

THERMOGRAVIMETRIC PYROLYSIS OF WALNUT SHELL AN ASSESSMENT OF KINETIC MODELING

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Abstract

Pyrolysis is considered as a possible thermal technique to convert biomass into value added chemicals and energy. Knowledge of the chemical composition, the thermal behavior and the reactivity of the biomass is very important for the effective design and operation of the thermochemical conversion units. Thermoanalytical techniques, in particular thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), allow this information to be obtained in a simple and straight forward manner. Thermogravimetric analysis (TGA) is one of the commonly used techniques to study thermal events during the pyrolysis process of fuel. The current research studied the thermal behavior of walnut shell (WS) by dynamic TGA under inert atmosphere at two different heating rates (5 and 15 °C/min). Three devolatilization stages for WS degradation were determined as removal of water, decomposition of hemicellulose and cellulose (active pyrolysis zone), and decomposition of lignin (passive pyrolysis zone). The use of these dynamic results to define the reaction kinetics necessitates the selection of an appropriate reaction mechanism, and 21 models have been proposed by Coats Redfern method in literature considering the rate limiting step being diffusion, nucleation or the reaction itself. According to the model assessment, the concepts of diffusion model kinetics provide the most suitable design approach. Activation energies were determined as 192 and 180 kJ mol⁻¹ from Zhrualev-Lesokin-Tampelman function of diffusion (3D) model for the heating rates of 5 and 15 °C min⁻¹, respectively.

Keywords: Pyrolysis, walnut shell, TGA, kinetics, modeling

1. Introduction

The use of biomass to substitute fossil fuels for the production of heat, electricity, transportation fuels and various types of chemicals, plastics and other materials has an increasing interest [1]. Waste biomass and residue using for energy production is encouraged by international organizations such as International Energy Agency because it can generate profit, contribute to mitigation of greenhouse gas emissions [2]. Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which each pyrolyses or degrades at different rates and by various mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicellulose, which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis. The rate and extent of decomposition of each of these components depends on the process parameters such reactor (pyrolysis) temperature, biomass heating rate and pressure [3].

Kinetic analysis of thermal decomposition processes has been the subject interest for many investigators all along the modern history of thermal decomposition. The interest is fully justified. On one side, kinetic data are essential for designing any kind of device, in which the thermal decomposition takes place; on the other side, kinetics is intrinsically related with the decomposition mechanisms. The knowledge of the mechanism allows the postulation of kinetic equations or vice versa, and kinetics is the starting point to postulate mechanisms for the thermal decomposition. Although kinetic studies can be performed in different devices, thermogravimetry (TG) is, by large, the mostly used technique [4]. The advantages of TGA are fast and repeatable data collection of pyrolysis rate, which facilitates a deep investigation of kinetic parameters [5]. So in a TG experiment, a modern equipment typically registers hundreds or thousands of experimental points that can be used for kinetic analysis of the reaction. It is clear that the selection of correct model is a critical point in kinetic analysis. Knowing how a model can justify experimental data has been evaluated by many researchers [6-8].

The aim of this work is specifically to show the utility of kinetic analysis method based on the complementary use of Coats-Redfern methods to identify the pyrolysis reaction model from non-isothermal TGA data. In this work, the TGA study of walnut shell was realized using non-isothermal method in order to determine the activation energy and the pyrolysis reaction model.

2. Materials and methods

Walnut shell sample has been taken from Bilecik located in the Northwest Turkey. Raw material was dried at room temperature, ground by rotary cutting mill and sieved. 425-600 μm mesh size samples were used in all experiments. Ultimate and component analyses performed for walnut shell and the properties of raw material are given in Table 1. The weight fractions of Carbon, Hydrogen and Nitrogen were determined by using elemental analyser Leco CHN628 Series. Elemental analysis of walnut shell is presented in Table 2. Du-Long's formula (Eq. 1) was used for the calculation of calorific values using elemental compositions. According to the results, calorific value of walnut shell was calculated as 16.7 MJ kg^{-1} [9].

$$Q_{GVC} = 338.2C + 1442.8 \left(H - \frac{O}{8} \right) + 94.2S \quad (\text{kJ kg}^{-1}) \quad (1)$$

C, H, N, O and S are the mass fractions of carbon, hydrogen, nitrogen, oxygen and sulphur.

The sample was subjected to TGA in an inert atmosphere of nitrogen. Seteram LabSys Evo analyzer was used to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Thermogravimetric curves obtained at two different heating rates (5 and 15 $^{\circ}\text{C min}^{-1}$). Nitrogen was used to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample.

Table 1. Properties of *juglans regia* shell

	wt. %
<i>Proximate analyses</i>	
Moisture	8.06
Ash	0.33
Volatile matter	76.38
Fixed carbon ^a	15.23
<i>Component analyses</i>	
Holocellulose	46.13
Oil	3.29
Lignin	48.11
Extractives	3.78
Hemicellulose	22.18
Cellulose ^a	23.95

^a By difference**Table 2.** Elemental analysis of *juglans regia* shell and scrap tyre

Substance	C (%)	H (%)	N (%)	S (%)	O (%) ^a
<i>Juglans regia</i> shell	47.50	6.39	0.46	-	47.65

^a By difference

3. Theoretical approach

In the non-isothermal TGA experiments, the mass of the sample is measured as a function of temperature, while the reaction proceeds for a fixed regime of temperature ramps, β (K/min) [10].

The decomposition rate of a solid is:

$$\frac{d\alpha}{dt} = k(T)f(x) \quad (2)$$

The conversion, α , can be written as a function of the temperature and the rate constant, k , can be described by the Arrhenius expression.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (3)$$

Integration and recombination of Eqn. 3 gives [4]:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{g(\alpha)} \int_0^T e^{-E_a/RT} dT \quad (4)$$

where $g(\alpha)$ represents the integrated form of the conversion dependence, however without specific analytical solution. Several expressions for $g(\alpha)$ have been proposed in the literature as a function of different reaction mechanisms, all of which are based on three concepts: diffusion, nucleation and the order of the reaction. Expressions of $g(\alpha)$ were summarized from previous literature and are given in Table 3, showing the 21 models available. $g(\alpha)$ can be solved as:

$$g(\alpha) = \frac{AE_a}{\beta R} \int_x^{\infty} \frac{e^{-x}}{x^2} dx = \frac{AE_a}{\beta R} p(x) \quad (5)$$

A solution for the p(x) can be found by solving the integral and using a Taylor approximation. The method of Coats-Redfern (1964) solves Eqn. (5) by limiting the number of terms in the Taylor series expansion:

$$\ln \left[-\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \right] \left(1 - \frac{2RT}{E_a} \right) - \frac{E_a}{RT} \quad (6)$$

By plotting the left hand side of the equation versus 1/T, the activation energy, E_a, can be determined from the slope of the linear expression [10, 11].

4. Results and discussion

Thermal degradation of walnut shell

Devolatilization stage plays an important role in the conversion processes. Particularly, attention should be paid to the light hydrocarbons which are producing at the end of thermal degradation [12]. The results of TG curves of the walnut shell at different heating rates as function of temperature are given Figure 1.

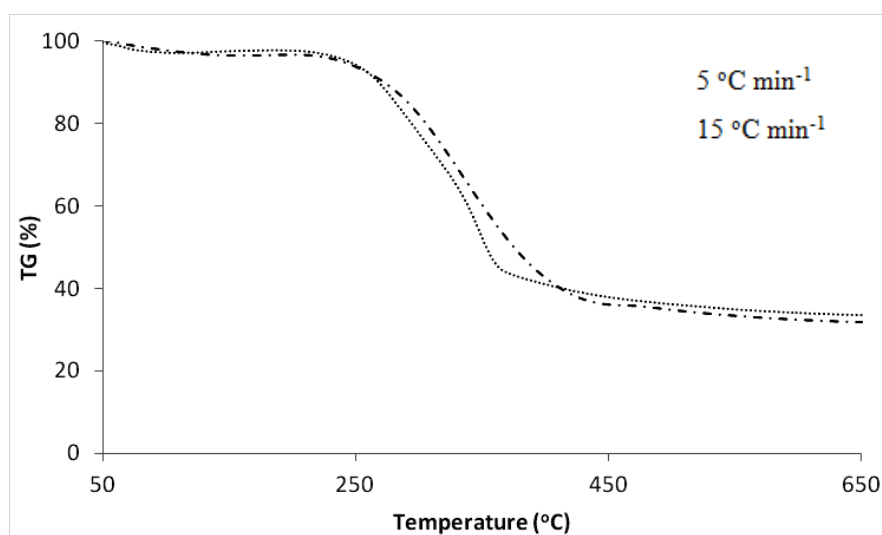


Figure 1. TG-DTG curves of walnut shell

According to TG curves, the mass loss range can be divided into three steps because of variable-slope curves. The first step started at about 50 °C and finished at about 130 °C with respect to the applied heating rate. This could have been owing to the vaporization of the moisture in consequence of physically absorbed water of the sample. This step was specified as a small peak on the most left hand side on the DTG curve (Fig.2).

Following the TG curve the main devolatilization step began at about 208 °C and finished at about 372 °C in terms of heating rate and this step indicates decomposition of hemicellulose and cellulose referred as active pyrolysis zone since mass loss rate is high. After 415 °C passive pyrolysis zone started and mass loss rate was lower at this step. Then, there was no further weight loss essentially. These thermal behaviors clarified by the components of walnut shell. Walnut shell is mainly consisted of hemicellulose, cellulose and lignin like all other lignocellulosic materials. The thermogravimetric behavior of these components have been studied before and it is well known that hemicellulose, cellulose and lignin accomplished their decomposition within the temperature

ranges of 210-325, 310-400, and 160-900 °C, respectively [13, 14]. Predicate on these intervals the minor and major reactions observed in active pyrolysis zone can be attributed to decomposition of hemicellulose and cellulose. From Table 1 the sum of hemicellulose and cellulose amount was calculated as 46.13% and the average mass loss of walnut shell at active pyrolysis zone was determined as about 45%. This case is another evidence of hemicellulose and cellulose decomposition occurs in the active pyrolysis zone.

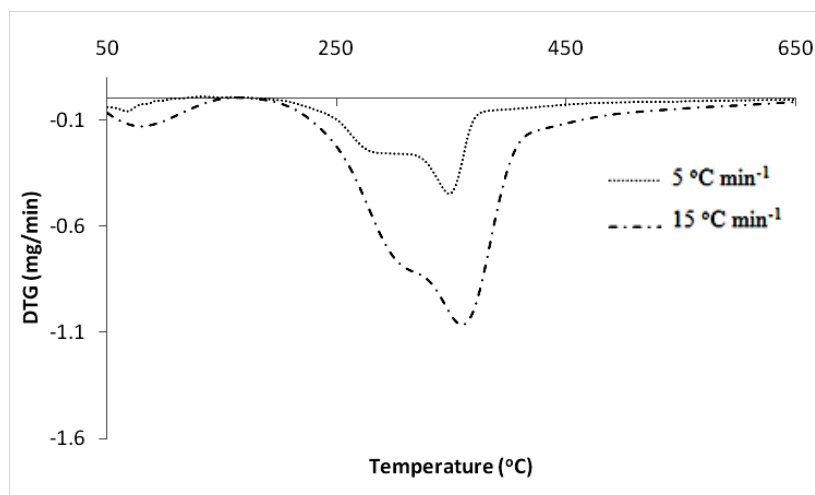


Figure 2. DTG curves of walnut shell

Kinetic parameters for walnut shell pyrolysis

The transformation of the experimental results using the model equations of $g(\alpha)$ was further represented at the heating rate of 5 and 15 °C min⁻¹ per mechanism investigated, i.e. diffusion (Fig.3), nucleation (Fig.4) and reaction order and shrinkage (Fig.5). Mechanism-applications were numbered according to the reference of Table 3.

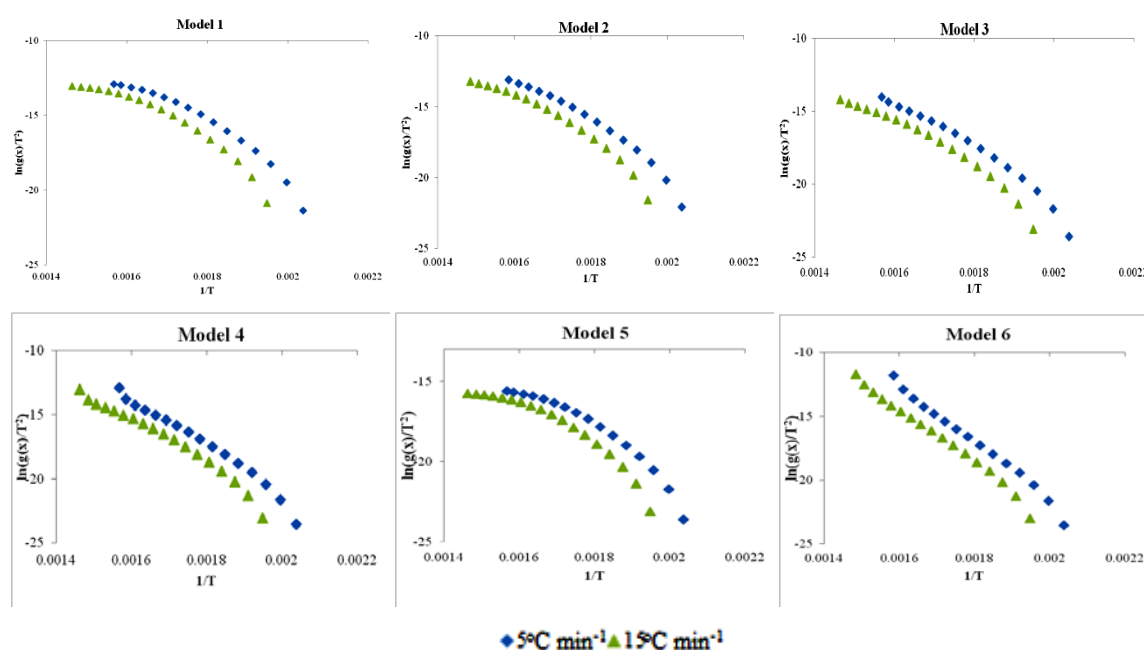


Figure 3. Diffusion models of walnut shell with heating rates of 5 and 15 °C min⁻¹

Table 3. Kinetic integration functions $g(\alpha)$ for different reaction mechanisms [4, 10, 11]

n°	Function	Mechanism	$g(\alpha)$
<i>Diffusion models</i>			
1	Parabolic law	Diffusion, 1D	α^2
2	Valensi (Barrer)	Diffusion, 2D	$\alpha + (1-\alpha)\ln(1-\alpha)$
3	Ginstling-Broushtein	Diffusion, 3D (column symmetry)	$\left(1 - \frac{2\alpha}{3}\right) - (1-\alpha)^{2/3}$
4	Jander	Diffusion, 3D (spherical symmetry)	$\left(1 - (1-\alpha)^{1/3}\right)^2$
5	Anti-Jander	Diffusion, 3D	$\left[(1+\alpha)^{1/3} - 1\right]^2$
6	Zhrualev, Lesokin and Tempelmen	Diffusion, 3D	$\left[\left(\frac{1}{1-\alpha}\right)^{1/3} - 1\right]^2$
<i>Nucleation models</i>			
7-11	Avrami-Erofeev	$n = 1; 1.5; 2; 3; 4$	$[-\ln(1-\alpha)]^{1/n}$
12	Power law		α
13	Power law		$\alpha^{1/2}$
14	Power law		$\alpha^{1/3}$
<i>Reaction order and geometric contraction models</i>			
15	Shrinkage geometry	Column symmetry	$1 - (1-\alpha)^{1/2}$
16	Shrinkage geometry	Spherical symmetry	$1 - (1-\alpha)^{1/3}$
17-20	Reaction order	$n = 0.25; 1.5; 2; 3$	$\frac{(1-\alpha)^{1-n} - 1}{n - 1}$
21	Mampel	$n=1$	$-\ln(1-\alpha)$

The illustrations in Fig.3 were related to the diffusion approaches. For mechanism 6, a linear fit was observed for both heating values. The illustrations of Fig. 4 and 5 related to the nucleation and geometric contraction models. Most often, a linear fit was not obtained for these models. The isothermal activation energy was determined as 192 and 180 kJ min⁻¹ for the heating rate is 5 and 15 °C min⁻¹, respectively. The pre-exponential factor of the Arrhenius equation was calculated as 5.3×10^8 and 2.1×10^7 for the heating rate is 5 and 15 °C min⁻¹, respectively.

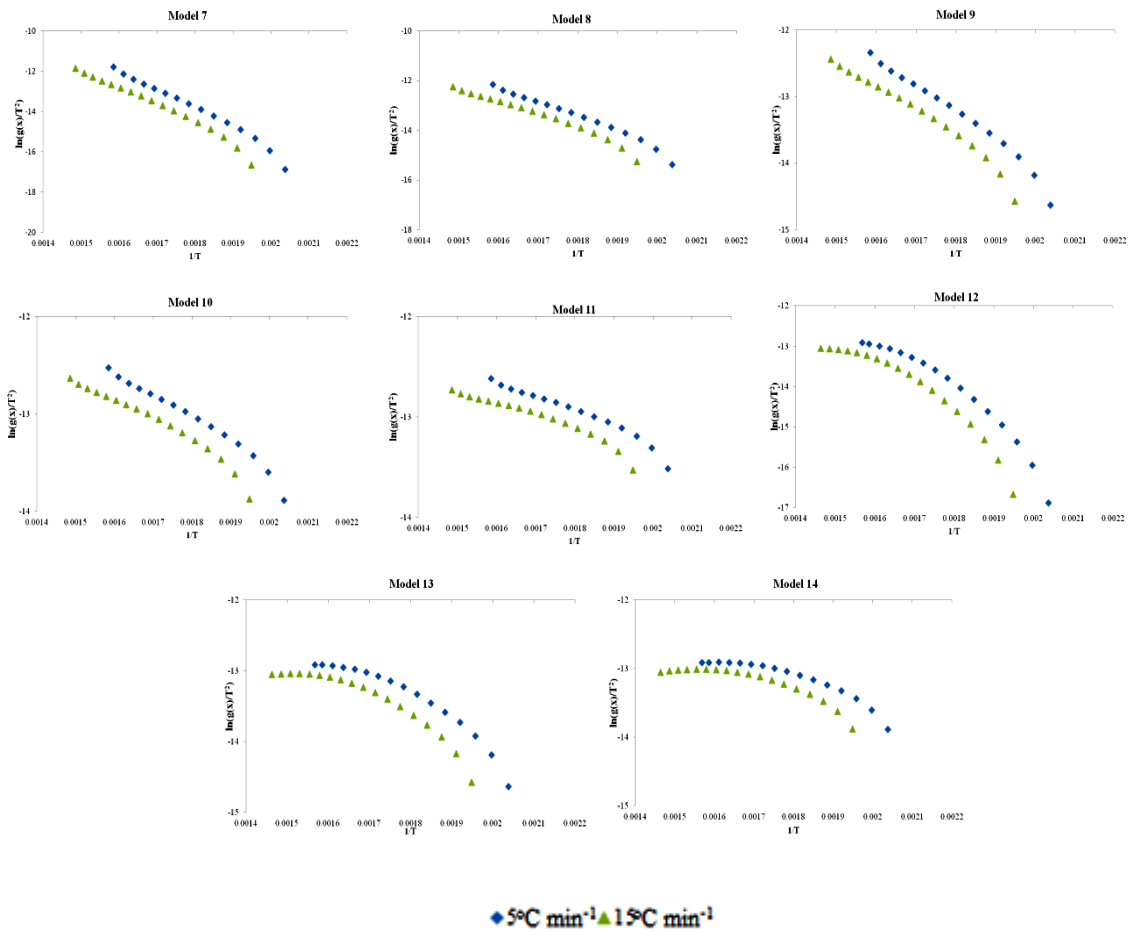


Figure 4. Nucleation models of walnut shell with heating rates of 5 and 15 °C min⁻¹

4. Conclusion

According to the model assessment, the concepts of first or second order kinetics provide the most suitable design approach. A first order kinetics is commonly proposed in literature for a variety of biomass. The paper used dynamic TGA-results to define the reaction kinetics of walnut shell pyrolysis. Application of the majority of the models to experimental findings demonstrated that they do not meet fundamental kinetic considerations of required linearity of $\ln(g(\alpha)/T^2)$ versus $1/T$ and are questionable in their use. Further research will repeat the analyses for pyrolysis of additional biomass, and the same analysis can also be applied to the pyrolysis of plastics, currently widely investigated.

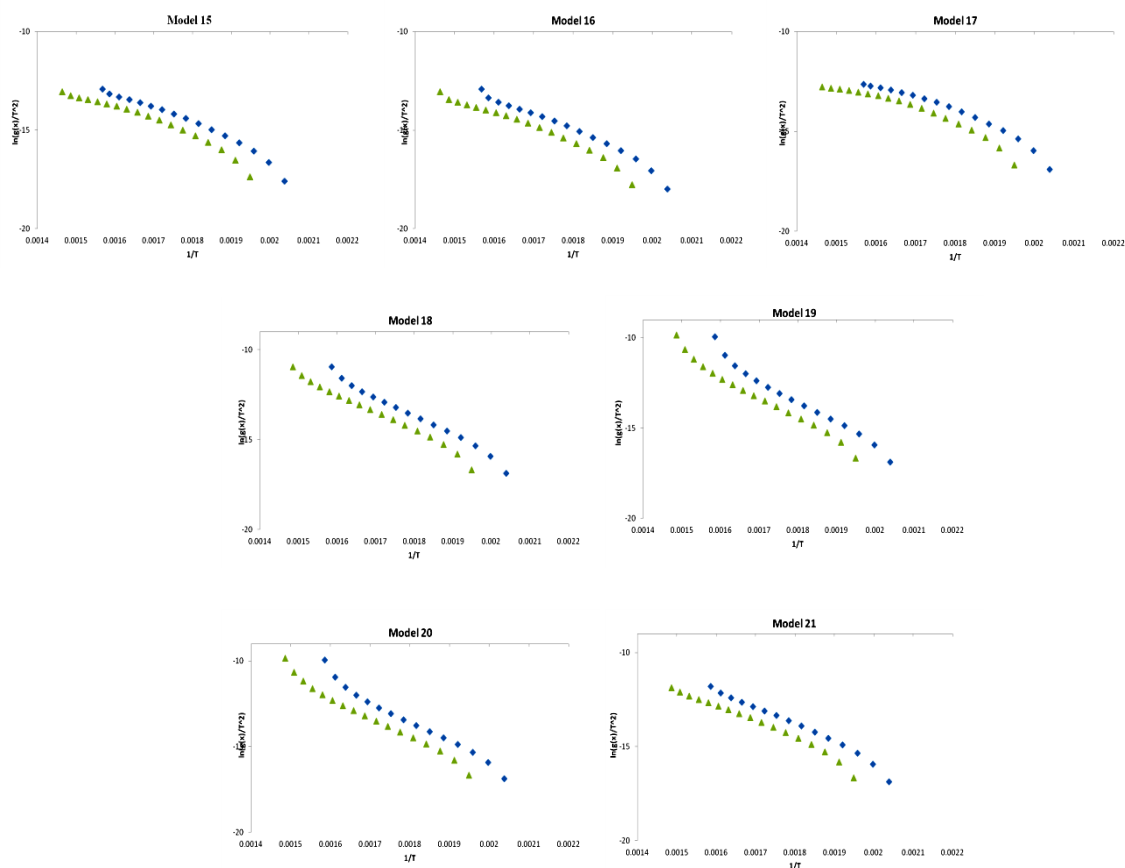


Figure 5. Reaction order and geometric contraction models of walnut shell with heating rates 5 and 15°C min⁻¹

5. References

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