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Research article

Valorization of hazelnut shell waste in hot compressed water

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ABSTRACT

Hydrothermal conversion of waste hazelnut shell in hot compressed water, green and environmentally friendly medium, was investigated under different operating conditions to clarify the effects of reaction temperature, reaction time, acid concentration and acid kind (H_2SO_4 and H_3PO_4) on the production of value-added chemicals with high temperature/high pressure autoclave. In literature, to our best knowledge, there is no study about the production of levulinic acid, as a high value chemical, from waste hazelnut shell in hot-compressed water without using any mineral and heterogeneous catalyst. Hydrothermal reactions were conducted at 150–280 °C for reaction times of 15 to 120 min with various H_2SO_4 and H_3PO_4 concentrations varying from 0 to 125 mM. The detailed liquid product species were identified with High Performance Liquid Chromatography (HPLC) and gaseous products were analyzed by Gas Chromatography with a Thermal Conductivity Detector (GC-TCD). The main identified liquid compounds were levulinic acid, acetic acid and furfural while carbon dioxide and carbon monoxide were the major gaseous products. Increasing the reaction temperature (280 °C) and reaction time (120 min) resulted in a significant increment on the conversion (65.40%) as well as levulinic acid yield (13.05%). The production of levulinic acid was enhanced with H_2SO_4 addition; whereas treatments with H_3PO_4 improved the furfural production.

1. Introduction

Population growth, scarce of petroleum reserves and environmental concerns improved the interest of investigation of alternative and renewable resources [1,2]. The utilization of biomass seems the most important alternative to fossil fuels in the production of value-added chemicals due to being carbon neutral source, not having and contribution to net CO_2 concentration in the atmosphere and reduce the waste problem with effective conversion [3].

A wide variety of bio-based chemicals (i.e. levulinic acid, acetic acid and furfural) can be produced from the degradation of different biomass types. Among them levulinic acid is a versatile chemical that can be used to produce a great number of derived products such as pharmaceutical and flavouring agents, resins, herbicides, plasticisers, anti-freeze agents and biofuel additives. Several technologies such as mineral acids, solid catalyst, ionic liquids and sub- or supercritical fluids have been performed during the production of levulinic acid from different raw materials [4]. To our best knowledge, this study is the first one that investigates levulinic acid production from waste hazelnut shell in hot-compressed water, which is environmentally friendly, non-toxic, cheap, non-flammable and abundant.

Near critical point (374 °C and 22.1 MPa), water exists in liquid state under enough pressure [5] which possesses unique solvation and physicochemical properties. Temperature increment results in reduce in water polarity (non-polar) [6] and the solvation power of organic compounds enhances [7]. The ion product (K_w) of water increases with temperature and reaches to 10^{-11} that is approximately three orders of magnitude higher than the ion product of ambient water and the dielectric constant (ε) of ambient water is reduced from 80 to 10 at around 374 °C [8,9]. Furthermore, low dielectric constant boosts ionic reaction and the high concentration of H_3O^+ and OH^- ions enables to water acts as an acid or base catalyst in subcritical water region [8].

Several researchers reported natural biomass conversion in subcritical water. Chan et al. [10] conducted series of experiments for the comparison of chemical species from subcritical and supercritical hydrothermal liquefaction of various biomasses: empty fruit bunch, palm mesocarp fiber and palm kernel shell. They stated that content of biomass had remarkable influence on the distribution of the products. Higher amounts of phenolic compounds were produced from palm mesocarp fiber and palm kernel shell while alcohol and ester were only formed from palm kernel shell. Kruse and Gawlik [11] described possible reaction pathways from the degradation of phytomass, which was mainly composed of cooked carrots and potatoes. The degradation of HMF occurred with two different pathways: the formation of 1,2,4-benzenetriol and the formation of levulinic acid (via acid catalyst). They also identified key components including HMF, levulinic acid,

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acetic acid and furfural. In another study, the hydrothermal degradation of switchgrass at 250–350 °C and 20 MPa with 1–300 s residence time to obtain the maximum conversion and desired product yield (5-HMF and furfural) were examined and rapid switchgrass conversion (90 wt%) was achieved which is <60 s [12]. Moreover, many researches have focused on the influence of different acid addition on the conversion of biomass and valuable chemical production. Takeuchi et al. [13] noticed that the production of valuable chemical species from carbohydrate biomass (glucose) vary with respect to acid type. The production of 5-HMF increased in the presence of H_3PO_4 while H_2SO_4 enhanced the levulinic acid production. Asghari and Yoshida [14] evaluated that the effect of dilute phosphate buffer at pH 2 on the conversion of Japanese red pine wood under subcritical water. When compared to uncatalyzed conditions, Japanese red pine wood decomposed into higher amount of sugars within shorter time and the yield of HMF and furfural were nearly doubled with a further treatment. Tymchyshyn and Xu [15] reported that the degradation of sawdust and cornstalks into phenolic compounds at 250–350 °C and 2 MPa H_2 with the addition of $Ba(OH)_2$ and $RbCO_3$ catalysts. Addition of catalysts greatly enhanced the bio-oil yield whose composition mainly consisted of 2-methoxy-phenol, 4-ethyl-2-methoxy-phenol and 2,6-dimethoxy-phenol.

Among different biomasses in literature, it was noticed that limited number of studies focused on the hydrothermal conversion of nut wastes (walnut, peanut etc.) in subcritical water. Zhu et al. [16] studied hydrolysis kinetics of waste peanut shell in subcritical water and possible reaction mechanisms. The yield of reducing sugars increased to 40.5%. Liu et al. [17] examined the catalytic degradation of walnut shells under hot compressed water (200–300 °C and 1.5–8.6 MPa) with the addition of KOH and HCl. They concluded that the methoxy phenolic compounds, cyclopentene derivatives C12–C18 fatty acids were detected in the KOH (0.5 M) catalyzed treatment while the presence of HCl improved the levulinic acid yield up to 12%. The majority of the studies about waste nut shell degradation under hydrothermal conditions focused on the product distribution, reaction mechanism and kinetics. In order to have idea about bioactivity results (total phenolic content, antioxidant activity, etc.) of the products obtained from waste nut shells, extraction studies in the literature would be reviewed. Shahidi et al. [18] evaluated that the extracts of hazelnut byproducts (skin, hard shell, green leafy cover and tree leaf) had higher amount of antioxidants and phenolic content than hazelnut kernel extract after ethanol extraction. Contini et al. [19] compared the total phenolic content of hazelnut shell, whole and chopped roasted hazelnut skins with using 80% (v/v) acetone, methanol and ethanol. The total phenolic content of hazelnut shell from acetone extract (72.2 mg of gallic acid equivalent (GAE)/g extract) was higher than those of ethanol (59.6 mg of GAE/g extract) and methanol extracts (56.6 mg of GAE/g extract). The highest phenolic content was obtained from whole roasted hazelnut skin for three solvents.

Hazelnut is an agricultural crop that is cultivated in substantial amount in Turkey. Turkey leads in hazelnut production with supplying 75% of the global hazelnut production in the World (650,000 tons/year). Large amount of waste hazelnut shells are produced during hazelnut processing and most of them are used for heating [20]. Therefore, the utilization of waste hazelnut shell in the production of value-added chemicals can contribute both in value gaining and being natural alternative resource.

To our best knowledge, conversion of waste hazelnut shell to valuable chemicals such as levulinic acid in hot-compressed water was done for the first time in literature. The main objective of this study is to investigate the potential role of waste hazelnut shell as a biomass feedstock for the production of mainly levulinic acid under hydrothermal conditions. The effect of reaction temperature (150–280 °C), reaction time (15–120 min), acid concentration (0–125 mM), and acid type (H_2SO_4 and H_3PO_4) on the conversion of hazelnut shell and the selectivities of valuable chemicals in the liquid product solution were investigated. The total phenolic content and the antioxidant activity of the product solution were also analyzed.

2. Materials and methods

2.1. Materials

Hazelnut shell was used as biomass feedstock from Ordu, Turkey. Samples were dried in an oven at 60 °C and ground into small pieces (~1 mm) with a laboratory type grinder. Elemental analysis of hazelnut shell was conducted via elemental analyzer (CHNS-932, Leco, USA). Moisture and ash contents of biomass were determined with Thermal Gravimetric Analysis (TGA-51, Shimadzu, Japan) [21]. Ultimate and proximate analyses of feedstock are shown in Table 1. Cellulose, hemicellulose and lignin contents of hazelnut shell (Table 1) were identified by using Van Soest Method [22,23]. The reagents used as standards for HPLC analysis are as follows: fructose (≥99%), pyruvic acid (98%), glycolaldehyde, glycolic acid (99%), glycerolaldehyde (99%), levulinic acid (98%), 5-HMF (99%) and lactic acid (98%) were obtained from Sigma-Aldrich and also, furfural (98%), acetic acid (100%), glucose (≥99.5%) and formic acid (98–100%) were purchased from Merck. Sulfuric acid (96–98%) and phosphoric acid (85–90%) were obtained from Merck and Fluka, respectively. For bioactivity tests, gallic acid (97.5%), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (97%), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid (ABTS), sodium carbonate (99.5%) and potassium persulfate (99.9%) were purchased from Sigma-Aldrich and Folin-Ciocalteu's phenol reagent and ethanol were purchased from Merck. De-ionized water was used for preparing solutions in all experiments.

2.2. Hydrothermal conversion in subcritical water

The hydrothermal conversion of waste hazelnut shell in subcritical water was carried out in a batch reactor (Parr 5500 Series, USA) made of SS-316 with a 300 mL of total volume, 350 °C maximum temperature and 207 bar maximum pressure, as shown in Fig. 1. The reactor was initially loaded with 4 g of hazelnut shell and then the volume is completed to 100 mL by adding de-ionized water. For comparison, different concentration of acid (H_2SO_4 and H_3PO_4) was placed at the same reaction conditions. Nitrogen gas was flowed to remove air inside the reactor, which then heated up to the desired reaction temperature with stirring rate of 200–250 rpm throughout the experiment. During heating period, temperature and internal pressure increased until reaching desired reaction temperature and reaction time started when temperature reached desired value. Required heating time to reach desired reaction temperature varies according to reaction temperature, for instance; 23 min, 30 min, 65 min and 73 min for 150 °C, 200 °C, 250 °C and 280 °C (SI, Fig. S1), respectively. At the end of the reaction time, the heater was turned off and reactor was cooled by cooling water with

Table 1
Ultimate, proximate and structural analysis of hazelnut shell.

	Hazelnut shell
Ultimate analysis (wt%)	
C	50.44
H	6.76
N	0.76
S	0.11
O[a]	41.92
Proximate analysis (wt%)	
Moisture	8.93
Ash	1.48
Protein	3.11
Structural analysis (wt%)	
Cellulose	36.02
Hemicellulose	12.66
Lignin	40.14
Extractives	7.86

[a] Obtained from difference.