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Effect of different pre-treatment techniques on thermogravimetric characteristics and kinetics of lignocellulosic biomass pyrolysis

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ABSTRACT

In this study, effect of pre-treatments on biomass pyrolysis kinetics was evaluated. Fir wood sawdust (F), pine wood sawdust (P) and hazelnut shell (H) were selected as raw biomass sample. Acidic pre-treatment was applied by using 1M-H_2SO_4 at room conditions and hydrothermal pre-treatment applied by using high pressure and temperature reactor. Thermogravimetric analysis was executed to specify thermal degradation behavior of the samples. Thermogravimetric analysis was also used to determine kinetic parameters of thermal degradation for biomass and pre-treated biomass samples. Having knowledge thermal degradation behavior and kinetic parameters of pyrolysis process such as activation energy and reaction rate are very important for reactor design. Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Coats-Redfern (CR) methods were used to investigate the effect of different pre-treatment techniques on the kinetic parameters. Activation energies of pyrolysis reactions for F, P and H were found as 158.47 ± 1.08 kJ/mol, 126.0 ± 1.78 kJ/mol and 158.66 ± 1.24 kJ/mol, respectively. The calculated activation energy values increased while acidic and hydrothermal pre-treatment were applied to each biomass samples. In conclusion, acidic and hydrothermal pre-treatments influenced the serial and parallel reaction rates during the thermal degradation process and the calculated activation energy values changed accordingly. Inorganics that catalyzed the pyrolysis reactions were removed by acid pre-treatment. The condensed species during hydrothermal pre-treatment prevented the easy volatilization. As a result of experimental studies and kinetic calculations, it has been determined that pre-treatments applied to biomass increased the activation energy value in thermal degradation reactions.

1. Introduction

Concern in the valorization of various wastes in the production of valuable chemicals and fuel is increasing year by year [1,2]. Raw material resources are limited, chemical production costs are increasing, and it is important to keep the environment clean during production. For this reason, it has become necessary to use waste materials, which are easy to access and cheap, as raw materials for the production of valuable chemicals and fuel. As an alternative resource, biomass utilisation and biomass conversion technologies has become important day by day. Various renewable and recyclable biomass resources can be converted into valuable chemicals [3,4], hydrogen [5,6], biofuels [7], and environmentally friendly polymeric materials [8,9] by thermochemical, biochemical and catalytic methods.

Biomass is a term that includes all terrestrial, aquatic plants and animal wastes, forest and urban wastes. Biomass can be renewed in less than 100 years and grown anywhere in accordance with its climate. Thus, it keeps each country from dependency on foreign countries. Lignocellulosic biomass consists of cellulose (40–50% by mass), hemicellulose (20–30% by mass), and lignin (10–40% by mass). In addition to these main components, it is a composite material that contains a small amount of extractive (terpene, tannin, fatty acid and resin), moisture and some inorganic components [10–12]. While sugar-based macropolymers (hemicellulose and cellulose) in biomass can be significantly degraded and converted into their derivatives by fermentation, lignin cannot be converted by this method. Decomposition of lignin polymer into small subunits is very important for lignin evaluation. Monolignols in the lignin structure are very important for the production of phenolic and aromatic compounds in the chemical industry, especially since they consist of phenolic compounds containing different functional parts [13]. Researchers emphasized that different components such as methane and methanol were also obtained under different reaction

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conditions on the production of monomeric phenol from the lignin. Selection of the type of biomass, pre-treatment technique and the catalyst and are very important to control the repolymerization reactions and obtaining the desired product [13,14].

Pyrolysis is an important method used for the thermochemical conversion of lignocellulosic biomass. During the pyrolysis process, cellulose and hemicellulose depolymerize and anhydro sugars such as 1,6-anhydro-β-D-glucose (levoglucosan) and 1,4-anhydro-D-cyclopyranose are formed [15,16]. 5-hydroxymethyl furfural, furfural, hydroxyacetone, hydroxyacetaldehyde and some C_1–C_2 compounds are obtained, which are important in industrial terms, from the degradation of levoglucosan. Pyrolysis liquid product includes methanol, acetic acid, and acetone components with the degradation of 1,4-anhydro-D-cyclopyranose. On the other hand, lignin has a very complex structure compared to hemicellulose and cellulose. The degradation mechanism of lignin is based on the radical or heterolytic fission mechanism according to its side chain structure [17–19]. The unique mechanism of lignin degradation has a strong influence on pyrolysis reactions reactivity. Thus, it degrades in different temperature ranges compared to hemicellulose and cellulose [20]. The characteristic pyrolysis liquid products of lignin can be classified into three groups as phenol, guaiacol and catechol. The main products of biomass pyrolysis are char and tar. The valuable chemicals mentioned above are obtained in small amounts. In order to upgrading the pyrolysis products, catalytic pyrolysis [21,22], hydrothermal process [23], co-pyrolysis [24] and acid pre-treatment [25] applications can be done. Improving the pyrolysis product with solvolysis can be controlled easily by changing the reaction conditions such as solvent, catalyst and temperature. However, the inorganics in the biomass prevent the solvent from being used for a long time without regeneration. Solid catalysts can be used as an alternative to solvents in pyrolysis process but the accumulation of coke on the catalyst surface also limits the use of this method [26,27].

The cellulose is composed of β-D-glucose, which are linked to each other by β-1,4-glycoside bonds; hemicellulose, on the other hand, consists of sugars such as mannose, xylose and glucose, which are linked to each other by β-1,4-glycoside and β-1,6-glycoside bonds. Lignin comprises of coniferyl and sinapyl alcohol units linked by β-alkyl-aryl ether bonds. Accordingly, the agreed characteristic of cellulose, hemicellulose and lignin components is that they have C–O bonds. These bonds can hydrolyze in the presence of acid, so that smaller components can be obtained as a result of biomass pyrolysis [28]. Researchers emphasized that the yield and quality of the pyrolysis liquid product increased by using sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) [29,30]. In literature, pretreatment with acid is generally carried out at high temperature and pressure. In another study, cedar wood sawdust was pre-treated with H_2SO_4 at room temperature and atmospheric pressure to avoid unnecessary energy usage for heating and pressurization [28]. While they found the liquid product yield from biomass pyrolysis without pre-treatment to be 30.1%wt., they found the highest liquid yield as 46.8%wt with the pre-treated biomass sample pyrolysis. According to the results supported by thermogravimetric and mass-spectrometry (TG-MS) experiments, the liquid product obtained from acid-pretreated biomass is rich in short-chain components. In addition, according to gas chromatography mass spectrometry (GC-MS) results, it was observed that phenolic hydrocarbons, which are lignin derivatives, increased with acid pre-treatment. Hydrothermal pre-treatment, which is called in different terms such as wet torrefaction, auto-hydrolysis, pre-treatment with hot water, uses water at high temperature (about 140–220 °C) [31]. In the first step of the hydrothermal pre-treatment, hydronium ions (H_3O^+) are formed and the ions act as weak acids to depolymerize the hemicellulose. Thus, glycoside bonds are hydrolyzed and acetyl groups are separated from the hemicellulose structure [32]. Acetic acid is formed with the hydration of acetyl groups, and the formed acetic accelerates the hydrolysis process [33,34]. The most important advantage of hydrothermal pretreatment is that it is an environmentally friendly method that uses only water without the need for additional chemicals and catalysts [35]. This pre-treatment method is a proper, easy and economical method that can be used in biological conversion technologies in terms of providing enzymes to reach the biomass more easily, and in thermochemical conversion methods in terms of preparing the biomass for the thermal degradation process [36]. Researchers used hydrothermal pre-treated beech wood chips in pyrolysis reactions. According to the experimental results, they found that carboxylic acids and ketones were reduced in liquid product by hydrothermal pre-treatment [37]. In another study, it was emphasized that hydrothermal pre-treatment reduces nitrous compounds in the liquid product obtained by pyrolysis [38].

Several serial and parallel reactions take place during the pyrolysis of biomass. Thermal characterization methods are widely used to calculate activation energy, reaction degree and pre-exponential factor values in pyrolysis reactions. These parameters are very important in reactor design to adapt laboratory scale to industrial scale [39]. Thermal analysis is a technique in which the physical properties of the sample or reaction products are measured as a function of temperature with a controlled temperature program [40]. In the thermogravimetric analysis method, the mass of the sample in an inert or reactive atmosphere is recorded vs. increasing temperature or time [41]. Thermogravimetric methods can be used for thermal degradation and oxidation reactions, or physical processes such evaporation, sublimation and desorption, where temperature change creates a change in sample mass [42]. Kinetic parameters in pyrolysis process can be calculated by using Arrhenius [43–45], Coats-Redfern [44–46], Kissinger [47], Flynn-Wall-Ozawa [48], Friedmann [49,50], Criado [48], Kissinger-Akahira-Sunose [50,51], and Horowitz-Metzger [43] methods.

Turkey is an agricultural country. These agricultural products are used in many industrial areas such as furniture factory, silage industry, food factory etc. Due to the industrial efficiency, plenty of waste biomass is released while biomass is processed. In this study, fir wood sawdust and pine wood sawdust, which are furniture factory waste, and hazelnut shells, which are food factory waste, were selected as raw materials. While selecting the samples, it was taken into account that biomass samples had different physicochemical properties. Two different pre-treatments techniques (acid and hydrothermal) were applied to the different biomass samples. Thermogravimetric analysis and kinetic calculations were performed to determine the effect of the pre-treatment techniques on biomass pyrolysis reaction kinetics.

2. Materials and methods

The materials and experimental techniques used in the study are explained in detail.

2.1. Materials

Fir wood sawdust (F) and pine wood sawdust (P) samples were provided as sawdust from a furniture workshop in Bilecik. Hazelnut (H) shells were obtained from a dried-nut factory operating in Trabzon. The hazelnut shell sample was dried at room conditions, ground using a rotary cutting mill and used without sieving.

2.2. Acid pre-treatment

250 mL of 1 M acid solution prepared using 96% pure H_2SO_4 was added to 2.5 g of biomass. The heterogeneous mixture was stirred for 1 h on a magnetic stirrer at room conditions. The solid filtrated from the solution was washed with ultrapure water until the pH of the filtrate was equal to the pH of ultrapure water. The solid part was dried at room conditions and then kept in an oven for 24 h. The sample taken from the oven was cooled in a desiccator and then stored in a moisture-free environment. The biomass samples obtained by acid pre-treatment were codded as AF, AP and AH.

2.3. Hyrothermal pre-treatment

Hydrothermal pre-treatment experiments were carried out in a computer-controlled, 1 L high temperature and high-pressure autoclave system (PARR 4575B Reactor). Hydrothermal pre-treatment conditions were 5 bar the initial pressure, 5 min the reaction time, 190 °C the temperature and 1/5 the solid/water ratio. After the experimental setup was ready, nitrogen gas flowed to remove the air in the reactor before starting to heat. Then the reactor was pressurized with nitrogen gas and heated to the desired temperature. At the end of the reaction time, the solid-liquid mixture was filtered. The separated solid phase was dried at room conditions and then in an oven at 105 °C for 24 h. The sample taken from the oven was cooled in a desiccator and then stored in a moisture-free environment. The biomass samples obtained by hydrothermal pre-treatment were codded as HTF, HTP and HTH.

2.4. Thermogravimetric analyses

Thermogravimetric analyser (TGA) (SETARAM, LabSys evo) was used to examine the thermal degradation behavior of the samples. 10 mg sample placed in a 100 μL volume Al_2O_3 crucible was heated from ambient temperature to 1000 °C. Nitrogen flow rate was 20 mL/min during the experiment. In order to calculate the kinetic parameters, data at different heating rates were recorded. For this purpose, the samples were heated from room temperature to 1000 °C with heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min.

2.5. Kinetic analysis

In this study, Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW) and Coats-Redfern methods were used to calculate kinetic parameters. KAS and OFW methods consider the kinetic parameters are independent of the reaction mechanism. According to this assumption, at a constant conversion rate (x), the rate of reaction depends only on temperature and is independent of the heating rate. Based on KAS and OFW methods, the thermal degradation of raw materials can be considered as a one-step process [50,52]. Activation energy was calculated using the KAS and OFW methods, and the pre-exponential factor was calculated using the CR method.

In the thermal decomposition of a solid under non-isothermal conditions, while volatile matters are separated in gaseous form, some solid remains depending on the structure of the solid [49].

$$\text{aA (solid)} \rightarrow \text{bB (solid)} + \text{cC (gas)} \tag{1}$$

Solid state reaction kinetics are expressed as given in equation (2).

$$\frac{dx}{dt} = k(T)f(x) \tag{2}$$

Conversion, x, is given in equation (3).

$$x = \frac{w_i - w_t}{w_i - w_f} \tag{3}$$

Here,
w_i: initial mass of the sample, mg
w_t: mass of the sample at t, mg
w_f: final mass of the sample, mg
$k(T)$ function is defined as the temperature-dependent rate constant k according to the Arrhenius rate equation:

$$k(T) = Ae^{\frac{-E_a}{RT}} \tag{4}$$

Here,
E_a: activation energy, kJ/mol
T: temperature, K
R: ideal gas constant (8.314), J/mol.K
A: frekans factor (1/min)

$$\frac{dx}{dt} = Ae^{\frac{-E_a}{RT}}f(x) \tag{5}$$

Temperature is a function of time with the constant heating rate (β):

$$\beta = \frac{dT}{dt} = \frac{dT}{dx}\frac{dx}{dt} \tag{6}$$

Equations (5) and (6) are written together:

$$g(a) = \int_0^x \frac{dx}{f(x)} = \int_0^T \frac{A}{\beta}e^{-Ea/RT}dT = \frac{AE_a}{\beta R}\int_z^\infty u^{-2}e^{-u}du = \frac{AE_a}{\beta R}P(z) \tag{7}$$

Here, $z = E_a/RT$. $P(z)$ has no real-calculation. So, equation (7) can be solved by using mathematical methods and approaches [50].

Kissenger-Akahira-Sunose (KAS) method:

The KAS method applies the approximation $P(z) = z^{-2}e^{-z}$ for the $P(z)$ function in equation (7). Accordingly, equation (8) is obtained.

$$ln\left(\frac{\beta}{T^2}\right) = ln\left[\frac{A\,E_a}{R\,g(x)}\right] - \frac{E_a}{RT} \tag{8}$$

While the conversion values are changed between 0 and 1; the $1/T$ vs. $ln(\beta/T^2)$ values are plotted; the slope of the obtained curve gives the $-E_a/R$ value.

Ozawa–Flynn–Wall (OFW) method:

The OFW method uses the Doyle approximation (Doyle, 1965) to solve equation (7). According to the Doyle approximation, $log(P(z)) \sim 2.315 + 0.457z$. When equation (7) and doyle approximation are used together, equation (9) is obtained.

$$\log[\beta] = \log\left[\frac{A\,E_a}{R\,g(x)}\right] - 2.315 - 0.457\,\frac{E_a}{R\,T} \tag{9}$$

While the conversion values are changed between 0 and 1; the $1/T$ vs. $log(\beta)$ values are plotted; the slope of the obtained curve gives the $-E_a/R$ value. Accordingly, the activation energy can be calculated for each conversion value.

Coats–Redfern (CR) method:

The CR method is a model-independent method derived from the Arrhenius equation. While KAS and OFW methods can be used to calculate activation energy, CR method can be used to calculate pre-exponential factor, apparent reaction degree and activation energy. $f(x)$ for solid phase reactions:

$$f(x) = (1-x)^n \tag{10}$$

If equation (10) and equation (4) are substituted in equation (2), equation (11) is obtained.

$$\frac{dx}{(1-x)^n} = \frac{A}{\beta}e^{\frac{Ea}{RT}}(1-x)^n \tag{11}$$

The integral form of equation (11):

$$\frac{1-(1-x)^{1-n}}{1-n} = \frac{A}{\beta}\int_0^T e^{-E_a/RT}dT \tag{12}$$

Assuming $\int e^{-E_a/RT}dT$ as asympthotic series:

$$\frac{1-(1-x)^{1-n}}{1-n} = \frac{ART^2}{\beta E_a}\left[1 - \frac{2RT}{E_a}e^{-E_a/RT}\right] \tag{13}$$

Logaritmic form of equation (3):

$$ln\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right] = ln\left[\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{14}$$

Assuming $2RT/E_a \ll 1$:

$$ln\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right] = ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT}\ (n \neq 1) \tag{15}$$

$$ln\left[-\frac{ln(1-x)}{T^2}\right] = ln\left[\frac{AR}{\beta E_a}\right] - \frac{E_a}{RT} \quad (n=1) \tag{16}$$

In equation (15), $ln\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right]$ vs. $\frac{1}{T}$ and in equation (16) $ln\left[-\frac{ln(1-x)}{T^2}\right]$ vs. $\frac{1}{T}$ are plotted. The slope of the obtained linear graphs gives $-\frac{E_a}{R}$ and the intercept gives $ln\left[\frac{AR}{\beta E_a}\right]$. Activation energy and frequency factor can be calculated from these values. The x and T values in these equations are obtained from the TG analysis [53].

3. Results and discussion

The results obtained from experimental studies and kinetic calculations are given under this section.

3.1. Thermogravimetric characteristics of biomass and pre-treated biomass samples

The volatilization process is essential in thermal decomposition reactions such as pyrolysis. The thermal degradation process of a typical lignocellulosic biomass can be examined in three steps correlated with the different slopes on the TG curve. The first step occurs in the temperature range of approximately 100–120 °C and shows the vaporization of physically absorbed water in the biomass structure. The second step, active pyrolysis zone, starts at approximately 208–232 °C and finishes at 372–415 °C. The mass loss rate is high in the active pyrolysis zone. Hemicellulose and cellulose are thermally degraded in this temperature range. Above 415 °C, the passive pyrolysis zone begins and lignin decomposes in this zone. The mass loss rate is slow in this region [44]. In a lignocellulosic biomass sample containing hemicellulose, cellulose, and lignin, such as the biomass used in this study, these three regions are clearly observed in the TG and dTG curves.

The TG, dTG curves and characteristic thermal properties of the F, AF and HTF samples at different heating rates were given in Fig. 1 and Table 1.

According to the thermal decomposition behavior of the F at different heating rates, the characteristic temperatures increased as the heating rate increased. Increasing of the characteristic temperatures can be explained by the effect of heat transfer at different heating rates and the effect of delayed decomposition on thermal decomposition kinetics [43]. As the heating rate increased, the completion time of the reactions and the desire to interact with the volatilization process decreased. Thus, the temperature at which maximum mass loss was observed shifted towards higher temperatures [54]. Similarly in the TG and dTG curves of AF and HTF samples, the initial temperature of the pyrolysis reactions shifted towards higher temperatures as the heating rate increased, without significant changes in the thermogram behavior.

As mentioned before, the shift of the peaks towards high temperatures was based on the rate of heat transfer at different heating rates. The variation of heat transfer rate was affected reaction kinetics, directly [43,55]. Heating the biomass at low heating rates, a more homogeneous temperature profile was achieved up to the inner part of the biomass particle, and the heat transfer efficiency decreased at high heating rates [50]. In addition, the peak heights, which indicated the total mass loss also increased as the heating rate increased [55].

In Fig. 2 and Table 2, the TG, dTG curves and the characteristics of the thermal decomposition zone of the P, AP and HTP samples were given.

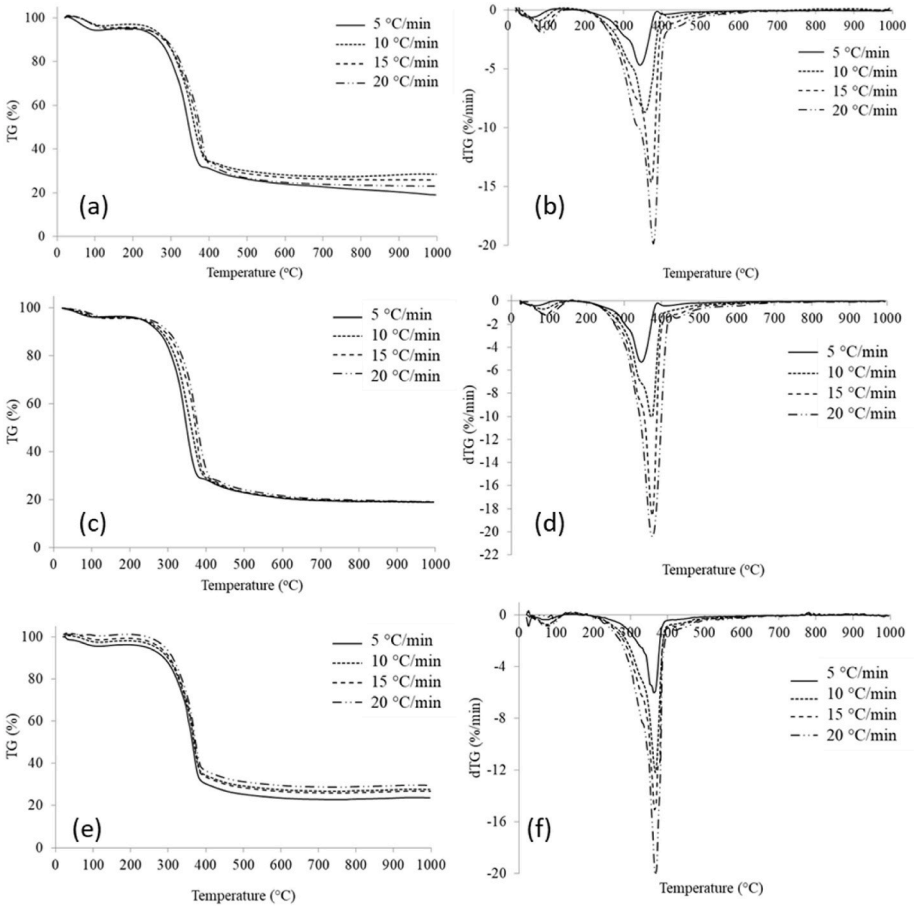

Fig. 1. Thermogravimetric analyses results of (a, b) Fir wood sawdust, (c, d) Acid pre-treated fir wood sawdust and (e, f) Hydrothermal pre-treated fir wood sawdust at different heating rates.

Table 1
Thermal characteristic properties of fir wood sawdust (F), acid pre-treated fir wood sawdust (AF) and hydrothermal pre-treated fir wood sawdust (HTF) at different heating rates.

β (°C/min)	F				AF				HTF			
	5	10	15	20	5	10	15	20	5	10	15	20
T_i (°C)	207	209	212	228	205	214	215	221	195	201	210	224
T_f (°C)	382	400	406	408	400	408	418	422	403	412	425	432
T_{max} (°C)	336	360	367	373	346	357	370	371	357	363	359	360
W_{max} (%/min)	−4.4	−8.3	−14.6	19.8	−5.3	−12.1	−18.5	−20.4	−5.4	−11.3	−12.8	−17.0
Mass loss (%)	63.10	62.58	62.82	62.49	68.16	43.20	67.66	67.53	66.17	64.86	67.73	65.78

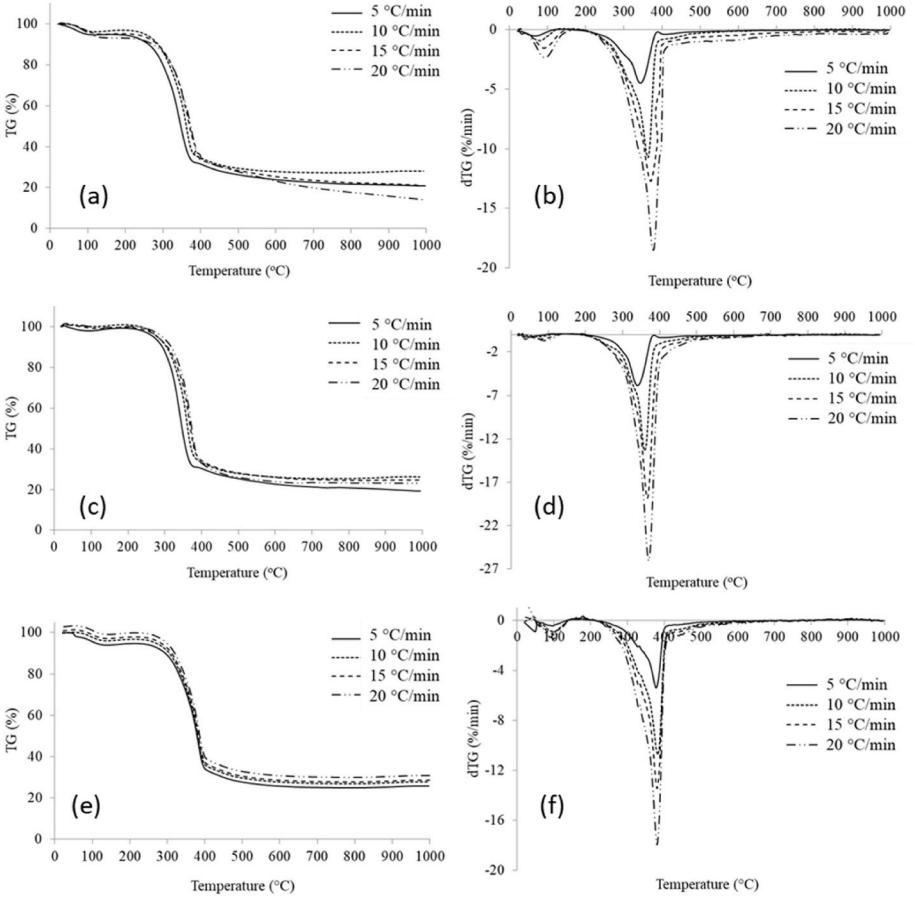

Fig. 2. Thermogravimetric analyses results of (a, b) Pine wood sawdust, (c, d) Acid pre-treated pine wood sawdust and (e, f) Hydrothermal pre-treated pine wood sawdust at different heating rates.

Table 2
Thermal characteristic properties of pine wood sawdust (P), acid pre-treated pine wood sawdust (AP) and hydrothermal pre-treated pine wood sawdust (HTP) at different heating rates.

β (°C/min)	P				AP				HTP			
	5	10	15	20	5	10	15	20	5	10	15	20
T_i (°C)	175	182	183	222	212	217	229	235	230	248	259	260
T_f (°C)	790	793	798	807	403	409	412	416	399	404	407	419
T_{max} (°C)	337	356	366	378	339	358	356	371	373	384	374	381
W_{max} (%/min)	−4.2	−10.7	−12.5	−18.4	−5.8	−13.2	−17.8	−26.0	−4.9	−12.3	−12.3	−17.9
Mass loss (%)	78.17	71.98	78.82	85.67	68.92	73.80	66.42	68.60	60.19	61.28	60.74	61.58

When the characteristic properties obtained according to the heating rate were examined, it was observed that the temperatures at which the active pyrolysis zone started and ended shift towards higher temperatures as the heating rate increased. The highest mass loss rate and the highest mass loss rate temperature were also increased with higher heating rate. Some researchers found similar results in their study. They explained that the heating rate, which was the driving force in the thermal decomposition process, was higher and the instantaneous heat energy was higher. So, thermal degradation rate was higher at higher heating rate [56].

Likewise, the increase in the heating rate in the AP sample caused the characteristic properties to shift to higher temperatures, no significant changes were observed in the total mass loss. While the total mass loss at 212–403 °C temperature range with the heating rate of 5 °C/min was 68.92%, the total mass loss at 235–416 °C temperature range with the heating rate of 20 °C/min was determined as 68.60%. As a result, it was determined that the change in the heating rate was not an effective parameter on the volatile matter ratio. The obtained result was in agreement with the literature [50]. Similarly, in the HTP sample, no significant change was observed in the total mass loss values, as well as the T_i, T_{max} and T_f values shifted to higher temperatures with the increase of the heating rate.

TG, dTG curves and characteristic properties of thermograms achieved by heating H, AH and HTH samples from 25 °C to 1000 °C at different heating rates were given in Fig. 3 and Table 3. Like other biomasses used in this study, the thermal degradation profile of these samples did not change as the heating rate changed, but this process shifted towards higher temperatures. The total mass loss during the pyrolysis reactions of H did not change significantly with the increase of the heating rate, it was determined as 44.04%, 45.83%, 46.17% and 48.48% for the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min, respectively. The thermal hysteresis was also seen in the pyrolysis profile of AH and HTH samples like the studies in literature.

In the pyrolysis experiments performed at different heating rates of bamboo [57], dried waste sludge [58], *phlomis bovei* biomass [59], and waste biomass [60] temperature shifts were determined which called thermal hysteresis or thermal lag.

The heating rate affects the pyrolysis of the biomass in two ways: *(i)* as the heating rate increases, the time required for the samples to reach the same pyrolysis temperature becomes shorter. However, in this case, the retention time required for the formation of volatile compounds that will occur in each temperature range is insufficient. For this reason, higher temperatures are needed for the degradation process to occur [61,62]. *(ii)* Besides, the increase in heating rate causes a larger temperature difference between the surface and inner part of the biomass particles, and the higher temperature difference, which is the driving force, furthers the overall volatilization process [60].

3.2. Kinetic analyses of biomass and pre-treated biomass samples

The graphs $ln(\beta/T^2)$ vs. $1/T$ and $log(\beta)$ vs. $1/T$ with varying conversion degree (0.1–0.8) by using the KAS and OFW methods for each example were given in the supplementary material file. Pyrolysis reactions were evaluated between these conversion values, since the correlation value was low at values below 0.1 and above 0.8 (Damartzis, vd., 2011). Activation energy values were calculated by using these curves for F, AF, HTF, P, AP, HTP, H, AH and HTH samples at different conversion values. The graphs $ln[(1-(1-x)^{(1-n)})/(T^2(1-n))]$ vs. $1/T$ at different heating rates using the CR method were also given in the supplementary material file. The pre-exponential factor values for each sample were calculated from CR graphs. Activation energy values calculated from KAS and OFW methods and pre-exponential factor values calculated from CR method for F, AF and HTF samples were given in Supplementary Information. The average activation energies of F calculated using the KAS and OFW methods were determined as 157.79 kJ/mol and 159.53 kJ/mol, respectively. Although the assumptions in the KAS and OFW methods were different, these calculated values were close to each other it proved that the methods were reliable [50]. Activation energy values increased while the conversion increased from 0.1 to 0.4. The activation energy from KAS method for the conversion

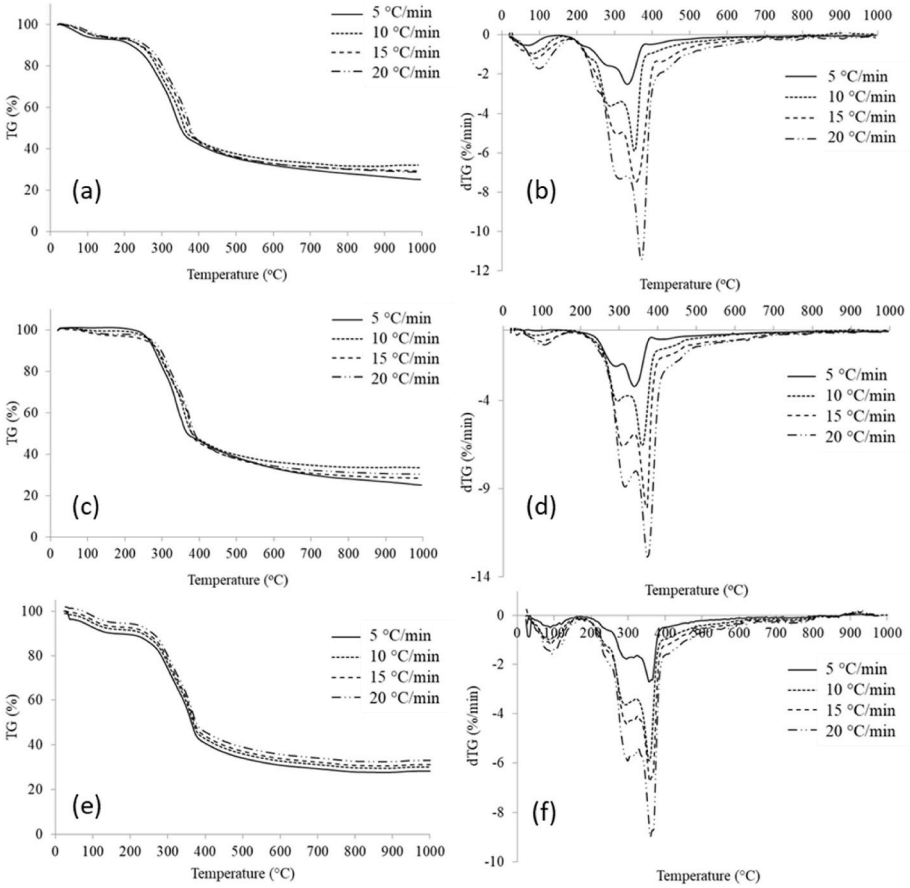

Fig. 3. Thermogravimetric analyses results of (a, b) Hazelnut shell, (c, d) Acid pre-treated hazelnut shell and (e, f) Hydrothermal pre-treated hazelnut shell at different heating rates.

Table 3
Thermal characteristic properties of Hazelnut shell (H), acid pre-treated hazelnut shell (AH) and hydrothermal pre-treated hazelnut shell (HTH) at different heating rates.

β (°C/min)	H				AH				HTH			
	5	10	15	20	5	10	15	20	5	10	15	20
T_i (°C)	202	210	214	221	203	226	235	240	207	212	220	228
T_f (°C)	359	370	381	390	371	382	392	403	370	386	390	401
T_{max} (°C)	332	346	358	369	336	356	373	372	355	351	352	353
W_{max} (%/min)	−2.5	−5.9	−7.4	−11.4	−3.1	−6.5	−10.0	−12.8	−2.6	−5.4	−6.5	−8.0
Mass loss (%)	44.04	45.83	46.17	48.48	50.63	48.40	49.85	51.29	43.24	47.41	47.18	47.55

values of 0.1 and 0.4 were 141.67 kJ/mol and 176.93 kJ/mol, respectively. The behavior of the activation energy values versus the conversion was the same in the OFW method. The activation energy values for the conversion 0.1 and 0.4 were determined as 143.07 kJ/mol and 177.80 kJ/mol, respectively. The reaction mechanism changing during the conversion caused the difference of activation energy values. Activation energy was defined as the minimum amount of energy required to start a reaction; a higher activation energy indicated that reactions took place more slowly [63]. In literature, the average activation energies calculated in the pyrolysis reactions of biomass were found to be 129 kJ/mol for corn cob [63], 224.1 kJ/mol for *cynara* waste [64] and 120 kJ/mol for orange waste [65]. When these results were compared with the activation energy results calculated for the pyrolysis reactions of F, it was seen that similar results were obtained with the literature. According to the CR results, the average reaction degree of F in the pyrolysis reactions was calculated as 0.8. The pre-exponential factor values varied between 8.6×10^6 and 2×10^8 min^{-1} depending on the conversion and heating rate. The average activation energies were calculated for the pyrolysis reactions of AF as 151.42 kJ/mol for the KAS method and 153.61 kJ/mol for the OFW method. The average reaction rate calculated according to the CR method was found to be 0.9. Compared to the activation energy values of F and AF, the energy requirement for the reactions increased with the acid pretreatment. Inorganic components in F and that removed from the structure by acid pre-treatment affected the pyrolytic behavior of the biomass [66].

As the conversion value increased from 0.1 to 0.4, the activation energy value also increased for HTF pyrolysis process. The activation energies were calculated as 249.02 kJ/mol by KAS method and 204.33 kJ/mol by OFW method at the conversion was 0.4. The change in the activation energy versus the conversion values was explained by the effects of the reactions taking place at that conversion value on the reaction rate [50]. The average activation energy values for the pyrolysis reactions of the HTF were calculated as 203.10 kJ/mol and 216.6 kJ/mol according to the KAS and OFW methods, respectively. The values were close to each other, indicated the reliability of the methods. The reaction degree calculated according to the CR method was 0.2, and the pre-exponential factor values were calculated in the range of 3.6×10^6- 3.2×10^8 min^{-1}. While the kinetic parameters result of the F and HTF samples were compared, the reaction degree decreased and the activation energy value increased by applying hydrothermal pretreatment to the biomass. The degree of reaction was a criterion of the interaction of molecules with each other. As the degree of reaction decreased, the possibility of free volatile components interacting with each other decreased. Accordingly, the energy requirement required for the reactions to take place also increased [67].

Activation energy values calculated from KAS and OFW methods and pre-exponential factor values calculated from CR method for P, AP and HTP samples were given in Supplementary Information. The activation energy required for the thermal degradation of the P sample continued to increase as the conversion increased and reached its highest value when the conversion value was 0.5. The variation in activation energy as the conversion altered was explained by the change in the mechanism and reaction degrees of the reactions that took place during the pyrolysis reactions [64]. The average reaction degree for the pyrolysis reactions of P was calculated as 1.9, and the pre-exponential factor value ranged between 1.9×10^7 and 2.5×10^9 (min^{-1}) by applied CR method. The average activation energy required for the pyrolysis reactions of the AP sample was calculated as 171.14 kJ/mol and 172.25 kJ/mol from the KAS and OFW methods, respectively. According to the CR method, the average reaction degree was calculated as 0.1 and the pre-exponential factor was determined between 1.9×10^8-5.9×10^9 values. As mentioned before, Acid pre-treatment of biomass caused an increase in the activation energy [66]. Activation energies from KAS and OFW methods varied at each conversion value. This can be explained by the complex structures of the raw material and the different thermal degradation characteristics of the ATP. The lowest activation energy obtained by breaking the weak bonds in the volatilization process of hemicellulose at the conversion value is 0.1 and 0.2. After the weak bonds were broken, the activation energy required for the reactions to occur increased as the bonds in the straight chain structure begun to break [68,69]. The average activation energy, reaction degree and pre-exponential factor values of the HTP sample calculated according to the KAS, OFW and CR methods were 190.31 kJ/mol, 201.33 kJ/mol, 0.2 and 2.5×10^6-2.5×10^8 min^{-1}, respectively. Activation energy values calculated from KAS and OFW methods and pre-exponential factor values calculated from CR method for H, AH and HTH samples were given in Supplementary Information. According to KAS and OFW methods, the average activation energy for the pyrolysis reactions of the H sample were 157.78 kJ/mol and 159.53 kJ/mol, respectively. While the conversion values changed in the range of 0.2–0.6 the activation energy did not change significantly. A rapid increase in activation energy was observed when the conversion value increased above 0.6. This result showed that the depolymerization reactions of cellulose and hemicellulose were completed in this range and lignin degradation reactions begun [70]. The reaction degree calculated from the CR method for the pyrolysis reactions of P was found as 0.4. The average activation energy values of the AP sample calculated according to the KAS and OFW methods were found as 213.40 kJ/mol and 210.02 kJ/mol, respectively. The reaction degree was also found as 0.1. from the CR method. The pre-exponential factor values at different conversion values ranged between 2.7×10^8 and 1.9×10^{10} min^{-1}. In the temperature range where the conversion value is 0.3 and 0.4, the degree of polymerization of cellulose in the AH structure decreased, the chain length in its molecule was shortened, and it transformed into active cellulose according to the Broido-Shafizadeh kinetic model [71]. The average activation energy required during this conversion was calculated as 226.77 kJ/mol from the KAS method and 224.98 kJ/mol from the OFW method. The degradation of low molecular weight active cellulose required lower energy than the previous steps [68]. The activation energy where the conversion at 0.5 was determined as 158.93 kJ/mol and 160.87 kJ/mol according to the KAS and OFW method, respectively. Carbon-rich structures begun to form at the conversion above 0.6. Cross-linking of polymer chains and polycondensation reactions occurred at this temperature [72].

The carbonization step also caused an increase in the activation energy value at the temperature where the conversion was 0.7 [69]. The average activation energy values of the HTH sample according to KAS and OFW methods were calculated as 186.36 kJ/mol and 206.47

kJ/mol, respectively. The degree of reaction calculated from the CR method was 0.2. The pre-exponential factor values were determined between 2.5×10^6 and 3.0×10^8 min^{-1} by using the activation energies obtained from the KAS and OFW methods. The average activation energy of pyrolysis of HTH was higher than H. These results showed that H volatilized easier than HTH and had a higher reaction rate. During the hydrothermal process applied to H, some volatile components were separated from the biomass, but most of them were recondensed on the HTH sample as a closed vessel reactor was used. These high-viscosity hydrocarbons caused an increase in the activation energy of the sample volatilization reactions. This result was in an agreement with the literature as pyrolysis of hydrothermal pre-treated karanj fruit [55] and pine tree waste [73].

3.3. Comparative results of biomass and pretreated biomass samples kinetic analysis

The comparative kinetic analyses results of biomass and pre-treated biomass samples were given in Table 4. Although different assumptions were accepted while deriving the KAS and OFW methods, the closer activation energy results showed that the reliability and applicability of the methods. The activation energy, pre-exponential factor and reaction degree values changed with the pre-treatment of biomass. A similar trend was observed in the change of activation energy values by applying different pre-treatments to the different biomass samples. This can be explained by changing the actual reaction rates due to the change in the biomass structure [50]. Acid pre-treatment of F provided the decrease on the pre-exponential factor and the activation energy values. With the application of hydrothermal pre-treatment of F, both the pre-exponential factor and the reaction degree values decreased, and accordingly, the desire of the molecules to come across and react with each other decreased. Thus, the activation energy value required for pyrolysis reactions also increased [63]. Similar to the hydrothermal pretreatment of F, the pretreatment of P and H decreased the reaction degree and pre-exponential factor values, which were the measure of the interaction of molecules, and accordingly, the activation energy values increased [67].

Possible reactions during the pyrolysis process were summarized in Table 5. At low conversion values (<0.2), weak bonds were broken. So that, the activation energy value was low in this conversion range. While conversion was between 0.2 and 0.6, the bonds in the straight chain structure began to break and the activation energy required for the reactions to occur increased. When the conversion value was higher than 0.6, lignin degradation reactions and forming carbon-rich structures began.

Table 4
Comparative results of pyrolysis kinetics of fir wood sawdust (F), acid pre-treated fir wood sawdust (AF), hydrothermal pre-treated fir wood sawdust (HTF), pine wood sawdust (P), acid pre-treated pine wood sawdust (AP), hydrothermal pre-treated pine wood sawdust (HTP), hazelnut shell (H), acid pre-treated hazelnut shell (AH) and hydrothermal pre-treated hazelnut shell (HTH) samples.

Biomass Sample	Ea (kJ/mol)		A (min^{-1})	n
	KAS	OFW	CR	CR
F	157.79	159.33	8.6×10^6-2.0×10^8	0.8
AF	151.42	153.61	3.1×10^6-1.9×10^8	0.9
HTF	203.10	216.60	3.6×10^6-3.2×10^8	0.2
P	124.74	127.26	1.9×10^7-2.5×10^9	1.9
AP	171.14	172.25	1.9×10^8-5.9×10^9	0.1
HTP	190.31	201.33	2.5×10^6-2.5×10^8	0.2
H	157.78	159.53	3.1×10^3-7.6×10^4	0.4
AH	213.40	210.02	2.7×10^8-1.9×10^{10}	0.1
HTH	186.36	206.47	2.5×10^6-3.0×10^8	0.2

Table 5
Possible reactions during the pyrolysis vs. conversion.

Conversion	Ea (kJ/mol)	Possible Reactions
0.1–0.2	Low	Scission of weak chain during hemicellulose volatilization
0.2–0.3	High	Scission of bonds in straight chains
0.3–0.4	High	Decreasing of polymerization degree of cellulose, shortening of chain length and conversion to active cellulose.
0.5	Low	Degradation of active cellulose
0.6	High	Degradation of lignin
0.7–0.8	High	The formation of carbon-rich structures by cross-linking of polymer chains and polycondensation reactions.

4. Conclusion

In this study, TG analyzes were performed at different heating rates in order to calculate the kinetic parameters for the pyrolysis reactions of biomass and pretreated biomass samples. The characteristic temperatures in the thermal decomposition zone increased by the heating rate increased and consummation time of the pyrolysis reactions decreased. In addition, the reaction zones shifted towards the higher temperature and the peak heights increased as the heating rate increased. It can be explained by a more homogeneous temperature profile was obtained up to the inner part of the particle by heating the biomass at low heating rates. Accordingly, the heat transfer efficiency was reduced at high heating rates. The calculated activation energy values with KAS and OFW methods were in harmony with each other. The pyrolysis reactions mechanism changed as the degradation continued throughout caused the calculated activation energy values to differ at varying conversion values. It was observed that when the conversion value was greater than 0.6, the depolymerization reactions of cellulose and hemicellulose were completed and the lignin degradation reactions started. Acid pre-treatment caused the increasing in activation energies of biomass samples except from F. According to the biomass type, the effect of pre-treatment techniques on thermal degradation reactions of biomass samples can be different. A higher activation energy indicated that the reactions took place more slowly. In case, hydrothermal pretreatment caused a decrease in the reaction degree and an increase in the activation energy in all three biomass samples. These results showed that the biomass samples volatilize more easily than pre-treated biomass samples. The reaction rate was also higher than the hydrothermal pre-treated biomass samples. In general, it was determined that the required energy for the pyrolysis reactions increased when different pre-treatment techniques was applied to the biomass samples. This result can be explained by the removal of inorganic components that catalyzed the pyrolysis reactions by applying acid pre-treatment. In addition to this, while applying hydrothermal pretreatment, the volatile components condensed again and accumulated on the biomass surface. The condensed species prevented the easy volatilization of biomass. In conclusion, the calculated kinetic parameters showed that the activation energy values in thermal degradation reactions of pre-treated biomass have been increased.

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Author contributions

EY: conceptualization, validation, investigation, formal analysis, resources, writing—original draft, NO: methodology, project administration.

Data availability

Not applicable.

Code availability

Not applicable

Conflicts of interest

The author doesn't have any conflicts of interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

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