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Investigation of Hazelnut Husk Combustion by using A Novel Non-linear Kinetic Model through Thermogravimetric Analysis

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Abstract

Considering economic and environmental issues, boosting renewable energy source is the main subject to fulfill energy demand in these days. Biomass as natural and abundant energy source can be typically used to produce electricity, fuels and heat applying thermochemical conversion processes such as combustion, pyrolysis or gasification. Biomass combustion is the most common process to produce electricity and useful heat in Turkey and all over the world. The aim of this study is to investigate the considerable influence of heating rates on combustion characteristics and kinetics employing a new developed non-linear kinetic model for hazelnut husk samples through thermogravimetric analysis. Furthermore, this work comprehensively assesses the variations in the reactivity of hazelnut husk combustion, expressed from thermogravimetric curves. The non-linear kinetic model developed in this study integrates the various kinetic pathway to estimate the major controlling parameter of combustion reactivity, its activation energy, pre-exponential factor and reaction order. According to comparison of results from the non-linear kinetic model for volatile combustion and fixed carbon combustion, correlation coefficients (R²) for both models are higher than 0.9985. These results proved the non-linear regression model for kinetic pathways in combustion reactivity worked properly to estimate thermal decomposition behavior.

Keywords: thermogravimetric analysis (TGA), combustion, kinetic analysis, non-linear regression, biomass

1. INTRODUCTION

The upsurge of environmental issues and energy crisis has been increased the attention of energy study about the sustainability and efficiency [1]. Energy production using the renewable energy source has become critical to sufficiently reduce consequence of greenhouse gas emissions and air pollution [2]. Turkey’s energy demand has been increasing rapidly in last years consequence of growing population and industry. Thus, by using the renewable energy source instead of fossil fuels which are the primary energy source in Turkey has been getting importance day by day [3]. Biomass has the critical advantage in terms of its abundant reserves and being carbon neutral material [4]. Turkey offers a broad potential of biomass particularly as agricultural wastes. There is diversity on the biomass characteristics depending on the agricultural crops grown

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naturally in different regions [3]. Black Sea region is the responsible of hazelnut production as highest amount in the worldwide that corresponds to 75% [5]. As follows, this amount of production accompanies with enormous quantity of hazelnut waste. Considering the hazelnut wastes such as husk and shell, they can be used in production of energy and valuable chemicals as a feedstock [6]. Thermochemical conversion of biomass to gas or liquid fuels is a good alternative instead of fossil fuels for outstanding contribution to renewable energy generation [7]. Innovative technologies of biomass conversion process like combustion, pyrolysis and gasification play a key role for the concept of biomass to energy [8]. Higher volatile content and lower ignition temperature of biomass improve the performance of conversion process [9]. Combustion process cleaves the chemical bonds of fuel and generates series of reaction presence of air or oxygen under the heat [10]. Combustion may be seen the most feasible and conventional way to utilize biomass as a renewable energy source [11-13]. In order to carefully evaluate combustion performance, it is important to recognize the chemical and physical characteristics of biomass. Thermogravimetric analysis (TGA) is typically used to investigate thermal decomposition characteristics of solid materials based on weight change at the determined heating rate as a function of time constant or temperature. TGA is a simple and fast method, which explains why it is commonly used in many studies [14, 15].

Knowledge about the combustion characteristics of biomass is important to conduct effective combustion process. Thermal behavior of the biomass samples should be known to develop and optimize the combustion processes. TGA describes the combustion profile at the different heating rates and obtained results can be used to calculate kinetic parameters for combustion reactions [16, 17]. Several studies have been carried out with TGA to reveal the thermogravimetric and kinetic characteristics of biomass combustion [18-21]. The calculation of kinetic parameters such as activation energy (Ea), pre-exponential factor and reaction order are very complex and needs to employ appropriate methods for successive reactions. K. Jayaraman used the Arrhenius and Coats & Redfern methods to investigate the kinetics of coal-biomass blends [22]. Another methods which are Ozawa-Flynn-Wall [23-25], Kissinger–Akahira–Sunose (KAS) [26], Friedman [27-29] have been used to calculate kinetic parameters for different applications in the literature. These methods can calculate kinetic parameters with some assumption and using equation constants that cause some deficiency to achieve kinetic parameters. Unlike the other methods, iteration can be conducted for non-linear regression analysis for confident prediction of the kinetic parameters. It has advantage to represent the multistep and complex reactions with good accuracy because there is no restriction related to complexity of the possible reactions [30]. However, only iterative procedures can be employed for estimation of the kinetic parameters non-linear regression method represents the multistep and complex reactions with good accuracy [31, 32].

The purpose of this work is investigation of the combustion characteristic of hazelnut husk as the agricultural waste. Experiments for TGA were properly conducted, and results were discussed considering the peak and burn-out temperature values, total mass changes at the three different heating rates. New developed non-linear regression model has been applied to achieve the combustion kinetics of hazelnut shell and determine the kinetic parameters.

2. MATERIALS AND METHODS

2.1. Material Selection and Characterization

This study focusses on to specify combustion mechanism and kinetics of hazelnut husk. Selection of hazelnut husk maintains the great importance because Turkey is the leading area for production [33, 34]. Thus, residues of the hazelnut can be obtained plenty amount as agricultural waste from Black Sea and northwest of Marmara Regions in Turkey [35]. The sample used in this work was collected from local growers from northwest of Marmara Regions in Turkey and
prepared at Marmara University. First, size of biomass sample was reduced using by IKA M20 Universal Mill Sample, then it was grinded and sieved under 250 µm. The proximate and ultimate analyze of hazelnut husk were conducted according to ASTM D3172 and D3176 test methods and results are presented in Table 1.

|                                | Hazelnut Husk |
|--------------------------------|---------------|
| Moisture (wt %)                | 3.96          |
| Fixed Carbon (wt %)            | 22.89         |
| Volatile Matter (wt %)         | 64.45         |
| Ash (wt %)                     | 8.70          |
| C (wt %)                       | 39.75         |
| H (wt %)                       | 5.06          |
| O (wt %)                       | 52.30         |
| N (wt %)                       | 0.82          |
| S (wt %)                       | 2.07          |

Table 1
Proximate and ultimate analysis results of the hazelnut husk

The proximate analysis were carried out via “NETZSCH 409 PC” thermogravimetric analysis device. Ultimate analysis results were performed in Advanced Technologies Application and Research Center, Hacettepe University by using LECO brand Truspec micro elemental analyzer. Results show that hazelnut husk sample compositions for ultimate and proximate analyses within the range for biomass. Ash content of agricultural wastes commonly varies between 0.5% and 10% [13].

2.2. TGA Experiments

Scope of this work, TGA method has been used to determine combustion characteristics of hazelnut husk. TGA was applied using STA409 device, made by NETZSCH GmbH, Germany, it can be seen in the Figure 1. Before staring the experiment, approximately 10 mg sample was put into a ceramic crucible (Al₂O₃) for each experiment. Then, sample was heated from ambient temperature (25°C) to 800 °C under 21% O₂ and 79% Ar atmosphere and the total gas flow was set to 100 mL/min. At the same experimental conditions, this study has been conducted at the heating rate of 10, 20, and 40 °C/min.

The weight loss of the sample was continuously monitored and recorded versus of temperature and time via STA409 software. Weight losses are calculated based on weight loss rate and DTG curve peaks. The ignition and burnout temperature values are important parameters to define combustion characteristics of fuel and they are determined based on TG/DTG curves. When the no weight loss rate at the starting of combustion that is defined as ignition temperature, moreover, if the no weight loss rate at the end of the combustion it can be defined as burnout temperature.

2.3. Combustion Index

Combustion index is used as a comprehensive analysis of the combustion characteristics of different fuels, which is described by using Eq. (1) [36].

\[
S = \frac{DG_{\text{max}} \times DTG_{\text{mean}}}{(T_i^2 \times T_b)}
\]  

The value of S indicates the insensitivity of combustion and the reactivity of fuels in combustion. \( T_i \) in Eq. 1 can be calculated based on a TG curve by using ignition temperature. \( T_b \) is determined by using burnout temperature. DTG\(_{\text{mean}}\) and DTG\(_{\text{max}}\) refer the average weight
2.4. Kinetic Analysis

Kinetic study is one of the important methods used to evaluate effect of operating parameters on the combustion reactivity. Kinetic analysis of hazelnut shell combustion process was studied in detail in this section. The kinetic parameters were obtained selecting the most probable kinetic model for the thermal breakdown in the Netzsch Thermokinetics-3 software. Non-linear regression analysis has been applied to find kinetic parameters of the combustion process based on the TGA results of experiments. Using initial values of linear regression, non-linear regression started from reaction mechanism (2).

Then, non-linear regressions were performed for reaction mechanisms (3) until reaching desired correlation coefficient $R^2$ value using by the data sets collected from experiments at three heating rates. For solving the reaction (3) and optimizing kinetic parameters, calculations of $E_a$, pre-exponential factor and reaction orders were conducted considering the iteration range at the evaluation range between 0.0005-0.9995.

\[ A \rightarrow 1 \rightarrow B \] with s reaction code (2)

\[ A \rightarrow 1 \rightarrow B \rightarrow 2 \rightarrow C \] with d:f reaction code (3)

For the three reaction mechanisms; A is the initial reactants, B is the intermediate product and C is the final crosslinked product. Reaction mechanism (3) named as d:f stated the two-steps consecutive reactions and 2 and 3 indicate the reaction steps. TGA curves for each heating rate were divided into two stages to evaluate combustion kinetics more accurately for volatile matter and fixed carbon combustion for each scan. Parameters in the Table 2 are optimized to obtain the results of each experiments.

Table 2

| Parameter | Description |
|-----------|-------------|
| log(A1/s^{-1}), log(A2/s^{-1}) | Logarithm of the pre-exponential factors for step 1 and 2 |
| E1/kJ.mol^{-1}, E2/kJ.mol^{-1} | Activation energies for step 1 and 2 |
| n\textsuperscript{th} order 1 and 2 | Reaction order (step 1 and 2) |
| FollReact. 1 | Share of step 1 (total mass loss) |
| Mass Loss 1/% | Total mass loss (scan 1) |
| Mass Loss 2/% | Total mass loss (scan 2) |
| Mass Loss 3/% | Total mass loss (scan 3) |

Parameters derived from calculations and experiments are compared and simulation run is ended when the $R^2$ value reaches to success. Initial and optimum values and standard deviations of parameters are recorded at the end of the simulation.

3. RESULTS

3.1. TG/DTG Analysis

The combustion characteristics of hazelnut shell has been obtained from TG/TG results, which can be seen in Figure 3. The main combustion parameters such as ignition and burnout temperature values and mass changes at the different points were derived from the TG/DTG curves for heating rates 10 °C/min, 20 °C/min, 40°C/min. Two main stages which are volatile and fixed carbon combustions can be observed in the combustion processes of hazelnut shell as seen in Figure 3.
(a)

(b)
In the Figure 3a, combustion reaction was conducted at the heating rate 10°C/min. Ignition temperature was recorded 216.8 °C and mass change rate reached the maximum value 5.41 %/min at the peak temperature 285.9 °C in the volatile combustion zone, the temperature varies between 150 °C and 370 °C. In the fixed carbon combustion zone, burnout temperature was saved 474.4 °C and mass change rate was obtained 3.18 %/min at the peak temperature 428.4 °C. Total mass loss values were recorded 58.41% and 30.27% for first and second stages separately, moreover residual mass was determined 6.18% when the mass change rate is being constant at the temperature 799.4 °C. According to mass loss in the first and second stages, it is obvious that mass loss in the volatile combustion zone is higher and faster than fixed carbon combustion zone because hemi-cellulose and cellulose thermally decompose in the volatile zone together [37].

TG/DTG analysis of hazelnut shell at the heating rate 20 °C/min is shown in the Figure 3b. Ignition and burnout temperature values were determined 221.9 °C and 532.5 °C. In the first stage, mass loss was recorded 55.07% and maximum value of mass change rate has been seen 9.72 %/min at the peak temperature 293.4 °C.

Mass loss in the second stage and residual mass at the end of the combustion were obtained 33.06% and 7.54% respectively. Maximum mass change rate of the second stage were obtained at the peak temperature 461.2 °C. Compared to DTG curves at the heating rates 10 °C/min and 20 °C/min, it is seen that peak value of the mass change rate at the heating rate 20 °C/min is not as sharp as at the heating rate 10 °C/min, in the second stage. Furthermore, temperature ranges of the each stages were expanded, for instance, in the first stage of combustion at the heating rate 10 °C/min is in the range between 150 °C and 370 °C whereas same stage at the heating rate 20 °C/min is in the range between 140 °C and 380 °C. As seen in the Figure 3a and 3b, increase of heating rate caused the shifting of decomposition peaks to higher temperature because of the shorter residence time and bad thermal conductivity. These results show the good consistency with the literature studies [27, 38].
Besides, Figure 3c. displays the thermal decomposition of hazelnut shell when the heating rate is the fastest of this study. Unlike the other two heating rates, only one peak is seen clearly in the DTG curve at the heating rate 40 °C/min. Ignition and burnout temperature values are 216.4 °C and 689.7 °C and peak temperature values for first and second stages are 289.5 °C and 415.5 °C respectively.

Total mass loss has been found 53.36% and maximum mass change rate was obtained 20.74 %/min for the first stage. Even the peak point cannot be seen in the second stage, mass change rate was determined 5.90 %/min and total mass loss was recorded 33.96% in the second stage. In accordance with the experimental conditions of combustion, hemicellulose, cellulose and lignin in the content of biomass sample can be decomposed at the different temperature. TG/DTG results prove that peak temperature values for the first stage where the hemicellulose and cellulose decomposition generally take place in here are different for each heating rates in Figure 3. Researchers have studied about the biomass structure since many years and their results show that hemicellulose and cellulose content of biomass are higher than lignin content [37, 39, 40]. Consequently, total mass losses in the second stage are higher than in the second stage for each experiment regardless of heating rates because the thermal decomposition of hemicellulose and cellulose occurs in the first stage and hemicellulose and lignin decomposition occurs in the second stage as mentioned above. Residual mass amounts are shown in the Fig 3. for each experiment, it displays that increasing heating rate caused the bad thermal conductivity and was increased the residual mass amounts.

### 3.2. Combustion Index

Based on the Eq. 1, combustion index (S) has been calculated for the all heating rates which are studying in this work. Calculation results and performance parameters of combustion are presented in the Table 3.

| Heating Rate (°C/min) | 10  | 20  | 30  |
|-----------------------|-----|-----|-----|
| T_i (°C)              | 216.8 | 221.9 | 216.4 |
| T_b (°C)              | 474.4 | 532.5 | 689.7 |
| DTGmax (%/min)        | -5.41 | -9.72 | -20.74 |
| DTGmean (%/min)       | -2.32 | -4.04 | -6.18 |
| S                     | 6.99E-08 | 1.99E-07 | 5.55E-07 |

As seen in the above Table 3, increase of heating rate influenced the ignition and burnout temperature values. Their effects on the combustion characteristics has been increased the combustion index values. The higher heating rate was decreased the residence time, but it was increased the amount of decomposed fuel per unit time. Thus reactivity of fuels in combustion increased with increases of heating rate [22].

### 3.3. Non-Linear Regression Analysis

Comparison of experimental and calculated TGA results are presented in Figure 4. for the different heating rates. Stage 1 and 2 which are represented volatile and fixed carbon combustion zones were evaluated separately and results were discussed based on regression coefficient R².
In the first stage is shown in Figure 4a, hemicellulose and cellulose combustion has been executed using by two-step reaction mechanism ($A \rightarrow 1 \rightarrow B \rightarrow 2 \rightarrow C$). The correlation coefficient ($R^2$) of 0.9998 support that this mechanism was represented volatile combustion zone for each heating rate successfully. The two-step reaction mechanism was used for the second stage as well as for the first stage. Figure 4b illustrates of the credibility of the reaction
mechanism for hemicellulose and lignin decomposition process. It is clear from the curves at the different heating rates and R² = 0.9985 that the experimental and non-linear model results are very similar. As seen in Figure 4 (a) and (b), the non-linear regression model displayed the great performance based on R² values.

3.4. Kinetic Parameters

Kinetic parameters of combustion process are presented after conducting non-linear regression analysis. R² values were found in the satisfactory limits for each stage, thus the kinetic parameters were proved to be correct. Kinetic parameters were listed in the Table 4 and 5 for volatile and fixed carbon combustion zones separately.

| Parameters | Optimum Value |
|------------|---------------|
| log(A1/s⁻¹) | 10.3736 |
| E₁/kJ.mol⁻¹ | 135.6839 |
| React. Ord.₁ | 2.6841 |
| log(A2/s⁻¹) | 6.9187 |
| E₂/kJ.mol⁻¹ | 67.7445 |
| React. Ord.2 | 1.2508 |
| FollReact. 1 | 80.4621 |
| Mass Loss 1/% | -58.0000 |
| Mass Loss 2/% | -60.0000 |
| Mass Loss 3/% | -63.0000 |

According to results presented in Table 4, activation energies (E₁ and E₂) for two step reaction were found 135.68 kJ.mol⁻¹ and 67.74 kJ.mol⁻¹ respectively. Reaction orders were determined 2.68 for reaction step 1 and 1.25 for reaction step 2. Pre-exponential factor for each reaction step and total mass losses at the different heating rates are also presented in Table 4.

Table 5
Kinetic Parameters for Fixed Carbon Combustion Zone

| Parameters | Optimum Value |
|------------|---------------|
| log(A1/s⁻¹) | -1.4534 |
| E₁/kJ.mol⁻¹ | 14.3585 |
| React. Ord.₁ | 0.5913 |
| log(A2/s⁻¹) | 13.0922 |
| E₂/kJ.mol⁻¹ | 210.9523 |
| React. Ord.2 | 0.5471 |
| FollReact. 1 | 0.6436 |
| Mass Loss 1/% | -33.3044 |
| Mass Loss 2/% | -32.2621 |
| Mass Loss 3/% | -29.4685 |

In the Table 5, kinetic parameters are listed for two step reaction mechanism that is occurred in the fixed carbon combustion zone. Activation energies were found 14.3585 kJ.mol⁻¹ and 210.9523 kJ.mol⁻¹ for reaction step 1 and 2 respectively. Reaction orders were determined 0.59 for reaction step 1 and 0.54 for reaction step 2. Based on the values in Table 4 and 5 and selected reaction mechanisms for each stage showed good results when compared with experimental data. Kinetic study results also showed good agreement with proximate analysis results presented in Table 1. Total mass losses in the first stage (58%, 60%, 63%) for each heating rate are higher than in the second stage (33.30%, 32.26%, 29.47%) because volatile content of hazelnut husk is higher than fixed carbon content.

4. CONCLUSIONS

The experiments of hazelnut husk combustion were conducted at three different heating rates and combustion characteristics were determined using by TGA. Combustion behavior and kinetic analysis of hazelnut husk were presented and discussed in this study. Results showed thermal decomposition characteristics of hazelnut husk have been affected changing of heating rate. TGA
results were evaluated considering two main parts: then the ignition and burnout temperature values and total mass changes were recorded for each heating rate. Results displayed a good consistency with literature in terms of mass losses which is greater in the volatile combustion zone than fixed carbon combustion zone. Combustion index is a criterion to show reactivity of hazelnut husk increased with enhancing of heating rate. Ea, reaction orders and pre-exponential factors were estimated for two stages by non-linear regression method. According to comparison of TGA curves for experimental and calculated data sets, R² values were found 0.9998 and 0.9985 for volatile and fixed carbon combustion zones respectively. R² values proved that the new developed non-linear model worked properly to estimate thermal decomposition behavior and calculate kinetic parameters of combustion process. This study will be a good reference for biomass combustion plants and other industrial applications of hazelnut husk that currently use or will be used in the future.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

The authors contributed equally to the study.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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