Complex Fertilizer Production from the Residue in Producing Furfural Using Straw: Study on the Additives and Reaction Conditions

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Abstract: The complex additives which contain (ω) 4%~6% phosphoric acid, 4%~6% calcium triple superphosphate, 80%~90% calcium phosphate, 2%~3% calcium carbonate, 2%~4% sodium hydrosuphite, 2%~4% ferric sulfate and 2%~4% aluminum sulfate were used to produce furfural by straw hydrolysis with sulfuric acid. The effect of reaction conditions on residue acidity and furfural productivity were investigated. The experimental results showed that the suitable conditions are sulfuric acid concentration 16% (ω), the added sulfuric acid amounting to 6% of all raw materials, the weight ratio of liquid to solid 2:1, the content of additives in straw 6%, temperature 100~130^{o}C and reaction time of 2 h, under which the productivity of furfural was 9.6% of rice straw and 10.5% of wheat straw respectively(or 80%~85% of the theoretical value), meanwhile the residue became a compound fertilizer.

Key words: straw; furfural; residue; additive; compound fertilizer

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1 INTRODUCTION

Furfural is an important raw material in chemical industry, and its production is increasing annually. In the process of producing furfural, a large amount of waste residue is formed and must be treated safely and economically, because the waste residue contains much acid and its disposal is rather inconvenient. Current available treatments are (1) used as boiler fuel directly, which saves fuel coal but leads to severe problem of corrosion; (2) used as paper pulp material[1] and building raw material[2]; (3) used to produce active carbon, acetyl aceton acid and sorbitol etc., which is also difficult for practical application for it needs complicated technology and equipment. Poptosov[3] used the waste from furfural production as raw material to produce fodder yeast. Russians reported using monocalcium phosphate[4,5], superphosphates[6,7] or metal sulfate[8,9] separately as catalyst to produce furfural so as to delete the waste settlings affecting environment. It was established that under homogeneous conditions with the same pressure and temperature, trivalent cations display higher catalytic activity as compared with di- and monovalent cations[10], but the productivity of furfural is only 30%~35% of theoretical value. The authors reported the research of transforming waste settlings into neutral organic compound fertilizer in furfural production, in which adding only calcium superphosphate, calcium triple superphosphate, or some other additive is needed[11, 12]. In this paper, the production of furfural by straw atmospheric hydrolysis with addition of compound additive was reported, and the effects of content of additives and the conditions of hydrolysis on acidity and furfural productivity were discussed. Compared with the previous results, the ratio of the additive added and the liquid−solid ratio are reduced significantly due to adding metal sulfate, the production cost is expected to decrease because the energy consumption for the purification of product is decreased, and furfural productivity is higher than the results from Russian papers.

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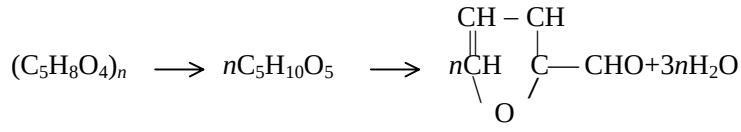
2 THEORETICAL ANALYSIS

The purpose of additives such as calcium carbonate, calcium phosphate, and sodium hydrosulphite is to neutralize sulfuric acid and to transform the residue directly into neutral compound fertilizer. In the same time, it produces hydrolysis catalyst such as calcium triple superphosphate and phosphoric acid to increase furfural productivity. In addition, calcium triple superphosphate, aluminum sulfate, ferric sulfate and sodium hydrosulphite etc. are added to catalyze the hydrolysis of xylan in straw. The major reactions are shown as follows:



$$H_2SO_4 + Ca_3(PO_4)_2 \longrightarrow CaSO_4 + H_3PO_4$$

$$H_3PO_4 + Ca_3(PO_4)_2 \longrightarrow Ca(H_2PO_4)_2$$

$$NaHSO_3 + H_2SO_4 \longrightarrow SO_2 + Na_2SO_4 + H_2O$$

$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2$$

3 EXPERIMENTAL

3.1 Raw Materials and Instruments

3.1.1 Main Raw Materials

Straw of rice and wheat was taken from local countryside. Phosphoric acid, sulfuric acid, sodium hydrosulphite, ferric sulfate and aluminum sulfate were chemical grade regents. Calcium phosphate, calcium triple superphosphate and calcium carbonate were of technical grade.

3.1.2 Instruments

Three-neck flask(5000 ml, Changsha Glass Factory), adjustable electric heater (RT102, Shanghai Specimen Instrument Factory), temperature controller(T205, Shanghai Analysis Instrument Factory), acidimeter (type 25, Shanghai Analysis Instrument Factory).

3.2 Experimental Methods

200 g straw was cut into 1~3 cm long pieces, then well stir-mixed with 400 g sulfuric acid solution and the additives(containing phosphoric acid, calcium triple superphosphate, calcium phosphate, sodium hydrosulphite, calcium carbonate, ferric sulfate and aluminum sulfate) to homogeneity in 30 min. The mixture was loaded into the three-neck flask, stirred and distilled at ambient pressure, 100~130^{o}C, and the fraction was collected.

3.3 Analysis Method

3.3.1 Determination of furfural

The content of furfural was determinated by titration with chloric hydroxy amine.

3.3.2 Determination of acidity of the residue

20 g settlings was dispersed into 500 ml water and stirred for 12 h. Then its pH value was determined with the acidimeter.

3.3.3 Determination of the content of effective constituent in the residue

The contents of P_2O_5 and K_2O in the residue were determined by conventional chemical methods.

3.4 Calculation of Productivity

$$\text{Productivity of furfural (\%)} = \frac{\text{Quality of furfural}}{\text{Quality of the straw}} \times 100\ \% .$$

4 RESULTS AND DISCUSSION

4.1 Effect of the Phosphoric Acid Content on Acidity of Settlings and Productivity of Furfural

The effect of different content of phosphoric acid in the additives on the acidity of the settlings and productivity of furfural was investigated under the otherwise same conditions (100°C, atmospheric pressure, calcium triple superphosphate 5%, calcium phosphate 76.5%~86%, sodium hydrosulphite 2%, calcium carbonate 3%, ferric sulfate 2% and aluminum sulfate 2%, the total additive constituting 5% in the straw, liquid–solid ratio of 2:1).

As shown by experimental results in Fig.1, the acidity of the settlings and the productivity of furfural increase with the increase of content of phosphoric acid, because phosphoric acid has high activity for the hydrolysis. As the acid becomes excessive, more free acid is present in the system, making the acidity of the settling increased. Therefore, in the additive the suitable content of phosphoric acid is 4%~6%.

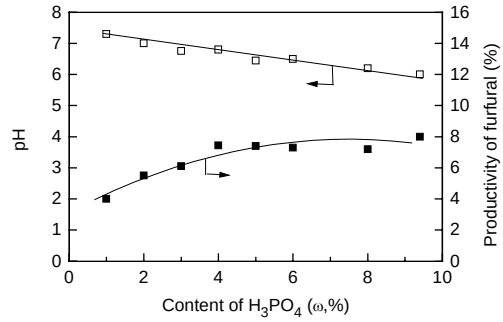


Fig.1 Effect of the phosphoric acid in the additive on acidity of the residue and productivity of furfural

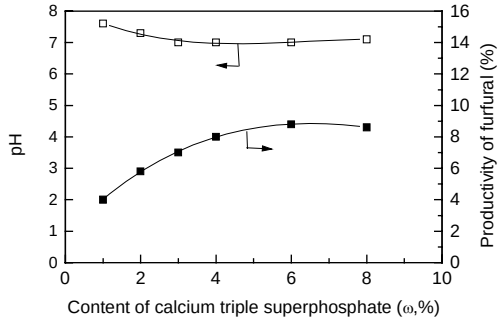


Fig.2 Effect of the calcium triple super phosphate content in the additive on acidity of the residue and productivity of furfural

4.2 Effect of Content of Calcium Triple Superphosphate

As shown in Fig.2, with the increase of calcium triple superphosphate in the additive the acidity of the residue decreases and the productivity of furfural rises. When the content of calcium triple superphosphate in the additive is about 4%, and thereafter, the productivity of furfural increases only slowly. Calcium triple superphosphate contains mainly mono-calcium phosphate. Since mono-calcium phosphate has high activity for hydrolysis, the catalytic activity increases as the content of calcium triple superphosphate raises. The suitable content of calcium triple superphosphate in the additive is about 4%~6%. Besides, in calcium triple superphosphate a little calcium phosphate is contained, and the acidity of the residue decreases when calcium triple superphosphate increases because the neutralization of calcium phosphate.

4.3 Effect of Other Assistants Content

The effect of the contents of sodium hydrosulphite, calcium carbonate, ferric sulfate and aluminum sulfate in the additive on the residue acidity and the productivity of furfural were studied under the otherwise same conditions (100°C, ambient pressure, phosphoric acid 5%, calcium triple superphosphate 5%, calcium phosphate 82%~90%, the total additive in the rice straw 5%, liquid–solid ratio was 2:1). The results are shown in Fig.3.

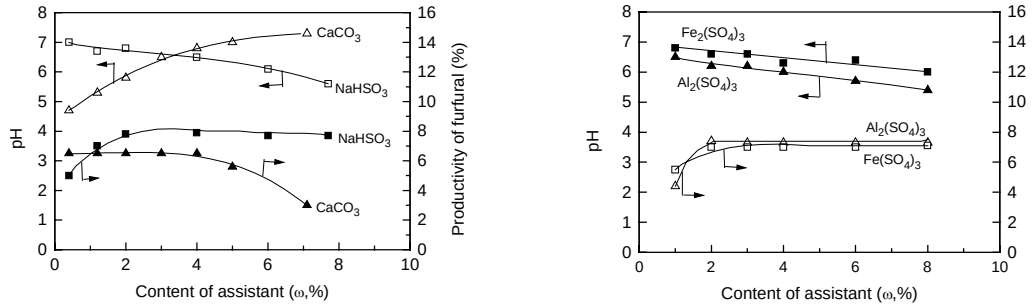


Fig.3 Effect of the assistant content in the additive on acidity of the residue and productivity of furfural

As shown in Fig.3, the acidity of the residue decreases when the content of calcium carbonate increases, but adding too much leads to the decrease of productivity of furfural, because excessive consumption of sulfuric acid occurs with the increase of calcium carbonate, making the hydrolysis incomplete. The acidity of the residue increases slowly with the increase of sodium hydrosulphite. The productivity of furfural raises quickly with the increases of sodium hydrousphite. When its content is over 2% the productivity rises slowly, at the same time the amount of sulphur dioxide increases. To absorb it, the consumption of calcium carbonate is increased and it will affect the productivity of furfural. When the content of sodium hydrosulphite is 2%~4% and calcium carbonate is 2%~3% in the additive the productivity of furfural is higher and the residue becomes neutral. The effects of ferric sulfate and aluminum sulfate content on acidity of the residue are small. In the lower range of content, the productivity of furfural increases quickly with the addition of ferric sulfate and aluminum sulfate, but when the content is about 2% for each, the productivity of furfural levels off, so the suitable content of ferric sulfate and aluminum sulfate in the additive is 2% for the both.

4.4 Effect of the Additive Content in the Straw

Figure 4 shows the effect of amount of additive(containing 5% phosphoric acid, 5% calcium triple superphosphate, 80% calcium phosphate, 3% calcium carbonate, 3% sodium hydrosulphite, 2% ferric sulfate and 2% aluminum sulfate) in the straw on acidity of the residue and productivity of furfural under the otherwise same conditions (100°C, ambient pressure, the weight ratio of liquid to straw 2:1). It is observed that the acidity of the residue decreases and the productivity increases with increasing content of the additive in straw. But when the additive is over 6%, the productivity increases little. The suitable content of the additive in the straw is 6% and under this condition, the productivity of furfural is high enough and the residue is neutral.

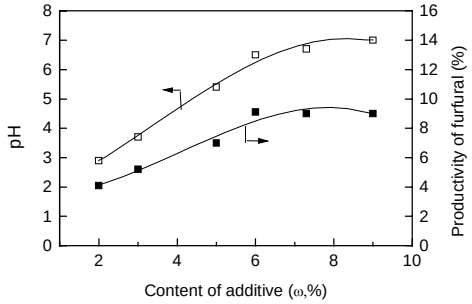


Fig.4 Effect of the additive content in the straw on acidity of the residue and productivity of furfural

4.5 Effect of the Conditions

The effects of the conditions of reaction such as the distillation temperature, time and the ratio of liquid to solid were examined under the otherwise same conditions (ambient pressure, the additive contains 5% phosphoric acid, 5% calcium triple superphosphate, 80% calcium phosphate, 3% sodium hydrosulphite, 3% calcium carbonate, 2% ferric sulfate and 2% aluminum sulfate, the content of the additive in the straw was 6%). The experimental results shown in Table 1 suggest that the acidity of the residue decreases with the increase of temperature, because at high temperature the neutralization become more completely. Also, the productivity of furfural increases with the increase of temperature. So it is beneficial to control the temperature at a high level. But the distillation temperature is limited by pressure and concentration of salts, and it is not easy to raise temperature freely. The acidity of the residue decreases with reaction time since the additives react with sulfuric acid more completely. But if the time is too long, the furfural is easy to undergo side reactions such as oxidation and polymerization to make the productivity decrease. Therefore, it is important to design a highly efficient reactor (e.g., to enlarge the ratio of height to radius) so as to shorten the distilling time, meanwhile ensuring efficient neutralization between the additive and acid. All the measures can reduce the residue acidity and increase the productivity. The productivity of furfural increases with the ratio of liquid to solid, but a too large liquid–solid ratio will increase the cost of production, so the suitable ratio of liquid to solid is 2:1.

Table 1 Effect of the reaction conditions on the acidity of residue and productivity of furfural

Reaction condition			Productivity (%)		pH of the residue
Temperature (^{o}C)	Time (h)	Liquid– solid ratio	Straw of rice	Straw of wheat	
100	2.0	3	10.2	11.5	7
100	2.0	2	9.6	10.6	6
100	2.0	1	7.0	7.6	5
100	3.5	2	5.8	6.2	7
150	2.0	3	11.2	12.5	7
130	2.0	3	12.5	13.8	7
130	1.5	3	12.8	13.9	6
130	2.5	3	11.8	12.2	7

4.6 Comparison of Furfural Productivity and Effective Fertilizer Ingredient in Residue

Table 2 shows the comparison of this method with the others to produce the furfural from straw. The reaction conditions of this method were as follows: additive containing phosphoric acid 5%, calcium triple superphosphate 5%, calcium phosphate 80%, calcium carbonate 3%, sodium hydrosulphite 3%, ferric sulfate 2% and aluminum sulfate 2%, total additive to straw 6%, straw 200 g, liquid 400 g, at 100^{o}C and ambient pressure, 2.5 h. It is demonstrated that when producing furfural with the straw of wheat and rice by this method, the residue is neutral, and the productivity is higher than other methods.

Table 2 Productivity of furfural and pH of the residue

Method	Productivity of furfural (%)		pH of residue
	Straw of wheat	Straw of rice	
6% HCl	8.2	7.0	<1
6% H_2SO_4	5.6	4.5	<1
This method	10.6	9.6	6

It is also determined that in the residue (after distillation, 200 g residue well stir-mixed with 200 g powdered rock phosphate, aging for 72 h) and the content of ingredient P_2O_5(14.68% by dry weight) and K_2O (0.76% by ash from burning the residue) meets the standard of the compound fertilizer. And when the straw decomposes, the manurial effect will be higher. The settling do not contain harmful substances. It has no pollution to the environment and does not harm soil and crops.

5 CONCLUSIONS

Using additives such as phosphoric acid, calcium triple superphosphate, calcium phosphate, calcium carbonate, sodium hydrosulphite, ferric sulfate and aluminum sulfate at a suitable content and controlling the conditions of reaction, the residue has been transformed into a neutral compound fertilizer and the productivity of furfural is almost doubled compared with the method of normal sulfuric acid catalysis. The suitable content of ingredients in the additive are as follows: phosphoric acid 4%~6%, calcium triple superphosphate 4%~6%, calcium phosphate 80%~90%, calcium carbonate 2%~3%, sodium hydrosulphite 2%~4%, ferric sulfate 2%~4% and aluminum sulfate 2%~4%. The suitable content of the total additive in the straw is 6%. Since distillation is at ambient pressure, it only needs simple technology and equipment, and low investment. It will not bring new pollution. It seems that this method is very promising for production.

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