

CHEMISORPTION AND LOW-TEMPERATURE PYROLYSIS OF WOOD CHARs IN SMOLDERING COMBUSTION

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ABSTRACT

This paper examines the chemisorption in air-preheated and nitrogen-heated wood chars that were created at heat treatment temperature as low as 140°C and 150°C and for extended preheating period up to 50 days that more closely resemble those encountered in built environment. The effect of chemisorption was examined in terms of consequent change in ignition temperatures and its correlation with the combustion behaviour. Chemisorption kinetics was studied using Elovich equation; gasification investigated by Arrhenius equation. A numerical analysis has been devised from Semenov model of thermal ignition to interpret the change in ignition temperature on the pyrolysis kinetics of wood chars and evaluate the kinetic significance of preheating duration and/or change in heat treatment temperature. This paper found that long-term air-preheated wood chars are capable of chemisorption, just as nitrogen-heated wood chars, ensued by ignition. Lower ignition temperatures have been noted in air-preheated samples. The change in ignition temperatures however is not thermally significant on the pyrolysis kinetics, as the Arrhenius parameters do not show a quantum leap to signify a change in pyrolysis pathways.

KEYWORDS: Chemisorption, Gasification, Elovich kinetics, Arrhenius kinetics, Semenov model, Smoldering combustion

NOMENCLATURE

A	: Pre-exponential factor (s^{-1})
E	: Activation energy (kcal/mol)
Q	: Exothermicity (kcal/g)
R	: Gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
S	: Sample surface area (m^2)
T	: Temperature (K)
V	: Sample volume (m^3)
W	: Mass uptake due to amount of oxygen absorbed (mg/g)
a	: Elovich constant (mg/g min)
e	: Semenov model constant = 2.71828
h	: Heat transfer coefficient (W/m^2K)
t	: Time (min)
α	: Elovich constant (mg/g) ⁻¹
σ	: Reactant density (kg/m^3)

INTRODUCTION

Chemisorption of oxygen on carbonized cellulose is a precursor leading to gasification. Still, there exists a main disparate view on whether gasification and chemisorption are two distinct processes or an interrelated one in the modelling of char combustion^{1,2}. Typically, the relation of the two processes is studied via experiments with chars prepared from the doped samples with additives^{3,4}. Their effect on pyrolysis kinetics and chemisorption kinetics of the doped samples hitherto provides the required arguments to support or counteract the proposition. In all such studies, the need to understand the

relation between the two processes is motivated by the better understanding that could enhance the modelling and the control of the smouldering combustion of cellulosic materials.

Chemisorption of oxygen by carbonaceous materials has been well researched. However, the char samples investigated were exposed to high heat treatment temperature in the range of 400°C to 800°C¹. The basis to draw inferences on the reactivity and kinetics onto a lower heat treated wood chars is questionable. The nature of wood chars changes by the rate and the final heat treatment temperature it is pyrolysed. Add to these variables is the duration for which the isothermal heating is being maintained. One could get a glimpse of the enormity of the issue by looking at the combination of these variables.

This study is interested in chemisorption and combustion behaviour of low temperature chars created at 140°C and 150°C exposed to long-term heating in air. Since maximum chemisorption kinetics is reported for nitrogen pyrolysed chars created at HTT of 550°C⁵, it would be of interest to examine the chemisorption kinetics of the same inert chars that are created at a much moderate temperature of 300°C. The temperatures at which these categories of wood char - both oxidatively and non-oxidatively pyrolysed, more closely resemble the cases encountered in built environment.

In this paper, chemisorption kinetics is studied using Elovich equation; gasification investigated by Arrhenius equation to seek a relation between the two processes. Pyrolysis kinetics and the change in ignition temperatures arising from heat pre-exposure and chemisorption are interpreted in the framework of Semenov model of thermal ignition.

MATERIALS AND METHODS

Materials and Sample Preparation

Kapur, a widely used hardwood species is used to create wood chars under low temperature, in both long-term preheating in air and rapid pyrolysis in nitrogen in thermogravimetric analyzer. The untreated Kapur is of empirical formula $C_{3.9}H_{6.5}O_{2.9}$.

To prepare air-preheated chars, wood blocks measuring 32 x 32 x 102mm were heated isothermally in air at heat treatment temperature (HTT) of 140°C for 50 days and HTT of 150°C for 30 days in Carbotlite oven. The powder air-preheated wood chars were obtained by grinding the wood discs sliced from the wood blocks and stored at 50%RH at 23°C. These wood chars are designated as K140 and K150 respectively.

Inert-heated samples were prepared by heating fresh Kapur wood powder at HTT of 300°C for 1.5 minutes under nitrogen at atmospheric pressure in TGA. The 1.5 minutes of pyrolysis time is selected to approximate the condition of char formation by a smouldering combustion front⁶. These nascent wood chars are immediately subjected to chemisorption after a few minutes of holding time in TGA to allow the respective chemisorption temperatures to equilibrate. This process eliminates the formation of surface oxides arising from separate char preparation and chemisorption runs. These inert-heated wood chars are designated as K300. Table 1 shows the elemental composition of the respective wood chars.

Experimental

Physical adsorption and chemisorption of oxygen on char samples were conducted in SDT 2960 simultaneous DTA-TGA Thermogravimetric Analyzer © TA Instruments. The wood char samples were subjected to chemisorption temperatures (CST) at 74°C, 109°C, 139°C, 168°C, 185°C and 207°C.

TABLE 1. Elemental analysis of wood chars samples

Sample	Composition		
	Carbon	Hydrogen	Oxygen ^a
Kapur- untreated	47.30	6.56	46.14
K 300-1.5mins-N ₂	54.20	5.70	40.10
K 150-30days-air	47.37	6.01	46.62
K 140-50days-air	47.34	5.88	46.75

^a composition obtained by difference

For inert-heated samples, as soon as the chars were pyrolysed for 1.5 minutes in TGA, the furnace temperature was immediately cooled to the chemisorption temperature for the respective chemisorption runs in inert atmosphere. In each run, a few minutes of holding time were allowed for the chemisorption temperature to equilibrate and to establish the weight of the sample prior to chemisorption. Air with a flow rate of 60 ml/min was then valved into the furnace maintained at isothermal temperature. The weight gain during chemisorption was monitored for 15 hours.

For air-preheated samples, the same procedure and condition is adopted, where the air-preheated wood powders were heated from 25°C to the chemisorption temperature and the weight gain was observed for 15 hours. However, these air-preheated wood chars were not pre-treated to clean the surface oxides. This is because the removal of surface oxides would require the heating of these wood chars to high temperatures. Unlike other works^{1,7} where the high their heat treatment temperatures (HTT) have made the cellulose chars much stable, with HTT ranging from at least 375°C to 800°C, the low HTT of 140°C and 150°C for air-preheated chars in this study created very reactive char. Preheating at high temperatures, even at 275°C for 30 minutes as suggested in Hshieh and Richards⁵ works would induce further pyrolysis and change the nature of these air-preheated wood chars composition. Such preheating would defeat the purpose for which these air-preheated wood chars were created and studied.

RESULTS & DISCUSSION

Chemisorption for Samples Preheated in Nitrogen

Fig. 1 shows oxygen chemisorption (21% oxygen in air) on Kapur char that has been pyrolysed at heat treatment temperature (HTT) of 300°C for 1.5 minutes in TGA which were then subjected to chemisorption runs at a series of chemisorption temperatures (CST). Because of the low heat treatment temperature, the wood chars were invariably very reactive. Indeed, for chemisorption temperatures above 140°C, gasification set in early. For the 207°C run, gasification was dominant and this data has to be excluded. The chemisorption data for 168°C and 185°C were truncated before gasification set in. On the other hand, wood chars tested at low chemisorption temperatures equal and below 140°C did not show any weight loss, henceforth, these wood chars data could be interpreted for the full run for chemisorption. Since gasification products could not be detected below 140°C threshold for wood chars³, and desorption of surface oxides are negligible below 1000°C⁸, it permits these chemisorption runs to be treated as a single oxygen adsorption process.

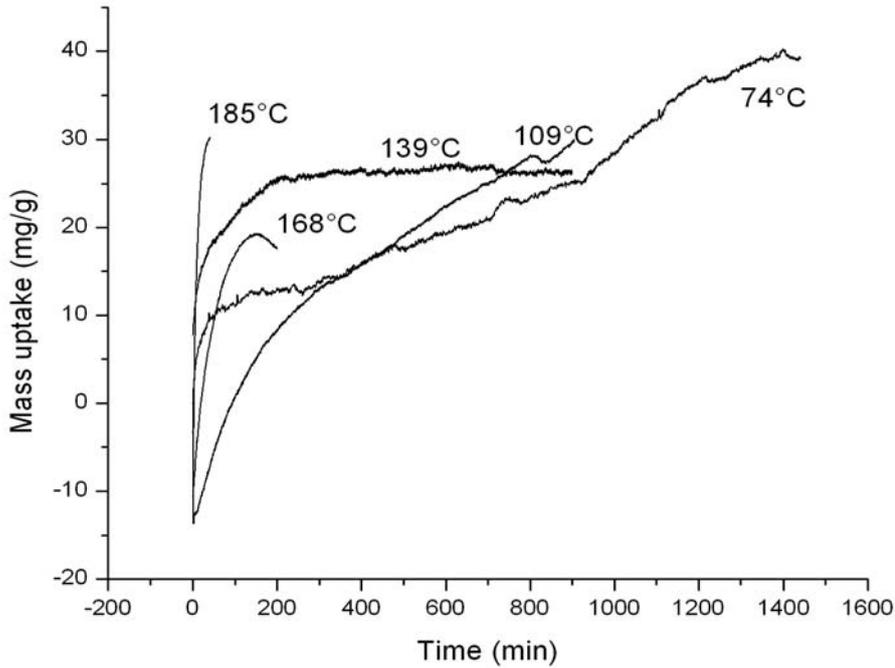


FIGURE 1. Oxygen chemisorption of lignocellulosic char in air in isothermal heating under atmospheric pressure

The mass uptake is plotted for 15 hours for low chemisorption runs. As usual, the initial reaction was rapid, but the rate declined with time until it reached equilibrium. For reactive wood chars, the mass uptake has yet to reach equilibrium especially at low chemisorption temperature of 74°C, for which case the mass uptake has been extended up to 24 hours. This observation is not of any surprise since chemisorption is highly temperature dependent. The lower the chemisorption temperature, the longer the time it is required to reach site saturation. Increasing the chemisorption temperature would of course increase the rate of chemisorption. However, the increase in temperature would entail the set in of particularly gasification process in these reactive chars, and therefore curtail the mass uptake measurement from chemisorption, as seen from wood chars subjected to chemisorption temperatures of 168°C and 185°C.

The observed chemisorption behaviour of gases on heterogeneous surfaces of wood chars above can be described by the Elovich equation as:

$$\frac{dW}{dt} = ae^{-\alpha W} \quad [1]$$

Where a and α are the Elovich constants. To solve for the constants, McLintok⁹ method is used which consists of linearising equation [1] by using a logarithmic form

$$\ln\left(\frac{dW}{dt}\right) = -\alpha W + \ln a \quad [2]$$

By plotting $\ln(dW/dt)$ against W , α is obtained from the slope and a as the intercept of the linear plot. The Elovich parameters are tabulated in Table 2.

TABLE 2. Elovich constants for oxygen chemisorption on Kapur Char based on 15 hour adsorption

Temperature (°C)	a (mg/g min)	α (mg/g) ⁻¹	Time constraint (min)
74	2.957	0.2133	Full run ^a
109	3.052	0.1769	Full run
139	10.744	0.0089	Full run
168	2.45	0.90949	<215
185	4.06	0.08526	<30

^a Full run denotes 900 minutes duration.

The parameter a represents the initial reaction rate of chemisorption. It increases with increasing temperature. Similar trend is also observed with the shorter chemisorption runs for wood chars at 168°C and 185°C. For parameter α , it decreases with increasing chemisorption temperature. The trend is also consistent with other published works^{10,11}.

The parameter a is said to be a measure of the intrinsic reactivity of the char sample towards oxygen². Using this parameter as a benchmark for reactivity, it is found that the brown coals char in Allardices'¹² work has a magnitude of a of 101 mg/g min at 110°C and that of pure carbon in Teng et al.⁸ work of 88 mg/g min at 100°C. As compared to the coal and carbon as a well known source for fuel and energy, the initial rate of chemisorption in wood chars pyrolysed at low heat treatment temperature as subjected to chemisorption temperature of 109°C is less by one to two orders of magnitude.

It is also noted that for chemisorption performed in air (21% oxygen), the magnitude of a is approximately five times lower than that performed in oxygen. This finding concurs with Bradbury & Shafizadeh's⁶ observation, and a clear illustration can be seen from the comparison of the parameter a of wood chars with cellulose chars in that of Bradbury & Shafizadeh's work¹, as tabulated in Table 3.

TABLE 3. Comparison of Elovich parameters for lignocellulosic char exposed to air and oxygen at 139°C chemisorption temperature

HTT (°C)	Pressure (mmHg)	a (mmol/g min)	α (mmol/g) ⁻¹
300	760	0.010	2.06
550	680	0.042	2.23

When the values of a at different temperatures were plotted on an Arrhenius scale (Fig. 2), the slope of the plot yields an activation energy of 16 kcal/mol. This apparent activation energy is in good agreement with the range of activation energies found for cellulosic chars, of which 12.6kcal/mol is the lowest limit of the reported range¹. The activation energy of 16 kcal/mol is higher than the range of 3.1 to 12.4 kcal/mol of activation energies found for the chemisorption on an ultraclean carbon¹³. The apparent activation energy in Kapur wood chars therefore shows that there are different types of active sites responsible for chemisorption in wood chars and that of the more mature and graphitic carbon chars.

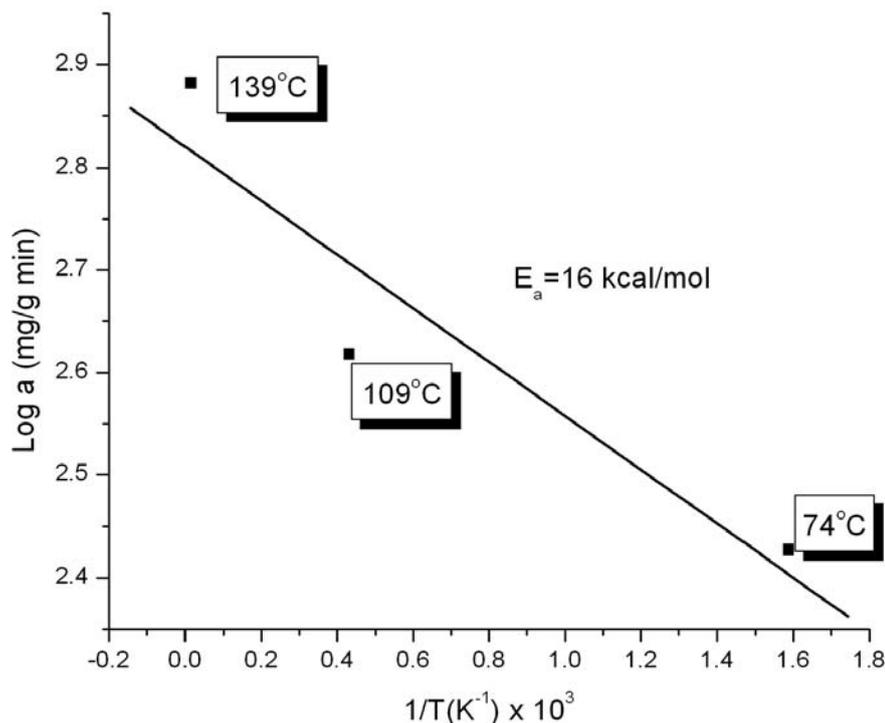


FIGURE 2. Arrhenius plot of of Log a on Arrhenius scale of Kapur char pyrolysed in nitrogen in air chemisorption

Hshieh et al. ³ have suggested that these low activation energies of this order indicates that the chemisorption process in both the compact solid wood char and the comparatively fibrous cellulose chars is a diffusion controlled process. However, diffusion control phenomenon rarely influences the kinetics of combustion at temperatures below 650°C ¹⁰, much less on the even slower chemisorption process at the low temperatures investigated here. The more probable reason for the low activation energies for zero-order gas-solid reaction in which desorption is negligible is often that of rate control by surface re-arrangement of adsorbed species ¹⁴, just as the case of wood chars here.

Chemisorption for Samples Preheated in Air

For samples preheated in air, there was no immediate weight gain due to surface adsorption of gases. The already formation of surface oxides during the preheating treatment at 140°C and 150°C for 50days and 30days respectively in air possibly blocked the surface for gases adsorption. Chemisorption however occurred after some periods of isothermal heating in TGA (Figs. 3 and 4) – the occurrence of chemisorption proves that continued heating removes the surface oxides, and re-exposes surface active sites for further chemisorption.

Since the desorption of surface oxides is temperature-dependent, the chemisorption was more marked in both air preheated samples of K150 and K140 at 109°C, as compared to the lower chemisorption temperature of 74°C. For chemisorption temperature at 109°C, K150 showed a remarkable weight gain due to gases adsorption, and ensued by a precipitous weight loss thereafter, indicating ignition. For K140, chemisorption occurred after some period of isothermal heating, leading to rapid gasification at the end of the chemisorption run. The weight variations of K140 and K150 are shown in Fig. 3. The same pattern is also observed at chemisorption runs conducted at 74°C, albeit to a less magnitude in both the mass gain and the duration for which it occurs, as seen in the weight variations graphs in Fig. 4.

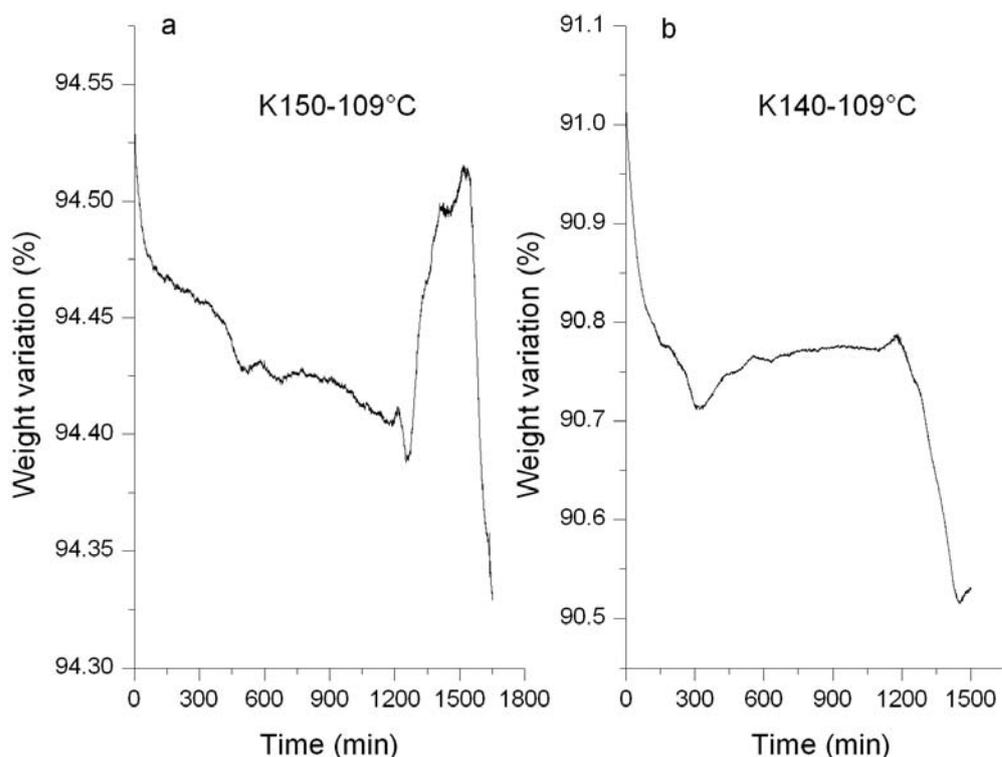


FIGURE 3. Weight change in air-preheated wood chars at chemisorption temperature of 109°C for (a) Kapur char heated at 150°C for 30 days; (b) Kapur char heated at 140°C for 50 days

There is no conclusive evidence in this study to predict when chemisorption might occur in air-preheated samples, and if ignition might take place at all, unlike inert-heated samples where chemisorption is immediate upon exposure to oxygen and in certain cases, the heat flux generated by the rapid initial oxygen chemisorption is sufficient to induce ignition at low temperature⁶. Nonetheless, this study provides a significant experimental evidence to suggest that air-preheated samples at temperatures as low as 140°C and 150°C for extended heating are capable of chemisorption, and they might lead to possible ignition at low temperature when the rate of heat generation exceeds the rate of heat loss.

Ignition Temperature and Pyrolysis Kinetics

Chemisorption is noted to occur in both air-preheated and nitrogen-preheated wood chars. The fact that chemisorption is exothermic could lead to ignition at a lower than expected temperature, since thermal runaway occurs when the heat flux generated by chemisorption in the sample exceeds heat loss. Lower ignition temperatures have been found for the long-term air-preheated wood char samples in this study (Table 4). The air-preheated wood chars have reported lower ignition temperatures in the range of 414.9°C to 421°C, as compared to the untreated fresh wood powder of 430°C found in Hshieh and Richards's work¹⁵.

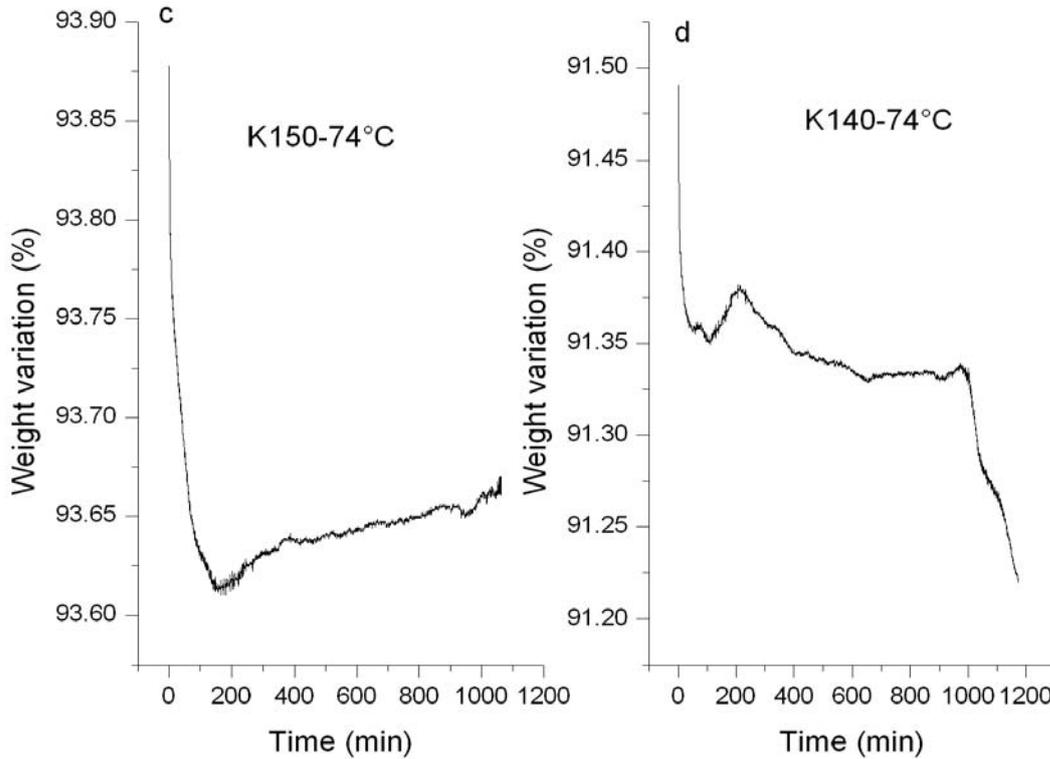


FIGURE 4. Weight change in air-preheated wood chars at chemisorption temperature of 74°C for (c) Kapur char heated at 150°C for 30days; (d) Kapur char heated at 140°C for 50days

TABLE 4. Effect of long-term preheating in air of wood on the ignition temperature in air

Sample	Preheating time (days)	Weight loss (%) ^a	Ignition temperature (°C) ^b
K150	30	20.5	414.9
K140	50	21.0	418.1
CW150 ^c	30	9	421.0

^a Air-dry basis

^b Heat from 25°C at 5°C/min in air

^c Cotton wood disc preheated in air - data taken from Hshieh et al. (1989)

The impact of a lower ignition temperature on the pyrolysis kinetics on wood chars however remains unknown. There is a question whether lower ignition temperature means a change in the pyrolysis kinetics of wood chars, and hence an alteration in the pyrolysis pathways. Alternatively, it is also a question if the different ignition temperatures between subsequent extension of preheating duration and/or change in heat treatment temperature are kinetically significant, thereby providing a clue as to how chemisorption has affected the combustion behaviour of solid.

The Semenov model of thermal ignition is applied to investigate the results where

$$\frac{R(T)^2}{E} \frac{S}{V} \frac{h}{\sigma QA} \exp[E/RT] = e \quad [3]$$

Assuming S, V, σ and Q do not differ much between samples, as porosity does not increase significantly for heat treatment below 500°C¹, and h remains unchanged between experiments,

applying equation [3] between two samples of two difference ignition temperatures could be re-written as:

$$\frac{(T_1)^2}{E_1 A_1} \exp[E_1 / RT_1] = \frac{(T_2)^2}{E_2 A_2} \exp[E_2 / RT_2] \quad [4]$$

Equation [4] is linearised by applying natural logarithm to both sides, where

$$E_1 / RT_1 + \ln \frac{(T_1)^2}{E_1 A_1} = E_2 / RT_2 + \ln \frac{(T_2)^2}{E_2 A_2} \quad [5]$$

Each side of the equation [5] represents a linear graph. Given that both graphs are identical, equating the constants terms and re-arranging yields:

$$\frac{E_1 A_1}{E_2 A_2} = \left(\frac{T_1}{T_2} \right)^2 \quad [6]$$

To examine if the effect of heat treatment and/or preheating duration which lowers the ignition temperature affects is kinetically significant, equation [6] is applied to analyse the temperature difference in ignition temperatures (Table 4) observed between K140 preheated for 50 days and K150 preheated for 30 days. By substituting $T_1 = 414.9^\circ\text{C}$ and $T_2 = 418.1^\circ\text{C}$ into equation [6], it is found that $E_1 A_1 = 0.984 E_2 A_2$. The analysis shows that the different ignition temperatures, which arises from a combination of different preheating duration and heat treatment temperature is almost kinetically comparable. In another case where ignition temperature changes as a consequence of preheating duration as found in Hshieh and Richards' work¹³, the analysis shows for $T_1 = 430^\circ\text{C}$ and $T_2 = 441^\circ\text{C}$ for wood discs preheated in air between 0 and 4 hours, $E_1 A_1 = 0.969 E_2 A_2$. In this case, neither does the effect of preheating duration is kinetically significant.

Equation [6] also indicates the scope of variation of E and A between the two samples. Using the case of a temperature difference as varied as 11°C , the permitted ratio between two groups of A and E is 0.969. Non-conformance firstly indicates that the pair of A and E are significantly different in kinetics, and secondly the resulting change in A and E implies a changing kinetics pathway altogether, depending on the value of the parameters. Tinney¹⁶ has suggested that the reasonable estimate for the pyrolysis of wood in the temperature interval of 220°C to 400°C is $E = 30\text{kcal/mol}$, and A spans the range of $6E07\text{ s}^{-1}$ - $7E08\text{ s}^{-1}$. Using $A_2 = 33.26\text{ kcal/mol}$ and $E_2 = 7.738E07$ found for Balau hardwood in temperature interval of 210°C to 300°C from S.M. Lim's work¹⁷, and assuming $A_1 = 30\text{ kcal/mol}$, numerical analysis shows that for the ratio of 0.969, E_1 works out to be $8.31E7$. This value of E conforms to the span suggested by Tinney. Therefore, with the change in temperature variation as much as 11°C , the activation energies fall within 30 kcal/mol to 33.26 kcal/mol , the values of which are typical for dehydration pathway. A switch in pathway to depolymerisation would require a leap in A to the range of $37\text{-}43\text{ kcal/mol}$ with E in the span of $4E08\text{ s}^{-1}$ - $2E09\text{ s}^{-1}$. The numerical analysis illustrates that chemisorption may lower the ignition temperatures of wood due to exothermicity of the reaction, but for the reported range of temperature variation, chemisorption does not seem to impact on the pyrolysis kinetics.

CONCLUSIONS

The results of Elovich kinetics parameters strongly indicates that these low temperature wood chars possess altogether a different type of active sites responsible for chemisorption activities, which are remarkably different from the more carbonized and mature graphitic carbon polymers. Other than inert-heated wood chars, chemisorption also occurs in long-term air-preheated wood chars. Lower

ignition temperatures have subsequently been noted for preheated wood chars. The experimental findings show that air-preheated wood chars would also undergo chemisorption if continued heating removes the surface oxides and reactivates the surface active sites. Despite the fact that chemisorption leads to a lower ignition temperature, the observed range of lowered ignition temperatures is not shown to be kinetically significant on wood pyrolysis, neither does the change in ignition temperature suggests a switch in pyrolysis pathway in wood decomposition.

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