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Algorithm design of the ratio control of chlorine and hydrogen in hydrogen chloride synthesis

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ABSTRACT

The mechanism of hydrogen chloride synthesis is analyzed, and the main factors affecting the ratio of chlorine and hydrogen in hydrogen chloride synthesis are found out. For hydrogen chloride synthesis procedure which is nonlinearly coupling, lagged, multivariate and multiple correlation control object, a chain system control method is brought forward to control the ratio of chlorine and hydrogen in hydrogen chloride synthesis process. The cause and effect relationships of key factors are analyzed, then build the model which consisted of four unit models and two causality chains. Through the field data simulation, the results show that the chain system model has strong real-time performance, stability, anti-interference ability, and the control effect is good.

Keywords: hydrogen chloride synthesis; control; chain system model; chain control system

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INTRODUCTION

With the rapid development of Chlor-alkali industry, the production capacity of synthetic hydrochloric acid is getting bigger. The Chlor-alkali enterprises use chlorine and hydrogen make direct synthesis of hydrogen chloride usually, then hydrochloric acid was product though water absorbing the hydrogen chloride. The hydrogen and chlorine are inputted into the synthesis furnace, the molecule ratio of hydrogen and chlorine is not only affects the product quality, but threats the safety of production process. To protect the security and stability of hydrogen chloride production process, we must effectively control the amount of chlorine and hydrogen inputting into the furnace, so as to ensure that the molecule ratio of chlorine and hydrogen satisfies the production conditions.

The ratio control of chlorine and hydrogen inputting into the furnace has been greatly concerned on many aspects, consequently, many kinds of control schemes appear. The old control method, based on artificial detection of flame color and pressure fluctuations inside the furnace, which manual adjust valve open degree to the production process. Although this method is reliable，which waste human resource and the control accuracy is not high，and it will cause accident when the operation staff are unable to focus on that. Now someone has already designed proportion controller to control the chlorine and hydrogen flow [1,2]. So as to control the flow easier and more accurate, adopts one big and one small automatic control valves[3], the minor caliber automatic valve adjust compensation when the indicator minute fluctuate; when process indicators fluctuations, minor caliber automatic control valve is not enough to adjust the hydrogen, the compensation feedback to the large automatic control valve to adjust the compensation. Someone has designed fuzzy control system with the adaptive ability [4], which is based on operational experience of artificial detection of flame color inside the furnace. However, due to the large lag, multiple interference and other issues of hydrogen chloride synthesis, the previous established models have not yet reach satisfactory results in practical applications [5].

This paper considers comprehensively from the safety of the production process and the product quality, taking the safety and the product quality as the control goal. It adopts the chain system control method to analyze the mechanism of the methanol synthesis, finds out the main factors which influence the quality of hydrochloric acid and the safety of the process. Then sets up a chain systematic structure model. This model offers strong stability, anti-interference ability and fault-tolerance to the hydrogen chloride synthesis system with a big lag. The model of the hydrogen chloride synthesis system is made up of four unit models and two interrelated causality chains. One is a quality chain, and the other is a safety chain. At last, we will realize the object of paper, it sets up dynamic mathematics model with the chain system structure which improves the quality and safety through prediction and control.

EXPERIMENTAL SECTION

Although the used synthetic furnace for hydrochloric acid is different, the production process of synthesis hydrochloric acid is basically same. The production of hydrochloric acid includes 3 processes, such as hydrogen chloride synthesis, hydrogen chloride gas cooling and hydrogen chloride gas absorption [6].

The hydrogen is produced by electrolysis of water, then hydrogen was treated by the flame arrester, last the hydrogen and the chloride from compressor are inputted into the synthetic furnace lamp caps within the same time at a certain degree of mole ratio (1.00: 1.05~1.00: 1.10).Chlorine gas and hydrogen gas are mixed in the combustion nozzle, after the ignition of hydrogen, the chlorine gas and the hydrogen gas are burned completely and the hydrogen chloride gas is generated.

The temperature of hydrogen chloride out of the synthetic furnace is very high, then the temperature of hydrogen chloride drops to 40 degrees Celsius through two stage cooler cooling. The qualify hydrochloric acid is produced when the cool hydrogen chloride gas is inputted into a falling film absorption tower and the dilute hydrochloric acid from the tail absorption tower is absorbed. The hydrogen chloride gas out of falling film absorption tower, which is not completely absorbed in the tail absorption tower. The hydrogen chloride gas is further absorbed in the tail absorption tower. The dilute hydrochloric acid is used as absorption liquid in the falling film absorption tower. A little amount of exhaust gas is discharged behind the water jet pump to a water seal [1]. The overall reaction in the chlorine and hydrogen synthesis reaction is as follows [6]:

Reaction $H_2 + Cl_2 \rightarrow 2HCl + 184.096$ kJ

The study is under the condition which the pressure of hydrogen and chlorine input the synthesis furnace is constant, and the controlled targets are the quality of hydrochloric acid, safety and reliability of production process.

We know that in the hydrogen chloride synthesis process of hydrogen combustion in chlorine, the excess hydrogen or chlorine not only influence product quality but threat the safety of the production process. So we must effectively control the amount of chlorine and hydrogen inputting into the synthesis furnace according to the technological conditions in order to guarantee hydrogen chloride production's safety and stability. Hydrogen is excess in the normal production process. If the chlorine is excess, the chlorine and hydrogen form an explosive mixture of gas ,the gas will threat the safety of the production [7].

If the pressure of hydrogen and chlorine inputting to the synthetic furnace is constant, the hydrogen chloride synthesis mainly control the hydrogen chloride ratio through the flow control of hydrogen and chlorine inputting into the synthetic furnace However, due to various reasons, the hydrogen chloride ratio often deviates because the production condition changes. For example, the variation of air temperature and seasonal climate changes will cause the gas density changes, and the ingredient of hydrogen and chlorine in the synthetic furnace will change accordingly; The other, although the flow does not change, the purity change of the chlorine and the hydrogen also may cause the actual ratio change [1].

According to the above analysis， we respectively take the opening degree of hydrogen flow valve and chlorine flow valve as control variables, and the opening degree of chlorine is primary control variable, the opening degree of hydrogen is secondary control variable. In addition, the model take the quality and safety as the thinking factors to establish the quality causality chain and the safety causality chain. In the fact, we control the quality based on the safety of the process. The actually the hydrogen is excess, the excess amount is generally between 5% and 10%. The more excess hydrogen in the synthesis process can cause the purity decrease of hydrogen chloride which is adverse to following production processes; the excess hydrogen also can lead to synthesis gas flow increase relatively, hydrogen chloride absorption system parameter fluctuations, synthetic furnace pressure fluctuation impact absorption operation and hydrochloric acid quality fluctuation. In addition, when the excess hydrogen does not participate in the reaction of combustion, the flame will be instability and pale [7,8]. If the chlorine is excess, the excess chlorine does not participate in combustion, flame color will be yellow, when serious the color will be red; If the chlorine is excess, the flame color will be pale ,and the chlorine and the hydrogen form an explosive mixture gas which threats the safety of the entire production device [7].

Combination of the above analysis, determined the following four controlled parameter:

1) Outlet gas pressure of hydrogen chloride synthesis furnace
The actual operation which the hydrogen is excess, the excess amount is generally between 5% and 10%. The more excess hydrogen will caused synthetic furnace pressure fluctuation.
2) Hydrogen chloride purity of synthesis furnace outlet gas
Hydrogen chloride purity affect hydrogen chloride absorption, which will caused the quality fluctuation of hydrochloric acid.
3) Synthesis furnace flame color

Because the hydrogen combustion in chlorine is intense chemical reaction, high temperature induced free radical chain reaction which generates hydrogen chloride, at the same time, emit a lot of heat, while the excited state hydrogen and chlorine atom will radiate out specific spectrum, it performance in different flame color according to hydrogen chloride ratios. The flame color is unstable and white when hydrogen excess, at normal ratio the flame color is pale, the flame color is yellow if chlorine excess. Therefore, we can control the components of product by observing the flame color of synthesis furnace [8].

The colorimeter is used to detect synthesis furnace flame color, any beam visible light is characterize by three-dimensional coordinates X, Y, Z of XYZ Chroma space in the 1931CIE-XYZ standard colorimetry system. In CIE (XYZ) color map, each point represents a certain color. However, the human eye cannot distinguish the color change when the coordinates of the point changes , the color change which is called tolerance. Studies have shown that, in the CIE (XYZ) color map, various regions' tolerance is different [5].Doing the projection transformation to (X, Y) plane, The coordinate transformation is as follows:

Reaction 1 $$u = \frac{4x}{x + 15y + 3z}$$

Reaction 2 $$v = \frac{9y}{x + 15y + 3z}$$

then

Reaction 3 $$u = \frac{4x}{3 - 2x + 12y}$$

Reaction 4 $$v = \frac{9y}{3 - 2x + 12y}$$

$$w = 1 - u - v$$

At uniform chromaticity scale map, take the distance e which is between the measured working point from standard working point's distance as the controlled parameters[5,8]. That is as follows:

Reaction 5 $$e = \sqrt{(u - u_0)^2 + (v - v_0)^2}$$

Among them, u_0 and v_0 are standard working point's chroma coordinate, u and v are measured as working point's Chroma coordinate.

4) Free chlorine content of synthesis furnace outlet gas
In normal production process, the hydrogen is excess. If chlorine excess occur, chlorine and hydrogen form an explosive mixture gas which threat the safety of the entire production device. The content of free chlorine gas is detected by chlorine RJM/HT-68 online detector, the detection method is simple and rapid, only need to put the film probe mount on the gas outlet, the content of free chlorine gas can be detected online

Analyzing the causality according to the mechanism of the hydrogen chloride synthesis, this paper finds out two pieces of causal chains. The first is the quality chain L1, and the second is the safety chain L2. On this basis, the following hypothesis is made:

Supposing that, the opening degree of the hydrogen flow valve is Z_{10}; The pressure of hydrogen chloride synthetic furnace outlet gas is Z_{11}; the purity of hydrogen chloride of synthetic furnace outlet gas is Z_{12}; The comprehensive effect of influences on Z_{10} by the purity, composition and temperature of hydrogen, etc. is regarded as the perturbation v_{10}, and K_1=2. The quality chain L1 of the reaction tower is defined as

$$L1=\{<z_{10}, z_{11}>, <z_{11}, z_{12}>\}, k_1 = 2$$

Supposing that, the opening degree of the chlorine flow valve is Z_{20}, the flame brightness of the synthetic furnace is Z_{21}, and the content of free chlorine out of the synthetic furnace is Z_{22}. The comprehensive influences on Z_{21} by Purity, composition and temperature of the input chlorine, etc. is regarded as the perturbation v_{20}, and K_2=2. The safety chain L2 is defined as

$$L2 = \{<z_{20}, z_{21}>, <z_{21}, z_{22}>\}, k_2 = 2$$

The block diagram of the hydrogen chloride synthesis systemic chain system model is given in Figure 1.

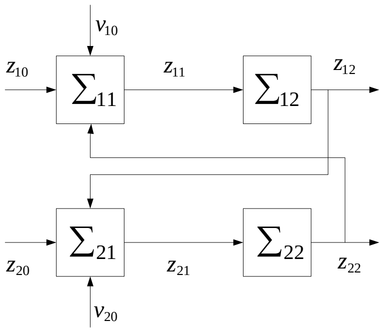

Fig.1.The block diagram of the hydrogen chloride synthesis systemic chain system model

Supposing that, the dynamic model of the subsystem in hydrogen chloride synthesis systemic is Σ_{ij} take the shape [9,10]:

$$z_{ij}(t+1) = F_{ij}(X_{ij}(t))z_{ij-1}(t-d_{ij-1}^{ij}) + v_{ij}$$

Among them, X_{ij} is a variable string set that is related with the output. It is made up of two parts: one is the control input which has a direct effect on Σ_{ij}, and the other is the measured output which has correlation interaction to Σ_{ij}; $z_{ij}, z_{ij-1} \in Z$. z_{ij-1} are inputs which have direct influence on unit Σ_{ij} output z_{ij}; d_{ij-1}^{ij} is the lag step that z_{ij-1} is opposite to z_{ij}. F_{ij} is a set of parameters to be identified, v_{ij} is a perturbation. So every unit model can be obtained as follows:

Reaction 6 $z_{12}(t+1) = a_1 z_{12}(t) + a_2 z_{11}(t - d_{11}^{12})$

Reaction 7 $z_{11}(t+1) = b_1 z_{11}(t) + b_2 z_{10}(t - d_{10}^{11}) + b3 z_{22}(t - d_{22}^{11}) + v_{10}$

Reaction 8 $z_{22}(t+1) = c_1 z_{22}(t) + c_2 z_{21}(t - d_{21}^{22})$

Reaction 9 $z_{21}(t+1) = d_1 z_{21}(t) + d_2 z_{20}(t - d_{20}^{21}) + d3 z_{12}(t - d_{12}^{21}) + v_{20}$

Among them, $a_1, a_2, b_1, b_2, b_3, c_1, c_2, d_1, d_2, and\ d_3$ are all obtained by the Method of the Least Squares.

There is a large lag existing in the hydrogen chloride synthesis system. And the most effective method which can overcome it and improve the control quality is prediction. In the chain system of single sampling cycle, the lag step, the cause variable z_{ij-1} as to effective variable z_{ij} , is $d_{ij-1}^{ij}+1$ .But the lag z_{i0} as to z_{ij} is $D_{ij} = \sum_{m=1}^{j}\left(d_{im-1}^{im}+1\right)$, so that the quality chain's predictive model is:

Reaction 10 $\hat{z}_{11}(t+D_{11} \mid t) = b_1\hat{z}_{11}(t+D_{11}-1 \mid t)+b_2 z_{10}(t)+b_3 z_{22}(t+D_{11}-d_{22}^{11}-1)+v_{10}$

Reaction 11 $\hat{z}_{12}(t+D_{12} \mid t) = a_1\hat{z}_{12}(t+D_{12}-1 \mid t)+a_2\hat{z}_{11}(t+D_{10} \mid t)$

Similarly, the safety chain's predictive model can be written out. Supposing it as follows [11,12]:

$$P\hat{z}_{12}(t+D_{12} \mid \mathrm{t}) = Hz_{12}^{*}(t+D_{12})$$

Among them：

$P = 1-P_1 z^{-1}, H = 1-P_1$, $z_{12}^{*}(t)$ is the expected value of $z_{12}(t)$.

Reaction 12 $\hat{z}_{12}(t+D_{12} \mid \mathrm{t}) = p_1\hat{z}_{12}(\mathrm{t}+D_{12}-1 \mid \mathrm{t})+(1-p_1)z_{12}^{*}(t+D_{12})$

With the same method, the following can be got.

Reaction 13 $\hat{z}_{11}(t+D_{11} \mid \mathrm{t}) = p_2\hat{z}_{11}(\mathrm{t}+D_{11}-1 \mid \mathrm{t})+(1-p_2)z_{11}^{*}(t+D_{11})$

Among them p_1, p_2 are design parameters.

Here, (12), (13) combined with (10), (11) can get the following control algorithm of the safety chain.

Reaction 14

$$z_{10}^{**}(t) = [(1-\mathrm{p}_2)z_{11}^{*}(t+D_{11})+(\mathrm{p}_2-\mathrm{b}_1)\hat{z}_{11}(t-D_{11}-1 \mid t)-b_3 z_{22}(t+D_{11}-d_{22}^{12}-1)-v_{10}]/\,\mathrm{b}_2$$

Reaction 15

$$z_{11}^{**}(t+D_{11}) = [(1-\mathrm{p}_1)z_{12}^{*}(t+D_{12})+(\mathrm{p}_1-a_1)\hat{z}_{12}(t+D_{12}-1 \mid t)]\,/\,a_2$$

Among them $a_1, a_2, b_1, b_2, and\ b_3$ are identification parameters, p_1, p_2 are design parameters, $z_{11}^{*}\ and\ z_{12}^{*}$ are the expected value of $z_{11}\ and\ z_{12}$ respectively, $\hat{z}_{11}\ and\ \hat{z}_{12}$ are the predictive value of z_{11}, z_{12} respectively. The control method of the quality chain can be got by the method above as well.

The pressure of the hydrogen which input into the synthesis furnace is 0.075MPa, chlorine gas pressure is 0.08 MPa[7].

Restraint condition:

Control target:

The hydrogen chloride mass fraction of the synthetic furnace outlet gas is 95±1%,the exhaust free chlorine content is 0.

Simulation method: According to the actual condition of the factory, the systematic data is gathered once every 10 minutes with 120 groups of data together. Then, according to the scene gathered data, we adopt least squares method to carry out the parameter identification to the system model. Finally, the control method is obtained via the prediction method. In addition, at the time of 40-45, a perturbation is added to the open degree of flow valve of hydrogen and chlorine. The following figure 2 and figure 3 is the simulation results of the quality chain and the safety chain obtained by the Matlab 6.0 simulation.

The adjustment scope of the open degree of flow valve of hydrogen and chlorine ranges from 0 to 10.

RESULTS AND DISCUSSION

The simulation results show that, using the chain system control method, we can control the content of free chlorine in the required range, it avoids explosion occurring in the production process, so that it ensure the production process safety first of all. Secondly, it ensure that high quality hydrochloric acid is produced through controlling the purity of hydrogen chloride at a relatively high level. Once again, in the case of interference, the system can suppress the disturbance in a certain degree and resume steadiness quickly, guaranteeing rapidity of system reaction. Finally, the system is designed independently, if one part breaks down, it is easy to deal with the troubles and guarantee overall performance.

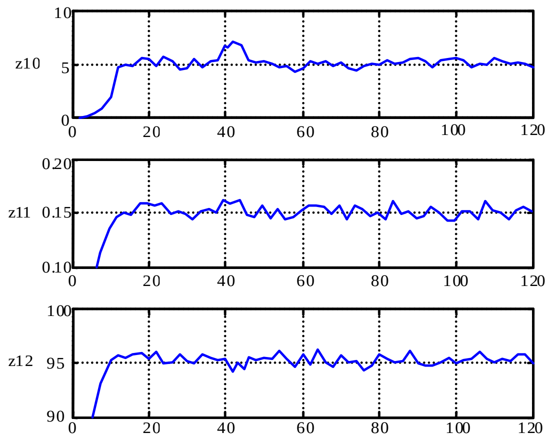

Fig.2. The simulation results of the quality chain

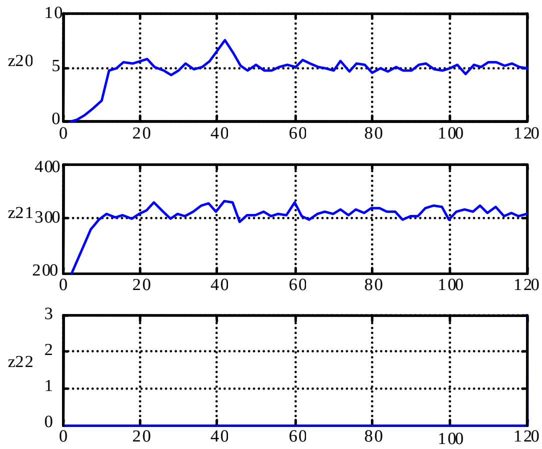

Fig. 3. The simulation results of the security chain

CONCLUSION

The chain system model of the hydrogen chloride synthesis system, set up by the chain system method, is a new exploration to the research of the hydrogen chloride synthesis control method. The chain system method is essentially a structure-decentralized method, which bestows the hydrogen chloride synthesis system model with better adaptability, stability and dependability. In short, the control target based comprehensively on higher quality and higher security is very meaningful.

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