



Recovery of municipal green bio-waste by the way of chemical transformation into valuable chemical products: intermediates of bio-polymers, green solvents and bio-components of fuels

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Abstract: In this paper, studies on transformation of various types of waste municipal bio-mass into furfural by acidic hydrolysis were presented. The amount of obtained furfural was 0.12-2.47% wt., based on the dry weight of biowaste subjected of hydrolysis. The yields of furfural strongly depend on the type of biomass used in the processes. What is more, obtained water solutions of furfural, without any purification, were used in the catalytic reduction processes over 5%Pd/Al₂O₃ catalyst. Furfuryl alcohol and tetrahydrofurfuryl alcohol were the only products of reactions of furfural reduction carried out at the temperature of 90° C and under the pressure 20 atm of H₂.

Introduction

The development and wide-scale implementation of clean, effective and renewable technologies for the production of valuable chemicals, including green-solvents, bio-fuels and bio-components from municipal green biowaste, is currently an area of key concern to government, scientists and industry [7,14]. One of the considered way for producing valuable chemical compounds from biomass is acid hydrolysis and further chemical transformation of its products [5]. One of the most important products of acid hydrolysis of biomass is furfural, which is regaining attention as a possible bio-based alternative for use in the production of a wide range of products, from antacids and fertilizers to plastics and paints. Furfural may be widely used in the industry as a versatile building material because its molecule contains two reactive functional groups (a carbonyl group and furan ring). The aldehyde group (C=O) of furfural may undergo typical reactions such as acylation, acetylation, reduction to alcohols, aldolisation and Kno-

evenagel condensation, decarboxylation, oxidation to carboxylic acids, and Grignard reactions. The double bonds of the furan ring (C=C-C=C) can undergo hydrogenation, oxidation, alkylation, halogenation, ring opening and nitration reaction [22,3,16].

The growing importance of furfural in chemical processing led to the increasing in production of this compound in the world. Furfural production is based on the Quaker Oats process, which uses biomass such as corn cobs, wood, cottonseed hulls, or straw. The annual world production of this compound is about 280,000 tons. China, Dominican Republic and South Africa are the leading producers of furfural, where overproduction of waste biomass takes place, labor is cheap and there is not restrictive legislation on environment protection [18]. Some time ago, furfural was also produced in Poland by the way of acidic hydrolysis of waste from the wood industry. However, the production of this chemical ceased to be profitable in Poland. The situation changed dramatically with the adoption by Pol-

ish Parliament of the new law on waste, which obliges local government units to organize of the green biomass collection and disposal. The new model of waste management also takes into consideration the green municipal waste as chips from the trees and shrubs, leaves and grass. The amount of these biomass reaches up to 30% of all collected municipal waste. This kind of biowaste may be successful converted into furfural and then catalytically reduced into more valuable compounds. The additional advantage of this method is that the local governments have to pay for disposal or recovery of biowaste and from this reason the manufacturer receives additional income by the using of biowaste as a raw materials. In this case, in the total calculation, furfural production becomes profitable.

Apart from being valuable platform chemical, derived from renewable biomass feedstock, furfural is also the precursor for many furan-based chemicals and solvents [18]. The hydrogenation of furfural yields valuable products, including furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, etc., which can be obtained through the reduction of furfural with hydrogen gas over catalysts such as copper chromites [12,15], Raney Ni [20], Raney Co [1], Raney Cu [8], nickel amorphous alloy [8,10], Al, Fe or Mn-doped mixed copper-zinc oxides [11], or alternatively over homogeneous complexes of Ru, Rh or Pt [2,6]. These systems are often promoted using Na, Ca, Co, La or Ni [4,13,21]. Selective reduction of furfural can lead to partially hydrogenated products, such as 2,5-dihydroxymethylfuran, and fully hydrogenated materials such as 2,5-bis(hydroxymethyl)tetrahydrofuran. Each of these materials can serve as alcohol components for the production of new polyester, and their combination with FDCA would lead to a new family of completely biomass-derived products. The utility of FDCA as a PET/PBT analog offers an important opportunity to address a high volume, high-value chemical market.

In this publication, the processes of acidic hydrolysis of 10 kinds of municipal green bio-waste were presented. For the selected samples of furfural obtained from bio-waste, processes of hydrogenation under high pressure in water phase were performed over supported palladium catalysts.

Material and method

Preparation of furfural; Furfural was obtained towards acidic hydrolysis of waste biomass. Each time 25 grams, dried to a constant weight, was placed in a 1 L round bottom flask and 33 mL of sulfuric acid (VI) (95% H₂SO₄, P.P.H. "Stanlab" Sp. J.) and 92 mL of water were added. The mixture in the flask was heated to boiling and distilled. Condensates were collected and subjected to HPLC (LaChrom, Merck-Hitachi, column: Kromasil 100 C18, mobile phase: acetonitrile / phosphate buffer = 5:95 (v/v), pH = 4.5, Cphosphate= 0.01, UV: λ = 210 nm) and GC (PerkinElmer GC-MS; Clarus 580 with MS Clarus SQ 8 S; Elite-5MS capillary column: 30 m length, 0.25 mm i.d. and 0.5 m filmthickness). For the chosen samples of condensates, after neutralization (pH = 7) with saturated sodium carbonate solution (Na₂CO₃ analytically pure POCh Gliwice SA), catalytic tests were performed.

Hydrogenation of furfural; Hydrogenation of 25mL of furfural in aqueous solution was performed in a 50 mL autoclave (Parr Company) at a temperature of 90° C and under 20 bar of H₂ pressure with equal amounts of catalyst ($m_{cat}=0.5$ g) in each experiment. The mixture was stirred at 500 rpm. The autoclave was pressurized with hydrogen to 20 atm, and the temperature gradually raised to 90° C with a heating rate of 20° C min⁻¹. The reaction was sustained for 2 h. Products of furfural hydrogenation were detected by HPLC and additionally screened by using GC-FID analysis (Hewlett Packard 5890A; packed column 8% Carbowax 1540 on Chromosorb W; injection port temperature: 170° C, injection volume: 5 μl; FID detector temperature: 250° C; column oven temperature: 190° C; He (Linde, 99.999%): 30 mL min⁻¹) as well as analyzed by GC-MS techniques (the method is described previously).

Results and discussion

Furfural yields are in the range 0.12-2.47%-wt. The highest concentration of furfural was observed for the samples obtained from corn leaves and walnut shells. The lowest amount of furfural is present in condensates obtained for blue spruce needles. The average content of furfural in the test samples is 1.34%-wt. The yields of furfural estimated for all types of biomasses used are presented on Fig.1. The condensates were also tested by GC-MS for the presence of other compounds of the decomposition of biomass under the action of concentrated H₂SO₄. In all of the analyzed condensates, in addition to furfural, acetone was also present, but the amount of this ketone was trace. Other compounds present in trace amounts in the condensates obtained by the hydrolysis of biomass were: formic acid, methyl acetate, 2-butanone, acetic acid, etc.

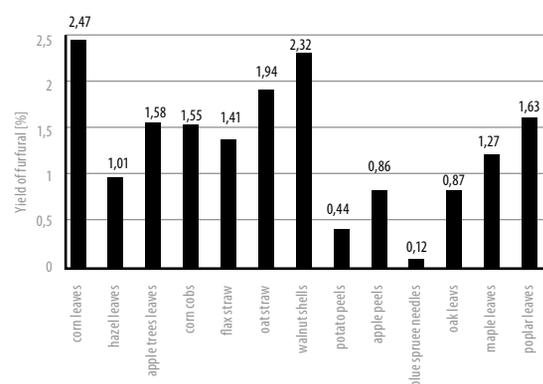


Fig.1 The yields of furfural obtained from various type of waste bio-mass expressed as a percentage by mass, based on the dry weight of the raw material.

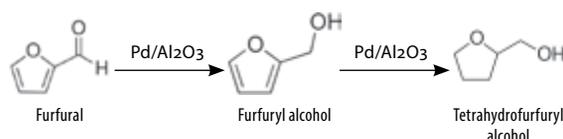
Two condensates obtained from oat straw and flax straw were used as a substrate in the catalytic reduction of furfural over 5%Pd/Al₂O₃ system (Fig.2). Catalytic results are expressed as conversion (X, %) and selectivities (S, %). Those parameters were defined as:

$$x = \left[1 - \left(\frac{c}{c_0} \right) \right] \cdot 100\%$$

$$s = \left(\frac{c_p}{c_0 - c} \right) \cdot 100\%$$

where C_0 is a molar concentration of furfural at the beginning of the hydrogenation process, C is a molar concentration of furfural after time t , C_p is a molar concentration of product (FA or THFA) after time t . The tests of catalytic activity were conducted for each medium three times and the presented results constitute arithmetical mean of these three measurements.

The hydrogenation of furfural over Pd/Al₂O₃ catalysts yields valuable products, such as furfuryl alcohol (FA) and tetrahydrofurfuryl alcohol (THFA) (Scheme 1). The most popular product of the furfural hydrogenation is furfuryl alcohol (FA). Above 60% of the annual production of furfural is converted to this alcohol. FA is used, for example, for the production of cross-linked polymers, characterized by unique chemical, thermal and mechanical properties. Moreover, FA, due to the high corrosion resistance, is used in the production of furan fiber-reinforced plastics for the construction of pipelines [22]. The second important product of deeper furfural hydrogenation is tetrahydrofurfuryl alcohol (THFA). It is considered a green solvent used in agriculture, industrial printing inks as well as cleaning agents in electronics [4].



Scheme 1 The hydrogenation of furfural over Pd/Al₂O₃ catalysts.

There is only little information in the literature on the hydrogenation of furfural over catalysts based on Pd [17,9], although the usefulness of such systems in various hydrogenation reactions realized in liquid phase is known [19]. On pure 5%Pd/Al₂O₃ catalyst, from pure furfural present in water phase the furfuryl alcohol is produced and further reduced to tetrahydrofurfuryl alcohol. This is probably connected with the activation of H₂ on the surface of palladium and the production of hydrogen species active in the reduction of double C C bonds in the furfuryl alcohol ring [9]. From the presented in Fig.2 results, it can be concluded that supported palladium catalyst shows particularly high activity in the studied process. The hydrogenation of water solution of pure furfural leads to the formation of tetrahydrofurfuryl alcohol (THFA) as a main product. However, the presence of trace amount of additional compounds in reaction mixture influences the activity and the selectivity to individual reaction products. In the case of using condensate from hydrolysis of straw as substratum of the increase in selectivity to furfuryl alcohol (FA) was detected.

Conclusion

It is possible to obtain furfural from all tested samples of biomass, but the commercial using of this method requires the optimization of temperature, kind of using acid as a catalysts, etc. and the optimization of method for the preparation of samples of biomass. It is known, that the pretreatment of biomass by physical and physicochemical methods, may be influenced on the structure of the lignocellulosic biomass, facilitating the availability of pentoses. The influences of the pretreatment using ultrasounds, mi-

crowaves and steam will be studied in the next stages of our investigations.

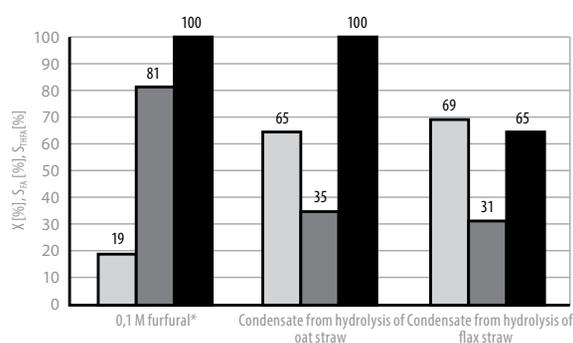


Fig. 2 The results of catalytic furfural reduction over 5%Pd/Al₂O₃ in water phase. X – furfural conversion, S_{FA} – selectivity to FA, S_{THFA} – selectivity to THFA, furfural* – commercial compound.

Depending on the used waste biomass, various amounts of furfural in condensates were stated. Moreover, depending on the used biomass, furfural was obtained with a different degree of contamination. Based on the results of catalytic reduction of furfural, it can be concluded that the amount of impurities present in the condensate has a significant influence on the course of the reaction. In this connection, the most promising for further research are these types of biomass, from which condensates containing not only a large amount of furfural, but also trace amounts of other compounds can be obtained. ■

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