Evaluation of hydrochars from lignin hydrous pyrolysis to produce biocokes after carbonization

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ABSTRACT

Hydrochars were obtained after hydrous pyrolysis of a pine Kraft lignin using different reaction conditions (temperature, water content and residence time) and the residues were characterized through a wide range of analytical techniques including high-temperature rheometry, solid-state ^{13}C nuclear magnetic resonance (NMR), thermal gravimetric analysis (TGA), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and field emission scanning electron microscopy (FE-SEM). The results indicated that an increase in reaction temperature, an increase in residence time or a decrease in water content reduces the amount of fluid material in the residue. The hydrous pyrolysis conditions studied were not able to increase the maturation of lignin, which would result in an increase in the resolidification temperature, but reduced the amount of mineral matter in the hydrochar produced. On the other hand, the hydrochars obtained from pristine lignin, torrefied lignin (300 °C, 1 hour) and their 50:50 wt.%/wt.% blend at temperatures of 350 °C after 6 hours using 30 ml of water had lower ash contents (<2 wt.%) than the parent lignin (2.5 wt.%) and a high rank good coking coal (10 wt.%). However, the reactivity of the resulting biocokes (>45%) is excessively high compared to that of the good coking coal (10%) and the micro-strength of the biocokes (R_1<1%) is much lower than that of the coal (R_1=17%). These findings could be rationalized by the high total porosity (>39%) and high microporous surface areas (>400 m^2/g) of the biocokes and high alkalinity index of the lignins (>27%) compared to those of the coke (27% and 145 m^2/g) and coal (0.6%), respectively. Furthermore, the biocoke derived from the hydrous pyrolysed torrefied lignin did not agglomerate, which could not be explained by changes in the chemical properties of the material and requires further investigation.

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1. Introduction

The substitution of coking coals with biomass materials is receiving a lot of attention in recent times due to the simultaneous reduction in material costs and non-renewable carbon emissions in the carbonization process [1−11]. The resultant coke obtained by the partial substitution of coal by biomass during coke making has been termed biocoke. It has been suggested that biomass addition can be increased without impairing biocoke strength and yield by increasing the biomass particle size and its density through compressive forming [12]. Charcoal has also been studied to reduce non-renewable carbon emissions [4,13,14]. The substitution of coal with 2−3 wt.% charcoal has been proven to produce biocoke with similar reactivity behavior to CO_2 to that of coke from coal [13]. Even an increase to 5 wt.% charcoal addition in the biocoke could have a beneficial impact in CO_2 emissions by reducing the thermal reserve zone temperature of the blast furnace that leads to a reduction in coke rate. Other researchers [15] have also suggested that hydrothermal carbonization (also termed as hydrous pyrolysis) of biomass can produce residues with properties similar to those of cokes obtained from coal, basing this assumption on the tensile strength of the residues at ambient temperature. However, none of these studies take into consideration the hot mechanical strength of the biocoke, which is one of the main criteria in order to establish the suitability of the biocoke for industrial application.

It is also well known that the char yield obtained from biomass is limited by the different extents of thermal degradation and concentrations of its main constituents hemicellulose, cellulose and lignin. Indeed, the biomass constituent lignin produces higher char yields than cellulose and hemicellulose since it is the only one with aromatic structures. Lignin is an interesting feedstock for biocoke production because it has H/C and O/C ratios closer to those from coal than the parent biomass, it is produced in vast quantities as a by-product in the pulp and paper industry (mainly as Kraft lignin) and will be obtained as a waste product in future bio-refineries [16]. For instance, lignin has been used as a binder of anthracite fines to produce foundry coke briquettes and the strength of the briquettes increased with an increase in hardwood lignin concentration up to around 6 wt.% [17]. However, lignin is also characterized by a high degree of swelling upon heating that can cause operational problems in the coke oven (e.g. high wall pressures, hard pushes during oven discharge) and diminish the biocoke strength. Torrefaction, which consists on a pyrolysis treatment at temperatures between 200−300 °C and has been used to increase the energy density of lignin [18], can reduce the level of swelling and increase its bulk density.

Therefore, the aims of this work are to elucidate whether torrefaction can improve the coking properties of a pine Kraft lignin and whether the residues obtained after hydrous pyrolysis of lignin in pristine and torrefied forms can be used to produce a fully renewable biocoke with good hot mechanical strength and reactivity. In this work, biocoke will be referred to as the coke obtained from hydrochars derived from pristine lignin, torrefied lignin and their 50:50 wt.%/wt.% blend without the presence of coal.

2. Materials and methods

2.1. Materials

The pine Kraft lignin used in this study was obtained from MeadWestvaco (USA) and supplied as a dark brown powder (>99.5 wt.% lignin). The pine Kraft lignin was torrefied at 250 °C and 300 °C for 1 hour to increase the char yield. Lignin torrefaction was carried out by pelletizing the lignin powder to produce discs of 25 mm in diameter using approximately 4 g of lignin. These lignin discs were placed inside a ceramic boat and the boat was

introduced in the quartz tube reactor of a horizontal tube furnace. Heating rates of 3 °C/min and 20 °C/min were used from room temperature to the final temperature. A constant flow of N_2 at 100 ml/min was used throughout the test.
A high rank good coking coal and its coke were used as reference to evaluate the hydrochars obtained after hydrous pyrolysis of pristine lignin, torrefied lignin, their 50:50 wt.%/wt.% blend and the biocokes produced from the carbonization of the hydrochars.

2.2. Hydrous pyrolysis and carbonization tests

The equipment used for hydrous pyrolysis comprised of a Parr 4740 series stainless steel 75 ml cylindrical pressure vessel connected to a pressure gauge rated to 690 bars. Heat was applied by means of a fluidized sand bath, which was controlled by an external temperature controller. The temperature was monitored by means of an additional K-type thermocouple connected externally to a computer that records the temperature every 10 seconds. Each hydrous pyrolysis experiment was conducted on 6 g of pristine lignin using different temperatures, residence times and water contents. In addition, pristine lignin, torrefied lignin (300 °C, 1 hour, 3 °C/min) and their 50:50 wt./wt. blend were hydrous pyrolysed at 350 °C for 6 hours using 30 ml of water to prepare hydrochars for carbonization tests. In this case, the amount of pristine lignin used for each test was 15 g whereas the amount of torrefied lignin and the 50:50 wt./wt. blend was 18 g. In all experiments performed, the reactor was flushed with nitrogen gas to reduce the oxygen content in the system. Afterwards, 2 bars pressure of N_2 was pumped into the system to keep it inert throughout the experiment. The sand bath, which was connected to an external temperature controller and compressed air source, was pre-heated to the required temperature and left to equilibrate. The pressure vessel was then lowered onto the sand bath and the experiment left to run with a constant air flow through the sand bath. At the end of the experiment, the reactor was removed from the sand bath and allowed to cool to room temperature. To recover the residues or hydrochars, the reactor including the pressure gauge was first disconnected from the experimental set up and transferred to a fume cupboard where the generated gas was released. This was followed by dismantling the reactor, after which the hydrochar was transferred to a vacuum oven and dried for 3−4 hours at 40 °C.
Carbonization tests were carried out in a sole heated oven. For each test, a sample of 80 g with particles < 1 mm was compacted in a stainless steel crucible, which was covered with a perforated ceramic top to allow the release of volatiles. The sole in the oven was pre-heated to 1050 °C and then the stainless steel crucible configuration containing the sample was placed inside the oven. The sample was heated from the sole at 1050 °C for 4 hours. The test was carried out in inert atmosphere as the volatiles generated by the sample impeded the contact with air.

2.3. Proximate, ultimate and inorganic matter analyses

Proximate analysis was carried out following the standard ISO 562 and ISO 1171 procedures for humidity, ash and volatile matter determination. For ultimate analysis, the standard procedures ASTM D5016-98 and ASTM D5373-02 were used for the determination of C, H N and S using LECO CHN-2000 and LECO S-144 DR instruments. The inorganic matter composition of each sample was analyzed by X-ray fluorescence (XRF) in a SRS 3000 Bruker spectrometer in accordance with the ASTM D4326-04 standard procedure. The alkalinity indexes for lignin, torrefied lignin and the coking coal were calculated using Eq. 1. This index gives an indication of the reactivity of the material whereby the higher the index the higher the reactivity and the less suitable for blast furnace operation [13].

$$\text{Alkalinity index (\%)} = \frac{[Fe_2O_3]+[CaO]+[MgO]+[K_2O]+[Na_2O]}{[SiO_2]+[Al_2O_3]} \times \text{Ash (\%)} \qquad (1)$$

2.4. CP/MAS and SPE/MAS solid-state ^{13}C nuclear magnetic resonance (NMR)

Cross polarization (CP) and single pulse excitation (SPE) coupled with magic angle spinning (MAS) solid-state ^{13}C NMR analyses were performed in a Bruker Avance 200 spectrometer at a field strength of 4.7 Tesla corresponding to 50 MHz for ^{13}C and 200 MHz for ^{1}H. CP/MAS analyses were performed with pristine lignin, torrefied lignin (300 °C, 1 hour, 3 °C/min) and three hydrochars obtained from pristine lignin at 240 °C, 280 °C and 320 °C for 1 hour using 20 ml of water. SPE/MAS analyses were carried out with the hydrochars obtained from pristine lignin and torrefied lignin after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water. Samples were packed tightly into a zirconia rotor with a Kel-F rotor-cap and spun at the magic angle (54°44') with a spinning frequency of approximately 5 kHz. A contact time of 1 millisecond was used during the Hartmann-Hahn condition. The acquisition times in CP/MAS and SPE/MAS analyses were 1.5 seconds and 30 seconds, respectively. In both cases, the spectra were obtained after 2500 scans and the FIDs were processed using a line broadening factor of 50 Hz. Tetrakis(trimethylsilyl)silane (TKS) was used as an internal standard to calibrate the position of the peaks.

2.5. Thermal gravimetric analysis (TGA)

TG/DTG analyses of the raw materials were carried out using a TA Instruments SDT 2960 thermoanalyser. 10−15 mg of samples with particle sizes <0.212 mm were heated to 1000 °C at a rate of 10 °C/min under a N_2 flow of 100 ml/min. From the data obtained, the volatile matter evolved up to a specific temperature (VMT) and the derivative of the weight loss (DTG) curve were calculated. The temperature of maximum volatile matter evolution (T_{max}) was also obtained from the TG/DTG curves.

2.6. High-temperature SAOS rheometry

High-temperature small-amplitude oscillatory shear (SAOS) measurements were performed using a Rheometrics RDA-III high-torque controlled-strain rheometer. The amount of material used for each analysis was 1.5 g. The samples were compacted with a hydraulic press under 5 tons of force to form discs of 25 mm in diameter. The tests involved placing the sample disc between two 25 mm parallel plates which had serrated surfaces to reduce slippage. The pine Kraft lignin, torrefied lignin (300 °C, 1 hour, 3 °C/min), their blends and the hydrochar obtained from pristine lignin at 350 °C for 6 hours and using 30 ml of water were heated from 50 °C to 500 °C at 3 °C/min. The high rank good coking coal was heated from room temperature to 330 °C at 85 °C/min and from 330 °C to 500 °C at 3 °C/min. The furnace surrounding the sample was purged with a constant flow of N_2 to transfer heat to the sample and remove volatiles. The sample temperature was monitored using a thermocouple inside the furnace. A continuous sinusoidal varying strain with amplitude of 0.1% and frequency of 1 Hz (6.28 rad/s) was applied to the sample from the bottom plate throughout the heating period. The stress response on the top plate was measured to obtain the complex viscosity (η^*), which measures the resistance to deformation and flow of the material. The complex viscosity is calculated using Eq. 2, where G' is the storage or elastic modulus, G'' is the loss or viscous modulus and ω is the frequency [19].

$$\eta^*(\text{Pa.s}) = \frac{\sqrt{\{G'(\text{Pa})\}^2 + \{G''(\text{Pa})\}^2}}{\omega(\text{s}^{-1})} \quad (2)$$

2.7. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS spectra were measured using a Nicolet Magna-IR560 spectrometer with a diffuse reflectance accessory. A mercury-cadmium-telluride array detector (MCT-A) that operates at sub-ambient temperature was used. Pristine lignin, lignin torrefied (300 °C, 1 hour, 3 °C/min) and the hydrochars obtained from pristine lignin, torrefied lignin and their 50:50 wt.%/wt.% blend after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water were analyzed. The samples were dried overnight before analysis and the data were collected in the range between 650−4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.8. Field emission scanning electron microscopy

Field emission scanning electron microscopy (FE-SEM) images were obtained on a Quanta FEG650 microscope (FEI Company) at 25 kV.

2.9. Micro-strength and reactivity of biocokes/coke

The micro-strength of biocokes and coke was determined by the method used by Ragan and Marsh [20]. Briefly, two charges of biocoke or coke (2 g, particle sizes 0.60–1.18 mm) were placed into two separate cylinders of 25.4 mm internal diameter and 305 mm length and sealed by steel dust caps. Each cylinder contained 12 steel ball-bearings of 8 mm in diameter. The samples were subjected to 800 rotations at a speed of 25 rpm. Three indices were derived after sieving: R_1 (>0.6 mm), R_2 (0.6–0.212 mm) and R_3 (<0.212 mm). The higher the value of R_1 (or the lower R_3), the higher the micro-strength of the biocoke or coke. At least duplicate tests were performed on each sample.

The reactivity was measured following the ECE-INCAR method [21], which briefly consists on subjecting 7 g of biocoke/coke of particle sizes between 1−3 mm to a CO_2 flow of 120 ml/min at 1000 °C. The reactivity is expressed as the mass loss after 1 hour of reaction.

2.10. Porosity and surface area determination

In order to determine the microporous structure of the biocokes and coke, physical adsorption of CO_2 at 0 °C (273 K) was carried out in a Nova 4200e Quantachrome Instruments. Degassing was performed in vacuum for 24 hours at 200 °C prior to adsorption. The Dubinin-Radushkevich equation was applied to the CO_2 adsorption isotherms in order to obtain the volume of micropores (W_0) and the characteristic adsorption energy (E_0). Following the procedure of Stoeckli [22], E_0 was related to the average width of the micropores (L) and W_0 was related to the surface area of the micropores (S_{mi}) by means of the following empirical equations:

$$\text{L(nm)} = \frac{10.8}{\text{E}_0(\text{kJ/mol}) - 11.4} \quad (3)$$

$$\text{S}_{\text{mi}}(\text{m}^2/\text{g}) = \frac{2000 \times \text{W}_0(\text{cm}^3/\text{g})}{\text{L(nm)}} \quad (4)$$

The true density (ρ_{He}) of the biocokes and coke was measured by means of helium picnometry on a Micromeritics Accupyc 1330 Pycnometer. Their apparent density (ρ_{Hg}) was determined using mercury at 0.1 MPa on a Micromeritics autopore IV 9500 mercury porosimeter. The open porosity corresponding to pore sizes <12 μm (ε) was calculated using the true and apparent densities by means of the following equation:

$$\varepsilon(\%)= \left\{1 - \frac{\rho_{Hg}(g/cm^3)}{\rho_{He}(g/cm^3)}\right\} \times 100 \quad (5)$$

The total pore volume (V_T) was obtained from the equation:

$$V_T(cm^3/g)= \left(\frac{1}{\rho_{Hg}(g/cm^3)} - \frac{1}{\rho_{He}(g/cm^3)}\right) \quad (6)$$

The pore size distribution was calculated by applying increasing pressure to the sample from 0.1 to 227 MPa. This resulted in pore sizes in a range of 12 μm to 5.5 nm in diameter (dp) according to the Washburn equation. Pore sizes were classified into three categories: macropores (12 μm>dp>50 nm), mesopores (50 nm>dp>5.5 nm) and micropores (dp<5.5 nm).

3. Results and discussion

3.1. Characterization of pristine and torrefied lignins

The ash yield, volatile matter yield and elemental composition of the pristine pine Kraft lignin (PKL), the lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (TL) and the high rank good coking coal are presented in Table 1. Lignin torrefaction increases the ash yield from 2.5 wt% to 3.1 wt%. The volatile matter yield and oxygen content of torrefied lignin are reduced from 64 wt% and 19 wt% to around 39 wt% and 26 wt% respectively, but they are still significantly higher than those of the high rank coal (23 wt% and 4 wt%).

The composition of the mineral matter and alkalinity index for the pristine lignin, torrefied lignin and high rank good coking coal are displayed in Table 2. The amounts of SiO_2 and Al_2O_3 in the pristine and torrefied lignins (3% and 1.2%, respectively) are much lower than those in the good coking coal (61% and 32%). On the contrary, the concentrations of K_2O (5−6%) and especially Na_2O (35−39%) in pristine and torrefied lignins are much higher than those in the coal (0.8% and 0.4%). As a result, the alkalinity indexes calculated with Eq. 1 for the pristine and torrefied lignins are much higher than that for the good coking coal (>27% cf. 0.6%). These results suggest that pristine and torrefied lignins are highly reactive and unsuitable for cokemaking in their current form.

The solid-state CP/MAS ^{13}C NMR spectra of the pristine lignin and lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min are presented in Fig. 1. Table 3 presents the chemical shift assignments for the ^{13}C NMR peaks in lignin obtained from the literature [24,25]. The peak at 3.5 ppm in the spectrum of torrefied lignin corresponds to the internal standard TKS. The spectra indicate that torrefaction removes aliphatic C−C groups (around 33 ppm), polysaccharides (72 ppm), C−O carbons including methoxyl carbons (56 ppm, 74

ppm and 84 ppm) and carbonyl and carboxylic acid structures (180 ppm) and reduces significantly the amount of guaiacyl units as indicated by the reduction in the intensity of the peaks positioned at 115 ppm and 148 ppm.

The DRIFTS spectra of these two samples are shown in Fig. 2. Aliphatic C−H appears in the region 3000−2800 cm^{-1}, C=O groups produce a peak at 1700 cm^{-1}, aromatic rings produce peaks at around 1600, 1510, 1465 and 1430 cm^{-1}, syringyl groups produce a peak at 1370 cm^{-1}, guaiacyl groups produce a peak at 1270 cm^{-1} and C−O from methoxy groups appears at 1120−1050 cm^{-1} [26,27]. Torrefaction causes a reduction in all the peaks in the region 1600−900 cm^{-1}. Therefore, aromatic rings, guaiacyl groups and methoxy groups are the most affected and seem to confirm aforementioned findings from solid-state ^{13}C NMR.

The viscoelastic properties as a function of temperature of the pine Kraft lignin (i.e. pristine), torrefied lignin and the high rank coal were determined (Fig. 3). Pine Kraft lignin presents two minima in complex viscosity at around 220 °C and 340 °C. Torrefaction of lignin at 300 °C destroys the fluid components evolving at 220 °C whereas the fluid components evolving at 340 °C are still present. It could be argued that the fluid entities forming at 220 °C in pine Kraft lignin could mainly derive from the decomposition of C−C, polysaccharides, C−O, carbonyl and carboxylic acid structures identified by CP/MAS ^{13}C NMR and DRIFTS. Torrefaction is not able to increase the maturation of lignin as indicated by the overlapping of the complex viscosity curves during resolidification. The good coking coal presents a minimum in complex viscosity at around 460 °C, which is 130 °C higher than that of torrefied lignin. The thermoplastic temperature range of the coal is much narrower (75 °C) that that of pristine lignin (220 °C), which is clear evidence of the different chemical properties of the fluid entities in these materials.

The effects of torrefaction temperature and heating rate on the viscoelastic properties of lignin were also evaluated. Table 4 presents the minimum complex viscosity (η^*_{min}) and temperature of minimum complex viscosity or maximum fluidity (T_{mf}) for the high rank coal, pristine pine Kraft lignin and the lignin torrefied at 250 °C and 300° C using a heating rate of 3 °C/min and at 300 °C using a heating rate of 20 °C/min. An increase in torrefaction temperature causes an increase in the minimum complex viscosity (i.e. decrease in fluidity) and an increase in the temperature of maximum fluidity due to the partial disappearance of the peak at 220 °C. An increase in heating rate from 3 °C/min to 20 °C/min increases fluidity development and decreases slightly the temperature of maximum fluidity by around 7 °C. The temperature of maximum fluidity of the sample torrefied at 300 °C using a heating rate of 3 °C/min (328 °C) is the closest to that of the high rank coal (462 °C) and for this reason was selected for further testing.

Blends of pristine lignin and lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min were prepared and their viscoelastic behaviors were also determined (Figs. 3 and 4). The results indicate that the viscoelastic behavior of the blends shifts from the viscoelastic behavior of pristine lignin to that of torrefied lignin as the amount of torrefied lignin in the blend increases. Those blends that contain pristine lignin in percentages between 30–60 wt.% show very similar viscoelastic behaviors, which are characterized by minimum complex viscosity values in the order of 1.5×10^5–3.0×10^5 Pa.s between 200–325 °C. It was observed that the chars obtained at 500 °C from these blends possessed good mechanical strength, and thus, a 50:50 wt.%/wt.% blend was selected for hydrous pyrolysis tests in order to elucidate possible synergistic effects between the components.

3.2. Characterization of hydrous pyrolysis residues from pine Kraft lignin

The effect of hydrous pyrolysis temperature on the viscoelastic behavior of pine Kraft lignin was investigated. Fig. 5 shows the viscoelastic behavior of the hydrous pyrolysis residues (or hydrochars) obtained at temperatures ranging from 220 °C to 320 °C. The viscoelastic behavior of pristine pine Kraft lignin is also shown for comparison purposes. The scattering of data in the plot might be attributable to the release of gaseous products that cause force fluctuations on the rheometer's transducer. The results indicate that the amount of fluid material in the hydrochars decreases with hydrous pyrolysis temperature in the order: 300 °C > 280 °C > 220 °C > 240 °C > 310 °C > 320 °C. The highest amount of fluid material is obtained with the hydrochar produced at 300 °C and this sample also yields the widest thermoplastic temperature range (150–350 °C). The DTG profiles of the hydrochars obtained at 240 °C, 280 °C and 320 °C indicate that lignin undergoes major degradation at temperatures above 280 °C (Fig. 6). All these results suggest that hydrous pyrolysis of lignin at 280–300 °C promotes the formation of liquid entities as suggested by the high fluidity of the hydrochars at these temperatures compared to the fluidity of hydrochars produced at 220–240 °C. However, these fluid entities seem to convert into gaseous products and/or form precipitates by condensation reactions at hydrous pyrolysis temperatures >300 °C, which leads to the drastic reduction in hydrochar fluidity.

The solid-state CP/MAS ^{13}C NMR results for pristine pine Kraft lignin (Fig. 1) and the hydrochars obtained at 240 °C, 280 °C and 320 °C (Fig. 7) indicate that hydrous pyrolysis removes the peaks at around 33 ppm (aliphatic C−C groups), at 70–90 ppm (polysaccharides and aliphatic C−O carbons) and at around 180 ppm (carbonyl and carboxylic acid structures). These results indicate that hydrous pyrolysis causes similar structural modifications in lignin to those caused by torrefaction. Indeed, the spectrum of the hydrous pyrolysed lignin at 280 °C resembles that of torrefied lignin at 300 °C (Fig. 1). The spectra of the hydrochars obtained at 240 °C and 280 °C are fairly similar but different to the spectrum of the hydrochar obtained at 320 °C. These results indicate that there is significant reduction in methoxyl groups (56 ppm) and C-3 and C-4 carbons of guaiacyl units (148 ppm) at 320 °C, which could be mainly responsible for the reduction in hydrochar fluidity (Fig. 5) and the reduction in the maximum rate of volatile release observed in the DTG plots (Fig. 6).

The effect of hydrous pyrolysis time on the viscoelastic properties of the hydrochars is presented in Fig. 8. An increase in residence time causes a reduction in fluidity development. The hydrochar obtained after hydrous pyrolysis at 300 °C for 30 minutes and using 20 ml of water develops the same minimum in complex viscosity as the pristine lignin (ca. 10^3 Pa.s) but the temperature of maximum fluidity is approximately 50 °C higher. An increase in residence time from 30 minutes to 1 hour leads to a significant increase in the minimum complex viscosity from around 10^3 Pa.s to 3×10^3 Pa.s with the simultaneous increase in the temperature of maximum fluidity from 270 °C to 285 °C. A residence time of 2 hours almost completely destroys fluidity development (minimum complex viscosity of 3.2×10^4 Pa.s) and causes a further increase in the temperature of maximum fluidity to 290 °C. These results suggest that short residence times of less than an hour should be used to preserve the fluid material in the hydrochar whereas residence times >2 hours would be required to produce a hydrochar that resembles a semi-coke from coking coal.

The effect caused on the viscoelastic properties of the hydrochar by the amount of water used during lignin hydrous pyrolysis is presented in Fig. 9. The amount of fluid material in the hydrochar decreases with the amount of water in the order: 20 ml > 5 ml ≈ 10 ml > 30 ml >

15 ml > anhydrous. Based on previous research, it has been suggested that the ratio of water to biomass should be kept as low as possible to enhance polymerization [28]. Indeed, more liquid product was produced during hydrous pyrolysis of an immature Kimmeridge Clay source rock at 310 °C for 7 hours by increasing the water content [29], and it was found that the liquid yield increased with the amount of water in the system up to 20 ml when using 4 g of Kimmeridge Clay source rock (i.e. water to source rock ratio of 5:1) but it decreased with higher amounts of water. Analogously, the viscoelastic behaviors of the hydrochars obtained after hydrous pyrolysis of 6 g of lignin at 300 °C indicate that the water to lignin ratio required to promote maximum fluidity development is close to 3.3:1.

In summary, maximum fluidity (or minimum complex viscosity) in the hydrochar was obtained at hydrous pyrolysis temperatures of 280−300 °C with 20 ml of water and residence times of 30 minutes. However, none of the hydrous pyrolysis conditions studied was able to increase lignin maturation (i.e. cross-linking condensation of aromatic rings) as indicated by the almost perfect overlapping of the complex viscosity curves of the hydrochars during resolidification. This implies that pristine pine Kraft lignin cannot be converted into a coking coal-like material using the hydrous pyrolysis conditions studied herein.

3.3. Comparison of hydrochars from pristine lignin, torrefied lignin and their blend

A different approach focused on the modification of lignin through torrefaction prior to hydrous pyrolysis in order to improve its coking properties. Furthermore, the hydrous pyrolysis temperature, the residence time and the water content were increased to 350 °C, 6 hours and 30 ml respectively in order to produce a high carbon content material with no fluidity comparable to a semi-coke from coking coal. In this manner, hydrochars were produced from pristine pine Kraft lignin, lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min, and a 50:50 wt.%/wt.% blend of these pristine and torrefied lignins. Table 1 summarizes the results from proximate and ultimate analyses. A comparison of the results for the hydrochars with those for the pristine pine Kraft lignin indicates that hydrous pyrolysis lowers the ash content from 2.5 wt.% to 1.0 wt.%. The ash content in the hydrochar obtained from torrefied lignin (1.7 wt.%) is also lower than that in pine Kraft lignin but higher than the ash content in the hydrochar from pristine lignin, showing that torrefaction prevents the transfer of mineral matter to the aqueous phase during hydrous pyrolysis. The hydrochar from the 50:50 wt.%/wt.% blend has similar ash content to that in the hydrochar from torrefied lignin, suggesting that there could be synergistic effects between the pristine and torrefied lignin components during hydrous pyrolysis. All three hydrochars produce ash yields <2 wt.%, which are lower than that obtained with the good coking coal (10 wt.%) and could be beneficial for biocoke quality. However, it has to be noted that the alkalinity indexes of lignin and torrefied lignin are much higher than that of coking coal (Table 2). Unfortunately, metal contamination was observed during the characterization of the mineral matter in the hydrochars. Future work should focus on this task and also on the use of acid washing with the hydrochars in order to remove the catalytic alkali/alkaline earth metals and determine the extent of reactivity of the inherent char structure.

On the other hand, the volatile matter content of the hydrochar from torrefied lignin (25.8 wt.%) is similar to that of a medium rank coking coal whereas the volatile matter content of the hydrochar from lignin (31.2 wt.%) is similar to that of a low rank coking coal. The carbon content of all hydrochars is similar and comparable to that of the high rank coking coal (ca. 80 wt.%). Hydrous pyrolysis reduces the sulfur content in pristine lignin from 1.5 wt.% to <1.0 wt.% and the oxygen content from around 26 wt.% to 12 wt.%. However, the

oxygen contents in the three hydrochars (>11 wt.%) are much higher than that in the good coking coal (3.6 wt.%), which could result in a biocoke excessively reactive for blast furnace operation.

Table 5 presents the mean hydrochar yields obtained after carrying out several hydrous pyrolysis tests. As expected, the hydrochar yield increases by 24% after lignin torrefaction. The hydrochar yield from the 50:50 wt.%/wt.% blend (77%) is higher than that calculated from the individual components (73%), which is significant taking into account the standard deviation values obtained for the mean yields, and could be related to synergistic effects and/or mass diffusion limitations as the samples were hydrous pyrolysed in pellet form.

High-temperature rheometry testing of the hydrochar obtained from pristine pine Kraft lignin indicated that the material did not develop any fluid material (not shown). From these results and considering that pristine lignin develops more fluidity than torrefied lignin or the 50:50 wt.%/wt.% blend, it can be inferred that none of the hydrochars develop a fluid phase upon heating.

TGA/DTG profiles for the hydrochars and the high rank good coking coal are shown in Fig. 6. The three hydrochars present very similar patterns of volatile matter evolution but these are quite different from that of the good coking coal. The data presented in Table 6 indicate that the percentage of volatile matter evolving from the hydrochars at temperatures <400 °C is much higher than that evolving from the high rank coal. The opposite occurs between 400–500 °C with no significant changes in the percentage of volatile matter of the samples at temperatures between 500–700 °C. The hydrochars show three maxima in the rate of volatile matter evolution whereas the high rank coal only shows one maximum at 486 °C. Table 5 shows that the highest biocoke/coke yield as determined by thermogravimetric analysis is produced by the coal (77%), followed by the hydrochar from torrefied lignin (73%), the hydrochar from the blend (70%) and the hydrochar from pristine lignin (67%). Differing from hydrous pyrolysis tests results, the biocoke yield from the blend hydrochar can be calculated from the biocoke yields of the single hydrochars. This could be ascribed to the lack of diffusion limitations in thermogravimetric analysis due to testing of a small amount of sample (10−15 mg) in powder form.

The SPE/MAS solid-state ^{13}C NMR spectra of the hydrochars obtained from pristine lignin (HL) and torrefied lignin (HTL) are presented in Fig. 7. Two spinning sidebands (ssb) originate from the aromatic carbon positioned at 130 ppm and are positioned at equal distances of the aromatic peak (i.e. there is one spinning sideband positioned in the aliphatic region). The spectra show no significant differences in the aliphatic and aromatic carbon structures of the hydrochars. The DRIFTS spectra presented in Fig. 10 also suggest that there are not significant differences in the distribution of functional groups on the hydrochar surfaces. A comparison of the spectra from the hydrochars with that obtained from pristine lignin (Fig. 2) indicates that there are significant modifications in the lignin structure during hydrous pyrolysis. Similar results were observed by other authors with a dealkali lignin and the hydrochars obtained at 225–265 °C [26]. However, the DRIFTS spectrum from torrefied lignin in Fig. 2 is very similar to the spectra from the three hydrochars in Fig. 10.

3.4. Comparison of biocokes with coke

Carbonization tests were performed with the hydrochars obtained after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water from the pristine lignin, torrefied lignin and their

50:50 wt./wt. blend. Coal carbonization was also carried out to compare the results from the coke with those from the hydrochars. The biocoke obtained from the torrefied lignin hydrochar did not show agglomeration and disintegrated into a powder. Considering that the hydrochars from the pristine and torrefied lignins have similar chemical compositions, as indicated above, this behavior is not well understood and needs further investigation. The biocoke obtained from the torrefied lignin hydrochar was not tested any further.

Table 1 present the data from proximate and ultimate analyses for the biocokes derived from the hydrochars of pristine lignin (HL) and the 50:50 wt.%/wt.% blend (HB) and for the coke from coal as reference. Although the biocokes from lignin and the blend yield very low amounts of ash (1.2−2.5 wt.%) compared to the coke (16 wt.%), their oxygen contents are very high (ca. 1.5 wt.% cf. 0.1 wt.%).

The micro-strength results in Table 7 indicate that the biocokes possess very low cold mechanical strength compared to the coke. Indeed, the biocokes have values of R_1 below 1% compared to 17% for the coke. The biocoke obtained from the blend hydrochar has lower strength than the biocoke from the lignin hydrochar as denoted by the higher value of R_3 (74% cf. 69%). This finding was expected since the biocoke obtained from the torrefied lignin hydrochar did not agglomerate. Table 7 also shows that both biocokes possess very high reactivity (>45%) compared to the coke (10%) as determined by the ECE-INCAR method.

FE-SEM images of the hydrochar derived from pristine lignin, the biocokes from this hydrochar before and after the CO_2 reactivity test and the coke from coal indicate that there are significant textural differences between the lignin residues and coke (Fig. 11). Coke presents a well-defined porous structure with a wider range of pore sizes than the porous structure of the hydrochar or biocokes. Table 8 indicates that the microporous surface area of the biocoke obtained from the lignin hydrochar is much higher than the microporous surface area in the coke (414 m^2/g cf. 145 m^2/g). In addition, the total porosity of this biocoke is around 12% higher than that in the coke. This table also shows that the biocoke obtained from the blend hydrochar possesses higher porosity and microporous surface area than the biocoke obtained from the lignin hydrochar.

These results suggest that the poor mechanical strength and high reactivity of the biocokes could be ascribed to a combination of high porosity resulting in thin pore walls (i.e. brittle pore structures), high oxygen contents in the biocokes (ca. 1.5 wt.%) compared to the coke (0.1 wt.%) and high alkali and alkaline earth metals contents in the hydrochars. Therefore, hydrochars from Kraft lignin from pine wood cannot be used in their pristine and/or torrefied forms for the complete substitution of coking coals but still could potentially be added to coking blends if the cohesion with coking coals is acceptable. Pre-treatment of the pine Kraft lignin with inexpensive acids should be investigated in the future as a possible methodology to improve the coking properties of lignin hydrochars and resulting biocokes.

4. Conclusions

Pine Kraft lignin in pristine and torrefied forms and their 50:50 wt.%/wt.% blend have been used to obtain and characterize hydrochars through hydrous pyrolysis. These hydrochars have been used to produce biocokes after carbonization at 1050 °C. A high rank good coking coal and the coke obtained after carbonization have been used as reference materials to evaluate the properties of the hydrochars and biocokes, respectively. The highest fluidity in

the lignin hydrochar was achieved when hydrous pyrolysis was carried out at 280−300 °C for short periods of time (30 minutes) and using 20 ml of water. However, none of the conditions studied was able to increase the maturation of the hydrochar since resolidification occurred at the same temperature to that of the pristine lignin. These results indicate that lignin cannot be converted into a coking coal-like material through the hydrous pyrolysis conditions studied in this work.

Torrefaction causes significant changes in the chemical structure of lignin with the complete degradation of aliphatic C−C and C−O groups, polysaccharides, carbonyl and carboxylic acid structures, which are very similar to the modifications caused by lignin hydrous pyrolysis. However, the biocoke produced from the hydrous pyrolysed torrefied lignin did not agglomerate in contrast to the biocoke resulting from a 50 wt.%/50wt.% blend of pristine and torrefied lignins. This anomalous behavior is not well understood and requires further investigation.

The hydrochars obtained at 350 °C for 6 hours using 30 ml of water from pine Kraft lignin, torrefied lignin and the 50:50 wt.%/wt.% blend of pristine and torrefied lignins produce ash yields <2 wt.% that are lower than that obtained with the good coking coal (10 wt.%), which could be beneficial for biocoke quality. However, the reactivity of the resulting biocokes is excessively high compared to that of the good coking coal (>45% cf. 10%) and the micro-strength R_1 values of the biocokes are much lower than that of the coal (<1% cf. 17%). These results could be explained by the high total porosity of the biocokes (>39%) and their high microporous surface areas (>400 m^2/g) compared to those for the coal (27% and 145 m^2/g) and the high alkalinity indexes of pristine and torrefied lignins compared to that of coal (>27% cf. 0.6%).

These drawbacks need to be addressed in order to use pine Kraft lignin hydrochars for biocoke production and utilization in integrated steel plants. Therefore, further investigation would be required to determine whether the oxygen content and the amount of alkali/alkaline earth metals could be significantly reduced through economically viable Kraft lignin pre-treatments (e.g. acid washing) in order to increase the strength and lower the reactivity of the resulting lignin hydrochars and biocokes.

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Table 1. Proximate and ultimate analyses of pristine pine Kraft lignin (PKL), torrefied lignin at 300 °C for 1 hour using a heating rate of 3 °C/min (TL), hydrochars obtained at 350 °C for 6 hours using 30 ml of water from pristine lignin (HL), torrefied lignin (HTL) and their 50:50 wt.%/wt.% blend (HB), biocokes from the lignin and blend hydrochars, high rank good coking coal and coke. Weight percentages expressed on a dry basis (db).

	Ash (%, db)	VM (%, db)	C (%, db)	H (%, db)	N (%, db)	S (%, db)	O (%, db)
PKL	2.5	64.0	64.7	5.7	0.9	1.5	26.3
HL	1.0	31.2	82.0	4.6	1.1	0.8	11.5
Biocoke (HL)	1.2	1.1	96.7	0.6	1.5	0.5	1.4
TL	3.1	38.7	73.5	4.8	0.7	1.1	19.0
HTL	1.7	25.8	81.6	4.1	0.9	0.9	12.5
HB	1.7	28.8	82.5	4.5	0.9	0.9	11.2
Biocoke (HB)	2.5	1.7	94.7	0.4	1.2	0.8	1.6
Coal	10.1	22.9	79.5	4.5	1.9	0.5	3.6
Coke	15.9	0.5	81.7	0.4	1.6	0.5	0.1

Table 2. Mineral matter composition and alkalinity index of pristine pine Kraft lignin (PKL), lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (TL) and the high rank good coking coal.

	Fe_2O_3 (%, db)	CaO (%, db)	MgO (%, db)	K_2O (%, db)	Na_2O (%, db)	SiO_2 (%, db)	Al_2O_3 (%,db)	Alkalinity index (%)
PKL	0.3	1.0	1.0	4.7	38.5	3.0	1.2	27.1
TL	0.3	1.0	1.1	6.1	35.2	2.9	1.2	33.0
Coal	3.0	0.8	0.5	0.8	0.4	60.8	31.5	0.6

Table 3. Solid-state ^{13}C NMR chemical shift assignments for lignin.

Band (ppm)	Assignment
33	Aliphatic C−C groups
56	Methoxyl carbons
60	Aliphatic C−O carbons other than methoxyl
72	Polysaccharides
74	Aliphatic C−O carbons other than methoxyl
84	Aliphatic C−O carbons other than methoxyl
115	C-2, C-5 and C-6 carbons of guaiacyl units
135	C-substituted aromatic carbons C-1 or un-substituted aromatic carbons that are not ortho or para to O-substitution sites on aromatic rings
148	C-3 and C-4 carbons of guaiacyl units
180	Carbonyl and carboxylic acid structures

Table 4. Minimum complex viscosity and temperature of maximum fluidity for pristine pine Kraft lignin (PKL), lignin torrefied at different temperatures and using different heating rates (TL) and high rank good coking coal.

	PKL	TL (250 °C, 1 h, 3 °C/min)	TL (300 °C, 1 h, 3 °C/min)	TL (300 °C, 1 h, 20 °C/min)	Coal
η^*_{min} (°)	907	14700	79900	37600	14300
T_{mf} (°C)	218	257	328	321	462

Table 5. Mean hydrochar yields and their standard deviation values calculated from different hydrous pyrolysis tests and biocoke/coke yields obtained from the hydrochars and coal as determined by thermogravimetric analysis. Hydrochars were obtained at 350 °C for 6 hours using 30 ml of water from pristine lignin (HL), torrefied lignin (HTL) and their 50:50 wt.%/wt.% blend (HB).

	HL	HTL	HB	Coal
Hydrochar yield, mean (%)	60.7	84.3	77.4	–
Std. deviation	3.3	1.3	2.2	–
Number of hydrous pyrolysis tests	14	16	15	–
Biocoke/coke yield (%)	67	73	70	77

Table 6. TG/DTG analysis results for the hydrochars obtained at 350 °C for 6 hours using 30 ml of water from pristine lignin (HL), torrefied lignin (HTL) and their 50:50 wt.%/wt.% blend (HB) and for the high rank good coking coal.

	HL	HTL	HB	Coal
T_i (°C)	134	167	141	332
VM300 (%)	30.1	10.8	21.3	1.1
VM400 (%)	44.0	19.5	33.4	6.4
VM500 (%)	61.0	37.3	51.8	45.5
VM400−500 (%)	17.0	17.8	18.4	39.0
VM750 (%)	91.9	81.3	89.9	89.6
VM750−500 (%)	30.8	44.0	38.1	44.1
DTG_{max1}	0.585	0.209	0.413	–
T_{max1} (°C)	157	239	250	–
DTG_{max2}	0.612	0.718	0.71	–
T_{max2} (°C)	239	544	499	–
DTG_{max3}	0.670	0.288	0.205	1.560
T_{max3} (°C)	501	789	812	486
T_f (°C)	900	969	892	928

Table 7. Micro-strength indices and reactivity values measured with the ECE-INCAR method for the biocokes obtained from the lignin hydrochar (HL) and the 50:50 wt.%/wt.% blend hydrochar (HB) and for the coke obtained from the high rank good coking coal.

	Biocoke (HL)	Biocoke (HB)	Coke
R_1 (%)	0.4	0.8	16.9
R_2 (%)	30.6	25.2	44.1
R_3 (%)	69.0	74.0	39.0
Reactivity (%)	45.1	57.0	9.8

Table 8. Surface areas determined through CO_2 adsorption and textural parameters for the biocokes obtained from the lignin hydrochar (HL) and the 50:50 wt.%/wt.% blend hydrochar (HB) and for the coke obtained from the high rank coal.

	Biocoke (HL)	Biocoke (HB)	Coke
W_0 (cm^3/g)	0.135	0.204	0.046
E_0 (kJ/mol)	27.91	29.10	28.35
L (nm)	0.654	0.610	0.637
S_{mi} (m^2/g)	414	615	145
V_T (cm^3/g)	0.364	0.371	0.251
Macropore volume (%)	30.3	34.5	41.4
Mesopore volume (%)	7.2	4.3	2.8
Micropore volume (%)	62.6	61.2	55.8
ρ_{He} (cm^3/g)	1.781	1.919	1.473
ρ_{Hg} (cm^3/g)	1.081	1.120	1.075
Porosity (%)	39	42	27

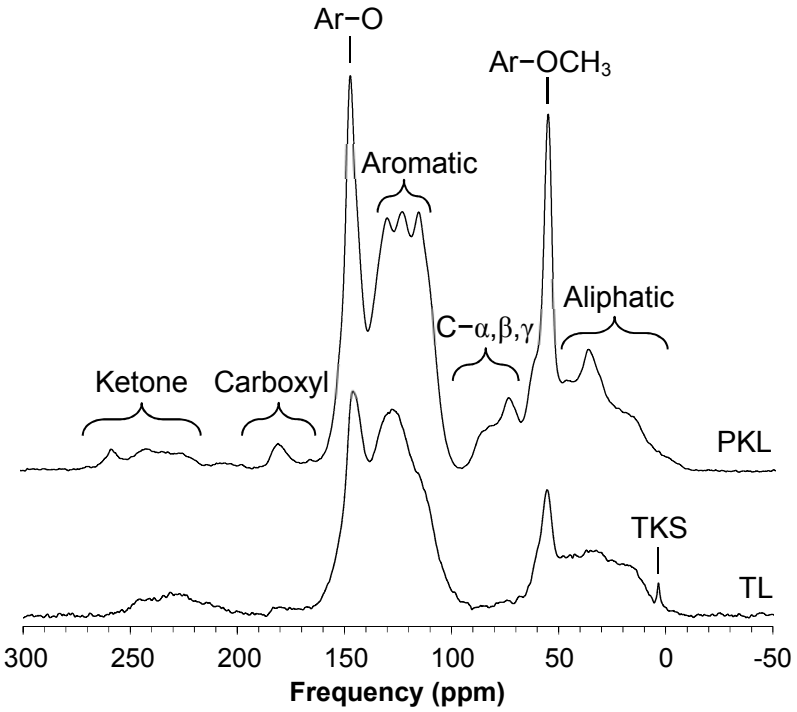

Fig. 1. Solid-state CP/MAS ^{13}C NMR spectra of pine Kraft lignin (PKL) and the lignin after torrefaction at 300 °C for 1 hour using a heating rate of 3 °C/min (TL). Peak assignments adapted from Sharma et al. [23].

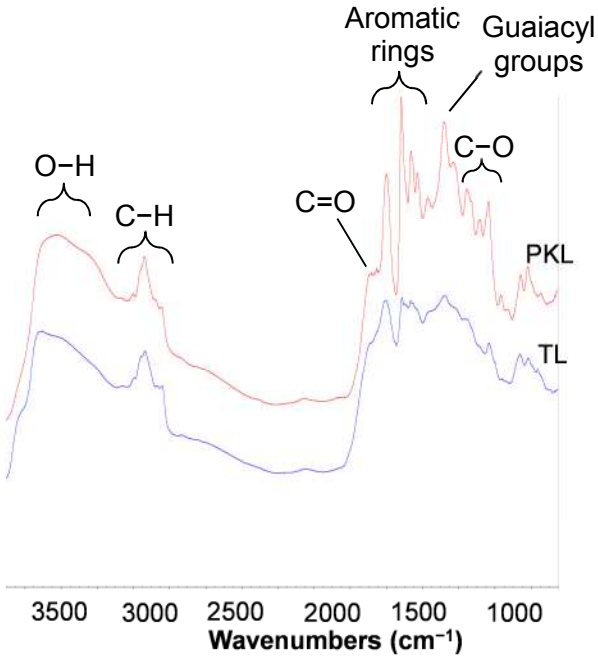

Fig. 2. DRIFTS spectra of the pristine lignin (PKL) and lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (TL). Peak assignments adapted from references [26,27].

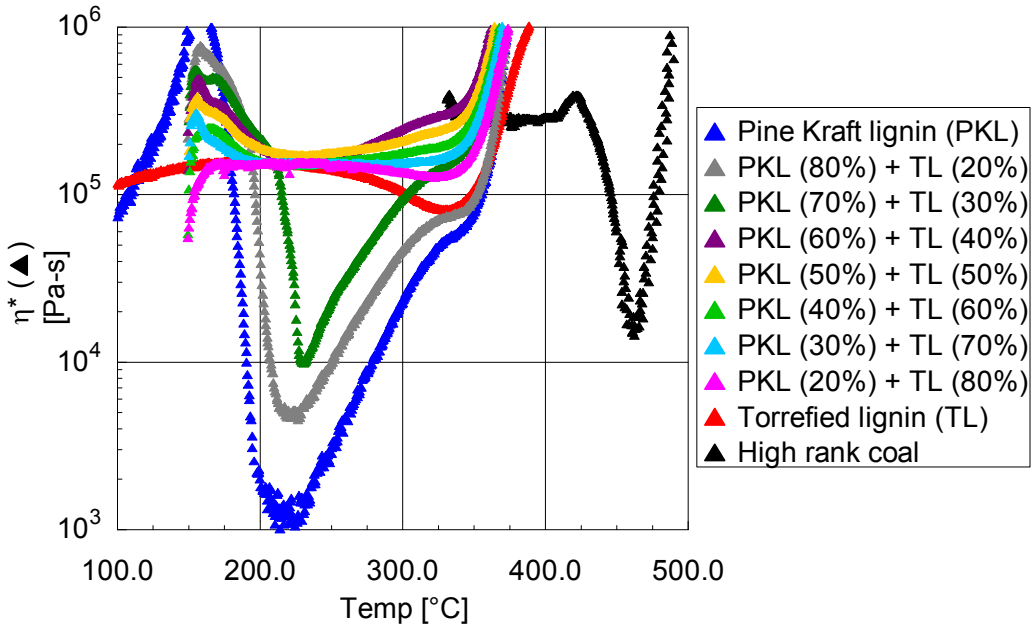

Fig. 3. Complex viscosity as a function of temperature for pristine pine Kraft lignin, lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min, their blends and the high rank good coking coal.

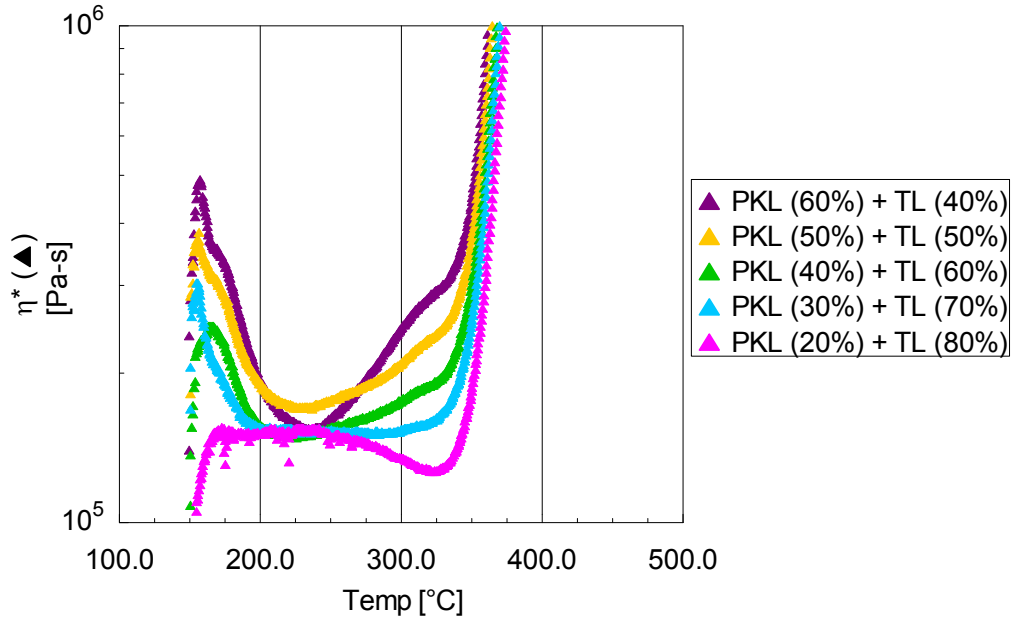

Fig. 4. Complex viscosity as a function of temperature for the blends of pine Kraft lignin (PKL) and lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (TL) containing between 20−60 wt.% of PKL.

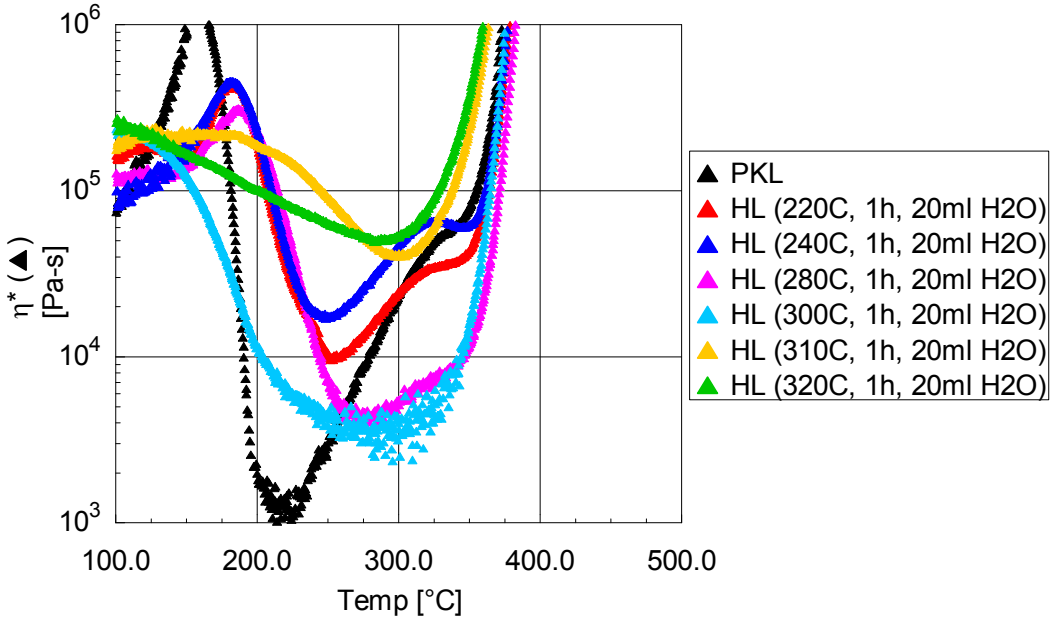

Fig. 5. Complex viscosity as a function of temperature for pine Kraft lignin (PKL) and the hydrochars obtained from lignin at different temperatures for 1 hour using 20 ml of water (HL).

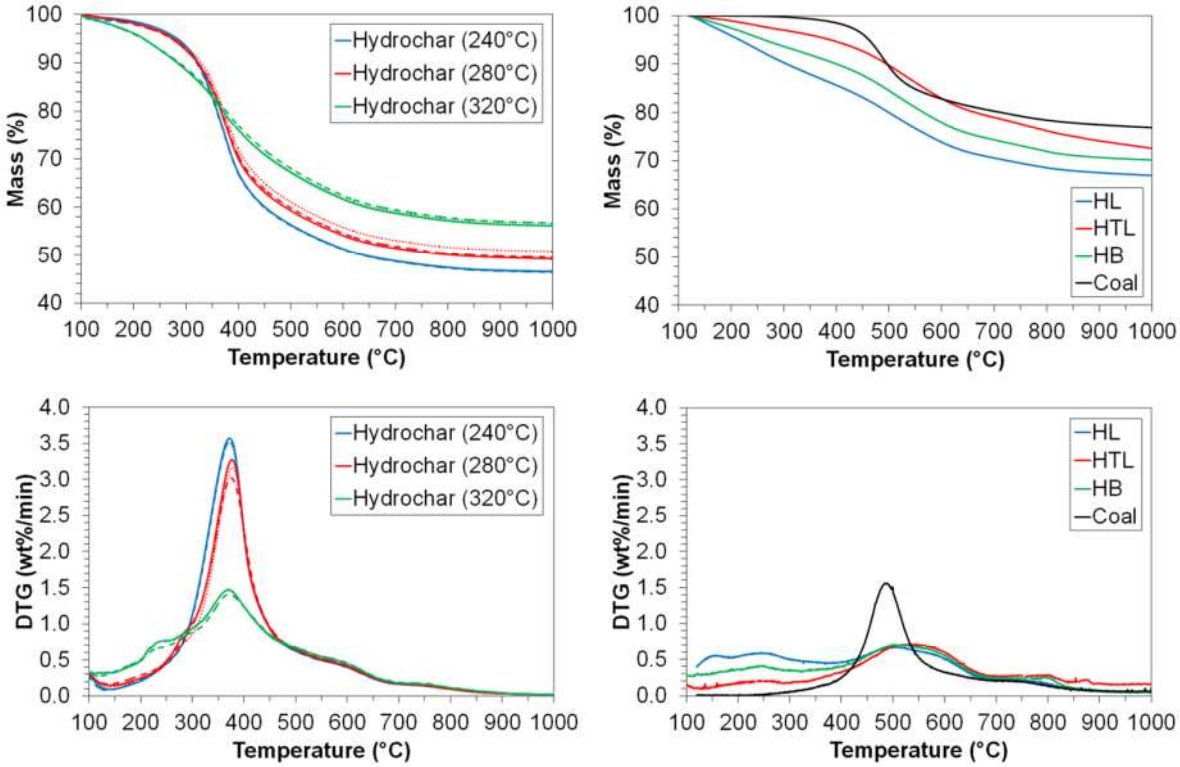

Fig. 6. TGA/DTG profiles as a function of temperature for the hydrochars obtained after hydrous pyrolysis of pine Kraft lignin at 240 °C, 280 °C and 320 °C for 1 hour using 20 ml of water (left) and for the high rank coking coal and the hydrochars obtained after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water of pristine lignin (HL), lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (HTL) and their 50:50 wt.%/wt.% blend (HB) (right).

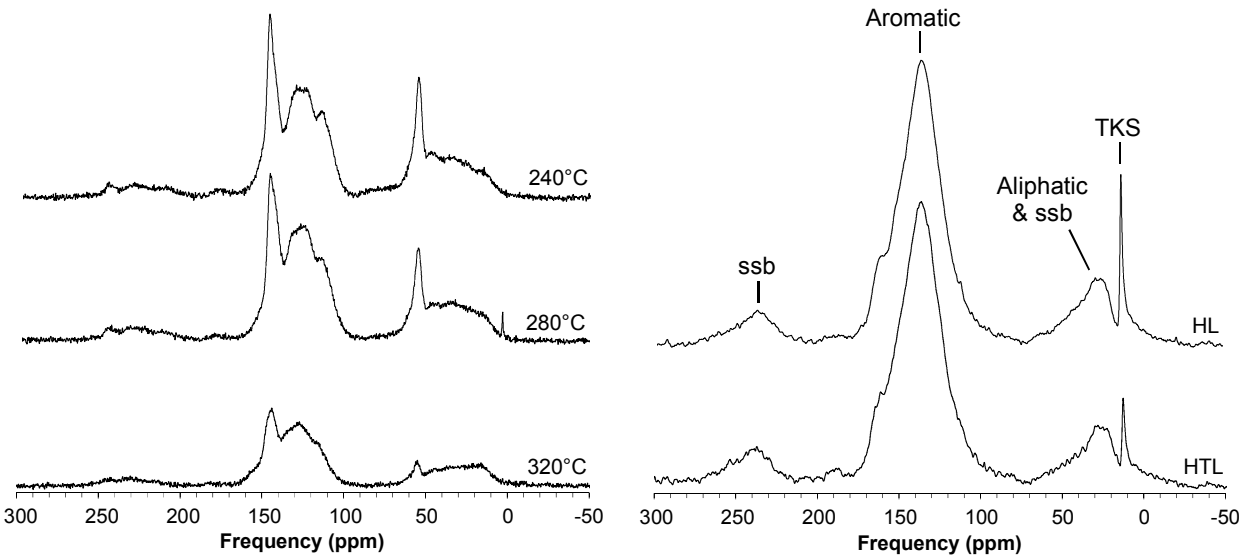

Fig. 7. Solid-state CP/MAS ^{13}C NMR spectra of the hydrochars obtained at 240 °C, 280 °C and 320 °C for 1 hour using 20 ml of water (left) and the hydrochars obtained after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water of pristine lignin (HL) and lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (HTL) (right). Spinning sidebands (ssb) originate from the aromatic carbon positioned at 130 ppm.

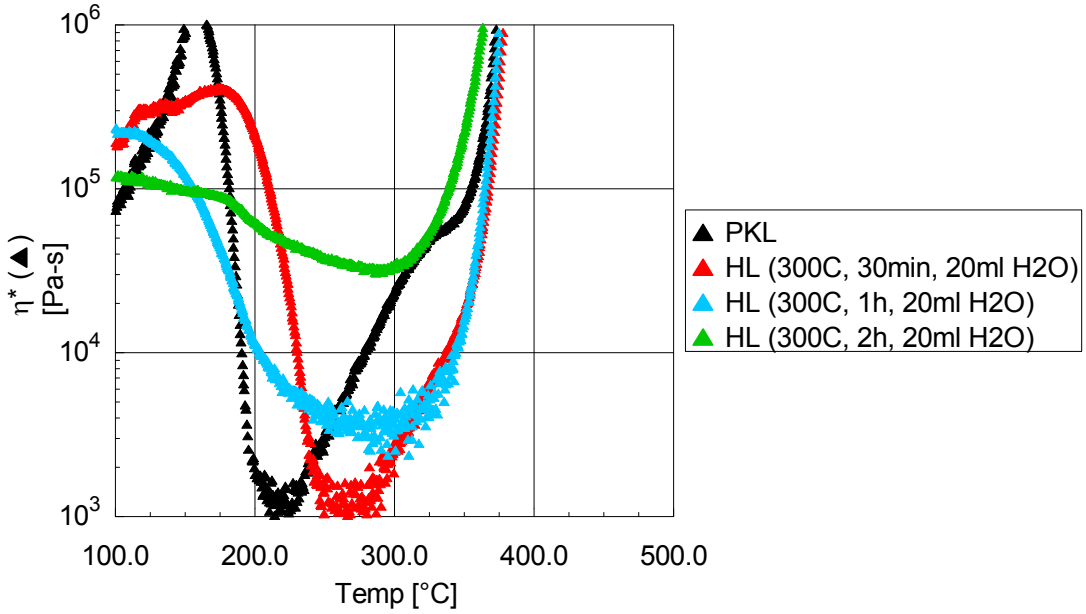

Fig. 8. Complex viscosity as a function of temperature for pine Kraft lignin (PKL) and the hydrochars obtained from lignin at 300 °C using 20 ml of water and different residence times (HL).

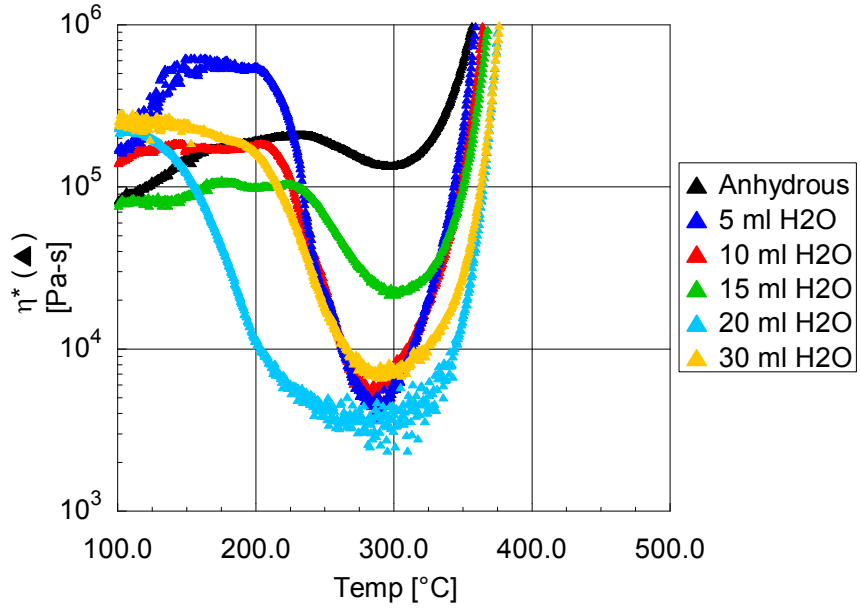

Fig. 9. Complex viscosity as a function of temperature for the hydrochars obtained from pine Kraft lignin at 300 °C for 1 hour using different amounts of water.

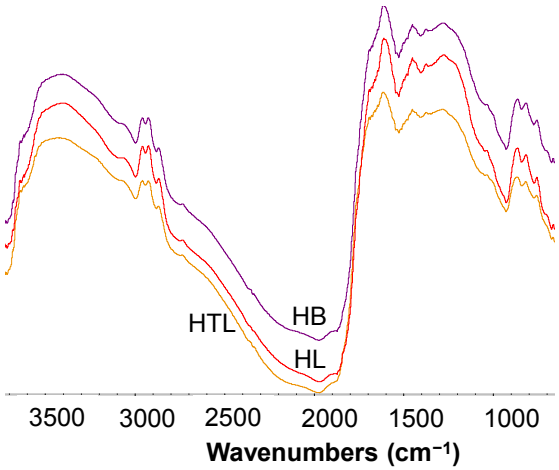

Fig. 10. DRIFTS spectra of the hydrochars obtained after hydrous pyrolysis at 350 °C for 6 hours using 30 ml of water of pristine lignin (HL), lignin torrefied at 300 °C for 1 hour using a heating rate of 3 °C/min (HTL) and their 50:50 wt.%/wt.% blend (HB).

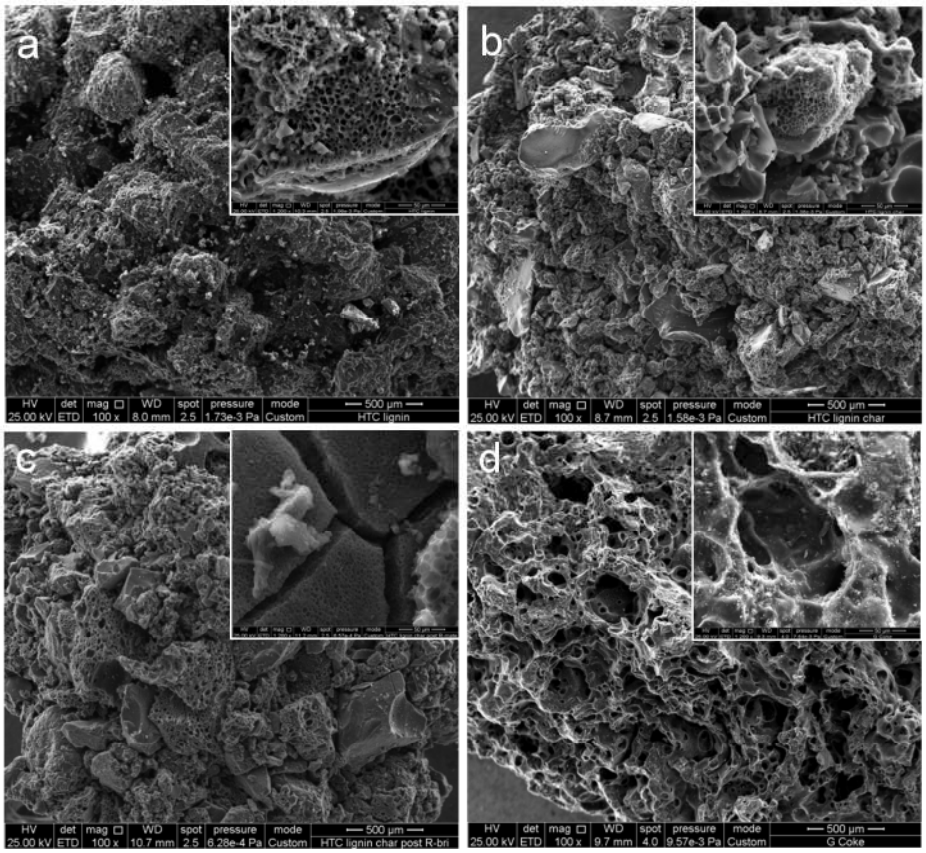

Fig. 11. FE-SEM images at magnification of ×100 of hydrous pyrolysed lignin at 350 °C for 6 hours using 30 ml of water (a), biocoke from hydrous pyrolysed lignin (b), biocoke from hydrous pyrolysed lignin and after CO_2 reactivity test (c) and coke from high rank good coking coal (d). Inner images taken with a magnification of ×1200.