Thermal Decomposition Kinetics of the Stalks of *Cynara Cardunculus* L. under Non-Isothermal Conditions

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Abstract

This paper is concerned mainly with the kinetics of the thermal decomposition of the stalks of an energy crop, Cynara Cardunculus. Cynara Cardunculus, as a candidate source of energy, can present a continuous stock of solid, liquid, and gaseous fuels by means of thermal and biological conversion processes. Nonetheless, a thorough grasp of thermal properties and reaction kinetics of Cynara Cardunculus plays a remarkable role in the effective design, operation and modeling of these processes. The pyrolysis reactivity and kinetic characteristics of Cynara Cardunculus were investigated in an inert atmosphere from the ambient temperature up to a temperature of 700 °C at four different heating rates. There were three distinct regions in the thermochemical conversion process of Cynara cardunculus. Almost the whole thermal degradation took place in the range of 181 and 415 °C. The Coats-Redfern method was employed to calculate non-isothermal kinetic parameters. The thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles were examined to evaluate the kinetic parameters such as the activation energy (E) and pre-exponential factor energy. The activation energy and pre-exponential factor were in the ranges of 61.13 to 66.44 KJ/mol and of 4.56×10^7 to 8.63×10^7, respectively, depending on the heating rates. Increasing the heating rates increased both the thermal degradation rate and markedly decreased the initial degradation temperature.

Index Terms– Biomass, Cynara Cardunculus, Thermogravimetric analysis, Non-isothermal kinetics, Arrhenius parameters

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I INTRODUCTION

All fossil fuels, coal, petroleum, and natural gas, contain carbon and hydrogen and were the remains of organic matter produced by photosynthesis which occurred as a result of millions of years of geological evolution. These fuels are nonrenewable and will ultimately be come to an end. As they rely upon limited resources and their distributions on earth are greatly restricted in certain areas of the world, they will become expensive. In addition, energy production from fossil fuels including coal, petroleum and natural gas via combustion irreversibly damages the environment with pollutants and causes greenhouse gas emission [1]. In order to maintain the future of the world with a cleaner environment, renewable energy is the only choice compared to other energy sources. Renewable energy sources include solar energy, wind energy, geothermal energy, nuclear energy, ocean energy, hydrogen, and biomass [2]. Biomass is the chemically stored energy in plant and animal tissues, which can be used as an alternative fuel. It is regarded as one of the most important resources on the earth. Besides a biological sustenance for ecosystem, biomass has a wide area of use from fabrics, medicines, valuable chemicals to construction materials [3].

The chemical composition of biomass depends greatly on the various types of tissues found in plant and animal species. In general, plant structure is composed of long-chain polysaccharides, a short-chain polysaccharides, and amorphous complex phenolic compounds. The polysaccharide fraction consists of glucose monomers linked together in long chains or polymers [4-5]. Biomass used in order to obtain energy includes herbaceous and woody energy crops, forestry crops and their residues, industrial residues, animal and food residues, municipal solid waste and sewage. The process of

conversing these sources of biomass with the purpose of energy into valuable products can be classified as two categories: biological conversion and thermal conversion. The thermal biomass conversion process can be divided into four main groups: combustion, liquefaction, pyrolysis, and gasification [6-9]. Among these conversion processes, pyrolysis, thermal decomposition of biomass in the inert atmosphere, is a promising technology for liquid oil production, biochar and gases [10]. Bio-oil obtained from the pyrolysis of biomass contains so many simple and complex compounds from aliphatics, furans to oxygenates and inorganics species. Pyrolysis gas comprises mainly of CO_2, CO, CH_4 and H_2 and some other light hydrocarbons. Biochar mainly contains elemental carbon and carbonaceous compounds along with hydrogen and various inorganic species in small quantities [9]. The term thermal analysis (TA) is a general term describing analytical instrumental technique which analyzes the behavior of a substance as a function of varying time and temperature. The most basic thermal analysis techniques are differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA), thermo-optical analysis (TOA) and thermogravimetric analysis. Thermogravimetric anlaysis or thermal gravimetric analysis (TGA) is a technique used for determining the overall mass of the analyte as a temperature-dependent property in a controlled atmosphere. The kinetic analysis of biomass can be carried out under different types of temperature programs, such as isothermal [11], and non-isothermal [12-13]. These types of the temperature programs entail handling the data to regress the kinetic parameters using different methods [14]. According to the atmosphere used, thermo-gravimetric analysis is employed frequently as an analytical method under nitrogen

[13], oxygen [15], air [16], helium [17], and argon [18-19] atmospheres. Empirical kinetics classified as a one-step single model [20], competing model [21], parallel model [22], or parallel-series model [23, 24] have also lately been used in various pyrolysis studies. Many researchers have investigated the pyrolysis kinetics of energy crops [25-27] and agricultural residues [28-30].

There have in general been two different of methods using non-isothermal data to evaluate the kinetic parameters used in the following equation known as the Arrhenius equation.

$$\frac{dm}{dt} = -Ae^{-E/RT}m \qquad (1)$$

where m is weight fraction, t the reaction time, A the pre-exponential or frequency factor, E the activation energy, T the absolute temperature and R is the universal gas constant. In order to solve Eq. (1) one of the methods used directly requires a linearization of the Eq. (1) by dividing by the mass and then taking the logarithm or natural logarithm of both sides. The resulting equation is shown Eq. (2) and is known as the derivative method.

$$ln\left(-\left[\frac{dm}{dt}\right]/m\right) = \ln{(A)} - \frac{E}{RT} \qquad (2)$$

Eq.(2) is a linearized form and when $ln\left(-\left[\frac{dm}{dt}\right]/m\right)$ is plotted on the ordinate and 1/T is plotted on the abscissa, the graph will yield a straight line when the thermal decomposition reaction is first-order. The slope of this line gives the activation energy, and the pre-exponential factor can be calculated from the ordinate intercept. The most frequently used method for calculating kinetic parameters from non-isothermal data is to employ an integral method. This method is much simpler than the derivative. Integrating the right-hand side of Eq. (1) has no analytical solution and for the exact solution, there are many methods reported in the literature. One of

the methods is the Coats and Redfern method which employs an approach of the integral form of an infinite sum [14,31].

In this study, the pyrolysis behavior of the stalks of an energy crop, Cynara Cardunculus was investigated by means of thermogravimetric analysis (TGA). The kinetic parameters, A, and E of the biomass were calculated using the Coats-Redfern method.

II THERETICAL BACKGROUND

One of the most applied kinetic models in the literature is the Coats-Redfern approximation [32-42]. Because biomass is a multi-component material that is comprised of lignin and carbohydrates (cellulose and hemi-cellulose), it is not easy to investigate the different and complex pyrolysis reactions individually. A simple kinetic approach to modelize the scheme. Thermal decomposition of the biomass in a solid state is the one-step first order rate model [43]. The overall pyrolytic decomposition process can be simplified as

$$\text{Biomass} \longrightarrow \text{Char} + \text{Volatile} \qquad (3)$$
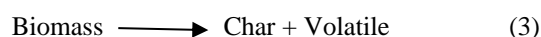
The kinetic rate expression of the non-isothermal pyrolysis of a reaction (3) is dependent on the following equations [31].

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (4)$$

$$k = Aexp\left(-\frac{E}{RT}\right) \qquad (5)$$

$$T = T_0 + \gamma t \qquad (6)$$

where α is the fraction thermally decomposed, $f(\alpha)$ a function depending on the degree of the reaction, k the reaction rate constant, t the reaction time, γ the linear heating rate and T is the absolute temperature.

Eqs. (4) and (6) can be arranged into the following equation.

$$\frac{d\alpha}{dt} = f(\alpha)\frac{A}{\gamma}\exp(-\frac{E}{RT}) \qquad (7)$$

In this paper, α is defined as m_0

$$\alpha = \frac{1 - m_i}{1 - m_0} \qquad (8)$$

where m_i and m_0 are the instantaneous and the final values of the mass fractions, respectively. $f(\alpha)$ can be defined as

$$f(\alpha) = (1 - \alpha)^n \qquad (9)$$

Putting Eq. (9) into Eq. (7) yields

$$\frac{d\alpha/dT}{(1-\alpha)^n} = \frac{A}{\gamma}\exp(-\frac{E}{RT}) \qquad (10)$$

Coats and Redfern [31] integrated Eq (10) by expanding it into a series with boundary conditions of $\alpha = 0$ for $T = T_0$ and $\alpha = \alpha$ for $T = T$ for the boundary conditions. For $n \neq 1$, the result is

$$\frac{1 - (1-\alpha)^{1-n}}{(1-n)T^2} = \frac{AR}{\gamma E}\left(1 - \frac{2RT}{E}\right)\exp(-\frac{E}{RT}) \qquad (11)$$

Assuming $2RT/E \ll 1$ Eq. (11) can be simplified into the form

$$ln\left(\frac{1 - (1-\alpha)^{1-n}}{(1-n)T^2}\right) = ln\left(\frac{AR}{\gamma E}\right) - (\frac{E}{RT}) \qquad (12)$$

For $n \neq 1$, the integration of Eq. (12) yields

$$ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = ln\left(\frac{AR}{\gamma E}\right) - (\frac{E}{RT}) \qquad (13)$$

The basic assumptions in the above equation are that the reaction is completely kinetic controlled and pyrolysis conforms to a first order reaction. By using the α values from the TGA data, a plot of left side of Eq. (13) versus $1/T$ will yield straight lines. The values of the Pre-exponential factor (A) and the Activation energy (E) can be found from the ordinate intercept and the slope of this line [33].

III EXPERIMENTS

III.I Preparation of biomass samples

The authors sampled the stalks of an energy crop, Cynara Cardunculus. This is an abundant species in the Mediterranean region. Around 100 g of plant were brought to the laboratory, washed with ultra-pure water and oven-dried for 24 hours at 100 °C. Dry samples were then grounded and sieved to pass through 250 μm mesh, then kept to the desiccators. The sieved sample was stored in plastic jars for experiments. All the thermal analysis was performed on this sample. The proximate analysis was carried out through the method in the American Society for Testing Materials (ASTM) (D 2016-74, D 1102-84, and E 870-82). The ultimate analysis was carried out using an element analyzer (LECO CHNS 932). Inorganic contents of the samples were performed using AAS-310 Flame Photometer. The calorific value of the samples was determined using Gallenkamp Auto Bomb Calorimeter. The results of the proximate, ultimate and inorganic elemental analysis of the biomass sample are shown in Table 1.

Table 1
Promimate, ultimate, and inorganic content of the biomass samples

Proximate analysis (wt%, dry ash free)	
Moisture	6.79
Volatile matter	72.16
Fixed carbon	10.81
Ash	10.24
Ultimate analysis (wt%, dry ash free)	
C	40.49
H	5.43
O	51.28
S	Negligible
N	0.8
Emprical formula	$CH_{1.609}O_{0.949}N_{0.013}$
Calorific value (MJ/kg)	
Gross Calorific Value	21.02
Main inorganic elements (ppm)	
Ca	0.55
Mg	0.1
Fe	508
Zn	78
K	0.15

III.II Thermogravimetric analysis

A Shimadzu Simultaneous 60H apparatus was used to give the TG and DTG experimental data for biomass decomposition at different heating rates. The experiments were performed with a carrier flow rate of N_2 50 ml/min. The heating rates were programmed at 5, 10, 20, and 30 °C min^{-1}. Throughout the experiments, the mass loss (TG signal) and the rate of mass loss (DTG signal) as a function of temperature were simultaneously recorded, as the samples were exposed to a adjusted temperature program. Although many mathematical methods can be used to calculate the kinetic of solid-state reactions, the Coats-Redfern method, in this study, was employed to determine the kinetic parameters.

IV RESULTS AND DISCUSSIONS

The TG weight loss curves of Cynara Cardunculus at different heating rates (5, 10, 20, and 30 °C/min) were obtained in order to study the effect of heating rates on non-isothermal kinetics (Figures 1-4) As can be seen from the Figures 1-4, the TG and DTG curves of the biomass at the different heating rates were similar, indicating three regions in the pyrolytic decomposition process. The TG and DTG results for each region in the pyrolysis of Cynara Cardunculus are shown in Table 2 for the heating rates of 5, 10, 20 and 30 °C min^{-1}. The first region is below 200 °C, where the water retained and the absorbed gases in the plant volatilize. The moisture and gases release of the sample started at around 60 °C and was completed in the interval of 181-211 °C, depending on the heating rates. In the first region, very little mass losses were observed (2.5-3.3 %). As the heating rate increases the drying temperature zone also increases. At the end of this region, the main thermal degradation took place between 181 and 415

°C. As can be seen in the sharp devolatilization process, the TG curves of the sample indicate two overlapping peaks. It has been well reported in the literature that lignocellulosic biomass is composed mainly of cellulose, hemicellulose and lignin and these compositions have a considerable effect on the biomass pyrolysis [40-45].
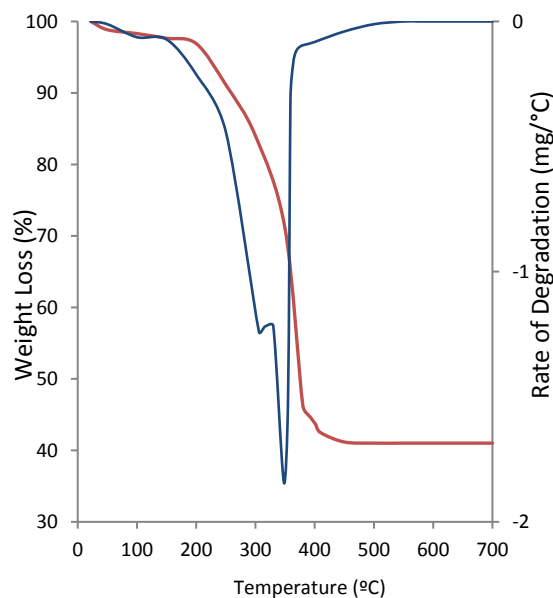

Figure 1. TGA and DTG curves of Cynara Cardunculus obtained with a linear rate of 5 °C/min under nitrogen atmosphere
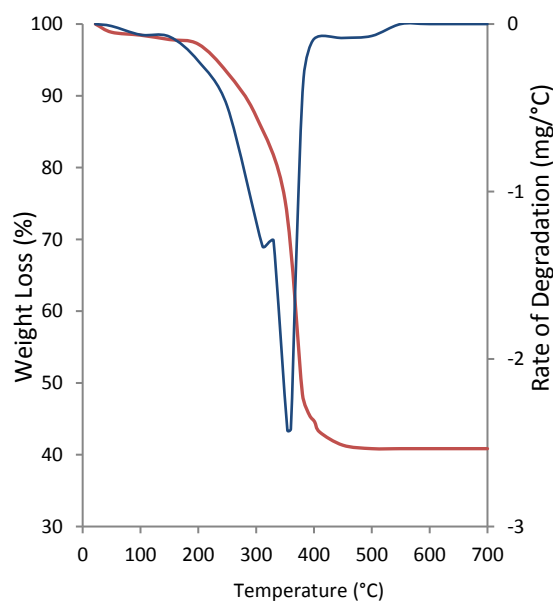

Figure 2. TGA and DTA curves of Cynara Cardunculus obtained with a linear rate of 10 °C/min under nitrogen atmosphere

Figure 3. TGA and DTA curves of Cynara Cardunculus obtained with a linear rate of 20 °C/min under nitrogen atmosphere

Figure 4. TGA and DTA curves of Cynara Carduclus obtained with a linear rate of 30 °C/min under nitrogen atmosphere
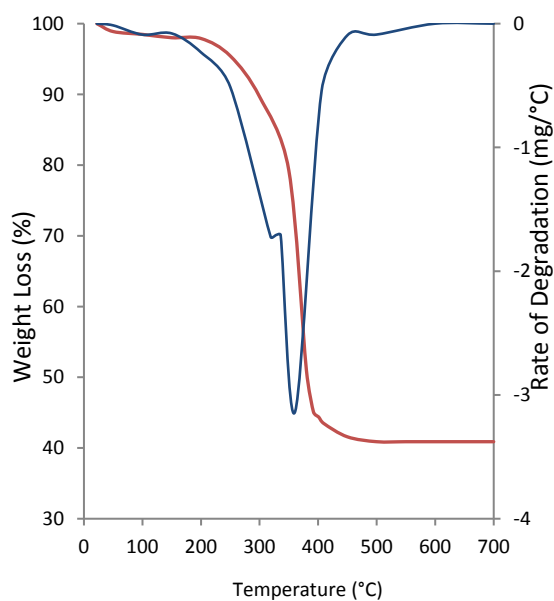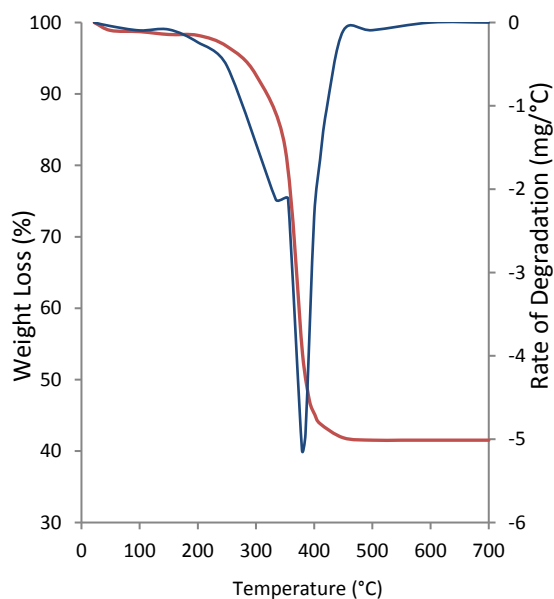
The derivative thermogravimetric (DTG) analysis of Cynara Cardunculus revealed that the thermal degradation of this biomass in the interval of 200-400 °C occurred in two peaks as shown in Figs. 1-4. The first peak occurred at 306-334 °C, while the second peak occurred at 348-379 °C, depending on the heating rates used. Wang et al. [46], Fernandez et al. [47], Moreira et al. [48], and Mansaray and

Ghaly [49] reported that three main constituents of biomass are chemically active and decompose thermocemically in the temperature range of 170-340 °C for hemicellulose, 280-360 °C for cellulose and 260-490 °C for lignin.

Table 2

TG and DTG results of cynara cardunculus (T_{max} is the peak temperature corresponding to a maximum mass loss for hemicellulose and cellulose, respectively,; T_f is the final temperature of the process; DTG_{max} is the largest value in the thermal decomposition process; and T_{DTGmax} is the temperature belonging to DTG_{max}; and R_s final residue at 700 °C)

Heating rate (°C min⁻¹)	5	10	20	30
Region 1				
Weight Loss (%)	3.3	3	2.7	2.5
Initial weight loss temperature	60	65	67	68
Maximum weight loss temperature	84	89	101	103
Final weight loss temperature	181	183	205	211
Region 2				
Weight Loss (%)	52.85	52.97	53.14	54.01
Initial weight loss temperature	181	183	205	211
T_{max1} (°C)	306	311	319	334
DTG_{max1} (mg/°C)	1.242	1.327	1.724	2.124
Maximum weight loss temperature (T_{max2})	348	354	361	379
DTG_{max2} (mg/°C)	1.843	2.426	3.131	5.128
Final weight loss temperature (T_f)	402	405	412	415
Region 3				
Weight Loss (%)	1.16	2	2.2	2.3
Initial weight loss temperature	402	405	412	415
Final weight loss temperature (T_f)	454	462	471	477
Residue, % R_s	38.47	39.15	39.89	41.03

Accordingly, the first step of weight loss in the second region could be ascribed to the thermal decomposition of hemicellulose and the first stages of cellulose, while the second thermal degradation step in this region belongs to the final stages of cellulose decomposition and the first stages of lignin decomposition. Therefore, the first peak corresponds to hemicellulose (306-334 °C) and the second one corresponds to cellulose (348-379 °C). The peak belonging to lignin is entirely overlapped by the

other two peaks. The cellulose thermal degradation was almost completed. It can be observed from Table 2 that it is clearly seen that the heating rates have a considerable effect on the maximum wieght loss and the rate of decomposition and also shift the wieght loss and rate of decomposition to higher temperatures. This can be ascribed to the increase in the rate of heat transfer and the longer exposure of the biomass particles to a particular temperature along with elevating heating rates. Thermal degradation percentages in the second region obtained at the final temperatures have been found to be very close (52.85-54.01 %). No significant differences have been observed in thermal degradation for the experiments carried out at the heating rates of 5, 10, 20 and 30 °C min^{-1}. Between the temperatures of 390-415 °C, a slow weight loss occurred. In the third region, over around 415 °C, the TG curves obtained at different heating rates reaches a common plateau value, approximately 40 wt%. Similar results were reported by Singh et al. [37] and Ali et al. [40] for banana leaves and Malaysian wood species, respectively.

In order to evaluate the decomposition kinetics of biomass particles, the kinetic parameters were calculated by applying Eq. (13) introduced and derived in Section II. Figure 5 shows that the plot of $-\ln\frac{-\ln(1-\alpha)}{T^2}$ versus $1/T$, indicating that the thermal decomposition reaction of Cynara Cardunculus could be assumed by a first order reaction in the studied temperature region for every heating rate from the slope and ordinate intercept of the line, the values of the Activation Energy, E, and Pre-exponential Factor, A, can be obtained. Table 3 indicates the Arrhenius parameters of thermal decomposition kinetics of Cynara Cardunculus at four different heating rates, using the Coats-Redfern method.

As can be seen from Table 3, all the regression coefficients (R^2) are larger than 0.998, which shows that the first order reaction model assumed conforms to the experimental data very well in the studied temperature zone. The heating rates have some impact on Arrhenius parameters, i.e. the activation energy and pre-exponential factor. The activation energy and pre-exponential factor rose from 61.13 KJ/mol and 4.56 x 10^7 min^{-1} to 66.44 KJ/mol and 8.63 x 10^7 min^{-1}, respectively, with the increase of the heating rate from 5 to 30 °C min^{-1}. This is attributed to the combined synergic effect of the heat transfer at different heating rates and thermal decomposition kinetics of Cynara Cardunculus [38-45].
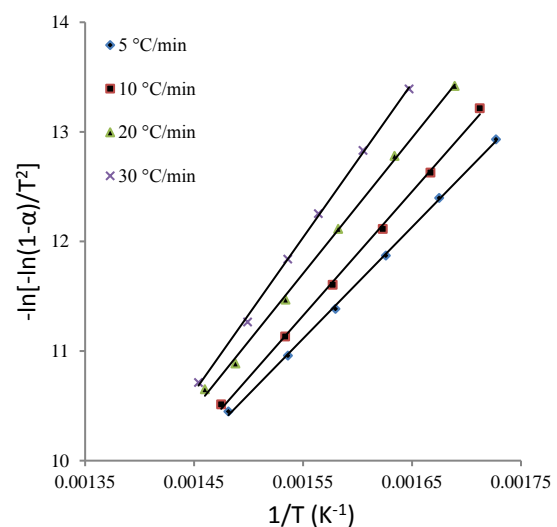

Figure 5. Plot of -ln[-ln(1-α)/T^2] versus 1/T of Cynara Cardunculus pyrolysis at different heating rates

Table 3

Kinetic Parameters of Cynara Cardunculus

Heating Rate	Studied Temperature Zone ($T_f - T_{max1}$)	$-(\frac{dw}{dt})_{max2}$	E	A	R^2
(°C min^{-1})	(°C)	(mg/°C)	(KJ/mol)	(min^{-1})	
5	306-402	1.843	61.13	4.56 x 10^7	0.999
10	311-405	2.426	64.12	5.12 x 10^7	0.998
20	319-412	3.131	65.21	6.29 x 10^7	0.998
30	334-415	5.128	66.44	8.63 x 10^7	0.999

V CONCLUSIONS

The thermogravimetric analysis helps investigate physical and chemical properties and thermal behavior of biomass sample. Evaluating the kinetic parameters also represents valuable information to design and operate more effective thermal conversion systems and optimum pyrolysis operating conditions. In this study, TGA and DTG data were employed under non-isothermal conditions at four different heating rates to investigate pyrolytic thermal decompostion of biomass (Cynara Cardunculus). The pyrolysis process of Cynara Cardunculus can be divided into three regions. The first region is a loss of moisture from the sample. The second region occurs around 181-415 °C and reflects largely the thermal degradation of cellulose, hemicellulose and lignin. In the third regions, the TG curves obtained at different heating rates reached a common value, approximately 40 wt%. The overall thermal degradation was observed in the range of 181 to 415 °C. The kinetics of Cynara Cardunculus thermal decomposition can successfully be modeled by a scheme consisting of single step decomposition reactions of three main components, cellulose, hemicellulose and lignin. The kinetic parameters were calculated with the Coats-Redfern method, depending on a first-order reaction. The regression analysis data of Cynara Cardunculus thermal decomposition fitted the fist-order kinetics very well ($\sim R^2 = 0.998$) The Arrhenius parameters, Activation Energy (E) and Pre-exponential Factor (A) were calculated for the heating rates of 5, 10, 20 and 30 °C min^{-1}. The authors found that the values of the activation energy and pre-exponential factor were in the range of 61.13 to 66.44 KJ/mol and of 4.56 x 10^7 to 8.63 x 10^7 min^{-1}, respectively, depending on the heating rates. The heating rate has some effect on the thermal decomposition kinetics of Cynara Cardunculus.

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