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BLACK POPLAR (*Populus nigra* L.) WOOD WASTES AS A RESOURCE FOR FURFURAL AND TANNINS PRODUCTION

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ABSTRACT

The possibility of producing furfural from black poplar (*populus nigra* L.), wood wastes was studied using acid hydrolysis (hydrochloric acid HCl at concentration of 13.2%) method. The extraction of tannins from the wood industry wastes (sawdust) was also investigated in this study. The results of the study showed that up to 10% of furfural and 4.07% of tannins can be obtained from wood industry wastes (sawdust) for subsequent applications and utilization in some more valued industrial uses.

انتاج مادتي الفورفورال والتانين من مخلفات خشب اشجار القوغ الاسود

يونس حسين سليمان

قسم البستنة وهندسة الحدائق / كلية الزراعة / جامعة تكريت

الخلاصـــة

تمت دراسة امكانية انتاج مادة الفورفورال من مخلفات خشب اشجار القوغ الاسود بطريقة التايين الحامضية باستعمال حامض الهيدروكلوريك بتركيز 10% – 16%. كما تمت ايضا عملية استخلاص التانين من المخلفات. من العوامل التي تؤثر علي التفاعل تم اختيار درجة الحرارة وتركيز الحامض بالإضافة الي وقت المعاملة . اوضحت الدراسة بانه يمكن الحصول علي نسبة فورفورال بحدود 10%، وتانين بنسبة 4,07% من المخلفات لاستعمالات اقتصاديه لاحقه.

كلمات مفتاحية :
فورفورال ، تانين ، مخلفات ، القوغ الاسود .
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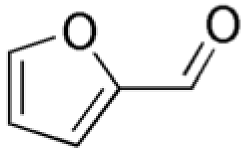
INTRODUCTION

The increasing demand on wood products due to increasing population for different needs, affected the wood industry by creating millions of tons of wood wastes (Ebert, 2011). These wastes could be re-used when treated efficiently. The production of useful chemicals from these wastes is a major approach which is added to other approaches such as using the wastes in creating energy by direct combustion to supply the wood industries mills with energy (Demirbas, 2001).

The production of chemicals from these wastes is a new approach to help humanity exploring multisource of materials to meet the needs and over a chance to reduce depending on petroleum to produce chemicals and make the wood wastes as another source in producing chemicals for human need in addition to petroleum. The producing of furfural and tannins from wood wastes (sawdust) is an alternative which is used in large scale internationally (Gravitis et al., 2001).

Furfural is the organic compound derived from a variety of agricultural by-products such as corncobs, oat hulls, and wheat barn. In addition to that furfural can be extracted from wood wastes. Furfural is produced by removing water from or dehydrating five carbon sugars such as xylose which is commonly obtained from hemicelluloses fraction of biomass wastes. The xylose hydrolysis leads to dehydration of three water molecules to produce furfural ($C_5H_4O_2$ Furan2-Carbaldehyde).



Furfural is used as an industrial solvent for refining and lubricating, and starting material for the production of chemicals and polymers (Busing et al., 1978), it is also used as a binder or substituted chemical in formulation of wood based panels' binders lately (Kim et al., 1994 and Dao and Zavarin, 1996). Furfural is used as a fungicide, and also is used in production of tetrahydrofuran (THF) which is an important industrial solvent and as a solvent for agricultural formulation to help herbicides penetrating the leaf structure (weed killer) (Gravitis et al., 2001 and Win, 2005). Furfural can be produced from xylan-rich agricultural wastes in which the amount of hydrolyzed xylose to produce furfural is about 25%. In addition to hardwood by two-stage hydrolysis via xylose as intermediate product or directly in one stage, the amount of recovered furfural from wood hydrolysis exceeds 11% (Maloney, 1978, and Ko et al., 2008). The monosaccharide products including furfural can be isolated from pulping spent liquors (Herrick and Hergert, 1977). The dilute-acid hydrolysis in one single step can produce furfural from different lignocellulosic materials (Goldstein, 1981 and 1988).

Tannins are water-soluble polyphenolic compounds having wide prevalence in plants. Hydrolysable and condensed tannins are the two major classes of tannins. These compounds have a range of effects on various organisms – from toxic effects on animals to growth inhibition of microorganisms. The tannin compounds are widely distributed in many species of plants, where they play a role in protection from predation, and perhaps also as pesticides, and in plant growth regulation. The tannins are important commercial products primarily used in the leather and dye industries. Most of the leather in the US was earlier treated with domestic tannin extracted from hemlock and oak bark or chestnut wood (Hillis, 1962). In addition to tanning industry, tannins are used in adhesives and plastic industries (Hillis, 1962), and finally, tannins are used as a protective film of metallic boards and tubes underground against soil micro-organisms, (White, 1958). The most promising utilization at present and in the future is the substitution of phenol in phenol-formaldehyde resins for the production of plywood, particleboards and laminated beams in which tannin based adhesives were approved with successful results and gaining increasing industrial and technical acceptance, (Leyser, 1990, Lu et al., 1995 and 1995b, Pizzi, 1995, Zhoo et al., 1995, Santana et al., 1995, and Vazquez et al., 1996). There is much experience in this field in Australia, New Zealand and the US and the industrial application of wattle tannin-based adhesives was well established in South Africa. In Germany the total amount of exterior-grade particleboard and plywood production was based on wattle tannins replacing phenol and partially urea in formaldehyde resins (Pizzi et al., 1981). The concentration and the diversity of tannins in forest trees are different (Fengel and Wegener, 1983). Recent studies have demonstrated that products containing chestnut tannins included at low dosages (0.15–0.2 %) in the diet can be beneficial (Schiavone et al., 2008). Some studies suggest that chestnut tannins have been shown to have positive effects on silage quality in the round bale silages, in particular reducing NPNs (non-protein nitrogen) in the lowest wilting level (Tabacco et al. 2006).

In this study, two approaches were investigated and they are: the possibility of furfural production from wood hemicelluloses sugars (pentosans) of poplar wood wastes (sawdust) via acid hydrolysis using hydrochloric acid, and the extraction of tannins from these wood wastes.

MATERIALS AND METHODS

The sawmill wastes (sawdust) of black poplar (*Populus nigra* L.) wood machining were used to produce furfural and tannins.

Furfural was produced via 13.2% HCl hydrolysis of alcohol-benzene extracted sawmill wooden powder (sawdust) in a reflux extraction with small amount of Sodium chloride for 90 minute at 105-110^{o}C. The purification of furfural was done using the volumetric Bromate-Bromide method and titration with Thiousulphate (Browning 1967).

The tannins samples (sawdust) were collected from three different mills and in each mill, three locations (area where they collected the trunks from) were chosen to randomize the results. The tannins were extracted from wood sawdust using American Leather Chemists Association ALCA method (browning, 1967). The samples of wood (sawdust) were extracted with water for 7 hours, then the extracts were analysed for solids and solutes using Kaolin. The analysis of non-tannins fraction was done using of hide powder and chrome alum solution. Tannins fraction was determined on the difference of weight of soluble and non-tannins, the purification of tannins was done by extraction with Ethyl acetate (Browning 1967).

RESULTS AND DISCUSSION

The results of the major effective factors in this study appeared in Tables 1 and 2 and figure 1.

Furfural :

Effect of the reaction temperature:

Table 1 shows the effect of the reaction temperature on the final yield of furfural in which the optimum temperature is 105-110^{o}C, the higher temperature above 110^{o}C reduced the amount of furfural due to breaking down of hemicelluloses under acid hydrolysis, while the low temperature (lower than 105^{o}C) resulted in low furfural percent due to lower hydrolysis rate of hemicelluloses which is the main source of furfural.

Effect of acid concentration:

The acid concentration effect was very much similar to temperature effect as the high concentration of HCl resulted in lowering furfural due to break down of wood carbohydrates, while the low concentration of HCl lowered the yield of furfural because of lower hydrolysis rate as can be seen in table 1.

The results of this study in table 1, is in the range of furfural percentage of hardwoods species as table 1 shows a yield of furfural ranged from 6.93% to 10.62%. The furfural main resource is the wood xylose five carbon sugar which makes of 21.2% of the poplar wood polyoses (five carbon wood sugar), (Timell, 1969, and Lai, et al., 1977). There is a percentage found of polyoses in hardwoods at 31.7%, (Fengel and Wegener, 1983).

The effect of reaction temperature on furfural yield was clear in table 1 as the temperature increased from 95^{0}C to 120^{0}C. The yield increased at 105-110^{0}C (from 8.10 at acid concentration of 10% to 9.55% at the same concentration) was due to enhanced breaking effect of glycoside linkages of carbon-oxygen in the structures of xylose as the reaction to produce furfural is through reduction of hydroxyl groups. When the reaction temperature increased to 120^{0}C the yield of furfural decreased (from 9.55% to 9.37% at the same acid concentration). The effect of acid concentration was also clear in table 1 as the acid concentration increased from 10% to 13.2%, then to 14% and finally to 16% with the three reaction temperatures. The furfural yield increased by increasing of the acid concentration from 10% to 13.2% but decreased after at 95^{0}C, while it increased more from 10% to 14% and decreased after at 105-110^{0}C (9.55% at 10% increased to 10.11% with concentration of 13.2% and to 10.62% with

concentration of 14%. When the reaction temperature increased to 120^{0}C, the concentration of acid clearly showed a decrease of the furfural yield. The acid concentration of 10% gave a yield of furfural 9.37% but declined after the acid concentration increased (to 8.62% with 13.2% concentration and to 6.93% with 16% concentration) at the same reaction temperature.
When the reaction temperature and the acid concentration are combined the furfural yield was clearly affected. Table 1 shows the yield of furfural with both reaction temperature and acid concentration, as they increased the yield also increased to mild conditions but when reaction temperature was increased to 120^{0}C, the yield was decreased with all four concentrations compared to reaction temperature of 95^{0}C and 105-110^{0}C. The trend of yield with both reaction temperature and acid concentration is controlled by both factors as the acid hydrolysis of five carbon sugars or even six carbons sugars based on the conditions of acid interaction with the reactant and how much the acid can go between those structures and breaks the glycoside linkages of carbon-oxygen in the structure of five carbon sugars. The penetration of acid between those linkages is enhanced by reaction temperature to a limit but after it will break other linkages which is not favoured for the production of furfural in which the yield of furfural was reduced with increasing of the reaction temperature and acid concentration. The rate of sugar hydrolysis is controlled by them and when it is not optimum the breaking of the produced furfural will also occurred, (Szejtli, 1976).

Tannins :

The results of the final yield of tannins appeared in table 2 and fig.1; the tannins are in the good range in the wood wastes as it is from 3.85% to 4.24%. Generally no significant variation appeared with different sawmills and the origin (site) of the cultivated trees. The extraction time is effective on the amount of tannins as appeared in figure 1. The tannins amount increased slightly with extraction time increase.

The results of tannin yield from poplar wood sawdust in table 1, are in agreement with other findings as the tannins are formed about 1.8-6.0% of the total extractives of hardwoods, in which this study results ranged from 3.85% to 4.24%, (Fengel and Wegener, 1983). This could be promising fact to extract tannins and use them in many applications in industry and medical fields since it adds a value to the wood wastes (sawdust). The results in fig.1 are confirmed the fact that with longer time of treating the sawdust, more of tannins could be recovered by extraction.

CONCLUSIONS

The results of the final yield of furfural and tannins from black poplar wood wastes (sawdust) are as good as enhancing the investigation of turning these wastes into higher valued end products. The ratio of furfural which produced from wood five carbon sugars (pentosans) was about 10% of wastes (sawdust), and tannins were about 4.07% of wastes (sawdust). These findings could make turning of the wood wastes (sawdust) into such useful chemicals as a promising route of industrialized wood industry waste (sawdust) applications. These findings also suggest that we should introduce more tree species to the country to improve the yield of the tannins which is good multipurpose intermediate for human uses. Some of the reaction factors that affect the conversion of the sawdust into useful by-products also need to explore to maximize the final yield.

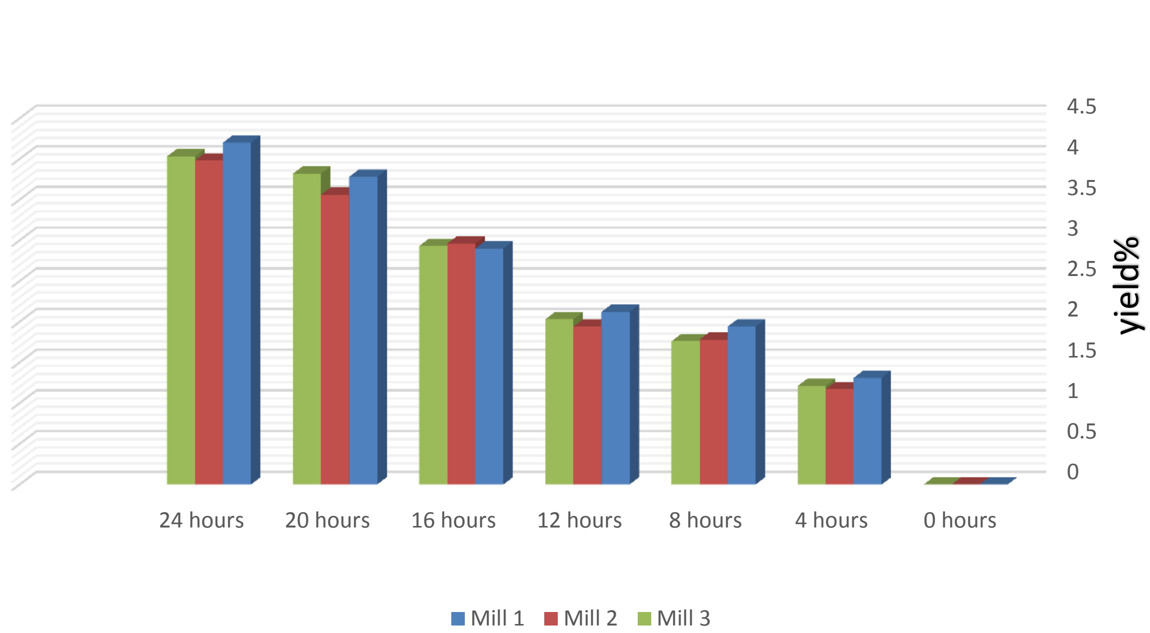
Table 1. Furfural yield (%) from the wood wastes (sawdust) after 90 minutes at different temperatures and acid concentration.

Temperature °C	Acid concentration %	Yield %
95	10.00	8.10
	13.20	8.41
	14.00	8.16
	16.00	7.82
105-110	10.00	9.55
	13.20	10.11
	14.00	10.62
	16.00	10.04
120	10.00	9.37
	13.20	8.62
	14.00	7.78
	16.00	6.93

Table 2. Tannins yield (%) from wood wastes (sawdust) with different sawmills at 95-100°C

Source	Location	Yield %
Mill 1	A	4.19
	B	4.24
	C	4.17
Mill 2	D	4.03
	E	4.06
	F	3.85
Mill 3	G	3.93
	H	4.09
	I	4.07

Fig. 1. Effect of extraction time on the yield of tannin



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