REACTION CONSTANTS AND ACTIVATION ENERGIES IN PYROLYSIS FOR *POPULUS ALBA*

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White poplar (Populus alba) is considered a good candidate for biomass production in Romania and Europe and can be used as a feedstock for production of bio-based fuels and energy. The present paper is focused on the determination of overall thermal behavior and the corresponding decomposition kinetics during pyrolysis of poplar wood. The biomass utilized was from different parts of the tree, namely small branches, twigs, buds and trunk. The proximate analysis indicated that the biomass is composed of volatile matter 79.23% and char 20.78%, (ash 4.25%, fixed carbon 16.25%). The moisture of 12.59% was measured on the samples as received. The mass variation revealed that the mass drop is not linear and varies from minute to minute starting with 0.08 % at 300°C to 22.73% at 800°C. The activation energy was computed for each temperature, from 300°C to 800°C, and it has been compared with the results from literature. The activation energy value for the range of temperatures, 300-800°C, is 29.65 kJ/mol, and the frequency factor is 2.8[s^{-1}].

Keywords: batch reactor, biomass, poplar wood, pyrolysis, activation energy

1. Introduction

The fossil fuels depletion and the immediate need for greenhouse gas emissions reduction are among the most discussed topics related to a sustainable industrial development through enhanced energy security. Global leaders, such as European Union (EU) committed to reaching a share of 20% of energy consumption from renewable sources (including bioenergy) by 2020 [1]; the same target is expected in Australia and U.S.A by 2030 [2-4].

By 2050 the bioenergy produced from biomass and waste could cover between 25%-33% from the global energy delivered [5]. Biomass represents an alternative for fossil fuels, being a renewable, environmental friendly and widely available source for energy and fuel production [6-9]. Depending on specific source, the biomass is composed of 10–20% lignin, 20–35% hemicellulose, 35–50% cellulose and other compounds such as: lipids, proteins, sugars and starches,

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to which it can be added the inorganic matter and water [10]. Lignocellulosic biomass is the most widely spread and sustainable energy source of biomass and can be used in biochemical production of ethanol [11] or thermochemical bio-oil production [12]. Even though technological systems based on thermal treatment solutions, such as pyrolysis, for bioenergy and biofuels production have been implemented at small scales, their sustainability at larger scale is still being investigated and needs further improvements [13]. These improvements can be achieved if a fundamental understanding of devolatilization kinetics, such as the one presented in this paper, is known. Biomass pyrolysis is a thermochemical process, consisting of thermal decomposition of the material, in an oxygen-free atmosphere, mainly used for generation of non-condensable gas products, liquid products (bio-oils, tars) and carbonaceous residues with some inorganic solid particles (biochar). The energetic potential of the pyrolysis gas is given by the chemical composition of the fuel, the process conditions and thermodynamic efficiency [14]. The pyrolysis gas is composed largely of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and small molecular weight hydrocarbons, such as methane (CH_4), ethane (C_2H_6), and ethene (C_2H_4), with traces of propane (C_3H_8), ammonia (NH_3), nitrogen oxides (NOx), sulfur oxides (SOx) and alcohols with a low carbon number. For biomass, the primary gas released during pyrolysis process are CO and CO_2, followed by CH_4 and H_2 which is formed at higher temperatures [15]. The amount of CO_2 released is mainly due to the decomposition and reformation of carboxyl functional groups, the C = O, COOH and CO are formed due to the cracking of the carboxy and carbonyl groups COC, C = O [16].

According to Tingting Qu et. al, carbon monoxide is formed due to the cracking of carboxyl and carbonyl groups which leads to large volume fraction of CO from cellulose pyrolysis, while hydrogen and CH4 are formed due to the cracking of C=C and CH respectively, methoxy-O-CH3 groups. Carbon dioxide is formed from hemicellulose pyrolysis on large volume fraction due to higher carboxyl content. On the other hand, a large volume fraction of methane forms from lignin pyrolysis – high concentration in methoxyl [17]. Pyrolysis gas has potential applications:

a) direct use by burning it to produce thermal and / or electrical energy (by spark or compression-ignition engine);

b) directly or in mixture with other fuels to produce individual gases including H_2, CH_4 and other volatiles or bio-synthetic liquid fuels;

c) the hot gases may be used in the process by preheating the reactor or the inert gases.

For most biomass pyrolysis systems, the main objective is to increase the yield of bio-oil production and improve its quality by producing bio-fuel. Among the liquid products resulted from the biomass pyrolysis, methanol and phenols are among the most valuable oxygenated products [18]. The energy potential of bio-oil resulting from the pyrolysis of biomass is strongly influenced by the high level of oxygenates present in the material. The High Heating Value (HHV) of the bio-oil resulted from biomass ranges between 16.79-19 MJ/kg, which is close to ethanol [19]. For fuel application, it is desirable for the oxygen content to be reduced, in order to make the bio-fuel more compatible with the existing petroleum-derived fuels [20]. The bio-char can be used as fertilizer and as a pollutant absorbent of soil quality improvement [21].

2. Materials and methods

The study presented here is focused on white poplar wood (*Populus Alba)*. The biomass has been collected from Valcea county in South of Romania. According to first cycle of national forest inventory (2008-2012), poplar represent 7% of forest in Romania. The biomass has been collected during spring season from different poplar trees. Due to the season the small branches were green and presenting a high humidity. Also, the buds were already existing. Thus, the collected biomass consisted of small branches, buds, leaves from last autumn, twigs and trunk. The biomass has been dried at 105˚C for 24 hours, to remove the excess moisture, which was found to be 12% by weight. After moisture removal, the biomass was ground into fine particles. The content of volatile matter, ash fraction and fixed carbon content from poplar were determined using a calcination furnace (Fig.1.). For volatile matter the calcination furnace temperature was established at 800˚C with a residence time of 40 minutes. The sample was weighted and placed into a refractory crucible steel which was covered with a tap, in order to reproduce the pyrolysis process required to remove the volatile fraction. After the established residence time the sample was weighted again, and char content was determined. The difference from the initial sample weight and char content was considered to be the content of volatile matter. For ash content, the furnace was set at 900˚C and the residence time for the sample (in the crucible without the cover to reproduce the combustion process) was 15 minutes. The content of fixed carbon was determined as the difference between the weight of the initial sample and volatile matter, char and ash. The determinations have been performed according to ASTM E871-82(2013) [22], ASTM D1762-84(2013) [23] and ASTM E1755-01(2015) [24].

Another suite of experiments was undertaken in the calcination furnace (Nabertherm L9/11/SW No. 192068/2007) to determine the mass variation through time, by maximizing the highest heating rate allowable by the furnace for 6 different temperatures (300°C-800°C). Mass loss rates were determined using a custom-made system composed of an analytical balance supporting the crucible and reactor through the furnace’s lower side. The samples were weighted and placed into the covered refractory steel reactor. For 300°C the time required for char stabilization was about approximately 60 minutes, and as the temperature was raised, the stabilization time decreased. Mass values were collected every 60 seconds, and the mass loss rates were determined subsequently using Microsoft Excel (Microsoft Inc., Seattle, WA, USA). All experiments were performed in triplicate, with the exception of mass loss in time at 300°C and 400 °C, which were conducted in six replicates due to the longer time required for char stabilization.

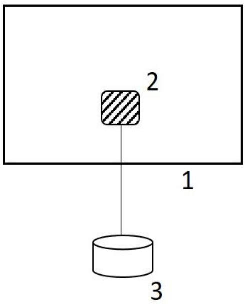

Fig. 1.Calcination oven external heated (1); Sample in refractory crucible steel (2); Analytical balance (3)

3. Results and discussions

A. Thermal behavior and experimental results

The determinations were performed on dried samples. Prior to eliminating the water, the twigs, branches, etc., were shredded to be easily manipulated and homogenized. After grinding, about 50% of the sample were less than 4 mm in size, more than 30% were less than 2 mm and the smallest, less than 8µm, were considered sawdust. The full-size distribution the ground poplar wood is presented in Fig. 2.

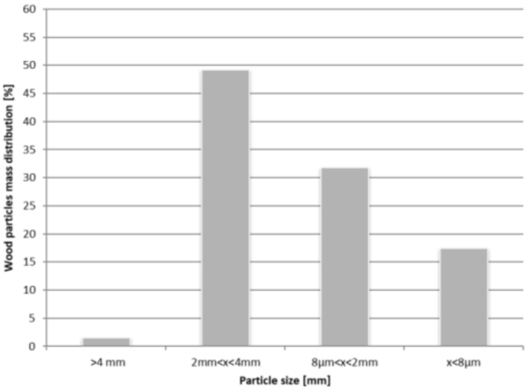

Fig. 2. Poplar wood size distribution

As the samples were homogenized prior to pyrolysis, no effect of particle size was investigated in the current study. However, literature data indicates that particle size significantly affects the pyrolysis products yield [25] and composition, as the pyrolysis of individual particles is controlled by the heat and mass transfer rates, which are dependent on size [26].

In order to observe the devolatilization period and the stabilization of the char in time, the sample was introduced in the refractory crucible steel and placed into the calcination furnace at the ambient temperature, then heated progressively until temperature stabilized at around 800°C. Determinations have been repeated three times to see if the pattern of devolatilization is maintained. In Fig. 3. is presented the variation of the mass with the temperature of poplar sample, until the char is stable, including the standard deviations.

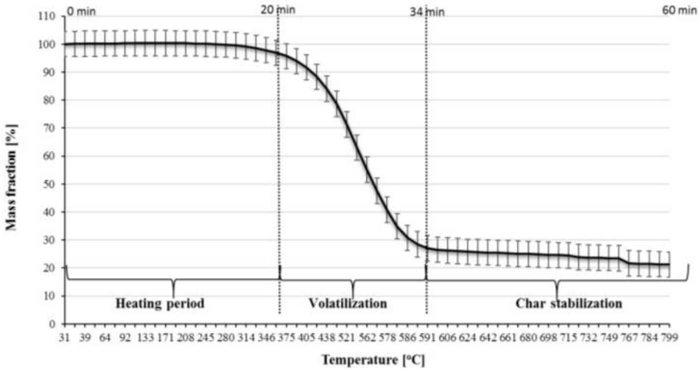

Fig. 3. Mass variation with temperature

During the variation of the mass with the temperature, the time was also measured. The results (Fig. 3.) indicate that the heating period required by the samples to reach pyrolysis stage is around 20 minutes, which is expected since the decomposition of lower carbon-number hemicellulose and cellulose compounds starts only around 300 °C [27]. A significant devolatilization only starts around of 360˚C, where the bulk of the solid matrix of the sample starts to decompose. Volatilization stage is shorter in time, only approximately 14 minutes, where the temperature reaches almost 600˚C. Following this period, the char stabilization occurs for the longest period of about 26 minutes. As an entire process, it is a relatively symmetrical with respect to time, 20 minutes required by the heating period and 26 minutes required by the char stabilization period. From Fig. 3, it can be observed that the maximum rate of mass loss appears to be around minute 30, corresponding to a temperature of 530 °C.

To determine the decomposition kinetics of the white poplar biomass, the mass variation in time was quantified for six different temperatures (Fig. 4.).

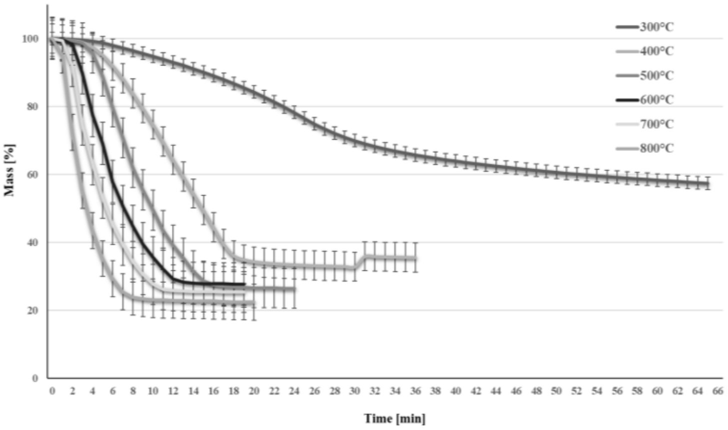

Fig. 4. Mass variation in time for 6 temperatures

As it is presented in Fig. 4 the time for char stabilization at 300°C is almost double as for 500°C. At the same time, the initial heating period and the volatilization periods are longer. In the first minute, at 300°C the mass loss is 0.09%, while at the other temperature the mass losses are 0.3%, 0.31%, 0.39%, 0.64 %, and 4.9%, at 400, 500, 600, 700 and 800°C, respectively. For the second minute the values are higher: from 300°C to 800 °C, the mass losses are, respectively, 0,14%, 0,25%, 0,36%, 1,3%, 7,62%, and 22,73%. Therefore, the pattern is clear, as the temperature increase, the mass losses at equivalent time increase as well.

B. Kinetic model and parameters for poplar wood pyrolysis

A detailed kinetic scheme of biomass pyrolysis considering the distribution of molecular weight requires the solution of a high-dimensional system of differential equations. The kinetic models of thermal cracking of biomass by itself and its components (cellulose, hemicellulose and lignin) can be classified into two major parts on the basis of their complexity; simple models with one to five lumps and the models with more than five lumps or models requiring more computational efforts (detail models requiring more than a few hundred species and a few thousand reactions) classified as complex models [28]. For simplicity purposes, usually only one step global reaction is considered which, however, does not allow the dependence of product yields on reaction conditions to be predicted. Conversely, the semiglobal model includes both primary and secondary reactions with pyrolysis products lumped into groups (tar, char, gas) [29]. In current work the one step global model for prediction of devolatilization profile of poplar wood (*Populus Alba*) was evaluated, under pyrolysis reaction in the temperature region 300°C-700°C in this reactor. To calculate the apparent kinetic parameters for pyrolysis of poplar wood, a pseudouni-molecular kinetics was applied, in which the empirical rate of decomposition of poplar wood is first order [Equation 1]

$$\text{Poplar wood} \rightarrow \text{Product} \tag{1}$$

and expressed by the following equation at given temperature:

$$A = A_0 * e^{-kt} \tag{2}$$

Where A and A_0 are initial and current mass amounts (in percentage) of poplar wood, respectively and *k* is the pseudo unimolecular reaction rate coefficient in the Arrhenius equation,

$$k = e^{(-\frac{E}{RT})} \tag{3}$$

Using [Equation 2] and [3], the rate constant can be derived from the slope of the dependence log A/A_0 versus pyrolysis time, t (in seconds) [Equation 4].

$$\log\frac{A}{A_0} = -\frac{k*t}{2.3} \tag{4}$$

The activation energy *E* and the pre-exponential factor *A* from equation (3) has been determined based on dependence of an Arrhenius plot of *log k* versus *1/T*.

$$\log k = log A - \frac{E}{2.3RT} \tag{5}$$

From [Equation 5] it is evident that the slope of the Arrhenius plot is equal to -*E*/2.3*R* and from the intersection with the axis, *log A*, the pre-exponential factor, *A* (in 1/sec) can be derived [30].

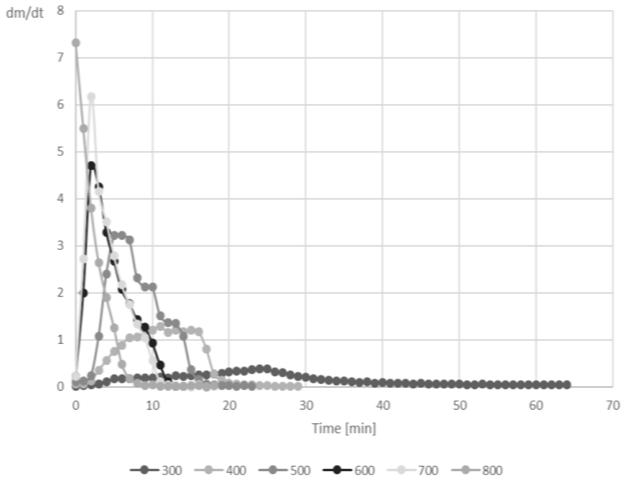

Fig. 5. Mass vaporization rates at different temperatures

In Fig. 5, the maximum mass vaporization rates are depicted. The time at maximum mass vaporization rate has been calculated at maximum mass vaporization rate at each temperature as a slope of the dependence of the fractional conversion at each time versus time. The maximum rates were used to calculate the reaction rate constants *k*, which were then used to calculate the activation energy E_a and the pre-exponential molecular constant *A* (Fig. 6).

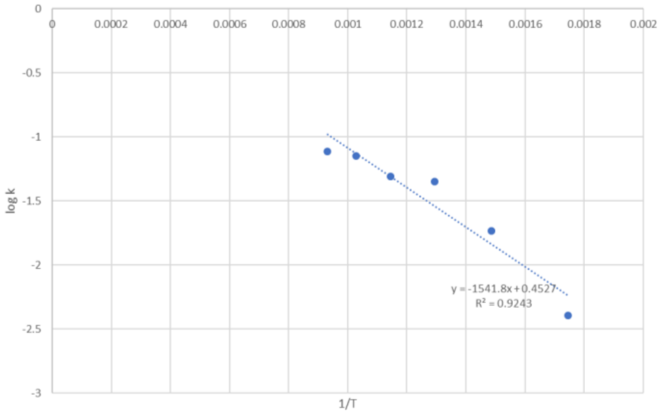

Fig. 6. The Arrhenius dependence of the pseudo-1st order monomolecular decomposition of poplar wood product

Thereby the activation energy computed for poplar wood is 29,65kJ/mol. It can be seen than in this particular process, the activation energy is lower than the what was previously reported in the literature: 153-158 kJ/mol reported by Slopiecka et al. [30] and 54.1 kJ/mol reported by Van de Velden et al. [29]. Such phenomenon is typical in pyrolysis processes due to numerous parameters that affect the kinetic calculations, but in particular the specific configuration of the reactor conditions.

4. Conclusions

During mass variation determinations, the small sizes of the particles of poplar can be entrained by the volatiles released and can lead to combustion inside the oven (not inside the crucible). This is perfect normal as the volatiles reacts with the Oxygen outside the crucible and has no influence on the process inside. Char stabilization is three times faster at 800°C than at 300°C. It is required a time of 21 minutes for 800°C and up to 66 minutes for 300°C. The heating period to reach the maximum process temperature decreases when increasing the temperature. The char stabilization period is also shorter, so the process can be considered to be symmetrical with respect to heating rate ratio at any temperature. The differences between the values of activation energy for the same biomass achieved by different authors is due to the fact that pyrolysis represents a complex process during which simultaneous physical processes (melting, phase changes) and chemical reactions (destruction of bonds, new bond formation, oxidation, etc.) occur. The experimental setup used in this study was designed for larger sample amounts compared to the literature. Therefore, the utilized samples were more representatives to the biomass feedstock. Also, the laboratory scale installation and the conditions to which the sample was subjected are closer to the industrial applications, the current results bringing an important contribution to the field.

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