RESEARCH ON QUANTIFICATION OF HAZOP DEVIATION BASED ON A DYNAMIC SIMULATION AND NEURAL NETWORK

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Hazard and operability (HAZOP) analysis has become more significant as the complexity of process technology has increased. However, traditional HAZOP analysis has limitations in quantifying the deviations. This work introduces artificial neural networks (ANNs) and Aspen HYSYS to explore the feasibility of HAZOP deviation quantification. With the proposed HAZOP automatic hazard analyzer (HAZOP-AHA) method, the conventional HAZOP analysis of the target process is first carried out. Second, the HYSYS dynamic model of the relevant process is established to reflect the influence of process parameters on target parameters. Third, to solve the problem of deviation identification based on multi-attribute and a large dataset, we use the ANN to process the input data. Finally, HAZOP deviation can be quantified and predicted. The method is verified by the industrial alkylation of benzene with propene to cumene. The results show that the predicted deviation severity can be close to the actual deviation severity, and the accuracy of prediction can reach nearly 100%. Thus, the method can diminish the probability of conflagration, burst, and liquid leakage.

Keywords: HAZOP; Deviation Quantification; Dynamic Simulation; Artificial Neural Network

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1. INTRODUCTION

Hazard and operability analysis (HAZOP) is a risk assessment method expanded by Imperial Chemical Industries. This technique is widely used in industrial production. However, with the continuous expansion of process capacity, the risk also posed by HAZOP has also increased. Therefore, dealing with deviation scenarios in the process industry in a timely and effective manner has become an increasingly complex problem. Nevertheless, traditional HAZOP analysis is time-consuming, laborious, and excessively dependent on expert opinions. Thus, realizing intelligent HAZOP analysis has become an inevitable trend of HAZOP development.

Currently, the development trend of HAZOP analysis methods is divided into three categories:

(1) HAZOP qualitative analysis: This method mostly replaces some regular steps with computer programming languages. Some programs also provide users with a user interface to enable users to enter model information and formulate rules for hazard identification procedures (Parmar and Lees, 1987). Bartolozzi et al. (2000) proposed combining HAZOP analysis with logic-function models to find the causes and consequences of variable deviations. This program ultimately generates a model library for the support system to reduce the time of HAZOP analysis. ExpHAZOP+ applies knowledgebased expert systems for automatic HAZOP analysis and combines the Expert Knowledge Database with a fault propagation algorithm to improve the practicability of HAZOP analysis by shortening repetitive work effectiveness (Rahman et al., 2009). Zhang et al. (2015) used the directed graph model of Petri net based on fuzzy logic to express the mass transfer and interrelationship between process variables to solve the abnormal situation during discontinuous operation. Single et al. (2020) proposed a knowledge-based framework for the automatic generation of HAZOP worksheets. In the course of this, expert knowledge from the process and plant safety domain is embedded within the ontological model. Javed et al. (2021) used HAZOP and fault tree analysis techniques to identify and mitigate/eliminate potential hazards. Subsequently, safety cases were constructed using the OpenCert platform, and safety contracts were associated with them to enable necessary changes during runtime. Finally, they used a simulation-based approach to identify and resolve the deviations between the system understanding reflected in the safety cases and the current system operation. The aforementioned approaches treat all process parameters that deviate from normal values as deviations with terrible consequences (Hoseyni et al., 2014). Nevertheless, most modern processes are equipped with a distributed control system

(DCS) with proportional-integral-differential (PID) controllers, which have an automatic adjustment function. Some deviations do not have serious consequences.

- (2) The intelligent HAZOP quantitative analysis method based on empirical knowledge (Zhou et al., 2018): Based on the existing SDG-HAZOP model, Wang et al. (2009) suggested a signed digraph-based HAZOP. It is used to identify the most likely operating mistakes that may cause certain process variables to deviate from their normal value. Hu et al. (2009) introduced fuzzy information fusion theory with HAZOP. After that, they used variable nodes with different attributes in the system corresponding to various fuzzy quantization methods to establish a directed graph model for HAZOP analysis. Marhavilas et al. (2019) integrated HAZOP with a decision matrix risk assessment and analytic hierarchy process. A new framework for identifying potential hazards thus came into being. In addition, probabilistic fault-tree analysis (Abuswer et al., 2013) and the layer of protection analyses (Johnson, 2010) were employed for semi-quantitative analysis in combination with HAZOP. These kinds of ideas solve the problem of quantifying the consequences of HAZOP accidents to a certain extent, but they still have a high degree of subjectivity and cannot quantitatively analyze the deviation of HAZOP.
- (3) Intelligent HAZOP quantitative analysis method based on dynamic simulation (Zhou *et al.*, 2018): Process simulation is one of the most successful technologies for the integration of computers and modern industry. It is based on the mechanism of the process and uses a mathematical model to represent the process. Eizenberg *et al.* (2006) applied Polymath 6.1 to model the basic model of the semi-batch reactor with an exothermic reaction and then imported it into MATLAB for simulation to calculate the actual threshold of process deviation. Enemark-Rasmussen *et al.* (2012) used K-Spice® to predefine the deviations of process equipment, systematically generate failure scenarios, and then use sensitivity to summarize the consequences of each failure scenario and rank the failure scenarios.

Kang and Guo (2016) presented the HAZOP analysis approach based on a sensitivity evaluation. In this approach, the sensitivity evaluation is introduced into HAZOP deviation analysis to measure the effect degree caused by each cause on the corresponding deviation. Danko *et al.* (2019) introduced a new framework methodology for a simulation-based HAZOP tool. This framework uses a layer of protection analysis concept of independent protection layers testing. The control system integrated into the raw process design represents the first of various protection layers of the LOPA concept. As a case study, a CSTR chemical production with nonlinear behavior under PID actions as the predominant type of classical feedback control strategy was used. In addition, most scholars, such as Huang *et al.* (2002), Carlos *et al.* (2018), and Zhu *et al.* (2019), have integrated HAZOP with another chemical simulative software, which has further promoted the development of HAZOP deviation quantitative analysis. The above viewpoint can not only reveal the influence of deviation size on the process system but also discuss the influence of deviation duration. These approaches make the HAZOP analysis more reliable.

Nonetheless, the reality is that many kinds of chemical process anomalies need to be considered, and relying on a single attribute parameter (e.g., temperature, pressure, and rate of flow) often cannot detect early slight deviations in time. Therefore, anomaly detection based on a large sample and multi-attribute process data is more in line with the actual needs of process safety. The artificial neural network (ANN) is a mathematical model similar to the structure and function of a biological neural network, which is widely adopted in the modeling of diverse nonlinear problems (De Fenza *et al.*, 2015). Owing to its unique advantages in cluster, regression, and pattern recognition, it is widely used in data analysis. To identify general indicators influencing forest fire and compare forest fire susceptibility maps, Pourtaghi *et al.* (2016) used boosted regression tree, generalized additive model, and random forest data mining models. The results show that the main drivers of forest fire occurrence were annual rainfall, distance to roads, and land-use factors. The results can be applied to primary warning, fire suppression resource planning, and allocation work. Li *et al.* (2019) considered that in some circumstances, the historical fault data are insufficient for use in performing statistical analysis, so they proposed a method to predict the dynamic failure rate of a chemical process system based on the backpropagation (BP) neural network and two-parameter Weibull distribution. Owing to the demand for determining the value at risk caused by forecasting errors, Boltürk and Öztayşi (2018) also applied ANNs to deal with the time-series data and proved the advantage of the ANN.

In this contribution, our goal is to propose the HAZOP-AHA method, which integrates HAZOP with Aspen HYSYS and an ANN. Aspen HYSYS is a process simulation software of Aspen Tech. It is mainly suitable for use in the design and calculation analysis of oilfield surface engineering construction as well as petroleum and petrochemical engineering (Liu and Karimi, 2018). Compared with other process simulation software, Aspen has the most comprehensive database and fastest convergence. In this study, HYSYS is taken to reflect the influence of process parameters on target parameters. An ANN is used to analyze the state parameters and predict the deviation severity. The industrial alkylation of benzene with propene to cumene is taken as an example to describe the HAZOP-AHA method. In this chemical process, we select deviation scenarios that have a significant impact on the process to simulate and display the results of HAZOP quantification.

2. METHODOLOGY

2.1 Technology roadmap

Figure 1 shows the specific process of HAZOP-AHA. In this method, Aspen HYSYS is applied to model the chemical process. According to the specific evaluation needs, typical deviation scenarios can be selected for the simulation, and the analog data are recorded. Based on the simulation data of Aspen HYSYS, an ANN is used for data processing and finally predicts the quantified deviation for the HAZOP evaluation. The specific steps of the HAZOP-AHA method are as follows:

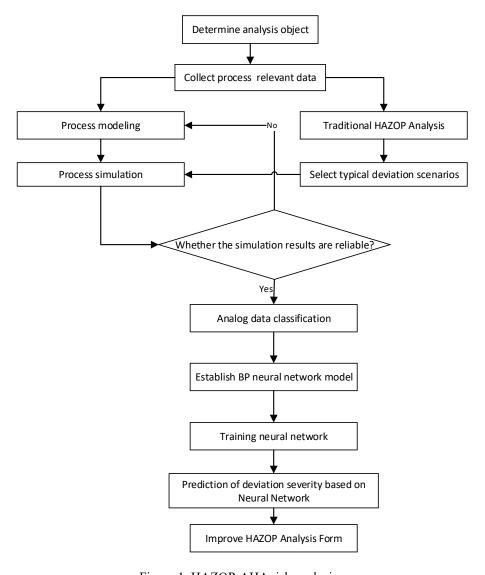


Figure 1. HAZOP-AHA risk analysis process

- 1) Determine the analysis object.
- 2) Collect relevant information. Assemble and analyze the PID diagram, PFD diagram of the chemical process, process operating conditions, product specifications, related facilities parameters, and logistics flow.
- 3) Perform conventional HAZOP analysis on the process flow.
- 4) Process modeling. Enter the relevant process parameters into HYSYS to establish the steady-state model under normal operating conditions and verify whether the model is consistent with the actual situation. Convert the static model to a dynamic model, initialize the dynamic model, and record the state parameters of the analysis node.
- 5) Choose and simulate typical deviation scenarios. According to traditional HAZOP analysis results, the most

crucial parameters reflecting the production status are gained. One of the parameters is adopted as the independent variable, and the other parameters are used as dependent variables. By constantly changing the operating conditions of the process, the staff should grasp the trend of each dependent variable and judge the rationality of simulation results in the meantime. If the simulation results coincide with the actual situation, the simulated data of several groups of dependent variables that change significantly are output. Conversely, the workers should find out the relevant reasons, modify the model, and continue the simulation again.

- 6) Classify the simulation data. We need to preprocess the data.
- 7) Establish the BP neural network. Because of the nonlinear and discrete nature of the process, we must establish a suitable BP neural network.
- 8) Train the neural network. Input preprocessed data to the ANN and then train it repeatedly until the training accuracy has been reached. Lastly, save the trained network.
- 9) Predict the deviation based on the neural network. Enter the test dataset into the ANN and analyze the data that have been processed to estimate the severity of deviation.
- 10) Improve the HAZOP analysis form.

2.2 Establishment of the BP neural network model

Figure 2 shows the structure of a multi-input multilayer, multi-output neural network.

 \mathbf{x} is the input vector, which represents the input state parameter, such as the condenser liquid level. R represents that there are R input vectors. L represents the number of layers of the multilayer neural network. In this paper, L = 3. \mathbf{y}^L is the output vector, and S = 5 represents the number of output vectors.

Each layer (L) has its weight matrix (ω^L) and deviations column vector (\mathbf{b}^L).

 $b_{s_L}^L$ means that there are S deviations in the L layer, and $y_{s_L}^L$ means that there are S outputs in the L layer.

The value of R is not necessarily equal to the value of S.

The number of neurons in each layer can be different, and its number is defined as S_L because there are three hidden layers in this paper, $S_L = [5 \ 4 \ 4]$.

The input data (x) can be considered in the 0 layers, so its number (R) is defined as S_0 .

So
$$\boldsymbol{\omega}^{L} = \begin{bmatrix} \boldsymbol{\omega}_{1,1}^{L} & \boldsymbol{\omega}_{1,2}^{L} & \cdots & \boldsymbol{\omega}_{1,S_{L-1}}^{L} \\ \boldsymbol{\omega}_{2,1}^{L} & \boldsymbol{\omega}_{2,1}^{L} & \cdots & \boldsymbol{\omega}_{2,S_{L-1}}^{L} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{\omega}_{S_{L},1}^{L} & \boldsymbol{\omega}_{S_{L},2}^{L} & \cdots & \boldsymbol{\omega}_{S_{L},S_{L-1}}^{L} \end{bmatrix} \mathbf{x} = \begin{bmatrix} x_{1} \\ x_{2} \\ \vdots \\ x_{R} \end{bmatrix} \boldsymbol{b}^{L} = \begin{bmatrix} b_{1}^{L} \\ b_{2}^{L} \\ \vdots \\ b_{S_{L}}^{L} \end{bmatrix} \boldsymbol{y}^{L} = \begin{bmatrix} y_{1}^{L} \\ y_{2}^{L} \\ \vdots \\ y_{S_{L}}^{L} \end{bmatrix}.$$

$$x_{1} \bullet \boldsymbol{\omega}_{1,1}^{L} \bullet \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L} \cdot \boldsymbol{\lambda}^{L} = \boldsymbol{\lambda}^{L}$$

Figure 2. The structure of the neural network

Hence, the regression equation of layer L is

$$y_i^L = f^L \left(\omega_{i,1}^{L-1} y_i^{L-1} + \dots + \omega_{i,S_{I-1}}^{L-1} y_{S_{I-1}}^{L-1} + b_i^L \right), i = 1, 2, \dots, S_L$$
 (2)

The *tanh* function is selected as the activation function (f) of the hidden layer, whose expression is $f(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$, and the transfer function f of the output layer is a linear function.

The training function is "trainlm."

Backpropagation is used to calculate the Jacobian (ix) of the performance with respect to the weight and bias variables (x). Each variable is adjusted according to the Levenberg–Marquardt algorithm.

$$\mathbf{j}\mathbf{j}=\mathbf{j}\mathbf{x}^{*}\mathbf{j}\mathbf{x}$$

$$\mathbf{je} = \mathbf{jx} * \mathbf{E} \tag{4}$$

$$d\mathbf{x} = -(\mathbf{j}\mathbf{j} + \mathbf{I} * \mathbf{m}\mathbf{u}) \setminus \mathbf{j}\mathbf{e} \tag{5}$$

E represents the errors, and I is the identity matrix. **mu** is the adaptive value.

The training stops when any of these conditions are met:

- The maximum number of **epochs** =1000.
- 2) The maximum amount of **time**.
- The performance is minimized to the **goal** = 0.0001.
- The performance gradient falls below min grad.
- mu exceeds mu max.
- The validation performance has increased more than max fail =24 times since the last time it decreased (when using validation).

3. CASE STUDY

This paper takes the industrial alkylation of benzene with propene to cumene as an example to establish the reaction flow model. The main chemical equation of this process is

Main reaction:
$$C_6H_6 + C_3H_6 \rightarrow C_9H_{12}$$
 (6)

Side reaction:
$$C_9H_{12} + C_3H_6 \rightarrow C_{12}H_{18}$$
 (7)

The reactants produce the target product under the action of the catalyst. Then, the target product and other impurities enter the flash tank through the heat exchanger and cooler for gas-liquid separation. Moreover, the liquid phase stream of the flash tank is cooled and enters the rectification tower C1. Furthermore, the excess benzene is rectified from Rec Ben-1 into the reactor for recycling, and then the bottom stream enters the rectification column C2 for further purification. Finally, cumene is separated. The PFD diagram of the process is demonstrated in Figure 3. The vaporizer has a diameter of 1.724 m and a height of 3.447 m. The flash tank V-100 has a diameter of 1.271 m and a height of 2.542 m. Table 1 shows the design dimensions of the distillation column.

Table 1. Dimensions of the distillation columns

	Distillation section		Stripping section		Reboiler		Condenser	
Name	Plate	Tower	Plate	Tower	Diameter	Length/m	Diameter/m	Length
	distance /m	diameter /m	distance /m	diameter /m	/m	Lengui/in	Diameter/iii	/m
C1	0.6	1.0	0.6	1.2	1.591	3.182	0.708	1.416
C2	0.6	1.2	0.6	1.2	1.329	2.658	0.935	1.870

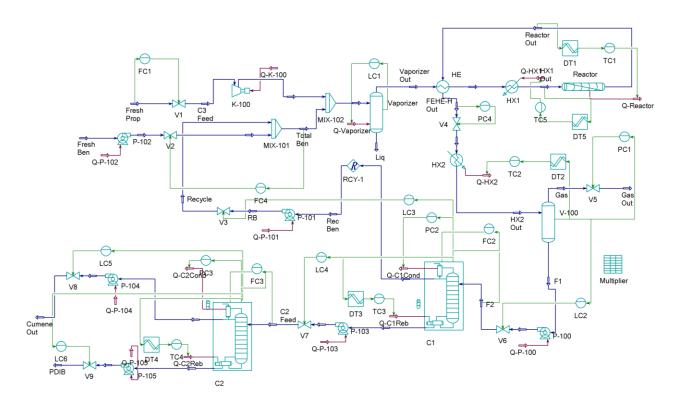


Figure 3. PFD diagram of the industrial alkylation of benzene with propene to cumene

3.1 Traditional HAZOP analysis

This industrial chemical process is divided into nine process nodes, comprising the propylene feed line, benzene feed line, heater unit, heat exchanger unit, reactor unit, cooler unit, flash tank unit, distillation column unit C1, and distillation column unit C2. In this article, we conduct a detailed HAZOP analysis on the rectification column C2.

Table 2 shows part of the HAZOP analysis results. See Appendix A for details on the whole HAZOP analysis.

Table 2. Traditional HAZOP analysis of distillation column C2

Process parameters	Guide word	Reason	Consequence	Recommended measure	
Flow (feed)	Less/None 1. The valve fails to close. 2. The pump efficiency is not enough or stops running. 3. The manual adjustment is wrong.		Low liquid level of distillation tower bottom	Set feed flow detection	
	More	 The valve failure to open. The pump flow is large. The bypass valve is opened mistakenly. 	Liquid level rise of rectification tower	 Set up feed flow detection. Set up direction identification for the pipeline valve. 	
Liquid level (reboiler)	More	 The steam quantity of the reboiler is small. The energy flow Q-C2Reb valve is blocked. The pump failure stops at the tower bottom. The V1 opening is too large. The V8 opening is too small. The outlet pipeline at the tower bottom is blocked. 7. The feed flow of the tower is too large 8. The reflux flow at the top of the distillation tower is too 	 Affect product quality. Flood tower. Exceed the normal pressure. Damage and shorten equipment life. Cause poor thermosiphon effect. Affect heat exchange effect of reboiler. 	 1. Set level controller and pressure relief valve. 2. Set the DCS status display and alarm of the discharging pump. 3. Set the standby pump for discharging from the tower bottom. 4. Set thermal insulation measures for discharging a pipeline to prevent condensation. 5. Set the detection display and alarm of reflux flow. 	

Process parameters	Guide s word Reason		Consequence	Recommended measure		
-		large. 1. The feed volume is too low. 2. The instrument control has malfunctioned.	Product composition changes.	 Set the indicator for the discharge pipe. Set the reboiler temperature 		
	Less	 The discharge is too fast, or the bypass valve is open. The reboiler temperature control has broken down; the heating volume is too large. The valve opening is too high. The top of the rectification tower has lost cooling or has no reflux. 	 Product output is decreased. The liquefied gas in the reboiler evaporates to dryness, causing the tower to flush. 	 control valve group. Set a high-temperature alarm at the bottom of the tower. Set a temperature alarm at the top of the tower. Set the feed flow detection and flow control valve group. 		

3.2 Aspen HYSYS modeling

3.2.1 Establishment of the Aspen HYSYS dynamic model

First, the NRTL model is considered an activity coefficient model. As shown in Table 3, the material information of Fresh Prop, Fresh Ben, and Rec Ben is entered. Then, the steady-state model is established systematically. Because the Aspen HYSYS dynamic model is pressure-driven, the static-state model demands a pump and valve to ensure the relationship of pressure–flow between different units. Afterward, the dynamic regulations must be input. Next, the homeostatic model should transform the dynamic model. Finally, the control structure must be added and adjusted slowly.

Fresh Ben Rec Ben Name Fresh Prop 25°C 25°C 60°C Temperature 101.3 kPa 175 kPa **Pressure** 101.3 kPa **Molar Flow** 110 kmole/h 104.2 kmole/h 80 kmole/h Composition **Mole Composition** 0.95 Benzene **Propene** 0.95 0.04 Cumene **Propane** 0.05 0.01 14-ip-BZ

Table 3. Material information and composition

3.2.2 Initialization of dynamic models

The initial simulation time uniformly sets the current time to 0 min and the end time to 60 min. The dynamic simulation initialization results of the C2 rectification tower are shown in Table 4.

Operating parameters	Steady value	Operating parameters	Steady value
Reboiler liquid level	0.6649 m	Reboiler pressure	114.2 kPa
Condenser liquid level	0.4674 m	Condenser pressure	100 kPa
Reboiler heat load	1142 kW	Discharge from tower top	75.76 kmole/h
Condenser liquid level	1290 kW	Discharge flow of tower bottom	1.162 kmole/h
Reflux molar flow	47.74 kmole/h	Reboiler pressure	215 °C
Condenser Temperature	151.8 °C		

Table 4. Summary of dynamic simulation initialization results

3.2.3 Screen of deviation scenarios of the distillation tower C2

According to the internal structure of the rectification tower, two deviation scenarios, namely the abnormal feed flow rate

and malfunction of the Q-C2Reb control valve, are selected for the simulation in this work.

3.3 Deviation scenario 1: The feed flow rate of Fresh Prop is abnormal

3.3.1 The effect of a feed valve V1 failure

The feed stream of Fresh Prop is mainly conducted by valve V1. By controlling the opening of V1, we can observe the variation of the C2 condenser heat load. The specific steps are listed below.

- 1) Simulate for 1 h under normal conditions with 50% valve opening. Then, adjust the opening of V1 to 45%, 40%, 35%, and 30% for 4 h.
- 2) Classify the simulation data. Take the heat load of the C2 condenser as the dependent variable. The severity of the deviation is defined as follows. If the heat load deviation of the condenser is $\pm 5\%$ away from normal operation, the output is *I*. If the deviation changes from $\pm 5\%$ to $\pm 10\%$, the output is *II*. In case the range of change is from $\pm 10\%$ until $\pm 15\%$, the result is *III*. If the amplitude reaches $\pm 15\%$ to $\pm 20\%$, the output is *IV*. Moreover, if the amplitude reaches more than $\pm 20\%$, the outcome is *V*. The simulated data are shown in

Figure 4.

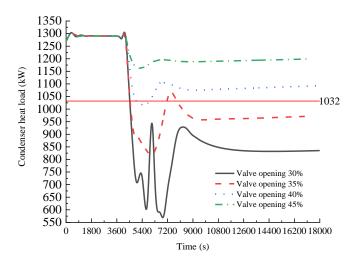


Figure 4. Condenser thermal load deviation

From

Figure 4, if the valve V1 openings are different, the influence of this deviation on the thermal load of the condenser is also distinct. When V1 is turned on to about 35%, the heat load of the condenser is below 1032 kW (the normal value is 1290 kW) for most of the time during 5 h. The deviation severity is V, which needs to be rectified immediately.

3.3.2 The forecast of deviation severity based on the ANN

According to the dynamic simulation results, six process parameters with an obvious change, comprising the condenser liquid level, condenser heat load, reboiler heat load, reflux, tower top discharge flow, and the sensitive tray temperature of distillation tower C1, are seen as the dependent variables for further data analysis. The deviation severity is computed on each variable separately, and then the severity of the whole system is defined as the maximum of the severities computed over all the parameters. Take the condenser heat load as an instance. If the deviation severity of the condenser heat load is V, and the deviation severity of others is IV, the deviation severity of the whole process is V. In this study, we use "fitnet" to simulate the neural network.

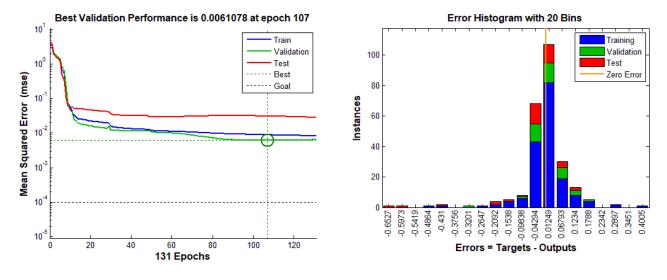


Figure 5. Mean square error analysis

Figure 6. Error histogram

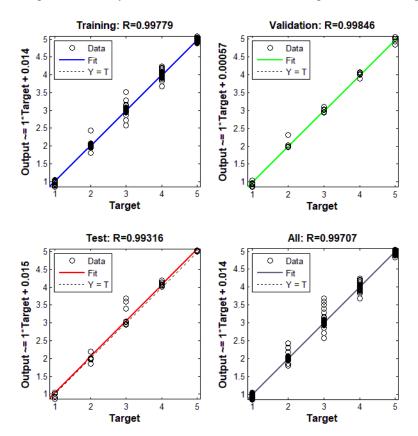


Figure 7. ANN linear regression graph

Figures 5, 6, and 7 demonstrate that in the 107th iteration, the error of the verification set is the smallest. The error is mostly distributed in [-0.04294,0.06793]. The mean square error (MSE) of the verification set is 0.0118. The R-values of the training, verification, and test sets are all above 0.99, so the fitting effect is precise.

As shown in Table 5, there is little difference between the predicted and actual deviation levels except in group 6, group 7, and group 10. The predicted accuracy is about 88%. The predicted accuracy may be stimulated by improving the algorithm. See Appendix B for details on the complete ANN forecast data.

C2 Reflux Condenser Reboiler C2 out Actual Condenser C2 distillation Pre. No. Liquid heat Molar stream deviation heat loss/kW temperature/°C Dev.Sev.1 level/m loss/kW Flow/kmole.h-1 flow rate severity 0.467381 1290.346 1142.455 47.74254 75.75849 1.0164 1 145.503 I 0.467381 1290.342 47.74251 1.0164 2 1142.454 75.75834 145.5029 I 3 0.467381 1290.341 1142.453 47.74251 75.75821 145.503 1.0162 I 4 0.467381290.338 1142.455 47.74249 75.75808 145.5029 1.0164 I 5 0.467381290.337 1142.455 47.74253 75.75796 145.5031 I 1.0163 6 0.467529 1287.045 1136.634 47.58038 75.79565 137.714 II 1.6172 7 II 0.46746 1286.563 1135.666 47.64084 75.77193 136.2245 1.7858 8 II 0.467373 1286.045 1134.771 47.7043 75.74249 134.7905 1.9684 9 75.70782 133.4346 II 0.467271 1285.504 1133.998 47.76852 2.1559 10 0.467154 1284.961 1133.389 47.83142 75.66858 132.1733 II 2.3397 0.467452 1224.29 43.74958 III 11 1028.135 75.57403 124.202 3.0065 12 0.466807 1216.889 1022.207 43.59417 75.34259 124.9467 III3.0010 13 0.466117 1209.315 1016.431 43.43688 75.0969 125.7585 III 2.9967 14 0.4653861201.613 1010.82 43.27804 74.83792 126.6386 III2.9905 15 0.464617 1193.8 1005.382 43.11754 74.56669 127.5878 III 2.9840 16 0.466411280.245 48.07488 IV 3.9191 1128.821 75.41508 123.5878 17 0.466229 1279.802 1129.434 48.11344 75.35558 122.7383 IV 3.9806 18 0.466055 1279.493 1130.353 48.1406 75.29887 IV 121.9866 4.0131 19 0.465892 1279.335 1131.567 48.1558 75.2465 121.3205 IV 4.0246 20 0.465747 1279.345 1133.046 48.15868 75.20006 120.7279 IV 4.0186 21 905.4851 37.54734 V 0.41494917.2867 59.09102 152.558 5.0031 22 0.415193 905.5465 37.5664 59.17122 V 5.0004 918.2758 152.4594 23 0.415435919.2003 905.5896 37.58448 59.24742 152.3612 V 4.9986 24 0.415665 920.0761 905.6175 37.6016 59.31974 152.2637 V 4.9976 25 0.415883 920.8908 905.6306 37.61776 59.38818 152.1664 V 4.9973

Table 5. Partial ANN forecast data of deviation scenario 1

3.3.3 HAZOP analysis results based on AHA

It can be seen from Table 6 that in this working condition, engineers should pay more attention to the data changes of the heat load and liquid level of the condenser. If the condenser liquid level is too low, local concentration of hydrocarbons is likely to occur, which will block the main cooling pipe and cause the main cooling explosion. We need to install more sensitive safety accessories, such as a safety valve and emergency cut-off valve, and clean the condenser frequently. Compared with traditional HAZOP, this method is more specific.

Process parameters	Guide word	Reason	Consequence
Flow (Feed)	Obviously low	 The valve V1 is blocked, or the opening is not enough; The pump efficiency is not enough, or the pump stops due to 	 The liquid level and heat load of the condenser decrease. The heat load of the reboiler decreases greatly, and the liquid level fluctuates to a certain extent. This may cause the pressure drop of the empty reactor tower, resulting in the gas-liquid two-phase imbalance in the tower, which cannot maintain normal production When the valve opening is 35%, the severity of condenser thermal load deviation within 4535 seconds is V.
	Low	failure; 3. The manual	1. The heat load of the condenser decreases, and the liquid level of the condenser decreases slightly . The heat load of the reboiler

Table 6. HAZOP analysis based on AHA

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^a Pre. Dev. Sev.is abbreviation of predictive deviation severity

Process parameters	Guide word	Reason	Consequence
		adjustment is wrong.	decreases and the liquid level of the reboiler fluctuates slightly. 2. The deviation severity of the condenser heat load reached <i>V</i> in 4967 s, but it returned to <i>IV</i> in 5936 s
	Slightly low		 The heat load of the condenser decreases. The liquid level of the condenser slightly decreases. The heat load of the reboiler decreases When the valve opening is 45%, the deviation severity of the condenser heat load is stable at II.

3.4 Deviation scenario 2: Malfunction of the Q-C2Reb control valve

3.4.1 The result of an abnormal valve opening

We can change the liquid level of the reboiler by controlling the opening of the Q-C2Reb valve. The detailed procedure is shown below.

- 1) Run under normal conditions for 1 h. The opening of the Q-C2Reb control valve is automatically adjusted from 49.46% to 50.23% and eventually stabilizes to 49.67%. Assuming that the PID controller of the Q-C2Reb valve fails, the opening of the Q-C2Reb control valve stays at 48%, 49%, 50%, 51%, and 52%. These deviation scenarios disappear for 4 hours.
- 2) Classify the simulation data. Take the distillation column C2 reboiler level as the dependent variable. Repeat the steps described in Section 3.3.1. The results are shown in Figure 8.

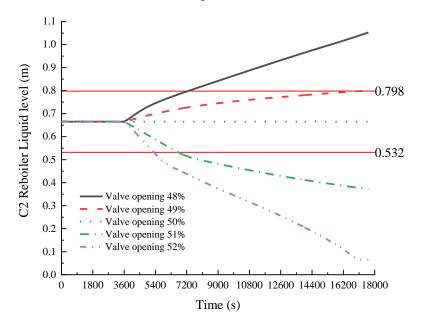


Figure 8. The liquid level of the C2 reboiler in the distillation column

From Figure 8, when the control valve opening of Q-C2Reb is 51%, the reboiler level drops to 80% (0.532 m) of the normal level (0.6649 m) at around 6700 s. The severity reaches V. When the control valve opening is 52%, the reboiler level drops to 0.532 m at around 5300 s. Similarly, when the control valve opening is 49%, the reboiler level rises to 120% (0.798 m) at about 17,700 s. When the control valve opening is 48%, the reboiler level rises to 0.798 m in approximately 7,260 s.

3.4.2 The prediction of deviation severity based on the ANN

The temperature of the 15th tray of the distillation column C2, the outlet flow rate of Cumene Out, the liquid level of the reboiler, the heat load of the condenser, and the reflux flow rate serve as dependent variables. The author of this article uses "fitnet" to fit the neural network. The adaptive value $\mathbf{mu} = 1$, \mathbf{mu} inc = 1.5, \mathbf{mu} dec = 0.8, and \mathbf{min} grad = 1e-8.

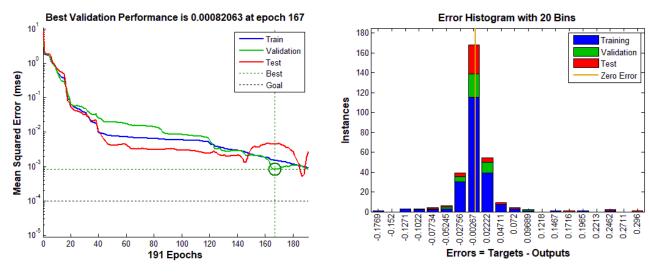


Figure 9. ANN mean square analysis

Figure 10. ANN error histogram

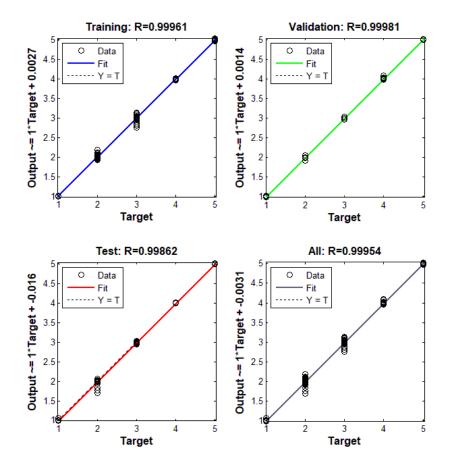


Figure 11. ANN linear regression graph

From Figures 9, 10, and 11, we can draw some conclusions. In the 167th iteration, the error of the verification set is the smallest. The mean error is mostly distributed in [-0.02756, 0.04711]. The MSE of the verification set is $\theta.0018$, and the R-values of the training set, verification set, and test set are mostly about $\theta.999$. Consequently, the fitting effect is good.

Table 7 shows the selection of any 25 sets of the abovementioned data. As demonstrated in Table 7, the proposed method's accuracy rate can almost reach 100%.

Table 7. Partial ANN forecast data of deviation scenario 2

No.	Sensitive plate temperature of distillation column/°C	Cumene Outflow rate/kmole.h ⁻¹	Reboiler Liquid level/m	Condenser heat load/kW	C2 Reflux Molar flow/kmole.h- ¹	Actual deviation severity	Predictive deviation severity
1	182.212	75.50053	0.666554	1291.768	47.87419	I	0.998172
2	182.2333	75.54777	0.66655	1292.904	47.8707	I	0.998179
3	182.2617	75.59736	0.666537	1294.02	47.86695	I	0.99819
4	182.2967	75.64872	0.666514	1295.104	47.86376	I	0.998202
4 5	182.3382	75.70129	0.666482	1296.151	47.85983	I	0.99823
6	169.3713	72.16483	0.684575	1222.893	47.78293	II	1.997096
7	169.0847	72.1423	0.685106	1222.616	47.78176	II	1.998675
8	168.8021	72.12117	0.685639	1222.359	47.78036	II	2.000104
9	168.5236	72.10137	0.686171	1222.116	47.77894	II	2.001102
10	168.2493	72.08289	0.686703	1221.897	47.77778	II	2.001434
11	164.4588	71.92439	0.69517	1220.155	47.75714	III	2.988787
12	164.2598	71.92109	0.695692	1220.133	47.75591	III	3.009667
13	164.0651	71.91836	0.696213	1220.118	47.75487	III	3.008615
14	163.8747	71.91618	0.696733	1220.114	47.75365	III	2.999256
15	163.6885	71.91455	0.697251	1220.115	47.75249	III	2.991652
16	156.5787	72.9619	0.766858	1238.305	47.73175	IV	3.99813
17	156.5756	72.96366	0.767141	1238.332	47.73186	IV	<i>3.9986</i>
18	156.5726	72.96538	0.767423	1238.359	47.73197	IV	3.999377
19	156.5696	72.96707	0.767705	1238.389	47.73209	IV	4.000066
20	156.5666	72.96874	0.767986	1238.424	47.7322	IV	3.999481
21	156.3593	72.99962	0.804127	1238.88	47.73674	V	4.996561
22	156.3584	72.99908	0.804385	1238.867	47.7367	V	5.001536
23	156.3578	72.99854	0.804642	1238.856	47.73671	V	5.005168
24	156.357	72.99799	0.8049	1238.849	47.73672	V	5.007279
25	156.3563	72.99744	0.805157	1238.839	47.7367	V	5.007925

3.4.3 HAZOP analysis results based on AHA

It can be seen from Table 8 that when the control valve of Q-C2Reb is abnormal, the technicians have 6700 s to take targeted measures. Similarly, when the reboiler liquid level is too low, the reboiler is prone to overpressure and high temperature, which will eventually cause the reboiler to explode. The engineers should also replace the control valve within the allowed time and use detergent to clean the material dirt. If necessary, a safety interlock device shall be adopted.

Table 8. HAZOP analysis based on AHA

Process parameters	Guide words	Reason	Consequences	Recommended suggestions
Liquid level (reboiler)	More	 Too small steam quantity of the reboiler; Small opening of energy flow Q-C2Reb valve; failure of the tower bottom pump; Excessive opening of V1; The small opening 	 Affect product quality. Flood tower. Exceed the normal pressure. Damage and shorten equipment life. Cause poor thermal siphon effect. Affect the heat exchange effect of the reboiler. When the opening of the energy flow Q-C2Reb valve is 51%, the reboiler level deviation can touch the highest severity (V) within 6700 s. The temperature of the C2 main tower's 15 trays rises from 183°C to 211.3°C within 1.7 h. 	

Process parameters	Guide words	Reason	Consequences	Recommended suggestions
	Obviously more	of V8; 6. Blocked outlet pipeline at the tower bottom; 7. Excessive feeding flow of the tower; and 8. Excessive reflux at the tower top	 Affect product quality. Flood tower. Exceed the normal pressure. Damage and shorten equipment life. Cause poor thermal siphon effect. Affect the heat exchange effect of the reboiler. When the opening of the energy flow Q-C2Reb valve is 52%, the reboiler level deviation can reach V within 5406 s. The temperature of the C2 main tower's 15 trays rises from 183°C to 211.7°C within 1.4 h. 	
	Low	 Excessive low feeding; Instrument control failure; Excessive discharge or bypass valve opening; Temperature control failure of the 	 The content of cumene in PDIB increases. Product output is decreased. Liquefied gas in the reboiler is steamed and dried, which finally results in the flushing of the tower. When the opening of the energy flow Q-C2Reb valve is less than 49%, the reboiler level deviation severity reaches V within 17472 s. The temperature of the C2 main tower's 15 trays decreases from 183°C to 156.7°C within 2.6 h. 	Set indicative signs on the discharge pipeline. Set the reboiler temperature control valve block. Set the high-
	reboiler; 5. Excessive opening of V8; 6. Tower top cooling loss or no reflux:		 The content of cumene in PDIB increases. Product output is decreased. Liquefied gas in the reboiler is steamed and dried, which finally results in the flushing of the tower. When the opening of the energy flow Q-C2Reb valve is less than 48%, the reboiler level deviation severity reaches V within 7260 s. The temperature of the C2 main tower's 15 trays drops from 183°C to 156.4°C within 1.9 h. 	temperature alarm at the tower bottom; 4. Set a temperature alarm on the top of the tower. 5. Set feeding flow detection and the flow control valve block.

4. CONCLUSIONS

This paper proposed the quantitative analysis method of HAZOP-AHA. In this scheme, the traditional HAZOP identifies the deviation scene in the process. Aspen HYSYS is used to simulate the numerical deviation. The deviation severity is defined according to the deviation range of state parameters. In the end, the ANN is employed to classify and predict the data generated in dynamic simulation. Based on the simulation fruit of HYSYS, industrial members are supported to formulate safety measures that are more in line with an actual situation.

This method was applied in the industrial alkylation of benzene with propene to cumene. Two deviation scenarios (abnormal feeding flow rate and failure of flow control valve) were regarded as the analysis objects. The deviations of state parameters at different time points were divided into five severities, that is, I, II, III, IV, and V, according to the deviations of 0–5%, 5–10%, 10–15%, 15–20%, and more than 20% from initial values. We inputted the above data into the ANN as the training set and then modeled the appropriate ANN model. The results indicate that the severity of ANN's forecast deviation nearly matches the severity of the actual deviation. The real-time prediction of a system deviation ought to be realized. Therefore, by implementing HAZOP-AHA, industrial managers can take rational action more easily. The risk of accidents in the chemical process should also be reduced. The downtime caused by the accident will also be shortened. The method proposed in this paper can be applied to other processes, and the scalability is strong. The key is to obtain the dynamic simulation data of specific processes, and then the traditional HAZOP results can be modified by using the method in this paper.

HAZOP analysis, as the most widely used analysis method in process risk assessment, identifies potential hazards and operation problems of a process system systematically and logically. It puts forward suggestions and measures that have broad development prospects. Based on previous studies, this paper proposed a new method of HAZOP deviation recognition and quantification based on dynamic simulation and machine learning. We did not cover in detail the impact of this method on reducing the evaluation time of traditional HAZOP analysis because this paper mainly showed how to quantify the deviations in HAZOP analysis, namely the severity of deviations and the time to reach the deviations. In our follow-up work, we will continue to test and evaluate the improvement of this method on the time of HAZOP analysis. In addition, the following aspects can be improved: (1) This paper has mainly studied the numerical deviation, and

quantitative research on the non-numerical HAZOP deviation needs to be carried out. (2) Currently, there is still a lack of research on the transmission path of deviation, and there is even less research on the transmission mechanism of deviation. (3) The influence of multiple deviations on the system will be studied.

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APPENDIX A

Table A1. Traditional HAZOP Analysis of process

Process parameters	Guide word	Reason	Consequence	Recommended measure
Flow (feed)	Less/None	1. The valve fails to close. 2. The pump efficiency is not enough or stops running. 3. Manual adjustment is wrong	Low liquid level of distillation tower bottom	Set feed flow detection
	More	Valve fault open. Pump flow large. 2. Bypass valve open mistakenly.	Liquid level rise of rectification tower	Set up feed flow detection.2. Set up direction identification for pipeline valve
Liquid level (Reboiler)	More	Steam quantity of reboiler is small. 2. Energy flow Q-C2Reb valve is blocked. 3. Pump failure stops at tower bottom 4. V1 opening is too large. 5. V8 opening is too small 6. Outlet pipeline at the tower bottom is blocked 7. The feed flow of the tower is too large 8. Reflux flow at the top of distillation tower is too large	Affect product quality. 2. Flood tower; 3. Excess the normal pressure 4. Damage and shorten equipment life 5. Poor thermosiphon effect 6. Affect heat exchange effect of reboiler	Set level controller and pressure relief valve Set DCS status display and alarm of discharging pump. Set standby pump for discharging from tower bottom Set hermal insulation measures for discharging pipeline to prevent condensation 5. Set detection display and alarm of reflux flow.
,	Less	The feed volume is too low 2. The instrument control is malfunctioned 3. The discharge is too fast or the bypass valve is open 4. The reboiler temperature control has been broken down; the heating volume is too large 5. The valve opening is too high 6. The top of rectification tower loses cooling or no reflux	Product composition changes; 2. Product output loss; 3. The liquefied gas in the reboiler evaporates to dryness, causing the tower to flush	Set indicator for discharge pipe; 2. Set reboiler temperature control valve group; 3. Set a high-temperature alarm at the bottom of the tower; 4. Set temperature alarm at the top of the tower; 5. Set feed flow detection and flow control valve group
Temperature (main tower sensitive	Low	1. The liquid level valve fails to close; 2. Low-pressure steam pressure; 3. Low feed temperature; 4. The return flow at the top of the tower is large; 5. The reboiler is	Low tower pressure	Set a temperature alarm Reflux flow detection display and alarm are set on the top of the tower

plate of rectification		not heated; 6. Too much dirt in Reboiler		3. Formulate rules and regulations for reboiler inspection/maintenance/cleaning	
tower)	More	The liquid level valve fails to open; 2. High low-pressure steam pressure; 3. The heat input of the reboiler is large; The reboiler pipe is broken; 4. The temperature indicator fails; 5. Tower top return flow decreases	Tower over temperature and high pressure Product output is affected	Reflux flow detection display and alarm are set on the top of the tower Set a temperature alarm	
	Less/No	1. The pressure valve is open; 2. The steam volume of the reboiler is small; 3. Large reflux at the top of the tower; 4. There is no liquid level in the tower kettle; 5. The reboiler is not heated	Unstable tower pressure, affecting separation	Set pressure control system and safety valve Set the temperature control valve group of the tower kettle reboiler Set the feed flow detection and regulating valve group	
Pressure (main tower of rectification tower)	More	1. The pressure valve fails to close; Insufficient circulating water of condenser; 2. The reboiler has a large amount of steam; 3. Large amount of preheating steam; 4. Inaccurate instrument indication; 5. The tower is blocked, and the airflow is blocked in the following parts of the tower; 6. The heat input of the tower kettle is too large; 7. The reboiler pipeline leaks or breaks; 8. There is water in the feed hot oil; 9. Excess materials enter the tower; 10. The overhead condenser loses its function, and the overhead reflux loses	Unstable tower pressure affects separation; 2. Excessive venting and material loss; 3. The pressure in the tower rises, affecting production, and there is a risk of positive pressure overpressure	Set the interlock shut-off valve for heating steam of reboiler with a high and high-temperature limit of tower kettle; 2. Reflux flow detection reality and alarm are set on the top of the tower	
Liquid level (reboiler)	More	1. The steam volume of the reboiler is small. 2. Q-C2reb valve of energy flow is closed in fault. 3. The tower bottom pump is stopped in fault; 4.V1 is too large; 5.V8 spent; 6. The outlet pipeline at the tower bottom is blocked;7. The feed flow of the tower is too large; 8. The reflux at the top of the tower is too large	1. Affect product quality; 2. Flooding tower; 3. Overpressure will damage equipment and shorten the service life of equipment; 4. The thermal siphon effect should be poor; 5. Affect the heat exchange effect of Reboiler	Set liquid level controller; Pressure relief valve; 2. Set DCS status display and alarm of discharge pump; 3. The tower bottom discharge is equipped with a standby pump; 4. The discharge pipeline shall be provided with thermal insulation measures to prevent condensation and blockage; 5. Set the reflux flow detection display and alarm	
` '	Less	The feeding amount is too low; 2. Instrument control failure; 3. Discharging is too fast or the bypass valve is opened; 4. Temperature control failure of reboiler, excessive heating; 5. The valve is opened too large; 6. The tower top loses cooling or has no reflux	Changes in product composition; 2. Loss of product output; 3. The liquid liquefied gas in the reboiler is evaporated to dryness, resulting in tower flushing	The discharge pipe shall be set with indication signs; 2. Set the reboiler temperature control valve group; 3. Set a high-temperature alarm at the bottom of the tower; 4. Set temperature alarm on the top of the tower; 5. Set the feed flow detection and flow control valve group	
Leakage	Abnormal	There are sand holes in pipelines and equipment; 2. The flange sealing gasket is invalid, or the model of maintenance spare parts is wrong; 3. Pump seal failure; Condensate drain valve leaks; 5. Insufficient sealing torque of flange bolts; 6. The pipeline stress exceeds the standard	Environmental pollution, personnel poisoning, fire and explosion in serious cases	Set combustible gas alarm; 2. Check whether the layout of the fire and gas system is reasonable; 3. Set plug or blind plate for condensate drain valve; 4. Formulate bolt fastening maintenance procedures; 5. Purchase, install and pressure test in strict accordance with the design requirements; 6. Pipe reasonably to eliminate pipe stress	
Reflux ratio	More	Reflux ratio controller failure; Improper design parameters	The downcomer flow is not timely, resulting in flooding of the tower	Check the reflux ratio controller and readjust the corresponding parameters	
	Less	Reflux ratio controller failure; Low design parameters	Reduced product quality		
Power On/Off	Other	Containers and pipelines are not fully replaced, and there is an explosion hazardous environment; 2. There are construction debris in pipeline equipment; 3. The system safety facilities have not been restored or put into use, such as filters, pressure relief valves, on-site and remote instruments, etc.; 4. Disposal of toxic or combustible substances	Personnel poisoning; Fire and explosion risk; Risk of equipment damage	Set purging and replacement utility pipes and corresponding regulations; 2. Set temporary filters to remove construction debris; 3. Strictly implement the system of equipment during start-up; 4. Formulate toxic and combustible discharge regulations and set up corresponding collection and disposal facilities	

APPENDIX B

Table B1. ANN Forecast Data deviation scenario 1

No	Condenser Liquid level/m	Condenser heat loss/kW	Reboiler heat loss/kW	C2 Reflux Molar Flow/kmole.h ⁻¹	C2 out stream flow rate	C2 distillation temperature/°C	Actual deviation severity	Pre. Dev.Sev.
1	0.41494	917.2867	905.4851	37.54734	59.09102	152.558	V	4.982553
2	0.415193	918.2758	905.5465	37.5664	59.17122	152.4594	V	4.989231
3	0.415435	919.2003	905.5896	37.58448	59.24742	152.3612	V	4.99527
4	0.415665	920.0761	905.6175	37.6016	59.31974	152.2637	V	5.000703
5	0.415883	920.8908	905.6306	37.61776	59.38818	152.1664	V	5.005362
6	0.41609	921.6441	905.6303	37.63296	59.45289	152.0694	V	5.009258
7	0.416287	922.3437	905.6178	37.64724	59.51397	151.9725	V	5.012306
8	0.416473	923.0087	905.5966	37.66062	59.57156	151.876	V	5.014587
9	0.416649	923.6148	905.5692	37.6731	59.6257	151.7794	V	5.01598
10	0.416815	924.1799	905.5317	37.68472	59.67662	151.6828	V	5.016524
11	0.360137	569.3351	629.9581	27.63221	40.7707	174.6996	V	5.001964
12	0.359812	569.3077	632.0012	27.71239	40.66874	174.6343	V	5.001794

13	0.359508	569.501	634.3506	27.79472	40.57362	174.5679	V	5.001605
14	0.359227	569.9207	636.9948	27.8791	40.48658	174.501	V	5.001402
15	0.358975	570.5759	639.9203	27.96538	40.40878	174.4336	V	5.00119
16	0.358751	571.4679	643.1115	28.05347	40.34089	174.3652	V	5.000974
17	0.358564	572.6098	646.5491	28.14324	40.28457	174.2959	V	5.000761
18	0.358414	573.999	650.2131	28.23459	40.24089	174.2257	V	5.000561
19	0.358305	575.631	654.0821	28.32744	40.21038	174.1545	V	5.000381
20	0.358237	577.5012	658.1321	28.42169	40.19372	174.0821	$\overset{\cdot}{V}$	5.000232
21	0.42487	969.0588	938.0727	39.18469	61.97942	145.4059	V	4.993577
22	0.424873	969.0788	938.0871	39.18532	61.98037	145.4057	$\overset{\cdot}{V}$	4.994309
23	0.424876	969.0969	938.1004	39.18594	61.98124	145.4055	$\overset{\cdot}{V}$	4.995027
24	0.424879	969.1195	938.115	39.18656	61.98227	145.4055	$\stackrel{'}{V}$	4.995907
25	0.424882	969.1387	938.1301	39.18719	61.98319	145.4053	$\stackrel{'}{V}$	4.996653
26	0.424884	969.1614	938.1444	39.18782	61.98414	145.4052	$\stackrel{'}{V}$	4.997493
27	0.424887	969.1771	938.1577	39.18845	61.98506	145.4054	V	4.998342
28	0.42489	969.2	938.1729	39.18905	61.98599	145.4051	V	4.999101
29	0.424893	969.2197	938.1855	39.18969	61.98693	145.4053	V	4.999978
30	0.424896	969.2403	938.201	39.19032	61.98785	145.4053	V	5.000815
31	0.426038	1004.583	984.525	40.75855	62.61469	154.0975	V	5.053792
32	0.426437	1007.139	985.9184	40.81051	62.74759	153.6835	V	5.045452
33	0.426835	1007.137	987.2721	40.86101	62.87993	153.2753	V	5.034943
34	0.427232	1012.171	988.5845	40.90998	63.01166	152.8733	V	5.021133
35	0.427626	1012.171	989.8533	40.95743	63.14269	152.4778	V	5.002946
36	0.428019	1017.084	991.0783	41.00327	63.27288	152.0892	V	4.980002
37	0.428409	1017.084	992.2545	41.04753	63.40216	151.7075	V	4.951357
38	0.428796	1019.492	993.3851	41.0902	63.5304	151.3332	V	4.917324
39	0.42918	1021.802	994.4673	41.1312	63.65752	150.9662	$\stackrel{r}{V}$	4.877423
40	0.42916	1024.193	995.4994	41.17057	63.7834	150.6069	$\stackrel{r}{V}$	4.832477
41	0.434832	1028.558	983.8834	40.94676	64.8277	162.402	V V	4.902157
42	0.43469	1028.023	983.9163	40.93113	64.78614	162.5834	$\stackrel{r}{V}$	4.922272
42	0.434557	1028.023	983.9431	40.91596	64.74741	162.7632	$\stackrel{\scriptstyle V}{V}$	4.942044
44	0.434432	1027.066	983.9605	40.91390	64.71136	162.7632	$\stackrel{r}{V}$	4.961505
45	0.434432	1027.000	983.9678	40.88699	64.67787	163.1173	$\stackrel{\scriptstyle V}{V}$	4.980616
46	0.434205	1026.237	983.9631	40.87317	64.64683	163.2917	$\stackrel{r}{V}$	4.999548
47	0.434102	1025.866	983.9468	40.85975	64.61809	163.4643	$\stackrel{r}{V}$	5.018172
48	0.434102	1025.513	983.9166	40.84673	64.59152	163.6349	$\stackrel{\scriptstyle V}{V}$	5.036686
49	0.433917	1025.186	983.8723	40.83418	64.567	163.8037	$\stackrel{\scriptstyle V}{V}$	
50	0.433917		983.8129	40.82196	64.5444	163.9704	$\stackrel{\scriptstyle V}{V}$	5.054899 5.072936
51	0.46641	1024.876 1280.245	1128.821	48.07488	75.41508	123.5878	IV	3.686922
52	0.466229	1279.802	1129.434	48.11344	75.35558	122.7383	IV IV	3.823484
53	0.466055	1279.493	1130.353	48.1406	75.29887	121.9866	IV IV	3.924797
54	0.465892	1279.335	1130.555	48.1558	75.2465	121.3205	IV IV	3.994467
55	0.465747	1279.345	1133.046	48.15868	75.20006	120.7279	IV IV	4.037188
56	0.465622	1279.538	1134.759	48.14914	75.16112	120.7279	IV IV	4.057947
57	0.465522	1279.924	1136.663	48.1273	75.13089	119.72	IV IV	4.061429
58	0.465451	1279.924	1138.714	48.09349	75.11071	119.72	IV IV	4.05174
59	0.465413	1280.303	1140.862	48.04798	75.10159	118.8855	IV IV	4.032413
60	0.465409	1281.283	1140.862	47.99145	75.10139	118.5139	IV IV	4.006293
61	0.43342	1048.339	1003.245	41.49292	65.05122	147.149	IV IV	4.195923
62	0.433732	1048.339	1003.606	41.51229	65.15307	146.8777	IV IV	4.145242
63	0.434037	1049.978	1003.000	41.52996	65.25215	146.6134	IV IV	4.101866
64	0.434334	1051.329	1003.91	41.54613	65.34841	146.3561	IV IV	4.06055
65	0.434623	1053.025	1004.133	41.56065	65.44175	146.1054	IV IV	4.023875
66	0.434902	1055.795	1004.342	41.5736	65.53203	145.8612	IV IV	3.992234
	0.40-4-0	40.55		44 50 50 6	C# C4040			
67 68	0.435173 0.435434	1057.073 1058.282	1004.55 1004.571	41.58502 41.59491	65.61918 65.70308	145.624 145.3931	IV IV	3.964265
69	0.435686	1058.282	1004.571	41.60333	65.78366	145.1688	IV IV	3.940259 3.922622
70	0.435928	1060.454	1004.338	41.61026	65.86086	144.9511	IV IV	3.908217
71	0.455928	1122.143	964.1839	41.62445	71.74368	138.836	IV IV	3.818844
72	0.455458	1114.352	960.3821	41.4567	71.74308	140.2773	IV IV	4.006698
73	0.453438	1114.332	956.7073	41.28939	71.06541	141.7236	IV IV	4.087714
73 74	0.45345	1099.023	953.1512	41.12293	70.72411	143.1637	IV IV	4.06613
75	0.452438	1099.023	949.7041	40.9577	70.38215	144.5877	IV IV	3.994121
76		1091.499	946.3569	40.79403	70.04002	145.9848	IV IV	3.930637
77	0.451423 0.450406	1076.767	943.102	40.63231	69.69814	147.3461	IV IV	3.913752
78	0.449389	1069.567	939.9344	40.47286	69.35683	148.6634	IV IV	3.955277
79	0.448371	1062.485	936.8484	40.31603	69.01632	149.9296		4.048739
80	0.448371	1055.528	933.8358	40.31603	68.67679	151.1391	IV IV	4.179244
80 81	0.436989	1066.876	1018.178	42.30295	65.94191	162.2018	IV IV	4.179244
82	0.436989	1068.012	1018.178	42.30293 42.32897	65.99224	161.9651	IV IV	4.236672
				42.32897	66.04307			
83	0.437284	1069.143 1070.282	1019.567 1020.248	42.38002	66.04307	161.7256	IV IV	4.145971 4.099965
84	0.437434					161.4838		
85 86	0.437586	1071.423	1020.92	42.40501 42.42964	66.14606 66.19817	161.2397	IV IV	4.053614
86	0.437739	1072.56	1021.582			160.9937	IV IV	4.007167
87	0.437892	1073.702	1022.231	42.45386	66.25065	160.7461	IV IV	3.960519
88	0.438048	1074.839	1022.868	42.47765	66.30346	160.4974	IV IV	3.913973
89	0.438204	1075.973	1023.49	42.501	66.35657	160.2476	IV IV	3.867552
90	0.438361	1077.106	1024.097	42.52387	66.40996	159.9972	IV IV	3.821349
91	0.468592	1303.029	1151.476	46.91994	76.20726	120.5057	IV IV	4.024045
92	0.468914	1303.838	1149.636	46.80952	76.31422	120.3054	IV	4.02197

93	0.469232	1304.401	1147.371	46.69695	76.41917	120.1219	IV	4.01778
94	0.469542	1304.688	1144.68	46.58226	76.52032	119.9574	IV	4.011149
95	0.469838	1304.671	1141.57	46.46569	76.61595	119.8138	IV	4.001666
96	0.470116	1304.324	1138.051	46.34722	76.70446	119.6932	<i>IV</i>	3.988826
97	0.470371	1303.624	1134.139	46.22696	76.78423	119.5971	IV.	3.972054
98	0.470597	1302.548	1129.852	46.10491	76.8537	119.5276	IV	3.950753
99	0.470792	1301.081	1125.214	45.9811	76.9114	119.4868	IV W	3.924251
100	0.470951	1299.211	1120.246	45.85554	76.95606	119.4756	IV	3.891981
101	0.467452	1224.29	1028.135	43.74958	75.57403	124.202	III	2.987371
102	0.466807	1216.889	1022.207 1016.431	43.59417 43.43688	75.34259 75.0969	124.9467 125.7585	III III	2.96414 2.954543
103 104	0.466117 0.465386	1209.315 1201.613	1010.431	43.43688	73.0969	125.7385	III	2.9562
104	0.464617	1193.8	1005.382	43.11754	74.56669	127.5878	III	2.967945
106	0.463812	1185.898	1000.119	42.95563	74.28418	128.6058	III	2.987668
107	0.462975	1177.937	995.0325	42.79227	73.99147	129.6914	III	3.013025
108	0.462108	1169.937	990.1234	42.62769	73.68966	130.8422	III	3.044019
109	0.461214	1161.916	985.3905	42.46207	73.37977	132.0552	III	3.083872
110	0.460297	1153.896	980.8311	42.29548	73.06276	133.325	III	3.140873
111	0.46689	1283.933	1132.815	47.94536	75.58018	129.9657	III	2.571747
112	0.466748	1283.495	1132.902	47.99304	75.5334	129.0218	III	2.718996
113	0.466607	1283.143	1133.254	48.03283	75.48672	128.1797	III	2.868898
114	0.466468	1282.894	1133.875	48.06373	75.44159	127.4317	III	3.016596
115	0.466338	1282.773	1134.755	48.08504	75.39949	126.7686	III	3.156946
116	0.46622	1282.792	1135.879	48.09628	75.36191	126.1808	III	3.287087
117	0.466118	1282.969	1137.218	48.09731	75.33022	125.6574	III	3.404787
118	0.466037	1283.311	1138.742	48.08809	75.30571	125.1893	III	3.509554
119	0.465979	1283.828	1140.408	48.06876	75.2896	124.7669	III	3.601219
120	0.465949	1284.518	1142.171	48.03968	75.28284	124.3818	III	3.680445
121	0.441621	1097.88	1032.249	42.87044	67.50304	155.1472	III	3.097243
122	0.44176	1098.631	1032.378	42.87987	67.54906	154.9577	III	3.078982
123	0.441897	1099.355	1032.484	42.88863	67.59406	154.7728	III	3.06203
124	0.442031	1100.055	1032.562	42.8968	67.63803	154.5929	III	3.046121
125 126	0.442161 0.442289	1100.722 1101.358	1032.617 1032.648	42.90431 42.91121	67.68087 67.72254	154.418 154.2484	III III	3.031615 3.018407
126	0.442412	1101.961	1032.653	42.91752	67.76299	154.0835	III	3.006322
128	0.442533	1102.532	1032.639	42.92323	67.80216	153.9235	III	2.995452
129	0.442649	1102.332	1032.6	42.92833	67.84	153.7683	III	2.985526
130	0.442762	1103.583	1032.539	42.93291	67.87651	153.6177	III	2.976271
131	0.444091	1107.046	1027.846	42.93221	68.28657	151.2678	III	2.93514
132	0.444104	1106.917	1027.554	42.92926	68.28909	151.1786	III	2.937846
133	0.444113	1106.769	1027.266	42.92617	68.29026	151.0902	III	2.940724
134	0.444118	1106.603	1026.979	42.92297	68.29011	151.0023	III	2.943817
135	0.444119	1106.424	1026.699	42.91968	68.28869	150.9147	III	2.946938
136	0.444116	1106.226	1026.425	42.91629	68.28608	150.8275	III	2.950624
137	0.44411	1106.016	1026.157	42.91284	68.28229	150.7406	III	2.954261
138	0.444101	1105.792	1025.897	42.90932	68.27742	150.6537	III	2.958174
139	0.444088	1105.561	1025.645	42.90579	68.27154	150.5665	III	2.961963
140	0.444073	1105.316	1025.403	42.90219	68.26463	150.4794	III	2.966217
141	0.443397	1100.066	1022.872	42.82679	68.01302	148.5723	III	3.037723
142	0.443363	1099.883	1022.859	42.82331	68.00103	148.4791	III	3.037946
143	0.44333	1099.703	1022.852	42.81982	67.98937	148.3863	III	3.038442
144	0.443298	1099.532	1022.847	42.81633	67.9781	148.2937	III	3.038451
145	0.443268	1099.372	1022.849	42.81284	67.96723	148.2015	III	3.038005
146	0.443238	1099.221	1022.853	42.80932	67.95678	148.1102	III	3.037053
147	0.44321	1099.078	1022.859	42.80579	67.94677	148.0188	III	3.035726
148 149	0.443183 0.443157	1098.936 1098.812	1022.867 1022.876	42.80223 42.79867	67.93717 67.92806	147.928 147.838	III III	3.034872 3.03257
150	0.443133	1098.695	1022.884	42.79507	67.92806	147.7489	III	3.029793
150	0.443133	1287.045	1136.634	47.58038	75.79565	137.714	II	1.808402
152	0.46746	1286.563	1135.666	47.64084	75.77193	136.2245	II	1.949218
153	0.467373	1286.045	1134.771	47.7043	75.74249	134.7905	II	2.072611
154	0.467271	1285.504	1133.998	47.76852	75.70782	133.4346	II	2.188081
155	0.467154	1284.961	1133.389	47.83142	75.66858	132.1733	II	2.305667
156	0.467026	1284.428	1132.985	47.89093	75.62566	131.0158	II	2.433202
157	0.468813	1261.414	1076.935	45.37515	76.12859	130.9923	II	2.063559
158	0.468492	1257.09	1072.833	45.28397	76.01089	131.4137	II	2.047365
159	0.46814	1252.608	1068.788	45.19214	75.88281	131.8609	II	2.033389
160	0.467757	1247.982	1064.812	45.09974	75.74466	132.3332	II	2.0207
161	0.467345	1243.232	1060.914	45.00684	75.59678	132.8301	II	2.008388
162	0.466904	1238.367	1057.104	44.91349	75.43944	133.3505	II	1.996527
163	0.466437	1233.403	1053.392	44.81976	75.27344	133.8939	II	1.985488
164	0.465944	1228.35	1049.785	44.72562	75.09927	134.4593	II	1.976352
165	0.465428	1223.232	1046.289	44.63124	74.91749	135.045	II	1.969206
166	0.46489	1218.061	1042.908	44.53661	74.72874	135.6501	II	1.966109
167	0.464331	1212.847	1039.648	44.44189	74.53353	136.2728	II	1.969867
168	0.463753	1207.605	1036.511	44.34711	74.33246	136.9116	II II	1.983487
169 170	0.463159 0.4672	1202.351 1286.725	1033.498 1136.369	44.25236 47.83059	74.12618 75.68932	137.5647 136.1901	II II	2.009986 1.858814
170	0.4672	1195.797	1086.239	45.38557	73.88932	145.438	II	1.987122
172	0.455599	1195.808	1086.239	45.38597	71.94057	145.4383	II	1.987199
. ,	0	11/5.000	10001210	.5.56571	, 11, 11, 11	1.0000		1.,011,7

173	0.4556	1195.824	1086.254	45.38627	71.94206	145.438	II	1.986653
174	0.455602	1195.836	1086.262	45.38662	71.94259	145.4382	II	1.986816
175	0.455604	1195.847	1086.269	45.387	71.94312	145.438	II	1.986939
176	0.455605	1195.86	1086.277	45.38735	71.94365	145.4379	II	1.98672
177	0.455607	1195.873	1086.285	45.38769	71.94418	145.4378	II	1.986651
178	0.455608	1195.887	1086.294	45.38803	71.94472	145.4377	II	1.986434
179	0.45561	1195.899	1086.301	45.38839	71.94526	145.4377	II	1.986372
180	0.455612	1195.911	1086.311	45.38873 45.40683	71.94579 71.97391	145.4375 145.4371	II II	1.986571
181 182	0.455698 0.4557	1196.605 1196.618	1086.746 1086.753	45.40683 45.40713	71.97391	145.4371	II II	1.980615 1.980502
183	0.455702	1196.634	1086.762	45.40753	71.97507	145.4372	II	1.980089
184	0.455704	1196.644	1086.769	45.40787	71.97562	145.4374	II	1.980456
185	0.455705	1196.66	1086,778	45.40822	71.97619	145.4373	II	1.980051
186	0.455707	1196.672	1086.786	45.40859	71.97676	145.4373	II	1.980237
187	0.455709	1196.686	1086.792	45.40892	71.97733	145.4374	II	1.979962
188	0.455711	1196.697	1086.8	45.40932	71.97787	145.4376	II	1.980124
189	0.455712	1196.711	1086.807	45.40963	71.97841	145.4375	II	1.97988
190	0.455714	1196.725	1086.814	45.40995	71.97896	145.4376	II	1.979531
191	0.455266	1193.163	1084.591	45.3159	71.83363	145.4388	II	2.008602
192 193	0.455268 0.455269	1193.178 1193.192	1084.598 1084.605	45.31625 45.31659	71.83416 71.83468	145.4387 145.4388	II II	2.008239 2.007871
193	0.455271	1193.192	1084.614	45.31693	71.8352	145.4387	II	2.00/8/1
195	0.455273	1193.214	1084.622	45.31728	71.8357	145.4388	II	2.008134
196	0.455274	1193.227	1084.628	45.31762	71.83621	145.4385	II	2.007814
197	0.455276	1193.239	1084.636	45.318	71.83671	145.4386	II	2.00783
198	0.455277	1193.252	1084.644	45.31833	71.83722	145.4388	II	2.007701
199	0.455279	1193.265	1084.653	45.31869	71.83773	145.4391	II	2.007598
200	0.45528	1193.278	1084.661	45.31902	71.83824	145.4389	II	2.007473
201	0.467381	1290.346	1142.455	47.74254	75.75849	145.503	I	1.049617
202	0.467381	1290.342	1142.454	47.74251	75.75834	145.5029	I	1.049757
203	0.467381	1290.341	1142.453	47.74251	75.75821	145.503	I	1.049577
204 205	0.46738 0.46738	1290.338 1290.337	1142.455 1142.455	47.74249 47.74253	75.75808 75.75796	145.5029 145.5031	$rac{I}{I}$	1.049718 1.049724
206	0.467379	1290.334	1142.455	47.74247	75.75782	145.503	I	1.049724
207	0.467379	1290.33	1142.455	47.74246	75.75769	145.5031	Ī	1.050068
208	0.467379	1290.331	1142.457	47.74239	75.75758	145.5032	Ī	1.049841
209	0.467378	1290.329	1142.457	47.74242	75.75749	145.5032	I	1.049865
210	0.467378	1290.33	1142.457	47.74243	75.75741	145.503	I	1.049544
211	0.468908	1297.968	1139.794	47.7982	76.27011	145.6038	I	0.941815
212	0.468841	1297.255	1139.278	47.79791	76.24554	145.6088	I	0.953102
213	0.468767	1296.531	1138.823	47.79768	76.21875	145.6136	I	0.964958
214	0.468688	1295.81	1138.428	47.7975	76.19011	145.6177	I	0.976303
215 216	0.468603 0.468514	1295.092 1294.381	1138.096 1137.825	47.7974	76.15987 76.12835	145.6215 145.6245	$rac{I}{I}$	0.987954 0.999667
217	0.468421	1293.688	1137.623	47.79728 47.79717	76.12833	145.627	I	1.011012
217	0.468327	1293.088	1137.473	47.79717	76.06276	145.627	I	1.022069
219	0.468231	1292.369	1137.388	47.79705	76.02929	145.6309	Ī	1.032989
220	0.468134	1291.757	1137.36	47.79689	75.99579	145.6319	Ī	1.042849
221	0.467378	1290.328	1142.459	47.7424	75.75731	145.5032	I	1.049748
222	0.467377	1290.326	1142.459	47.7424	75.75721	145.5031	I	1.049927
223	0.467377	1290.323	1142.462	47.74237	75.75713	145.5032	I	1.050212
224	0.467377	1290.325	1142.462	47.74236	75.75706	145.5032	I	1.049833
225	0.467377	1290.321	1142.463	47.74236	75.75698	145.5033	I	1.05027
226	0.467377	1290.324	1142.464	47.74231	75.75693	145.5032	I	1.049905
227	0.467376	1290.323	1142.465	47.74233	75.75688	145.5031	I	1.049895
228 229	0.467376 0.467376	1290.322 1290.325	1142.465 1142.465	47.7423 47.74227	75.75682 75.75681	145.5035 145.5028	I I	1.04999 1.04948
230	0.467376	1290.323	1142.466	47.74227	75.75676	145.5033	I	1.049849
231	0.467827	1293.395	1143.179	47.76542	75.90779	145.4814	Ī	1.000576
232	0.467827	1293.278	1142.979	47.76529	75.90715	145.4813	Ī	1.002001
233	0.467823	1293.141	1142.788	47.76512	75.90553	145.4814	I	1.004642
234	0.467817	1293.005	1142.608	47.76499	75.90306	145.4816	I	1.006239
235	0.467809	1292.851	1142.438	47.76486	75.8997	145.4822	I	1.008953
236	0.467798	1292.694	1142.282	47.76475	75.89558	145.4828	I	1.011267
237	0.467785	1292.531	1142.137	47.76465	75.89077	145.4835	I	1.013833
238	0.46777	1292.363	1142.008	47.76453	75.88531	145.4844	I	1.016635
239 240	0.467754 0.467735	1292.192 1292.019	1141.892 1141.788	47.7644 47.76428	75.87927 75.87272	145.4851	$rac{I}{I}$	1.019516 1.022442
240	0.467/35	1303.216	1141.788	47.76428 47.80761	75.87273 76.339	145.4863 145.5242	$\stackrel{I}{I}$	0.862238
241	0.469043	1303.216	1147.373	47.80594	76.34948	145.5345	I	0.865341
243	0.469108	1302.601	1145.632	47.80448	76.35576	145.544	I	0.869458
244	0.469121	1302.184	1144.78	47.80323	76.35794	145.5532	Ī	0.876029
245	0.469122	1301.715	1143.952	47.80209	76.35608	145.5623	Ī	0.882808
246	0.469112	1301.19	1143.154	47.80112	76.35031	145.5702	I	0.890654
247	0.469091	1300.612	1142.39	47.8003	76.3408	145.5782	I	0.899919
248	0.469059	1299.999	1141.668	47.79959	76.3278	145.5852	I	0.909294
249	0.469018	1299.347	1140.991	47.79905	76.3115	145.5919	I	0.919608
250	0.468967	1298.669	1140.366	47.79858	76.2922	145.5979	I	0.93048