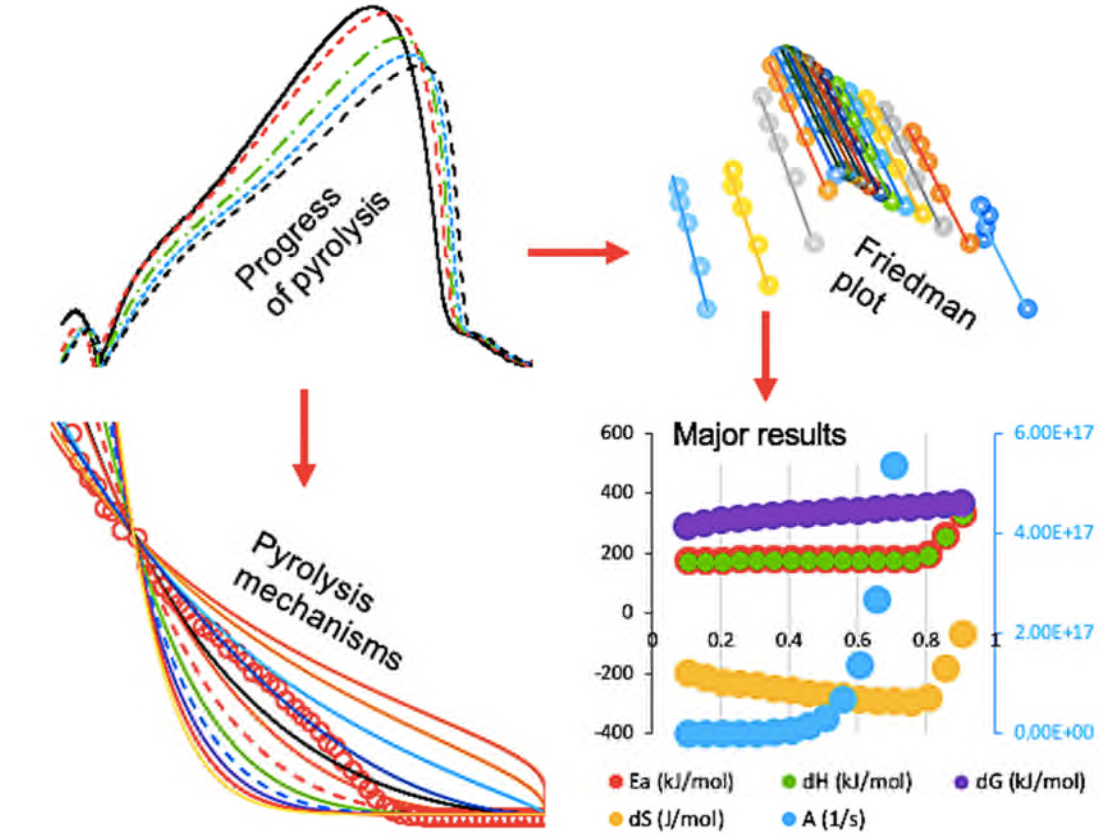
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Determination of Kinetic Parameters and Thermodynamic Properties of Ash (Fraxinus) Wood Sawdust Slow Pyrolysis by Thermogravimetric Analysis

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Abstract

Ash (Fraxinus) wood sawdust pyrolysis under nitrogen was conducted using 2, 5, 10, 15 and 20 ^{o}C/min heating rates. Friedman and Starink methods were used for kinetic analysis while y(α) master plots were used for pyrolysis mechanisms prediction. The mean activation energy were 198 and 202 kJ/mol for Friedman and Starink respectively. The master plots predicted that the pyrolysis process could be a combination of diffusion, geometrical contraction, nucleation, and reaction order models. The pre-exponential factors were in the range 10^{12} to 10^{19} s^{-1}. Gibbs free energy was 180 -185 kJ/mol. The entropy values were negative up to α = 0.75 indicating high orderliness of products relative to reactants but changed to positive at higher conversions implying likely disorderliness of the products compared to reactants. The calorific value of Ash (Fraxinus) wood sawdust was 18.3MJ/kg.

Key words: Ash (Fraxinus), Kinetic parameters, Thermodynamic properties, Calorific value, Slow Pyrolysis.

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1. Introduction

Energy sources have shifted from biomass to fossil fuels and back to biomass in less than 300 years due to economic and technological developments. The need for renewable sources is on the rise due to their environmental friendliness and sustainability. Globally, 19% of the energy needs are met using renewables, with 9% being contributed by biomass. It is envisaged to increase at a rate of 2.5% per year (Ahmad et al. 2017). However, investigation of the material properties has to be made to ensure suitability for any probable bioenergy production like bio-char. Several researchers have analyzed and characterized a number of biomass resources including beech wood (Ding et al. 2016), pine wood (Mishra, Kumar, and Bhaskar 2015), bamboo (Chen, Liu, et al. 2015) among others for their energy

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potential. Due to the abundant nature of biomass, many materials still remain not fully or uninvestigated yet they also present enormous potential for bio-oil, bio-char and other useful products.

Pyrolysis and torrefaction (Chen, Zheng, et al. 2015) are key methods used for processing biomass materials for potential energy production. Thermogravimetric (TG) techniques have been used to study pyrolysis since they are effective and provide a controllable atmosphere and heating rate, with negligible thermal gradients and mass transport (Ding et al. 2016). TG can be used alone or combined with other techniques like spectrometry (Gu et al. 2014) to study biomass materials. The application of TG analysis is appropriate to obtain chemical kinetic parameters, such as activation energy employing differential and integral methods (Wang et al. 2016). However, identifying the appropriate pyrolysis mechanism for processes with changing activation energies across the entire range of conversion requires careful application of model free and model fitting methods (Vyazovkin et al. 2011). Master plots have been used extensively for predicting pyrolysis mechanisms for biomass pyrolysis (White, Catallo, and Legendre 2011).

In this study, Ash (Fraxinus) sawdust, material from a perennial plant found in many parts of the world, were investigated. Ash (Fraxinus) trees grow to 40-80 feet tall, are heavily branched and resistant to severe environmental conditions. This study performs characterisation and in-depth analysis of Ash (Fraxinus) physiochemical properties, kinetic parameters, thermodynamic properties and pyrolysis mechanisms. The study gives high-lights and potential application of this plant (material) for energy and the results add to the body of knowledge for biomass materials whose properties are already known.

2. Methods and materials

2.1. Sample preparation and characterisation

Sawdust samples from Ash (fraxinus) tree were ground to fine powder using a laboratory vibratory pulveriser (Essa LM2 pulverising mill) and sieved to less than 200μm particle size. They were then further dried in an oven at 105^{o}C prior storage.

Elemental analysis for carbon, hydrogen and nitrogen was carried out by the Cranfield University School of Water, Energy and Environment, following British standard BS EN 13654-2:2001 and BS7755, using a Vario EL elemental analyser. Oxygen levels were determined by difference.

An automated thermogravimetric analyzer (TGA/DSC3+ STAR system – Mettler Toledo, EAG.EID 304 model) was used to measure the moisture content, volatiles, fixed carbon and ash content as per the D7582-15 standard method. In this method (with slight modifications), approximately 8-mg aliquots of dry sawdust, pulverized to <200 μm particle size in 70 ml alumina crucibles, were loaded into the TGA instrument and heated in N_2 and air environments at (50/60) ml/s and (25/60) K/s heating rate. For moisture determination, the sample was heated from 303 K to 383 K and held at that temperature for 10 min in N_2. For volatiles, the sample used for moisture was heated further to 1073 K and held at that temperature for 10 min in N_2. For ash, the same sample used for volatiles was heated further at 1073 K for 40 min in air. Fixed carbon (FC) was determined by difference. This procedure was done in triplicate.

The same TGA used for proximate analysis was used for pyrolysis (mass loss determination as a function of temperature and time). Approximately 5mg of sawdust of less than 210μm particle size were loaded into 70 ml alumina crucibles and heated at five different heating rates: 2/60, 5/60, 10/60, 15/60, and 20/60 K/s. Samples were heated from

303K to 1073K in Nitrogen environment at (50/60)*10^{-6} m^3/s. Mass loss with temperature and time was recorded automatically. The pyrolysis thermal analysis was done in triplicate.

The calorific value determinations were done at Cranfield University – Bedfordshire campus using the 6400 Automatic Isoperibol Calorimeter. The calorimeter has a precision of 0.1%, temperature resolution of 273.1501 K, calorie sample range of 5000 – 8000, and a linearity across operating range of 0.05%. The analysis was done in triplicate.

2.2. Kinetic properties

The kinetic parameters were determined taking into account the mechanisms for the degradation process of Ash sawdust. The reaction rate is related to the degree of conversion (α) according to Eq.1 below;

$$\alpha = \frac{M_o - M_i}{M_o - M_\infty} \quad (1)$$

where: M_o, M_i, and $M\infty$ are the initial mass, instantaneous mass and the final mass. The degradation kinetics (Islam, Asif, and Hameed 2015) can be represented through the expression shown in Eq. 2.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

The temperature dependence of the rate of degradation is related to the Arrhenius Eq. 3:

$$k = A\ exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where: A, E_a, R and T are the pre-exponential factor, activation energy, gas constant and absolute temperature. Substituting Eq.3 into Eq.2 gives,

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (4)$$

The isoconversional differential method by Friedman and the integral method by Starink were used for determination of activation energy since both are believed to more

accurate than similar methods (Starink 2003). These methods take the forms shown in Eqs 5 and 6.

$$In\left[\beta_k\left(\frac{d\alpha}{dt}\right)_{\alpha,k}\right] = InA_\alpha f(\alpha) - \left(\frac{E_\alpha}{R}\right)\left(\frac{1}{T_{\alpha,k}}\right) \qquad (5)$$

$$In\left(\frac{\beta_k}{T_{\alpha,k}^{1.92}}\right) = In\left(\frac{A_\alpha R}{g_{(\alpha)}E_\alpha}\right) - 1.0008\left(\frac{E_\alpha}{R}\right)\left(\frac{1}{T_{\alpha,k}}\right) \qquad (6)$$

where:

β_k - k^{th} heating rate,

$T_{\alpha,k}$ - temperature for a given α of k^{th} heating rate,

Ea - apparent activation energy,

A_α - pre-exponential factor of given conversion.

A plot of $In\left[\beta_k\left(\frac{d\alpha}{dt}\right)_{\alpha,k}\right]$ OR $In\left(\frac{\beta_k}{T_{\alpha,k}^{1.92}}\right)$ Vs $\left(\frac{1}{T_{\alpha,k}}\right)$, enables one to estimate Ea from the slopes.

2.2.1. Master plots

The Ea values obtained by the Friedman method were used to determine experimental values for master plots. The approximate constant value of Ea was replaced by the average value $Ea_{(o)}$ that was inserted into the $y(\alpha)$ function, Eq. 7.

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)_{\alpha,k}\exp\left(\frac{E_{a(o)}}{RT_{\alpha,k}}\right) = \beta_k\left(\frac{d\alpha}{dT}\right)_{\alpha,k}\exp\left(\frac{E_o}{RT_{\alpha,k}}\right) = Af(\alpha) \qquad (7)$$

where $d\alpha/dT_{(a,k)}$ is the differential conversion to temperature (T) at given α and a specified heating rate, β, and $E_{a(o)}$ is the mean value of the Ea. The experimental y(α) can be obtained by substituting the $E_{a(o)}$, β_k, R, dα/dT and T_α into Eq.7. And theoretical y(α) are obtained by substituting the given α into different f(α) described elsewhere (L. Vlaev et al. 2008). Since the pre-exponential factor (A) of Eq.7 is still unknown, experimental and theoretical y(α) have to be normalized (Vyazovkin et al. 2011), using Eq. 8.

$$y(\alpha)_{norm} = \frac{y(\alpha)}{y(0.5)} \quad (8)$$

2.2.2. Thermodynamic parameters

The thermodynamic parameters including pre-exponential factors (A), enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were calculated from the Eqs. 9-12 (Ahmad et al. 2017).

$$A = \beta . Ea_\alpha \, exp\left(\frac{Ea_\alpha}{RT_m}\right) / R . T_m^2 \quad (9)$$

$$\Delta H = Ea_\alpha - RT \quad (10)$$

$$\Delta G = Ea_\alpha + R . T_m . In\left(\frac{K_b . T_m}{h . A}\right) \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (12)$$

where K_b =1.38*10^{-23} J/K), h = 6.626*10^{-34} Js), and T_m is the DTG peak temperature.

3. Results and Discussion

3.1. Proximate, ultimate and heating values

Table 1 shows the results for proximate, ultimate and heating values of raw Ash (fraxinus) sawdust. These properties, are very comparable to and to some extent better than many biomass materials that have been investigated before (Chen, Zhou, and Zhang 2014). Low moisture content allows Ash sawdust to have a rapid heat transfer during pyrolysis (Varma and Mondal 2016) and a high combustion yield. (Singh, Mahanta, and Bora 2017) characterised several biomass materials and found them to have a moisture content of 8.2-13.9wt% which was higher than the 5.7±0.04wt% observed for Ash sawdust. High volatile matter means the material can easily be devolatilised. The ash content was low (3.13±0.02wt%) meaning that devolatilisation is not interrupted much and less fouling

occurs, little slag formation leading to high thermal efficiency and low operating costs (Peter 2002).

Table 1: Properties of selected materials compared with raw Ash (fraxinus) used in this study

Sample	HHV (MJ/kg)	Proximate analysis				Ultimate analysis					Ref.
		M	V	FC	A	C	H	N	S	O*	
Ash (fraxinus)	18.29	5.66	70.14	21.07	3.13	49.12	6.64	0.35	-	43.89	This study
[a]Ash tree	17.23 - 22.06	7.6-4.2	86.8-69.3	12.3-26.1	0.9-0.4	48.9-57.3	5.9-5.8	<0.1-0.4	0.2-0.3	44.9-36.2	(Haykiri-Acma, Yaman, and Kucukbayrak 2016)
Moso Bamboo	16.85	-	85.53	13.33	1.15	47.58	6.13	0.52	0.04	45.73	(Chen, Zhou, and Zhang 2014)
S. African Coal	27.37	2.70	26.90	56.30	14.10	67.50	4.26	1.76	0.44	11.58	(Wu et al. 2017)

HHV-Higher heating value; *determined by difference; M-moisture content, V-volatile matter, FC-fixed carbon, A-Ash, C-carbon, H-hydrogen, N-nitrogen, S-sulphur, O-oxygen; [a]values were taken before and after torrifaction at 300^{o}C

The calorific value of Ash sawdust was 18.29±0.02 MJ/kg in its raw form. This value is higher than that for many other biomass fuels like Moso Bamboo (16.85 MJ/kg) (Chen, Zhou, and Zhang 2014), palm fibre (17.60 MJ/kg), palm sludge (13.80 MJ/kg) (Chong et al. 2017) cotton stalk (15.78 MJ/kg), wheat straw (17.90 MJ/kg), corn stalk (17.79 MJ/kg), vineyard (16.68 MJ/kg), corn cobs (17.99 MJ/kg), sugar beet leaves (17.70 MJ/kg), rice straw (12.13 MJ/kg) (Skoulou and Zabaniotou 2007) but lower than 19.00MJ/kg for wood reported by (Koyuncu and Pinar 2007). On torrifaction (Daood et al. 2010), Ash sawdust properties were enhanced making it suitable for co-firing or for industrial and domestic settings without any addition of other materials.

3.2. Mass loss and conversion

Figure 1A and **B** shows the mass loss and mass loss rate as a function of temperature. Ash sawdust underwent slow pyrolysis following three major phases. The first phase occurring between 50-200^{o}C attributed to loss of moisture. The second occurred between

200-450°C attributed to degradation of hemicellulose and cellulose and the last one occurring between 450-800°C (for all heating rates) attributed to degradation of lignin.

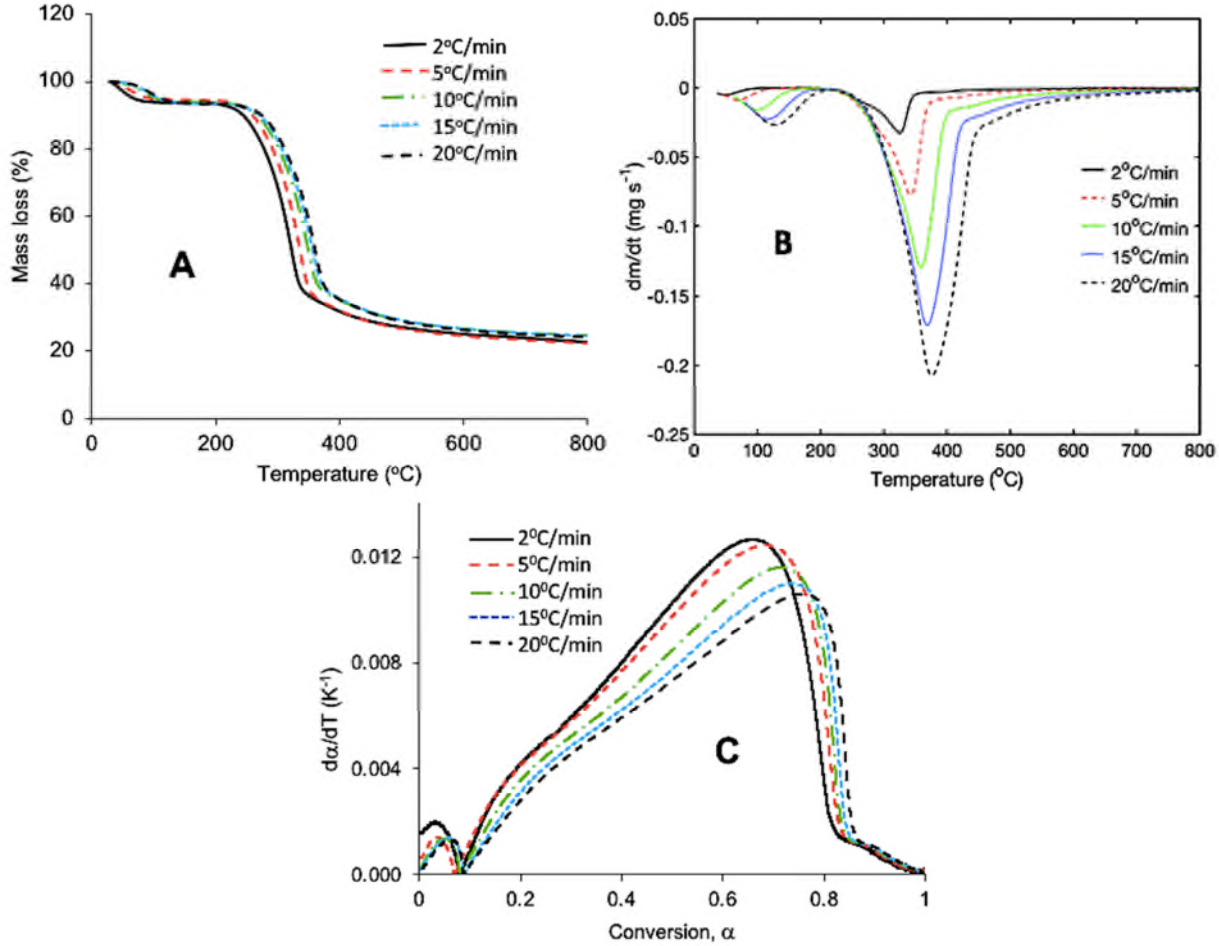


Figure 1: A - Mass loss; B - mass loss rate; C - dα/dT as a function of conversion

There is a shift in the attainment of the peak on the mass loss rate graph for each heating rate: 325, 334, 348, 356, and 359°C for 2, 5, 10, 15, and 20°C/min heating rates respectively.

The hydrophilic nature of sawdust especially the non-crystalline parts and voids allow water molecules to be accommodated in the structure. Sawdust is composed of cellulose (α-cellulose), hemicellulose, lignin, pectin and waxes with the first three representing up to 99% of sawdust composition. Water is linked to the amorphous region of cellulose through intra- and intermolecular hydrogen bonds on hydroxyl groups and free radicals on cellulose and

hemicellulose (Manaila et al. 2016). During phase I (50-200^{o}C), the main event that took place is dehydration of the sawdust. Dehydration reactions are both endothermic and may be reversible involving interface reactions and diffusion. This may involve rapid initial nucleation on the surface followed by advance of the coherent interface thus formed. Nucleation may be at specific surface sites followed by growth or no growth at all. Structural re-organization leads to development of cracks, channels or pores through which moisture may escape from the interface (Bamford and Tipper 1980).

In stage II (200-450 ^{o}C), the main reactions that take place are the pyrolysis of hemicellulose and cellulose. Hemicellulose is amorphous with a linear framework of xylans and glucomannans. Its conversion takes place mainly in the 200-350^{o}C region catalyzed by mineral matter releasing moisture, CO_2 and other volatiles forming char (Collard and Blin 2014). Cellulose on the other hand has both the crystalline and the amorphous phases. The main conversion of cellulose takes place between 300-450^{o}C. Decomposition reactions of cellulose at ~300^{o}C are responsible for most mass loss as well as release of CO, CO_2, and other organic compounds.

In the final phase (stage III; 450-800 ^{o}C), lignin breakdown leads to formation of pyrolysis gases, and tars which condense on the char wall surfaces (Brebu and Vasile 2010). Several mechanisms describe this region including chemical reactions (Jeguirim et al. 2014), random nucleation and growth, phase boundary mechanisms, and diffusion.

Figure 1C presents the dα/dT as a function of conversion, with a sigmoidal type that are common in linear non-isothermal TGA (Wang et al. 2016), (Khawam and Flanagan 2006). For $0<\alpha<0.1$, we observe a prominent peak corresponding to moisture loss. This is followed by a shoulder peak up to $\alpha\sim0.3$ corresponding to hemicellulose and maximum peak for $0.6<\alpha<0.75$ attributed to cellulose decomposition. At $0.85<\alpha<1.0$, we observe another shoulder peak corresponding to lignin decomposition reactions. Furthermore, for

$0.00<\alpha<0.10$ range was related to 50°C<T<220°C for all heating rates, related to diffusion reactions of moisture through the pores of sawdust. The second conversion range $0.1<\alpha<0.8$ corresponded to 180°C<T<450°C for all heating rates. For $0.80<\alpha<1.00$, the main reaction corresponds to lignin breakdown and were within 360<T<800°C for all heating rates. We also observe in (**Figure 1C**), that the derivative $d\alpha/dT$ peak height decreased with increasing heating rate attributed to combined effects of heat and mass transfer within the sample (Wang et al. 2016).

3.3. Activation energy

Iso-conversional methods were used for the estimation of activation energies at different degrees of conversion for pyrolysis of Ash (fraxinus) sawdust. **Figure 2A** and **2B** show the Friedman, and Starink plots that were used for calculation of activation energies. These methods gave similar and sensible values at each degree of conversion implying that these methods are appropriate for describing the pyrolysis profile of Ash sawdust. This is further strengthened by the high regression coefficients (0.999) for $0.2 < \alpha < 0.8$, **Figure 2C**.

The activation energy values obtained could be divide into two main categories; 180-184 (kJ/mol) for $0.1 < \alpha < 0.8$ conversion and 195-350 (kJ/mol) for $\alpha > 0.8$. For $0.1 < \alpha < 0.8$, relatively weak bonds (Reza et al. 2013) of hemicellulose and cellulose are being broken. However, for $\alpha > 0.8$ relatively stronger bonds of lignin components are being broken (Islam, Asif, and Hameed 2015), hence, the higher activation energies observed.

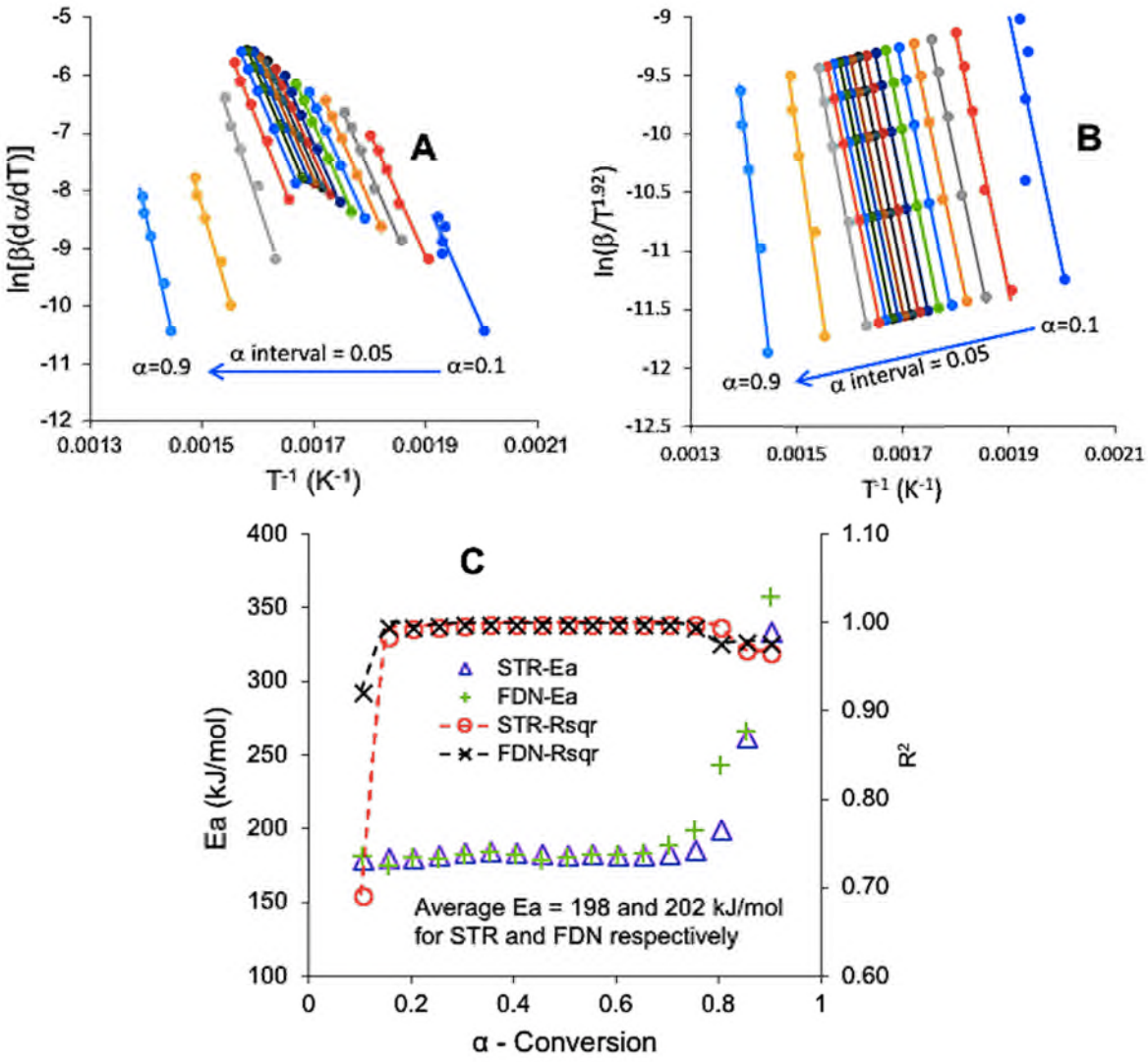


Figure 2: A – Friedman (FDN) plot; B – Starink (STR) plot and C – Activation energy and regression coefficients for STR and FDN respectively

Ash (Fraxinus) wood sawdust, Ea (198 kJ/mol – 202 kJ/mol) is similar to waste tea pyrolysis (Ea: 208kJ/mol – 223 kJ/mol) (Tian et al. 2016). The results still show that Ash sawdust was not so easy to pyrolyse compared to beech wood (Ea: 147-174kJ/mol) (Ding et al. 2016), moso bamboo (Ea: 96-113kJ/mol) (Chen, Zhou, and Zhang 2014), and other biomass with lower activation energy (Ceylan, Topcu, and Ceylan 2014), (Ceylan and Topcu 2014), (Slopiecka, Bartocci, and Fantozzi 2012), (Sonobe and Worasuwannarak 2008). However, Ash sawdust pyrolysis seems to be easier to pyrolyse than Corallina pilulifera (Ea: 248 kJ/mol) (Tian et al. 2016), Enteromorpha (Ea: 228 kJ/mol) (Tian et al. 2016), and Rice husks (Ea: 230 kJ/mol) (Tian et al. 2016).

3.4. Reaction mechanism prediction using master plots.

Vyazovkin *et al.* (Vyazovkin et al. 2011), recommended that when the Ea values obtained vary significantly with conversion, i.e., when the difference between the maximum and minimum values of Ea is more than 20-30% of the average Ea, it is important to integrate over small segments (minimum of α=0.05 intervals) to avoid systematic errors in Ea.

In this case the pyrolysis process is multi-step and follows several mechanisms. As seen from **Figure 3**, the deviations from $E_{a(o)}$ got higher than 30% once the conversion exceeded 0.8 for Starink method and 0.75 for Friedman method. These deviations could be attributed to secondary reactions between the volatiles and char (Wang et al. 2016).

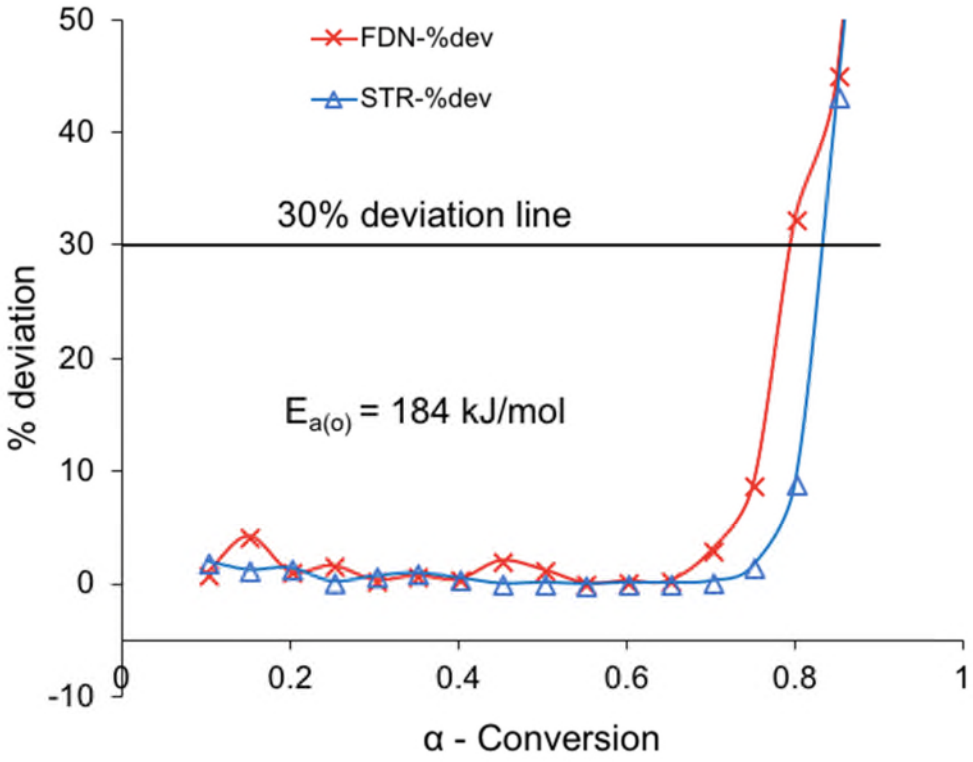


Figure 3: Deviation of E_a from $E_{a(o)}$

After excluding the Ea values higher than 30% of deviation, $E_{a(o)}$ was calculated from the Friedman method as 184kJ/mol since differential methods are considered more accurate

that integral methods (Vyazovkin et al. 2011). As shown in **Figure 4A** master plots, the experimental y(α) master plot did not fit exactly any of the theoretical master plots. However, Fraxinus pyrolysis plots have a shape similar to diffusion especially 5-D at lower conversions (α<0.5). In the same region, Ash sawdust pyrolysis master plot is similar to, and intercepts several reaction order master plots especially n=2 to n=8.

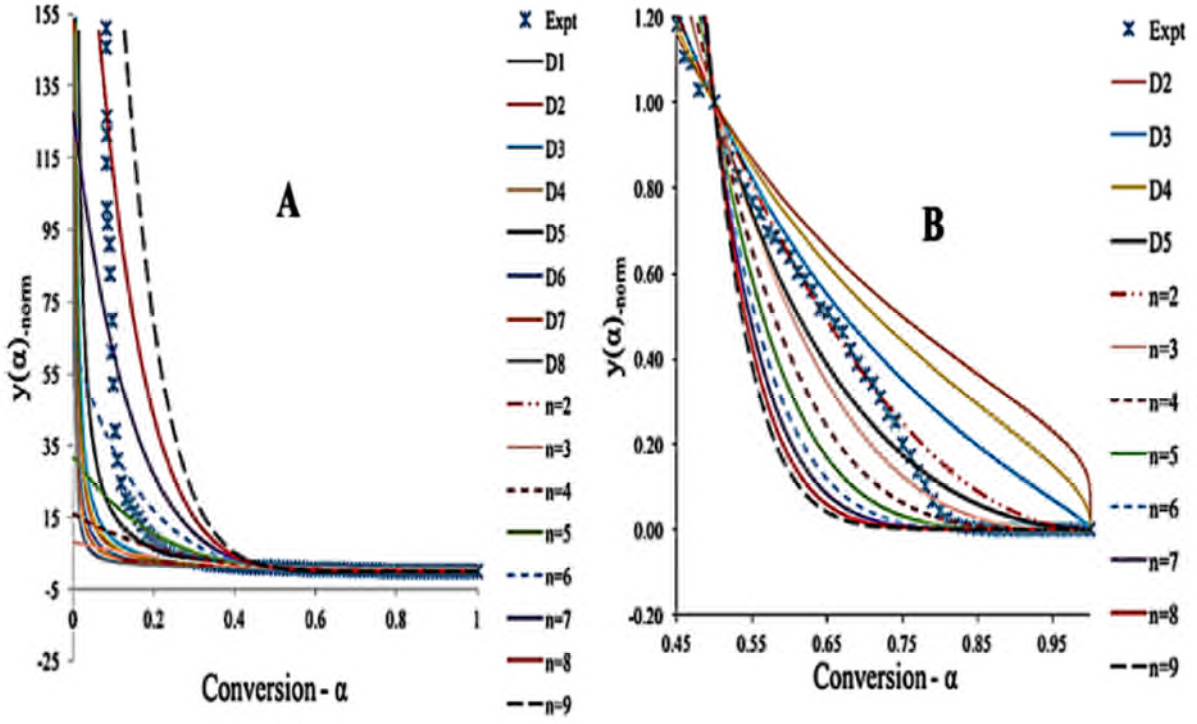


Figure 4: Generalized y(α) master plot (A), and master plot for α > 0.45 (B)

At higher conversions (α>0.5), Ash sawdust pyrolysis master plot resembles the diffusion models D3, and D5 as well as reaction order especially n=2 for 0.5<α<0.75. For α>0.75, Ash (Fraxinus) master plot pattern follows reaction order mechanisms especially n=2-9 and still continued to be similar to D5 model **Figure 4B**. However, the overall pyrolysis process could be a combination of several mechanisms involving diffusion (D3 and D5), geometrical contraction (G2 and G3), reaction order models (n=2-9) or nucleation (Wang et al. 2016).

3.5. Thermodynamic parameters

The pre-exponential factor (A), enthalpy (ΔH), Gibbs energy (ΔG), and entropy (ΔS) were calculated using Eqs. 9-12. The A values obtained in this study were in the range 10^{12} to 10^{19} except at α>0.8. ΔG values were constant at 185 kJ/mol and only decrease slightly at α>0.8 (**Table 2**).

Table 2: Thermodynamic parameters for pyrolysis of Ash (Fraxinus)

	Friedman				Starink			
α	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)
0.10	7.29E+12	176.80	185.29	-13.31	4.95E+12	174.80	185.35	-16.53
0.15	2.21E+12	170.66	185.48	-23.23	6.52E+12	176.22	185.31	-14.25
0.20	6.85E+12	176.48	185.30	-13.82	6.10E+12	175.88	185.32	-14.80
0.25	5.70E+12	175.53	185.33	-15.36	9.37E+12	178.09	185.26	-11.23
0.30	8.83E+12	177.79	185.27	-11.72	1.37E+13	180.04	185.20	-8.09
0.35	1.37E+13	180.06	185.20	-8.06	1.49E+13	180.50	185.19	-7.35
0.40	8.68E+12	177.70	185.27	-11.86	1.28E+13	179.69	185.21	-8.66
0.45	4.88E+12	174.74	185.35	-16.64	1.06E+13	178.75	185.24	-10.17
0.50	6.34E+12	176.08	185.32	-14.48	9.80E+12	178.33	185.25	-10.85
0.55	9.72E+12	178.28	185.25	-10.92	1.01E+13	178.46	185.25	-10.64
0.60	9.10E+12	177.95	185.26	-11.46	9.72E+12	178.29	185.25	-10.92
0.65	1.18E+13	179.30	185.22	-9.29	9.77E+12	178.31	185.25	-10.88
0.70	3.08E+13	184.24	185.08	-1.32	1.17E+13	179.23	185.22	-9.40
0.75	2.44E+14	194.92	184.79	15.88	1.88E+13	181.69	185.15	-5.43
0.80	1.05E+18	238.27	183.75	85.45	2.58E+14	195.21	184.78	16.34
0.85	9.49E+19	261.66	183.27	122.88	4.97E+19	258.30	183.33	117.51
0.90	3.52E+27	352.57	181.71	267.80	4.51E+25	329.80	182.06	231.56

The values of A for reactions in the solid state vary between 10^6 to 10^7 orders of magnitude. Usually, first order reactions have A in the range of 10^5 to 10^{18} s^{-1}. Low A values are indicative of surface reactions, but if the reactions are independent of the material surface area, the low A factors would indicate that the activated complex is a 'sophisticated' one, while high A factors indicate a simple complex (L. Vlaev et al. 2008). Entropy change values obtained had negative values up to α=0.7 for Freidman and up to α=0.75 for Starink, indicating that the final products could have been more ordered than the initial reactants (Alves, Maia, and Morais 2016). The positive entropy values obtained at high conversions indicate that the orderliness of the final products were likely to be less than the original materials (Turmanova et al. 2008). Furthermore, entropy (ΔS) values are directly related to

Ea and A; the higher are the values of Ea and A, the higher are the values of (ΔS) (L. T. Vlaev, Georgieva, and Genieva 2007). The occurrence of positive and negative values of (ΔS) shows that the pyrolysis process was complex (Ahmad et al. 2017).

4. Conclusions

This study investigated the kinetics, and thermodynamics of Ash (Fraxinus) wood sawdust slow pyrolysis. The activation energy values were 180-350 (kJ/mol). The pyrolysis process could have involved diffusion, geometrical contraction, reaction order models or nucleation. The pre-exponential factors were in the range 10^{12} to 10^{19} s^{-1}. The entropy were negative up to $\alpha = 0.75$, but changed to positive at higher conversions implying likely disorderliness of final products compared to reactants. The calorific value of Ash (Fraxinus) wood sawdust was 18.3MJ/kg which is comparable to other biomass.

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