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Furfural residues from straw become complex fertilizer by addition method

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Abstract: The additives such as phosphoric acid, calcium phosphate, calcium super phosphate, calcium over-super phosphate, calcium carbonate, sodium hydrosulphite, etc. were used to produce furfural from the straw by hydrolysis with sulfuric acid. The effect of amount of the additives, the content of the added substance and the conditions of distillation on the acidity of the residues were studied. The experiment results showed that the all residues became neutral complex fertilizer, and the productivity of furfural increases under the following conditions: sulfuric acid concentration is 20% (by weight), the ratio of liquid to solid is 3:1—4:1 (by weight), the ratio of the additives to straw is suitable.

Key words: straw; furfural; residues; complex fertilizer

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Introduction

Furfural is a kind of important raw material in chemical industry. With the growth of its use, its production is increasing annually. But in the process of producing furfural, a large number of waste residues are brought. So it is very important to deal with the residues. At present, the methods to deal with it are as follows: (1) used as boiler fuel directly. This method can save fuel coal but has strong corrosiveness; (2) used as paper pulp material (Li, 1994). But the waste residues contain much acid and this disposal is rather inconvenient; (3) used to produce active carbon, acetyl acetonate acid, sorbitol, and so on. This way is also difficult to spread because it needs higher technology and complicated equipment. Vedernikov reported that using super-phosphates as a catalyst to produce furfural (Vedernikov, 1993a, 1993b). The research of transforming waste residues in furfural producing into neutral organic complex fertilizer, only adding calcium super phosphate, calcium over-super phosphate, and some other additives was reported (Liu, 1996). This paper presents the method that using straw to make furfural by atmospheric hydrolysis, and discussed the effects of the content, the amount of additives, and the conditions of hydrolysis on acidity of residues and using both phosphoric acid and calcium phosphate, or calcium over-super phosphate, selecting other assistants, and controlling suitable ratio of additives and distillation condition, the productivity of furfural can be raised 70%, mean while, the waste residues can be transformed completely into neutral organic complex fertilizer, and the cost of production can be reduced.

1 Experimental

1.1 Raw materials and instruments

Main raw materials: Straw of rice and wheat straw were taken from local countryside. Phosphoric acid, sulfuric acid, and sodium hydrosulphite are chemical pure. Calcium phosphate, calcium over-super phosphate and calcium carbonate are industrial pure.

Instruments: 1L three-neck flask, adjusted electric heater, temperature controller, 25-type acidimeter.

1.2 Experimental methods

Reaction: first, straw was cut into 1—3 cm long pieces, added sulfuric acid, soaking. Then the additives were added in, mixed evenly. Last, the mixture was put into the three-neck flask and distilled at normal pressure, and the fraction was collected.

Determination of acidity of the residues: 20g residues was filtrated into 500 ml water and stirred 12h. Then its pH value can be determined with the acidimeter.

Determination of the content of efficient constituent in the residues: the content of P_2O_5 and K_2O in the residues was determined by normal chemical method.

1.3 Experimental principle

The method of the adding substances such as calcium phosphate, sodium hydrosulphite etc. has been used to neutralize sulfuric acid in process of producing furfural, so the residues transform directly into neutral complex fertilizer. The major reactions are shown as follows:

$$H_2SO_4 + Ca_3(PO_4)_2 \longrightarrow CaSO_4 + H_3PO_4,$$
$$H_3PO_4 + Ca_3(PO_4)_4 \longrightarrow Ca(H_2PO_4)_2,$$
$$NaHSO_3 + H_2SO_4 \longrightarrow SO_2 + Na_2SO_4 + H_2O,$$
$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2.$$

2 Results and discussion

2.1 Effect of the ratio of phosphoric acid and calcium phosphate to raw materials on acidity of residues

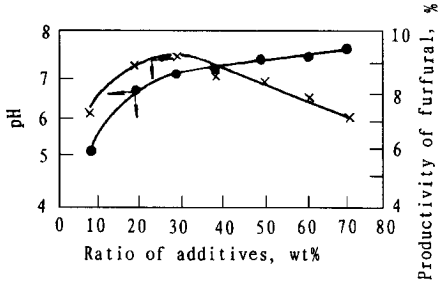

Fig. 1 Effect of ratio of additives to straw on the acidity of the residues

The ratio of phosphoric acid to calcium phosphate is unchanged, it has experimented in the effect of different ratio of additives to straw on the acidity of the residues. The results are shown in Fig. 1.

As seen in Fig. 1, with the ratio of the additives to straw raising, the acidity of residues decreased. But the productivity of furfural is decreased when the ratio of the additives to straw is much higher. So suitable ratio of the additives to straw is 20%—30%. Following above conditions, the productivity of furfural is higher and the residues is nearly neutral.

2.2 Effect of ratio of phosphoric acid to calcium phosphate on acidity of the residues

It has experimented in the effect of different ratio of phosphoric acid to calcium phosphate on the acidity of the residues under the same conditions for the rest as before. The results of the experiment are shown in Fig. 2.

As seen in Fig. 2, the acidity of the residues increases with the increase of phosphoric acid. So the content of phosphoric acid can not be much higher. But if its content is very small, the productivity of furfural shall decrease. The suitable content of phosphoric acid is 8%—10%.

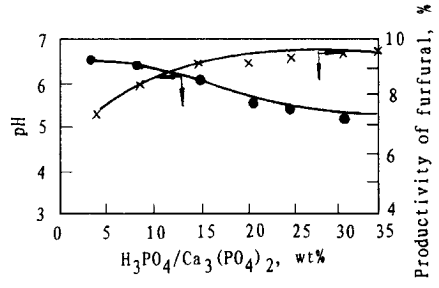

Fig. 2 Effect of ratio of phosphoric acid to calcium phosphate on acidity of residues

2.3 Effect of content of assistants on acidity of the residues

It has experimented in the effect of the content of sodium hydrosulphite and calcium carbonate on the acidity of the residues under the same conditions for the

rest as before. The results are shown in Fig.3.

As seen in Fig. 3, when the content of calcium carbonate increased, the acidity of the residues decreased. But too much its content will make the productivity of furfural decrease because hydrolysis is uncompleted. With the content of sodium hydrosulphite increased the productivity of furfural increased, and the acidity of the residues reduced, but the amount sulphur dioxide increased. To absorb this gas, the exhausted amount of calcium carbonate increased. When the content of sodium hydrosulphite is 4%—6% (among additives, wt %, the same as below), and calcium carbonate is 6%—8%, the productivity of furfural is higher, and the acidity of the residues is nearly neutral. The effect of content of assistant (Ⅲ) on the acidity of the residues is small, but the productivity of furfural increases much with the addition of assistant (Ⅲ). Because of its higher value, the amount of assistant (Ⅲ) can not be added too much.

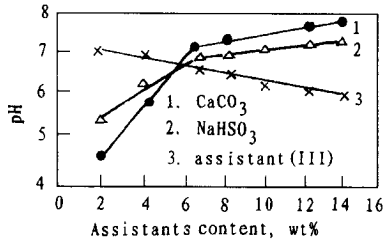

Fig.3 Effect of content of assistants on acidity of residues

2.4 Effect of amount of calcium over－super phosphate on acidity of residues

The effect of amount of calcium over-super phosphate on the acidity of the residues is shown in Fig.4. As seen in Fig.4, with the amount of calcium over-super phosphate increased, the acidity of residues decreased, and the productivity of furfural raised. But the cost of the production increased. So the added amount of calcium over-super phosphate is about 20% (to straw, by weight).

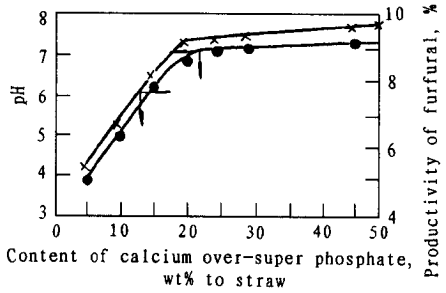

Fig. 4 Effect of content of calcium over － super phosphate on acidity of residues

2.5 Effect of conditions of distillation on acidity of residues

Under the other same conditions, the effect of the conditions of distillation such as the distilling temperature, time, the ratio of liquid to solid has been investigated. The experiment results are shown in Fig.5, Fig.6 and Fig.7 respectively. As seen in these figures, the acidity of the residues decreased with the temperature of distillation raised. The reason is that when temperature raised, the neutralization finished more completely. Also, the productivity of furfural increased with temperature raised. So raising the temperature to be suitable higher, the productivity of furfural is high, and the residues is nearly neutral. But the distilling temperature is limited by the system pressure and by the concentration of the salts. It is very difficult to raise temperature freely. With the distilling time extending, the additives react more completely, and the acidity of the residues decreased. But if the time last too long, the furfural is easy to produce side reactions such as oxidation and polymerization to make the productivity decrease. So designing high efficient reactor (e. g. to enlarge ratio of highness to radius) to shorten the distilling time, at the same time ensuring the neutralization between additives and acid efficiently. All these can reduce the acidity of the

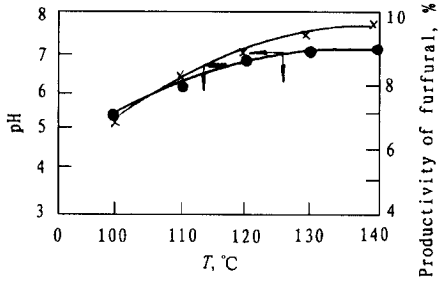

Fig.5 Effect of temperature on acidity of residues

residues. From the results in Fig. 7, it is seen that when the water content ranges between 200% and 300% (to straw, wt%), the acidity value of the residues is above 6. If the content of water is too much, it will increase the cost of the production.

2.6 Efficient constituent compound in residues

The content of efficient constituent phosphorus and potassium in the residues after distillation are shown in Table 1.

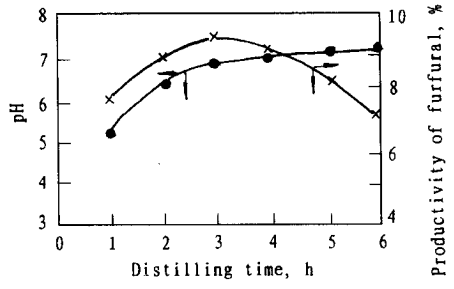

Fig. 6 Effect of distilling time on acidity of residues

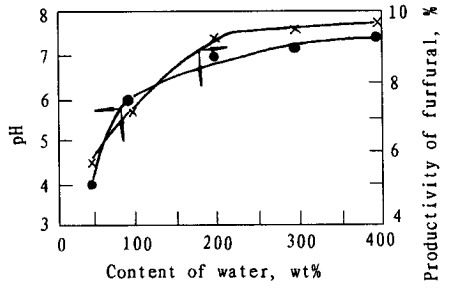

Fig. 7 Effect of content of water on acidity of residues

Table 1 Efficient constituent in residues

Efficient constituent	P_2O_5	K_2O
Content, wt %	14.68	0.76

As seen in Table 1, the content of efficient constituent phosphorus and potassium coincides the standard of phosphor-kalium complex fertilizer. And when the straw decomposes, the manurial value will be higher. The residue does not contain harmful substances. It has no pollution to the environment and does not harm to soil and crops.

3 Conclusions

Using additives such as phosphoric acid, calcium phosphate, calcium carbonate, sodium hydrosulphite, and calcium over-super phsopate, etc., controlling suitable content, the residues are changed into the neutral complex fertilizer.

The suitable ratio of each substance added to the whole additives is as follows: phosphoric acid is 6%—8% (by weight, the same as the bellow), calcium phosphate is 70%, calcium carbonate is 8%—10%, sodium hydrosulphite is 4%—6%, and the other assistant 5%— 10%.

If using calcium over-super phosphate as the additive, the amount of addition is 10%—15% (wt%, to straw). In the same time, adding other additives, the productivity of furfural will increases largely.

To use normal pressure distillation, it only needs simple technology, low demand of equipment, and low investment. It will not bring new pollution. So this method may possess better commercial value.

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