Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
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Journal of Applied Sciences 10 (12): 1122-1127, 2010
ISSN 1812-5654

Thermal Decomposition Kinetics of Forest Residue

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Abstract: The aim of this study is to obtain the kinetics parameters of combustion for forest residue from white spruce, white pine and balsam fir needles under inert atmosphere. The biomass material particle size of 150 μm prepared from each of these species was subjected to the combustion process at five different heating rates: 10, 20, 30, 40 and 50°C min^{-1}. TGA was used to analyse the data of the weight degradation over the increase in temperature up to 800°C. The experimental data was then used to develop a reaction kinetic model to obtain the activation energy, E. The proximate and ultimate analysis of the species was carried out. The conversion degree α occurred at different temperature range when different heating rates were applied. The activation energy related to the combustion of white spruce needles was the highest (262.4 kJ mol^{-1}) compared to white pine (197.14 kJ mol^{-1}) and balsam fir needles (139.94 kJ mol^{-1}).

Key words: Activation energy, degradation, white pine, kinetic parameters

INTRODUCTION

Biomass is one of the major energy sources today, contributing approximately 14% of the world annual energy consumption in comparison to 12% from coal and 15% from gases (Senneca, 2007). Physical and chemical structure of biomass is extremely important for chemical conversion or production of biofuels. There is a tremendously growing interest of developing efficient biomass thermal conversion technologies including combustion, gasification and liquefaction for power generation (Kazagic and Smajevic, 2007) and production of liquid biofuels (Asadullah *et al*., 2007, 2008; Putun *et al*., 2005). Chemicals (Valero and Uson, 2006; Orecchini and Bocci, 2007) and charcoal (Senneca, 2007; Prauchner *et al*., 2005; El-Hendawy, 2007; Prins *et al*., 2006a) that can be used as activated carbon for absorption as well as domestic fuels. A good understanding of the decomposition of forestry biomass during thermochemical conversion is important for developing efficient processing technology.

Woody biomass is mainly composed of hemi-cellulose, cellulose and lignin, which decompose at the temperature range of 225-325, 305-375 and 250-500°C, respectively (Prins *et al*., 2006b). The variation of constituent fractions in biomass, types of species and plant origin gives different thermal behaviour and products namely non-condensable gases, heavy volatiles (tar) and char (Rath *et al*., 2007). Most reported studies about the kinetics of biomass decomposition (Senneca, 2007; Valero and Uson, 2006; Prins *et al*., 2006b; Volker and Rieckmann, 2002; Sanchez *et al*., 2009; Sonobe *et al*., 2008; Kumar *et al*., 2008; Leroy *et al*., 2006; Dimitrakopoulos, 2001; Lapuerta *et al*., 2004) focused on pyrolysis of cellulosic materials under inert atmospheres using either experimental or theoretical methods. The kinetics of decomposition of biomass under inert atmospheres are influenced by type of equipment, experimental conditions (temperature, pressure and heating rate), the physical properties of material (moisture content and particle size) and the chemical composition of the solid (three main constituents and inorganic components). The effects of the above parameters on the behaviour of biomass decomposition under inert atmospheres have been mostly investigated but are limited for such kind of forestry residue. The purpose of this study is to obtain activation energy in relation with the calorific value and degree of conversion at different heating rates for white spruce, white pine and balsam fir needles.

EXPERIMENTAL

Sample preparation: White spruce, white pine and balsam fir, were obtained from local supply. Prior to the TG analysis species samples were identified for their characteristics and behaviour for consistency

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to demonstrate reproducible tests and values. Characteristics such as drying behaviour, gross calorific values, ultimate and proximate analysis for each species were determined.

Moisture analysis: Samples of about 100 g of each species were dried at 105°C for 3 h in the Dispatch Oven for moisture content determination. The weight of the biomass sample was taken periodically every 15 min until the weight was constant and no further change was observed. The moisture content of the species was between 50-100 weights percent on wet basis. The desired moisture content for test samples was 2-5 weight percent. The samples, which are chopped first between sizes 4-5 mm, were then milled and sieved into 150 μm mesh sizes. Small biomass particle sizes of less than 2-3 mm are needed to achieve high biomass heating rates and the rate of particle heating is usually the rate-limiting step (Bridgwater, 2007). Harun *et al*. (2009) studied effect of particle sizes of 300 and 425 μm on reaction rate, lower particle size (300 μm) gave out higher reaction rate than greater size (425 μm). Dall'Ora *et al*. (2008) has pointed out that when the fuel particle size increases, the particle might not experience a uniform rapid heating to high temperature and this could limit the extent of melting leaving a char more similar to the original wood particle.

Ultimate analysis The ultimate analysis was obtained by using Carbon Nitrogen Sulphur (CNS) Analyzer. The samples, which weight around 1.5 to 2.0 mg in an aluminium container, are ensured prior to entering the analyzer. The analyzer was then displayed the composition of that carbon, nitrogen and sulphur contained within the material in percentage value. The hydrogen and oxygen composition were calculated by the difference method using the elemental composition and the calorific values equation (Ruyter, 1982) as following:

$$CV = 0.34\%C + 1.40\%H-0.16\%O \ (MJ\ kg^{-1})$$

Calorific value analysis: The calorific value of biomass samples was measured using Parr 1341 Plain Jacket Oxygen Bomb Calorimeter. Samples in pellet form with weight about 1 gram were prepared. The calorific value was then determined by plotting a graph and calculation using a spread sheet program.

Thermogravimetric analysis: The proximate analysis was carried out using Thermogravimetric Analyzer (TGA). Prior to the analysis, the samples were prepared and weighed approximately 5mg to 10mg to fit the small pan of TGA. Then, a program is initialized to ensure the result align with the objectives. The program was set as follows:

Heating Ramp from 30 to 800°C at several heating rate i.e., 10, 20, 30, 40 and 50°C min^{-1} were applied with nitrogen flow rate of 100 mL min^{-1}. The pressure gauge was 1.5 bars (150 kPa). Each set of conditions was repeated for three times.

Theory of kinetic reactions: Thermochemical conversion model for biomass is difficult to derive because of multiple components, anisotropic properties and large number of reactions. The reactions that are coupled with the effects of chemistry and transport phenomena result more complex of reaction model. But most authors have used an overall reaction kinetics concept, which products are often categorized into volatiles and char as in Eq. 1. A kind of model-free kinetics or isoconversional, which is sufficiently flexible to allow for a change of mechanism during the reaction and reduces mass transfer limitations when multiple heating rates are employed, is used in this study.

Reaction mechanism:

$$\text{Wood} \xrightarrow{k} \text{Char} + \text{Volatiles} \quad (1)$$

Differential conditions of thermal analysis were taken as relevant data to any fuel combustion system because it is related to chemical kinetics and mass transport (Sanchez *et al*., 2009). For solid fuel, char reactivity is defined in terms of conversion rate as below:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

Where:
α = Degree of conversion
n = Reaction order
t = Time
k = Reaction rate

Based on the Arrhenius relationship the reaction rate, k is:

$$k = A\exp(-\frac{E}{RT}) \quad (3)$$

Where:
A = The pre-exponential Arrhenius factor
E = The activation energy
R = The gas constant

The reaction rates can be expressed as a function of temperature (T) at a constant heating rate:

$$\beta = \frac{dT}{dt} \quad (4)$$

The non-isothermal rate expression is obtained by inserting Eq. 4 into 2 and 3:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} A e^{(-\frac{E}{RT})} k(1-\alpha)^n \quad (5)$$

The experiment was carried out at different heating rates that involved isoconversional methods to obtain activation energy from dynamic data. Equation 5 is integrated to obtain a linear form of equation that includes the term β and 1000/T. The activation energy can be estimated by plotting β vs. 1000/T (Flynn and Wall, 1966). Variation in the degree of conversion with temperature and heating rate may be described as:

$$\alpha(T) = 1 - \exp[\frac{-k(T)}{\beta^n}] \quad (6)$$

Taking the double natural logarithm of both sides of equation 6 with equation 3 inserted, should obtain a linear form of equation whose slope is the reaction order. The method applied to this modeling process is also described by Flynn, Wall and Ozawa method (Flynn and Wall, 1966; Ozawa, 1970).

RESULTS AND DISCUSSION

Characterization of material: Figure 1a-c show rapid weight loss within 2, 1.45 and 2.45 h for white spruce, white pine and balsam fir needles, respectively. The samples weight was then remain unchanged. The residence time of drying was extended to more than 24 h to obtain the desired moisture content of 2-5% for gross calorific values determination, CHNSO and TG Analyses.

Plain Jacket Oxygen Bomb Calorimeter-1341 was used for calorific values determination. The CHNSO elemental compositions also have been tested for each species that were milled 150 μm. All the results are given in Table 1.

Among the three species white pine has the highest moisture content because it was collected fresh but balsam fir and white spruce have very similar moisture content as they were one year old and were in freezer. However, all species have similar values of C but white pine showed a higher S and N content than both white spruce and balsam fir that may be due to fresh and old conditions of the species that caused the contents comparable. Carbon to oxygen ratio for white pine and white spruce has highest values than balsam fir. This has shown similar relationship of their HHV values where

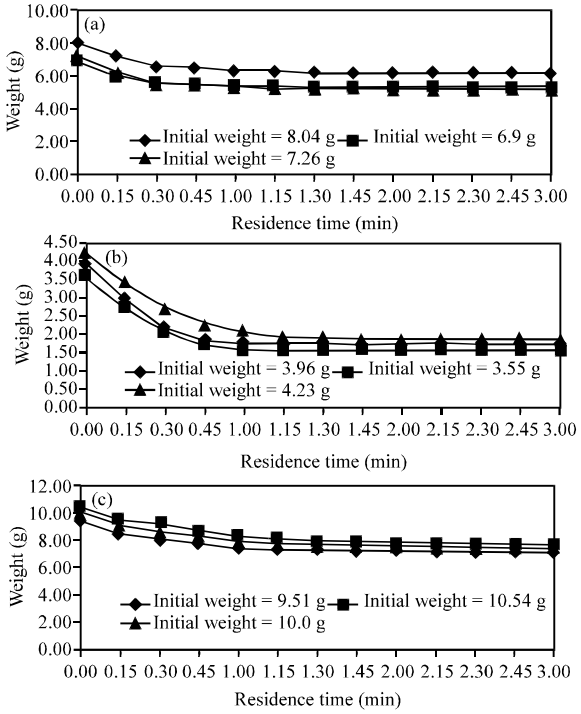

Fig. 1: Drying of (a) white spruce (b) white pine and (c) balsam fir needles at 105°C for 3 h, particle size ≤5 mm

Table 1: Moisture Content (MC), Gross Calorific Values (HHV) and CHNSO composition of white spruce, white pine and balsam fir

Species	MC (%db)	HHV (MJ kg^{-1})	C (% db)	S (% db)	N (% db)	H (by calc.)	O (by calc.)
Spruce	33.2	21.16	53.7	0.05	0.63	13.4	32.2
Pine	128.0	19.93	53.9	0.09	1.19	13.9	30.9
Fir	33.4	16.6	55.2	0.05	0.60	8.59	35.6

white spruce and white pine has higher HHV than balsam fir. It can be concluded that white spruce has highest energy among the three species because of its HHV of 21.16 MJ kg^{-1}.

TGA results: The Thermogravimetric analysis for white spruce, white pine and balsam fir for combustion was carried out in a TA Instruments model SDT Q600. Samples of about 10 mg were fed in the furnace of the instrument for combustion under controlled temperature. The corresponding weight degradation of TG curves as shown in Fig. 2a-c for each biomass were obtained for degree conversion, α and activation energy, E, analyses. White pine, balsam fir and white spruce needles for this experiment were prepared for particle size 150 μm, to run at five different heating rates, β of 10, 20, 30, 40 and 50°C min^{-1}.

Based on the TG curves obtained, there are three main regions which are the moisture content represented

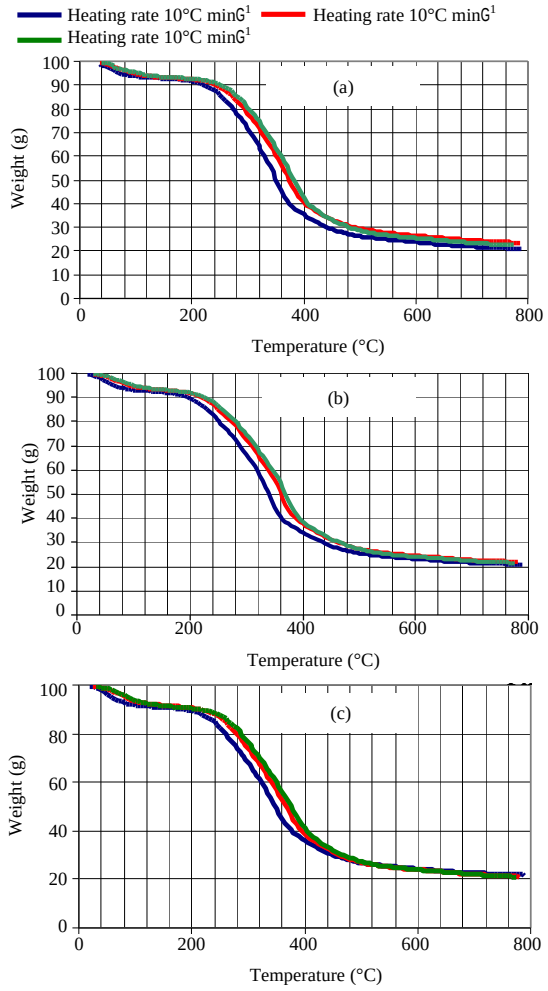

Fig. 2: TG curves for (a) white spruce (b) white pine and (c) balsam fir needles, particle size 150 μm at heating rate 10, 30 and 50°C min^{-1}

Table 2: Proximate Analysis Corresponding to combustion of white spruce, white pine and balsam fir needles at different heating rates

Species	Heating rate (°C min^{-1})	Moisture (%)	Volatiles (%)	Fixed carbon (%)	Ash (%)
Spruce	10	6.97	3.03	67.18	20.82
	20	4.98	5.02	66.35	23.65
	30	7.00	3.00	66.55	23.45
	40	7.98	2.02	67.41	22.59
	50	6.97	3.03	67.56	22.44
Pine	10	7.07	2.87	69.12	20.94
	20	6.08	2.76	68.77	22.39
	30	6.01	2.65	69.25	22.09
	40	7.12	1.94	69.12	21.82
	50	6.09	2.91	69.41	21.59
Fir	10	8.01	2.98	67.12	21.89
	20	9.05	2.80	67.74	20.41
	30	7.27	3.01	68.49	21.23
	40	8.12	2.67	68.08	21.13
	50	8.02	2.75	68.11	21.12

Table 3: The degree of conversion (α) occurs at different temperature range as different heating rate applied to the process

Biomass	Degree of conversion (α) (%)	Heating Rates (°C min^{-1}) 10	20	30	40	50
Spruce	10	222.6	249.0	243.5	242.4	252.3
	20	273.7	290.9	293.1	294.6	301.9
	30	305.0	320.7	325.0	326.1	333.4
	40	330.3	345.9	351.6	352.3	360.0
Pine	10	195.6	216.7	220.8	215.0	226.9
	20	252.3	267.3	273.5	273.3	281.1
	30	288.4	302.9	309.0	308.4	316.3
	40	318.6	333.1	339.4	338.7	346.7
	50	340.5	355.0	361.9	362.6	370.2
Fir	10	184.7	173.0	215.0	200.3	213.8
	20	260.1	269.2	279.9	280.6	287.7
	30	293.4	302.6	312.1	312.3	320.0
	40	323.3	332.9	341.8	341.2	350.2
	50	347.7	358.2	367.0	367.1	376.0

by the first slope, the volatile matter represented by the second slope and the fixed carbon represented by the third slope.

As observed in Fig. 2, with the increase in temperature, as combustion took place; the corresponding decrease in sample weight is observed. Once the fuel content of the biomass exhausted, the weight remains stable. The profiles were analysed for proximate analysis of each heating rate applied to the combustion of samples in the TA instrument.

The results of the proximate analysis in Table 2 showed the highest of volatiles and fixed carbon to degrade over the temperature profile for white spruce at heating rate 20 and 50°C min^{-1}, respectively. As for white pine, the highest volatiles and fixed carbon were determined at heating rate 50°C min^{-1}. Balsam fir showed the highest volatiles and fixed carbon to degrade at heating rate 30°C min^{-1}. This implied that different species degraded into different amount of composition when different heating rates were applied to the combustion process. This also shows that a certain heating rate is optimum to degrade effectively for certain species in combustion. However, no trend was observed on the yield of ash and all species produced lowest yield when lower heating rate was applied (Table 2).

Several conversion degrees,α, of the process are pointed out in each curve: 10, 20, 30, 40 and 50% to calculate the activation energy as given in Table 3. The activation energy is calculated based on the slope of the linear line corresponding to each conversion degree.

The linearity of these conversions according to Ozawa-Flynn-Wall kinetic method should be obtained by plotting βvs. 1000/T, while the slope of curve is representing the term to calculate the activation energy, E (kJ mol^{-1}). The linear of fitting to the kinetic equation model with the correlation coefficients (R^2) are shown in

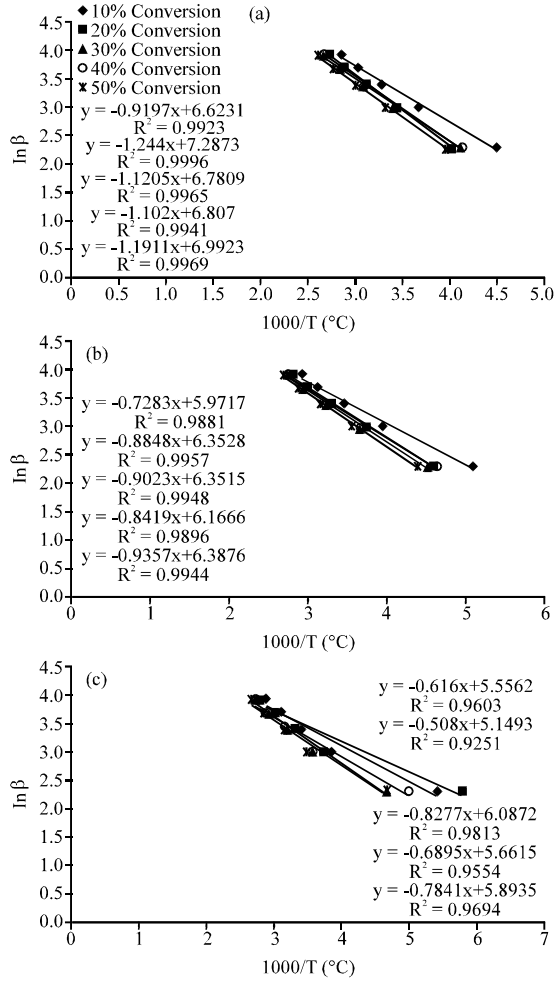

Fig. 3: Linear of fitting to kinetic model at various conversion percentages correspond to (a) white spruce (b) white pine and (c) balsam fir needles at different heating rate

Table 4: Calculated activation energy, E (kJ mol^{-1}), comparison between white spruce, white pine and balsam fir needles based on kinetic model, gross calorific value, HHV (MJ kg^{-1}), measured by Bomb Calorimeter and C/O analysed by CHNS

Biomass species	Average activation energy, E (kJ mol^{-1})	HHV (MJ kg^{-1})	C/O by CHNS
Spruce	262.40	21.16	1.66
Pine	197.14	19.93	1.74
Fir	139.94	16.60	1.55

Fig. 3a-c for each biomass species (Flynn and Wall, 1966; Ozawa, 1970).

The calculated activation energy is presented in Table 4. The activation energy for each conversion stage was calculated based on the slope at each linear line as proposed in the kinetic model by Flynn and Wall (1966). The average arithmetic of activation energy for white spruce needles for a range from 10 to 50% conversion is 262.40 kJ mol^{-1}. The average arithmetic of activation energy for white pine and balsam fir needles are 197.14 and 139.94 kJ mol^{-1}, respectively for the same range of degree conversion.

Since, it is observed that lower heating rate gives out higher conversion percentage of volatiles and fixed carbon while lower percentage of ashes, therefore this study is looking for the comparison of activation energy between species. Table 4 shows the comparison values of activation energy E for all species at lower heating rate.

In comparison to the HHV measured by bomb calorimeter and carbon content analysed by CHNS elemental analyser, the activation energy values calculated using kinetic model corresponding to the white spruce species is the highest as compared to other species, white pine and balsam fir. From the TG profile balsam fir at heating rate 10°C min^{-1} also has a relative high volatiles and fixed carbon content determined by the decomposition region over high temperature process.

CONCLUSION

The thermal decomposition of white spruce, white pine and balsam fir needles were carried out experimentally and theoretically. The kinetic parameter, activation energy (E) of three species: white spruce, white pine and balsam fir has their own profile of decomposition over high temperature range. Both experimental and kinetic model used to determine the energy potential have shown a good agreement between the methods and correspondence species. White spruce has the highest energy potential as compared to white pine and balsam fir.

ACKNOWLEDGMENTS

The authors appreciate the financial assistance from Natural Sciences and Engineering Research Council of Canada. The authors would also like to thank Dr. Mladen Eic and Dr. Q. Huang in the Department of Chemical Engineering, University of New Brunswick for use of TGA-DSC.

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