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ORIGINAL ARTICLE

Hydrothermal vs. dilute acid pre-treatments: comparison of the biomass properties, distribution of pyrolysis products, and bio-oil characteristics

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Abstract

In this study, hydrothermal and acid pre-treatments were applied to improve the raw material properties of the bean pod. To evaluate the biomass as a fuel, it is superior to have low moisture content, high volatile matter, and carbon content. As acid concentration changed in acid washing and impregnation, different trends were observed in these contents. The optimum working concentration to meet all these properties was chosen as 1 M acid. In hydrothermal pre-treatment, as the temperature increased with constant reaction time, the moisture content of the biomass decreased while the amount of volatile matter was raised. According to the SEM, FT-IR, TGA, and preliminary and elemental analysis characterization results, the samples with high C and low O content after evaluating in hydrothermal pre-treatment at 190 °C for 20 min and hydrothermal pre-treatment at 150 °C for 20 min, washing with 1 M H_3PO_4, and impregnating with 1 M H_3PO_4 were subjected to pyrolysis process. When the tar yields obtained from impregnating with 1 M H_3PO_4 and washing with 1 M H_3PO_4 samples were compared, it was seen that the washing process gave a higher (19.56%) tar yield. In the pyrolysis experiments, the highest tar yield (22.18%) was achieved by using the hydrothermal pre-treatment at 190 °C for 20 min sample with a volatile matter content of 71.59%. Total volatile matter yields of pyrolysis were listed as (hydrothermal pre-treatment at 190 °C for 20 min) > (washing with 1 M H_3PO_4) > (impregnating with 1 M H_3PO_4) > (hydrothermal pre-treatment at 150 °C for 20 min). As a result, it can be concluded that the processes performed as hydrothermal method or acidic pre-treatment compared to raw biomass have an important role in obtaining the desired product distribution and properties in biofuel production.

Keywords Biomass · Hydrothermal pre-treatment · Acidic pre-treatment · Characterization · Pyrolysis

1 Introduction

Because population increases and technology develops, the demand for energy and chemical raw material input in the world is increasing day by day. Also, the fact that most chemicals are obtained from fossil sources, that the fossil sources are limited, and that they will be exhausted in the near future also indicates the search for alternative energy and raw material sources. Many researchers are working towards making more use of renewable resources rather than consumable resources [1]. One of the most important renewable resources is biomass. The biggest advantages of using biomass as a source of raw materials are that it can be renewed in less than a century and can be grown in every country in a manner suitable for its climate. Thus, it saves the countries from foreign dependency. Lignocellulosic biomass is 40–50% cellulose by mass, 20–30% hemicellulose, and 10–40% lignin and, besides these main compounds, is a vegetable composite material that contains a small amount of extractive (terpene, tannin, fatty acid, and resin), moisture, and some inorganic components [2].

The pyrolysis method, one of the thermochemical conversion processes, is a method used to convert lignocellulosic biomass into valuable chemicals. During the pyrolysis process, cellulose and hemicellulose form anhydrous sugars such as 1,6-anhydrous-β-D-glucose (levoglucosan) and 1,4-

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anhydrous-D-cyclopyranose with depolymerization reactions [3]. 5-Hydroxymethyl furfural, furfural, hydroxyacetone, hydroxyacetaldehyde, and some C_1-C_2 components are obtained from the industrially important organic compounds by the degradation of the intermediate levoglucosan during pyrolysis. As 1,4-anhydrous-D-cyclopyranos continues to degrade during the pyrolysis process, methanol, acetic acid, and acetone components, which are important chemical raw materials, are included in the pyrolysis liquid product [4]. The third of the main components of lignocellulosic biomass, lignin, is more complex than hemicellulose and cellulose and degrades at higher temperatures. The degradation mechanism is based on the radical or heterolytic fission mechanism according to its side chain structure and provides the formation of phenol, guaiacol, and catechol components in the pyrolysis products [5]. The products obtained by the pyrolysis of biomass are a large amount of char and tar. The precious chemicals mentioned are obtained in small amounts and the raw material or pyrolysis process should be improved to increase their efficiency. For these improvement studies, researchers have tried methods such as catalytic hydrodeoxygenation [6], hydrothermal process [7, 8], acid-catalyzed hydrolysis [9], and solvolysis [10, 11] to improve the pyrolysis product. Pre-treatment of biomass is one of the important steps in the biological transformation of lignocellulosic biomass into biofuels and by-products. The main purpose of the pre-treatment is to reduce the crystallinity of the cellulose, remove the lignin, or increase the surface area, thereby ensuring the biodegradability of carbohydrates. Today, chemical and thermochemical methods are the most effective among the pre-treatment techniques [12]. The common feature of hemicellulose, cellulose, and lignin in the biomass structure is that they have C-O bonds. These C-O bonds are hydrolyzed in the presence of acid and lower carbon number components can be obtained [13]. It has been determined in previous studies that the yield and quality of the pyrolysis liquid product increased using sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) [14, 15]. However, high temperature and pressure were generally used in these studies. These pre-treatments should be conducted at room temperature to avoid the energy to be used in the heating and pressurization process. Kumagai et al. [13] pre-treated the cedar wood shaving at atmospheric pressure and room temperature with H_2SO_4 and determined that pyrolysis liquid yield increased by 55% with this pre-treatment. Besides, it has been observed that the liquid product obtained is rich in short-chain components, and the phenolic hydrocarbons, which are lignin derivatives, increase by acidic pre-treatment. Hydrothermal pre-treatment, another method of pre-treatment, uses water at a temperature of around 140–220 °C [16]. In hydrothermal pre-treatment, hydronium ions are first formed in the environment; these ions act as weak acids, allowing hemicellulose to be depolymerized, and acetyl groups are separated from the hemicellulose structure [17]. The acetic acid in the environment is formed by hydration of acetyl groups and accelerates the hydrolysis process [18]. The fact that only water is used in the process without the need for a harmful chemical and additional catalyst makes hydrothermal pre-treatment an environmentally friendly method [19]. Hydrothermal pre-treatment is one of the easy and economical pre-treatment methods preferred because it enables the enzymes to reach the biomass easily in the biological transformation of the biomass, and in the thermochemical conversion, it prepares the biomass for the heat degradation process [20]. Stefanidis et al. [21] applied hydrothermal pre-treatment to beechwood shavings, and determined that the amount of unwanted acids and ketones decreased in the pyrolysis liquid product they obtained from this sample.

In this study, bean pods without food value were selected as biomass samples and it was aimed to improve the quantity and quality of pyrolysis liquid product to be obtained by pre-treatments applied to this biomass. Dry bean is an important food source in Turkey and the bean pod waste generated during dry bean production has no nutritional value. It is important to utilize the abundant amount of bean pods that are disposed of during dry bean production as an energy source or valuable chemical raw material. Although the bean pod selected as biomass has a lignocellulosic structure, it has lower lignin content compared to woody biomasses, so the tar yields in the pyrolysis products will be lower than those of woody biomass. The effects of different pre-treatments and parameters changed during these processes on biomass properties and the effects on pyrolysis product distribution were examined.

2 Experimental studies

The materials and experimental methods used during the experimental studies were explained in detail in this section. Two different methods, impregnation and washing in room conditions, and three different acid concentrations were used to avoid unnecessary energy while applying pre-treatment with acid. In the hydrothermal pre-treatment, reaction temperature and duration were examined as process parameters. Pre-treatment and pyrolysis experiments were carried out three times under the same conditions for each parameter to ensure repeatability and the average values from the three experimental runs were used.

2.1 Materials

During experimental studies, bean pods (*Phaseolus vulgaris*) (BK) were selected as biomass. In 2017, dry bean production in Turkey was 239 thousand tons, and according to studies, it is expected that 245 thousand tons will be produced with increased consumption in 2020. In 2016, 19% of the dry bean, which was consumed a lot in the world, was produced by Myanmar (5.190 thousand tons), 14% by India (3.898 thousand tons), and 9% by Brazil (2.616 thousand tons). That same year, Turkey was involved in the production of beans with an 8.4% share of the world [22]. During the production of dry beans, the pods of the plant emerge as vegetable waste that cannot be consumed as food. Therefore, it was aimed to evaluate the dry bean waste as biomass in this study. In this study, bean pod samples obtained from the Marmara region as food factory waste were first dried under room conditions. The dried biomass was ground and sieved to give particle size (D_p) fractions of $224 < D_p < 425$ µm, $425 < D_p < 600$ µm, $600 < D_p < 850$ µm, $850 < D_p < 1250$ µm, and $1250 < D_p < 1800$ µm. For all experiments in this study, 224–425-µm-sized samples were used.

2.2 Application of acidic pre-treatment of biomass

Washing and impregnation were carried out using three different concentrations of phosphoric acid (H_3PO_4) (Merck, 85%): 0.5 M, 1 M, and 1.5 M to pre-treat the bean pod with acid:

i) In the acid washing process, 500 mL of H_3PO_4 solution at the desired concentration was added to 5 g bean pod and mixed for 1 h at room temperature. The solid part separated from the solution by filtration was washed with distilled water until its pH was neutral and dried in the oven at 105 °C for 24 h. After being removed from the oven, the samples cooled to room temperature in the desiccator were stored in a desiccator. The bean pod samples that were subjected to acid washing using different acid concentrations were named 0.5Y, 1Y, and 1.5Y, respectively.

ii) In the acid impregnation process, 100 mL of H_3PO_4 solution was added to the desired concentration on 5 g bean pod and the solution was kept in a fume hood until it completely evaporated away from the biomass. The acid evaporation process lasts about 48 h. Samples taken from the fume hood were dried for 24 h in an oven at 50 °C. After being removed from the oven, the samples cooled to room temperature in the desiccator were stored in a desiccator. The bean pod samples that were subjected to acid impregnation using different acid concentrations were named as 0.5E, 1E, and 1.5E, respectively.

2.3 Application of hydrothermal pre-treatment to biomass

High-pressure and high-temperature reactor (PARR, 4575B) was used when applying hydrothermal pre-treatment to the bean pod. Keeping the solid/water ratio constant at 1/10, 100 mL of ultrapure water was added to 10 g bean pod and placed in the reactor. Reaction temperature (150 °C and 190 °C) and pre-treatment time (10 min and 20 min) were fixed as reaction parameters. The codes of the samples named according to the fixed parameters are given in Table 1. Before the reactor started to be heated, sweeping with high purity nitrogen gas was carried out to remove the air in the environment and to prevent possible reactions with air. The reactor was then heated to the desired working temperature in an inert atmosphere with a heating rate of 5 °C/min. When the hydrothermal pre-treatment time was completed, the reactor was cooled to room temperature with a stream of cold water passing from the outside. The solid-water mixture taken from the reactor was filtered; the solid product was dried in the oven at 105 °C and stored in a desiccator.

2.4 Characterization of biomass and pre-treated biomass

Bulk density [23] and true density (gas pycnometer, Micromeritics-AccuPyc II 1340) values were measured to determine the difference between the porosities of the bean pod and pre-treated bean pod samples. The weight fractions of moisture (moisture analyzer, Sartorius-MA 150), ash [24], and volatile matter [25] were determined. The weight fraction of fixed carbon was also calculated from the difference (fixed carbon% = 100 − (moisture% + ash% + volatile matter%)). Elemental analysis (LECO CHN/S 628) was used to determine the effect of pre-treatments on the amount of carbon, oxygen, hydrogen, and nitrogen, and the Dulong formula [26] was used to determine the effect of the higher calorific value.

Fourier transform infrared spectroscopy method (FT-IR, Perkin Elmer Spectrum 100) was used to determine the functional groups, the status of the bonds in the structure, and the binding sites. During the analysis, 4000–380 cm^{-1} wavelength range and attenuated total reflection module (ATR) technique were used. The thermogravimetric analysis method (TGA; Setaram-LabsysEvo) was used to determine the thermal stability and thermal degradation behavior of the samples. For this, the ~ 10 mg sample placed in Al_2O_3 crucibles was heated from ambient temperature to 1000 °C with a heating

Table 1 Coded names of hydrothermal-pre-treated samples

Coded names	Temperature (°C)	Time (min)
HT 150-10	150	10
HT 150-20	150	20
HT 190-10	190	10
HT 190-20	190	20

rate of 10 °C/min at a nitrogen flow rate of 20 mL/min. Thermal degradation behaviors of the samples obtained from TG and dTG data were examined. Surface images were taken by scanning electron microscopy (SEM, ZEISS-SUPRA 40VP) to determine the effect of pre-treatments applied to the samples on the morphological structure of the samples. SEM images of the Pt-coated samples were taken using a secondary electron (SE) detector, with 15-kV acceleration voltage and 10-mm operating distance.

2.5 Pyrolysis experiments and characterization of the liquid product

The pyrolysis behavior of the bean pod samples pre-treated acidic and hydrothermally was examined and the effect of the applied parameters on the pyrolysis product distribution was investigated. When the effect of the three different concentrations applied in acid pre-treatment on the carbon content in the biomass structure was examined, the highest C and the lowest O content was reached when 1 M H_3PO_4 was used. For this reason, biomass obtained during the impregnation and washing processes using 1 M H_3PO_4 in pyrolysis experiments was studied. However, at the end of 20 min of pre-treatment in the hydrothermal pre-treatment, a solid product with higher C content was obtained. Pyrolysis experiments were carried out in a Heinze-type reactor at 500 °C pyrolysis temperature in a static environment to increase the heating rate 10 °C/min. In the pyrolysis process, a 5 g sample was weighed and placed in the fixed bed reactor; after the reactor was heated to 500 °C, 20 min was waited to complete the reaction. The codes of these samples were BK, 1Y, 1E, HT 150-20, and HT 190-20 respectively.

At the end of the pyrolysis process, the mixture containing the liquid product (tar + aqueous phase) in the traps was taken with dichloromethane (DCM), and after the liquid product and aqueous phase were separated, the solvent was removed with the aid of a rotary evaporator. While the solid product remaining in the reactor is weighed directly, the yield of the gas product is determined according to the total mass balance. All the yields were given on an ash-free and dry basis, and their values were calculated as the average of two parallel tests within error less than ± 0.5%. Elemental analysis of pyrolysis liquid products was carried out and the effect of pre-treatments on the carbon content of the product was examined. Elemental analysis, FT-IR, and gas chromatography-mass spectrometry (GC-MS) techniques were used to characterize the pyrolysis liquid product. For elemental analysis and FT-IR analysis, the analysis was made under the conditions applied while characterizing biomass and pre-treated biomass. While performing the GC-MS (HP 6890, 5793 mass selective detector) analysis, the HP-5 capillary column (Hewlett-Packard) was used. In the temperature program, the initial and final temperatures are set at 40 and 280 °C, respectively. Retention time is 10 min and the heating rate is 8 °C/min. The inlet temperature is 280 °C and the injection volume is 1 μL. At a purity of 99.999%, He gas was used as an immersive gas. The scanning range of the MS detector is 50–550 amu.

3 Results and discussion

3.1 Characterization results of bean pod

Bulk and true density values and proximate analysis results determined after size reduction of bean pod are given in Table 2. Elemental analysis of raw bean pod and pre-treated samples is shown in Table 3. The bulk and true densities of the bean pod were found as 0.41 g/cm^3 and 1.44 g/cm^3, respectively. The fact that the true density value was higher than the bulk density value indicated that the bean pod had a porous structure. The moisture content of the raw material was measured as 10.52 wt.%. It was aimed to reduce the amount of moisture by treating the bean pod, whose moisture content was more than the average amount of biomass, with acid. Moisture content is a factor that directly affects the fuel properties of biomass and it is aimed to increase the thermal value by reducing the amount of moisture contained in the biomass. The ash amount of the bean pod was found to be 8.39 wt.% and the amount of volatile matter was 59.62 wt.%. The carbon and oxygen contents of the bean pod were 39.45 wt.% and 53.89 wt.%, respectively. HHV of the bean pod was also calculated as 12.87 MJ/kg (Table 3).

The FT-IR spectrum, which showed that the bean pod had different functional groups, is given in Fig. 1. It referred to the large peak hydroxyl group observed around 3337 cm^{-1}. The region in 2887 cm^{-1} belonged to the C-H tension vibrations in the methyl and methylene groups. Carbonyl groups (C=O) were located in the region of 1860 cm^{-1}. The most severe peak alcohol in the 1100 cm^{-1} region and the 1037 cm^{-1} region belonged to the C-O tension vibration of the phenol, ether, and ester groups. They were the out-of-plane bending vibrations of the C-H bond in the peak benzene derivatives observed after the 800 cm^{-1} regions. According to the FT-IR spectrum, it was determined that the bean pod contained carbonyl groups, ethers, esters, alcohols, and phenol groups.

The TG and dTG curves of the bean pod are given in Fig. 2. According to the TG curve, mass loss was observed in three regions. The first zone started at 50 °C and ended at about 150 °C. The weight loss in this region was determined as 5% from the TG curve. In the dTG curve, the first region was seen as a small peak on the leftmost. The second region was observed in the temperature range of 201–397 °C. The second region was the region with the greatest loss of mass, which was called the active pyrolysis region [27]. The bean pod lost about 57% of its mass in the active pyrolysis zone.

Table 2 Preliminary analysis results of samples

	Raw BK	Acid pre-treated						Hydrothermal pre-treated			
		0.5Y	1Y	1.5Y	0.5E	1E	1.5E	HT 150-10	HT 150-20	HT 190-10	HT 190-20
Density											
Bulk density (g/cm^3)	0.41 ± 0.02	0.34 ± 0.03	0.32 ± 0.11	0.31 ± 0.05	0.38 ± 0.03	0.51 ± 0.05	0.55 ± 0.04	0.40 ± 0.02	0.32 ± 0.09	0.31 ± 0.02	0.29 ± 0.01
True density (g/cm^3)	1.44 ± 0.04	1.45 ± 0.06	1.48 ± 0.01	1.50 ± 0.02	1.48 ± 0.04	1.42 ± 0.04	1.49 ± 0.02	1.35 ± 0.07	1.38 ± 0.05	1.37 ± 0.10	1.40 ± 0.06
Proximate analysis											
Moisture (%)	10.52 ± 1.01	5.15 ± 0.92	4.98 ± 0.84	4.21 ± 0.75	7.48 ± 0.93	6.49 ± 0.39	6.78 ± 0.95	7.49 ± 0.82	6.94 ± 0.49	4.06 ± 0.21	3.95 ± 0.12
Ash (%)	8.39 ± 0.95	7.36 ± 0.84	5.15 ± 0.51	4.96 ± 0.38	7.59 ± 0.15	6.78 ± 0.37	5.97 ± 0.50	5.98 ± 0.24	4.09 ± 0.10	4.65 ± 0.21	4.69 ± 0.39
Volatile matter (%)	59.62 ± 2.98	69.14 ± 3.78	71.26 ± 3.21	73.19 ± 2.79	67.29 ± 1.99	66.84 ± 1.73	63.15 ± 2.45	60.48 ± 1.32	61.49 ± 2.04	65.36 ± 1.36	71.59 ± 3.04
Fixed carbon (%)*	21.47 ± 0.92	18.35 ± 1.22	18.61 ± 0.45	17.64 ± 1.09	17.64 ± 1.97	19.89 ± 1.02	24.10 ± 1.42	26.05 ± 1.82	27.48 ± 2.00	25.93 ± 1.92	19.77 ± 0.98

*Estimated by difference

The third region started from 397 °C and continued to 800 °C. The speed of mass loss slowed down in this region. This region, where the rate of mass loss was slow, was called the passive pyrolysis zone. The decomposition temperatures of hemicellulose, cellulose, and lignin are in the range of 210–325 °C, 310–400 °C, and 160–900 °C, respectively. Accordingly, the peaks in the active pyrolysis zone resulted from the degradation of hemicellulose and cellulose. Lignin started degradation in the active pyrolysis zone, but since the degradation rate was very slow, it continued to degrade in the passive pyrolysis zone by not giving a characteristic peak in this region [9].

SEM images of 1× 000 and × 500 magnification values of bean pod are given in Fig. 3. From these images, it was seen that the bean pod had a layered structure.

3.2 Characterization results of acid-pre-treated bean pods

Density, proximate, and ultimate analysis results of the bean pod applied with an acid washing and acid impregnation using 0.5 M, 1 M, and 1.5 M H_3PO_4 are given in Table 2 and Table 3, respectively. In the acid washing process, as the acid concentration increased, the bulk density did not change significantly, while as the acid concentration in the acid impregnation process increased, the bulk density was also raised.

It was predicted that, due to the H_3PO_4 accumulated between the layered structure of the bean pod during the impregnation process, the bulk density was increased. For biomass to be used efficiently in the pyrolysis process, this raw material was desired to have low moisture content and high volatile content [28]. While, the moisture content and volatile content of the bean pods were 10.52% and 59.62% (Table 2), respectively, and the amount of moisture decreased and the amount of volatile material increased as a result of pre-treatment with acid.

In acid-washed bean pod samples, it was observed that the amount of carbon increased by mass and the amount of oxygen decreased compared to the raw material (Table 3). Accordingly, the higher heating values of the 0.5Y, 1Y, and 1.5Y samples were higher than the higher heating value of the bean pod. In acid-impregnated bean pod samples, no significant change in the amount of carbon and oxygen was observed, while the higher heating values were very close to the higher heating value (12.87 MJ/kg) of the bean pod.

FT-IR spectra of the bean pod applied with acid washing and acid impregnation pre-treatments are given in Fig. 4. According to the FT-IR spectrum of bean pod washed with acid at a concentration of 0.5 M and 1 M, aldehydes, ketones, esters, and peaks of carboxylic acids were around 1723 cm^{-1}, and C-O stretching vibrations were seen around

Table 3 Elemental analysis results of samples

	Raw BK	Acid pre-treated				
		0.5Y	1Y	1.5Y	0.5E	1E
C (%)	39.45 ± 0.45	45.08 ± 0.97	47.18 ± 0.78	45.95 ± 0.91	39.48 ± 0.39	41.59 ± 0.48
H (%)	6.41 ± 0.14	6.48 ± 0.28	6.98 ± 0.09	7.01 ± 0.71	5.98 ± 0.49	6.15 ± 0.72
N (%)	0.24 ± 0.01	0.26 ± 0.02	0.27 ± 0.19	0.25 ± 0.15	0.23 ± 0.03	0.26 ± 0.11
O (%)*	53.89	48.16	45.55	46.78	54.29	51.97
H/C	1.95	1.72	1.77	1.83	1.81	1.77
O/C	1.02	0.80	0.72	0.76	1.03	0.93
Molar structure	$CH_{1.95}N_{0.005}O_{1.02}$	$CH_{1.73}N_{0.005}O_{0.80}$	$CH_{1.78}N_{0.005}O_{0.72}$	$CH_{1.83}N_{0.005}O_{0.76}$	$CH_{1.81}N_{0.005}O_{1.03}$	$CH_{1.78}N_{0.006}O_{0.93}$
HHV (MJ/kg)	12.87	15.92	17.82	17.22	12.19	13.57

	Acid pre-treated	Hydrothermal pre-treated			
	1.5E	HT 150-10	HT 150-20	HT 190-10	HT 190-20
C (%)	40.25 ± 0.27	39.48 ± 0.32	41.67 ± 0.78	40.62 ± 0.24	42.83 ± 0.55
H (%)	5.99 ± 0.96	7.59 ± 0.19	6.49 ± 0.69	7.53 ± 0.54	7.15 ± 0.98
N (%)	0.27 ± 0.04	0.20 ± 0.09	0.19 ± 0.01	0.32 ± 0.04	0.25 ± 0.03
O (%)*	53.46	52.73	51.65	51.53	49.77
H/C	1.78	2.30	1.87	2.22	2.00
O/C	0.99	1.00	0.92	0.95	0.87
Molar structure	$CH_{1.79}N_{0.006}O_{1.00}$	$CH_{2.30}N_{0.004}O_{1.00}$	$CH_{1.87}N_{0.004}O_{0.92}$	$CH_{2.22}N_{0.007}O_{0.95}$	$CH_{2.0}N_{0.005}O_{0.87}$
HHV (MJ/kg)	12.62	14.797	14.160	15.311	15.841

*Estimated by difference

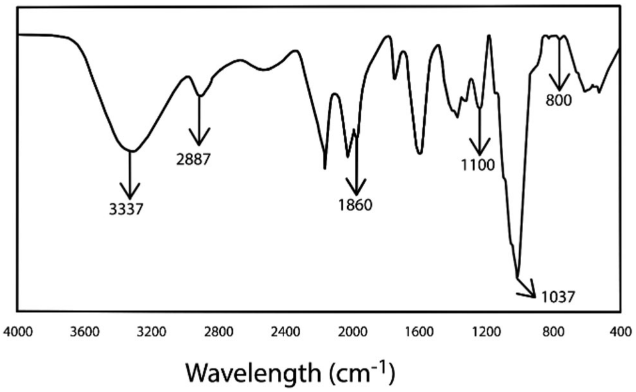

Fig. 1 FT-IR spectrum of bean pod

1000 cm^{-1}. C-H tensile vibrations of alkanes were observed in the region, which was around 2896 cm^{-1} according to the FT-IR spectrum of samples impregnated with acid at a concentration of 0.5 M and 1 M. In the region of 1720–1728 cm^{-1}, there were aldehydes, ketones, esters, and carboxylic acids having C=O bond, and moderate bending vibrations of alkene derivatives of C-H bond in the range of 954–962 cm^{-1}. When the bean pod was impregnated with acid at a concentration of 1.5 M, C-H tensile vibrations of alkanes were seen in the region around 2912–2710 cm^{-1}, and ketones, esters, aldehydes, and carboxylic acids (C=O) in the region around 1720–1623 cm^{-1}; and mild-low C-H bonds were seen in the region around 946 cm^{-1}. When compared with the FT-IR spectrum of the bean pod, it was observed that the intensity of the peaks decreased significantly by pre-treating with acid and increasing the acid concentration.

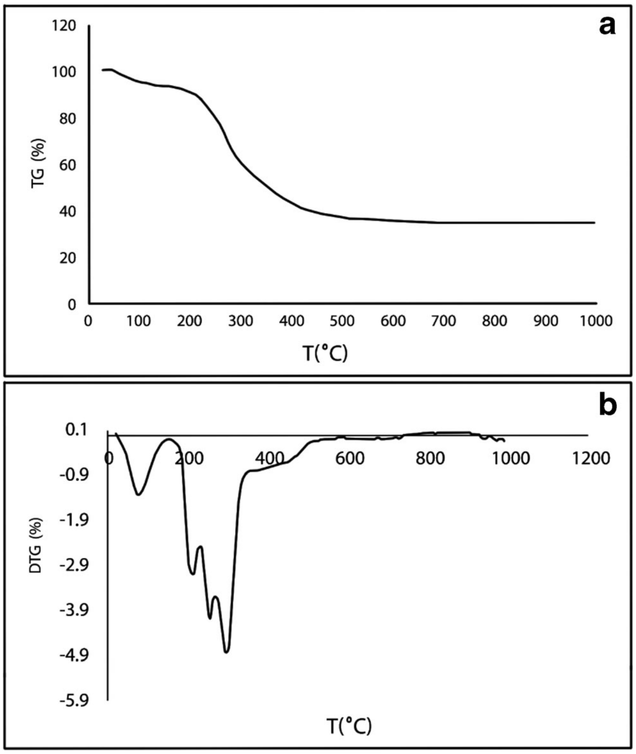

Fig. 2 TG (**a**) and dTG (**b**) curves of bean pod

TG and dTG curves for bean pod applied with acid washing and acid impregnation pre-treatments are given in Fig. 5. The first region in the thermal degradation behavior of the 0.5Y and 1Y samples occurred with the degradation of hemicellulose and cellulose in the range of 221–422 °C. In this TG curve, the fact that the mass loss region showing the moisture loss did not give a significant peak was due to the decrease in the moisture of the raw material as a result of acid washing. Mass loss was approximately 65% in the first loss region, which was the region where the mass loss was greatest. The second region was the region that was 422–922 °C; the mass loss was about 7%. In TG curves of 0.5E and 1E samples, the first region was between 25 and 120 °C, and there was a mass loss of approximately 7–10%. This value was also compatible with the moisture determination specified in short analyses, and the humidity moved away from the structure with the increase in temperature. In acid-impregnated biomass, a different thermal degradation behavior was observed compared to the bean pod. Accordingly, the second region of thermal degradation was between 120 and 550 °C, and approximately 65% mass loss was experienced in this region. The third region was between 550 and 800 °C and there was approximately 10% mass loss in this region. With the impregnation of biomass with H_3PO_4, the phosphorus accumulated on the surface of the biomass provided a sharp separation of the active and passive pyrolysis zone.

SEM images taken at × 1000 magnification of bean pod, where acid washing and acid impregnation pre-treatments were applied, are given in Fig. 6. As a result of acid washing, it was observed that the pore structure developed as the acid concentration increased. As a result of the acid impregnation process, as the acid concentration increased, the phosphorus in the phosphoric acid structure accumulated in the pores and covered the pores. Rosas et al. stated that, when the concentration of acid increased in the production of activated carbon, phosphoric acid was agglomerated in a monolith-like structure [29, 30]. Nowakowski et al. also proved that the phosphorus salts catalyzed the pyrolysis and that the yields of pyrolysis products were modified [31]. According to the study of Guo et al., activation using H_3PO_4 leads to a more heterogeneous pore size distribution [32].

3.3 Characterization results of hydrothermal-pre-treated bean pods

The results of the bulk density and actual density values, moisture, ash, and volatile matter amount of the bean pod, where hydrothermal pre-treatment was applied at a constant solid/water ratio at different temperatures and times, are given in Table 2. When the results were compared to the analysis results of bean pods, hydrothermal pre-treatment usually

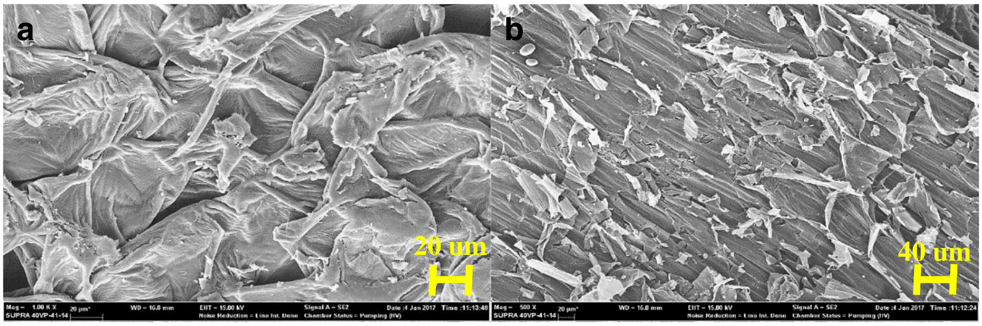

Fig. 3 SEM images of bean pod. **a** × 1000. **b** × 500

reduced the bulk density, moisture, and ash content of the raw material. Comparing the pre-treatment results performed with 10 and 20 min at 150 °C and 190 °C, it was seen that, while the time and the temperature increased, the bulk density decreased and the actual density did not change significantly. This showed that, as the hydrothermal pre-treatment time increased, the porosity of the biomass was also raised. With hydrothermal pre-treatment, volatile matter was increased. Thus, bean pod became a more suitable raw material for the pyrolysis process.

The carbon, hydrogen, nitrogen, and oxygen amounts; H/C and O/C ratio; and higher heating value results of the bean pod applied hydrothermal pre-treatment at different temperatures and times at a constant solid/water ratio are given in Table 3. When these values were compared with the analysis results of bean pods, it was determined that hydrothermal pre-treatment increased the carbon content of the raw material and decreased the oxygen content. The higher heating values calculated using the elemental analysis results, on the other hand, varied in the range of 14.16–15.84 MJ/kg values, which were higher than the higher heating value of bean pod of 12.87 MJ/kg.

Functional group analysis results obtained by applying FT-IR analysis to bean pod samples with hydrothermal pre-treatment are given in Table 4. The peaks of the O-H stretching band of the hydroxyl, acid, and phenol groups at about 3500 cm^{-1} [33] in the FT-IR spectrum of the bean pod were not seen when hydrothermal pre-treatment was applied to the raw material. C-H stretching band peaks which belonged to symmetrical and asymmetrical aliphatic CH_3 and CH_2 were not seen in the FT-IR spectrum of HT 150-20 sample. Similar to the FT-IR spectrum of the bean pod, C = 1625–1590 cm^{-1}, 1600–1580–1450 cm^{-1}, and 1241–1036 cm^{-1} wavelength olefinic structures; aromatic structures; and alcohol, phenol, ether, and ester C-O stretching band peaks were observed in each sample pre-treated with hydrothermal treatment. The peak belonging to the C-H bending band of benzene derivatives was not included in HT 190-10 and HT 190-20 samples obtained by increasing the temperature from 150 to 190 °C.

SEM images of HT 150-10, HT 150-20, HT 190-10, and HT 190-20 samples obtained from the application of hydrothermal pre-treatment at different temperatures and times at a constant solid/water ratio to the bean pod are given in Fig. 7. When the temperature and time increased during the hydrothermal pre-treatment, it was determined from SEM images that the surface roughness and porosity of the bean pod increased.

3.4 Pyrolysis experiment results

Pyrolysis product yield distributions of biomass samples produced as a result of raw materials and pre-treatments are given in Fig. 8. The yield of tar and the solid product obtained from the pyrolysis of bean pod at 500 °C was 11.23% and 26.11%

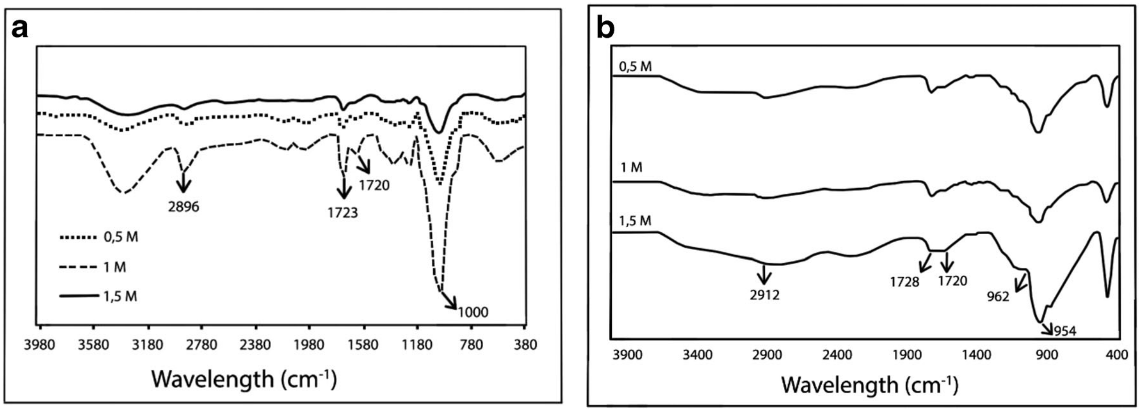

Fig. 4 FT-IR spectrums of acid-pre-treated bean pod. **a** Acid washing. **b** Acid impregnation

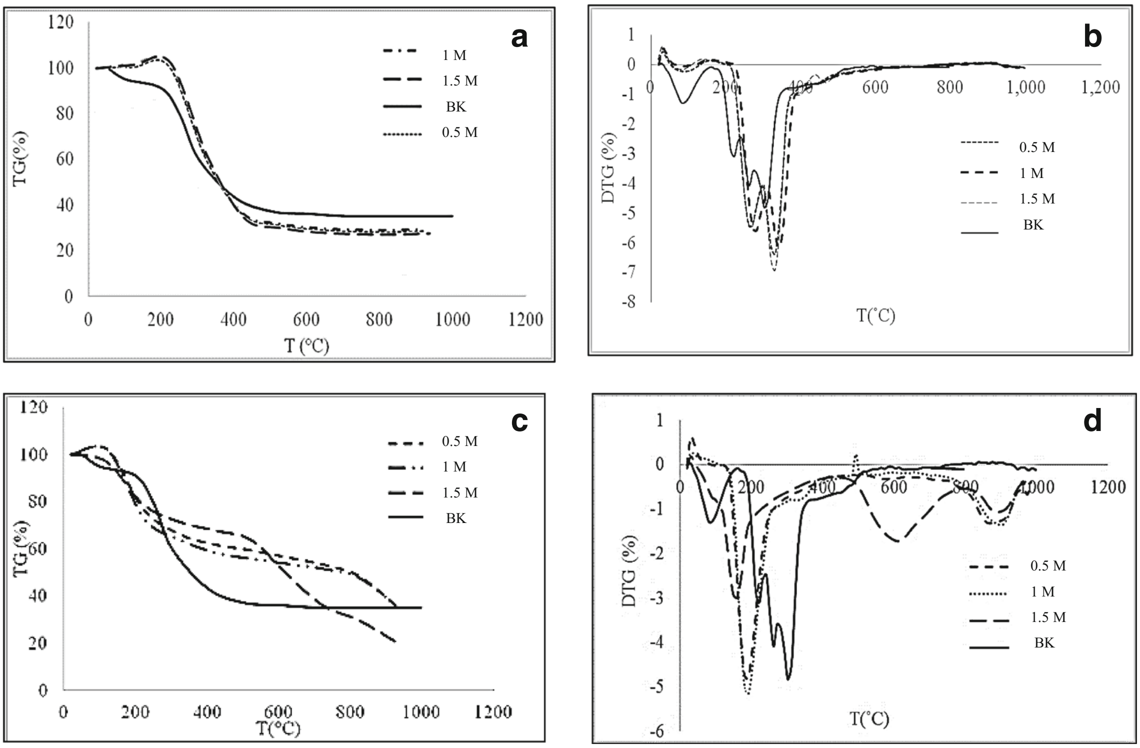

Fig. 5 TG and dTG curves of acid-pre-treated bean pod. **a**, **b** Acid washing. **c**, **d** Acid impregnation

by weight, respectively. When the pre-treatment conditions were changed, it was determined that the highest tar yield was reached as 22.18%, by applying the hydrothermal process at 190 °C and 20 min to the biomass. It was observed that the tar yields obtained by applying acid impregnation and washing processes were higher than those of the hydrothermal-pre-treated sample at 150 °C compared to the pyrolysis liquid product. It was determined that 18.29% tar yield was achieved with the impregnation process. The presence of phosphoric acid agglomerated on the biomass sample after impregnation was seen from the SEM images given in Fig. 6. The reason for the high yield of a liquid product as a result of this process was that the phosphoric acid was not removed from the structure by washing after the process, so it showed a catalytic effect during the pyrolysis process. In the literature, the activation temperature is chosen as 450 °C for chemical activation with H_3PO_4 [34]. Accordingly, it was seen that the structure of the acid-absorbed sample at 500 °C pyrolysis was broken down to give a highly volatile substance (gas and liquid product) as a result of the chemical activation process. When comparing the washing and impregnation processes, it was noteworthy that the biomass applied with washing had a higher (19.56%) tar yield. The reason for this was that the acid remaining in the structure after impregnation re-breaks the high molecular weight pyrolytic liquid components through secondary reactions and acts in a way to increase gas yield. When the

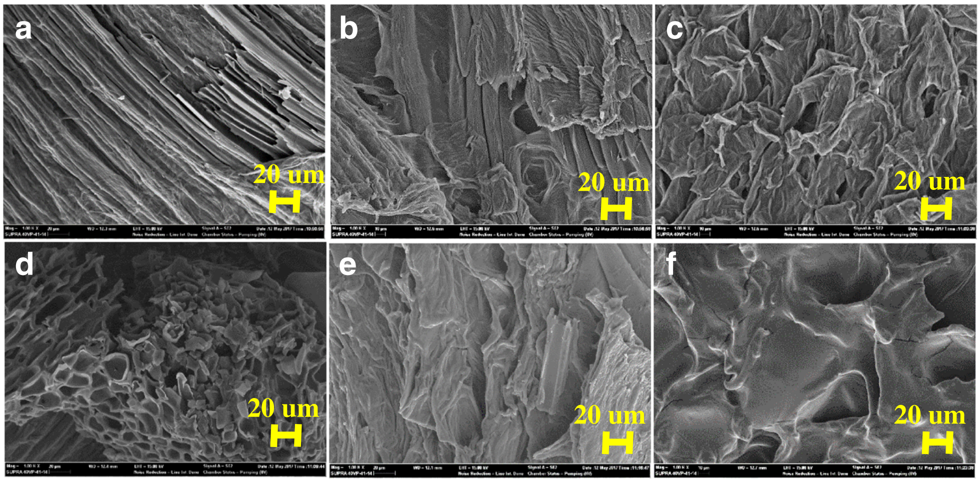

Fig. 6 SEM images of acid-pre-treated bean pod. **a** 0.5Y. **b** 1Y. **c** 1.5Y. **d** 0.5E. **e** 1E. **f** 1.5E

Table 4 FT-IR analysis results of hydrothermal pre-treated bean pod

Wavelength (cm^{-1})	Functional group	Atomic structure and groups	HT 150-10	HT 150-20	HT 190-10	HT 190-20
3600–3300	O-H stretching band	Hydroxyl, acid, phenol	−	−	−	−
2950–2800	C-H stretching band	Symmetric and asymmetric aliphatic CH_3 and CH_2	+	−	+	+
1770–1650	C=O stretching band	Carbonyl group	+	−	+	+
1625–1590	C=C stretching band	Olefinic structures	+	+	+	+
1600–1580, 1450	C=C stretching band	Aromatic structures	+	+	+	+
1241–1036	C-O stretching band	Alcohol, phenol, ether and ester	+	+	+	+
900–840	C-H bending	Benzene derivatives	+	+	−	−

+, existent; −, non-existent

pyrolysis solid product (tar) yields of the pre-treated biomass were examined, it was observed that HT 190-20 and HT 150-20 samples had the lowest and highest tar yield of, respectively, 20.08% and 24.58%. Total volatile matter yields were listed as HT 190-20 > 1Y > 1E > HT 150-20.

The volatile matter is the gas phase formed from the thermal decomposition of the material, which can be divided into two parts: light volatiles and tar containing larger molecules that condense at ambient temperature. Volatile matter content is naturally high for many types of biomass. This feature facilitates the ignition of biomass. Volatile matter from biomass has low lower heating value due to its high oxygen content. The amount of volatile material available largely depends on the properties of the pyrolyzed material and the pyrolysis conditions, temperature, and heating rate. The amount of tar produced depends on these parameters [35].

Elemental analysis results and calculated higher heating values of tar obtained as a result of the pyrolysis of biomass at 500 °C are given in Table 5. It was determined that, when the pre-treatments were applied in case the carbon content of the bean pod was 39.45% and the thermal value was 12.87 MJ/kg, content C of biomass increased. However, tars obtained from the pyrolysis of pre-treated biomass were seen to have a high carbon content in the range of 61.46 to 68.66%. Also, when the calculated thermal values were examined, it was determined that the higher heating value of tars was higher than of the raw material.

FT-IR analysis is an advantageous method for associating various functional groups with the chemical structure. The liquid product obtained by the pyrolysis method has a rather complex chemical structure and the FT-IR method is often used to illuminate this structure [36, 37]. FT-IR spectra and functional groups of liquid products obtained by the pyrolysis process of bean pod and pre-treated bean pod samples at 500 °C are given in Fig. 9. It was seen that the pre-treatments applied caused differences in the chemical structure of the liquid products obtained according to Fig. 9. The peaks seen in the 3390–3450 cm^{-1} region belonged to the O-H strain

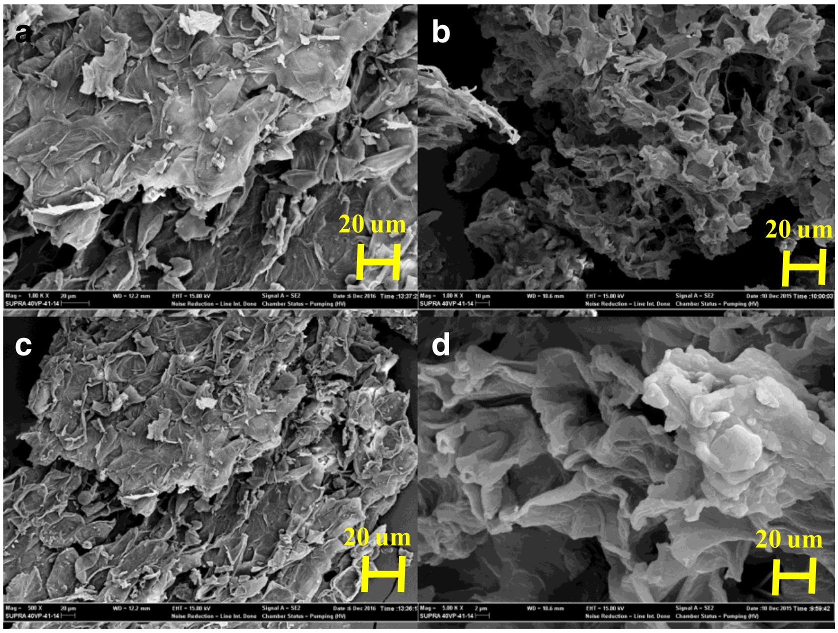

Fig. 7 SEM images of hydrothermal-pre-treated bean pod. **a** HT 150-10. **b** HT 150–20. **c** HT 190-10. **d** HT 190-20

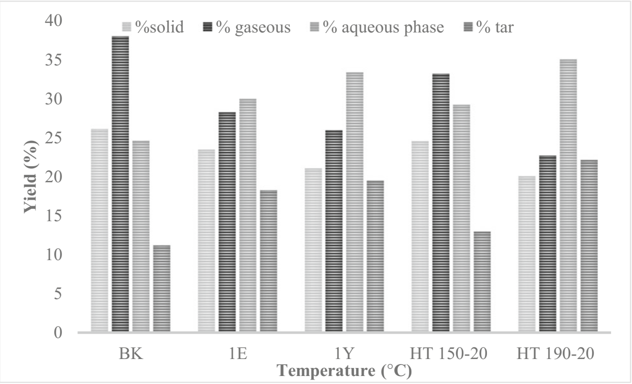

Fig. 8 Effect of pre-treatment type on pyrolysis product distribution for bean pod

vibration [38] and resulted from acid and/or alcohol structures. The peak in the 3050 cm^{-1} bands belonged to the C-H olefinic structures and indicated the presence of aliphatic hydrocarbon [39]. Although the peaks in the 2700 cm^{-1} region showing the C-H aliphatic groups were quite evident in the bean pod, the lowest intensity of these peaks was seen in the HT190-20 sample. It referred to the C=O groups in the most important peak structure in the 1750–1770 cm^{-1} region. The carbonyl group indicated that there were ester and/or carboxylic acid structures in the liquid product content [38]. As a result of acid washing, a decrease in this peak intensity belonging to the carbonyl group was observed. The low-intensity peaks were seen in the region of 1450–1600 cm^{-1} which belonged to the C=C stretching vibration in the aromatic structure. This peak intensity in the 1Y sample showed that washing with acid increased the aromatic structures in the liquid product. The coexistence of C-O and O-H stretching vibrations was another proof that there were carboxylic acids and derivatives in the structure. The fact that both C-O and O-H peaks decreased in the 1Y sample showed that the amount of carboxylic acid decreased in the liquid product obtained as a result of acid washing [36]. The peaks in the region of 700–850 cm^{-1} indicated the presence of aromatic rings in the structure. All liquid products obtained as a result of the study had similar functional groups with different intensity values.

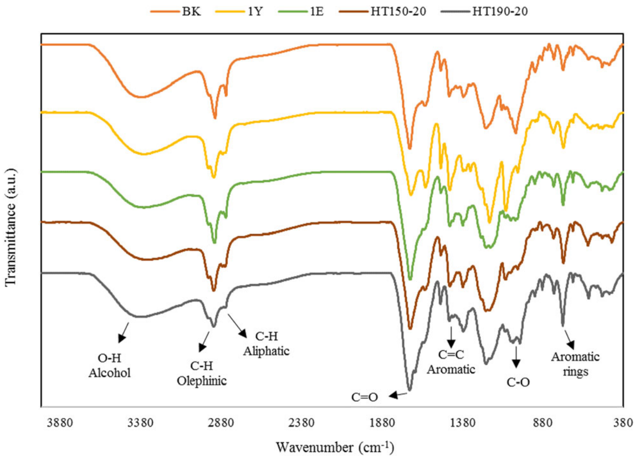

Fig. 9 FT-IR spectrums of pyrolysis liquid products obtained at 500 °C

GC/MS chromatograms of liquid products obtained from pyrolysis of bean pod and pre-treated samples are shown in Figs. 10, 11, and 12. Compounds assigned for each peak defined in the GC/MS chromatograms of pyrolysis liquid products are given in the Supplementary Data (SP-1). It was seen that bean pod pyrolysis liquid products were a very complex mixture of organic compounds with 4–24 carbons. According to the results of the analysis, it was determined that there were lignin-derived phenols, alcohols, aldehydes, esters, fatty acid methyl esters, ketones, amides, long-chain alkanes, furans, naphthalene, and various aromatics in tar structure. Products with a peak area of around 2% or more are the following:

i) For bean pod tar: 2-furancarboxaldehyde, 1-(2-furanyl)-ethanone, 5-methyl-2-furancarboxaldehyde, phenol, 3-methyl-1,2-cyclopentanedione, 2-methyl-phenol, 4-methyl-phenol, naphthalene, hexadecanoic acid, and tetracosane;

ii) For 1E tar: 2-furancarboxaldehyde, 1-(2-furanyl)-ethanone, 5-methyl-2-furancarboxaldehyde, phenol,

Table 5 Elemental analysis results and higher heating values of pyrolysis liquid products obtained at 500 °C

Coded names	BK	1E	1Y	HT 150-20	HT 190-20
Carbon (%)	50.99	65.21	66.47	61.46	68.66
Hydrogen (%)	7.34	7.91	8.16	7.06	7.57
Nitrogen (%)	1.31	0.94	1.08	0.69	1.36
Oxygen (%)*	40.36	25.94	24.29	30.79	22.41
H/C	1.73	1.46	1.47	1.38	1.32
O/C	0.59	0.30	0.27	0.38	0.24
Molar structure	$CH_{1.73}N_{0.022}O_{0.59}$	$CH_{1.46}N_{0.012}O_{0.30}$	$CH_{1.47}N_{0.014}O_{0.27}$	$CH_{1.38}N_{0.009}O_{0.38}$	$CH_{1.32}N_{0.017}O_{0.24}$
Higher heating value (MJ/kg)	20.57	28.80	29.89	25.42	30.11

*Estimated by difference

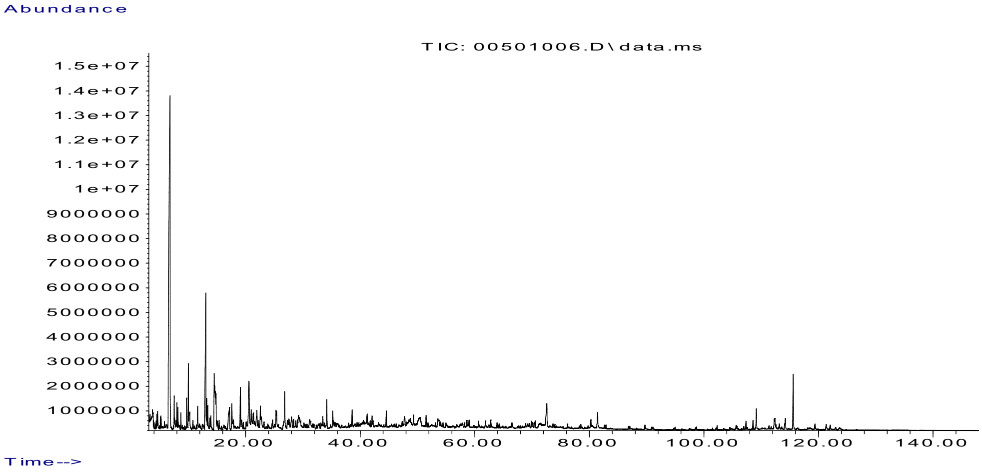

Fig. 10 GC-MS chromatogram of the raw bean pod pyrolysis liquid product obtained at 500 °C

2,3-dimethyl-2-cyclopenten-1-one, 2-methyl-phenol, 4-methyl-phenol, 2,4-dimethyl-phenol;

iii) For 1Y tar: 2-furanmethanol, phenol, 2-methyl-phenol, 4-methyl-phenol, 3,5-dimethyl-phenol, 2,6-dimethoxy-phenol, 4-methyl-syringol;

iv) For HT 150-20 tar: 2-furancarboxaldehyde, 5-methyl-2-furancarboxaldehyde, 2-methyl-phenol, 4-methyl-phenol;

v) For HT 190-20 tar: 2-furancarboxaldehyde, 2-furanmethanol, 2-methyl-2-cyclopentenone, 1-(2-furanyl)-ethanone, 3-methyl-2-cyclopentenone, phenol, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 2,3-

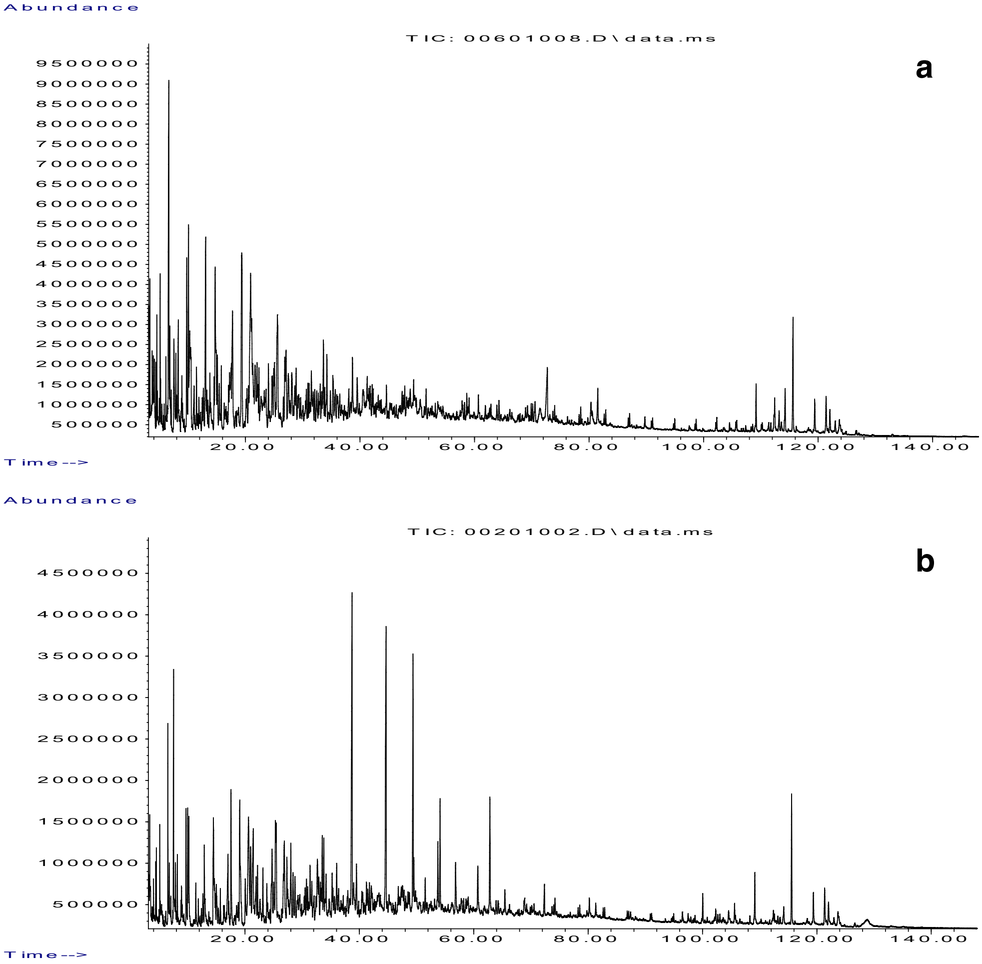

Fig. 11 GC-MS chromatogram of the pyrolysis liquid products obtained at 500 °C. **a** 1E. **b** 1Y

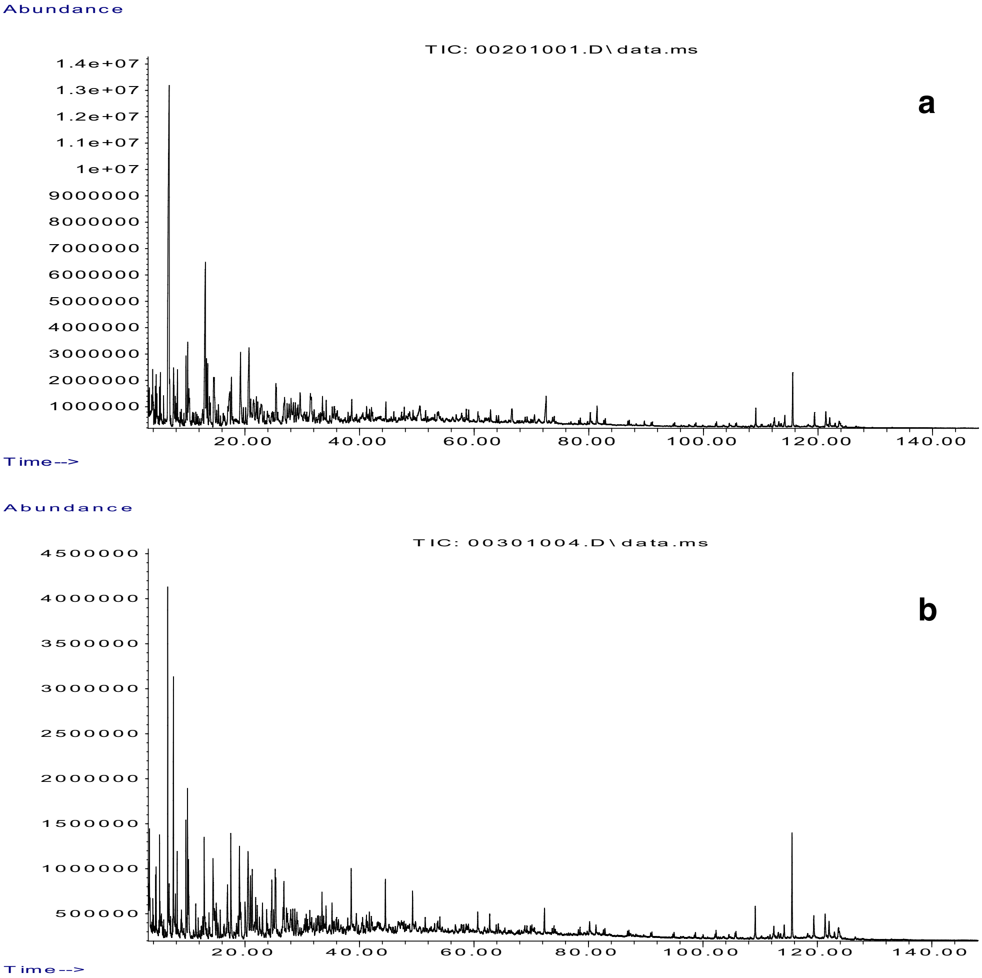

Fig. 12 GC-MS chromatogram of the pyrolysis liquid products obtained at 500 °C. **a** HT 150-20. **b** HT 190-20)

dimethyl-2-cyclopenten-1-one, 2-methyl-phenol, 4-methyl-phenol, 2-methoxy-phenol,, 2-ethyl-phenol, 2,4-dimethyl-phenol is 3,5-dimethyl-phenol. Apart from these, although the peak areas are low, there are many compounds in the structure.

Bio-oil can be used as a clean and renewable fuel compared to fossil fuels, or as a promising source to generate a variety of high value-added chemicals. Depending on the application area, the properties of the bio-oil such as pH and CHO contents, hence the HHV value, can be adjusted by various procedures (physical, thermal, chemical, and catalytic) from diverse steps of pyrolysis such as pre-pyrolysis, during pyrolysis, and after pyrolysis. As it is known, highly reactive oxygens originating from carboxylic acids, aldehydes, and phenols in the structure of bio-oil both cause acidic pH and react with other reactive organic compounds, thus reducing the stability of the bio-oil during storage [40]. Acid pre-treatment and hydrothermal pre-treatment (wet torrefaction) are both classified as chemical methods. Inorganic minerals, which can be found in the form of phosphates, carbonates, sulfates, or chlorides in lignocellulosic biomass structure, can affect the pyrolysis process by providing catalytic activity. Accordingly, the properties of bio-oil such as viscosity, pH, stability, and corrosion activity change limit the application area of the bio-oil. It has been proven by the studies in the literature that pre-treatment performed with both acid and hydrothermal processes reduces inorganic compounds in biomass structure and thus improves the fuel properties of biomass. In this study, acid and hydrothermal pre-treatments were applied to minimize the unfavorable properties of bio-oil. When the compounds determined in the structure by GC/MS analysis were compared according to the treatment type, the following results were found to be compatible with the literature. In the literature, it is stated that the number of aliphatic hydrocarbons increases in the bio-oil content obtained after the pre-treatment of biomass with weak acid, whereas the ratio of acids and other oxygenated compounds decreases [41]. Thus, the physical properties of the bio-oil are also improved [42]. The change in bio-oil content was also in agreement with the FT-IR results, and a significant decrease in the intensity of the hydroxyl stretching vibration was observed when biomass was pre-treated with acid. The determination of guaiacol and syringol compounds in the GC/MS chromatogram indicated that the lignin component in the biomass structure was thermally degraded, that is, the αC — βC bonds and β — 5 bonds in the structure were broken by pre-treatment [43]. By applying hydrothermal pre-treatment to lignocellulosic biomass, hemicellulose in the structure is almost totally dissolved, the interactions of lignin are disrupted, and cellulose is left almost remained in the solid product. Therefore, more cellulose and lignin-derived compounds are detected in the bio-oil content produced from hydrothermal-pre-treated biomass. The bio-oil obtained after hydrothermal pre-treatment of bean pod also contained phenolic compounds, organic acids, furans, and furfural, which was consistent with other studies in the literature [44, 45].

4 Conclusion

In this study, it was aimed to improve the raw material properties and increase the pyrolysis liquid product yield by applying hydrothermal and acid pre-treatment to the bean pod, which was a food factory waste. The pre-treatment for the improvement of the biomass structure should be low cost firstly to realize low consumption of cheap chemicals. It is also important to underline application of lignocellulosic raw materials, providing a high rate of lignin removal and minimal carbohydrate loss. Biomass resources should have low moisture and ash contents and high volatile content. Prior to the results, these properties of raw materials were improved with pre-treatments. Hydrothermal pre-treatment reduced the bulk density, moisture, and ash content of the raw materials and increased the amount of volatile matter. The highest volatile matter content and the lowest moisture content were obtained in the HT190-20 sample (71.59% and 3.95%, respectively). Apart from the pre-treatment studies, biomass is considered as a renewable energy source in pyrolysis processes where its valuable liquid product obtained is expected to have low oxygen content and high carbon content, so its higher heating value would be high. According to the results of the optimum pre-treatment condition evaluation, it was determined that the highest tar yield was reached as 22.18% with the HT 190-20 sample at 500 °C pyrolysis temperature and the produced tar contained 68.66% C and 22.39% O according to the elemental analysis result and the higher heating value was 30.11 MJ/kg. It was observed that the pre-treatments applied to biomass changed the ratio of moisture, ash, and volatile components in the structure, and the tar yield obtained from the pyrolysis process increased in line with the amount of volatile matter in the structure. In brief, it can be concluded that (i) the biomass structure is improved by hydrothermal method or phosphoric acid impregnation and washing; thus, its usability as a biofuel precursor is provided in the pyrolysis process; (ii) the product distribution and tar properties can be adjusted depending on the pre-treatment conditions.

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