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Characterization of lignocellulose biomass and model compounds by thermogravimetry

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ABSTRACT

In this research, combustion characteristics of lignocellulose biomass (hazelnut shell) and three main components (cellulose, hemicellulose, and lignin) were investigated using thermogravimetry (TGA-DTG) technique at different heating rates. The ignition, peak, burn-out temperatures, and the heat liberation of lignocellulose biomass and three main components were also measured. Two different model-free kinetic methods, known as Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS), were used in order to determine the activation energy values. Throughout the study, it is observed that the activation energy values of the biomass compounds varied between 83.8 and 191.7 kJ/mol for OFW and KAS methods, respectively.

KEYWORDS

Biomass model compound; combustion; hazelnut shell; hemicellulose; kinetics; lignin; lignocellulose; thermogravimetry

Introduction

In recent years, combustion characteristics of biomass fuels have been studied by thermo-analytical techniques. The most common were thermogravimetry (TGA), differential thermogravimetry (DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR), and thermogravimetry-mass spectrometry (TG-MS) techniques.

Biomass fuels are chemically complex polymeric lignocellulose materials. Lignocellulose biomass is composed of cellulose, hemicellulose, and lignin. The carbohydrate polymers (cellulose and hemicellulose) are tightly bound to the lignin. These model compounds cellulose, hemicellulose, and lignin determine the physical and chemical properties of the biomass fuels based on their arrangement in the fuel (Sjostrom, 1993).

The lignocellulose biomass samples such as miscanthus, wheat bran, hazelnut shell, rice husk, poplar wood, and many others were used in different power plants for energy production. Some researchers (Jayaraman and Gokalp, 2014–2015; Magdziarz and Wilk, 2014; Coimbra et al., 2015; Wilk et al., 2016) have reported the thermal characteristics of biomass samples and their blends in different atmospheres (oxygen, argon, air, nitrogen, and steam) using various thermal analysis techniques. Besides, pyrolysis and combustion properties of wood chips mixture, main wood, poplar wood, corn stalks, straw, rice husks, sawdust, and other agricultural residues were studied at different heating rates using thermogravimetric techniques.

On the other hand, some researchers have investigated the pyrolysis characteristics of model compounds, while some researchers have tested the combustion behavior of model compounds. Ferdous et al. (2002) have studied the pyrolysis of lignin in a fixed-bed reactor and in a thermogravimetric analyzer (TGA) using helium and nitrogen. The distributed activation energy model has been used to analyze complex reactions involved in the lignin pyrolysis

process. It has been observed that, for the pyrolysis in TGA, the activation energies for lignin varies from 129 to 361 kJ/mol. Yang et al. (2007) have used DSC and TG-FTIR to investigate the three model compounds. It has been observed that pyrolysis of hemicellulose and cellulose occurs quickly; however, lignin is more difficult to decompose. The main gas products from pyrolyzing the three components are similar, including CO₂, CO, CH₄, and some organics. It has been observed that hemicellulose has higher CO₂ yield, cellulose generates higher CO yield, and lignin owns higher H₂ and CH₄ yield. Ramiah (1970) has used DTA and TGA to study the thermal degradation of samples of cellulose, hemicellulose, and lignin. It has been observed that cellulose has the highest thermal stability. The results calculated from static and dynamic TGA indicate that the activation energy *E* for thermal degradation for different cellulosic, hemicellulose, and lignin samples is in the range of 150–250, 63–150, and 55–80 kJ/mol, respectively. Shukry et al. (1991) have studied the thermal degradation of bagasse and rice straw hemicelluloses by DTA. It has been observed that bagasse hemicellulose exhibit three overlapping exothermic effects, while rice straw hemicellulose display two exothermic effects. Different activation energies have been observed for each exothermic reaction. Tsujiyama and Miyamori (2009) have used DSC to investigate the effects of model compounds on biomass degradation. The common outcome for the studies in the literature is the high stability of cellulose for the thermal degradation. However, the output data regarding the combustion of biomass model compound are poor. On the other hand, some researchers have investigated the pyrolysis characteristics of model compounds, while some researchers have tested the combustion behavior of model compounds (López-González et al., 2013).

In this research, combustion behavior of lignocellulose biomass (hazelnut shell) and three main components (cellulose, hemicellulose, and lignin) were investigated from the point of view of reaction regions, peak and burn-out temperatures and kinetics using thermal analysis technique known as thermogravimetry. The reason to conduct this study was to obtain the combustion behavior of lignocellulose biomass and model compounds that provide information for the combustion of biomass fuels.

Experimental

In this research, combustion experiments of lignocellulose biomass (hazelnut shell) and three main components (cellulose, hemicellulose, and lignin) were performed using *TA* differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA-DTG) equipment. The model compounds tested were CF11 fibrous cellulose powder, hemicellulose (xylan) from birch wood, and loblolly pine lignin: CF11 fibrous cellulose powder and xylan (hemicellulose) from birch wood, provided by Whatman Company (Buckinghamshire, UK), and loblolly pine lignin, provided by the College of Agricultural Sciences at Penn State University. They include no impurities.

The lignocellulose biomass and model compound samples used in the analysis were less than 60 mesh size, and the mass was around 10 mg. The experiments were carried out with the powdered sample, whereas the air flow rate (50 ml/min) has been kept constant during the experiments. All the experiments have been conducted in the temperature range of 20–600°C for DSC and 20–800°C for TGA at three different heating rates such as 10, 20, and 30°C/min.

Prior to experiments, the DSC system has been calibrated for temperature readings using indium as reference standard. On the other hand, the TG-DTG system has been calibrated for buoyancy effects to allow quantitative estimation of weight changes. The system was kept isothermal at 110°C for 5 min to remove moisture from samples. Experiments have been performed twice to ensure repeatability, and it has been observed that the experiments show good repeatability with standard errors $\pm 1^\circ\text{C}$ (within a confidence interval of 95%). Proximate and ultimate analysis of lignocellulose biomass (hazelnut shell) is given in Table 1.

Table 1. Proximate and ultimate analysis of lignocellulose biomass (hazelnut shell).

Moisture Cont.(%)	Volatile Matter (%)	Fixed Carbon (%)	Ash Content (%)	Heating Value (cal/kg)
1.5	69.5	28.9	0.1	4872
C (%)	H (%)	N (%)	S (%)	O (%)
50.5	5.63	0.18	0.08	43.61

Results and discussion

Theoretically, when biomass samples were subjected to heat, they follow parallel and consecutive reactions and undergo permanent molecular change, and it is known that the temperature, composition of the fuel, and the oxygen supply dictate the nature of these reactions.

In thermogravimetry (TGA-DTG) curves of lignocellulose biomass (hazelnut shell) with increasing temperature, continuous mass loss of the sample was observed. TGA-DTG curves of lignocellulose biomass (hazelnut shell) represented three different mass loss stages in each heating rate studied (Figure 1). In general, the first stage corresponds to loss of moisture and decomposition of very light volatile compounds. The temperature interval for this stage was below 160°C. The second stage, known as decomposition of hemicellulose, cellulose, and lignin, takes place around 209–395°C, and the last stage, which is the combustion of complex and thermally stable structure (char forming), takes place around 395–571°C for lignocellulose biomass. It was observed that the reaction regions (all the three stages) shifted to the higher temperature intervals, and peak burn-out temperatures was increased as the heating rate was increased from 10 to 30°C/min (Table 2).

From the TGA-DTG curves of model compounds (cellulose, hemicellulose, and lignin) different mass loss stages were observed. Cellulose has one main peak because of its structure, which is in a good order without branches; hemicellulose and lignin have two main peaks due to the presence of

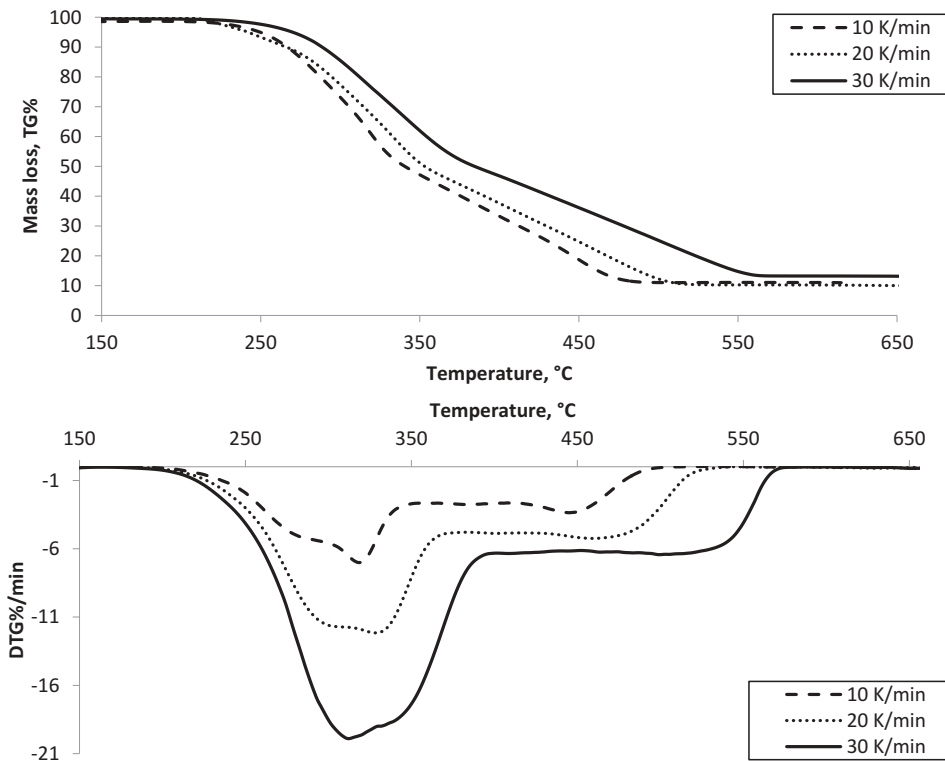
**Figure 1.** TGA-DTG curves of lignocellulose biomass at different heating rates.

Table 2. Combustion properties of lignocellulose biomass (hazelnut shell) at different heating rates.

Properties	10°C/min	20°C/min	30°C/min
Reac. Region-II (°C)	201–350	207–371	209–395
Peak temperature (°C)	315	321	327
Mass loss (%)	54.0	57.0	57.0
Reac. region-III (°C)	350–502	371–532	395–571
Peak temperature (°C)	443	458	498
Mass loss (%)	36.2	34.0	34.8
Burn-out temp. (°C)	505	535	575
Residue left (%)	9.8	9.0	8.2

Table 3. Reaction regions (°C) of model compounds.

Samples	Reaction Type	10°C/min	30°C/min	50°C/min
Cellulose	Combustion of light compounds	273–405	369–440	383–463
	Combustion of heavy compounds	405–535	440–568	463–591
Hemicellulose	Combustion of light compounds	210–350	238–379	251–382
	Combustion of heavy compounds	350–475	379–500	382–523
Lignin	Combustion of light compounds	240–361	252–385	264–412
	Combustion of heavy compounds	361–577	385–615	412–675

Table 4. Ignition, peak, and burn-out temperatures of model compounds.

Sample	Ignition Temp. (°C)	Peak Temp. (°C)	Burn-out Temp. (°C)
10°C/min			
Cellulose	273	353	535
Hemicellulose	210	411	475
Lignin	240	517	577
20°C/min			
Cellulose	369	379	568
Hemicellulose	238	417	500
Lignin	252	582	615
30°C/min			
Cellulose	383	394	591
Hemicellulose	251	438	523
Lignin	264	600	675

light and heavy compounds in their complex branched structures. That is why combustion of hemicellulose and lignin occur in a wide range. Similar peak temperatures, reaction intervals, and thermal profiles have also been observed in the literature (Shukry et al., 1991).

It was observed that the combustion of light and heavy compounds take place in different temperature intervals depending on the heating rate and the type of biomass model compounds (Table 3). On the other hand, ignition, peak, and burn-out temperatures were increased as the heating rate was increased. Since hemicellulose has the highest moisture content and lignin is the highest heavy compound among the model compounds, the mass losses were due to its high volatile matter and carbon content. Finally, no relationship between heating rate and mass loss has been observed possibly because of model compound's high reactivity that eliminates other experimental effects (Table 4).

Kinetic analysis

The non-isothermal kinetic study during combustion process of lignocellulose biomass (hazelnut shell) and model compounds was extremely complex because of the presence of numerous components and their parallel and consecutive reactions. In this research, model-free methods known as Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) were used to obtain the activation energy values.

OFW method

The OFW method (Skoog et al., 1998) was based on a simplified model for determining kinetic parameters for complex reactions. This simplified model does not require a priori assumption and mathematical model fitting for obtaining the kinetic parameters. For OFW method, several TGA-DTG curves (three or more) can be used simultaneously to determine the activation energy values. TGA-DTG curves were used simultaneously to determine the activation energy values at the same conversion levels, using the following relationship which was from the P function of Doyle's approximate expression. From the slope of the plot of $\log(\beta)$ vs. $1/T$ at given conversions, activation energy can be calculated.

$$[d(\log \beta)/d(1/T)] = 0.4565(E/R) \quad (1)$$

KAS method

KAS method was accepted as more accurate than OFW method due to its better approximation of the temperature integral (Slopiecka et al., 2001). In this method, some part of the approximation was neglected and oversimplified. In KAS method, apparent activation energy was obtained from a plot of $\ln(\beta_i/T_{\alpha i}^2)$ vs. $1000/T_{\alpha i}$ for a given value of conversion, α , where the slope is equal to $-E_{\alpha}/R$. The final form of the equation which was used to determine the apparent activation energy is given below:

$$\ln(\beta_i/T_{\alpha i}^2) = \ln[(A_{\alpha}R)/(E_{\alpha}g(\alpha))] - (E_{\alpha}/RT_{\alpha i}) \quad (2)$$

where E is activation energy, J/mol; R is ideal gas constant, 8.314 J/mol/K; T is temperature, K; β : is heating rate, K/min; α is ratio of conversion.

In general, model-free methods allow the calculation of kinetic properties at progressive conversion degrees without any reaction model, $f(\alpha)$ estimation. To carry out a model-free method, a series of experiments are performed at different heating rates and then, the temperature values at fixed conversion degrees are measured for each heating rate. The conversion intervals were selected between the beginning of first reaction regions and the end of second reaction regions for the simplicity of the processes and comparisons. Mass in the kinetic methods is considered as the organic material burnt in the reaction regions.

Throughout the study, it was observed that the activation energy values of lignocellulose biomass (hazelnut shell) and model compounds varied between 93.6 and 191.1 kJ/mol for OFW and 83.8 and 141.4 kJ/mol KAS methods, respectively (Tables 5 and 6). The kinetic parameters calculated were in a similar magnitude, and the deviations in each model were so close to each other. It was observed that the cellulose has the highest activation energy value among the model compounds and hemicellulose has the lowest value, for all the kinetic methods studied. Although

Table 5. Activation energy values of lignocellulose biomass and model compounds different values of conversion (KAS method).

Samples/Conversion Ratio	10	20	30	40	50	60	70	80	90	Aver E. (kJ/mol)
Hazelnut shell	128.7	110.8	111.9	100.1	91.9	53.6	52.4	51.9	52.1	83.8
Cellulose	142.7	143.0	145.6	145.9	152.1	153.1	153.5	153.1	153.2	149.1
Hemicellulose	130.9	132.2	132.9	134.8	137.6	138.9	140.3	140.4	141.2	136.6
Lignin	133.0	135.0	136.7	138.0	145.5	146.1	145.9	146.2	146.1	141.4

Table 6. Activation energy values of lignocellulose biomass and model compounds different values of conversion (OFW method).

Samples /Conversion Ratio	10	20	30	40	50	60	70	80	90	Aver E. (kJ/mol)
Hazelnut shell	145.3	124.5	124.6	111.1	101.3	59.5	57.9	57.5	57.4	93.3
Cellulose	183.3	185.2	186.3	189.0	189.5	190.2	194.1	194.1	196.0	189.7
Hemicellulose	171.4	173.2	176.3	177.9	179.5	181.5	183.2	184.1	185.6	179.2
Lignin	185.4	186.9	187.2	189.9	191.7	192.5	193.2	195.3	198.1	191.1

different activation energy values were obtained for each kinetic method, the trend of the values was same for all the kinetic methods (Kok et al., 2000, 2003, 2012).

Conclusions

In the research, combustion behaviors of lignocellulose biomass (hazelnut shell) and model compounds were determined using TGA-DTG technique at different heating rates. Lignocellulose biomass (hazelnut shell) combustion took place into three main stages. Different reaction regions intervals, peak, and burn-out temperatures have been observed at different heating rates. The differences in activation values were due to the different equation parameters and assumptions of the kinetic methods used.

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