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Study of the decomposition of kraft lignin impregnated with orthophosphoric acid

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Abstract

The aim of this study was to analyze the pyrolysis of Kraft lignin impregnated with orthophosphoric acid by thermogravimetry (TG-DTG). We studied the effect of various parameters on both the char yield and the rate of mass loss: heat treatment temperature up to 650 °C, impregnation time, inclusion of isothermal periods, acid to lignin mass ratio (P/L) and gaseous atmosphere. Decomposition of pure lignin showed two maxima in the mass loss corresponding to evolution of moisture at 92 °C and to lignin decomposition in a broad temperature range from 150 to 650 °C, respectively. When orthophosphoric acid was added, lignin dehydration proceeded to a larger extent, decomposition occurred in a narrower temperature range and decomposition ended at lower temperatures with higher char yields. There was an optimum P/L at values between 0.8 and 1.0, and further increasing P/L had low influence on the decomposition mechanisms. Differential Thermal Analysis (DTA) showed that reactions occurring upon impregnation of lignin with orthophosphoric acid at room temperature are finished after only 1 h, which confirmed the TG-DTG results. Impregnation times longer than 1 h and inclusion of isothermal periods did not affect significantly the subsequent char yield. Concerning the gaseous atmosphere, identical char yield were obtained whether the samples be prepared in nitrogen or in air at 450 °C. However, decomposition in air at 650 °C produced a decrease in the char yield when compared to pyrolysis in nitrogen due to the evaporation of P_2O_5 and the subsequent oxidation of the unprotected carbon.
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1. Introduction

The kraft method produces black liquor, a residue composed by lignin (30–40%) and other inorganic compounds, that is used as in-house fuel for the recovery of both energy and residual inorganic matter. The trend towards larger plant capacities and the optimization of the pulping process to improve cost effectiveness have led to the plants producing more by-product lignin than the amount that is needed to cover their energy consumption. The separation of lignin after water evaporation of black liquor could be an alternative to its incineration. Lignin is a bountiful and renewable source and could represent an attractive field for future in-

dustrial chemistry (i.e., as a substitute in the formulation of phenol–formaldehyde resins and adhesives). Another interesting option among these potential uses for lignin is the production of activated carbons.

Several authors have reported the use of kraft lignin as activated carbon precursor. Del Bagno et al. [1] investigated char and activated carbon manufacture from black liquors at a pilot-plant scale. Rodríguez-Mirasol et al. [2] prepared activated carbons from carbonization of eucalyptus kraft lignin. The latter research group also studied the chemical activation of this precursor by using $ZnCl_2$ [3] and obtained microporous activated carbons with a BET surface area as high as $1800 \, m^2 \, g^{-1}$. However, the use of $ZnCl_2$ has declined due to the environmental problems [4] and orthophosphoric acid (PA) is preferred as activating-dehydrating agent.

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PA promotes the bond cleavage in the biopolymers and dehydration at low temperatures [5], followed by extensive cross-linking that bonds volatile matter into the carbon product and so an increase in carbon yield. Benadi et al. [6] showed that the mechanism of PA activation of biomass feedstocks occurs through various steps: cellulose depolymerization, biopolymers dehydration, formation of aromatic rings and elimination of phosphate groups. This allows activated carbons to be prepared with good yields and high surface areas.

The use of PA as activating agent has been reported with various agricultural by-products [7–20], wood [21,22], natural carbons [4,23,24] and synthetic carbons [25,26]. As far as we know, there is only one paper wherein the possibility of chemical activation of kraft lignin with PA among other activating agents has been examined [27]. The authors carried out carbonization over the temperature range of 500–900 °C held for 1 h and under N_2 flow: maximum surface areas of more than $1300 \, m^2 \, g^{-1}$ were found at 600 °C.

This paper deals with the thermal decomposition of kraft lignin activated with PA in order to analyze the effect of the operation conditions on the char yield and on the rate of mass loss. The operation conditions studied were the impregnation time, the inclusion of isothermal periods, the PA to lignin mass ratio and the gaseous atmosphere. The role of PA as activating agent but also as inhibitor of carbon oxidation are herein analyzed.

2. Experimental

Kraft lignin was provided by Lignotech Iberica S.A. (Spain). Table 1 shows the proximate and ultimate analysis of lignin. The proximate analysis was carried out according to ISO standards following the weight losses at 100 °C/air (moisture), 900 °C/non-oxidizing atmosphere (volatile matter) and 815 °C/air (ash). An 85 wt.% H_3PO_4 aqueous solution (Panreac, Spain) was used as activating agent. Ultimate analysis was carried out in a EA1108 Carlo Erba Elemental Analyser. Results presented in Table 1 are very similar to those already reported [28].

Table 1
Lignin analysis (wt.%)

Proximate analysis (wt.%, wet basis)	
Moisture	14.5
Ash	9.5
Volatile matter	45.0
Fixed carbon[a]	31.0
Ultimate analysis (wt.%, ash and moisture free)	
Carbon	59.5
Hydrogen	5.1
Nitrogen	0.1
Sulphur	2.2
Oxygen[a]	33.1

[a] Estimated by difference.

Lignin was mixed with varying amounts of H_3PO_4 in the range of 0.3–1.8 PA to lignin mass ratio (P/L). The slurry was left for impregnation times from 1 to 22 h at room temperature and under air, then transferred to a Perkin-Elmer TGA 7 thermobalance wherein decomposition was carried out at temperatures up to 650 °C. In this study, approximately 30–50 mg of sample was heated up to a maximum temperature of 650 °C and in a flow rate of $50 \, cm^3 \, min^{-1}$ measured at room temperature and atmospheric pressure.

Experiments were repeated three times to be sure of the reproducibility, which was found to be quite satisfactory. Average data obtained at each set of operation conditions were considered for results and discussion. For comparison purposes between the various activation parameters, we used a sample impregnated for 1 h with a P/L of 1.4 and pyrolyzed with a heating rate of $10 \, °C \, min^{-1}$ up to 650 °C in nitrogen. The operation conditions were varied with regard to this reference. The effect of impregnation time was studied for samples left for 1 and 22 h at room temperature. The inclusion of isothermal periods was studied holding temperature for 15, 30 or 60 min at 150 °C or for 60 min at 300 °C and heating the sample at $10 \, °C \, min^{-1}$ up to 650 °C afterwards. The effect of P/L was studied for samples with a P/L of 0.3, 0.6, 0.8, 1.0, 1.4 and 1.8. Finally, the effect of gas atmosphere on decomposition was studied using nitrogen or air and heating the sample to a maximum temperature of either 450 or 650 °C, which temperatures were held for 120 min.

Differential thermal analysis (DTA) was performed by simply recording the voltage drop at both ends of a differential chromel–alumel thermocouple, having one temperature probe embedded within the 1.4 P/L mixture (i.e., the sample), while the other one was inside a fine powder of dry α-alumina (i.e., the reference). The experiment was carried out at room temperature, and the P/L mixture was stirred by the thermocouple probe itself. For that purpose, any part of the experiment (thermocouple, sample and reference), was handled using metallic tongs, in order to avoid parasitic heating due to the fingers of the operator.

3. Results and discussion

Fig. 1(a) and (b) shows thermogravimetric (TG) and differential thermogravimetric (DTG) curves, respectively, for pure lignin, PA and 0.3 P/L mixture when heated at $10 \, °C \, min^{-1}$ up to a temperature of 650 °C in nitrogen. The three samples were next maintained 2 h long at this latter final temperature. At the initial stage of the thermal treatment, pure lignin losses moisture from room temperature (T_{1a}) to 131 °C (T_{1b}). The dehydration proceeds with a maximum rate at 60 °C (T_{1max}), reaching a constant weight of 87% at 131 °C. Degradation of pure lignin occurs over a broad temperature interval (150–650 °C), with a maximum weight-loss rate between 300 and 370 °C. The decomposition of lignin is highly complex and depends on several factors such as its origin. The occurrence of lignin degradation in a wide range of temperatures
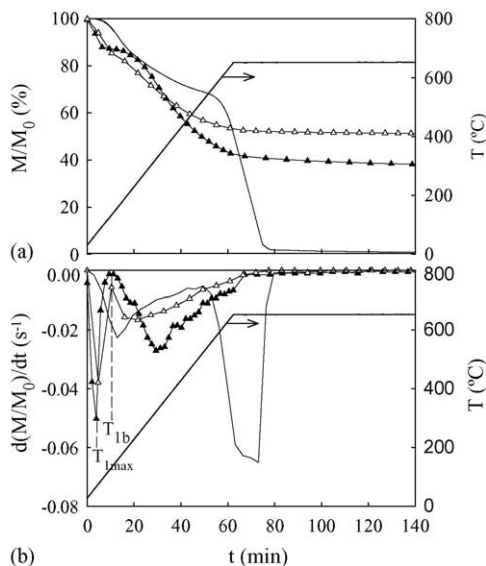
Fig. 1. (a) TG and (b) DTG curves for decomposition of pure lignin (▲), PA (—), and the 0.3 P/L mixture (△) in nitrogen. The thermal treatment is also shown on the plot.

Fig. 2. (a) TG and (b) DTG curves for the decomposition of the 0.3 P/L mixture experimental (△) and calculated (· · ·) assuming a weighted combination of the TG and DTG curves for PA and lignin.

has been described by several authors [29,30]. Negligible weight losses were observed while lignin was held 2 h long at 650 °C in nitrogen, hence the *x*-axis in Fig. 1 was limited to a maximum value of $t = 140$ min.

PA losses water at higher temperatures than pure lignin due to the different nature of the water eliminated. Water from lignin corresponds only to moisture whereas water from PA comes from moisture and the water generated by H_3PO_4 thermal degradation into P_2O_5. Indeed, when orthophosphoric acid is heated it dehydrates to form pyrophosphoric acid, $H_4P_2O_7$, as a result of the condensation of two phosphoric acid molecules. Continued heating leads to a mixture of orthophosphoric and polyphosphoric ($H_{n+2}P_nO_{3n+1}$) acids called superphosphoric acid. At higher temperatures metaphosphoric acid, HPO_3, is formed and it decomposes to P_2O_5 [31]. Thus, a maximum weight-loss rate was observed at 170 °C and the sample continued loosing weight up to 300 °C, which can be attributed to the successive dehydration reactions to P_2O_5. As temperature increased above 300 °C, weight loss continued at slower rate due to the sublimation of P_2O_5 that starts at this temperature [31]. Sublimation continued steadily up to $T = 580$ °C where a sharp increase in the weight-loss rate of the sample was observed, due to P_2O_5 melting and evaporation at 580–585 °C [31]. The sample weight when temperature arrived at 650 °C was of 52% and, as the temperature was held for 2 h, the sample was totally evaporated.

The 0.3 P/L mixture showed an intermediate behavior between those shown by lignin and PA. Fig. 2(a) and (b) shows experimental and calculated TG and DTG curves of the 0.3 P/L mixture; the calculation was made on the basis of a weighted combination of the experimental curves of pure PA and pure lignin. Doing so, the calculated carbon yield measured during heating was found to be lower than the
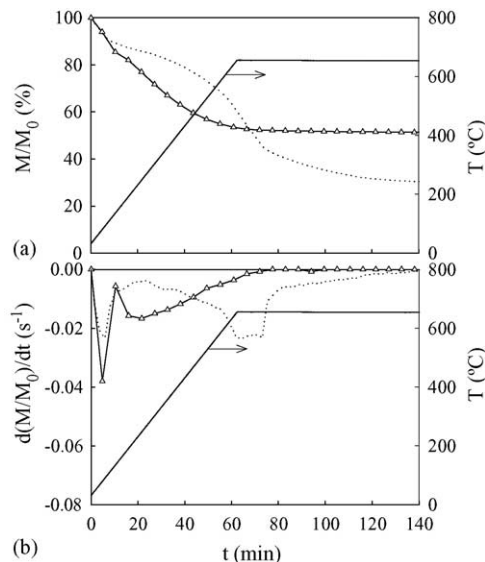
experimental one. However, when temperature was held at 650 °C for 2 h the calculated carbon yield decreased under the experimental one, 29 and 51%, respectively. The experimental weight-loss was higher than that calculated at temperatures lower than 150 °C and between 200 and 450 °C, and the weight of the sample was almost constant at temperatures higher than 600 °C.

These results clearly indicate that lignin reaction with PA during impregnation results in a complex mixed substrate, and that the PA/lignin mixture decomposes according to a reaction path, which is different from that of pure lignin. The PA-impregnated lignin follows a different reaction path during decomposition from that observed in pure lignin. Reaction of lignin with PA starts at room temperature as soon as the components are mixed since, according to the DTA curve given in Fig. 3, the temperature of the P/L sample increases immediately. This observation is in agreement with Lai [32]
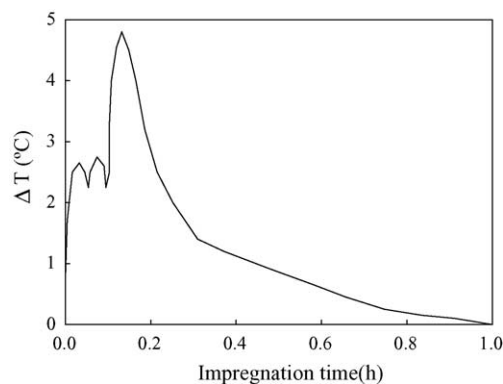

Fig. 3. DTA as a function of the impregnation time of the 1.4 P/L mixture in air and at room temperature. The first two peaks are artefacts only related to the stirring of the formerly inhomogeneous P/L mixture.

who reported the cleavage of aryl ether bonds in accompanied by dehydration, degradation and condensation reactions together with the formation of ketones by hydrolysis of ether linkages at low temperatures. PA promotes dehydration producing an important reordering of the structure and decreasing the volatile compounds emitted during decomposition and so increasing the carbon yield. Therefore, the first weight loss at temperatures lower than 150 °C can be attributed to the increase of dehydration and the higher rate of mass loss between 200 and 450 °C can be attributed to the decomposition of the depolymerized fractions of lignin that degrade at lower temperature than 'pure' lignin. The mass loss rate calculated as the weighted combination of the curves for PA and lignin is very different from the experimental one at temperatures higher than 500 °C (see Fig. 2). Whereas the weight of the sample remained approximately constant at 51% the calculated weight decreases steadily up to 29% due to P_2O_5 evaporation at temperatures above 580 °C. This result agrees with the total reaction of PA with lignin once they are mixed with a P/L of 0.3.

3.1. Effect of the impregnation time

In order to study the effect of the impregnation time, two samples with a P/L = 1.4 and impregnation times of 1 and 22 h were pyrolysed with a heating rate of $10 °C \, min^{-1}$ up to 600 °C in nitrogen. TG curves showed nearly the same evolution with temperature. The char yield at 600 °C was of 56 and 55% for the samples with 1 and 22 h of impregnation time, respectively. This little difference is within the uncertainties of the method and it is difficult to conclude from these results that impregnation time has a real effect on the char yield.

Fig. 3 shows a DTA curve of a sample during the impregnation time with a P/L = 1.4 in air and at room temperature. The temperature difference between the sample and the reference is seen to be almost zero after 1 h impregnation time, evidencing that no chemical reaction still occurs after that time. Therefore, the expected differences, if there are, will be of minor importance for carbons prepared with impregnation times longer than 1 h. In that sense, DTA results are in good agreement with TG-DTG analysis and hence the effect of the other operating conditions can be studied using only 1 h impregnation time.

3.2. Effect of intermediate isothermal periods

Yoon et al. [33] reported an increase of char yield by maintaining the sample at constant temperature for a certain period of time at the beginning of the weight loss. Therefore, we have studied the effect of including isothermal periods at 150 and 300 °C, temperatures at which maximum weight-loss rates in PA-lignin mixtures were observed.

The PA-lignin decomposition was studied for a sample with a P/L = 1.4 and an impregnation time of 1 h, intercalating isothermal periods of 15, 30 and 60 min at 150 °C. Fig. 4 shows the mass loss of these samples and that of the ref-
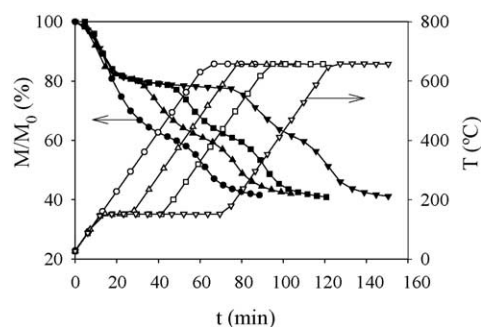

Fig. 4. TG curves of the 1.4 P/L mixture in nitrogen when intercalating isothermal periods at 150 °C ((●) 0 min-reference, (▲) 15 min, (■) 30 min, (▼) 60 min). The thermal treatment is also shown on the plot ((○) 0 min-reference, (△) 15 min, (□) 30 min, (▽) 60 min).

erence sample without including isothermal periods. Except for the step at 150 °C, the shape of the curves was essentially the same with a slight variation in the slope of the mass loss between 250 and 400 °C due to the higher extent of lignin degradation with longer isothermal periods. Thus, the differences observed at the end of the isothermal period at 150 °C were small 81, 79 and 77% after 15, 30 and 60 min, respectively. However, once the temperature arrived to 650 °C and after holding for 30 min the char yield was of 42, 41 and 41% for the same samples, respectively, and also of 41% for the reference sample. Therefore, intercalating isothermal periods does not produce changes in the char yield.

Although the differences of char yield upon addition of an isothermal period at 150 °C were not very important, including an isothermal step at this temperature can be of practical interest. Biomass is usually ground and pelletized before carbonization for commercial purposes. As the maximum weight-loss rate corresponding to moisture vaporization during the decomposition of lignin takes place at approximately 150 °C, the rapid water vaporization could crack-up the pellet. Carbonization of lignin in pellets indeed evidenced that intercalating an isothermal period between 100 and 150 °C allows a steady vaporization of lignin moisture, finally leading to pellets free of cracks.

We also studied the PA-lignin decomposition with a P/L = 1.4 and with the inclusion of isothermal periods of 1 h at 150 or 300 °C. The inclusion of an isothermal period of 1 h at 150 °C or at 300 °C did not produce any change in the char yield that was about 41% after holding for 30 min once the temperature arrived to 650 °C. These results are in agreement with the works of Rodríguez-Reinoso et al. [34] and Tascón et al. [35] who found no change in carbon yield with inclusion of intermediate isothermal periods during the course of decomposition of viscose rayon cloth and apple pulp, respectively.

3.3. Effect of phosphoric acid to lignin mass ratio (P/L)

Fig. 5 shows the DTG curves of PA-lignin mixtures, varying P/L from 0.3 to 1.8. As the P/L increased, the tempera-
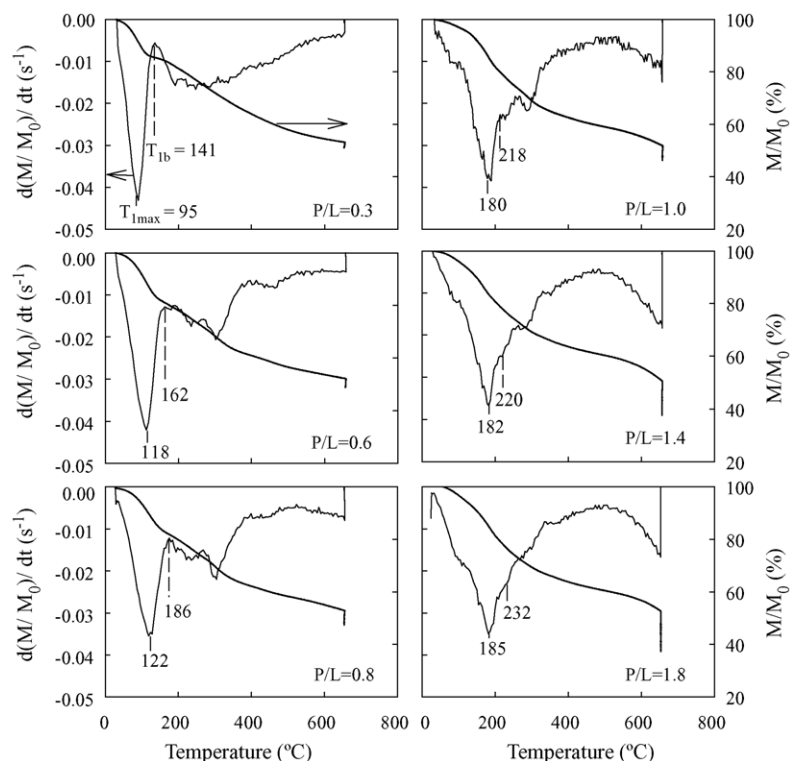
Fig. 5. TG and DTG curves of the decomposition of PA/lignin mixtures, varying P/L from 0.3 to 1.8, heating at 10 °C min^{-1} up to 650 °C and holding the final temperature for 2 h.

ture at which the rate of weight loss was maximal raised up to P/L = 1.0. At P/L ≥ 1.0, T_{1max} remains practically unchanged at a temperature of around 180–185 °C. We can also observe in the figure that increasing P/L from 0.3 to 0.8 makes the lignin to be completely degraded at decreasingly lower temperatures, from 620 to about 400 °C. By contrast, P/L ≥ 1.0 lead to almost identical end of degradation temperatures, lower than 400 °C.

Jagtoyen and Derbyshire [21] reported that CO_2 and CO begin to evolve from biomass in presence of PA just below about 100 °C and their production increases sharply to achieve a maximum at about 200 °C. In Fig. 5, it may be observed that T_{1max} becomes higher than the temperature of maximal rate for PA dehydration (170 °C) and so there is not a clear difference between dehydration of the PA-lignin mixture, dehydration of the PA in excess and lignin degradation with increasing P/L. However, it seems clear that there is a P/L value where PA totally reacts with lignin and so higher P/L should not produce any effect on the decomposition of lignin. In order to confirm the existence of this optimum P/L, the inflexion point of the TG curve after T_{1max} was assumed to mark the end of the dehydration peak, and hence to correspond to the limiting temperature T_{1b} between dehydration and decomposition. The percentage of mass loss due to the reaction of PA with lignin, %$ML_{P/L}$, could thus be quantified, and was calculated as follows:

$$\%ML_{P/L} = \frac{ML_{T_{1b}} - [X_P ML_P + X_L ML_L]}{ML_{T_{1b}}} \times 100$$

where $ML_{T_{1b}}$ is the percentage of mass loss at the inflexion point of the curve, T_{1b}, for a mixture PA-lignin. ML_P and ML_L stand for the water loss of PA and lignin respectively when pyrolyzed independently. X_P and X_L are the weight fraction of PA and lignin in the PA-lignin mixture at a given P/L.

Fig. 6 shows the %$ML_{P/L}$ calculated as defined above as a function of P/L. The mass loss due to the addition of PA increases nearly linearly between a P/L of 0 and 0.8 and remains approximately constant for P/L ≥ 1.0 within the error in the estimation of $ML_{T_{1b}}$. This figure confirms that it exits a maximum of acid that can react with lignin. Using P/L ≥ 1.0 does not increase dehydration: the acid in excess degrades
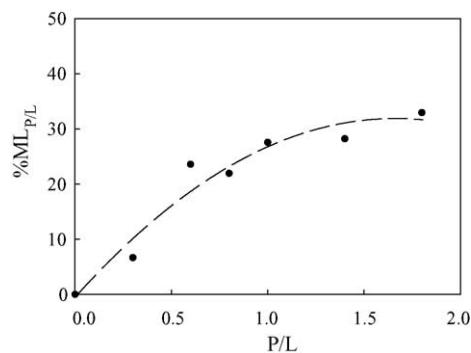

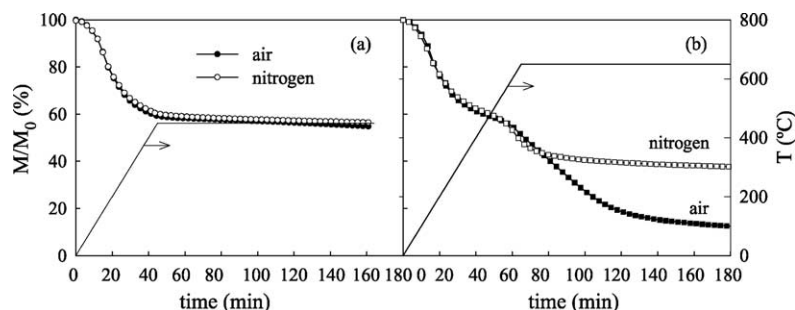Fig. 6. Percentage of mass loss due to the reaction of PA with lignin as a function of P/L.

Fig. 7. TG curves of the 1.4 P/L mixture in nitrogen and air when heating at $10\,^\circ C\,min^{-1}$ up to (a) $450\,^\circ C$ and (b) $650\,^\circ C$, and holding the final temperature for 2 h.

up to P_2O_5 and evolves, which is confirmed by the weight loss produced at $P/L \geq 1.0$ and at temperatures higher than $550\,^\circ C$ observed in Fig. 5.

It may be seen from Fig. 5 that, at $P/L = 0.3$, the plateau indicating that no more reaction takes place while the material is heated (i.e., the lignin degradation is finished), occurs near $600\,^\circ C$. Increasing P/L makes the end of the degradation occur at decreasing temperatures as far as P/L remains below 1.0. The DTG curves for $P/L \geq 1.0$ evidenced the same behavior, i.e., the lignin degradation took place at lower ($<400\,^\circ C$) and almost identical temperatures, and the weight-loss rate was nearly constant at temperatures from 450 to $550\,^\circ C$. The melting and vaporization of P_2O_5 of the unreacted PA could explain the increase in weight-loss rate from 550 to $650\,^\circ C$. This observation supports the hypothesis of an optimum on P/L at values between 0.8 and 1.0 as argued above. It seems clear that since PA reacts with lignin, the optimum P/L will depend on the lignin origin.

3.4. Effect of the gaseous atmosphere

Materials impregnated with PA are usually pyrolyzed in nitrogen. However, earlier studies have shown that chemical activation with PA in air produced carbons with the greatest total number of functional groups when compared with activation under nitrogen flow [25,36,37]. Therefore, excluding obvious economical concerns, activation in air is an interesting option when activated carbons are used for the removal of metals in water treatment because metal uptake appears to be directly correlated with the number of functional groups [36].

To study the effect of the gaseous atmosphere in the process, a sample of PA-impregnated lignin was heated at $10\,^\circ C\,min^{-1}$ up to 450 or $650\,^\circ C$ in air and in nitrogen and both final temperatures were held for 2 h. Fig. 7(a) shows TG curves of PA-lignin decomposition with $P/L = 1.4$ in nitrogen and air when heating at $10\,^\circ C\,min^{-1}$ up to $450\,^\circ C$. The TG curves for these two experiments exhibit exactly the same shape, i.e., the sample losses weight in the same way and independently of the atmosphere used. Moreover, there was no significant weight loss for 2 h once the temperature of the sample arrived to $450\,^\circ C$.

Fig. 7(b) shows the same as in Fig. 7(a) but the final temperature was $650\,^\circ C$, held 2 h long. Again, the TG curves for both nitrogen and air atmospheres exhibit exactly the same shape up to $650\,^\circ C$. However, if temperature was held at $650\,^\circ C$ for a longer time, the samples behaved differently in air and in nitrogen. The sample pyrolyzed in nitrogen showed a sharp decrease in the weight from 51 to 43% during the first 15 min and afterwards the weight remained approximately constant with time. On the contrary, the sample pyrolyzed in air showed a continuous decrease during 80 min reaching a mass percentage of 14.5% meaning the total combustion of the sample. Indeed, due to the phosphatation of the ashes, a residual mass higher than that given in Table 1, 9.5%, was recovered. The low mass variation (8%) of the sample pyrolyzed in nitrogen can be attributed to the P_2O_5 vaporization whereas the low char yield in air is the result of the P_2O_5 vaporization of the PA used in excess and the combustion of unprotected carbon. Examining Fig. 7, one can extract a conclusion of practical and economical importance: char yield is nearly independent of the gaseous atmosphere at moderate temperatures and with the adequate P/L.

4. Conclusions

When lignin and PA are mixed together, they react completely in less than 1 h and longer impregnation times or inclusion of isothermal periods do not have any influence on the char yield. The product of the reaction between PA and lignin pyrolyses following a reaction path different from that of pure lignin. PA acts on lignin increasing dehydration and anticipating its complete degradation at temperatures as low as $400\,^\circ C$. There exits an optimum P/L at values between 0.8 and 1.0 that allows the complete reaction of lignin, and further increases in P/L do not produce changes on the pyrolysis process. H_3PO_4 in excess dehydrates progressively into P_2O_5 which finally melts and evaporates. P_2O_5 protects carbon from oxidation and once evaporated at temperatures higher than $580\,^\circ C$ the carbon is totally oxidized in air whereas the char yield in nitrogen remains constant. Char yield is nearly independent of the gaseous atmosphere at moderate decomposition temperatures as long as lignin has reacted completely with PA.

Acknowledgements

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