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Experimental Research on a Process for the Recycling of Yellow Phosphorous Tail Gas to Produce Formic Acid

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ABSTRACT

This study provides details of a novel continuous process to eliminate the pollution of yellow phosphorus tail gas, which can also produce high quality and low cost formic acid, with a particular focus on the high and variable viscosity of the system and the rationality of energy utilization. A compact acidification reactor was developed as the key equipment used in this novel process, based on integrating the reaction, heating and condensation reflux. In addition, the effects of the mole ratio of the reactants, formic acid additive content, reaction time, reaction temperature and agitation speed on product concentration and yield were also researched experimentally. The experimental results show that as the mole ratio of the reagent increases, the product yield rises significantly while the concentration only increases slightly. The concentration and yield of the product decrease if less formic acid additive is added to the system. As the reaction time increases, both the concentration and yield of formic acid are increased, especially when the reaction time is over two hours. The reaction temperature has little effect on the product concentration, whereas the product yield would increase first and then decrease as the reacting temperature increases. The effects of agitation speed on the concentration of formic acid are not significant.

Keywords: Yellow phosphorous tail gas; Formic acid; Process; Equipment; Optimization.

INTRODUCTION

Yellow phosphorous tail gas produced during the electric furnace smelting process of phosphate ore contains about 90% carbon monoxide. Other constitutes are mainly sulfide, phosphide, ash, etc. (Yan, 2009). Generally, when 1t yellow phosphorous was produced, about 2800 m^3 tail gas which has a higher calorific value than water gas would be let out. Due to its complex composition, difficult recycling and large investment, the tail gas was often burned directly and then let out into the air by many enterprises in China, resulting in not only waste of energy and resources but also environmental pollution. So it is of great significance for energy conservation, emissions reduction and development of circular economy to recycle yellow phosphorous tail gas.

At present the recycled yellow phosphorous tail gas was mainly used as heat source, resource for electricity generation and raw materials (Duan, 2010; Zhang *et al.*, 2012). Among them, using yellow phosphorous tail gas to produce chemicals with high added value and high quality is one of the most potential and promising approaches. According to analysis, the formic acid is in great market demand and has good economic benefits (Han, 2001). The combination of recycling of yellow phosphorous tail gas and formic acid production can give full play to the resource advantages of yellow phosphorous production enterprises and integrate well with its existing production, thus reducing cost of formic acid production and improving the added value of yellow phosphorous tail gas. So it has competitive advantage and broad market prospect compared with enterprises specialized in producing formic acid.

NOVEL PROCESS FOR THE RECYCLING OF YELLOW PHOSPHOROUS TAIL GAS TO PRODUCE FORMIC ACID

Yellow phosphorous tail gas, rich in carbon monoxide, contains many impurities like sulfur, phosphorus, arsenic, fluorine, carbon. It must be purified first in order to produce high-quality formic acid. Then formic acid and sodium tripolyphosphate can be obtained through the processes of alkalization, acidification, distillation, firing, etc. Specific process is shown in Fig. 1, and involving reactions are as follows:

$$CO + NaOH \rightarrow NaCOOH \quad (1)$$

$$H_3PO_4 + NaCOOH \rightarrow HCOOH + NaH_2PO_4 \quad (2)$$

$$2NaH_2PO_4 + Na_2CO_3 \rightarrow 2Na_2HPO_4 + H_2O + CO_2 \quad (3)$$

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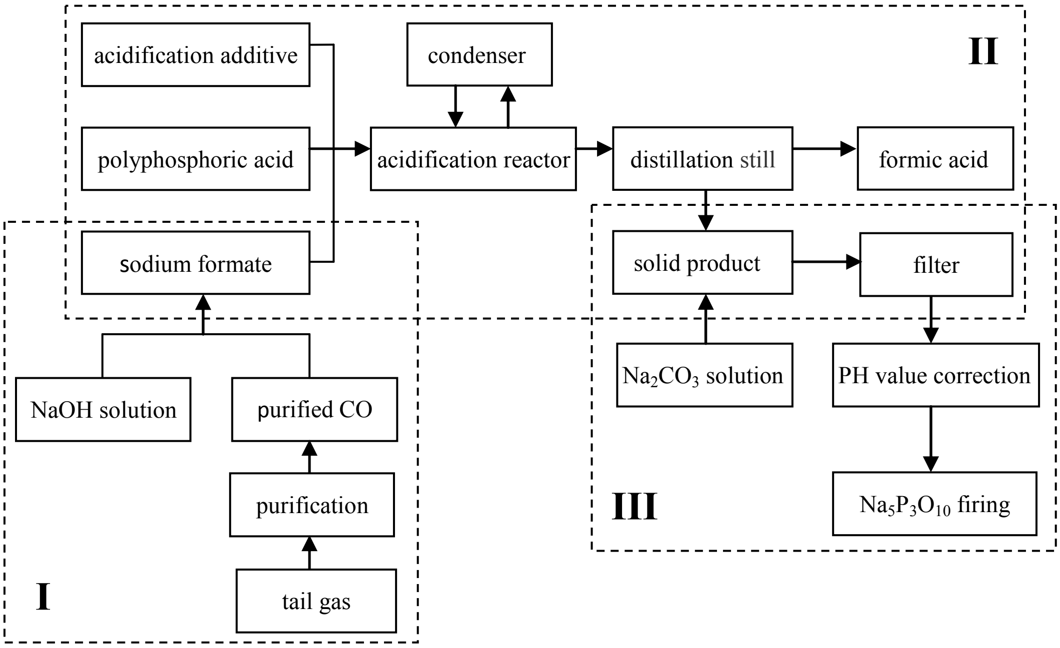

Fig. 1. Process for the recycling of yellow phosphorous tail gas to produce formic acid.

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O \quad (4)$$

It can be easily seen that the process can be divided into three parts generally: I producing sodium formate through alkalization with purified yellow phosphorous tail gas; II producing high-quality formic acid by distilling after phosphoric acid acidification of sodium formate; III producing sodium tripolyphosphate by sintering sodium phosphates. Wherein, purified yellow phosphorous tail gas can be obtained by several proven methods, such as water wash and caustic wash, catalytic oxidation, temperature & pressure swing adsorption. which can meet the requirement of raw materials in C1 chemical (Ning and Ren, 2003; Ma *et al.*,2008),and the production of sodium tripolyphosphate by sintering also has relatively mature technology. So the key to realize the novel process of the effective recycling of yellow phosphorous tail gas to produce formic acid with high added value lies in process II.

Producing high-quality formic acid by distilling after phosphoric acid acidification of sodium formate has caused industry attention (Zuo, 2007; Luo *et al.*, 2009). But most existing technologies adopt intermittent operation. For example, in patent 200610200857.3, Zuo Jianguo proposed a method of producing 95% formic acid through intermittent phosphoric acid acidification of sodium formate and distillation. These intermittent methods of producing formic acid not only need more human resource, which complicate operations and may lead to higher cost and possibility of incorrect operations, but also limit the production capacity of formic acid enterprises and is adverse to the recycling of large quantity of yellow phosphorus tai gas. Meanwhile, existing technologies generally have following key shortages: (1) They do not take full account of the change of system viscosity in production process. (2) Overall consideration of the rationality of system energy utilization is lacking. (3) Equipment used in those processes is not involved. So getting through the bottleneck of formic acid production through acidification of sodium formate is of great significance for effective recycling of yellow phosphorous tail gas.

Concentration of phosphoric acid has a direct influence on the quality of formic acid product and the system's viscosity. Low concentration will cause the formation of azeotrope of water and formic acid, preventing the production of high-concentration formic acid, while high concentration will lead to high system viscosity that will affect the mixing of reactants and increase difficulty of continuous operation. Meanwhile, the continuous process provides higher demands on procedure parameters and equipment matching. So the continuous process of formic acid production through phosphoric acid acidification of sodium formate shown in Fig. 2 was developed on the basis of the consideration of safety, energy conservation and environmental protection.

During the operation, formic acid additive and 116% polyphosphoric acid are pumped into premixing tank firstly, then start agitator and add solid sodium formate continuously into multistage acidification reactor using spiral feeder, next, pump the well premixed materials into multistage acidification reactor. Materials will react gradually when they are heated to appropriate temperature in acidification reactor, and continuously volatilized or evaporated formic acid flowing out from the top will flow back into acidification reactor after condensed in condenser to guarantee the fluidity of the system. The generated mixture in reaction which is rich in formic acid and sodium dihydrogen phosphate will be separated through the combination of atmospheric distillation and vacuum distillation. Most formic acid will be distilled out of the mixture by atmospheric distillation, leading to higher viscosity, then vacuum pressure distillation with greater driving force is adopted to distill the rest formic acid out sufficiently. As viscosity of the system will

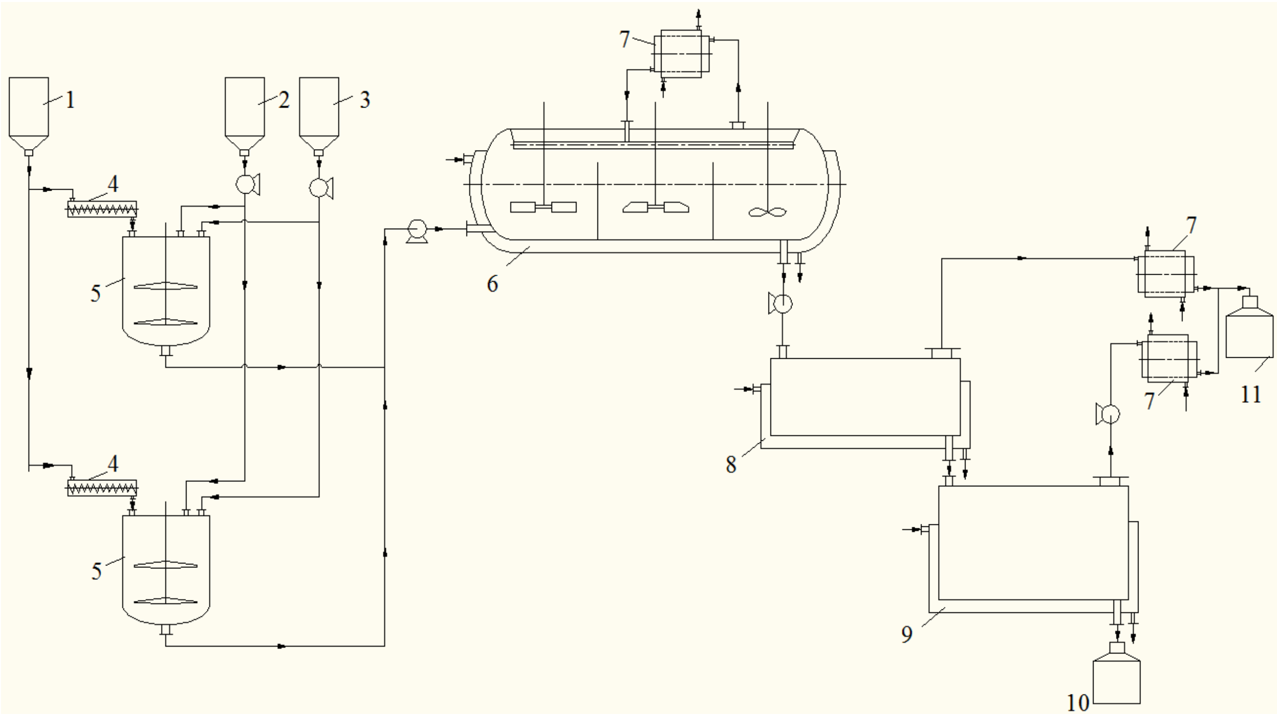

Fig. 2. Continuous process for the production of formic acid by phosphoric acid acidification method (1 sodium formate storage tank 2 polyphosphoric acid storage tank 3 acidification additive storage tankn4 spiral feeder 5 materials premixing tank 6 multi-chamber acidification reactor 7 condenser 8 atmospheric distillation unit 9 vacuum distillation unit 10 compound phosphate storage tank 11formic acid storage tank).

turn into high viscosity during distillation, both atmospheric distillation unit and vacuum distillation unit are equipped with spiral rotor to update the external distillation surface of the system in order to enhance distillation. The separated formic acid will be collected after condensed in condenser, and the solid product is compound phosphate which mainly contains NaH_2PO_4 (Liu *et al.*, 2011a).

Compared with other processes for the production of formic acid through acidification of sodium formate, the process shown in Fig. 2 has the following characteristics:

(1) Continuous operation and high efficiency. With parallel premix procedures installed, the process and device provide uniform, steady and continuous material for subsequent acidification and distillation. On the one hand, it overcomes some shortcomings caused by high viscosity of system, such as long production cycle, inadequate reaction. On the other hand, it realizes the continuous operation of the whole system, shortening the production cycle and improving the efficiency by intermittent operation of parallel premixers and coupling with continuous acidification reactor as well as atmospheric and vacuum distillation devices.

(2) Flexibility and wide adaptability. The scale and number of parallel premixers in the system, number, height and interval of baffles in acidification reactor, number and type of agitators and the structure and heating medium of heating units can be adjusted flexibly based on the condition of reaction process, so it can meet the needs of different scale production systems.

(3) Rational utilization of system energy. Different agitators and drive systems are equipped in the process based on varied system viscosity during the reaction, achieving rational match between mixing devices and the mediums, thus avoiding the waste of energy and device potentials. Distillation of formic acid becomes more and more difficult as system viscosity becomes higher and higher, which is opposite to that in acidification stage. As the adoption of single type of agitator and vacuum distillation in the whole course will lead to high energy consumption, multistage distillation that consists of atmospheric distillation in the beginning and vacuum distillation later is adopted to reduce system energy consumption.

(4) High quality of product and evident benefit. Formic acid with high concentration and quality which can meet the requirements of high-class product specified in national standard GB/T2093 (Industrial Formic Acid) can be produced during this process. Formic Acid is important chemical raw material and intermediate with high added value which can meet the needs of various occasions.

KEY EQUIPMENT FOR THE RECYCLING OF YELLOW PHOSPHOROUS TAIL GAS TO PRODUCE FORMIC ACID

Specific principle of producing high-quality formic acid by polyphosphoric acid acidification of sodium formate is that sodium formate is double decomposed by the chemical energy of the first hydrogen ions in polyphosphoric acid, producing formic acid and compound phosphate which mainly contains NaH_2PO_4, under the condition of certain temperature and with the help of acidifier. The quality and yield of formic acid will be influenced by the mole ratio of reactants, temperature, pressure and reaction time of the acidizing reaction, so designing appropriate reaction device for acidification is the key to realize the process.

During the reaction process between sodium formate and polyphosphoric acid, the system viscosity is relatively high with the maximum being 60 Pa·s and varies a lot. Usually, it is very high at the beginning then becomes lower as the reaction proceeds because of the good fluidity of formic acid. Formic acid is volatile and will be evaporated when the reaction temperature is close to its boiling point, which means that content of formic acid in system must be controlled to ensure the fluidity of the system, or it is difficult for sufficient reaction. Therefore, continuous device for phosphoric acid acidification of sodium formate to produce formic acid must meet the following conditions simultaneously: (1) it must be able to adapt to the change of system viscosity during the reaction and provide rational and effective agitation. (2) It should be able to control the content of formic acid in the system, that is, the volatilized or evaporated formic acid can be complemented in time. (3) It should be able to provide effective heating modes to create an environment with stable reaction temperature. (4) It should have the function of continuous operation, achieving complete reaction during the interval between flowing in and out of the materials.

Structure of the reactor designed based on the above considerations is shown in Fig. 3. The reactor includes a closed vessel enclosed by left and right end plate and upper, middle and lower shell. Local heating jacket is arranged symmetrically on the outer surface of the vessel, and built-in condenser is hanged on the top of the inner side of the vessel. Inlet pipe of premixed materials is arranged on the left end plate, and outlet pipe of reaction liquid at the bottom of the right side of the vessel is led out through heating jacket. The vessel is divided into several reaction chambers each equipped with a different type of agitator according to local viscosity by baffles, whose number, interval and height are adjustable. Tubular structure is adopted in built-in condenser, and ends of heat exchange tubes are assembled in the right and left containers. Membrane wall structure is adopted for heating jacket which consists of two inlet pipes and two inlet containers of heat medium, several semicircle heating pipes, outlet container and outlet pipe of heat medium. Wherein the semicircle heating pipes are bended based on external diameter of the lower shell.

In the running process, premixed materials will be added into the closed vessel, in which temperature of the system will be controlled at about 100°C by heating medium in heating jacket, and polyphosphoric acid will react with sodium formate step by step with the existence of additive formic acid. The volatilized and evaporated formic acid will be condensed timely by the built-in condenser and then flow back to the system. Exactly complete reaction can be achieved by controlling the length of device, height of baffles, number of reaction chambers, feeding speed, etc. During the reaction, heating medium should be pumped into heating jacket continuously, and suitable and stable reaction temperature can be obtained by adjusting the flow rate and temperature of heating medium. Simultaneously, coolant should be added into the built-in condenser continuously to prevent deterioration of system fluidity due to the volatilization and evaporation of formic acid, thus avoiding bad effect on the reaction (Liu *et al.*, 2011b).

Compared with other stirred reactor, the reactor mentioned above can achieve acidizing reaction of polyphosphoric acid and sodium formate flexibly and efficiently, and its significant advantages are shown as follows.

(1) Systematic and integrated structure design mode. This acidizing reactor integrates the functions of reaction, heating and condensation reflux together to create optimized space for acidizing reaction of sodium formate. It also has the advantages of compact structure, small floor space and relatively low equipment investment.

(2) Membrane wall heating structure. Membrane wall heating structure consisting of several heat exchange tubes and containers is adopted in the reactor, which has higher heat transfer efficiency, structural strength and reliability than the traditional overall jacket.

(3) Rational energy utilization. System viscosity is relatively high at the beginning of the process of polyphosphoric acid acidification of sodium formate, while it becomes lower and fluidity becomes better as reaction proceeds due to the effective condensation and reflux of evaporated and volatilized formic acid. Selection of single

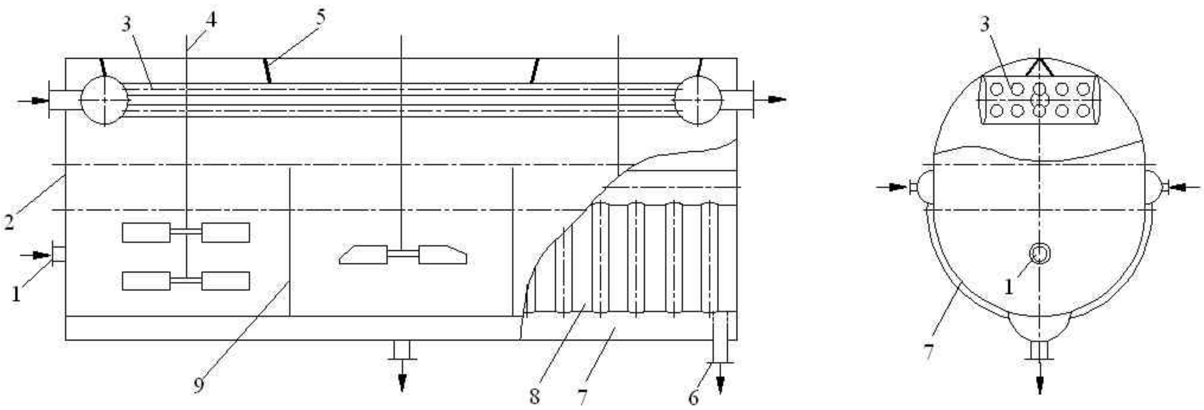

Fig. 3. Structure of multi-chamber acidification reactor (1 inlet pipe of premixed materials 2 end plate 3 built-in condenser 4 stirrer 5 mounting bracker 6 product outlet pipe 7 heating jacket 8 cylinder 9 baffles).

type of agitator based on initial viscosity will cause power surplus at later stage and the agitator can't well adapt to the later system; conversely, adoption of single type of agitator based on later viscosity will result in its abnormal function at the beginning of acidification reaction due to the insufficient power. Multi-chamber operation is adopted and different types of agitators are equipped in differ chamber based on varied system viscosity, which can not only optimize the mixing effect but also reduce energy consumption.

EXPERIMENT SECTION

The key to obtain formic acid with high quality and yield is the parameter optimization in acidification and distillation processes (Xiong *et al.*, 2010). Generally, the mole ratio of reactants, formic acid additive content, reacting time, reacting temperature and agitation speed all have influence on the product concentration and yield. The variation trends of product concentration and yield affected by above-mentioned factors in acidification and distillation processes were analyzed experimentally so as to achieve optimized operation of the system.

Reagents and Apparatuses

The main apparatus and reagents used in the experiments are listed in Table 1 and Table 2. The experimental apparatus of the sodium formate acidification and the formic acid distillation are specifically shown in Fig. 4. As formic acid and water can easily form azeotrope under the temperature of 107°C (Zhou *et al.*, 2008; Luo *et al.*, 2009), 116% polyphosphoric acid was used in the experiment, which can easily absorb water and is beneficial to improve the concentration of formic acid.

During the experiment, the temperature of oil bath pot can be adjusted flexibly through the temperature control device based on the different needs at different stages; power per unit volume needed in the system can be computed based on the current measured by ammeter which is connected to the powerplant of agitator; the condenser plays the role of refluxing formic acid, thus avoiding high system viscosity caused by the fast volatilization and evaporation of formic acid in the reaction stage, when its lower branch pipe valve keeps closed and its top hole is connected to the atmosphere via absorption tower and three-way valve. During distillation process, the branch pipe valve of the condenser is open and connects with vacuum pump via absorption tower, three-way valve and surge flask to achieve vacuum distillation. The condensed liquid flows into collection bottle through branch pipe; the paraffin wax and molecular sieve are filled into absorption tower to absorb organic gases and water in order to avoid environmental pollution.

Experimental Method

The acidizing reaction of polyphosphoric acid and sodium formate can make them convert into formic acid and compound phosphate using the chemical energy of the first hydrogen ions in polyphosphoric acid to double decompose sodium formate. Formic acid will be separated out via vacuum distillation after reaction, correlative main reaction is shown as follows:

$$H_3PO_4 + NaCOOH{\cdot}2H_2O \rightarrow NaH_2PO_4 + HCOOH + 2H_2O \quad (5)$$

Side reaction as follows:

$$H_3PO_4 + 2NaCOOH{\cdot}2H_2O \rightarrow Na_2HPO_4 + 2HCOOH + 4H_2O \quad (6)$$

The followings are the specific experimental procedures:

(1) Mixing acid. In order to ensure the fluidity of the reaction system, appropriate amount of formic acid additive

Table 1. Main laboratory apparatuses.

apparatus name	main technical specifications
electronic balance	accuracy 0.0001 g, AGE-220
agitator	speed 25–360 r/min, torque 0.99 N.m, power 90 W
ammeter	0–500 mA
oil bath pan	power 1.5 kW
temperature controller	temperature range 0–200 ± 0.2°C
vacuum pump	maximum vacuum degree 0.098 MPa
condenser for reflux and distillation	500 mL
Reaction flask with three nozzles	1000 mL

Table 2. Main laboratory reagents.

reagent name	specification	composition	plant
sodium formate	AR ≥ 99.5%	$NaCOOH{\cdot}2H_2O$	Chongqing Chuandong Chemical Co., Ltd.
polyphosphoric acid	technical grade 116%	H_3PO_4	Yunnan Tianyao Chemical Co., Ltd.
formic acid	AR ≥ 88%	HCOOH	Hangzhou Shuanglin Chemical Reagent Factory
sodium hydroxide	AR ≥ 96%	NaOH	Hangzhou Chemical Reagent Co., Ltd.
potassium hydrogen phthalate	AR ≥ 99.8%	$C_8H_5KO_4$	Shanghai Hushi Chemical Co., Ltd.
ethanol	AR ≥ 99.7%	CH_3CH_2OH	Shanghai Hushi Chemical Co., Ltd.
phenolphthalein	—	$C_{20}H_{14}O_4$	Shanghai San'aisi Reagent Co., Ltd.

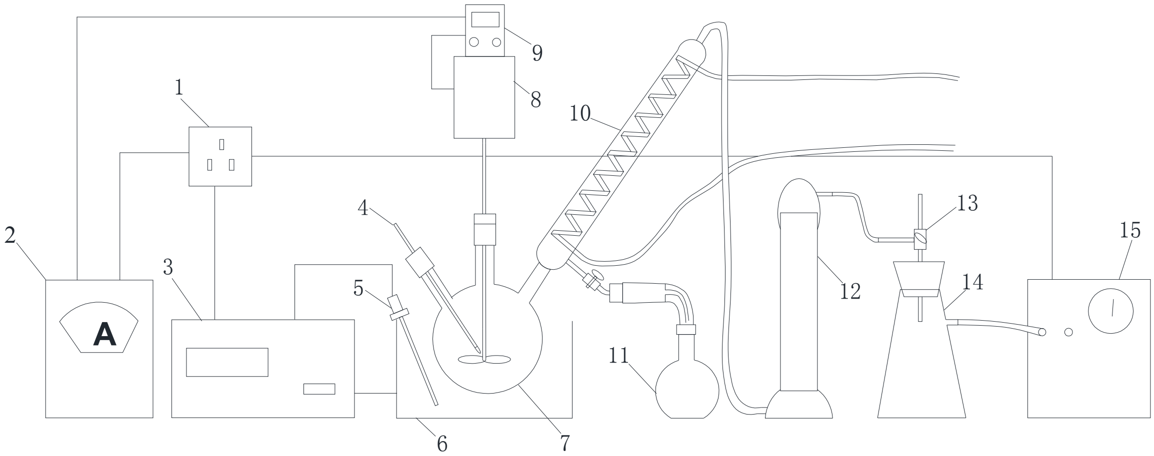

Fig. 4. Experimental facility for acidification and distillation (1 power panel 2 ammeter 3 temperature controller 4 thermometer 5 temperature transmitter 6 oil bath youyupan 7 Reaction flask with three nozzles 8 stirrer 9 speed controller 10 condenser for reflux and distillation 11 collection bottle 12 absorption column 13 three-way valve 14 surge flask 15 vacuum pump).

was added into a dry three-neck flask first, then desired amount of polyphosphoric acid was rapidly added. Cooling water should be pumped into condenser to make volatilized formic acid condense and flow back due to the heat released when polyphosphoric acid absorbs water. The agitator should work about 10 minutes to make the mixture clear and uniform

(2) Reaction. The prior weighed sodium formate was added into reaction flask and the oil bath pot was lifted up to submerge the reaction flask when temperature of oil reached reaction temperature. The reaction system should have relatively good fluidity to ensure complete reaction, so continuous and effective agitation was needed and formic acid should be condensed and flow back in time. Reaction temperature was measured by the thermometer submerged under fluid level during the reaction, which can be controlled by slightly adjusting the temperature of hot oil through temperature control device.

(3) Distillation. Vacuum distillation began when reaction system didn't have obvious change and the predetermined reaction time was up. Branch pipe valve of the condenser was opened and three-way valve was adjusted to unblock the pipeline that connects the top hole of condenser, absorption tower, three-way valve, surge flask with vacuum pump after the oil temperature was elevated to about 150°C. Then vacuum pump was open and vacuum degree of reaction flask was adjusted to the desired degree. Distillation was done after about 40 minutes when there's no condensed liquid distilled. At this moment, clarified formic acid product was obtained in collection flask, and white powder of phosphate was obtained in reaction flask.

(4) Post-processing of distillate. Neutral titration was used to determine the concentration of formic acid. Wherein NaOH standard solution used in titration was calibrated by potassium acid phthalate. The concentration of each sample was measured three times and adopted the average value in titration and calibration. Formic acid yield was determined based on material balance at the same time.

Data Processing Method

NaOH standard solution with the concentration of 0.5 mol/L which needed to be calibrated was used in titration when measuring the concentration of formic acid product, using phenolphthalein as the indicator.

Calibration of concentration of NaOH standard solution: add about 1g potassium acid phthalate to 30 mL distilled water, then add 2–3 drops of phenolphthalein, next add NaOH standard solution which was to be calibrated to the solution drop by drop until the color becomes light pink. Record the mass of potassium acid phthalate m_1 and the volume of NaOH standard solution V_1 during the process. At last, calculate the concentration of NaOH standard solution using the following formula:

$$C_{NaOH} = \frac{m_1}{204 \times V_1} \times 1000 \quad \text{(mol/L)} \tag{7}$$

Determination of the concentration of formic acid: add about 1 g formic acid into 20 mL distilled water, then add 2–3 drops of phenolphthalein, next add calibrated NaOH standard solution into the solution drop by drop until the color becomes light pink which doesn't fade in 30 s. The mass of formic acid sample m_2 and the volume of NaOH standard solution V_2 used were recorded. The mass fraction of formic acid product was then calculated by the following formula:

$$w = \frac{C_{NaOH} \times V_2 \times 46.03}{1000 m_2} \times 100\% \tag{8}$$

Calculation of formic acid yield: record the mass of empty reaction flask m_0, the mass of formic acid added in reaction m_3, the mass of sodium formate added in reaction m_4 and the gross mass of reaction flask after reaction m_5. Then calculate the yield using the following formula:

$$y = \frac{(m_0 + m_3 + m_4 - m_5) \times w - m_3 \times 0.88}{\frac{m_4}{104} \times 46.03} \times 100\% \tag{9}$$

RESULTS AND DISCUSSIONS

Industrial formic acid is divided into three grades: high-class product, first-class product and qualified product according to the Chinese standard GB/T2093 (GB/T 2093-1993, 1994). The price of formic acid with different grades varies a lot. Therefore, producing high-class formic acid becomes the target in order to realize high-value recycling of yellow phosphorus tail gas. According to the measurement, the appearance, color, dilution test and other impurities' content of the formic acid product obtained in the experiments can meet the technical requirements of high-class formic acid, only the concentration varies a lot under different operating conditions. The concentration of high-class formic acid is required to be no less than 90% according to Chinese standard GB/T2093 (GB/T 2093-1993, 1994), therefore, the effects of mole ratio of reactants, formic acid additive content, reacting time, reacting temperature, agitation speed and vacuum degree on product concentration and yield were investigated in the experiments. In addition, the different experimental phenomenon and results under different conditions were also discussed, and then the optimized operating parameter combinations were determined.

Effect of Mole Ratio of Reactants

As the direct product of recycling of yellow phosphorous tail gas, sodium formate should be used to produce formic acid with high added value. Excessive polyphosphoric acid is beneficial for the complete reaction of sodium formate. 1.0, 1.2, 1.3 and 1.4 were adopted respectively as the mole ratio of polyphosphoric acid and sodium formate in the experiments, while other parameters were constant: reacting time was 2 h, reacting temperature was 105°C, the mass ratio of polyphosphoric acid and formic acid was 2:1, agitation speed was 50 rpm and vacuum degree was 0.05 MPa.

The effect of different mole ratios of reactants on product concentration and yield is shown in Fig. 5. Fig. 5 shows that the product yield would increase significantly and the concentration has a little increase with increasing mole ratio of polyphosphoric acid and sodium formate. Usually, the increased amount of polyphosphoric acid is conductive to the conversion of sodium fotmate because the increase of one reactant is good for the reaction to proceed in the positive direction from the perspective of reaction equilibrium; furthermore, polyphosphoric acid is helpful to improve the concentration of formic acid product because of its absorbency of water. However, NaH_2PO4 is also produced during the reaction, and excess polyphosphoric acid is adverse to the process of NaH_2PO_4, so the mole ratio of polyphosphoric acid and sodium formate is appropriate to be controlled at 1.2.

Effect of Formic Acid Additive Content

The system would become more viscous after adding sodium formate into 116% polyphosphric acid whose viscosity is very high (about 60 Pa·s), and it is difficult to achieve complete dispersion and sufficient contact between reactants even though there's agitation. So it's necessary to add a certain amount of additive to reduce the viscosity of the system and make the reactants contact sufficiently. But the addition of the additive should not bring impurities, so formic acid, a product of the reaction, is the most appropriate additive. Formic acid additive used in the experiment was purchased. In practical production, appropriate system viscosity can be achieved by the reflux of partial formic acid product. However, reflux causes bad effect on distillation and power consumption, so it should be as few as possible under the premise of appropriate viscosity. The effect of mass ratio of polyphosphoric acid and formic acid was investigated in the experiments, whose value was 2.0, 2.4, 2.67 and 4 respectively. Other parameters were constant: reacting time was 2 h, reacting temperature was 105°C, the mole ratio of

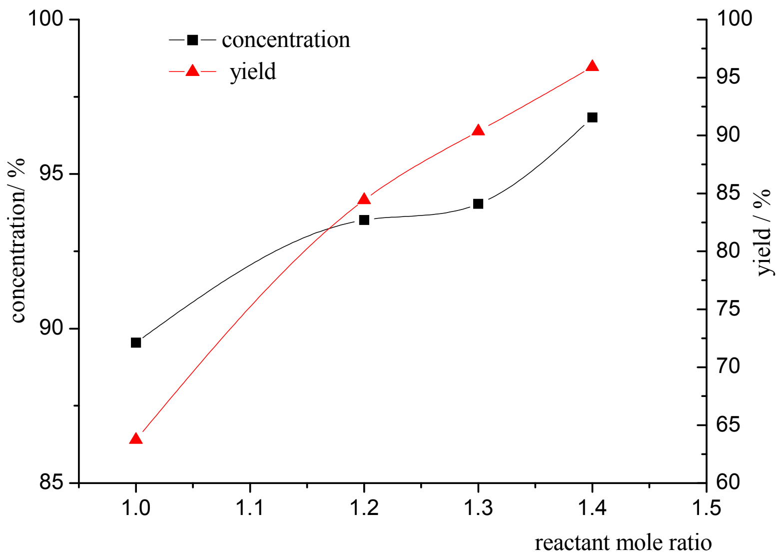

Fig. 5. Effect of reactant mole ratio on product concentration and yield.

polyphosphoric acid and sodium formate was 1.2, agitation speed was 50 rpm and vacuum degree was 0.05 MPa.

The effect of different formic acid contents on product concentration and yield is shown in Fig. 6. Fig. 6 shows that the product concentration and yield would decrease slightly with the increasing mass ratio of polyphosphoric acid and formic acid, therefore the smaller mass ratio of polyphosphoric acid and formic acid is preferable from the perspective of improving product concentration and yield. On the other hand, the larger mass ratio is preferable from the perspective of reducing power consumption. But when the mass ratio is more than 2.67, in particular reaches 4.0, the concentration of formic acid product has reduced to nearly 90% as shown in Fig. 6. Therefore, in order to obtain high-class formic acid, it is feasible to control the mass ratio of polyphosphoric acid and formic acid additive to be less than 2.67 with the mole ratio of polyphosphoric acid and sodium formate being 1.2.

Effect of Reacting Time

The longer reacting time is, the closer the reaction is to equilibrium point, and the yield increases accordingly. However, long reacting time will result in too much energy consumption, while the yield doesn't increase with corresponding magnitude, which causes the decline of production efficiency. So the effect of reacting time was investigated on the basis of the consideration to formic acid quality, yield and efficiency. 3 h, 2 h, 1.5 h, 1 h and 0.5 h were adopted respectively as the reaction time, while other parameters were constant: reacting temperature was 105°C, the mole ratio of polyphosphoric acid and sodium formate was 1.2, the mass ratio of polyphosphoric acid and formic acid was 2:1, agitation speed was 50 rpm and vacuum degree was 0.05 MPa.

The relationship between reacting time and the product concentration and yield is shown in Fig. 7, which shows that the product concentration and yield both improved with the extension of reacting time. When the reaction time is less than 2 h, the increase is obvious with the concentration and field increasing respectively from 84.27% and 77.97% at 0.5 h to 93.51% and 84.43% at 2 h, averaging 6.16% and 4.31% per hour; but the increase is not significant when the reaction time is over 2 hours with the average increase per hour being 0.82% and 1.37%, respectively. Besides, it is unable to meet the requirement of 90% of the concentration and 80% of the yield when reaction time is short. So, 2 hours is selected as the appropriate reaction time.

Effect of Reaction Temperature

Temperature is the dominant factor in determining the reaction rate. Usually, reaction rate will increase as the temperature rises. At the same time, temperature also has influence on state parameters such as density and viscosity, whose change will cause the change of reaction rate. The effect of different reacting temperatures on product concentration and field was analyzed. 100°C, 105°C, 110°C and 120°C were adopted as the reaction temperature respectively, while other parameters were constant: reaction time was 2 h, the mole ratio of polyphosphoric acid and sodium formate was 1.2, the mass ratio of polyphosphoric acid and formic acid was 2:1, agitation speed was 50rpm and vacuum degree was 0.05 MPa.

The effect of different reaction temperatures on product concentration and yield is shown in Fig. 8, which shows that temperature has little effect on the product concentration, which fluctuates around 93%; whereas it has certain influence on the product yield, which would increase when the temperature is below 105°C and decrease when the temperature is above 105°C with the increase of reaction temperature. Here is the reason: increase of temperature, leads to higher reaction rate, and 105°C is the boiling point of formic acid, so, when temperature is below 105°C formic acid yield increases with the increase of temperature under the condition of the same reaction time, while when temperature is above 105°C, formic acid yield would decrease with the increasing temperature due to the bad fluidity of

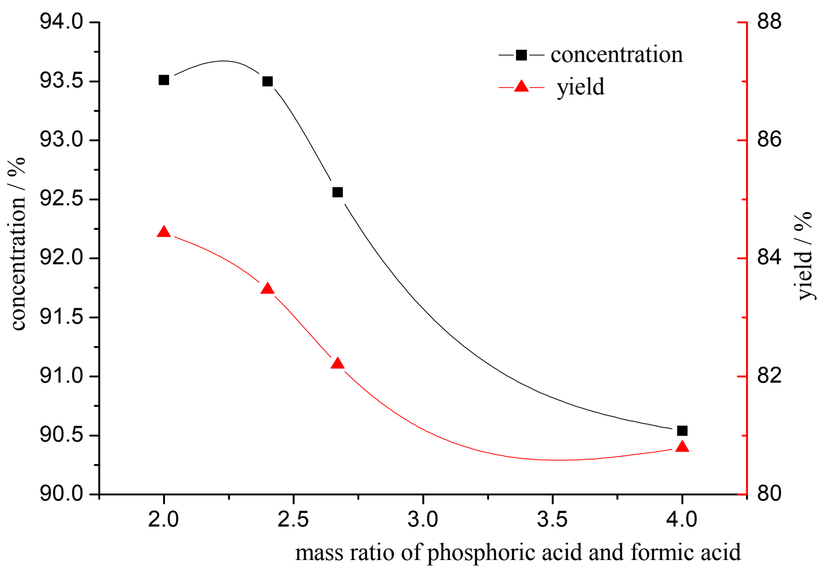

Fig. 6. Effect of formic acid additive content on product concentration and yield.

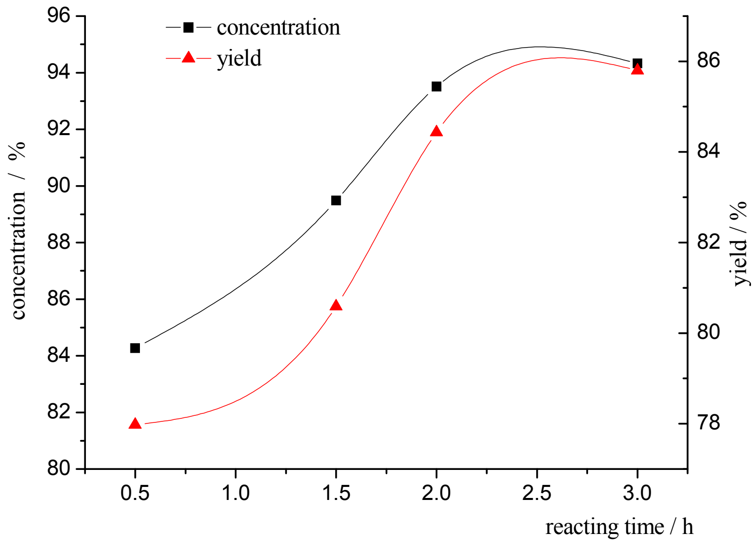

Fig. 7. Effect of reacting time on product concentration and yield.

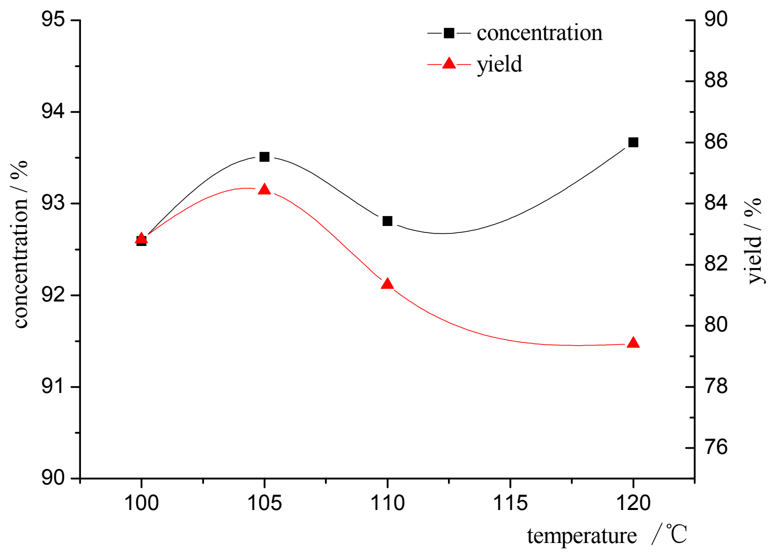

Fig. 8. Effect of reacting temperature on product concentration and yield.

the system caused by the fast distillation of formic acid. Besides, too high temperature will inhibit the reaction because it belongs to exothermic reaction. So appropriate reaction temperature is 105°C.

Effect of Agitation Speed

Without agitation, complete dispersion can't be achieved in high-viscosity system and the reaction can't proceed smoothly. While too high agitation speed not only provides no help for the dispersion, but also increases power consumption (Chen *et al.*, 2005). Therefore, the effect of agitation speed on product concentration and yield was analyzed giving consideration to efficiency and energy consumption under the premise of smooth reaction. 20 rpm, 30 rpm, 50 rpm and 70 rpm were adopted respectively as the agitation speed in the experiment, while other parameters were constant: reacting time was 2 hours, reacting temperature was 105°C, the mole ratio of polyphosphoric acid and sodium formate was 1.2, the mass ratio of polyphosphoric acid and formic acid was 2:1 and vacuum degree was 0.05 MPa.

The effect of agitation speed on product concentration and yield is shown in Fig. 9, which shows that agitation speed has little effect on the reaction, its concentration fluctuates around 93% and the fluctuation of yield is within 5%. So, 30 rpm was adopted as agitation speed giving consid eration to both product requirement and power consumption.

CONCLUSIONS

(1) The continuous process to produce formic acid with phosphoric acid acidification of sodium formate based on the recycling of yellow phosphorous tail gas is mainly composed of the following processes: premixing of raw materials, acidizing reaction of sodium formate, distillation of formic acid, etc. Full consideration is given to the high and variable system viscosity and the rationality of energy

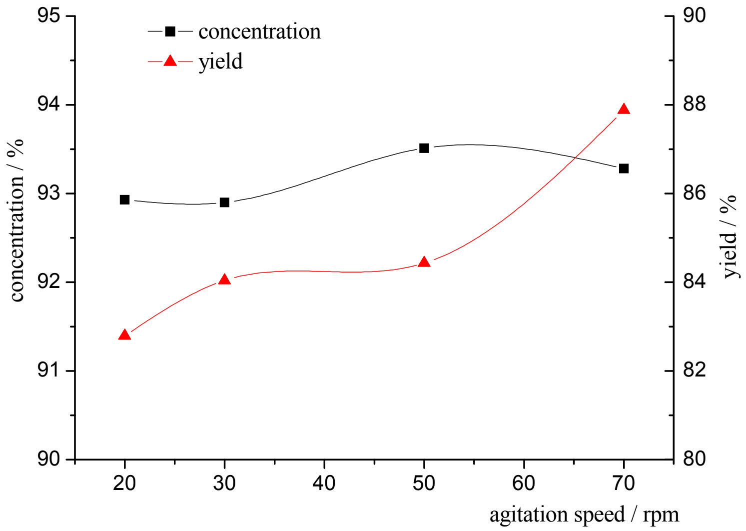

Fig. 9. Effect of agitation speed on product concentration and yield.

utilization in the process, achieving high efficiency, wide adaptability, energy conservation and environmental protection, high product quality and yield.

(2) Novel acidizing reactor is the core equipment in the continuous process for the production of high-quality formic acid through acidification of sodium formate by polyphosphoric acid. The reactor adopted integrated structure and consisted of reaction chambers that were equipped with different agitators, built-in tube condenser, membrane wall heating jacket, etc.

(3) With increasing mole ratio of reagent, the yield of formic acid product would increase significantly and the concentration has a little increase; the concentration and yield of product would decrease when less formic acid additive content was put in; the product concentration and yield both improved with the extension of reacting time, but the improvement magnitude before 2 hours is obvious while little 2 hours later; The increase of reacting temperature had little effect on the product concentration, whereas the product yield would increases first and then decreases, and 105°C is the turning point; The effects of agitation speed on the concentration of formic acid were not obvious.

(4) The optimized operating parameters of reaction and distillation process for the production of formic acid with the help of phosphoric acid acidification method were determined considering yield, efficiency and consumption synthetically under the premise of ensuring the concentration of formic acid product as follows: reacting time 2 hours, reacting temperature 105°C, the mole ratio of polyphosphoric acid and sodium formate 1.2, the mass ratio of polyphosphoric acid and formic acid 2.67:1, agitation speed 30 rpm. Under such conditions, the concentration of formic acid product is above 90%, and its yield is above 80%.

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