Activation Energy of Rape Residue

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Abstract

Thermal analysis describes the changes of physical and chemical properties of materials depending on increasing temperature. Thermogravimetric analysis of rape residue sample has been carried in inert atmosphere. The samples were heated over a range of temperatures that includes the entire range of pyrolysis with three different heating rates of 5, 10 and 15°C min^{-1}. Thermogravimetric (TG) curves were obtained from experimental data. The results obtained from thermal decomposition process indicate that there are main stages such as dehydration, active and passive pyrolysis. The first region from 50°C is related to the extraction of moisture and adsorbed water in samples. The main pyrolysis process proceeds in a range from approximately 250 to 450°C. The activation energy values as a function of the extent of conversion for the pyrolysis process of rape residue have been calculated by means of the Flynn–Wall–Ozawa method. The activation energy for the pyrolysis of rape residue was 99–189 kJ.mol^{-1} in the conversion range of 0.2–0.8. The average activation energy calculated by this method was 142 kJ.mol^{-1}.

Keywords: activation energy, microwave radiation, rape residue

Introduction

From the energy point of view in the world is devoted considerable attention to the use and processing of various types of biomass, for example in gasification process, pyrolysis process, extraction of organic compounds, and the subsequent use of pyrolysis oil e.g. in the flotation of coal and the like [1–6]. The effective use of new trends in the intensification of processes is conditional knowledge of thermogravimetric characteristics of irradiated biomass samples. The thermal decomposition of biomass in the world dealt at several authors [7–10]. Pyrolysis (thermal decomposition) is a complex phenomenon in which the thermal decomposition in the absence of oxygen enables the release of volatile compounds, leading to the formation of liquid (oil tar) and solid products (char) with more energetic density and high calorific value. The chemical and physical changes determine the decomposition reaction rates, which are dependent on kinetic parameters. The knowledge on the behavior of such parameters that accompanies the process can be useful to interpret the reaction kinetics mainly regarding the mechanism of the process. The kinetic study is related to the activation energy determination for the thermal degradation process of the samples under inert atmosphere. Studies on the kinetic analysis of major biomass constituents (hemicellulose, cellulose and lignin) have been conducted under inert atmospheres. For instance, Braga et al. (2013) reported activation energy of hemicellulose + cellulose of two biomasses (rice husk and elephant grass) using thermogravimetry. They found average activation energy values between 220 and 229 kJ.mol^{-1} [11]. Yao et al. (2008) studied ten different types of biomass and values ranged between 160–170 kJ.mol^{-1} [12]. Jereguirim and Trouvé, (2009) studied the biomass and found 110 kJ.mol^{-1} for activation energy of hemicellulose and for cellulose, values between 90–140 kJ.mol^{-1} [13].

Six lignocellulosic biomass samples (coffee husk, sugar cane bagasse, penut shell, rice husk and tucumã seed) with potential interest for energy production were evaluated under two aspects: physical chemical characterization and kinetic

study of pyrolysis. The activation energy of samples in the range 160–214 kJ.mol^{-1} was studied [14].

Activation energy calculation

The thermal degradation process of biomass is frequently described by a single reaction: solid – volatiles and char, where the conversion by pyrolysis depends on the conversion and residual mass, respectively, and on the temperature according to the following equation:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_A}{RT}\right)\cdot f(\alpha) \quad (1)$$

with α as the conversion of the convertible part of the biomass, defined as:

$$\alpha = \frac{m_o - m(T)}{m_o - m_k} \quad (2)$$

where:

m_o – initial mass of the sample, m (T) – mass of the sample at the temperature T, m_k – final mass of the sample.

The function *f*(α) (1) depends on the reaction mechanism of thermal decomposition.

The dependence of the activation energy on conversion was acquired using calculations according to Flynn-Wall-Ozawa (OFW) [15, 16]:

$$\log\beta = \log\left(A\frac{E_A}{Rg(\alpha)}\right) - 2.315 - 0.4567\frac{E_A}{RT} \quad (3)$$

where

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

The experimental values of the temperature for constant degree of conversion measurements for different heating rate are added to the equation. Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed by plotting logβ vs.1000/T, and the EA is obtained from the slope of the straight line.

Material and Methods

The experiments were realized with the samples of the rape residue (Stakčín, Slovak Republic).

The samples were subjected to comminution using the grinder MRC model FDV and in such way grain size was reduced to 1 mm. Thermogravimetric analyse was carried out using thermal analyser Derivatograf C, MOM (Hungary) under following conditions: samples weight 100 mg, argon atmosphere, heating rate 5°C, 10°C and 15°C/min. The experiments were realized with the samples of the rape residue (Stakčín, Slovak Republic).

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Results and discussion

Fig 1. shows the result of the mass loss during thermal degradation process of rape residue at the different heating rates.

The weight loss curve (TG) shows the loss of mass with temperature at different heating rates for samples (Fig. 1). The results obtained from thermal decomposition process indicate, that there are main stages such as dehydration, active and passive pyrolysis. The thermogravimetric analysis of rape residue revealed an initial slight weight loss between ambient temperature and about 100°C. This could be due to the elimination of physically absorbed water in the rape residue and superficial or external water bounded by surface tension. The loss of light volatiles could also be a contributing factor.

The main pyrolysis process proceeds in a range from approximately 250 to 450°C. As can be seen from the plot, the devolatilization process begins at about 250°C and proceeds rapidly with increasing temperature until about 450°C and then the weight loss decreases slowly to the final temperature 600°C. The solid residue yields are about 30% for sample.

The initial phase of decomposition is similar to all samples. First conversion samples increases only slowly and gradually increase accelerated after reaching a maximum rate of weight loss. To determine the activation energy was used the equation (3). As input data served previously described results obtained by thermogravimetric analysis.

The graphical representation of dependence to determine the activation energy is shown in Fig. 3. The activation energy was determined for the area of the major degradation of samples, that involve the steps of decomposition to 0.8.

The $\log(\beta) - 1/T$ plot according to Equation (3) confirms that the activation energy can be determined based on Ozawa's method (Fig. 3). The activation energy for each α was calculated from the slope of each straight line, as listed in Table 1.

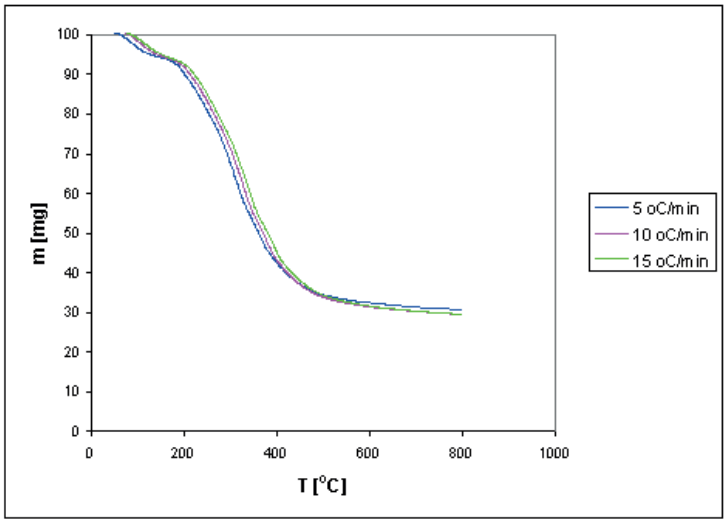

Fig. 1. TG analysis of rape residue at the different heating rates

Rys. 1. Analiza TG odpadów rzepaku w różnych temperaturach

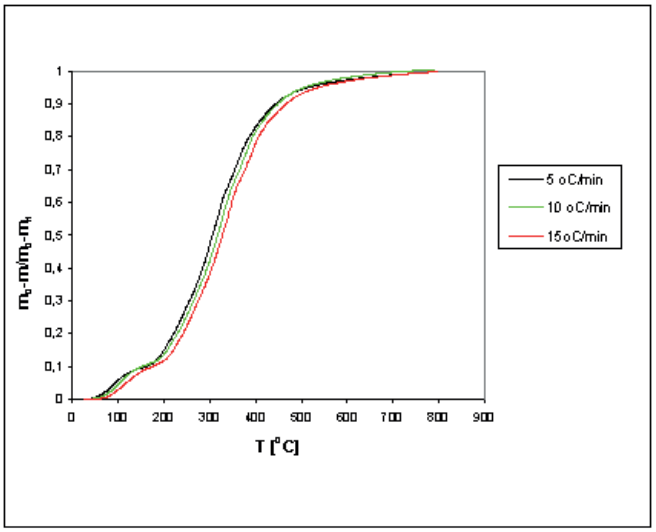

Fig. 2. Influence of the temperature on the conversion degree at the different heating rates

Rys. 2. Wpływ temperatury na przemiany dla różnej szybkości nagrzewania

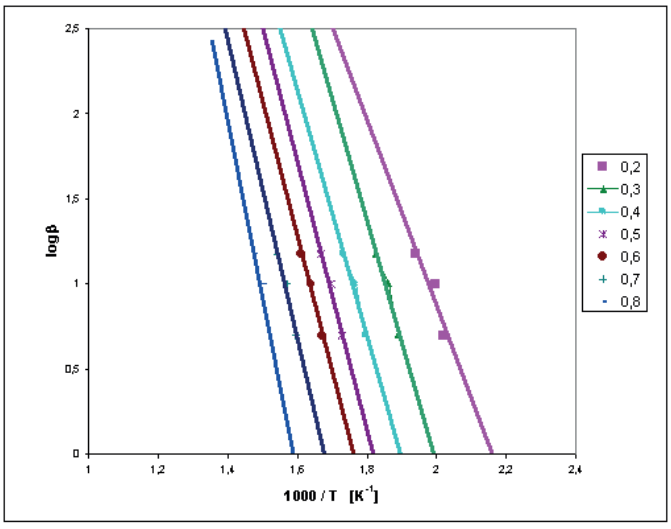

Fig. 3. Dependence described by Flynn-Wall-Ozawa method for selected conversion

Rys. 3. Opis przemian według modelu Flynn-Wall-Ozawa

Tab. 1. Activation energy after thermal degradation of rape residue

Tab. 1. Energia aktywacji odpadów rzepaku po obróbce termicznej

α	Linear expression (Fig. 2)	Activation energy [kJ/mol]
0.2	$y = -5.4489x + 11.773$, $R^2 = 0.8653$	99
0.3	$y = -7.1472x + 14.242$, $R^2 = 0.9475$	130
0.4	$y = -7.2015x + 13.659$, $R^2 = 0.9516$	131
0.5	$y = -7.8741x + 14.319$, $R^2 = 0.9723$	143
0.6	$y = -7.9117x + 13.939$, $R^2 = 0.9898$	144
0.7	$y = -7.7565x + 14.69$, $R^2 = 0.9634$	159
0.8	$y = -10.387x + 16.499$, $R^2 = 0.9355$	189

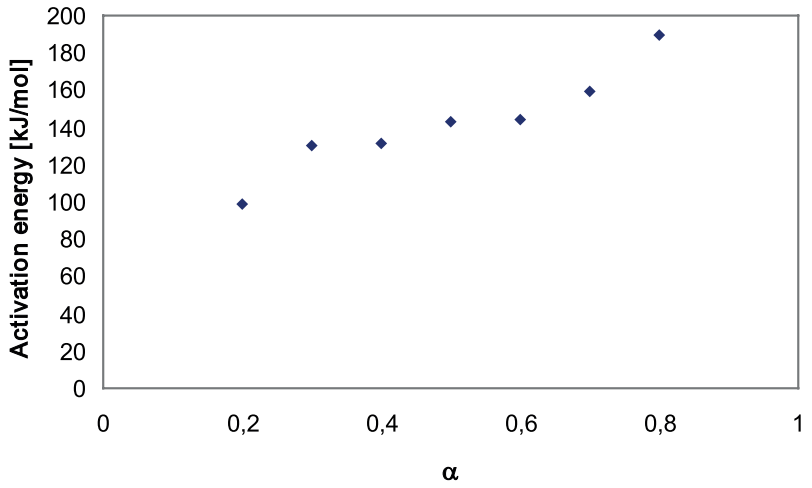

Fig. 4. Activation energy of pyrolysis of rape residue as a function of conversion

Rys. 4. Energia aktywacji po pirolizie odpadów rzepaku w funkcji przemian

The significant increase of activation energy is to achieve the degree of conversion of 0.3, then a slight increase in value of 0.6 and then the steeper increase. The average activation energy was in the calculation by this method are 142 kJ.mol^{-1}. This means that the reaction mechanism is not the same in the whole decomposition process and that activation energy is dependent on the conversion.

Conclusion

The attention was paid to the study of the thermal decomposition and the kinetics of rape residue sample based on thermogravimetric analysis. The main pyrolysis process proceeds in a range from approximately 250 to 450°C.

The activation energy values as a function of the extent of conversion for the pyrolysis process of rape residue have been calculated by means of the Flynn-Wall-Ozawa method. The activation energy for the pyrolysis of rape residue is 99–189 kJ.mol^{-1} in the conversion range of 0.2–0.8. The average activation energy calculated by this method is 142 kJ.mol^{-1}. On average, activation values found in this study are within the range reported in the literature for biomass.

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Energia aktywacji odpadów rzepaku

Analiza termiczna wykazała zmiany właściwości fizycznych oraz chemicznych materiałów w zależności od wzrostu temperatury. Analizę termograwimetryczną próbek odpadów rzepaku przeprowadzono w atmosferze gazów obojętnych. Próbki były podgrzane w różnym zakresie temperatur, który zawierał cały zakres pirolizy z trzema różnymi prędkościami ogrzewania wynoszącymi 5, 10 oraz 15°C min^{-1}. Krzywe termograwimetru (TG) otrzymano z danych eksperymentalnych. Wyniki uzyskane z termicznej dekompozycji wskazują na istnienie głównych faz takich jak dehydratacja, aktywna i pasywna piroliza. Pierwszy proces zachodzi w okolicy 50°C, występuje wtedy parowanie wilgoci i wody z próbek. Główny proces pirolizy zachodzi w zakresie od ok. 250°C do 450°C. Wartości energii aktywacji jako przedłużenie właściwości konwersji procesu pirolizy resztek rzepy zostały obliczone metodą Flynn-Wall-Ozawa. Energia aktywacji dla pirolizy odpadów rzepaku wyniosła 99–189 $kJ.mol^{-1}$ w zakresie konwersji od 0,2–0,8. Średnia energia aktywacji obliczona tą metodą wyniosła 142 $kJ.mol^{-1}$.

Słowa kluczowe: energia aktywacji, promieniowanie mikrofalowe, odpady rzepaku