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Research Progress on Furfural Residues Recycling: A Literature Review

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***Abstract*—Millions of tons of furfural residues from the furfural industry are produced every year in China. Proper recycling of these residues is highly desirable as it may reduce associated environmental problems and increase the economic viability of the furfural industry. Research progress on furfural residues recycling is reviewed. The residues have high potential for agricultural applications such as organic fertilizers, soil conditioners, artificial soil and culture media, as well as for the production of activated carbon, bioenergy, and for biobased chemicals such as ethanol.**

Keywords-recycling; furfural residues; agricultural utilization; activated carbon; bio-energy; bio-ethanol

I. INTRODUCTION

Economic factors such as increasing oil prices related to the depletion of fossil resources and environmental considerations have stimulated worldwide interest in the use of renewable resources. Biomass is a sustainable alternative for conventional fossil feedstocks, particularly when environmentally sound production and processing techniques are applied. Furfural from biomass is regarded an important bio-based chemical and has attracted large attention for its wide range of applications.

However, the furfural processing industry produces considerable amounts of waste and this restrains further developments in the furfural industry. In general, a furfural processing plant with an annual furfural production level of 1000t produces about 13000t/a of wastes. With an increasing environmental awareness and tightening legislation, treatment and utilization of these large amounts of waste from furfural industry is the preferred option [1]. To date, many studies have been performed on alternative disposal or reuse options for furfural residues. The research progress in furfural residues utilization is reviewed in this paper.

II. FURFURAL RESIDUES FOR AGRICULTURAL APPLICATIONS

Furfural residues are carbon rich, acidic (pH=2) and also contain valuable nutrients. For instance, it typically contains 5.0-6.0g/kg of N, 1.2-1.5g/kg of P_2O_5, 1.5g/kg of K_2O, 360g/kg of humic acids, more than 980g/kg of organic matter. Application of the residues for agricultural purposes showed positive effects on, for instance, soil alkalization, amelioration of solonetz and crop yields.

A. Residues as organic fertilizer

Fuyan Xin et al. [2] recently reported a production method for a soil fertilizer consisting of a mixture of solid residues from seaweed and furfural processing units. The seaweed residue is obtained from seaweed processing and involves the following steps: 1) adding water and potassium hydroxide into a reaction kettle, heating the mixture, and then adding dry brown seaweed, and digestion; 2) filtration of the digested brown seaweed dispersion; 3) neutralization of the filtrate by phosphoric acid to obtain seaweed extract to be directly used as a liquid seaweed fertilizer; and 4) mixing of the solid residue with furfural residues, followed by pelletizing and drying to obtain a solid soil fertilizer.

Another invention relates to a multifunctional organic fertilizer containing Chinese herbal medicines and furfural residues. The following raw materials are used in the formulation (weight portions): 5 portions of traditional Chinese medicines, and 95 portions of organic substances, including furfural residues. The traditional Chinese medicine ingredients are (weight percentage): 15-20% of kuh-seng, 10-15% of scutellaria, 15-18% of tripterygium wilfordii, 15-18% of kusnezoff monkshood root, 20-22% of meliaceae seeds, 5-15% of honey locust fruit, and 5-7% of stemona. The organic substances consist of the following raw materials (weight percentage): 15.8% of bean pulp, 21% of furfural residues, 31.6% of crop straw powder, and 31.6% of plant ash. The multifunctional organic fertilizer is easy to prepare at low integrated cost, has a wide application range and has shown to have remarkable positive effects on crop yields. Furthermore, due to the presence of the Chinese herbal medicines, it is highly acknowledged by people and society [3].

B. Residues as soil conditioner

In 1998, Cai Axing and coworkers [4] reported that furfural residues may be used to improve soil properties such as the pH (reduction of alkalinity), bulk density and compactness, water permeability and retention ability of the soil.

Li Qian et al.[5] studied the effects of furfural residues as well as by-products from flue gas desulphurization (BFGD) on ameliorating saline-sodic soil. The results showed that pH, soluble salts and the exchangeable sodium percentage (ESP) of the soil were decreased by applying both residues. Remarkably, a synergistic effect was observed when applying the BFGD and furfural residues together.

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Xianghao Cui et al. [6] disclosed a formulation to be used against moderate and severe soda salinization. The formulation consists of a modifier and an organic fertilizer. Modifier components are humic acids, zeolites, an acid conditioner, fly ash and furfural residues; the organic fertilizer comprises of fermented chicken manure, crushed straw and wood vinegar liquid. The formulation is applied at a level of 13-17t/hm^2 of saline-alkali land before harrowing and transplanting. The formulation is said to integrate physical- and chemical functions like complexing, neutralizing, ion exchange, adsorption, desorption, passivation, fixing, preventing salt accumulation and emulsion breaking. As a result, the cation exchange capacity (CEC) of the soil increases with times, the pH value decreases, the amount of soluble Na ions is reduced.

C. *Residues as artificial soil*

In 2006, Feng Yongjun et al. [7] examined the chemical properties of artificial soil formed by mixing organic furfural residues and inorganic fly ash. The results indicate that the artificial soil is suitable for agricultural applications after irrigation and desalination. The available nutrients in the artificial soil have a positive effect on plant growth and the inorganic components improve pH values to the desired neutrality.

D. *Residues as culture media to cultivate edible fungi*

A number of papers have appeared on the utilization of furfural residues as culture media for edible fungi such as Ganoderma lucidum, Auricularia and Eniki mushroom.

Naiquang Chen et al. [8] reported an invention for the production of culture media from industrial furfural residues for the breeding of edible fungi. The furfural residues are treated with lime and mixed with bran, cottonseed shell, urea, and a phosphorus containing fertilizer. The pH value of the product is between 5.5-6.5, the total nitrogen content between 0.8-1.2%, and the total P_2O_5 content between 0.2-0.3%. The operating conditions for culturing the edible fungi with the new culture media are similar to those for conventional ones. With the novel media, the biological efficiency is improved by 45-55% compared to conventional media from furfural residues.

III. FURFURAL RESIDUES FOR ACTIVATED CARBON PREPARATION

Activated carbon is typically produced from carbonaceous sources like nutshells, peat, wood, coir, lignite, coal and petroleum pitch. Furfural residues have a carbon content of over 40% and as such may serve as a source for activated carbon.

In general, activated carbon is produced by the following two processes: physical reactivation and chemical activation. Among the studies of furfural residues for activated carbon preparation, physical reactivation was the most studied method.

In 1992, first attempts to use furfural residues for the preparation of activated carbon were reported by Guangyu Cai, et al. [9]. A kind of furfural residues (corncob residues of furfural manufacture (CRFM)) activated carbon catalyst is obtained by using CO_2, ammonia, Ar or N_2 to proceed the modifying treatment in the course of preparation. This catalyst is used for eliminating and recovering SO_2 in the flue gas. The results indicate that the atmospheric pollution of SO_2 in the tail gas exhausted from sulfuric acid factory, smeltery, chemical plant and power plant can be effectively eliminated, at the same time, sulfuric acid with concentration about 30% can be recovered. The catalyst is especially suitable for decontaminating treatment for such flue gas as containing fair amount of dust and relatively low SO_2.

In 2004, Li Guobin and Yang Mingping [10] studied the synthesis of granular activated carbon from furfural residues. The optimum process conditions by using steam activation are as follows: carbonization temperature of 400 ℃, activation temperature of 800℃ and an activation time of 1h. The following product properties were obtained: strength of 93%, specific surface area of 45m^2/g, maximum iodine absorbance of 814mg/g, methylene blue adsorption levels of 198mg/g and a benzene absorption value of 22.4%-wt. These product properties fall within the range of activated carbons made from coal.

New technologies for the synthesis of activated carbon with the objectives to reduce costs and environmental impact are emerging. For instance, microwave heating has recently been introduced for the preparation of activated carbon. Wang Nanfang et al. [11] report the synthesis of activated carbon from furfural residues using microwave-CO_2 activation at a microwave power range between 160 - 800W. The results indicate that microwave irradiation mainly destroys in-plane crystallite size (La) of activated carbon and the pore structure is well developed at the microwave power of 640W. In addition, the total amount of acidic groups was reduced considerably, and this particularly holds for the amount of carboxylic groups (less than 0.0345mmol/g).

An invention of 2008 discloses an activated carbon production process using furfural residues. Impurities in the furfural residues are removed by a centrifugal winnowing type of separator. Subsequently, the water content of the furfural residues is reduced to 5% by microwave drying. In the next step, the activated carbon is prepared by placing the furfural residues in a carbonization furnace and the sample is heated up to 400℃ for 30min to complete the carbonization process [12].

In case of chemical activation method of activated carbon, the raw material is impregnated with certain chemicals prior to carbonization. Typically acids, strong bases, or salts are applied. $ZnCl_2$ is a well known example of the latter class. Furfural residues in combination with an acidic activating agent like H_3PO_4 to prepare activated carbon with desirable properties have been described [13,14].

IV. ENERGY POTENTIAL OF FURFURAL RESIDUES

Furfural residues contain large amounts of organic compounds and as such have potential to be used as an energy source. Energy from agricultural residues may be obtained by a range of conversion processes. The processes are used for furfural residues are mostly thermochemical (combustion, gasification, pyrolysis) in nature. Tab.1 lists

TABLE I. LIST OF PATENTS RELATED TO THE COMBUSTION OF FURFURAL RESIDUES

Patent or Application NO.	Inventor	Title	Publication date
CN201339016 (Y)	Chunlin Li	Sawdust and furfural residue carburizing device	2009-11-04
CN201306195 (Y)	Yujun Wu	Self-contained power station system with furfural waste residue boiler	2009-09-09
CN101196289 (A)	Shucai Zhao, et al.	High-efficiency boiler for combustion of furol waste slag	2008-06-11
CN200993368 (Y)	Shucai Zhao, et al.	Efficient furfural-residue-fired boiler	2007-12-19
CN2934944 (Y)	Shucai Zhao, et al.	High-efficiency furfural slag-combusting boiler for electricity generation	2007-08-15
CN2893427 (Y)	Shucai Zhao, et al.	Non-induced air furfural waste residue-combustion boiler	2007-04-25
CN2539059 (Y)	Yang Taimin	Boiler using furfural residue as fuel	2003-03-05
CN2256983 (Y)	Liu Fu, et al.	Efficient furol residue boiler	1997-06-25

patents related to the utilization of furfural residues for energy generation by combustion. A number of studies have been reported mainly involving high-efficiency boilers.

Li Zhujun et al. [15] reported an invention to produce oxidant- and binder-free charcoal briquettes by drying, crushing, moulding, carbonization a mixture consisting of mainly furfural residues, wood flour and soda. The briquettes show good burning properties without emissions of smoke and smell. The process is characterized by a simplicity of the technology and low production costs.

A number of studies report the conversion of furfural residues by pyrolysis, either using furfural residues alone or blended with other materials such as rice husk[16,17]. These studies indicate that the conversion of furfural residues to liquid energy carriers in the form of pyrolysis oil is well possible.

V. OTHER APPLICATIONS FOR FURFURAL RESIDUES

Furfural residues can be used for waste water treatment. Wang Hailiang et al. [18] found that the humic acids in furfural residues can chelate copper ions. This shows the potential for the use of furfural residues to treat wastewater containing high concentrations of copper ions. In addition, Gao Xiaorong and Ren Guangjun [19] studied the adsorption of dyes, e.g. present in waste water, on furfural residues. For congo red, the adsorption characteristics as a function of processing variables like contact time, temperature, absorbent particle size and absorbent intake were investigated. The adsorption isotherms at different conditions were determined. On the basis of these funding, it may be concluded that furfural residues are potentially attractive to be used as an absorbent to treat dye wastewater.

Zhang Lei et al.[20] studied the feasibility to use furfural residues (CRFM) to produce bio-ethanol by enzymatic hydrolysis. The results indicate that the efficiency of the enzymatic hydrolysis is promoted by a water pre-treatment. Jianxin Jiang et al. [21] also studied the conversion of furfural residues to bio-ethanol. Their invention provides a method for preparing absolute ethanol from the furfural residues. The method has the advantages that it combines rectification technology with a modern advanced separation technology to improve the production efficiency.

Another invention relates to a method for preparing microcrystalline cellulose and ethanol from furfural residues. It comprises of the following steps: (1) ethanol is taken as a solvent, a circulating ultrasonic extraction method is adopted, and the lignin is separated from the extraction liquid; (2) the extraction residues are treated with a complex enzyme mixture consisting of endoglucanase and beta-glucosaccharase for the enzyme-catalyzed hydrolysis, and the hydrolysate is fermented to ethanol; and (3) the hydrolysis residues are subjected to an acid-catalyzed hydrolysis to separate the microcrystalline cellulose. The extraction method has the advantages that it is green and environment-friendly, the enzyme-catalyzed hydrolysis is performed under mild conditions, the acid concentration for the acid hydrolysis is low, the reaction times are short, and the yields of each step are high [22].

According to Xu Chunjiu [23], the production process of packing paper can be improved by using waste residues from the furfural and xylitol industry. It includes the following steps: feeding the waste residues into a beating pool, beating and washing the residues, neutralization by adding lime hydrate and carboxymethyl cellulose (CMC), feeding the fine-beaten pulp material into a pulp storage pool, paper-making, pressing to reduce the water content, drying, regulation of the paper thickness, calendaring and rolling up. The invention thus uses furfural and relates residues to make packing- and corrugated paper using a simple process.

VI. CONCLUSIONS

Due to environmental concerns, landfilling of agricultural and food processing waste materials is not acceptable anymore and has declined in recent years. The utilization of furfural residues is essential to improve the economic attractiveness of the furfural industry and to contribute to sustainable development. This review gives an overview of possible valorization routes for furfural residues. The use of furfural residues has potential for agricultural applications (e.g. fertilizer, soil improver), for the production of activated carbon, as an energy source by combustion or pyrolysis, and to produce biobased chemicals such as ethanol by fermentation. Further research and development will be required to make successful large scale commercial implementation possible.

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