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Research Article

Levulinic Acid Production from Artichoke Leaves (Cynara Scolymus L.) by Catalytic Hydrothermal Reaction

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ABSTRACT

In addition to examining the highest yield production of Levulinic acid (LA) from artichoke leaves by the subcritical catalytic hydrothermal decomposition, the studies were carried out on also increasing the production yields of 5-Hydroxymethylfurfural (HMF), Acetic and Formic acid from this biomass. In order to obtain the most suitable reaction conditions, the effect of different reaction conditions, including different temperature, reaction time, pH and catalyst types, on the decomposition of artichoke leaves and product yields were investigated. The subcritical thermal decomposition studies of artichoke leaves were carried out in an autoclave system at temperatures (120°C, 140°C, 160°C, and 180°C) for reaction times of 10, 20, 30, 40, and 50 min in the presence of H_2SO_4, HNO_3, and HCL catalysts with different pH values; these reactions were realized also without adding a catalyst. As a result of the detailed research, it was seen that the most suitable experimental conditions for the production of LA with the highest yield from artichoke leaves could be achieved by adding sulfuric acid with a pH of 0.5 at a reaction temperature of 180°C and a reaction time of 50 min. The investigations were continued till achieving the highest product yields. After carrying out the experiments stated above, the optimal yields of the products produced from the artichoke biomass by the reactions were found as 209.39 g/kg biomass for LA, 117.40 g/kg biomass for formic acid, 72.27 g/kg biomass for acetic acid, and 39.04 g/kg biomass for 5-HMF.

1. Introduction

Due to the polarity of water and its ability to form hydrogen bonds, it is used as a solvent. These features enable the reaction to occur that will ensure the breakdown of biomass during the effective use of subcritical water. Polar molecules are more efficiently solubilized at temperatures near 150°C; if the temperature is raised from 100°C to near the critical point, the surface tension, viscosity and dielectric constant decrease and diffusion rates increase.

Levulinic acid ($C_5H_8O_3$) (LA) a polar organic solvent is soluble in both water and different organic solvents. LA, a high worth substance, is among one of the most needed chemicals in the world. It is one of the 12 most important chemicals, called platform chemicals, obtained from biomass with high efficiency [1]. LA, which can be converted into many valuable chemicals, is one of the best bio-based molecules.

The production of LA is dependent on both the feedstock and processing conditions, which are used. The most important intermediate obtained in the hydrolysis of LA is 5-HMF [2].

The use of LA as a raw material in the production of various chemicals gives it a special importance [3]. There are many useful compounds that can be converted from 5-HMF, including 5-aryl amino methyl-2-furanmethanol, 5-

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hydroxymethyl furoic acid, furfuryl alcohol, LA, levulinate esters, and 5-ethoxymethyl furfural [4].
5-HMF is usually produced by the dehydration hexoses and is primarily accepted as a valuable chemical. Hydrothermal transformation of LA from rice straw, corn meal, sweet sorghum meal and Miscanthus Grain LEA using acid catalyst has been examined [5]. A process to produce LA from cellulose with the help of zirconium phosphate catalyst (ZrP) has been studied [6]. Under optimum reaction conditions, the extraction of sugar and LA from seaweed biomass Gelidium amansii has been examined using acid catalyst [7]. The hydrothermal transformation of wheat straw, poplar sawdust, paper mill sludge, tobacco shredded, and olive tree pruning into LA in the presence of homogeneous acid catalysts has been investigated [8].

According to the known production amount, world artichoke production is more than 1678 ktons/year; artichoke waste biomass is about 80-85% of the all [9]. The transformation of the globe artichoke crop residues, which are lignocellulosic biomass, into bioethanol was investigated and it was shown that the ethanol yield after 24 h of fermentation may be 2399 kg of ethanol per hectare [10]. The suitability of artichoke crop residues for conversion to bioethanol was investigated from the field to the fermenter [11]. There have been many studies related to conversion of biomass into valuable chemicals via subcritical hydrothermal liquefaction [12-16].

In this study, it is aimed to develop a method to efficiently obtain valuable chemicals using artichoke leaves as a biomass in the subcritical water conditions. For this purpose, inulin-containing artichoke stems and bowls leaves were used as biomass to produce important chemicals by catalytic hydrothermal reaction.

2. Experimental

2.1. Materials

The leaves of the artichoke were selected as waste biomass. After drying artichoke leaves in an oven at 60°C, they were grounded so as to obtain the desired particle size using a crush mill and sieved to get below of 1mm fractions. The proximate analyses (moisture and ash) and ultimate analysis of the dried biomass samples are shown in Table 1. The ultimate elemental analysis of the biomasses was determined via an elemental analyzer (CHNS-932 by Leco, MI-USA).

The amount of cellulose, lignin, and hemicellulose contents in artichoke leaves and stalks, determined by the Van Soest method [17], are depicted in Table 2.

Table 1. Proximate and ultimate analysis of the artichoke leaves

	Artichoke Leaves
Proximate analysis (wt %)	
Moisture	7.73
Ash	5.54
Ultimate analysis (dry. wt %)	
C	46.33
H	5.70
N	2.16
S	0.03
O (from difference)	45.78

Table 2. The components of the artichoke leaves

Components (daf. wt %)	**Artichoke Leaves**
Cellulose	37.37
Lignin	4.13
Hemicellulose	7.92
Extractives	50.58

2.2. Experimental system

A SS 316 batch-type autoclave reactor device made of stainless steel with an internal volume of 100 cm^3 was used to perform the subcritical catalytic hydrothermal decomposition experiments of the artichoke leaves.

The reaction temperature was controlled using a Proportional Integral Derivative (PID) controller. The details and a schematic diagram of the experimental systems, used to produce valuable products from the biomass by hydrothermal reactions, were described in our previously published work [18].

2.3. Experimental procedure

The mineral acid catalysts (Hydrochloric, Nitric, and Sulfuric acids) at different pH values were used to increase the efficiency of products. In the experiments, the hydrothermal decomposition of the artichoke leaves to hexose (glucose, mannose and galactose), from them to 5-HMF, and from it (by rehydration) to LA + Formic acid were performed.

The first hydrothermal decomposition experiments were performed at the temperatures of 120, 140, 160 and 180°C and the reaction times of 10, 20, 30, 40 and 50 min in the presence of H_2SO_4 catalyst at pH 0.5, 1.0, 1.5 and 2.0; changes in the amounts of LA, Formic acid, Acetic acid and 5-HMF produced in these experiments were examined and the most suitable production conditions were tried to be formed. In the second experiments, the experiments were carried out with HNO_3 and HCl catalysts at different pH levels (0.5, 1.0, 1.5, 2.0) under the most suitable conditions.

After placing the biomass and water into the reactor, the air inside was purged from the device by using nitrogen gas three times, and then the reactor was heated using by PID temperature controller (EMKO-ESM 9920) heater at a heating rate of 15°C/min to the reaction temperature. Temperature and pressure values were measured every 10 minutes till the end of the experiment; after every experiment**,** the reactor was cooled to 25℃ using a cold water bath under atmospheric conditions. The reaction temperature was controlled using a Proportional Integral Derivative (PID) controller.

After the reactor expanding to the room pressure, analysis of the product gases, formed from the sample, during the catalytic hydrothermal reactions, were performed by the gas chromatography analysis; the collection and injection of the gases were realized by gas-tight analytical syringes. The solid residue in the reactor was separated from the aqueous solution through a special filter. H_2SO_4 was added so as to make the pH of the liquid product 2.0 to prevent the ionization of the organic acids. The residue, produced during the reaction, was dried in an oven. Tetrahydrofuran (THF) was used to obtain the viscous tar after washing the reactor. Although every care was taken to increase the accuracy of the measurement results, each experiment was repeated three times under the same conditions to increase the reliability of the results.

2.4. Analyses

A Shimadzu LC-20A HPLC was used to analyze the liquid products, produced during the catalytic hydrothermal reactions. The HPLC system consists of a DGU-20AS degassing module, CTO-10ASvp chromatography oven LC-20AT gradient pump and SPD-20 multiwavelength ultraviolet detector. The analysis of the gases, produced during the catalytic hydrothermal reactions, was conducted by a gas chromatography system (GC, HP-7890A) equipped with Flame ionization (FID) and thermal conductivity detectors (TCD). TOC-SSM (Solid Sample Module: Shimadzu SSM-5000A) analyzer was used to analyze the solid residues, produced by during the catalytic hydrothermal reactions, after drying them in an oven at 105℃ so as to reach free-water content. A TOC-5000A total organic carbon analyzer equipped with SSM (Solid sample module) was used to realize organic carbon content measurements.

The carbon content of the gaseous products, obtained through the catalytic hydrothermal reactions, was also determined basing on the results, obtained as a result of the Gas Chromatography (GC) measurements. Using the relevant analyzers, the product analyses were repeated two or three times according to the importance and the averages of these measurement results were used.

3. Results and Discussion

The production of LA, and the other valuable chemicals by the hydrothermal decomposition of artichoke were investigated. To be able to determine the most suitable reaction conditions in this study, which were performed under different experimental conditions, the effects of temperature, reaction time, and the different mineral acid catalysts with different pH value on yields of LA and the other products were investigated. The acquisition of the most efficient conditions and constant reaction times for the production of high-yield LA from artichoke leaves were provided. The subcritical thermal decomposition experiments were performed at increasing reaction times (10, 20, 30, 40, and 50 min) and at different temperatures (120°C, 140°C, 160°C, and 180°C) with H_2SO_4, HNO_3, and HCL catalysts. These experiments were repeated three times in the presence of the catalysts at different pH values (0.5, 1, 1.5, 2), and without catalyst.

The influences of the different reaction temperatures on the yield of LA and the other products produced in the presence of an H_2SO_4 catalyst (pH 0.5) and the reaction time of 50 min, are presented in Table 3. The best LA production yield was obtained as 209.4 (g/kg C in biomass) from the biomass by the hydrothermal reaction process (180°C for 50 min) in the presence of H_2SO_4 catalyst (pH 0.5) (Table 3).

Table 3. Effects of the different reaction temperatures and H_2SO_4 catalyst (pH 0.5) on the yield (g/kg C in biomass) of the aqueous products, produced from the artichoke leaves, for the reaction time of 50 min

Product Yields	120°C	140°C	160°C	180°C
LA	57.8	65.7	122.5	209.4
5-HMF	39.0	20.8	18.5	4.6
Acetic acid	72.3	66.1	60.4	58.1
Formic acid	61.5	71.4	80.3	117.4

Effects of the reaction times in the presence of H_2SO_4 catalyst (pH=0.5), and the reaction temperature of 180°C on the yield of the aqueous products, produced from the artichoke leaves, are shown in Table 4.

Effects of the different pH values of H_2SO_4 catalyst at the reaction temperature of 180°C on the amount of the aqueous products produced from the artichoke biomass are presented in Table 5.

In the presence of H_2SO_4 catalyst (pH 0.5), the highest yields of 5-HMF and Formic acid produced through the conversion process (180°C for 10 min) were determined as 41.2 and 135.5, respectively (Table 4). The highest yield of Acetic acid, produced under the same conditions of reaction temperature and reaction time in the presence of H_2SO_4 catalyst (pH 2.0), was determined to be 119.8 (Table 5).

Table 4. Reaction time dependence on the yield (g/kg C in biomass) of the aqueous products of the artichoke leaves in the conversion process (180°C), and the presence of H_2SO_4 catalyst (pH 0.5)

Product Yields	10 min	20 min	30 min	40 min	50 min
LA	35.04	105.9	113.6	145.2	209.4
5-HMF	41.2	17.7	16.8	13.7	4.6
Acetic acid	77.3	72.6	62.2	60.8	58.1
Formic acid	135.5	129.1	120.7	118.1	117.4

Table 5. Yields (g/kg C in biomass) of the aqueous products produced by the conversion process (180°C for 50 min) in the presence of the different pH values of H_2SO_4 catalyst

Product Yields	pH: 0.5	pH: 1.0	pH: 1.5	pH: 2.0
LA	209.4	177.9	21.9	15.5
5-HMF	4.6	5.4	11.3	19.2
Acetic acid	58.1	62.2	87.3	119.8
Formic acid	117.4	97.8	95.1	94.8

Effects of catalyst type (pH 0.5) on the yield (g /kg C in biomass) of the aqueous products produced by the conversion process (180°C for 50 min) is shown in Table 6.

Table 6. Dependence of catalyst (pH 0.5) on the yield (g/kg C in biomass) of the aqueous products produced by the conversion process (180°C for 50 min)

Product Yields	H_2SO_4	HNO_3	HCI
LA	209.4	13.9	12.33
5-HMF	4.6	16.6	1.0
Acetic acid	58.1	75.2	3.3
Formic acid	117.4	110.7	7.1

Raising the reaction temperature caused a significant increase in the production of LA and Formic acid from artichoke leaves (Table 3). In the presence of H_2SO_4 catalyst (pH 0.5), the reaction time of 50 min became effective more for LA production, and that of 10 min for Acetic acid, Formic acid and 5-HMF productions. However, in the presence of H_2SO_4 catalyst (pH 2.0), it was observed that Acetic acid production yield increased more than 1.5 times for the reaction time of 50 min comparing to the yield of Acetic acid produced in the presence of H_2SO_4 (pH 0.5) catalyst.

Raising the reaction temperature from 160^oC to 180^oC induced an increase in the yields of LA and Formic acid by 1.8 and 1.5 times, respectively, on the contrary the yield of 5-HMF decreased by 4 times (Table 3).

It was shown that yield percent of LA, produced from wheat straw by the hydrothermal conversion in the presence of HCL catalyst at 200^oC for 1 hour, was between 19.3 and 21.7 [8]. LA and Formic acid production from macroalgae has been examined using methanesulfonic acid (0.7 M) at 160^oC and a reaction time of 45 minutes. Both LA and Formic acid were obtained from red macroalga K.Alvarezii using with a product concentration of 5.69 and 14.51%, respectively [19].

Reaction temperatures were chosen to observe the effect of increasing heat on production efficiency and to reveal at which reaction temperature high efficiency can be achieved.
In the study of N. Pulidindi et al, the different reaction times were applied by keeping the reaction temperature at 150°C during the conversion of levulinic acid from various types of herbaceous biomass by the hydrothermal process [5]. In a study of Lappalainen et al [20], the highest production efficiency of levulinic acid produced from potato peel waste was detrmined to be 49% at 180°C in the presence of $CrCl_3$ and H_2SO_4 as catalysts. It was shown levulinic acid, obtained from corncob, to have yield of 78.49% at the reaction temperature of 180°C, and reaction time of 200 min in the presence of the catalysts, 6 wt% WO_3(10 wt%)/$ZnCO_2O_2$@CeO_2 [21].

Hydrothermal conversion of cellulose to levulinic acid using zirconium dioxide as a catalyst was investigated and a remarkably high yield (53.9 mol%) was achieved at 180°C reaction temperature and reaction time of 3 h with 2 wt % of catalyst [22]. Levulinic acid was produced from artichoke leftovers via the microwave-assisted subcritical water extraction (225℃, 2 min, 1500 W) at about a 37% yield (molar yield) in the presence of HCl and p-toluenesulfonic acid [23].

The present study results show that, acid catalyst type and their pH values also greatly affect the product yields of artichoke biomass, and also show how important reaction time, reaction temperature are, as well as the catalyst type and its pH value, in terms of increasing the yield of the LA, 5-HMF, Acetic, and Formic acid produced from the biomass.

4. Conclusion

In this study, the effects of reaction temperature, reaction time and acid catalysts with different pH values on the decomposition of artichoke leaves by hydrothermal conversion process were revealed and the most suitable reaction conditions were determined.

Arranging acid catalysts, used in the experiments, on the basis of their effectiveness in LA and Formic acid production from the artichoke biomass by the hydrothermal conversion process can be specified as H_2SO_4>HNO_3>HCL. The results obtained from this study will help to evaluate vegetable and food wastes and to develop methods to be used in the production of valuable chemicals.

Article Information Form

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the Data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science. In terms of LA production, the experiments related to this study show that the type of acid catalyst and pH values, reaction times and temperature greatly affect the product yield of artichoke biomass.

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