



Optimization of Pyrolysis Temperature and Particle Size on the Phenols and Hemicellulose Fast Pyrolysis Products in a Tandem Micro-Pyrolyzer

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ABSTRACT

Fast pyrolysis of sugarcane bagasse was investigated in a tandem micro-pyrolyzer. The effects of temperature and particle size on the phenolic compounds and hemicellulose products distribution were examined during fast pyrolysis process. For this, changes in the micro-reactor parameters were made (particle size between 0.1 and 0.5 mm and reactor temperature between 450 and 600 °C). Response Surface Methodology (RSM) was used to optimize pyrolysis parameters. The results indicated that the temperature had the highest effect on phenolic and furfural-type compounds, whereas the particle size did not exhibit significant effects on carboxylic acid products. The largest number of phenolic compounds were achieved upon decreasing the temperature and increasing particle size. The ANOVA analysis revealed that the full quadratic model was more adequate for phenolic and furfural compounds, whereas the linear square model was accurate for carboxylic acids. In general, a tandem micro-pyrolyzer interfacing with a GC-MS analysis facilitated a better understanding of a chemical composition of biomass and therefore, could remarkably improve the valorising of sugarcane bagasse application in biorefinery processes.

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1. INTRODUCTION

In recent years, many studies have been conducted to enhance the efficiency of processes for renewable energy. Biomass can be used for a partial or full replacement of fossil fuels given that it is a carbon-based energy resource with such benefits as potential for zero to net negative emission of carbon dioxide. Thermochemical and biological processes can transform biomass into high-energy fuels [1]. Thermochemical processes provide complex and multiple products in a short reaction time span; however, biological processes are more selective but require long processing times [2]. One of the commercially relevant thermochemical technologies for processing lignocellulosic materials into fuel and chemical products is fast pyrolysis [3, 4]. Using fast pyrolysis, the pyrolysis vapor is rapidly cooled to produce a liquid product (bio-oil), which is up to 75 wt % of the biomass feedstock and has a higher caloric value than the biomass [5]. While there are more than 300 oxygenated compounds in fast pyrolysis bio-oil, three classes of compounds can be typically identified in bio-oils [6] including sugars, small carbonyl compounds (e.g. furfurals and cyclopentanones), carboxylic acids and phenols, arguably derived from the three polymeric components of biomass, namely cellulose, hemicellulose, and lignin, respectively [7]. Recently, there is growing attention to

producing added-value chemicals from fast biomass pyrolysis. Furfural derived from hemicellulose is an effective organic chemical extensively applied to production of fibres, synthetic rubbers, resins, flavors, food additives, dyes and paintings, and liquid hydrocarbon fuels [8]. Cellulose is hydrolyzed and dehydrated to form the furfural on an industrial scale from biomass feedstocks such as bagasse and corncob in aqueous acid solutions. Moreover, enhanced furfural production was reported using catalytic pyrolysis of biomass with MgCl₂, ZnCl₂, H₂SO₄, and solid superacid as catalysts [9].

Lignin is a promising natural resource for aromatic compound productions compared to hemicellulose and cellulose due to its hydroxyphenyl, syringyl, guaiacyl, monomeric units [10]. The remarkable aromatic and highly functionalized nature of lignin make it appropriate for value-added aromatic products such as benzene, toluene, and xylenes [11]. However, recent research has also shown that these aromatic hydrocarbons can also be formed from intermediates compounds arising from cellulose and hemicellulose [12, 13]. For example, toluene can be produced from the Diels-Alder cycloaddition reactions of methyl furan and ethylene, followed by dehydration [14].

The yields and detailed compositions of fast pyrolysis products from the three main polymers of biomass have been mainly investigated by reacting each polymer separately [15, 16]. Except where the concept of fractionation is adopted in a biorefinery, fast pyrolysis of raw biomass feedstock involves co-processing of the component polymers under the same

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process conditions, which may lead to both beneficial and abortive interactions of intermediate reaction products. Such interactions may lead to enhanced yields of some reaction products in the bio-oil, while they could also decrease the yields of others. Processing parameters such as fast pyrolysis temperature, vapor residence times, biomass particle size, biomass type, biomass feeding rate, and reactor type are known to influence the yields and compositions of products in bio-oils [17-19]. Among these parameters, pyrolysis temperature, biomass type, and biomass particle size have been highlighted to have the predominant influence on bio-oil yield and composition [13, 20, 21]. Joubert et al. [22] studied the effects of the type of reactor and temperature on the fast pyrolysis of biomass. Using biomass particle size of >2 mm, they found that the ideal temperature for the production of the highest bio-oil yield (60 wt %) was 500 °C [23]. In addition, Park et al [24] and Amutio et al. [25] found that the yields of phenolic compounds depended mostly on the type of biomass, the amount of biomass feed, and pyrolysis temperature.

Karagoz et al [26] investigated online conversion of beech wood and microalgae on a laboratory reactor connected with GC-MS by using a catalyst. They reported that the relative yield of aromatic hydrocarbons such as Benzene, Toluene, and Xylenes (BTX) changed considerably depending on the biomass type. Wang et al. [27] compared the conversion of continuous and sequential pyrolyses of wood biomass using in-situ and ex-situ catalyses. The authors indicated that in-situ catalytic pyrolysis generated higher aromatic compounds than ex-situ under the same situations.

Fast pyrolysis of sugarcane bagasse, a vastly available biomass feedstock, has been studied by a number of researchers [1, 12, 28-30]. Sugarcane bagasse is obtained after the extraction of sugarcane juice (mostly hexose sugars) and therefore, is mostly composed of lignin and hemicellulose. The weight percentage of hemicellulose and lignin components in sugarcane bagasse is around 25 % and 23 %, respectively, with the elemental composition of about 42 % carbon, 5 % hydrogen, 52 % oxygen, and trace amounts of several metal ions [12]. This feedstock is therefore suitable to study the influence of processing parameters in a real biomass that will improve the understanding of the interactions among intermediate products of fast pyrolysis by following the yields of phenolic compounds, furfurals, and carboxylic acids. In this present study, the effects of temperature and particle size on these classes of bio-oil compounds have been investigated during ex-situ fast pyrolysis using Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC-MS), an analytical micro-pyrolyzer instrument. Response Surface Methodology (RSM) was employed to reveal the role of particle size and temperature in hemicellulose and lignin compounds in fast pyrolysis process. This is a novel approach to determining the contributions of effective parameters in the stepwise conversion process of hemicellulose and lignin (in sugarcane bagasse) into a selection of bio-oil compounds and the performance of value-added chemicals recovery from hemicellulose and lignin.

2. MATERIALS AND METHODS

2.1. Biomass collection and preparation

The sugarcane bagasse fiber feedstock was collected from an agro-based pulp and paper industry in the southwest of Iran, used as paper mill raw material. The average fiber size was

3-5 cm in length with approximate moisture content 50 % (w/w). The biomass was dried in the open using solar energy for two days; then, it was put in the oven at 105 °C to reach a moisture content below 10 % (w/w). Dried materials were ground by a mill and, then, sieved to particle sizes of diameters 100, 212, 300, 425, and 500 µm. The small size of sugarcane bagasse (300 g, dry weight) was subjected to soxhlet extraction with ethanol/Toluene solvent (2:1, v/v) for 5 h. In order to remove the toluene, the sample was dewatered for 3 h followed by vacuum drying at 105 °C over a day. Table 1 shows the result of proximate and ultimate analysis, adapted by the ASTM protocols established for biomass. Hemicellulose fraction was measured by precipitation of pre-hydrolysis followed by acid hydrolysis. The acid hydrolysis based on the Technical Association of the Pulp and Paper (TAPPI) standard methods (T264 om-88, T211 om-85) was carried out for acid-soluble lignin. Soluble lignin was calculated by UV spectrophotometry. To ensure the reproducibility of results, the chemical analysis procedures were conducted in triplicate. FTIR analysis was performed to characterize the hemicellulose and lignin from 4000 to 500 cm⁻¹ by platinum ATR Alpha instrument.

Table 1. The proximate and ultimate analysis of sugarcane bagasse

Component	Weight %	Standard method
Proximate analysis (wt %, ar*)		
Moisture	8	ASTM D 3173
Volatile	77	ASTM 3174
Fixed carbon	12.4	ASTM 3175
Ash	2.6	ASTM 3172
Ultimate analysis (wt %, db*)		
C	43.5	ASTM D 4239
H	6.4	ASTM D 4239
N	0.1	ASTM D 4239
S	0.01	ASTM D 4239
O	49.9	By difference
* ar = as received, db = dry base		

2.2. Fast pyrolysis experiment

A tandem micro-pyrolyzer system, Rx-300 TR, Frontier Laboratories, Japan was utilized for fast pyrolysis of the milled samples. The detailed schematic of the system can be found in another study (Wang et al. 2014). According to Figure 1, the micro-pyrolyzer consisted of two individual parts: first, pyrolysis reactor and second, the *ex-situ* catalyst bed reactor. Microgram quantities of biomass sample were weighed (around 1-2 µg) and placed into a stainless steel cup, which was then dropped into the pyrolysis reactor fitted with programmable temperature control. Rapid thermal degradation and devolatilisation of the biomass produced vapor streams, carried by helium gas at a rate of 1 ml/min through the catalyst bed reactor. At a temperature of 500 °C, the retention time of hot vapor at micro-pyrolyzer occurred in less than 2 seconds. Vapor products leaving the catalyst bed were detected by GC-MS interfacing with the pyrolysis system. The yield of each compound was estimated individually using their percentage peak areas.

2.3. Experimental design

Statistical and mathematical techniques such as response surface methodology are helpful in developing, optimizing,

and improving chemical processes. Moreover, these techniques can be employed for developing, designing, and formulating new products and enhancing the designs of existing products. The RSM is widely used for industrial purposes, especially in case of determining the effects of several input variables on quality characteristics of the products or performance measure or process [31]. Two-variable Central Composite Design (CCD) was used to optimize and study the influence of process conditions on the chemical compounds of fast pyrolysis. The CCD is an effective method for estimation of combined value and quadratic polynomials to optimize the response through a three-dimensional observation space regarding the reaction variables including the temperature and particle size. Design Expert 7 was employed for analyzing the results including phenolic compounds, furfural, and carboxylic acids.

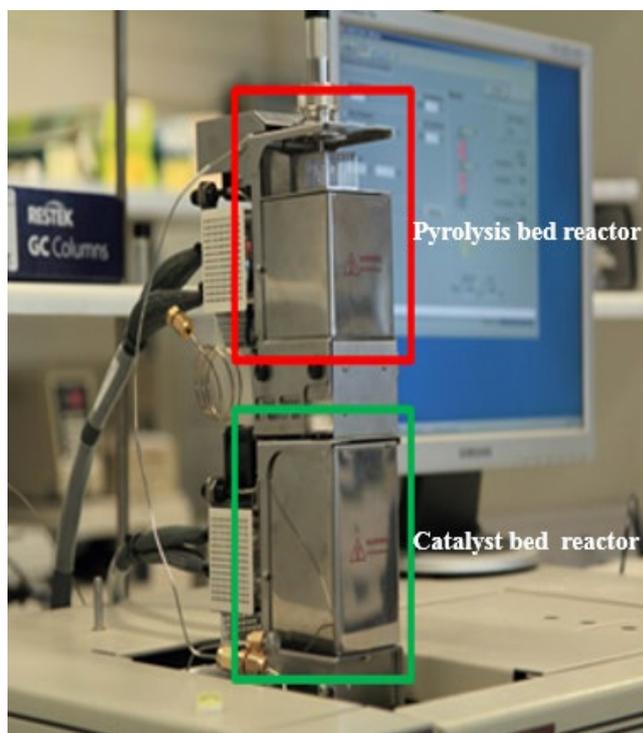


Figure 1. The tandem micro-reactor connected with GC-MS

3. RESULTS AND DISCUSSION

3.1. Characterization of hemicellulose and lignin

The FTIR analysis showed that the broad peak of 3500 cm^{-1} resulted from O-H stretching vibration, while 2900 cm^{-1} was attributed to C-H stretching of methyl compounds. The region between 3200 and 3600 cm^{-1} corresponds to hydrogen stretches in several compounds and amines and amides in amino acids. This band is broad because of the high number and large density of hydrogen bonds, mainly hydroxyl radicals in the polysaccharide pyronose rings. At 2888 cm^{-1} , the observed absorption band is related to the axial deformation of C-H group. The peak at 1721 cm^{-1} is characteristic of the carbonyl group (C=O) of the hemicellulose in the sugarcane bagasse. The aromatic ring bond from phenol is determined between 1650 and 1500 cm^{-1} . In fact, C=O bonds at 1650 cm^{-1} increase conjugated groups qualitatively with aromatic rings in lignin. The region between 1250 and 1000 cm^{-1} showed that the assignments mainly attributed to oxygenated group (C-O bonds) in alcohols, ethers, and carboxylic acids in sugar which were not affected by metal binding.

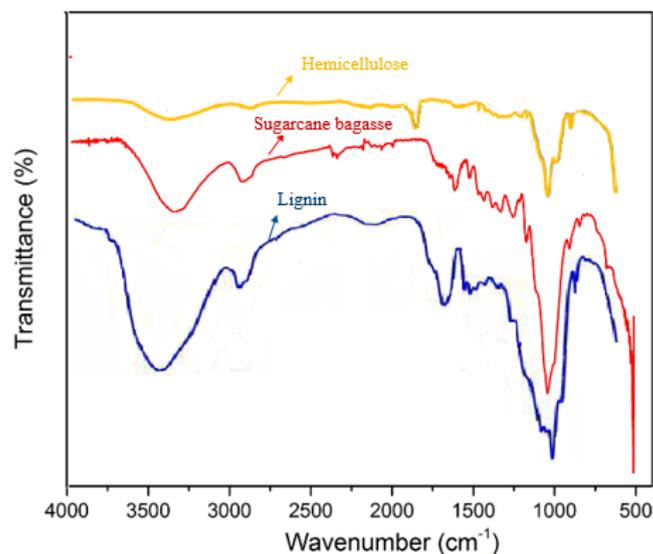


Figure 2. FTIR analysis of lignin, sugarcane bagasse, and hemicellulose

3.2. Hemicellulose and lignin production distribution from fast pyrolysis

In this study, the sugarcane bagasse product compositions and distribution were evaluated at different temperatures (450 – $600\text{ }^{\circ}\text{C}$) and particle size (100 – $500\text{ }\mu\text{m}$). The results showed that different compounds could be produced by changing the pyrolysis conditions. In addition, each biomass component generates a wide range of chemical compounds. For example, acetic acid, propionic acid, furfural, 5-hydroxymethyl furfural (HMF), and levoglucosan are generated from sugars, while lignin is a significant source of phenol, alkylphenols, and guaiacol. Figure 3 illustrates the main chemical compounds from the pyrolysis of sugarcane bagasse. In this study, the pyrolytic products were divided into three groups including carboxylic acids (sum of acids), furfural (furfural and HMF), and phenolic compounds (sum of lignin products). Among the carboxylic acids, the acetic acid, formic acid, and propionic acid were the main products of pyrolysis of sugarcane bagasse. All pyrolysis products were detected at temperatures above $450\text{ }^{\circ}\text{C}$.

Figure 4 presents the fast pyrolysis of hemicellulose and lignin compounds with different temperatures and particle sizes. The peak area % of carboxylic acids, furfural, and lignin compounds decreased as the temperature increased. Ben et al. [32] found that the yield of acetic acid dropped at higher temperatures. In this present work, at a temperature above $600\text{ }^{\circ}\text{C}$, the yield of lignin products declined from 5.9% to 2.8% . Lou et al. [33] reported that the amount of phenols slightly decreased at $550\text{ }^{\circ}\text{C}$. The results implied that the concentration of phenolic macromolecular compounds was enhanced when the temperature increased from $450\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$ due to effective primary thermal reactions occurring in this temperature range. At higher temperatures, the secondary reaction decomposes the macromolecular to form the mono-molecular compounds [34].

The effect of particle size showed that the contents of phenolic compounds increased with the increase of particle size, whereas there were no strong effects on carboxylic acids. Montoya et al. [30] showed that the yield of pyrolysis products increased by increasing the particle size of sugarcane bagasse between 0.425 and 0.600 mm . The average particle heating rates were enhanced by decreasing biomass particle

sizes, which favored the release of larger fragments by destroying cell structure. Therefore, selecting an appropriate particle size can improve biomass devolatilization timing and increase the formation of vapor rather than char during fast

pyrolysis. The particle size higher than 0.5 mm significantly decreased the contact time of volatiles with silica which led to a decrease in the yield of heavy compounds [35].

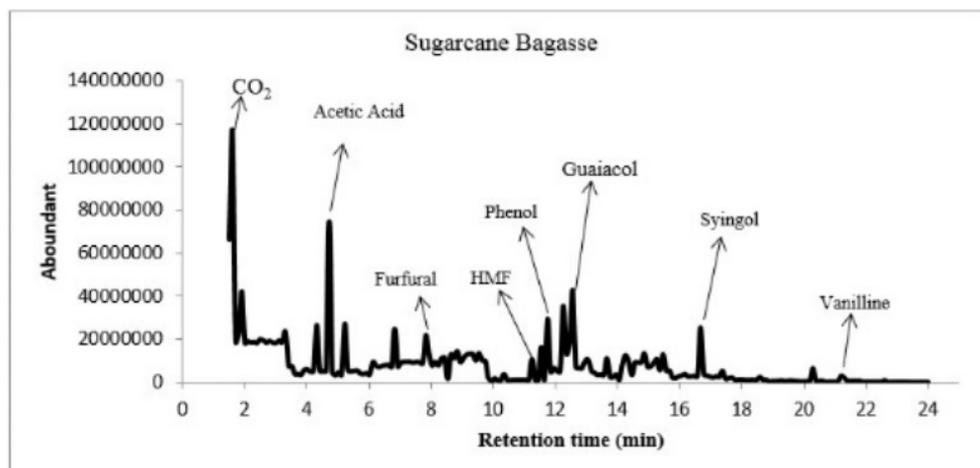
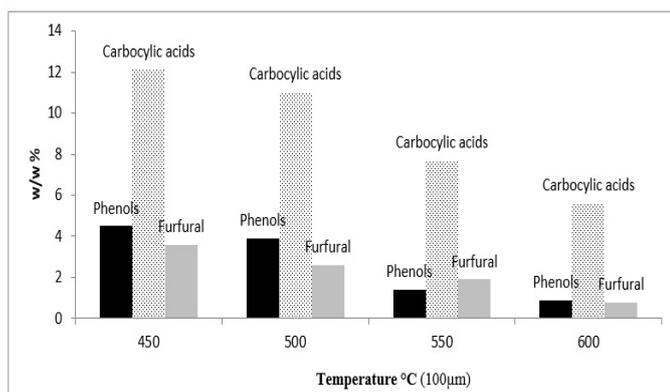
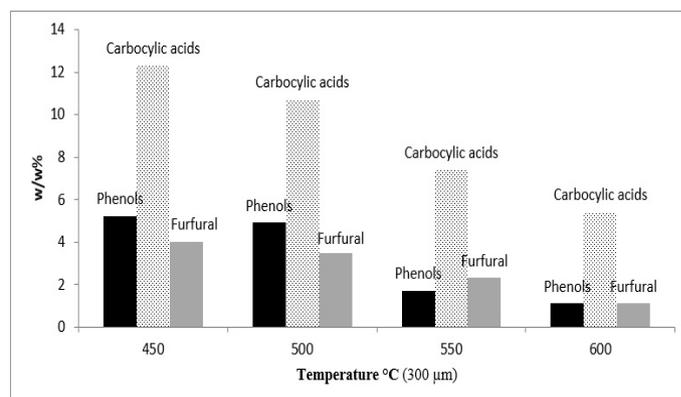


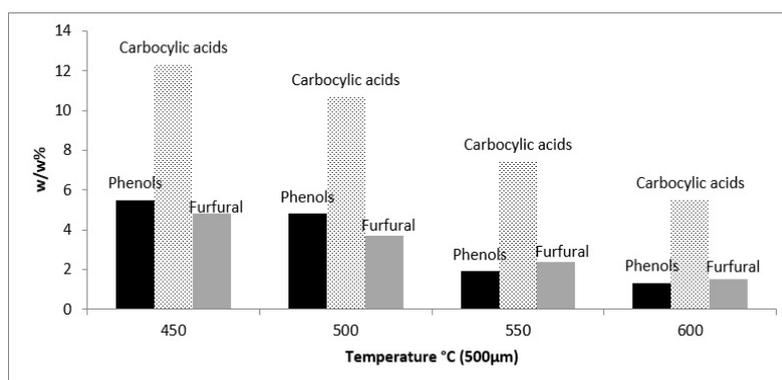
Figure 3. Py-GC-MS of sugarcane bagasse at 450 °C (Particle size 300 μm)



(a)



(b)



(c)

Figure 4. The effects of pyrolysis temperature and particle size on the w/w % of sugarcane bagasse: (a) particle size 100 μm , (b) particle size 300 μm , and (c) particle size 500 μm

3.3. Fitting the Response Surface Models

Initial comparison of statistical models indicated that the phenolic compounds and furfural were more desired with full quadratic models, while the carboxylic acids corresponded to the linear form (Table 2). The stepwise elimination of insignificant coefficients was deduced for the models based on each response at different temperatures, where X_1 and X_2 represent the temperature and particle size, respectively.

Phenolic compounds model (%): $+5.11 - 0.4X_1 + 0.95X_2 - 0.15X_{12} - 0.55X_{22}$

Furfural model (%): $+1.62 - 1.63 X_1 + 0.48X_1X_2 + 0.45X_{12} - 0.4X_{22}$

Carboxylic acids model (%): $+8.45 - 2.55 X_1 + 0.39 X_2 - 1.22X_{12} X_2$

The significance of temperature and particle size was evaluated by analysis of variance (ANOVA). The highly

effective parameters were validated by a large F-value and a small P-value. Therefore, the comparison between temperature (A) and particle size (B) found that the

temperature had more influence on the yields of phenolic compounds, furfural, and carboxylic acids during the process of fast pyrolysis (Table 3).

Table 2. The statistics of models

Models	Statistics	Response		
		Phenolic compounds	Furfural	Carboxylic acids
Linear	R ²	0.79	0.83	0.92
	R ² -adj.	0.75	0.79	0.9
	R ² -pred.	0.63	0.63	0.83
	Sdv.	2.35	0.3	0.66
Linear square	R ²	0.79	0.86	0.92
	R ² -adj.	0.72	0.82	0.90
	R ² -pred.	0.56	0.66	0.70
	Sdv.	2.4	0.3	0.69
Full quadratic	R ²	0.99	0.97	0.93
	R ² -adj.	0.98	0.94	0.88
	R ² -pred.	0.95	0.80	0.5
	Sdv.	0.5	0.1	0.7
Cubic	R ²	0.99	0.98	0.98
	R ² -adj.	0.99	0.97	0.96
	R ² -pred.	0.95	0.49	0.07
	Sdv.	0.4	0.1	0.4

Table 3. ANOVA for the models for phenolic compounds, furfural, and carboxylic acids

Response	Factors	DF	Mean of square	F-value	P-value
Phenolic compounds	A	1	1.26	112	0.0001
	B	1	7.21	641	0.0001
	A ²	1	0.16	13.97	0.0057
	B ²	1	2.07	184	0.0001
	AB	-	-	-	-
	Residual	8	0.01	-	-
	Lack of fit	4	0.017	3.23	0.14
	Pure error	4	0.13	-	-
	Total	12	-	-	-
Furfural	A	1	21.33	161	0.0001
	B	-	-	-	-
	A ²	1	1.39	10.45	0.01
	B ²	1	1.13	8.55	0.01
	AB	1	0.9	6.8	0.03
	Residual	8	0.029	0.13	-
	Lack of fit	3	0.25	14.6	0.013
	Pure error	4	0.017	-	-
	Total	12	-	-	-
Carboxylic acids	A	1	52.17	119	0.0001
	B	1	0.39	0.9	0.365
	A ²	-	-	-	-
	B ²	-	-	-	-
	AB	1	2.77	13.85	0.0045
	Residual	10	0.2	-	-
	Lack of fit	6	0.33	66	0.0006
	Pure error	4	-	-	-
	Total	12	-	-	-

3.4. Influence of the temperature and particle size on pyrolysis products

Figure 5(a) presents the interaction between the temperature and particle size on the phenolic compounds. As shown in the

figure, yields of phenolic compounds gradually decreased with increasing temperature. On the other hand, more phenolic compounds were generated at a larger particle size at a given temperature. It is illustrated in Figure 5(a) that yields of phenolic compounds considerably decreased at a temperature

above 550 °C. At high temperatures, the more single ring lignin compounds could be produced by cleavage of β -O-4, α -O-4, C-C bond [36]. Chu et al. [37] reported that the β -O-4 ether bond as the most abundant linkage from lignin structure was easily broken at low temperatures because of the lowest dissociation energy (90.9 kcal/mole). Jung et al. [10] found that the lignin began to decompose at a temperature around 170 °C while increasing the temperature led to the generation of more single-ring products from phenolic compound by demethoxylation during secondary reactions [9, 38].

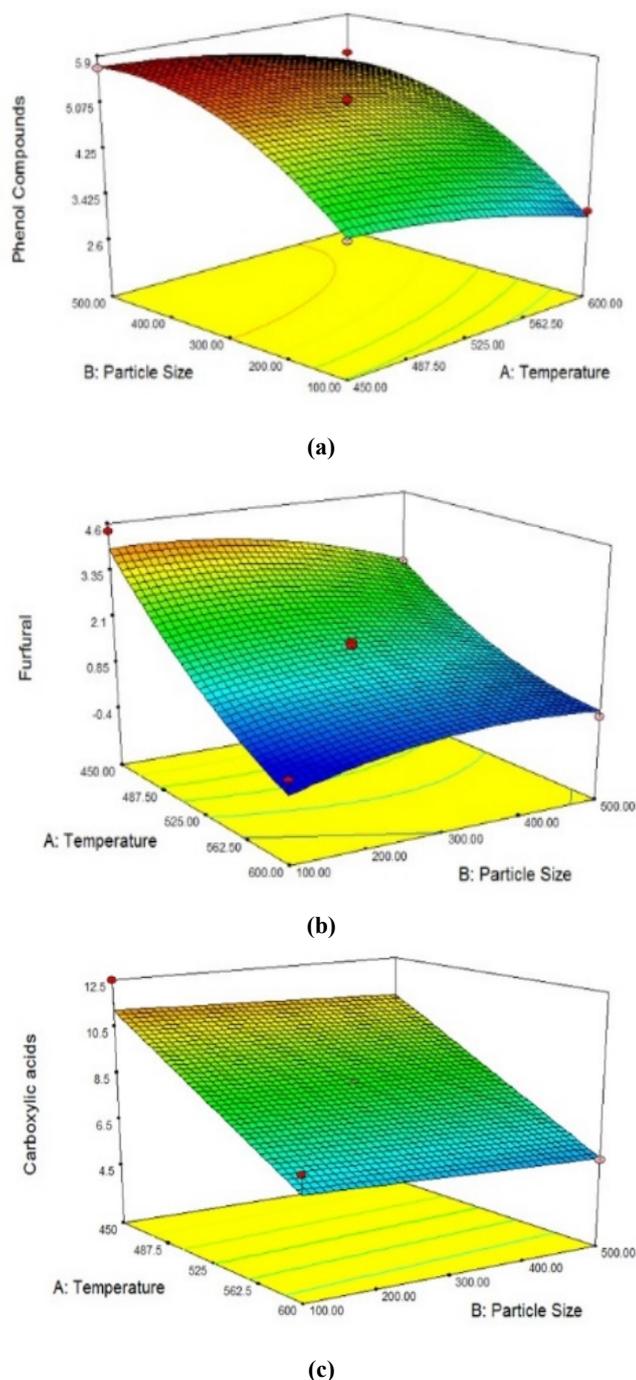


Figure 5. Three-dimensional surface of (a) phenolic compounds, (b) furfural and (c) carboxylic acids against temperature and particle size

Figure 5 (b) displays the interaction between temperature and particle size on the furfural. The furfural decreased by increasing the particle size, but it finally increased so that the

maximum furfural was achieved at a particle size of 300 μ m and at a temperature of 450 °C. It is noteworthy that the maximum furfural was obtained by decreasing the temperature of fast pyrolysis. The cleavage of C-H and C-OH bonding occurred during secondary reaction to break down the HMF from furfural at a temperature of 500 °C. Removal of hydroxymethyl group through dehydration of furanose generated the HMF and then, formed formaldehyde and furfural [33] (Lu et al., (2011)). The authors indicated that HMF and furfural were significantly promoted before reaching 550 °C, while the furans considerably increased after 600 °C, which is in agreement with this present work.

Figure 5 (c) exhibits that yields of carboxylic acids which were primarily decreased by elevating the pyrolysis temperature; however, this effect was not observed by increasing the particle size. Finally, this study shows that the maximum co-production yields of 5.8 % phenolic compounds, 3 % furfural, and 10.3 % carboxylic acids from sugarcane bagasse were found to be optimal conditions of temperature of 450 °C and particle size of 500 μ m, respectively.

4. CONCLUSIONS

In this study, the yields of hemicellulose and lignin products from fast pyrolysis of sugarcane bagasse were investigated. The fast pyrolysis yields of phenols, furfural, and carboxylic acid compounds in a tandem micro-pyrolyzer were influenced by the variables studied (temperature and particle size). Variation in temperature was determined as the most important variable using RSM analysis. As the temperature raised from 450 °C to 600 °C, the yields of furfural, carboxylic acids, and phenolic compounds decreased. In addition, the yields of phenolic and furfural compounds were clearly enhanced by increasing the particle size, whereas it was not shown to be a critical factor that could influence the yields of carboxylic acids. However, it was found that the maximum content of target compounds of sugarcane bagasse fast pyrolysis occurred below 450 °C and at a particle size of nearly 500 μ m.

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