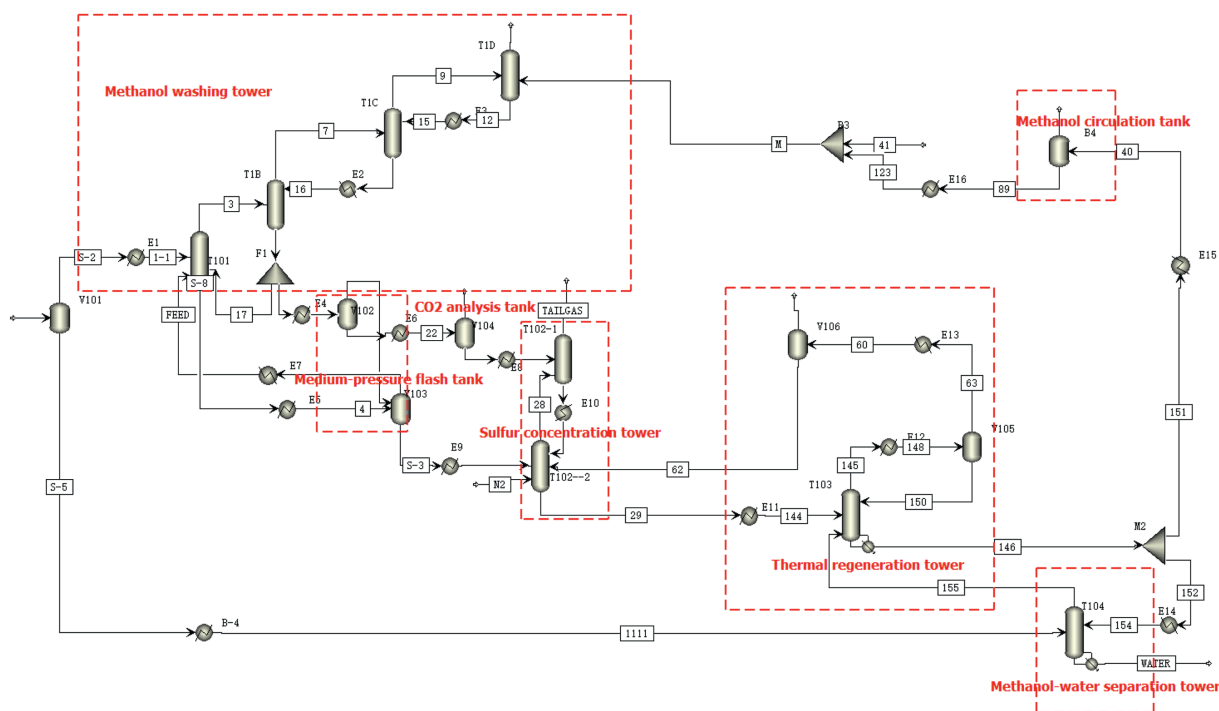


Fig. 2. Simulation flow chart of the rectisol process.

quantitatively, which could help to increase the intrinsic safety production of the system.

2. Methods

The quantitative HAZOP analysis method established in this study includes three main components: risk identification, risk evaluation and risk control. Risk identification adopts a combination of steady state simulation and dynamic simulation. The general chemical simulation software Aspen Plus is used to simulate the steady-state process and optimize the process operating parameters. However, the actual operation of the production is not carried out in an absolute steady state [29]. Therefore, the steady state model of the process is imported into Aspen Dynamics to simulate the degree of impact on the process target process variables when each deviation occurs with the same amplitude of perturbation. Then, the GM model is established according to the response speed, response time and the number of direct influences

of the deviation to the process index so that the risk ranking of the deviation can be carried out. The simulated deviation is divided into four risk levels: higher risk, high risk, medium risk and low risk deviations. Based on this, the quantitative HAZOP analysis is further carried out on the identified higher risk deviation.

Subsequently, the sensitivity analysis module in the Aspen Plus process simulation software extends the fluctuation range of the high risk deviation, simulates the variation of the process parameters and quantifies the deviation when it reaches the process control targets. Different ranges of quantified fluctuations

Table 1

Methanol washing tower process design parameters and simulation data.

Parameters	Data
Process simulation data	
Feed syngas	Mole composition(%): H ₂ (0.458), N ₂ (0.003), CO(0.214), CO(0.323), H ₂ S(0.001) Flow rate: 8159.75 kmol·h ⁻¹ Temperature: -31 °C; Pressure: 3.25 MPa
Purge gas	Composition: H ₂ , N ₂ , CO, H ₂ O etc. Flow rate: 5539.66 kmol·h ⁻¹
Heat load of E2	-3232.9 kW
Heat load of E3	-2290.87 kW
Design parameters of absorption tower	
T1A	Number of plates: 16; Pressure at the top of the tower: 3.2 MPa; Pressure drop: 0.02 MPa
T1B	Number of plates: 6; Pressure at the top of the tower: 3.19 MPa; Pressure drop: 0.01 MPa
T1C	Number of plates: 8; Pressure at the top of the tower: 3.17 MPa; Pressure drop: 0.02 MPa
T1D	Number of plates: 8; Pressure at the top of the tower: 3.15 MPa; Pressure drop: 0.02 MPa
Diameter of tower kettle	2.8 m
Height of tower kettle	5.6 m
Volume of tower kettle	34.51 m ³

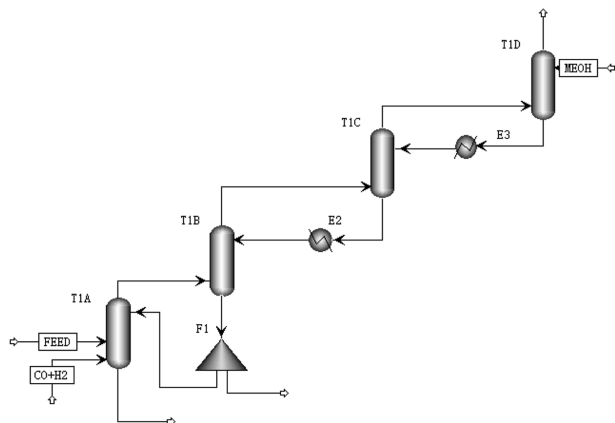


Fig. 3. Aspen Plus simulation flow chart of the methanol washing unit.

Table 2
Main process control indicators of the washing tower.

Numbers	Indicators	Safe scope of work
1	Molar fraction of CO ₂ in purge gas	<3%
2	Molar fraction of H ₂ S in purge gas	$<1 \times 10^{-7}$
3	Heat load of E2	-3879.47–0 kW
4	Heat load of E3	-2749.04–0 kW
5	Pressure at the top of the tower	<3.40 MPa
6	Tower kettle level	1.12–3.92 m

Table 3
The simulatable deviations of the methanol washing tower.

Numbers	Deviations
1	High syngas feed flow
2	Low syngas feed flow
3	High methanol feed flow
4	Low methanol feed flow
5	High return flow at the top of T1A
6	Low return flow at the top of T1A
7	High water content in methanol
8	Low water content in methanol
9	High syngas feed temperature
10	Low syngas feed temperature
11	High methanol feed temperature
12	Low methanol feed temperature
13	High pressure
14	Low pressure

Table 4
Risk identification indicators.

	Hazard analysis	Operability analysis
Risk identification indicators	Temperature of tower kettle	Molar fraction of CO ₂ and H ₂ S in purge gas
	Liquid level of tower kettle Temperature difference between inlet and outlet of cooler E2, E3	Flow rate of pure gas

correspond to different consequences, and as such, the steady-state model of the deviation is pressure-driven and imported into Aspen Dynamics software. By adding a parametric controller, transient changes in the deviation (e.g., temperature and pressure fluctuations) are quantified. The ultimate consequences and

hazard level of the deviation are further analyzed by combining qualitative analysis, historical failure accident statistics, and dynamic simulation results. The approach to consequence quantification using dynamic simulation in this study is based on highly accurate P&ID diagrams with boundaries of continuous processes, high-risk units and modelable conventional scenarios; not applicable to intermittent operations and mechanically constrained facilities. The fault propagation process is modeled with deviation as the top event and the cause of deviation as the basic event, and the FTA model is constructed for high risk deviations, which is calculated from the basic event failure frequency equation and the data to achieve the probability of the deviation [30]. The initial risk level of the deviation is quantitatively evaluated, and the accuracy of the GM is validated by combining the accident hazard level with the probability of accident occurrence through the risk matrix method. Finally, LOPA analysis is used to add an independent layer of protection to reduce the likelihood of these accidents so that the residual risk of deviation is reduced as much as possible to achieve risk control. Based on the above steps, the quantitative HAZOP analysis report is formed. The quantitative HAZOP analysis flow-chart is shown in Fig. 1.

Traditional HAZOP remains the cornerstone of comprehensive identification of bias, this study introduced a complementary technique to traditional HAZOP for quantitative risk analysis of conventional scenarios, research and discussion focusing on the methodological aspects of safety evaluation, supported by the framework of traditional HAZOP analysis. In this framework, the method of using dynamic simulation for deviation risk ranking and risk class classification is only for the simulatable deviations identified after the qualitative analysis of traditional HAZOP; at the same time, the method of using process simulation, FTA and LOPA analysis to determine the initial risk class of deviation is only for the identified high-risk scenarios. The results obtained verify the validity of the GM model on the one hand, and provide guidance for the actual safe production of the low-temperature methanol washing process on the other hand.

3. Case Studies

Among the key regulated hazardous chemical processes, the new coal chemical process (including coal gasification, direct

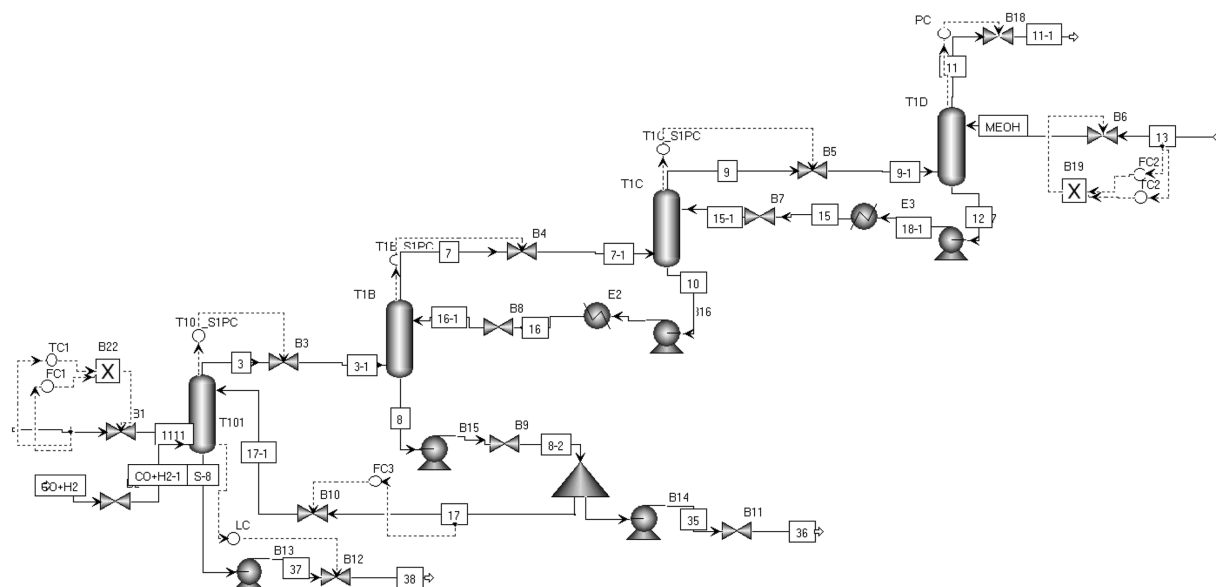


Fig. 4. The model of methanol washing unit and its parameter controller in Aspen Dynamic.

liquefaction, indirect liquefaction and other processes to produce chemical products) requires acid gas removal technology to achieve clean and efficient use of coal. The rectisol process is now recognized as the most economical, highest purification degree of gas purification technology, which uses cold methanol solvent to remove acid gases (such as CO_2 , H_2S , COS and others) under low-temperature and high-pressure conditions [31]. Its process involves low-temperature and high-pressure systems, and it is appropriate to choose the equation of state method, in which the PRRK equation is applicable to nonpolar and polar mixtures containing light gases (e.g., CO_2 , H_2S , H_2 , etc.), and therefore, this method is chosen in this study for calculating the binary interaction parameter of the mixed phases as well as the gas-liquid phase equilibrium. The Aspen Plus flow simulation of the low-temperature methanol wash process is shown in Fig. 2.

The process involves dangerous and harmful chemicals (CH_4 , H_2 , CO , H_2S etc.), which may cause serious personal injury, economic loss, unpredictable social and environmental hazards in case of leakage. Therefore, it is of practical significance to carry out risk analysis and safety countermeasure research on the rectisol process. This study takes the methanol washing unit in the rectisol process as an example to introduce the principle and process of the quantitative HAZOP method combining HAZOP, Aspen Dynamics, Aspen Plus, FTA, risk matrix and LOPA analysis, to carry out the risky ordering of deviation and semi-quantitative risk level classification.

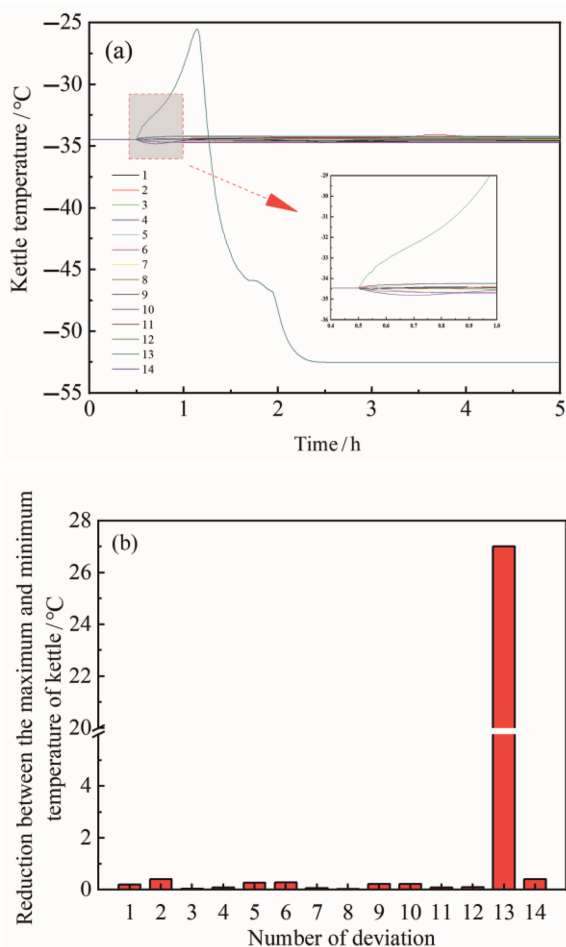


Fig. 5. 14 deviation fluctuations of 5% (a) effect on temperature of tower kettle; (b) difference between maximum and minimum of tower kettle temperature.

3.1. Risk identification

3.1.1. Steady state model and process control indicators

Fig. 3 shows the Aspen Plus simulation flow chart of the methanol washing unit in the rectisol process. Here, the methanol washing tower (T101) is divided into four parts from bottom to top: desulphurisation tower (T1A), crude decarbonisation tower (T1B), main decarbonisation tower (T1C), and fine decarbonisation tower (T1D). The absorption process of the absorbing tower belongs to the exothermic process while the absorption operation needs to be carried out at low temperatures. Therefore, circulating methanol coolers E2 and E3 are installed between each section of the absorption tower to draw out the methanol solution for cooling and to remove the dissolution heat of the acidic gas in the absorption process to maintain the absorption temperature.

Crude syngas containing H_2S , COS and CO_2 components is sent to the bottom of T101 at $-31\text{ }^\circ\text{C}$ and 3.25 MPa after separating water from the flash tank. The strong ability to absorb the acid gases at low temperatures which methanol holds is utilized to effectively achieve the removal of acid gases and gas purification. The purified syngas is recovered from the top of T101, the H_2S -rich, CO_2 -rich methanol flowing out of the bottom of the tower, CO_2 -rich methanol solvent drawn from the two separators enters the

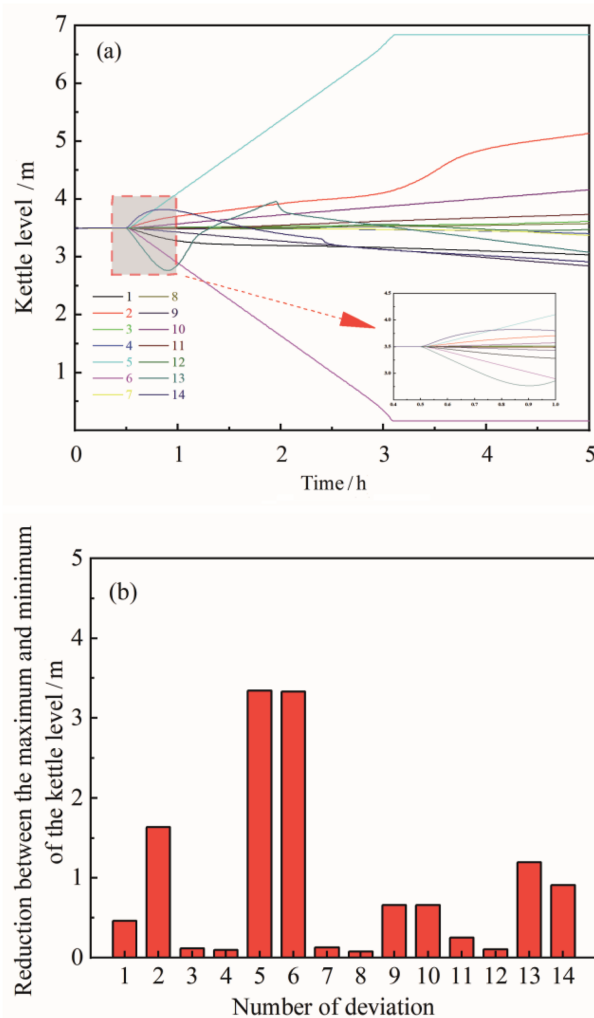


Fig. 6. 14 deviation fluctuations of 5% (a) Effect on the level of tower kettle; (b) Difference between the maximum and minimum values of the level of tower kettle.

two medium-pressure flash tanks after heat exchange and cooling, respectively. The dissolved H_2 , CO and other effective gases are flashed out and returned to the bottom of T101 for further absorption. The basic simulation data of the process are obtained from the literature [32], the design parameters of T101 are also shown in Table 1.

The CO_2 and H_2S in the purified gas in the process control index of T101 must meet the requirements of the process products. The heat loads of E2, E3 are -3232.9 and -2290.87 kW through the process simulation. According to experience, the two cooler heat loads of the safety margin to take 20% [33], thus, the E2, E3 heat loads of the safe operation of the ranges are $-3879.47-0$ and $-2749.04-0$ kW. According to the process design requirements, the tower kettle level is generally controlled in the range of 20% to 70% under normal working conditions, the pressure of the tower top exceeding 10% of the operating pressure is called the high tower top pressure [34], thus the safe range of the washing tower kettle level is 1.12–3.92 m, the range of process control of the tower top pressure is less than 3.40 MPa. The process control indicators of the methanol washing tower are shown in Table 2.

3.1.2. Modellable deviation and risk identification indicators

The overall Piping and Instrumentation Diagram (P&ID) of the methanol washing unit is shown in Fig. S1 of the Supplementary Material, including the process equipment, instruments and logic

interlocks devices of the system. Based on this P&ID diagram, the target analytical deviation of the methanol washing tower is first determined by using the traditional HAZOP analysis method, then, the simulation of the target deviation is classified, in which the simulated parameters include feed flow rate, temperature, pressure, level, etc. The non-simulated deviations mainly include leakage, rupture, and utility failures. The simulated deviations of T101 are shown in Table 3.

Risk identification indicators are based on two aspects of HAZOP analysis: hazard analysis and operability analysis. The hazard analysis mainly considers the safety problems that the process equipment and operators may face, which accounts for about 40% of the content of HAZOP analysis evaluation. Operability analysis is mainly about the stability of the process and product quality problems, which accounts for about 60% [35]. The risk identification indicators in this study are shown in Table 4.

3.1.3. Riskiness ranking and semi-quantitative analysis of risk level

After adding pressure-driven components such as pumps and valves to the steady-state model, it was imported into the Aspen Dynamic simulation software to establish a dynamic model for the methanol scrubbing unit. Here, 14 parametric controllers for simulating deviations listed in Table 3 were added to this model for simulation. The Aspen Dynamics simulation flow chart for the methanol scrubbing unit and its deviation controllers are shown in Fig. 4. It is determined that the variation amplitude of all disturbances is uniformly set to 5% deviation from the normal operating state based on the results of multiple simulations with Aspen

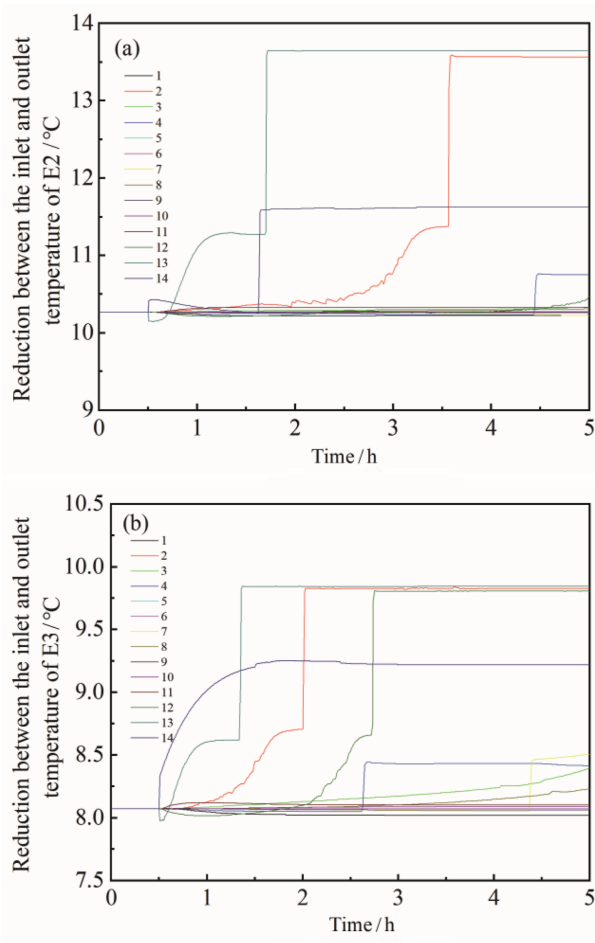


Fig. 7. Effect of 5% fluctuation of 14 deviations on the temperature difference between inlet and outlet of E2 and E3.

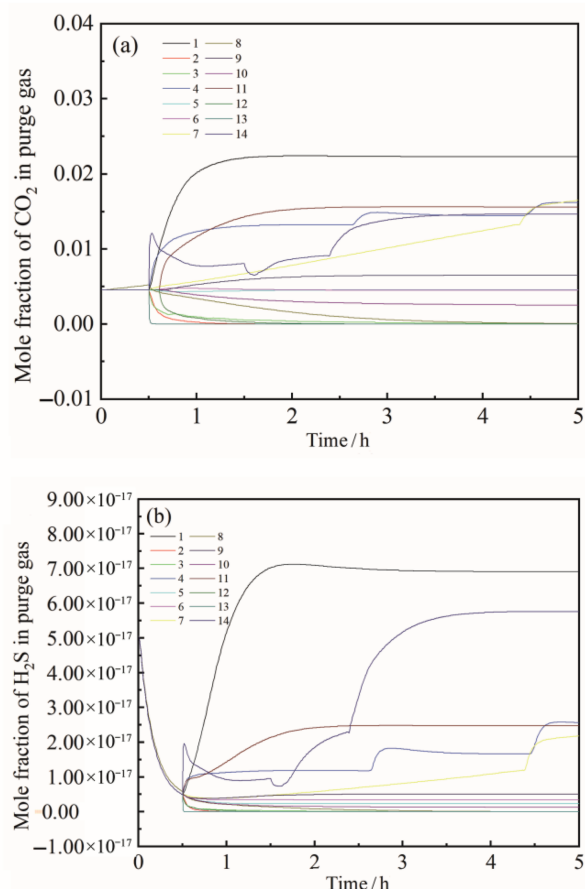


Fig. 8. Effect of 5% fluctuation of 14 deviations on the mole fraction of CO_2 and H_2S in purified gas.

Dynamics software. The initial values of the 14 simulated deviations in the steady state simulation are input into the controller in Aspen Dynamics for setting. After 0.5 h, 5% perturbation is added to carry out dynamic simulation for 5 h to observe the dynamic behavior of the system.

The effect of 5% perturbation of each deviation on the tower kettle temperature is shown in Fig. 5. The deviation high pressure leads to sharp fluctuations in the temperature of the kettle tower, while the large difference in temperature indicates that the system is in an unstable state when the pressure is too high, which means that it is easily lead to serious consequences. However, the pressure is too low, which does not cause large fluctuations in the temperature of the kettle tower, but is large in comparison with other deviation changes. Therefore, deviations between 13 and 14 have a direct effect on the temperature of the kettle tower.

Fig. 6 shows the effect of 5% perturbation of each deviation on the level of tower kettle. Deviation 2 responds quickly and causes the level to rise continuously, and there is no tendency to flatten out after 5 h. The level of tower kettle responds quickly with small wavy fluctuations to the perturbation of deviation 13 and 14. Deviation 5 and 6, which are a stream of the feed pipeline close to the tower kettle, respond quickly and stabilize in the end. Therefore, the deviations of 2, 5, 6, 13 and 14 have a direct effect on the tower kettle level.

Fig. 7 shows that the effect of each deviation perturbation of 5% on the temperature difference between the inlets and outlets of E2, E3. When the deviation between 2 and 13 fluctuates, the temperature differences between the inlets and outlets of the two coolers change rapidly, tending to stabilize after continuously increasing to a higher value, with the power of cooler rising, which is easy to produce greater consequences. When the deviation of 12 fluctuates for about 2 h, the temperature difference between the inlet and outlet of E3 changes greatly. 4, 14 deviation fluctuation

make inlet and outlet temperature difference of E2 increased slightly. 4, 7, 14 deviation fluctuation make inlet and outlet temperature difference of E3 increased slightly. Therefore, deviations 2, 4, 7, 12, 13 and 14 have a direct impact on the temperature difference between E2 and E3.

Figs. 8 and 9 show the effect of 5% perturbation of each deviation on the product purge gas. In Fig. 8, the fluctuations of deviations 1, 4, 7, 11, 14 all increase the content of CO₂ and H₂S in the purified gas, which reduces the quality of the detriment of production, in which the fluctuation of 1 causes the fastest response and highest increase. Fig. 9 shows that the fluctuation of deviation 13 causes a rapid decrease in the purified gas flow at the top of the tower, which affects the stability and production of the system, the fluctuation of deviation 2 causes a small decrease in the purified gas flow. Therefore, deviations 1, 2, 4, 7, 11, 13 and 14 have a direct effect on the purge gas.

The risk level classification and sort in descending order of simulated deviations of the methanol washing tower is shown in Table 5, where the deviations 'high pressure and 'low Syngas feed flow' are considered higher risk deviations.

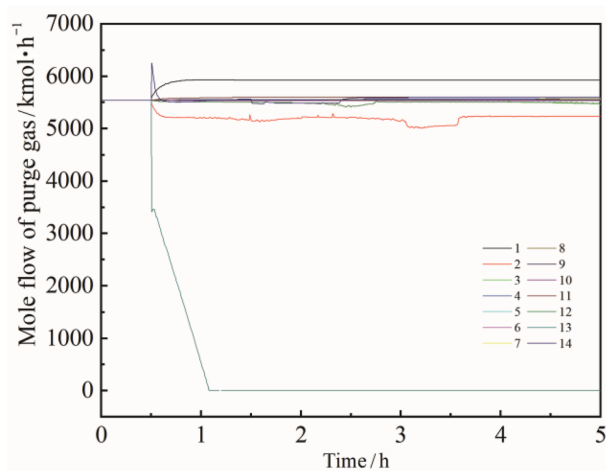


Fig. 9. Effect of 5% fluctuation of 14 deviations on purge gas flow.

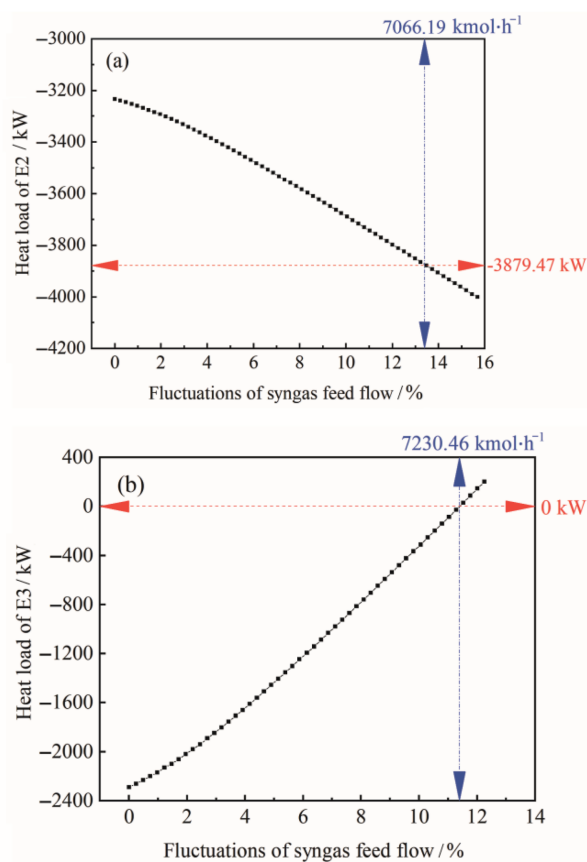


Fig. 10. Effect of syngas feed flow reduction on E2 and E3 heat loads.

Table 5

Classification of deviation risk levels.

Higher risk (Unacceptable)	High risk (Unacceptable)	Medium risk (Additional measures acceptable)	Low risk (Acceptable)
High pressure Low syngas feed flow	Low pressure Low methanol feed flow High syngas feed flow High water content in methanol	High methanol feed temperature High return flow at the top of T1A Low return flow at the top of T1A	High methanol feed flow Low water content in methanol High syngas feed temperature Low syngas feed temperature Low methanol feed temperature

3.2. Risk evaluation

Based on Section 3.1, two higher risk deviations (low syngas feed flow, high pressure) are targeted to establish the quantitative relationship among the range of deviation fluctuation, the probability of accident occurrence (L), the degree of accident risk (S) the risk level (R), in order to validate the accuracy of the GM as well as the feasibility of the quantitative analysis method of HAZOP proposed in this study.

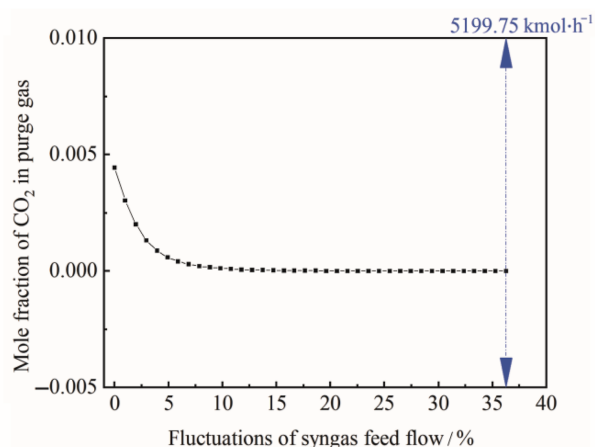


Fig. 11. Effect of reduced syngas feed flow rate on CO₂ mole fraction in purge gas.

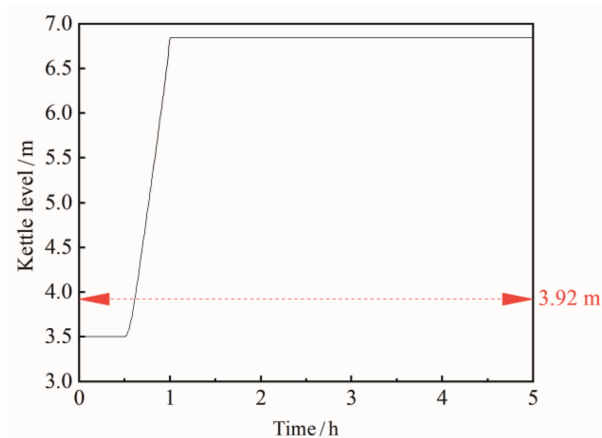


Fig. 12. Dynamic simulation results of tower kettle level when syngas feed flow is reduced to 7230.46 kmol·h⁻¹.

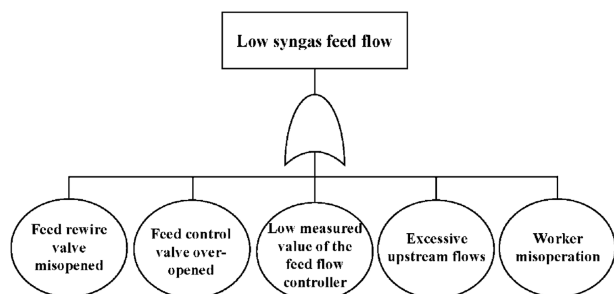


Fig. 13. FTA of low syngas feed flow event.

3.2.1. Low syngas feed flow

3.2.1.1. Quantifying the range of deviation fluctuations. The relationship between the deviation 'low syngas feed flow' and the heat load of the two circulating methanol coolers, obtained by sensitivity analysis with Aspen Plus software, is shown in Fig. 10. The relationship between them is nearly linear. The heat load of E2 reaches the safety threshold when the feed rate is 7066.19 kmol·h⁻¹ with a relative deviation of 13.4%. Meanwhile, the heat load of E3 reaches the safety threshold when the feed rate is reduced to 7230.46 kmol·h⁻¹ with a relative deviation of 11.39%. Prolonged overloading of the cooler may result in lower product quality at the top of the tower, affecting the absorption effect of the T101, thus the heat load of the cooler should be strictly limited within the safety threshold.

From Fig. 11, which shows the variation of CO₂ mole fraction in purified gas when the syngas feed rate is reduced, it can be seen that with the reduction of syngas feed, the mole fraction of CO₂ in purified gas decreases rapidly and then tends to level off. When the feed flow reduces to 5199.75 kmol·h⁻¹, the relative deviation is 36.28%, the calculation does not converge and the system could not operate. Therefore, the safe range of feed flow reduction is 7230.46–8159.75 kmol·h⁻¹, and the lower limit of feed flow rate deviation is 7230.46 kmol·h⁻¹.

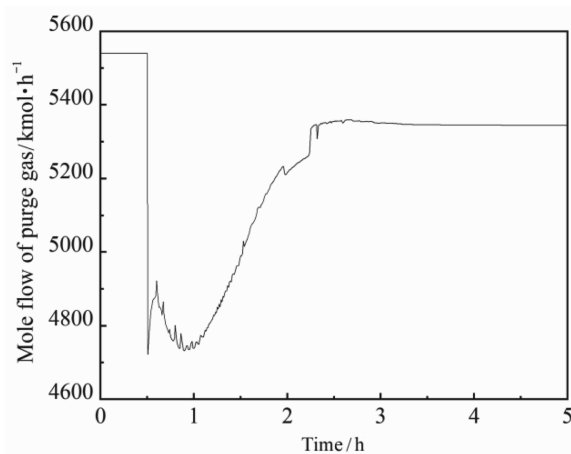


Fig. 14. Dynamic simulation results of purge gas flow rate when the pressure of the absorber tower rises to 3.16 MPa.

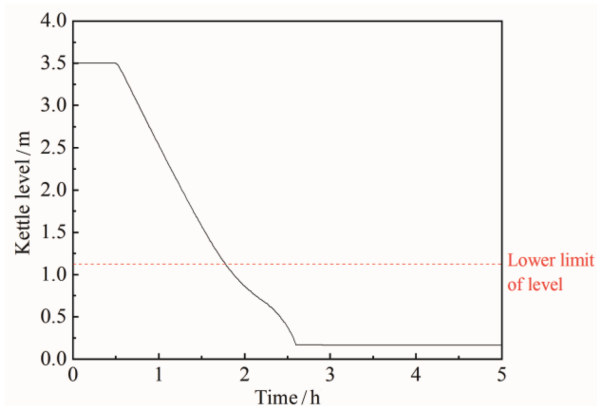


Fig. 15. Dynamic simulation results of the tower kettle level when the absorber tower pressure rises to 3.16 MPa.

3.2.1.2. *Quantifying accident hazard level.* The threshold value of the deviation fluctuation range obtained from the steady state simulation is imported into the dynamic simulation to further simulate the consequences of the accident. Fig. 12 shows that when the syngas flow rate is reduced to 7230.46 kmol·h⁻¹, the level of the tower kettle rises rapidly above the upper level limit and the level will be at a dangerous peak after 1 h, which may damage the equipment, affecting the life of the equipment as well as the normal operation of the process. According to Table S3 of the Supplementary Material, the accident hazard level is 2 when the syngas flow rate fluctuates from 5199.75 to 7230.46 kmol·h⁻¹, level 3 when it is less than 5199.75 kmol·h⁻¹.

3.2.1.3. *Quantifying the probability of accidents.* Based on the dynamic process simulation results and HAZOP analysis of the causes

leading to low syngas feed flow, the FTA constructed is shown in Fig. 13.

When the input event is an independent event [30],

$$P(X) = P\left(\bigcup_{i=1}^n x_i\right) = 1 - \prod_{i=1}^n P(1 - P(x_i))$$

Then the probability of the input event is [30]:

$$P(x_i) = 1 - e^{-\lambda_i t}$$

where x_i is input event, X is output event, λ_i is failure rate of x_i , where the failure rate data of the basic event is shown in Table S1, t is annual start-up time of the device, h.

According to the equation and data of the failure frequency of the basic events, the deviation is quantitatively evaluated. The

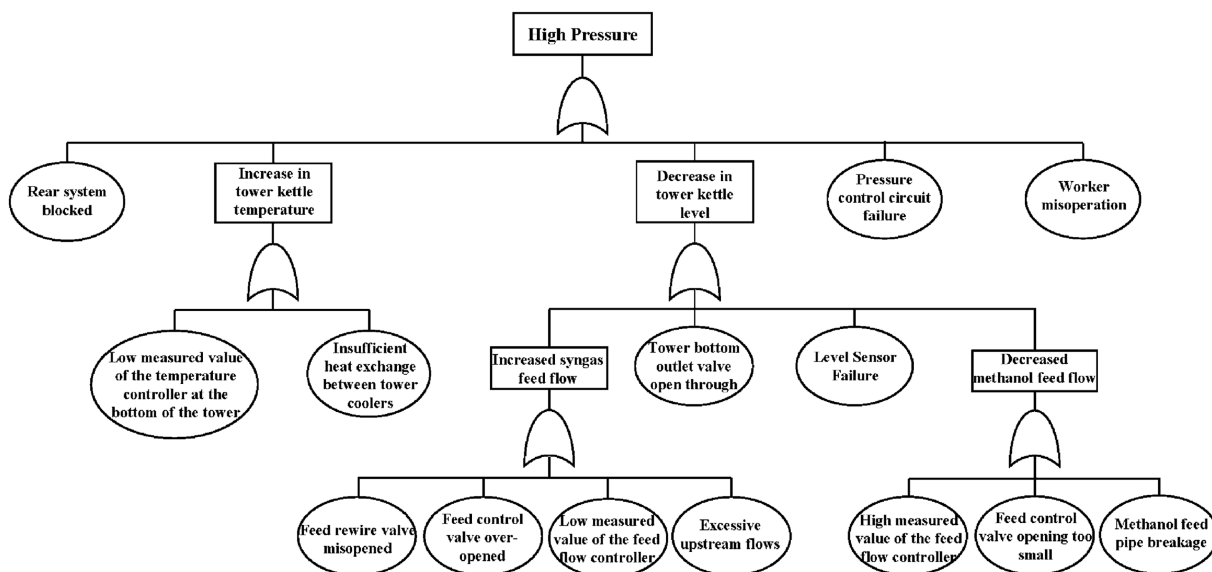


Fig. 16. FTA of high pressure event.

Risk Level	Level of accident occurrence probability					Risk level description:	
	1	2	3	4	5		
Severity level of the accident consequences	1	I 1	I 2	I 3	I 4	II 5	Low risk (1-4): No measures will be taken; Medium risk (5-9): Selective adoption of measures; High risk (10-14): Take measures within a specified period of time; Higher risk (15-25): Take measures immediately.
	2	I 2	I 4	II 6	II 8	III 10	
	3	I 3	II 6	II 9	III 12	IV 15	
	4	I 4	II 8	III 12	IV 16	IV 20	
	5	II 5	II 10	IV 15	IV 20	IV 25	

Fig. 17. Risk matrix hierarchy.

Table 6
HAZOP quantitative analysis results.

Deviation	Reason for deviation	Range of deviation	Simulated consequences	S	L	R	Existing protection measures	RI	Recommended protection measures	RII
Low syngas feed flow	<ol style="list-style-type: none"> 1. Leakage of feed pipe 2. Feed control valve opening too small 3. Feed flow controller measuring value is high 4. Upstream flow rate is too low 5. Improper human operation 	(11.39%, 13.4%)	<ol style="list-style-type: none"> 1. Level of tower kettle is too high 2. Cooler E3 is overloaded. 	2	5	10	<ol style="list-style-type: none"> 1. Set high-temperature detection alarm device at the outlet of cooler 2. Set high liquid level alarm device in the washing tower. 	8		
		(13.4%, 36.28%)	<ol style="list-style-type: none"> 1. Level of tower kettle is too high 2. Cooler E2, E3 is overloaded. 	2	5	10	<ol style="list-style-type: none"> 1. Set high-temperature detection alarm device at the outlet of cooler 2. Set high liquid level alarm device in the washing tower. 	8		
		>36.28%	<ol style="list-style-type: none"> 1. Level of tower kettle is too high 2. Cooler E2, E3 is overloaded. 3. CO₂ mole fraction in purified gas does not meet the standard 	3	5	15	<ol style="list-style-type: none"> 1. Set high-temperature detection alarm device at the outlet of cooler 2. Set high liquid level alarm device in the washing tower. 	12	Add product content analysis quality monitoring instruments in the top of tower outlet pipe	9
High pressure	<ol style="list-style-type: none"> 1. Pressure control circuit failure 2. Clogging of the rear system 3. Increase in washing tower temperature 4. Syngas feed flow increase 5. Methanol feed flow decrease 6. Improper human operation 	(2.1%, 10%)	<ol style="list-style-type: none"> 1. Decrease in purified gas flow 2. The level of the tower kettle is too low 	2	5	10	<ol style="list-style-type: none"> 1. Set low liquid level alarm device in the absorption tower. 2. Set absorption tower pressure transmitter remote alarm, the operator could respond to handle 	8		
		>10%	<ol style="list-style-type: none"> 1. Decrease in purified gas flow 2. The level of the tower kettle is too low 3. Overpressurisation of equipment, which may result in equipment or pipe rupture 	3	5	15	<ol style="list-style-type: none"> 1. Set low liquid level alarm device in the absorption tower. 2. Set absorption tower pressure transmitter remote alarm, the operator could respond to handle 	12	Set self-acting regulating valves in the washing tower for automatic pressure relief in case of overpressure.	9

occurrence probability of the basic events is calculated according to the annual operating time of the device of 8000 h. Since the FTA is an 'or-gate' relationship and the basic events are independent of each other, the occurrence probability of the top event is finally calculated as $0.2069 a^{-1}$.

3.2.2. High pressure

3.2.2.1. Quantifying the range of deviation fluctuations and accident hazard level. Based on the dynamic process simulation results, Figs. 14 and 15 show that when the pressure of T101 increases to 3.16 MPa and the relative deviation is at 2.1%, the flow rate at the top of T101 exhibits a tendency of decreasing, then increasing to a stabilized state. Compared with the small decrease in the purge gas flow at the top of the tower before the increase in tower pressure, the level of tower kettle exceeds the lower level limit after 1.78 h and continues to decrease to stabilize eventually. Equipment overpressure occurs when the pressure of T101 increases to a threshold value of 3.40 MPa with a relative deviation of 10%, which may result in equipment or pipeline rupture. When syngas leaks into the atmosphere and mixes with air, it forms an explosive mixture, which is prone to fire or explosion. Therefore, the accident hazard level is 2 when the tower pressure increases in the range of 3.1.6 to 3.40 MPa, level 3 when the tower pressure exceeds 3.40 MPa.

3.2.2.2. Quantifying the probability of accidents. According to the dynamic simulation and the reason caused the high pressure, the FTA is built with deviation as the top event, the cause of deviation as the basic event, as shown in Fig. 16. The occurrence probability of the top event is calculated to be $0.591 a^{-1}$ according to the same method in Section 3.2.1.

3.3. Risk controls

This study uses HAZOP to analyze a 5×5 risk matrix, with the severity level of the accident consequences in the vertical direction, and the level of accident occurrence probability in the horizontal direction. Based on the position of the risk in the planar matrix, the deviation is classified into four risk levels, represented by the color green, yellow, orange and red, as shown in Fig. 17.

The calculated accident probabilities of the two high-risk deviations and their resulting consequences, derived through a combination of process simulation, qualitative analysis, and historical accident statistics, are compared in Tables S2 and S3, to determine the deviation's accident probability level and accident consequence severity level. Finally, the risk matrix approach was used to determine the deviation's initial risk level. It is found that the fluctuation ranges of the two deviations are in the high risk and higher risk. This result verifies the validity of the GM model applied to deviation riskiness ranking and risk class classification. Therefore, the recommended measures need to be added to minimize the risk value of deviations.

In this study, LOPA analysis is carried out for the accident consequences which obtained from quantitative HAZOP analysis to achieve risk control. The probability of accident occurrence are reduced by adding IPL means [36] on the basis of the original HAZOP, thereby reducing the risk level of deviation and making its residual risk as low as possible [37], which is beneficial to improve the intrinsic safety level of the system. Among them, the typical IPL and the failure probabilities are shown in Table S4 of the supporting materials.

3.4. Quantitative HAZOP analysis

The risk analysis and evaluation of the methanol washing unit in the rectisol process are carried out by a combination of HAZOP,

Aspen Plus, Aspen Dynamics, FTA, risk matrix and LOPA analyses in this study. The quantitative results of HAZOP are obtained as shown in Table 6.

4. Conclusions

In this study, a methodology of applying the GM model to the risk ranking of deviations and risk class classification is used in the low-temperature methanol washing process as an example. The results of the study show that too high pressure in the methanol washing tower and too low syngas feed flow rate are high-risk deviations in the process. Then, the identified high-risk deviations are subjected to quantitative HAZOP analysis combining HAZOP, Aspen Plus, Aspen Dynamics, FTA, risk matrix and LOPA analysis to quantify their safety fluctuation ranges and corresponding consequences through software simulation, which provides guidance for actual production safety warnings; and through FTA, risk matrix and other methods, we get the root causes of accidents in the process and the accident risk level, determine the factors that should be focused on in the actual production process, and finally carry out risk control to form a quantitative HAZOP analysis report, which increases the readability and accuracy of the HAZOP analysis report, helps to improve the accuracy of process risk analysis and determine the effectiveness of safety measures, and provides a reference for risk analysis of similar chemical processes.

CRedit Authorship Contribution Statement

Haiyan Zhang: Writing – review & editing, Writing – original draft, Software, Resources, Methodology, Formal analysis, Data curation, Conceptualization. Peirui Li: Writing – review & editing, Validation, Software, Conceptualization. Zhonglin Zhang: Writing – review & editing, Validation, Software, Resources, Funding acquisition, Conceptualization. Xiaogang Hao: Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. Yuan Zhou: Writing – review & editing, Validation, Methodology. Xiaolu Wu: Writing – review & editing, Supervision, Resources, Methodology. Jingxuan Yang: Writing – review & editing, Supervision, Methodology. Abuliti Abudulad: Writing – review & editing, Supervision, Resources. Guoqing Guan: Writing – review & editing, Supervision, Resources, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

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