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11th International Conference on Renewable Electrical Power Sources



PROCEEDINGS

Editor
Milica Vlahović

Belgrade, November 02-03, 2023

PROCEEDINGS

11th International Conference on Renewable Electrical Power Sources



2023

PROCEEDINGS
11th International Conference
on Renewable Electrical Power Sources

Chamber of Commerce and Industry of Serbia,
Belgrade, November 2 and 3, 2023

Publisher

Union of Mechanical and
Electrotechnical Engineers and
Technicians of Serbia (SMEITS)
Society for Renewable Electrical
Power Sources
Kneza Miloša str. 7a/II,
11000 Beograd

President to the Society
for Renewable Electrical
Power Sources
within the SMEITS

Prof. dr Zoran Lazarević

Editor

Dr Milica Vlahović, Full Research Professor
University of Belgrade
Institute of Chemistry, Technology and Metallurgy
National Institute of the Republic of Serbia

Tiraž
100 primeraka

CD umnožava
MT-KOMEX doo, Beograd

ISBN
978-86-85535-16-1

CIP - Каталогизacija у публикацији
Народна библиотека Србије, Београд

502.171:620.9(082)(0.034.2)

INTERNATIONAL Conference on Renewable Electrical Power Sources (11 ; 2023 ; Beograd)

Proceedings [Elektronski izvor] / 11th International Conference on Renewable Electrical Power Sources, Belgrade, November 02-03, 2023 ; [editor Milica Vlahović]. - Beograd : Union of Mechanical and Electrotechnical Engineers and Technicians of Serbia SMEITS, 2023 (Beograd : BEOŽivković). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemska zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 100. - Apstrakti. - Bibliografija uz svaki rad.
ISBN 978-86-85535-16-1

a) Енергетски извори -- Одрживи развој -- Зборници

COBISS.SR-ID 129137161

Organizer

Savez mašinskih i elektrotehničkih
inženjera i tehničara Srbije (SMEITS),
**Društvo za obnovljive izvore
električne energije**

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Sponsors

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MS Kablovi, Paraćin



Endorsement

MT-KOMEX, Beograd



Održavanje 11. MKOIEE finansijski je pomoglo
Ministarstvo nauke, tehnološkog razvoja i inovacija
Republike Srbije



Република Србија

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FOREWORD

The conditions created by the development of technologies in which modern man lives have led to a complex and paradoxical effect: that by removing obstacles on the way to a more comfortable, simpler, faster and more efficient life and way of working, man also generates numerous misfortunes, attracting dark clouds of threats to the survival of the planet and humanity. The question that concerns and affects all of us - all people, all living beings, systems in which life takes place, large and small, strong and weak - boils down to the problem of the negative impact of man on the environment; this issue invites us to an urgent solution by looking at the causes, proposing solutions, evaluating them, changing approaches and ways of thinking, as well as drawing correct conclusions. Simply put, by adapting nature to one's own needs, man threatens and damages it. That is why, with the joint efforts of all of us, individuals, organizations and states, it is necessary to take all possible measures to immediately prevent the negative effects that are ahead of us.

The importance of renewable sources of electricity, which this international conference focuses on, is noticeable from two angles: the first - it is certain that fossil fuels as a resource will disappear and it is necessary to find alternative sources, the second - the use of renewable energy sources by its essence implies "clean" technology that significantly contributes to reducing CO₂ emissions and thus mitigating climate change and reducing pollution, while encouraging social and economic development in all spheres of life.

The 11th International Conference on Renewable Electrical Power Sources is organized by the Society for Renewable Electrical Power Sources (DOIEE) at SMEITS, with co-organizers: The Institute of Architecture and Urban & Spatial Planning of Serbia (IAUS) and the Chamber of Commerce and Industry of Serbia, with the support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The registered participants designed their papers according to the given conference topics:

- Energy sources and energy storage;*
- Energy efficiency in the context of use of renewable energy sources (RES);*
- Environment, sustainability and policy;*
- Applications and services.*

Eminent authors - scientists, teachers, experts in this field from fifteen different countries: Algeria, Belgium, Bosnia and Herzegovina, China, Croatia, Greece, Hungary, India, Portugal, Saudi Arabia, Serbia, Slovenia, Spain, the United Arab Emirates, and Ukraine, contributed to the conference through sixty-nine papers that were reviewed by the Scientific Committee of the Conference, and after the review process were accepted for presentation at the conference and for publication in the proceedings.

At the end of this short message and at the beginning of the proceedings I believe that it can be proudly said that scientists, researchers, policy makers and industry experts gathered in one place, in order to exchange experiences and knowledge with the aim of promoting scientific and professional ideas and results of research, technology improvement for the use of RES, promoting the rational use of electricity, affirming and proposing inventive solutions in the field of sustainable sources of electricity.

*Belgrade,
November 2023*

Milica Vlahović

KINETIKA TERMALNE DEGRADACIJE LIGNOCELULOZNOG OTPADA NA BAZI KOŠTICA BRESKVE

THERMAL DEGRADATION KINETICS OF LIGNOCELLULOSIC PEACH STONE WASTE

Zorica LOPIČIĆ^{1,*}, Anja ANTANASKOVIĆ¹, Slobodan CVETKOVIĆ², Vladimir ADAMOVIĆ¹, Tatjana SOSTARIĆ¹, Jelena AVDALOVIĆ², Mirjana KIJEVCANIN³

¹Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey 86, 11000 Belgrade, Serbia, z.lopicic@itnms.ac.rs (*Correspondence)

²University of Belgrade, Institute of Chemistry, Technology and Metallurgy-National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia

³University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

Apstrakt

Smanjenje rezervi fosilnih goriva, kao i zagađenja koja nastaju njihovom upotrebom, povećali su interesovanje ka obnovljivim izvorima energije iz biomase (drvena biomasa, energetski usevi i otpad poreklom iz poljoprivredne i prehrambene industrije). Posebno interesantna je otpadna lignocelulozna (LCW) biomasa, koja nastaje u velikim količinama nakon prerade sirove biomase, a poseduje određene energetske karakteristike koje bi mogle ispuniti zahteve održivosti. Ovaj rad opisuje termičku razgradnju otpadnih koštica breskve (PS), ispitanu termogravimetrijskim analizama (TG/DTG) u neizotermnim uslovima. TG/DTG analize pružile su niz eksperimentalnih podataka (pod uslovima varirane brzine zagrevanja), koji su modelovani kinetičkim modelima, u cilju dobijanja parametara koji bi mogli biti korisni za njihovu industrijsku primenu. Cilj ispitivanja kinetike termičke razgradnje je uspostavljanje veze između brzine razgradnje, stepena konverzije (α) i temperature. Ispitivanje kinetike termičke razgradnje izvedeno je u struji kiseonika, variranjem brzine zagrevanja od 5 do 20 °C/min. Energija aktivacije (E_a) termičke razgradnje PS određena je primenom Flynn-Wall-Ozawa (FWO) izokonzervacionog modela. Mogući reakcioni mehanizam ispitan je primenom Coat-Redfern (C-R) modela. Vrednosti E_a dobijene izokonzervacionim modelima nisu bile konstantne sa promenom stepena konverzije (α), što ukazuje da termička razgradnja PS predstavlja kompleksan proces koji se ne može opisati jednostepenom reakcijom u celom opsegu konverzije. Otpadni uzorci PS, ispitan u ovom radu, imaju određena fizičko-hemijska svojstva koja ispunjavaju zahteve za energetsku gustinu, nizak sadržaj pepela i sigurno sagorevanje. Prikazani rezultati podržavaju primenu lignocelulozne otpadne biomase u razvoju cirkularne ekonomije u Srbiji.

Ključne reči: lignocelulozna otpadna biomasa; koštice breskve; termalna razgradnja; izokonzervacione metode; C-R model

Abstract

The decrease of fossil fuel resources as well as associated pollution induced by its applications has increased the interest in findings of renewable fuels from various biomasses such as wood, energy crops, and various waste disposed from agricultural and food-industry activities. Especially interesting is lignocellulosic waste (LCW) biomass, found in large quantities after processing of the raw biomass, which pose certain energetic properties that might be used to fulfil future sustainability demands. This paper describes the thermal decomposition of waste peach stones (PS) investigated via thermogravimetric (TG) analyses. TG/DTG analyses provided a set of experimental mass loss data (obtained under different conditions), which were modelled by different kinetic

models, resulting in parameters that might be used for industrial application of the tested biofuel. The goal of analyzing the kinetics of thermal degradation was to establish a relationship between the rate of degradation, degree of conversion (α) and temperature. In this sense, the investigation of the kinetics of thermal degradation was performed in non-isothermal conditions, with the heating speed varying from 5 to 20 °C/min in an oxygen stream. Activation energy (E_a) of the PS thermal degradation was determined using Flynn-Wall-Ozawa (FWO) isoconversional model free method. The possible reaction mechanism that controls the process was investigated by the method of Coats-Redfern (C-R). The values of the E_a obtained by this method were not constant with the change in the degree of conversion (α), indicating that the thermal decomposition of PS represents a complex process that cannot be described by a one-step reaction in the entire range of conversions. PS waste samples investigated in this paper, have certain physical and chemical properties which satisfy request for energy density, small ash content and safe burn out. Presented results might support the value of biowaste in a future circular bio economy of Serbia.

Key words: *lignocellulosic waste biomass; peach stone; thermal decomposition; isoconversional methods; C-R model*

1 Introduction

The energy generation from renewable materials has gained much attention in the previous decade due to the negative environmental impact of nonrenewable energy sources uses. In the same time, the decline of accessible fossil fuel resources is widely present. EU Energy Security Strategy proposed by EC (2014), has identified renewable alternatives that can deliver clean and renewable energy (RE) in order to replace fossil fuels, identifying biomass as an important RE source to reach the EU objectives. These objectives were oriented toward the possible decrease of the EU dependence on traditional fossil fuels, diversifying supply of energy but also reducing greenhouse gas emissions [1]. According to the RS Strategy for energy sector development, the RE greatest potential relies to biomass (app. 3.4 toe), representing more than a half of renewables potential. Unfortunately, although significant, this potential is still underutilized [2].

Biomass sources ranges from lignocellulosic materials like forestry and agricultural residues, to energy crops, municipal wastes, industrial and animal residues, coupled with having a net carbon-neutral effect on the environment; this makes it as option for use as a renewable energy source [3]. Lignocellulosic waste biomass mainly consists of cellulose, hemicellulose, and lignin, with small amounts of extractives, moisture, and mineral matter [4]. This biomass is used as feedstock for various thermochemical conversion processes including pyrolysis, gasification (gaseous fuels and other products) or direct combustion. Lignocellulosic waste biomass could serve as feedstock for one of the thermochemical conversion processes mentioned, but its complex heterogeneous composition results in multiple reaction that occur during the process of conversion. The extent of progress of these reactions is dependent on several parameters dependent on the kinetic rates of the reaction such as reaction temperature, residence time, feed rate, and heating rate [5]. Because of this, it is important to study the kinetics of biomass thermal decomposition, as it will result in prediction of the conversion process and promote understand of the mechanisms involved.

Thermogravimetric analysis (TGA) is a widely used technique in solid-phase thermal degradation studies that measures mass changes of a material with temperature. At very low heat- and mass-transfer effects, mass change results in many information such as thermal stability of the investigated sample, reactivity, reaction mechanism, decomposition kinetics etc. [3]. Investigation of thermal decomposition kinetic using TGA provides the thermal response of material degradation as a function of temperature over a certain period and under controlled temperature regime. It has been widely used to study materials originating from different biomass residues [6, 7, 8]. Non-isothermal TGA involves material heating to a desired temperature at a desired constant heating rate with time. It has been shown to be a very useful method as being applicable to complex multi-staged reactions, with good reliability and replicability. The application of isoconversional models (either differential or integral) allows the activation energy (E_a) estimation, as a function of temperature at a certain conversion (α) without previous assumptions on the reaction mechanism (model-free methods). The

most widely used differential method is the Friedmann method [9], while, among the others, integral methods include the Flynn–Wall–Ozawa (FWO) [10] and Kissinger–Akahira–Sunose (KAS) [11, 12].

The purpose of this work is to investigate the kinetics of thermal decomposition of waste peach stones (*Prunus persica* L.) by TGA where the thermal analysis curves were recorded at several linear heating rates. The FWO model-free non-isothermal method was used to calculate activation energy (E_a) and pre-exponential factor (k_o). Coats-Redfern model was used for prediction of the possible reaction mechanism that controls the process. The effect of heating rate on decomposition was also studied.

2 Experimental section

2.1 Material

Lignocellulosic waste biomass samples, peach stones (PS), were taken from the local fruit processing factory where they have been disposed as a waste. After receiving, samples were washed with tap water and dried at room condition for several days. Grinding of the samples into powder was performed by ultra-centrifugal mill “Retsch ZM-1” (Retsch, Gemini BV, Netherland). Samples were further screened through the series of wire sieves. For the purpose of experiments described in this paper, particles with diameter less than 0.1 mm were used.

2.2 Methods

TGA of the PS biomass sample was performed „NETZSCH 409 EP“ TG Instrument. The samples were dried for 24 h at 60 °C in order not to lose some of the volatiles. After this period of time, samples were kept in desiccator for 24 h, at relative humidity of 23 %. About 20 mg of the sample was placed in crucibles and thermally treated in oxygen stream from 20 to 1000 °C under different heating rates: 5, 10, 15 and 20 °C/min.

2.3 Kinetic Theory

The kinetics of reactions in solid-state are described by the following decomposition rate equation, where the dependence of the process rate on temperature, $k(T)$, is expressed by Arrhenius equation:

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

where $k(T)$ represents rate constant, $f(\alpha)$ is a general expression of the reaction mechanism and α represents extent of conversion at time t . Conversion degree, α , represents normalized form of weight loss data of decomposed sample which is defined as:

$$\alpha = \frac{m_o - m_t}{m_o - m_\infty} \quad (2)$$

where masses m_o , m_t , and m_∞ refer to the initial, instantaneous, and final mass of the sample, respectively. The temperature dependence of the rate constant k is given by:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where E_a and A are the activation energy (kJ/mol) and the pre-exponential factor (1/min), R is 8.314 J/Kmol, and T is absolute temperature (K).

Combination of equations (1) and (3) gives the fundamental expression (4) of analytical methods to calculate kinetic parameters, on the basis of TGA results:

$$\frac{d\alpha}{dt} = k_o \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \quad (4)$$

For non-isothermal TGA experiments at linear heating rate $\beta = dT/dt$, equation (4) can be written as:

$$\beta \frac{d\alpha}{dT} = k_o \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \quad (5)$$

Integrating equation (5), at constant heat speed, an integral equation is obtained (6):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_o}{\beta} \cdot \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT = \frac{k_o}{\beta} p(E_a, T) \quad (6)$$

Previous equation represents mathematical connection between k_o , E_a and $f(\alpha)$ and might be solved by some of the approximations or numerical methods [13].

2.4 Model free methods

These methods allow obtaining the kinetic parameters of a solid-state reaction without knowing the reaction mechanism. Flynn-Wall-Ozawa method.

The FWO method represents of the most commonly applied isoconversional methods, which linearizes the temperature integral in equation (6) using Doyle's empirical approximation [14]:

$$\ln p(x) \cong -5.3305 - 1.052 \quad (7)$$

The mathematical expression of the FWO method is given by the following equation [13]:

$$\ln \beta_i = \ln \left(\frac{k_o E_a}{g(\alpha) R} \right) - 5,3303 - 1,052 \frac{E_a}{RT_{\alpha,i}} \quad (8)$$

where $T_{\alpha,i}$ represents the temperature at which the degree of conversion α is experimentally significant at the heating rate β_i , and the label i refers to the number of experiments performed at different heating rates. Using equation (8), it is possible to calculate the apparent value of the activation energy E_a at a certain degree of conversion α , from the slope of the graph $\ln(\beta_i)$ vs. $1/T_{\alpha}$.

When the activation energy for the degradation process is evaluated, the next step is to determine what reaction mechanisms control the process obtaining the form of the function $f(\alpha)$. For this study, the method of Coats-Redfern (CR), applied at conversion ranges in which the E_a can be considered approximately constant, is used. This method approximates $p(E_a, T)$ using a Taylor series expansion to yield the following simplified expression:

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \frac{k_o R}{\beta E_a} - \frac{E_a}{RT} \quad (9)$$

By plotting $\ln[g(\alpha)/T^2]$ vs $1/T$, the value of the E_a is obtained. From the results, it can be set as a reaction mechanism which governs the decomposition process, in the different range of conversion tested, one with which the energy values are closest to the values obtained using the FWO method. Some of the most important rate equations used to describe the kinetic behavior of solid state reactions ($g(\alpha)$), which might be applied on C-R method are listed in Table 2 of [15].

3 Results and Discussion

3.1 Biomass Characterization-Analysis of TG Curves

The thermal stability of the PS sample was analyzed in such temperature range where it was possible to observe three defined stages of the sample degradation. TGA showed that there are at least three different phases in the mass change of the PS sample. The mass of the sample constantly decreases, indicating first the dehydration process, and then the thermal degradation of the PS structural components-hemicellulose, cellulose and lignin. According to the results, the first loss of PS mass starts already at about 50 °C with loss of moisture, Figure 1.

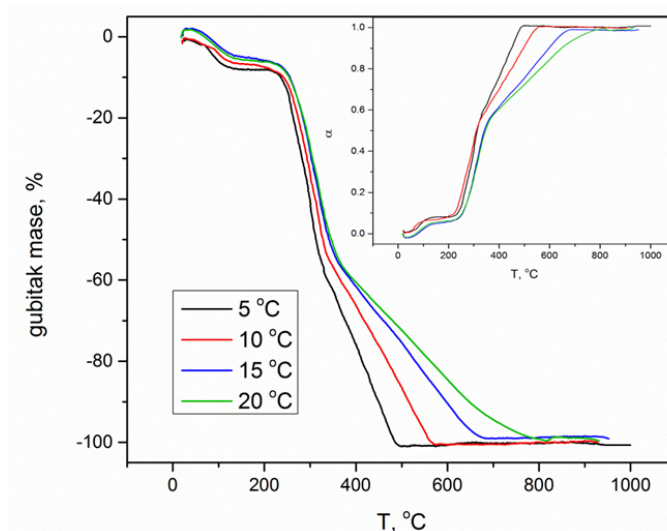


Figure 1. Weight loss as a function of temperature at different heat rates

Intense, asymmetric, endothermic DTG peak in the area of 50 - 125 °C (Figure not shown) with a maximum at 86 °C corresponds to dehydration of KB. In subsequent stages, the loss of more volatile components occurs, and the first exothermic DTG peak of decomposition of the most unstable structural component, hemicellulose, is observed in the area of 220-315 °C. The decomposition of hemicellulose takes place very quickly, with a peak on the DTG diagram observed at 265 °C and corresponding to a mass loss of approximately 25 %. The cellulosic component decomposes in a wider temperature range, from 285 to 390 °C, with a maximum conversion rate at 305 °C, which corresponds to a mass loss of about 45-50 %. Due to its structure, lignin decomposes the slowest, in a wide temperature range from 160 to 900 °C. The TG analysis showed that the total mass loss is about 99 %, which is in agreement with the other analysis which showed that the ash content in the PS sample was less than 1 %. The low ash content indicates good combustion behavior, high burning rate and acts positively on minimizing agglomeration, operational and disposal costs, avoiding slagging and fouling on the combustion units. PS poses other characteristics that are beneficial for their application as renewable fuel, such as: bulk density of 675 m³/kg (much higher compared to other biomass) and calculated caloric value of 18.97 MJ/kg, which is high enough to empower the utilization of this biomass type as energy source.

From Figure 1, it is also possible to see that an increase in the heating rate leads to a shift of the curves towards higher temperatures. This behavior can be attributed to very fast heat transfer [15]. It is possible to observe that with an increase in the heating rate, the degradation process is delayed: at higher heating rates, the samples are exposed to a certain temperature for a shorter time, which shifts the decomposition temperatures to higher values [16]. Slower heating of the sample leads to better and more efficient mass transfer within the sample particles, so the degree of conversion at a certain temperature is higher at lower heating rates.

3.2 Analysis of Thermal Degradation Kinetic by FWO Model

The kinetic parameters obtained by FWO method were calculated according to eq. (8) for a given value of conversion, α . Figure 2 shows the change of the conversion with temperature of the PS sample at any moment at different heating rate. To determine the kinetic parameters, the value of α from range 0.1 to 0.9 for all curves at different heating rate was used and the corresponding temperatures were found. The FWO plot of $\ln(\beta_i)$ versus $1/T_{ai}$ for different values of conversion are shown in Figure 2a. This Figure (Fig 2b) also shows the change in the calculated E_a with the increase in the degree of conversion for the tested model.

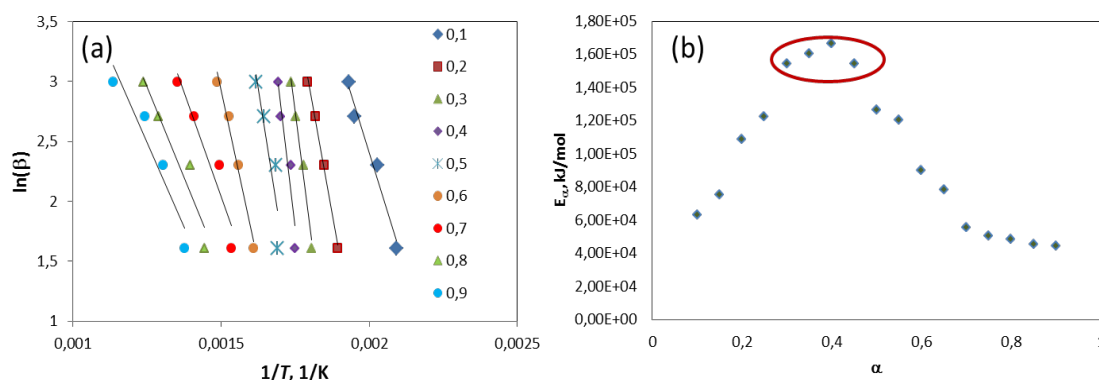


Figure 2. (a) FWO plot of poplar wood for different values of conversion and (b) $\alpha - E_a$ dependence (FWO model)

The apparent activation energies were obtained from the slope and pre-exponential factors from the intercept of regression line and are given in Table 1. The calculated squares of the correlation coefficients, R^2 , correspond to linear fitting in Figure 2a, and were in the range from 0.872 to 0.996.

Table 1. Values of E_a and correlation coefficients (R^2) determined by FWO method

Conversion degree, α	FWO	
	E_a , kJ/mol	R^2
0.1	62.81	0.872
0.2	108.41	0.996
0.3	154.08	0.981
0.4	166.26	0.910
0.5	126.04	0.982
0.6	89.73	0.984
0.7	55.46	0.912
0.8	47.94	0.919
0.9	44.24	0.912

The dependence $\alpha - E_a$ is extremely important for studying the kinetics of thermal degradation and the complexity of the process itself, because the variations of E_a indicate the existence of a kinetically complex process that takes place in several successive stages. Vyazovkin and Lesnikovich showed that the analysis of the dependence $\alpha - E_a$ reveals not only the complexity of the process, but also its possible mechanism [17]. This form of dependence indicates a multi-stage mechanism of thermal degradation, and can be attributed, based on the shape of the curve, to a mechanism dominated by the complexity of the process due to diffusion.

As can be seen from Table 1, the lowest correlation coefficients were observed for extreme levels of conversion, which can be attributed to the loss of moisture in the samples that occurs at lower temperatures, or, to the complex process of degradation of the solid residue (high degrees of conversion). Also, this table shows that the activation energy determined by isoconversional methods is not constant in the conversion function, and that the thermal decomposition of PS in the oxygen stream cannot be represented by a simple kinetic model in the entire process of thermal degradation. As can be seen, the apparent activation energy varies with the increase in the degree of con-

version, in the range from 44 to 166 kJ/mol, indicating different reaction mechanisms in certain stages of the process.

However, as it was shown by thermal analyses, three stages of decomposition can be observed in the decomposition of PS, each of which refers to the decomposition of individual components, hemicellulose, cellulose and lignin. The first stage of decomposition refers to the decomposition of hemicellulose and occurs in a conversion percentage of 20-30 %. The activation energy in this range of conversions is lower compared to the cellulose fraction due to the composition and lower thermal stability of hemicellulose. The second stage of decomposition refers to the decomposition of cellulose and occurs in the range of conversions around 0.3 to 0.5 with higher activation energies that arise due to the crystallinity of the cellulose fraction and the highly polymerized structure of the cellulose. The decrease in activation energy in the final stages of conversion occurs due to the thermal decomposition of lignin and indicates an easier process of degradation of this component. These results are in accordance with literatures.

After determining the E_a by FWO method, reaction mechanism that governs the degradation process is needed to determine the function $f(\alpha)$. For this purpose, the Coats-Redfern method is applicable in that conversion range for which the E_a value can be considered approximately constant [15]. From Figure 2(b) it is possible to adopt that the activation energy can be considered approximately constant in the range of conversions from 0.30 to 0.45 where the values of E_a vary approximately from 154 to 146 kJ/mol (for the applied FWO model). Therefore, in order to determine the reaction mechanism of degradation, the Coats-Redfern method was applied in this conversion range. Therefore, all possible mechanisms of thermal degradation were investigated, and based on the best match between the calculated activation energy and the one determined by FWO method, we have determined the approximate mechanism.

In the case of thermal degradation of PS, a range of conversions from 0.30 to 0.45 was observed, which corresponds to the thermal degradation of cellulose with the highest observed rate of thermal degradation (as indicated by the DTG peak in this area) and in which the value of the activation energy can be considered approximately constant. Numerical results of activation energy values obtained using the C-R method were calculated for a heating rate of 5 °C/min, although similar values were obtained using other heating rates.

Based on the results obtained, it can be concluded that the function $f(\alpha)$ that best fits the experimental data represents the reaction of the n^{th} order, where the determined order of the reaction is close to six (6). The values of the activation energies of the other models deviate significantly from the values obtained by the FWO model, although high values of the linear correlation parameters were also obtained for them. The calculated pre-exponential factor, k_0 , for this model is $2.66 \text{ E}+11$ 1/min. The obtained results are in agreement with the results obtained by Martin-Lara et al. [15], when they examined the thermal degradation of torrefied olive biomass, and obtained a fifth-order mechanism.

4 Conclusion

In this paper, an experimental kinetic study of lignocellulosic waste biomass of peach stone is presented. Thermogravimetric analysis was investigated under oxygen atmosphere at different heating rates. Thermal decomposition of PS samples proceeds in 4 consecutive steps: water evaporation, followed by passive/active decomposition of main structural properties, where the maximum weight loss occurred in the range from about 550 to 660 °C. Effect of heating rate on TG curve was also presented. Activation energy and pre-exponential factor were obtained by the FWO model-free method. The kinetic parameters calculated by FWO method shown that apparent activation energy and apparent pre-exponential factor vary with conversion and revealed the complex mechanism of reaction that occur during the thermal degradation. Experimental results showed that values of kinetic parameters are in good agreement with literature data but also indicate the complexity of devolatilization process, so the further analysis is needed.

Acknowledgements: This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-47/2023-01/200023).

5 References

- [1] **Martín-Lara, M. A., A. Pérez, M. A. Vico-Pérez, M. Calero, G. Blázquez,** The role of temperature on slow pyrolysis of olive cake for the production of solid fuels and adsorbents, *Process Safety and Environmental Protection*, 121 (2019), pp. 209-220.
- [2] **Lopičić, Z., A. Antanasković, T. Šošarić, V. Adamović, M. Orlić. J.Milojković, M. Milivojević,** Improvement of energy properties of lignocellulosic waste by thermochemical conversion into biochar, *Hemijaska Industrija*, 77 (2023), 2, pp. 147-153.
- [3] **Emiola-Sadiq, T., L. Zhang, A. K. Dalai,** Thermal and Kinetic Studies on Biomass Degradation via Thermogravimetric Analysis: A Combination of Model-Fitting and Model-Free Approach, *ACS Omega*, 6 (2021), 34, pp. 22233-22247.
- [4] **Orfao, J. J. M., F. J. A. Antunes, J. L. Figueiredo,** Pyrolysis kinetics of lignocellulosic materials - three independent reactions model, *Fuel*, 78 (1999), 3, pp. 349-358.
- [5] **Li, X. T., J. R. Grace, C. J. Lim, A. P. Watkinson, H. P. Chen, J. R. Kim,** Biomass gasification in a circulating fluidized bed, *Biomass Bioenergy*, 26 (2004), 2, pp. 171-193.
Patel, S., S. Kundu, P. Halder, L. Rickards, J. Paz-Ferreiro, A. Surapaneni, S. Madapusi, K. Shah, Thermogravimetric Analysis of biosolids pyrolysis in the presence of mineral oxides, *Renewable Energy*, 141 (2019), pp. 707-716.
- [6] **Gogoi, M., K. Konwar, N. Bhuyan, R. C. Borah, A. C. Kalita, H. P. Nath, N. Saikia,** Assessments of Pyrolysis Kinetics and Mechanisms of Biomass Residues Using Thermogravimetry, *Bioresource Technology Reports*, 4 (2018), pp. 40-49.
- [7] **Hu, M., Z. Chen, S. Wang, D. Guo, C. Ma, Y. Zhou, J. Chen, M. Laghari, S. Fazal, B. Xiao, B. Zhang, S. Ma,** Thermogravimetric Kinetics of Lignocellulosic Biomass Slow Pyrolysis Using Distributed Activation Energy Model, Fraser-Suzuki Deconvolution, and Iso-Conversional Method, *Energy Conversion and Management*, 118 (2016) pp. 1-11.
- [8] **Friedman, H. L.,** Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a Phenolic Plastic, *Journal of Polymer Science Part C: Polymer Symposia*. 6 (1964), pp. 183-195.
- [9] **Ozawa, T.,** New Method of Analyzing Thermogravimetric Data, *Bulletin of the Chemical Society of Japan*, 38 (1965), pp. 1881-1886.
- [10] **Kissinger, H. E.,** Reaction Kinetics in Differential Thermal Analysis, *Analytical Chemistry*, 29 (1957), 11, pp. 1702-1706.
- [11] **Akahira, T., T. Sunose,** Method of Determining Activation Deterioration Constant of Electrical Insulating Materials, *Research Report, Chiba Institute of Technology*, 16 (1971), pp 22-31.
- [12] **Brachi, P., F. Miccio, M. Miccio, G. Ruoppolo,** Isoconversional kinetic analysis of olive pomace decomposition under torrefaction operating conditions, *Fuel Processing Technology*, 130 (2015), pp. 147-154.
- [13] **Doyle, C. D.,** Kinetic analysis of thermogravimetric data, *Journal of Applied Polymer Science*, 5 (1961), pp. 285-292.
- [14] **Martín-Lara, M. A., G. Blázquez, M. C. Zamora, M. Calero,** Kinetic modelling of torrefaction of olive tree pruning, *Applied Thermal Engineering*, 113 (2017), pp. 1410-1418.
- [15] **Blázquez, G., M., Calero, C., Martínez, M. T., Cotes, A., Ronda, M. Á. Martín-Lara,** Characterization and modeling of pyrolysis of the two-phase olive mill solid waste, *Fuel Processing Technology*, 126 (2014), pp. 104-111.
- [16] **Vyazovkin, S. V., A. I., Lesnikovich,** An approach to the solution of the inverse kinetic problem in the case of complex processes. Part 1. Methods employing a series of thermoanalytical curves, *Thermochimica Acta*, 165 (1990), pp. 273-280.

