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	Organization	Sabancı University
	Address	Orhanli, Tuzla, Istanbul, 34956, Turkey
	Email	yyurum@sabanciuniv.edu
Author	Family Name	Dumanli
	Particle	
	Given Name	Ahu Gümrah
	Suffix	
	Division	Faculty of Engineering and Natural Sciences
	Organization	Sabancı University
	Address	Orhanli, Tuzla, Istanbul, 34956, Turkey
	Email	
Author	Family Name	Taş
	Particle	
	Given Name	Sinem
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Co-firing of biomass with coals. 1. Thermogravimetric kinetic analysis of combustion of fir (*abies bornmulleriana*) wood

Ahu Gümrah Dumanli · Sinem Taş ·
Yuda Yürüm

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Abstract The chemical composition and reactivity of fir (*Abies bornmulleriana*) wood under non-isothermal thermogravimetric (TG) conditions were studied. Oxidation of the wood sample at temperatures near 600 °C caused the loss of aliphatics from the structure of the wood and created a char heavily containing C–O functionalities and of highly aromatic character. On-line FTIR recordings of the combustion of wood indicated the oxidation of carbonaceous and hydrogen content of the wood and release of some hydrocarbons due to pyrolysis reactions that occurred during combustion of the wood. TG analysis was used to study combustion of fir wood. Non-isothermal TG data were used to evaluate the kinetics of the combustion of this carbonaceous material. The article reports application of Ozawa–Flynn–Wall model to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the combustion of the fir wood. The average activation energy related to fir wood combustion was 128.9 kJ/mol, and the average reaction order for the combustion of wood was calculated as 0.30.

Keywords Co-firing · Combustion · Thermogravimetric analysis · Non-isothermal kinetics · Activation energy of combustion

Introduction

Biomass (wood, agricultural residues, forestry residues, energy crops, etc.) is a renewable fuel and the fourth largest

following coal, oil, and natural gas [1]. Compared with fossil fuels, biomass has the advantages of being harmless in regard to the emissions of carbon dioxide, as this participates in biomass growth through the photosynthesis reactions, and reducing pollutant species generation, given the low sulfur and nitrogen contents. From an economic point of view, the possibility of co-firing of biomass with coal in power plants can be an interesting alternative, since it allows for the use of existing infrastructures already equipped with proper devices for emission control, reducing simultaneously fossil fuels consumption [2]. Information of the chemical composition and reactivity of the biomass, the thermal phenomena occurring during solid fuels combustion is very important for the effective operation of conversion units.

Thermal analysis methods have been extensively used in recent years, because they offer a quick quantitative technique for the assessment of pyrolysis or combustion processes under non-isothermal conditions and allow to guess the effective kinetic parameters for the various decomposition reactions [3–13]. Kinetics of coal-biomass combustion has been investigated by many research groups recently [14–17].

The reaction kinetics parameters of combustion of wood under differential oxidizing conditions were calculated with the method given in Sanchez et al. [18] as follows. The rate of heterogeneous solid-state reactions can generally be explained by

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (1)$$

where t is time, $k(T)$ the temperature-dependent constant, and $f(\alpha)$ a function described the reaction model, which expresses the dependence of the reaction rate on the extent of reaction, α . The temperature dependence of the rate

A1 A. G. Dumanli · S. Taş · Y. Yürüm (✉)
A2 Faculty of Engineering and Natural Sciences, Sabanci
A3 University, Orhanli, Tuzla, Istanbul 34956, Turkey
A4 e-mail: yyurum@sabanciuniv.edu

69 constant is explained by the Arrhenius equation. Thus, the
70 rate of a solid-state reaction can generally be illustrated by

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}} f(\alpha) \quad (2)$$

72 where A is the pre-exponential Arrhenius factor, E the
73 activation energy, and R the gas constant.

74 For dynamic data obtained at a constant heating rate

$$\beta = \frac{dT}{dt} = \text{constant}$$

76 this term is inserted in Eq. 2 so the above rate expression
77 can be converted into non-isothermal rate expressions
78 describing reaction rates as a function of temperature at a
79 constant β .

$$\frac{d\alpha}{dT} = \frac{1}{\beta} Ae^{-\frac{E}{RT}} f(\alpha) \quad (3)$$

81 Integrating up to conversion, α , Eq. 3 gives,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT \quad (4)$$

83 Isoconversional methods include carrying out a series of
84 experiments at different heating rates [19, 20]. In this study,
85 activation energies from dynamic data were obtained from
86 isoconversional method by Ozawa [21, 22], Flynn and Wall
87 [23] using the Doyle's approximation of $p(x)$ [24], which
88 involves measuring the temperatures corresponding to fixed
89 values of α from experiments at different heating rates.

$$\ln(\beta) = \ln \left[\frac{AE}{Rg(\alpha)} \right] - 5331 - 1052 \frac{E}{RT} \quad (5)$$

91 From this equation, the activation energy E may be
92 estimated by plotting $\ln(\beta)$ versus $1/T$.

93 To find out the reaction order, Avrami's theory [25–27]
94 was used to describe non-isothermal cases, where variation
95 of the degree of conversion with temperature and heating
96 rate can be explained as

$$\alpha(T) = 1 - \exp \left[-\frac{k(T)}{\beta^n} \right] \quad (6)$$

98 Taking the double natural logarithm of both sides of
99 Eq. 6, with $k(T) = Ae^{-E/RT}$, yields

$$\ln[-\ln(1 - \alpha(T))] = \ln A - \frac{E}{RT} - n \ln \beta \quad (7)$$

101 Therefore, a plot of $\ln[-\ln(1 - \alpha(T))]$ versus $\ln \beta$, which
102 is obtained at the same temperature from a number of
103 isotherms taken at different heating rates, should give in
104 straight lines whose slope will have the value of the
105 reaction order or the Flynn–Wall–Ozawa exponent n [21,
106 28]. Extra aspects of the technique applied to examine the
107 process are explained by Ozawa [22].

The aim of this study was to determine the chemical
composition and reactivity of fir wood under non-isothermal
thermogravimetric (TG) conditions. This study provided a
kinetic evaluation of the combustion of fir wood. The Ozawa–
Flynn–Wall model was used to deal with non-isothermal TG
data to calculate the activation energy of the fir wood
combustion. The data obtained will be useful to understand
the behavior of fir wood during combustion. The information
obtained will be used in the co-firing of the wood with low
rank Turkish coals.

Experimental

Materials and characterization

The fir wood sample used in this study was a bark-free fir
(*Abies bornmulleriana*) sawdust sample obtained from Bolu
forests (northwest Anatolia) in Turkey. The proximate and
elemental analyses of the wood sample were done at the
Instrumental Analysis Laboratory of the Scientific and Technical
Research Council of Turkey, Ankara, is given in Table 1. The
sawdust was ground and sieved to below 175 μm (–80 mesh)
size. Wood sample was characterized in terms of proximate
analysis according to the ASTM standards (ASTM E871, ASTM
D1102-84, ASTM D3172-89) using laboratory furnaces, ultimate
analysis using CHN-600 and S532-500 analyzers (ASTM
D3176-93, ASTM D3177-33). Calorific values of the samples
were determined with a Parr 6100 calorimeter according to
ASTM D2015-95 in our laboratories.

Thermogravimetric analysis

Wood combustion tests were performed in a Netzsch STA
449 C Jupiter differential thermogravimetric analyzer (precision
of temperature measurement ± 2 °C, microbalance sensitivity
 < 5 μg), with which the sample weight loss

Table 1 Proximate and elemental analyses of fir wood

Proximate analysis/% (as received)	
Volatile matter	85.5
Fixed carbon	10.5
Moisture	3.7
Ash	0.3
Elemental analysis/% (daf)	
Carbon	47.2
Hydrogen	6.1
Nitrogen	0.3
Oxygen (by difference)	46.7
H/C (atomic)	1.55

140 and rate of weight loss as functions of time or temperature
 141 were recorded continuously, under dynamic conditions, in
 142 the range 25–1000 °C. The experiments were carried out
 143 under an air atmosphere, with a flow rate of 60 mL/min,
 144 and combustion of the samples was performed in the fur-
 145 nace of the thermobalance under controlled temperature to
 146 obtain the corresponding TG curves with heating rates (β)
 147 of 5, 10, 20, and 30 °C/min as it was also conducted in
 148 current literature [29, 30]. Preliminary tests with different
 149 sample masses and sizes and gas flow rates were carried
 150 out, to check the influence of heat and mass transfer.
 151 20–25 mg of each material, of ~ 250 μm particle size, was
 152 found to be optimum to eliminate the effects of eventual
 153 side reactions and mass and heat transfer limitations, was
 154 thinly distributed in the crucible in the experiments. The
 155 experiments were replicated at least twice to determine
 156 their reproducibility, which was found to be satisfactory.

157 The TG–FTIR runs were carried out in a Netzsch STA
 158 449 C Jupiter TG system coupled to a Bruker Equinox 55
 159 FTIR spectrometer under a dynamic air atmosphere. TG
 160 analysis was done from 25 to 1000 °C at a linear heating
 161 rate of 10 °C/min. The output of the TGA system was
 162 connected to the FTIR spectrometer through a heated line.
 163 The balance adapter, the transfer line, and the FTIR gas
 164 cell can be heated until 250 °C, thus avoiding the con-
 165 densation of the less volatile compounds. On the other
 166 hand, the low volumes in the thermobalance microfurnace,
 167 transfer line, and gas measurement cell permit low carrier
 168 gas flow rates to be used and allow for good detection of
 169 the gases evolved in the pyrolysis process. In all the
 170 experiments, the transfer line and the gas measurement cell
 171 were maintained at 200 °C. Online gas analyses were
 172 performed for the detection of combustion gases fed to
 173 FTIR spectrometer, and experimental data were stored as a
 174 function of time.

175 FTIR spectra

176 FTIR spectra of the original and fir wood samples oxidized
 177 under an air atmosphere at 200, 300, 350, 380, 400, 500,
 178 and 600 °C were obtained using a Bruker Equinox 55 FTIR
 179 spectrometer equipped with an ATR system by co-adding
 180 20 scans over the range 600–4000 cm^{-1} performed at
 181 1 cm^{-1} of digital resolution. The assignment of the bands
 182 in the FTIR spectra was according to Shevla [31].

183 Scanning electron microscopy

184 Morphology of the wood and its ashes was examined by
 185 scanning electron microscopy. Leo Supra 35VP Field
 186 emission scanning electron microscope (SEM), Leo 32 and
 187 energy dispersive X-ray spectrometer (EDS) were used for
 188 images and analyses of the major ash-forming elements in

189 different ashes. Wood and ash samples were mounted on
 190 stubs and gold-coated before analysis, to make them
 191 electrically conductive. Imaging was generally done at
 192 2–5 keV accelerating voltage, using the secondary electron
 193 imaging technique.

194 Results and discussion

195 SEM–EDS analysis

196 Morphology of the wood and its ash obtained at 900 °C
 197 was investigated by SEM, Fig. 1. Physical appearances of
 198 wood and its ashes were quite different. The SEM photo-
 199 graphs indicated that these contained material with diverse
 200 morphology. While micro structure of the wood contained
 201 amorphous, the ash was consisted of some prismatic,
 202 mainly micron-scale cubical forms of 0.2 μm size. EDS
 203 analysis of the wood ash revealed, Table 2, that the ash
 204 contained unburned carbon and in the order of decreasing
 205 percentage oxides of calcium, aluminum, potassium,
 206 magnesium, and sodium. Ash elements can exert a catalytic

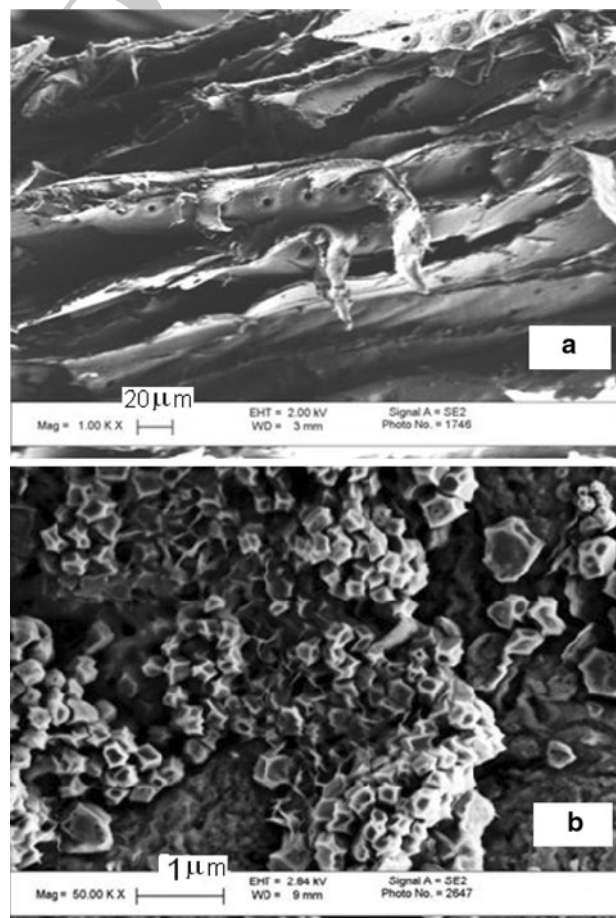


Fig. 1 SEM micrographs of a fir wood and b residue of fir wood fired at 900 °C

Table 2 EDS analysis results of the ash obtained at 900 °C

Element	Series	Net	Unnor. wt%	Norm. wt%	At.%
Carbon	K series	293	5.9456	5.2861	10.3084
Oxygen	K series	2458	39.9036	35.4771	51.9369
Magnesium	K series	164	1.2457	1.1075	1.0673
Calcium	K series	305	43.7126	38.8635	22.7127
Sodium	K series	76	0.5506	0.4895	0.4987
Aluminum	K series	1035	9.3138	8.2806	7.1883
Potassium	K series	197	11.8048	10.4953	6.2874

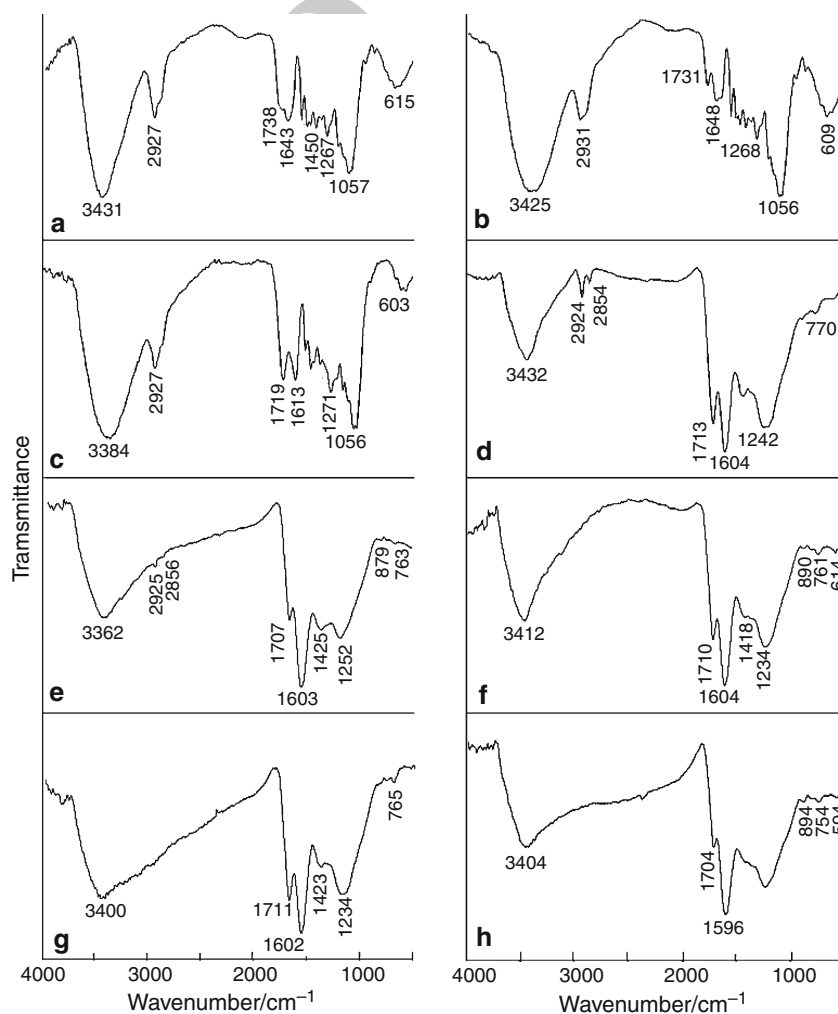
207 role on the reactivity of organic material during combustion of the wood. Karabakan and Yürüm [32] found that
 208 mainly carbonates of calcium and magnesium have a mild
 209 effect to promote the oxidation organic material in carbonaceous fuels.
 210
 211

212 FTIR analysis of the original and oxidized fir wood

213 FTIR spectra recorded in the 400–4000 cm^{-1} region of
 214 original fir wood and oxidized fir wood are presented in

Fig. 2. FTIR spectrum of the wood, Fig. 2a, contained a strong broad O–H stretching at 3300–4000 cm^{-1} , C–H stretching at 2800–3000 cm^{-1} , and several distinct peaks in the finger print region between 500 and 1750 cm^{-1} . Most of these bands have contribution from both carbohydrates (cellulose and hemicellulose) and lignin. More specifically, the bands at 3431 and 1450 cm^{-1} (characteristic of hydrogen bonded OH groups), 2927 and 1470 cm^{-1} (C–H stretching of methyl or methylene groups) [31]. The band at 1738 cm^{-1} in the spectrum of the wood is due to uranic acid and acetyl groups in the hemicellulosic material of the wood [33]. The presence of a sharp signal at 1643 cm^{-1} can be attributed to the aromatic rings in quinonic structures. Specific band maxima in 1260–1000 cm^{-1} regions were related with ring vibrations overlapped with stretching vibrations of (C–OH) side groups and the (C–O–C) glycosidic bond vibration, typical of xylans. Bands at 1267 and 1057 cm^{-1} are indicative of hemicelluloses. Bands in the range of 1270–1050 cm^{-1} belong to C–O and C–O–C groups [33].

Fig. 2 FTIR spectra of
 a original fir wood and fir wood
 oxidized at b 200 °C, c 300 °C,
 d 350 °C, e 380 °C, f 400 °C,
 g 500 °C, and h 600 °C



236 The FTIR spectra of the wood oxidized at 200, 300, 350,
 237 380, 400, 500, and 600 °C are presented between Fig. 2b
 238 and h, respectively. The significant change in the spectra of
 239 oxidized wood seemed in the intensity of C–H stretching of
 240 methyl or methylene peaks in the zone 2930–2924 cm⁻¹,
 241 decreased steadily until 380 °C and beyond this tempera-
 242 ture these functionalities appeared to be lost. The other
 243 significant change was the nascence of new absorption
 244 bands due to oxygenated functions such as C–O distin-
 245 guished in the zone of 1731 and 1704 cm⁻¹. As the oxi-
 246 dation temperature was increased from 300 to 600 °C
 247 intensity of the C–O band increased and the peaks shifted
 248 from 1731 to 1704 cm⁻¹ strongly suggesting a rearrange-
 249 ment among the C–O functionalities during oxidation, the
 250 1734 cm⁻¹ band is characteristic of non-conjugated car-
 251 bonyl group [34]. The third important change was sharp
 252 increase in the intensity of the absorption bands due to
 253 aromatic ring breathing vibrations near 1600 cm⁻¹, indi-
 254 cating the formation of a product of high aromaticity.
 255 Therefore, oxidation of the wood sample at temperatures
 256 near 600 °C caused the loss of aliphatics from the structure
 257 of the wood and created a char heavily containing C–O
 258 functionalities and of highly aromatic character.

259 TG–FTIR experiments

260 The evolution of gaseous species and products as a result of
 261 the oxidation of wood sample was simultaneously moni-
 262 tored by FTIR during the TG experiment at the heating rate
 263 of 10 °C/min. The FTIR spectra of the gases evolved
 264 during are presented in Fig. 3. The spectra were detected at
 265 increasing times, and the corresponding temperatures at
 266 which the spectra were recorded are denoted on the spectra.
 267 Spectra indicated the nascence and development of certain

268 peaks. Bernstein et al. [35] who investigated the infrared
 269 spectra of CO₂ indicated the following peaks were due to
 270 CO₂: 3720, 3600, 3300, 2375, 1620, 750, and 675 cm⁻¹.
 271 Lemus [36] who studied on infrared spectra of water vapor
 272 showed that the peaks at 3756, 3657, and 1594 cm⁻¹ were
 273 due to water vapor. Spectra recorded in this study con-
 274 tained the following peaks: 3720, 3563, 2375, and
 275 1688 cm⁻¹ due to CO₂, 3188 [37] and 1550 cm⁻¹ due to
 276 water vapor, and 844 cm⁻¹ due to hydrocarbons. The large
 277 peak at 3188 cm⁻¹ in the spectrum obtained in the 2833rd
 278 second that was due to water vapor indicated the combu-
 279 sion of hydrogen content of the wood, that was also an
 280 indication of high hydrogen content of the wood (H/
 281 C = 1.55). On-line FTIR recordings of the combustion of
 282 wood indicated the oxidation of carbonaceous and hydro-
 283 gen content of the wood and release of some hydrocarbons
 284 due to pyrolysis reactions that occurred during combustion
 285 of the wood.

Heat treatment of wood under oxidative and non-oxidative atmospheres

288 In this study, the wood sample was subjected to heat
 289 treatment at different temperatures between 100 and
 290 400 °C in the presence of air. The mass loss according to
 291 the heat treatment was recorded, and calorific values of the
 292 samples were measured using an adiabatic calorimeter. The
 293 results were compared with the untreated wood sample.
 294 Results are shown in Table 3. According to the calorific
 295 value results, during the heat treatment of the wood sample
 296 under an air atmosphere, up to 200 °C the calorific value of
 297 the wood increased from 18746 to 19521 kJ/kg due to the
 298 removal of the low volatile compounds. As the heat
 299 treatment temperature was increased to 300 °C and higher

Fig. 3 TGA–FTIR spectra of gases released during combustion of fir wood heated under a dynamic air atmosphere from 25 to 1000 °C by a heating rate of 10 °C/min

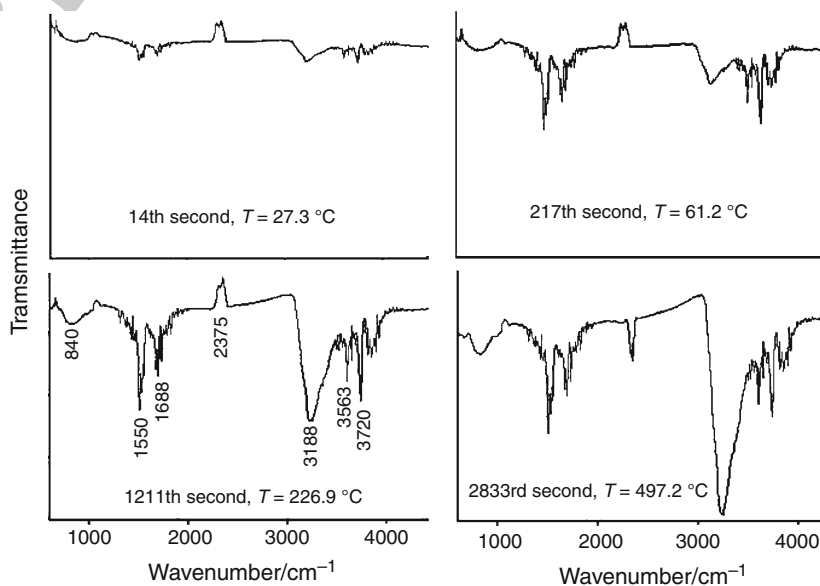


Table 3 Effect of heat treatment under an air atmosphere on the calorific values of the wood

Heat treatment temperature/°C	Mass loss/%	Calorific value/kJ/kg
Unheated	–	18746
100	5.9	19135
200	11.0	19521
300	32.0	3149
400	99.3	–

Table 4 Effect of heat treatment under an argon atmosphere on the calorific values of the wood

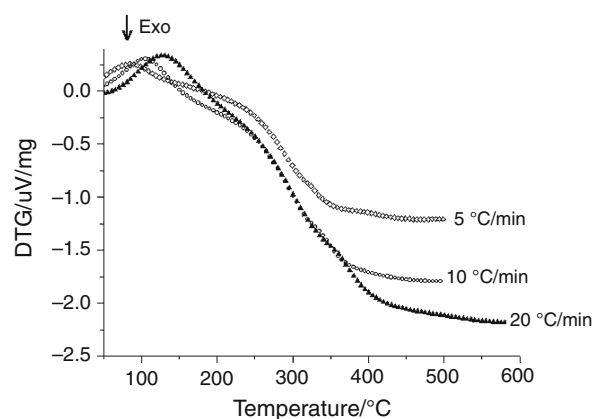
Heat treatment temperature/°C	Mass loss/%	Calorific value/kJ/kg
Unheated	–	18746
100	10.1	19001
200	11.7	19910
300	27.0	24210
400	97.1	–

300 temperatures, parallel to the pyrolytic losses of carbona-
 301 ceous material from the structure of the wood and combu-
 302 stion of the carbonaceous material the calorific values
 303 decreased sharply to 3149 kJ/kg.

304 The same experiment was repeated under an argon
 305 atmosphere, and the results are shown in Table 4. In these
 306 experiments, the calorific values steadily increased from
 307 18746 to 24210 kJ/kg due to the removal of volatiles
 308 producing residual matter rich in carbon. Further increase
 309 of the temperature volatilized all the carbonaceous mater-
 310 ial. The TG experiments gave information of the percent
 311 material loss during heat treatment.

312 TG experiments

313 This study on reactivity of wood, useful for kinetic anal-
 314 ysis, was mainly based on TG measurements. DTG tracings
 315 obtained during the oxidation of wood with different
 316 heating rates were presented in Fig. 4. The TG curves
 317 measured from the temperature programmed combustion
 318 of the wood samples at the heating rates (β) of 5, 10, 20,
 319 and 30 °C/min were illustrated in Fig. 5. As it might be
 320 examined, on raising the temperature, combustion of the
 321 sample occurred with a related mass loss. Once the fuel
 322 content of the wood was consumed, the mass correspond-
 323 ing to the ashes stayed constant. Given the small sample
 324 amounts and the relatively slow heating rates, the weight
 325 loss versus temperature curves showed several sequential
 326 zones, as in the example for wood exposed to air. The
 327 weight loss versus temperature curves showed several

**Fig. 4** DTG tracings obtained during the oxidation of wood with different heating rates

328 sequential zones, as in the example for wood exposed to
 329 air. The first zone of weight loss, temperatures below
 330 390 °C and conversion up to 60%, was the pyrolysis (or
 331 devolatilization) stage, whose characteristics were affected
 332 by the presence of oxygen in the reaction environment.
 333 Char oxidation, adjoining solid pyrolysis, was completed at
 334 about 875 °C.

335 Figure 5 shows the TG mass loss curve of the wood with
 336 at various heating rates (β) (5, 10, 20, and 30 K/min) to
 337 study the effect of heating rate on non-isothermal kinetics.
 338 There were two main temperatures for mass losses for
 339 every heating rate (Fig. 5). The first temperature range was
 340 339.2–381.1 °C; as the heating rate was increased the
 341 greater mass losses were detected at higher temperatures.
 342 The second temperature range at which more material loss
 343 occurred was 537.9–875.7 °C; in this range, higher heating
 344 rates caused higher losses at more elevated temperatures.
 345 Residual masses in the range of 1.01–2.24% were obtained
 346 at about 1009–1019 °C. So there were several steps for
 347 mass losses; at 95 °C humidity of the wood was lost,
 348 depending on the heating rate at about 340–380 °C,
 349 56–62% of the volatiles were lost and in the temperature
 350 range of 540–875 °C the total material loss reached to
 351 96–98%. Higher heating rates caused higher material loss
 352 compared to the loss of material at lower heating rates.
 353 Since small masses of wood (20–25 mg) were utilized in
 354 each experiment, and particle size of the wood was reduced
 355 to <250 μ m, mass and heat transfer limitations were
 356 eliminated. The data obtained using different heating rates
 357 during firing experiments, therefore, did not contain any
 358 restrictive resistances. As the heating rate was increased,
 359 the maximum mass loss and/or maximum rate of combu-
 360 stion shifted to higher temperatures. This was attributed
 361 to the changes in the rate of heat transfer with the increase
 362 in the heating rate and the short exposure time to a par-
 363 ticular temperature at high heating rates, as well as the
 364 effect of the kinetics of combustion.

Fig. 5 TG tracings obtained during the oxidation of wood with different heating rates in the temperature range of 25–1000 °C

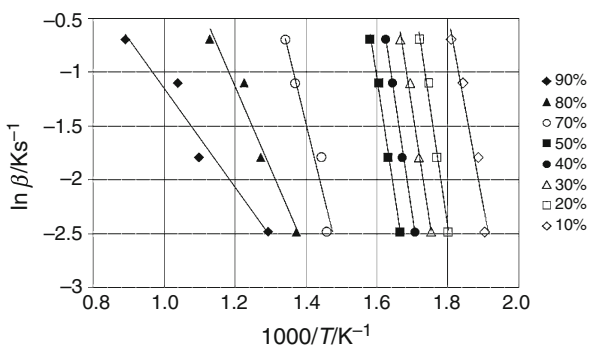
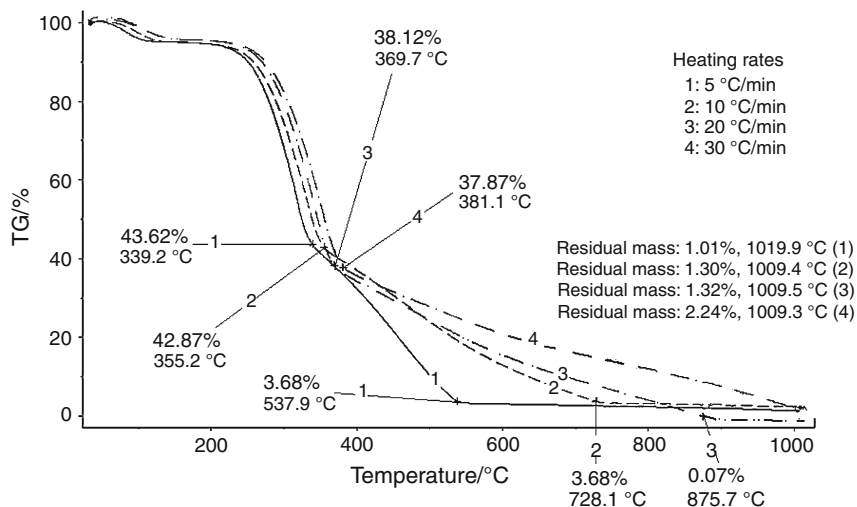


Fig. 6 Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the combustion of fir wood at different heating rates for the calculation of activation energies

365 Eight different percentages of conversion (α) are pointed
 366 out in each curve in Fig. 5: 10, 20, 30, 40, 50, 70, 80,
 367 and 90%. The plots of $\ln \beta$ versus $1/T$ corresponding to the
 368 several conversion degrees of the process were shown in

Fig. 6 for wood. Generally, there were linear relations for 369
 the conversion percentages so the activation energies were 370
 calculated from the corresponding slopes according to the 371
 Ozawa–Flynn–Wall kinetic method, Table 5. Raising the 372
 temperature, combustion of the sample occurred with mass 373
 losses and related decrease in activation energies. Activa- 374
 tion energy calculated at 10% conversion was 142.3 kJ/mol 375
 and steadily increased until 50% conversion to a value of 376
 169.8 kJ/mol then as the material loss increased beyond 377
 this point, the activation energy started to decrease until 378
 36.4 kJ/mol at conversion of 90%. It seemed that the first 379
 phase of reactions constituted the rate determining set of 380
 reactions with average activation energy of 165.8 kJ/mol. 381
 Beyond 70% conversion in combustion reactions, the 382
 average activation energy dropped to 67.6 kJ/mol. The 383
 overall average activation energy of the combustion of the 384
 wood was calculated to be 128.9 kJ/mol. This value 385
 calculated for fir wood seemed to be higher than those, 386
 54–92 kJ/mol, calculated by Kök [38] for some Turkish 387

Table 5 Slopes and correlation coefficients (R^2) corresponding to linear fittings to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the combustion of wood at different heating rates together with the resultant activation energy (E) values

Conversion/%	R^2	Slope	Activation energy/kJ/mol	Average activation energy/kJ/mol
10	0.953	-18.01	142.3	Rate determining phase 165.8
20	0.987	-22.51	177.9	
30	0.988	-21.07	166.5	
40	0.997	-21.83	172.5	
50	0.993	-21.48	169.8	
70	0.936	-13.44	106.2	Fast reactions 67.6
80	0.959	-7.61	60.1	
90	0.951	-4.61	36.4	
Overall average activation energy/kJ/mol				128.9

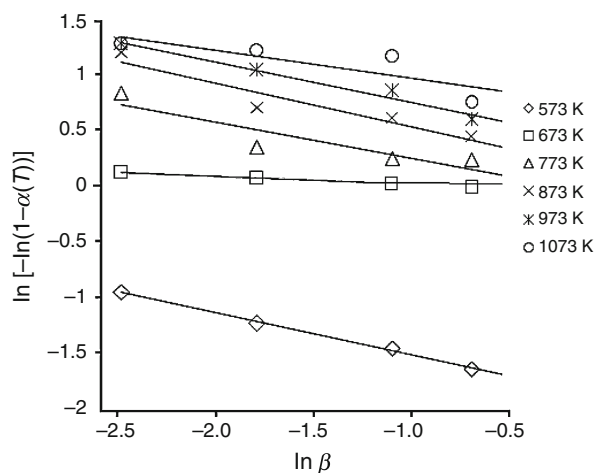


Fig. 7 Straight lines fitting to Ozawa–Flynn–Wall kinetic model for various conversion percentages corresponding to the combustion of wood at different heating rates for the determination of reaction order n

Table 6 Reaction order (n) as a function of temperature for the combustion of wood

$T/^\circ\text{C}$	Reaction order/ n
300	0.38
400	0.10
500	0.32
600	0.39
700	0.36
800	0.25
Average n	0.30

low rank coals using Coats and Redfern method [39], but lower than those calculated for the combustion of biomass using the Ozawa–Flynn–Wall kinetic method, 140 kJ/mol [18]. Otero et al. [40] using the Ozawa–Flynn–Wall kinetic method with a semianthracite coal calculated the average activation energy of combustion as 67.3 kJ/mol.

For the computation of the reaction order, the plots of $\ln[-\ln(1 - \alpha(T))]$ versus $\ln \beta$ have been represented in Fig. 7. The n values as a function of temperature for wood combustion are shown in Table 6. The values changed from very close to zero to around 0.3 and are dependent on the extent of the reaction, i.e., not constant during the reaction, which was an evidence of the multiple step processes such as devolatilization and combustion. The lowest value for n was measured at 400 °C at which the slope of the % TG versus temperature curves changed sharply indicating a change in the combustion regime. After this temperature, the order of the reaction again raised to values close to the average value of 0.30.

Conclusions

EDS analysis of the wood ash revealed that the ash contained unburned carbon and in the order of decreasing percentage oxides of calcium, aluminum, potassium, magnesium, and sodium. Oxidation of the wood sample at temperatures near 600 °C caused the loss of aliphatics from the structure of the wood and created a char heavily containing C–O functionalities and of highly aromatic character. On-line FTIR recordings of the combustion of wood indicated the oxidation of carbonaceous and hydrogen content of the wood and release of some hydrocarbons due to pyrolysis reactions that occurred during combustion of the wood. Heat treatment of the wood sample under an air atmosphere, up to 200 °C, caused the calorific value of the wood to increase from 18746 to 19521 kJ/kg due to the removal of the low volatile compounds. As the heat treatment temperature was increased to 300 °C and higher temperatures, parallel to the pyrolytic losses of carbonaceous material from the structure of the wood and combustion of the carbonaceous material the calorific values decreased sharply to 3149 kJ/kg. The weight loss versus temperature curves showed several sequential zones, as in the example for wood exposed to air. The first zone of weight loss, temperatures below 390 °C and conversion up to 60%, was the pyrolysis (or devolatilization) stage, whose characteristics were affected by the presence of oxygen in the reaction environment. Char oxidation, adjoining solid pyrolysis, was completed at about 875 °C. It seemed that the first phase of reactions constituted the rate determining set of reactions with average activation energy of 165.8 kJ/mol. Beyond 70% conversion in combustion reactions, the average activation energy dropped to 67.6 kJ/mol. The overall average activation energy of the combustion of the wood was calculated to be 128.9 kJ/mol. The value of order of reaction changed from very close to zero to around 0.3 and are dependent on the extent of the reaction, i.e., not constant during the reaction, which was an evidence of the multiple step processes.

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