How to Add Value to Waste Hazelnut Shell by Using Subcritcal Water as a Reaction Medium?

Aslı YÜKSEL[*], **Gökalp GÖZAYDIN**

İzmir Institute of Technology, Chemical Engineering Department, Gulbahce, Urla, İzmir, TURKEY

* asliyuksel@iyte.edu.tr

ABSTRACT

Hazelnut is one of the most widely cultivated agricultural crops in Turkey with supplying 70% of the world's total production. This production capacity causes generation of lots of biomasses mainly consisting of hazelnut shell. Therefore, in this study, it was aimed to valorize waste hazelnut shell by converting it into high value chemicals in subcritical water as a reaction medium.

Hydrothermal treatments have been attracting much as an effective decomposition method of biomass since one of the approaches being used in green chemistry practices is to use water as a solvent and reaction medium where possible. Much of this work deals with liquid water at temperatures exceeding the normal boiling point, which is denoted as subcritical water with higher ion product, higher H^+ and OH^- ion concentrations, much lower dielectric constant (i.e. from 80 at 298 K to 2 at 673 K), low viscosity, high diffusivity, etc.

Hydrothermal valorization of waste hazelnut shell in subcritical water was investigated under different operating conditions to clarify the effects of reaction temperature (150-280 ^{o}C), reaction time (15-120 min), acid concentration (0-125 mM) and acid kind (H_2SO_4 and H_3PO_4) on the production of value-added chemicals with high temperature/high pressure autoclave. The main identified liquid compounds were levulinic acid, acetic acid and furfural while carbon dioxide and carbon monoxide were the major gaseous products. The highest hazelnut conversion was achieved (65.4%) at 280 °C and 120 min reaction time with the addition of 50 mM H_2SO_4. Under these conditions, levulinic acid yield, which was one of the desired chemicals, was recorded as 13.1%. The production of levulinic acid was enhanced with H_2SO_4 addition; whereas treatments with H_3PO_4 improved the furfural production.

INTRODUCTION

Currently, the search and utilization of alternative and renewable resources for the production of valuable chemicals and fuels have been critical issue due to dependency of petroleum, environmental concerns and the growth of population. The valorization of waste and/or non-edible biomass have a significant potential in this sense. The enormous range of valuable bio-based chemicals such as levulinic acid, acetic acid furfural etc. can be formed from various biomasses, however; levulinic acid is seemed the most substantial chemical because of having high potential to derive different products including pharmaceutical agents, herbicides, plasticisers, biofuel additives and flavouring agents. There is found multiple biomass transformation options into levulinic acid like treatment of mineral acids and solid catalyst, ionic liquids and sub- and supercritical fluids [1].

An unique dissolution and physicochemical properties are enables near the critical point of water (374 °C and 22.1 MPa) due to the existence in liquid state under adequate pressure [2]. The increment of temperature leads to polarity change of water [3] and the ion product (K_w) of water becomes higher approximately three orders of magnitude higher than that of ambient water [4, 5]. Moreover, the dielectric constant (ε) reduces from 80 to 10 at critical point which enhances the ionic reaction and the dissociation of water into H_3O^+ and OH^- ions [4, 5].

Hazelnut has a significant role for Turkey's agriculture since Turkey is a global leader of the hazelnut shell production with 650,000 tons/year (75% of World production). In the hazelnut shell processing, a large amount of waste shell, which are used at ineffective options (heating) [6]. For this reason, the transformation of waste hazelnut shell into valuable bio-based chemicals can promote to value and being natural alternative.

This is the first study, to our knowledge, about the hydrothermal conversion of hazelnut shell to valuable chemicals in hot compressed water. The main objective of this study is to evaluate the influence of several reaction parameters such as temperature (150-280 °C), reaction time (15-120 min), acid types (H_2SO_4 and H_3PO_4) and acid amount (0-125 mM) in autoclave.

MATERIALS AND METHOD

Materials: Hazelnut shell was obtained from Ordu, turkey. Fructose ($\geq$ 99%), pyruvic acid (98%), glycolaldehyde, glycolic acid (99%), glycerolaldehyde (99%), levulinic acid (98%), 5-hydroxylmethyl furfural (99%) and lactic acid (98%) were purchased from Sigma-Aldrich. Furfural (98%), acetic acid (100%), glucose ($\geq$ 99.5%), formic acid (98%) and sulfuric acid (96-98%) were from Merck. Phosphoric acid (85-90%) was purchased from Fluka.

Methods: The hydrothermal treatment of waste hazelnut shell was performed in a batch reactor (Parr 5500) which is 300 ml of total volume, 350 °C maximum temperature and 200 bar maximum pressure. Initially, 4 g of hazelnut shell, 100 ml of de-ionized water and various amount of dilute H_2SO_4 and H_3PO_4 (50-125 mM) were loaded into reactor. After the reaction, gas product was collected into gas bas for GC-TCD analysis and then liquid product and solid product were separated by filtration paper. The liquid product was analyzed with HPLC (Shodex sugar column, SH 1011, with refractive index detector (RID), 0.5 ml/min flow rate of dilute H_2SO_4 (3.75 mM) as a mobile phase and 50 °C of column temperature). The residual solid product was dried at 50 °C and 24 h, and it was analyzed with SEM, FTIR-ATR, TOC and elemental.

RESULTS

The effect of reaction temperature, reaction time, dilute acid addition and acid type on the hydrothermal degradation of waste hazelnut shell under hot compressed water conditions was

evaluated. Furthermore, levulinic acid, acetic acid and furfural were qualified as desired products in this study.

Effect of reaction temperature: A typical reaction was carried out at 150-280 °C and 15-120 min in the presence of 50 mM H_2SO_4 in order to figure out the effect of reaction temperature on the hazelnut shell conversion and liquid products formation (Table 1). At each reaction time, the conversion of hazelnut shell increased with reaction temperature and reached to the highest level (65.40%) with a treatment of 280 °C, 120 min and 50 mM H_2SO_4. With the increment of reaction time, no significant conversion change was observed. As expected, a considerable amount of fructose did not converted to other compounds and no levulinic acid formation was observed at lower temperature (150 °C) because of the cellulose hydrolization into glucose and the isomerization to glucose primarily [7]. The fructose amount decreased to 0.11% (280 °C and 120 min) significantly with a further reaction temperature treatment which led to the increase of levulinic acid formation. The selectivity of levulinic acid reached to 13.26% and 13.05% for 250 °C and 280 °C in 120 min, respectively. This levulinic acid formation behavior can be caused by the structural changes of water through critical point of water since the hydrogen bonds are weakening and become less stable [3, 5]. On the other hand, dielectric constant decreases and self-dissociation of water increases which enhance the ionic reaction [4]. In contrast, relatively lower reaction conditions (150 °C and 120 min, 200 °C and 15 min) are more effective in the terms of furfural formation due to the low thermal stability of hemicellulose [8] and the selectivity of furfural decreased down to 0.04% with a higher temperature and longer time treatment (280 °C and 120 min). In the case of acetic acid, selectivity is comparatively high at 150 °C while it is quite stable between 200 °C to 280 °C.

Table 1. The effect of reaction temperature on the conversion and product selectivity in 50 mM H_2SO_4

T (°C)	t (min)	Conversion (%)	Selectivity	(%)		
			Fructose	Levulinic acid	Acetic acid	Furfural
150	15	35.79	41.96	0	11.58	1.54
	60	41.42	47.74	0	9.53	5.54
	90	42.14	43.11	0.10	11.09	6.60
	120	41.12	34.94	0.28	10.97	11.91
200	15	56.99	1.13	6.85	8.66	13.09
	60	59.32	0.58	13.33	8.43	7.73
	90	61.20	0.50	12.45	8.09	5.32
	120	58.39	1.24	13.01	8.68	5.72
250	15	61.66	1.08	10.91	8.05	0.92
	60	61.44	0.91	10.21	7.80	0.39
	90	61.02	1.09	10.87	8.72	0.22
	120	61.07	1.07	13.26	7.89	0.21
280	15	62.54	0.48	8.42	8.28	0.25
	60	64.64	0.35	11.85	8.09	0.18
	90	64.39	0.28	13.26	8.78	0.07
	120	65.40	0.11	13.05	8.76	0.04

The changes of raw hazelnut shell and solid residues' surface structure were monitored with SEM analysis (Figure 1). After the subjection of 150 °C and 50 mM H_2SO_4, hazelnut shell's complex layer with fiber (Figure 1a) started to decompose into small carbon spheres (Figure 1b). The reason of this situation can be easy decomposition of cellulosic and hemicellulosic component of hazelnut shell with higher diffusion characteristic of subcritical water [9]. The

particle size of carbon spheres were approximately 1-2 µm which found in tarry structures at 250 °C and 280 °C (Figure 1c-d).
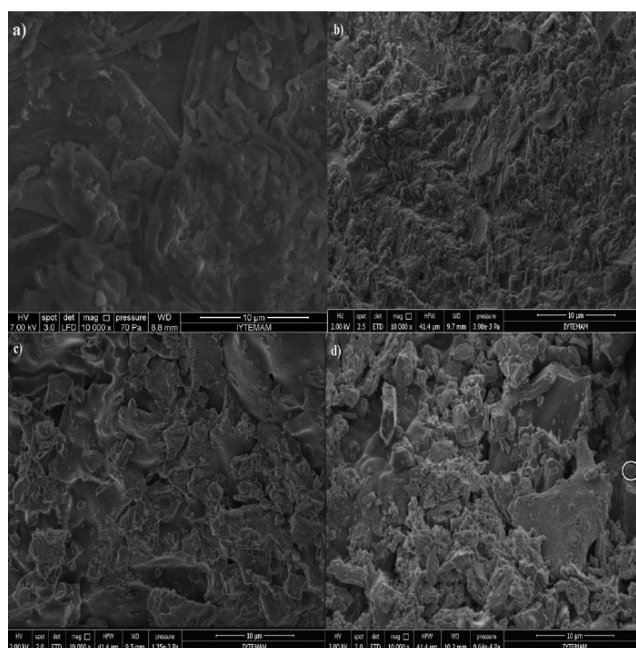

Figure 1. SEM images of a) untreated and solid solid residues after the treatment at b) 150 °C; c) 250 °C; 280 °C after 60 min and with 50 mM H_2SO_4 (at magnification of x10,000)

Furthermore, FTIR spectrum of untreated hazelnut shell and solid residues after the hydrothermal conversion at various reaction temperatures (150, 200 and 280 °C) are shown in Figure 2. The peaks at 1375 cm^{-1} and 2980 cm^{-1} are typical cellulose and hemicellulose structure [9, 10] and correspond to C-H bending of alkanes and saturated aliphatic C-H stretching respectively. These peaks of raw hazelnut shell were sharper than those of solid residues and also, the absorbance peak at 1375 cm^{-1} disappeared at higher temperature (280 °C). The peaks at 1215-1275 cm^{-1} are associated with stretching of aliphatic C-H groups. Moreover, the evidence of lignin presence in the hydrothermally treated solid residues can be concluded with 1600 cm^{-1} and 3330 cm^{-1} bands. These peaks are related to characteristic lignin structure [9, 11] and are observed in each treatment conditions since subjecting even 280 °C is not enough to cleavage of phenolic bonds.
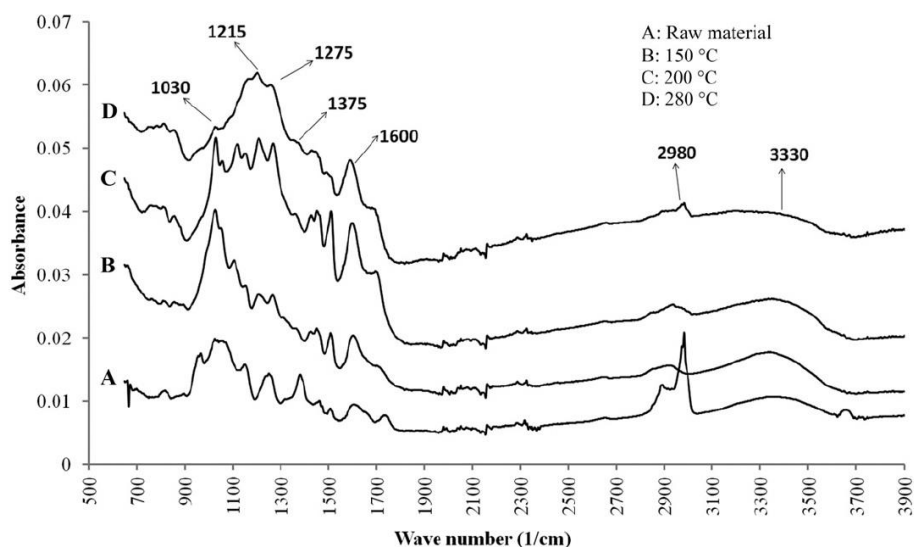

Figure 2. FTIR spectrum of untreated and treated hazelnut shell solid residues at different temperatures (60 min and 50 mM H_2SO_4)

In the terms of gas products distribution, relatively higher temperature conditions such as 250 °C and 280 °C for 120 min in the presence of 50 mM H_2SO_4 was considered for GC-TCD analysis due to the boost of the secondary decomposition reaction at elevated temperatures. Carbon monoxide and carbon dioxide were the main gas compounds that were identified from the hydrothermal conversion of hazelnut shell whereas trace amounts of hydrogen and methane were also observed (Table 2). While carbon monoxide concentration increased from 160.28 to 200.47 μg/ml, the concentration of carbon dioxide reduced from 637.26 to 591.12 μg/ml. Therefore, it can be concluded that the increment of temperature shifts the water gas shift reaction towards left-hand side (carbon monoxide). On the other hand, 1.78 μg/ml of methane concentration and 1.42 μg/ml of hydrogen concentration were determined in the 280 °C and 120 min in the presence of 50 mM H_2SO_4.

Table 2. The composition of gas products for 250 °C and 280 °C, 120 min and 50 mM H_2SO_4

Temperature (°C)	Gas	products	(μg/ml)					
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
250	2.77	160.28	0.29	637.26	0.20	0.06	0.57	0
280	1.42	200.47	1.78	591.12	0.36	0.65	1.25	0.32

Effect of acid addition: In this study, H_2SO_4 and H_3PO_4 were preferred to evaluate the influence of dilute acid addition on the conversion and liquid product formation from the waste hazelnut shell. To eliminate the corrosion problem, the effect of acid addition was studied at 200 °C and 60 min. The addition of H_2SO_4 and H_3PO_4 have a different conversion trend which increased until 75 mM H_2SO_4 then decreased slightly to 58.94% (125 mM H_2SO_4) whereas the continuous improvement (56.38%) was observed with the treatment of 125 mM H_3PO_4. As shown in Figure 3, the both acid type enhanced the different valuable chemicals production. While the formation of levulinic acid was significant in the presence of H_2SO_4 that was increased up to 15.40% (125 mM), the selectivity of levulinic acid was only 3.07% in the 125 mM H_3PO_4. In contrast to levulinic acid selectivity, relatively weaker acid, H_3PO_4, was more effective in the terms of furfural formation. The addition of 100 mM of H_3PO_4 increased the furfural selectivity to 16.74% whereas it had a reverse pattern and decreased to 3.62% with 100 mM of H_2SO_4. Two reasons can be caused to this difference: 1) the formation of char from furfural by polymerization [12] and 2) the structural difference of cellulose and hemicellulose. Furthermore, serious effect of acid type and amount on the acetic acid selectivity was determined.
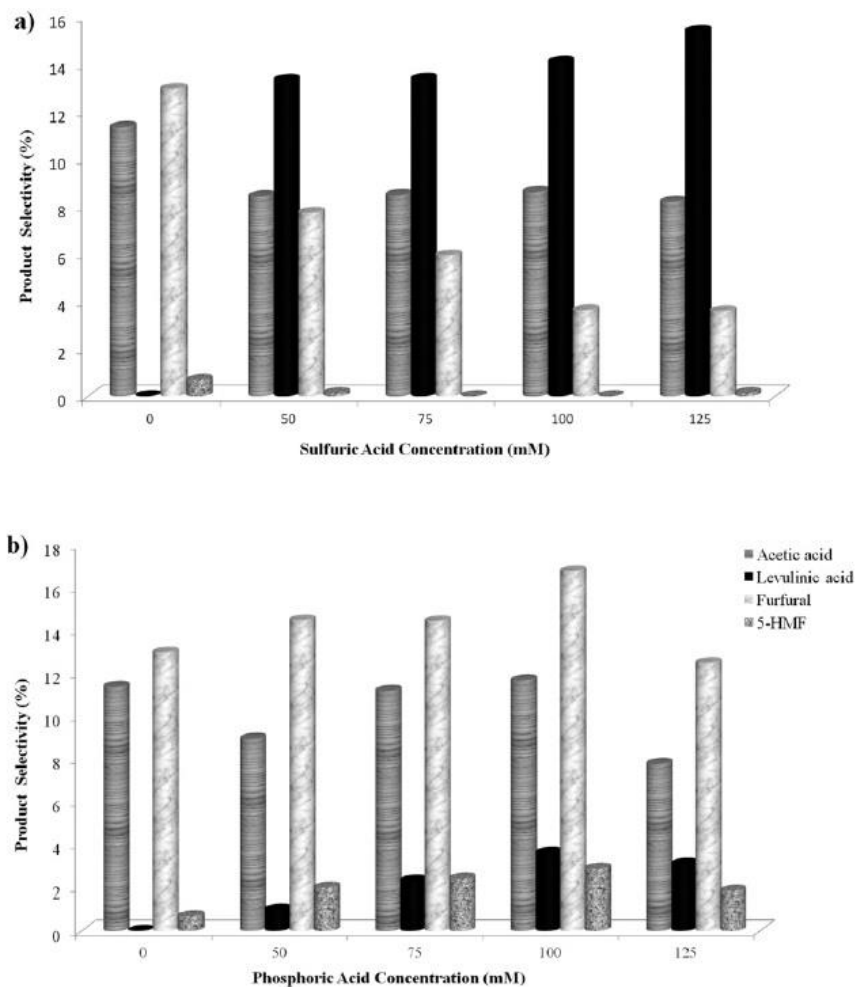
4

Figure 3. The effect of acid addition on the liquid product distribution at 200 °C and 60 min with a) H_2SO_4 and b) H_3PO_4

Effect of reaction time: The reaction time did not have significant influence on the conversion and acetic acid selectivity when compared to the effect of temperature and acid addition (Figure 4). With a longer reaction time, 5-HMF transformed to levulinic acid, whose selectivity is 13.01% at 120 min. However, the selectivity of furfural reduced considerably to 5.72% (120 min).
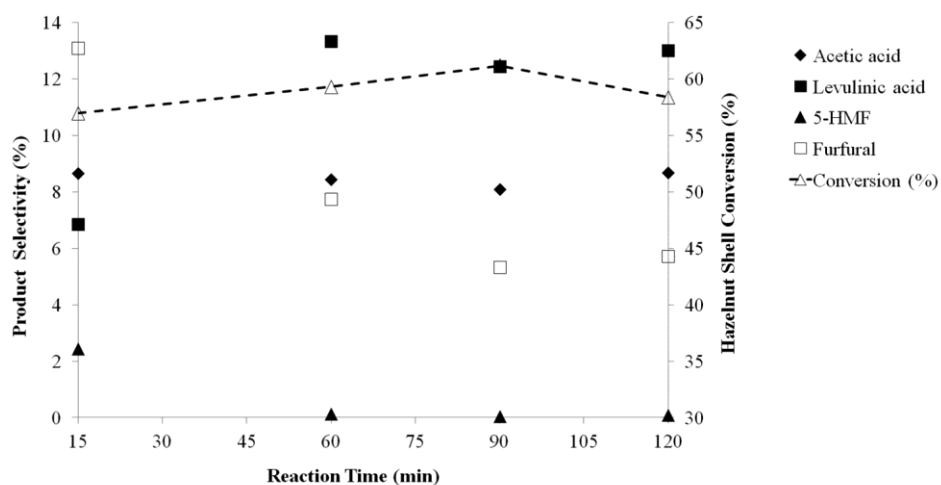

Figure 4. The effect of reaction time on the conversion and the selectivity of products (200 °C and 50 mM H_2SO_4)

5

Possible reaction pathways of hydrothermal conversion of hazelnut shell: As illustrated in Figure 5, the major possible reaction pathways of the hydrothermal degradation of hazelnut shell under subcritical water conditions were shown. In the case of cellulose, the hydrolization of cellulose into oligomers and the isomerization of glucose to fructose are rapid at low temperature (150 °C). At 200 °C, the addition of 75-100 mM of H_3PO_4 concentration increases the 5-HMF formation, however; the levulinic acid production enhances with the presence of 100-125 mM H_2SO_4 concentration and longer reaction time ($\geq$ 60 min). While the low presence of H_2SO_4 (0-5 mM) and high H_3PO_4 (75-100 mM) increase the acetic acid production via acetyl cleavage at 200 °C, 200 °C and 15 min with the presence of 50 mM H_2SO_4 is favorable for the furfural formation. On the other hand, the higher temperature (250-280 °C) and longer reaction time (120 min) treatments result in the char formation from furfural.
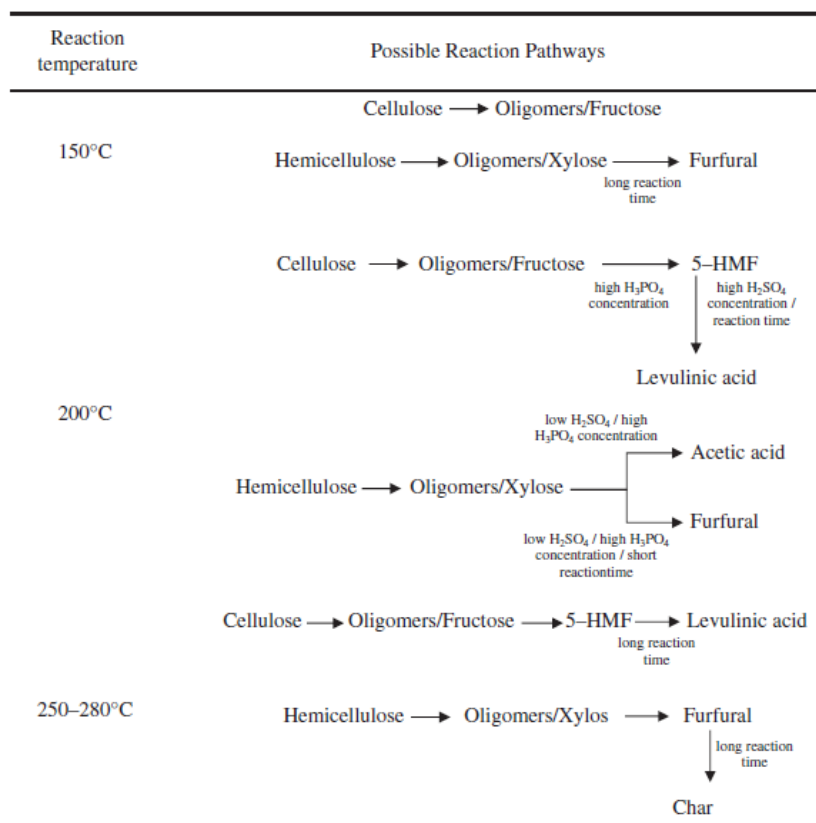

Figure 5. Possible reaction pathways of the hydrothermal decomposition of hazelnut shell at various reaction temperatures

CONCLUSION

The effect of reaction temperature (150-280 °C), reaction time (15-120 min), dilute acid type (H_2SO_4 and H_3PO_4) and acid amount (0-125 mM) on the hazelnut shell conversion and value-the production of added chemicals including levulinic acid and furfural in hot compressed water. The highest conversion (65.40%) was observed at 280 °C and 120 min with 50 mM H_2SO_4. The temperature and acid type affect the production of levulinic acid and furfural distinctly. While the formation of levulinic acid enhances through the critical point of water, the furfural formation has an opposite behavior. Furthermore, the rate of levulinic acid and furfural production are accelerated with the addition of H_2SO_4 and H_3PO_4, respectively.

REFERENCES

[1]   RACKEMANN D. W. and DOHERTY W. O. S., The conversion of lignocellulosics to levulinic acid, Biofuels, Bioproducts and Biorefining, 5, 2011, p. 198-214.

[2]   SASAKI M., OSHIKAWA T., WATANABE H., WAHYUDIONO, and GOTO M., Reaction kinetics and mechanism for hydrothermal degradation and electrolysis of glucose for producing carboxylic acids, Research on Chemical Intermediates, journal article 37, April 01 2011, p. 457-466.

[3]   KRUSE A. and DAHMEN N., Water – a magic solvent for biomass conversion, The Journal of Supercritical Fluids, 96, 2015/01/01/ 2015, p. 36-45.

[4]   KRUSE A. and DINJUS E., Hot compressed water as reaction medium and reactant: Properties and synthesis reactions, The Journal of Supercritical Fluids, 39, 2007/01/01/ 2007, p. 362-380.

[5]   AKIYA N. and SAVAGE P. E., Roles of water for chemical reactions in high-temperature water, Chemical Reviews, 102, 2002/08/01 2002, p. 2725-2750.

[6]   GUNEY M. S., Utilization of hazelnut husk as biomass, Sustainable Energy Technologies and Assessments, 4, 2013/12/01/ 2013, p. 72-77.

[7]   P. CARDENAS-TORO F., C. ALCAZAR-ALAY S., FORSTER-CARNEIRO T., and ANGELA A. MEIRELES M., Obtaining oligo- and monosaccharides from agroindustrial and agricultural residues using hydrothermal treatments, Food and Public Health, 4, 2014, p. 123-139.

[8]   CHAN Y. H., YUSUP S., QUITAIN A. T., UEMURA Y., and SASAKI M., Bio-oil production from oil palm biomass via subcritical and supercritical hydrothermal liquefaction, The Journal of Supercritical Fluids, 95, 2014/11/01/ 2014, p. 407-412.

[9]   CHENG L., YE X. P., HE R., and LIU S., Investigation of rapid conversion of switchgrass in subcritical water, Fuel Processing Technology, 90, 2009/02/01/ 2009, p. 301-311.

[10]   PAVLOVIČ I., KNEZ Ž., and ŠKERGET M., "Subcritical water - a perspective reaction media for biomass processing to chemicals : Study on cellulose conversion as a model for biomass," in *Towards sustainable technologies*, ed, 2013, pp. 73-82.

[11]   WAHYUDIONO, SASAKI M., and GOTO M., Noncatalytic liquefaction of tar with low-temperature hydrothermal treatment, Journal of Material Cycles and Waste Management, journal article 9, September 01 2007, p. 173-181.

[12]   PROMDEJ C. and MATSUMURA Y., Temperature effect on hydrothermal decomposition of glucose in sub- and supercritical water, Industrial & Engineering Chemistry Research, 50, 2011/07/20 2011, p. 8492-8497.