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Authors: Dilek SELVİ GÖKKAYA, Mehmet SAĞLAM, Mithat YÜKSEL, Levent BALLİCE

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Catalytic Hydrothermal Liquefaction of Artichoke Residues (Cynara Scolymus L.) to Valuable Chemicals

Dilek SELVİ GÖKKAYA *1, Mehmet SAĞLAM1 Mithat YÜKSEL *1,
Levent BALLİCE1

Abstract

Lignocellulosic biomass is accepted to be one of the best sustainable alternatives for overcoming fossil fuel dependence and to reduce environmental pollution. Intensive research studies have been carried out on conversion of this big potential source via chemical and biochemical processes to miscellaneous chemicals. According to one of the present methods of chemical conversion, cellulose and hemicellulose parts of the plant biomass can be converted to platform chemicals by hydrolysis, dehydration and rehydration reactions in the presence of acidic medium. In this study, the efficient conversion conditions of the Artichoke (Cynara Scolymus L.) leaves and stalks to the valuable chemicals (formic acid, acetic acid and 5-hydroxymetilfurfural) were investigated using acid (HCl, HNO_3 and H_2SO_4) catalyzed hydrothermal reaction. Experiments were performed in the temperature range of 150°C - 300°C and at the pH values 2.0 - 3.0 with a reaction time of 1 hour. Evolution of liquid parts and their variations with respect to reaction parameters were determined using HPLC via related analysis.

Keywords: Lignocellulosic biomass, artichoke, catalytic hydrothermal reaction

1. INTRODUCTION

Increasing energy demand, environmental pollution impacts of petroleum and oil prices lead to the search for new technologies to convert biomass into high worth chemicals. As a renewable energy source, plant biomass (e.g., energy crops, aquatic plants, agricultural and forest residues) has a significant potential for the bioenergy production, since it is one of the most available organic compound in the world. From lignocellulosic biomass, bioenergy, which includes liquid fuels (e.g., ethanol, butanol biodiesel), and various platform chemicals (e.g., acetic acid, formic acid, levulinic acid, furfural, 5-hydroxymethylfurfural) can be produced by chemical, thermochemical or biological processes.

A platform chemical is defined as a chemical that can be used as a substrate for the production of various other valuable products. US Energy Department issued the name of the twelve basic chemicals and

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* Corresponding author: dilek.selvigokkaya@gmail.com (D.GOKKAYA)
[1] Ege University, Izmir, Turkey
E-mail: mehmet.saglam@ege.edu.tr, mithat.yuksel@gmail.com, levent.ballice@ege.edu.tr
ORCID: https://orcid.org/ 0000-0002-3501-562X, , https://orcid.org/0000-0003-1784-4472 https://orcid.org/ 0000-0002-6287-3566, , https://orcid.org/ 0000-0002-3137-1352

more than 300 candidates, which are the basis of the biorefineries that is expected to take place the ordinary petrochemical refineries in the near future. In 2010, the DOE updated the Platform Chemical List which includes e.g. ethanol, furfural, hydroxymethylfurfural, succinic acid, levulinic acid, lactic acid, sorbitol, and xylitol [1]. All these identified platform chemicals can be produced from lignocellulosic biomass. Researches about hydrothermal biomass liquefaction analyzing influence of parameters such as temperature, pressure, catalyst type, pH value, biomass/catalyst ratio, catalytic effects, etc. have been conducted by many research groups [2 - 9]. Also the studies with biomass model compounds are helpful to develop the theoretical decomposition pathway depending on nature of feedstock [10 - 12].

Biobased platform chemicals can be produced effectively by hydrothermal biomass liquefaction in subcritical water ($T<374$ °C, $P<22.1$ MPa). The physicochemical properties of the hot compressed liquid water ensure many chemical advantages than the water at ambient conditions ($T = 25$°C, $P = 0.1$ MPa). Water at ambient conditions is immiscible with hydrocarbons because it is weak solvent for nonpolar compounds. As water is heated up along its vapor-liquid saturation curve the density decreases. The consequence of the lower density is that the dielectric constant decreases [2]. The reduced dielectric constant increases dissolving capacity of water [3]. In addition subcritical water has higher ion product, high diffusivity and low viscosity. The increased ion product cause to higher levels of hydronium ion in liquid water, which can accelerate the rates of the acid-catalyzed decomposition reactions [3]. All these thermodynamic properties give opportunity to water to decrease the required reaction temperature for the hydrothermal conversion and to increase decomposition efficiency for the hydrolysis of biomass in water.

The aim of this study is to investigate the conversion of Artichoke (Cynara Scolymus L.) leaves and stalks to valuable chemicals using subcritical water in a batch reactor and to support the progress of the subcritical reaction conditions by acid catalysts, to shift the product distribution toward more desirable platform chemicals. As a model lignocellulosic biomass residues of the artichoke was selected, since artichoke has a considerable amount of agricultural crop in Turkey and also in the world. As artichoke producer Turkey is the eleventh country in the world in 2016 according to the data from the FAOSTAT (Food and Agriculture Organization Corporate Statistical Database) [13]. This study can make a great contribution to solving the global bioenergy shortage and can be an effective waste management of the food industry. The efficient conversion conditions of Artichoke leaves and stalk to the valuable chemicals (formic acid, acetic acid and 5-hydroxymetilfurfural) were investigated in the presence of acidic medium. We focused our attention on the effects of HCl, HNO_3 and H_2SO_4 in subcritical water as a function of pH and temperature to shift the product distribution towards desired compounds. Additionally, the results presented in this paper have a novelty due to the examination of the feedstock.

2. EXPERIMENTAL

2.1. Materials

Artichoke leaves and stalks were dried in an oven at 60^{o}C and then, were grounded using a crush mill until the desired particle size was obtained and sieved to get below of 1mm fractions. The values of moisture content, proximate and ultimate analysis for the dried biomass samples are summarized in Table 1. Elemental analysis of the biomass residues were performed via an elemental analyzer (CHNS-932 by Leco, MI-USA). The composition of artichoke leaves and stalks was determined by the Van Soest method [14] and is given in Table 2.

Table 1 Proximate and ultimate analysis of the artichoke leaves and stalk

	Artichoke Leaves	**Artichoke Stalk**
Proximate analysis (wt %)	7.73	9.05
Moisture	5.54	6.90
Ash		
Ultimate analysis (dry. wt %)	46.33	41.57
C	5.70	5.85
H	2.16	1.15
N	0.03	0.04
S	45.78	51.43
O (from difference)		

Table 2 The components of the artichoke leaves and stalk

Components (daf. wt %)	**Artichoke Leaves**	**Artichoke Stalk**
Cellulose	37.37	31.41
Lignin	4.13	3.30
Hemicellulose	7.92	17.05
Extractives	50.58	48.24

2.2. Experimental Procedure

HTL experiments were performed in a stainless steel batch reactor (SS316) with an internal volume of 100 cm^3. The details about the experimental system used in this study and a schematic diagram of the experimental procedure employed for the products were explained in our previously published work [15]. In the HTL experiments, the reactor was loaded a total mass of 2 g of biomass and 18 ml of deionized water. For the catalytic HTL experiments, the same experimental procedure was applied by the adding catalyst solutions at the pH values 2.0 and 3.0. After loading the reactants, the inside air that was in the reactor was swept out three times by nitrogen and the reactor was heated (~15°C/min) by PID temperature controller (EMKO-ESM XX20) heater to the reaction temperature. At the end of the reaction time (60 min) the reactor was cooled to ambient temperature (~25°C) by a water bath. After the reactor expanded to ambient pressure, the product gas was measured with a gasometer. Gas-tight analytical syringes were used for the gas chromatography analysis. The solid residue and liquid products in the reactor were separated by filter paper, and then liquid products were analyzed using HPLC. After removal of the products in the reactor, the walls of reactor were rinsed with THF (tetrahydrofuran). The solids remaining on the filter paper were dried (at 105°C) before measuring its carbon content by TOC-SSM apparatus.

2.3. Analyses

Gas chromatography (HP 7890A), which was equipped with Flame ionization (FID) and thermal conductivity detectors, was used for the gas analysis. HPLC device (Shimadzu LC-20A with an Inertsil ODS-4 column) was used for identification of liquid products (aldehydes, ketones, carboxylic acids, furfurals and phenols). The HPLC system was equipped with a DGU-20AS degassing module, LC-20AT gradient pump, CTO-10ASVP chromatography, oven, and an SPD-20 multi wavelength ultraviolet detector. Dried solid residues were analyzed with a TOC-SSM (Solid Sample Module: Shimadzu SSM-5000A) device. Moles of carbon atoms in the liquid phase were calculated by measuring the total organic carbon in the liquid product by using TOC analyzer. And the carbon content of gaseous products was also calculated according to GC reports. So that carbon mass balance (92-97%) was determined using the results obtained for each carbon containing products. All the product analyses were repeated in duplicate or triplicate and their mean values were reported.

3. RESULTS AND DISCUSSION

Some of the important factors that are influencing hydrothermal liquefaction, which are reaction temperature, pH values and acid catalysts are investigated to optimize the reaction conditions. In this regard the experiments were performed at 150, 175, 200, 250 and 300°C and the pH values 2.0 and 3.0 values by using acid catalysts HCl, HNO_3 and H_2SO_4. The efficient liquefaction conditions of artichoke residues for production of high value chemicals were investigated in terms of the yield and chemical composition of the produced aqueous phase at a constant reaction time.

3.1. Effect of experimental parameters of hydrothermal liquefaction on liquid phase

The overall liquid yields were obtained from all the experiments in the range of 25 % to 64 % for the artichoke leaves and in the range of 24 % to 62 % for the artichoke stalks. Due to change of water characteristic properties by increasing temperature, liquid product yields were found to be at the minimum value at the highest reaction temperature (300°C). As the temperature increases hydrocarbons of liquid product decompose into gaseous products easily and carbohydrates at temperatures above 180°C completely decomposes into mono carbohydrates in hot compressed water [10, 16, 17]. So that yields of the liquid and solid products of the artichoke leaves and artichoke stalks were decreased by increasing the temperature from 175°C to 300°C. This effect on the product yields comes from the changing water properties such as the dielectric constant, density, viscosity, and ion product with temperature. Because of these thermodynamic properties solvation power of water increases and starts to dissolve hydrocarbons and salts in higher ratio. The lowest solid product yields 30.8 C% and 33.2 C% were obtained at 150°C by using HNO_3 at the pH of 3.0 for the artichoke leaves and stalks, respectively. The highest solid product yields were determined for the without catalyst experiments at the reaction temperature of 200°C, as 59.7 and 57.5 C % for the artichoke leaves and stalks, respectively.

The differences for the artichoke leaves and stalks come from the lignocellosic structure. Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses, lignin, extractives, and ash forming inorganic materials and their compositions vary depending on the source of the plant biomass. These major structural components have rough compositions of (30-50) % cellulose, (20-40)% hemicelluloses, (15-25) % lignin, and (1-3)% extractives. Cellulose ratio for the artichoke leaves (37.37 %) is higher than the artichoke stalks (31.41%) as seen from the Table 2. Cellulose is a complex carbohydrate, consisting of linear chain of d-glucose units and significant structural component of primary cell walls of plants. The structure of hemicellulose is more complex than cellulose which composed of carbohydrate polymers (e.g., pentoses, hexoses, glucuronic acid). Hemicellulose has a lower molecular weight than cellulose and its role is to connect lignin and cellulose fibers. Lignin is a long chain heterogeneous polymer generally contains functional groups including phenolic, hydroxyl, aliphatic and carbonyl groups. Cellulose, lignin, and hemicelluloses, show different chemical reactions in hydrothermal processes. So that important disparities are observed in the product gas composition and the quantity of organics in the liquid product distribution. For example furfural, 5-hydroxymethylfurfural, levulinic acid, xylitol and value added materials can be obtained by hydrolysis of hemicellulose [18].

From the Figures 1-4 liquid, yields from the hydrothermal liquefaction of artichoke leaves and artichoke stalks in the presence of acid catalyst can be seen. Both catalysts had a positive effect on liquid yields; high yields were obtained with the catalysts than in the non-catalytic experiments. The aims of using catalysts are to increase the liquid product selectivity and to decrease solid residue formation. The highest liquid yields were obtained at 150^{o}C by using HNO_3 at the pH of 3.0 as seen from the Figures 1-4. According to the experimental results, efficiency of the acid catalysts in hydrothermal liquefaction can be ordered as; $HNO_3 > H_2SO_4 >$ HCl. The experimental results of this study pointed that liquid phase production pathways are enhanced by HNO_3 at the highest rate.

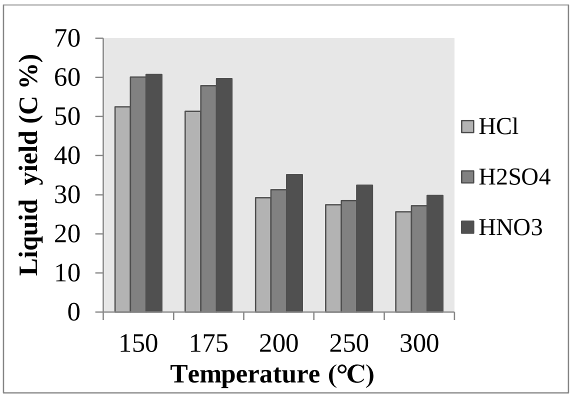

Figure 1 Effects of temperature and catalysts on the liquid yields of artichoke leaves at the pH 2.0.

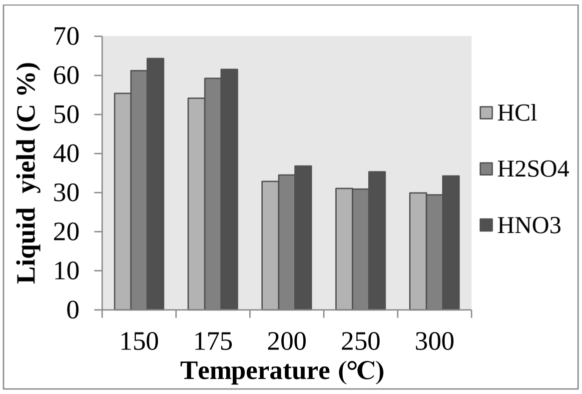

Figure 2 Effects of temperature and catalysts on the liquid yields of artichoke leaves at the pH 3.0.

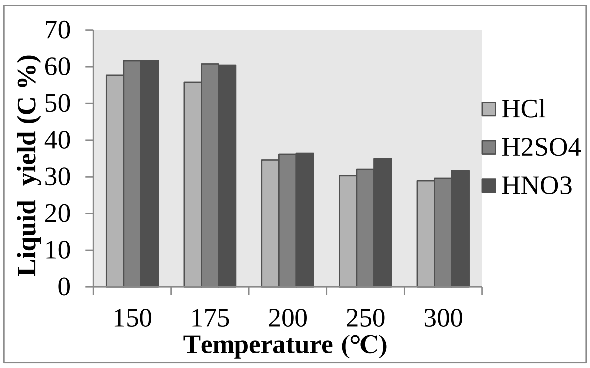

Figure 3 Effects of temperature and catalysts on the liquid yields of artichoke stalks at the pH 2.0.

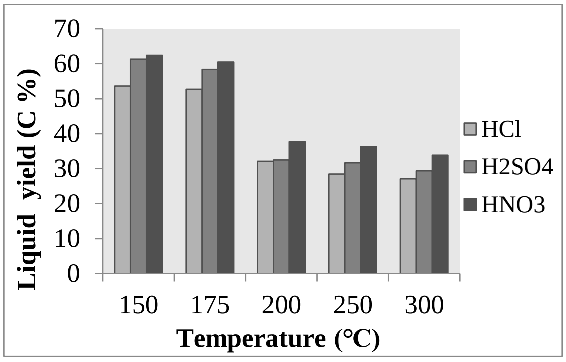

Figure 4 Effects of temperature and catalysts on the liquid yields of artichoke stalks at the pH 3.0.

3.2. Effect of experimental parameters of hydrothermal liquefaction on liquid product distribution

The aqueous products contained major organic compounds, which were carboxylic acids, furfurals, aldehydes and ketones. Their amounts were measured by using HPLC device to interpret the effects of the reaction conditions. Identified major organic compounds in liquid product from the hydrothermal liquefaction of artichoke leaves and stalks without catalyst are given in Figures 5 and 6, respectively, for the reaction temperatures (150°C - 300°C). According to the experimental results, HNO_3 led to highest increase of typical acidic intermediates; carboxylic acids and furfurals. Effects of temperature and HNO_3 on the liquid product yields of artichoke leaves and stalks at the pH 3.0 are given in the Figures 7 and 8, respectively.

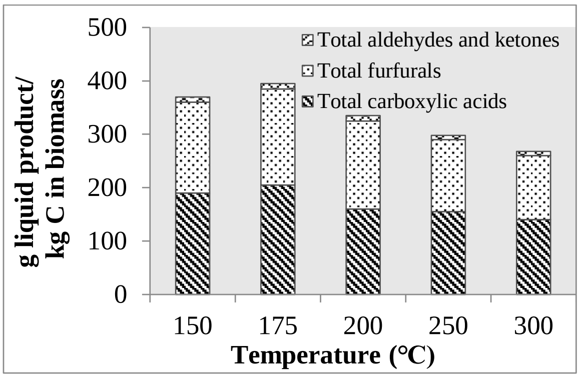

Figure 5 Effects of temperature on the liquid product yields of artichoke leaves.

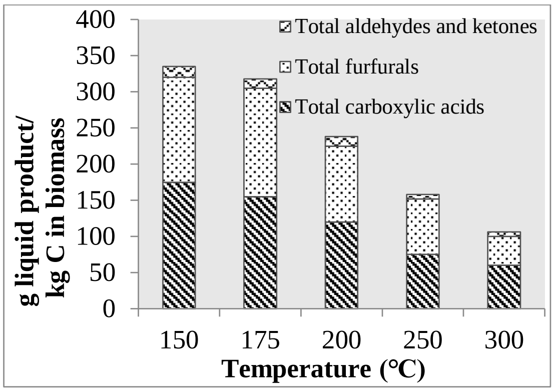

Figure 6 Effects of temperature on the liquid product yields of artichoke stalks.

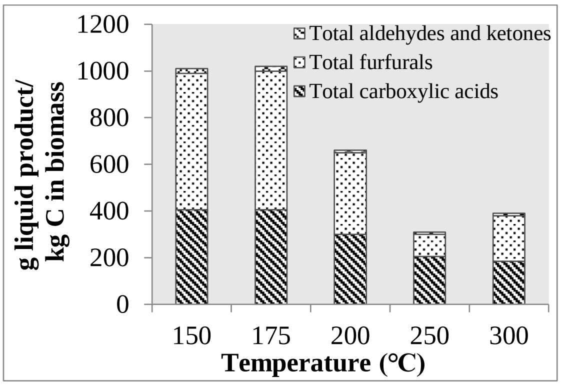

Figure 7 Effects of temperature and HNO_3 on the liquid product yields of artichoke leaves at pH 3.0.

Aqueous product contained high concentrations of carboxylic acids such as acetic acid and formic acid which are degradation products of furfural or 5-HMF. Effects of temperature and catalysts on the main aqueous products, formic acid, acetic acid and 5-HMF yields of artichoke leaves, and stalks at the pH 2 and pH 3 are shown in the Figures 9-14.

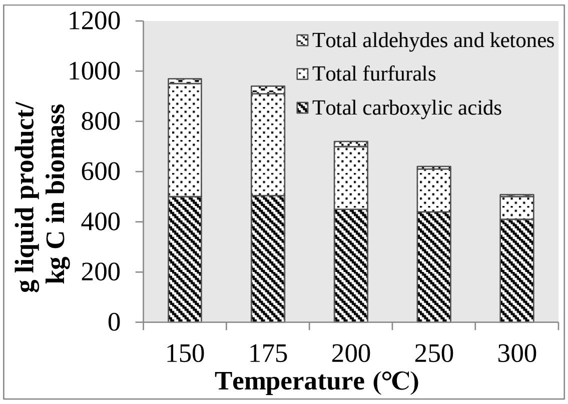

Figure 8 Effects of temperature and HNO_3 on the liquid product yields of artichoke stalks at pH 3.

The main aqueous products acetic acid and formic acid reached maximum value with HNO_3 catalyst at the pH 3. 5-HMF and reached maximum value with HCl catalyst at the pH 3. Especially, the main aqueous products were decreased sharply by increasing the temperature from 175°C to 200°C. Acetic acid was the highest product 268.52 (g aqueous product/kg C in biomass), and decreased to 103.59 (g aqueous product/kg C in biomass) at 300°C by using HNO_3. The highest formic acid was 72.12 (g aqueous product/kg C in biomass) and decreased to 26.82 (g aqueous product/kg C in biomass) at 300°C by using HNO_3. The highest 5-HMF was 176.24 (g aqueous product/kg C in biomass and decreased to 102.59 (g aqueous product/kg C in biomass) at 300°C by using HCl.

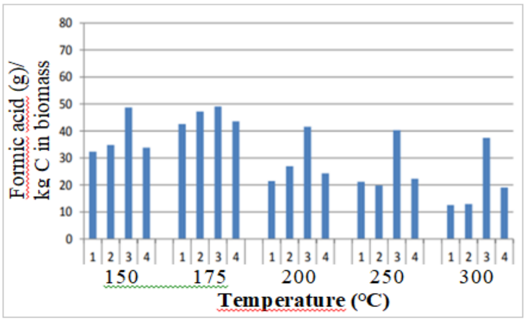

Figure 9 Effects of temperature and catalysts on the formic acid yields of artichoke leaves at pH 2. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

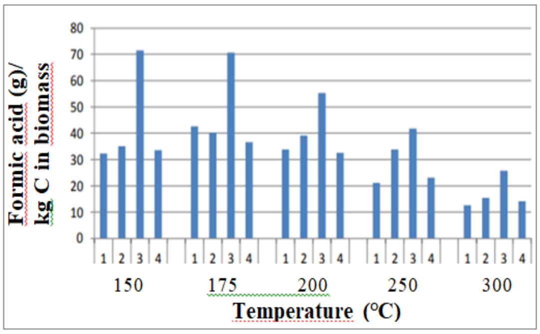

Figure 10 Effects of temperature and catalysts on the formic acid yields of artichoke leaves at pH 3. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

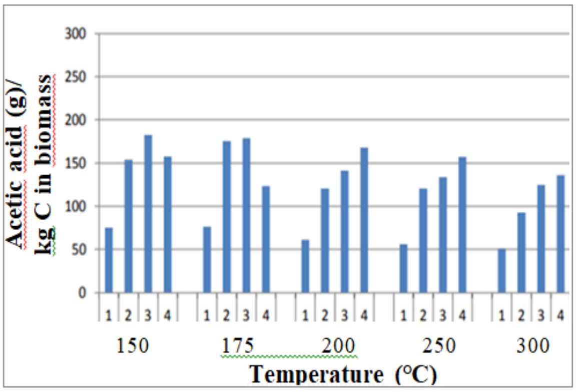

Figure 11 Effects of temperature and catalysts on the acetic acid yields of artichoke leaves at pH 2. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

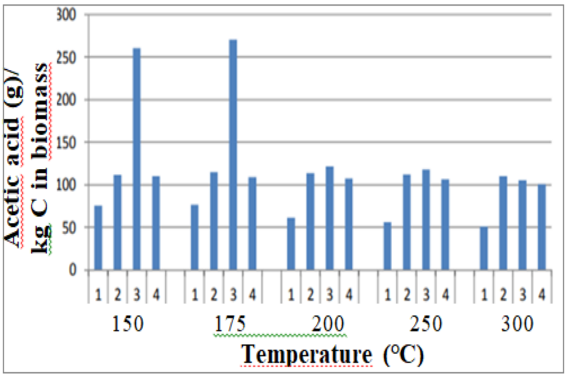

Figure 12 Effects of temperature and catalysts on the acetic acid yields of artichoke leaves at pH 3. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

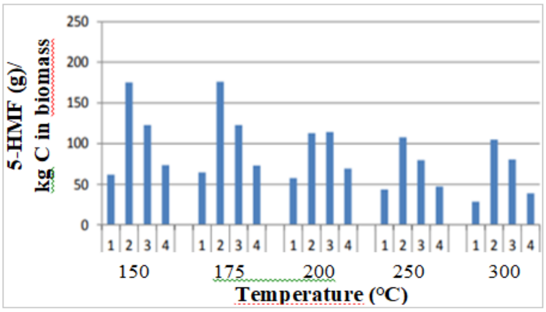

Figure 13 Effects of temperature and catalysts on the 5-HMF yields of artichoke leaves at pH 2. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

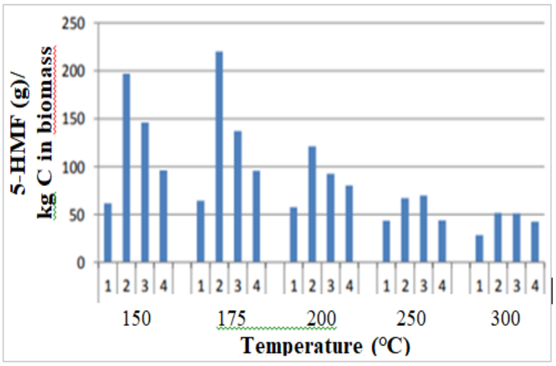

Figure 14 Effects of temperature and catalysts on the 5-HMF yields of artichoke leaves at pH 3. (1: without catalyst, 2: HCl, 3: HNO_3, 4: H_2SO_4).

4. CONCLUSION

This study was aimed to investigate the efficient conversion conditions of Artichoke residues to the valuable chemicals (formic acid, acetic acid and 5-hydroxymetilfurfural) by using acid (HCl, HNO_3 and H_2SO_4) catalyzed hydrothermal reaction as a function of pH and temperature. The experimental results of the hydrothermal liquefaction of the artichoke residues could be an alternative method to the waste management of the food industry. Additionally, the results presented in this paper have a novelty due to the examination of the feedstock. Experimental evolution of liquid parts and their variations with respect to the reaction parameters will be able to give more information about decomposition pathway depending on nature of feedstock. The experimental results of this study pointed that liquid phase production pathways are enhanced by HNO_3 at the highest rate. According to experimental results, efficiency of the acid catalysts in hydrothermal liquefaction can be ordered as: $HNO_3 > H_2SO_4 > HCl$. The aqueous products contain major organic compounds, which were carboxylic acids, furfurals, aldehydes and ketones. The main aqueous products acetic acid and formic acid reached maximum value with HNO_3 catalyst at the pH 3, at 175^{o}C and 150^{o}C, respectively. 5-HMF reached maximum value with HCl catalyst at the pH 3 at 175°C.

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The Declaration of Conflict of Interest/ Common Interest

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

Authors' Contribution

The first author contributed 60%, the other authors 40%.

The Declaration of Ethics Committee Approval

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

The Declaration of Research and Publication Ethics

The author of the paper declares that, international scientific, ethical and citation rules were followed for this study, and no falsification was made on the collected data Sakarya University Journal of Science and its editorial board have no responsibility for all ethical violations. All responsibility belongs to the responsible author and this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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