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2 **Evaluation of demineralized lignin and lignin-phenolic resin blends to produce**
3 **biocoke suitable for blast furnace operation**

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13

14 **Abstract**

15 Metallurgical coke makers could reduce carbon emissions and material costs by
16 introducing waste lignin in coke oven charges. Two approaches have been studied here
17 to increase the use of lignin in the preparation of metallurgical coke: lignin
18 demineralization with H₂SO₄ and lignin blending with a low rank coal using phenolic
19 resin as binder. The biocoke obtained after carbonization at 1000 °C from the
20 hydrochar of demineralized lignin (350 °C, 6 h, biomass/water=0.5 wt/wt) had much
21 higher reactivity than the coke obtained from the low rank coking coal, proving that
22 demineralization of lignin prior hydrothermal conversion is not a valid route for biocoke

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23 making. In the other approach, it was found that blends containing 70 wt% low rank
24 coal, 24 wt% torrefied lignin (before or after demineralization) and 6 wt% phenolic
25 resin produced biocokes with suitable mechanical strength for handling but higher
26 reactivity than the coke obtained from the low rank coking coal alone. The microporous
27 surface areas of the biocokes studied did not correlate with their reactivity values.

28

29

30 *Keywords:* Kraft lignin, demineralization, torrefaction, phenolic resin, biocoke.

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33 **1. Introduction**

34 Scarcity of prime coals for metallurgical coke making and more stringent reduction
35 targets for carbon emissions are two main challenges facing the steel industry.
36 Consequently, coke makers and steel producers must seek ways of lowering CO₂
37 emissions and decrease production costs without seriously undermining process
38 efficiency. The use of readily available biomass materials offers the advantages of
39 reducing non-renewable carbon emissions and reducing material costs. However,
40 partial replacement of metallurgical, or coking, coals with biomass materials to produce
41 biocoke in industrial coke ovens is limited by the deleterious effects of biomass on
42 biocoke reactivity, mechanical strength and yield. For instance, the use of wood
43 charcoal in integrated steelworks is limited by: i) its negative impact on coke quality
44 when added to coking coal blends; ii) its low mechanical strength that cannot support
45 the iron ore burden in large blast furnaces; iii) its low abrasion resistance; and iv) its ash
46 chemistry that can accelerate its reactivity towards CO₂ in the blast furnace.
47 Subsequently, the highest amount of pristine or thermally treated biomass that can be
48 added to a coal blend while maintaining biocoke quality suitable for blast furnace
49 operation is 5 wt% [1]. Recently, Xing et al. [2] introduced 7.5 wt% charcoal in a coal
50 blend using coal tar pitch (2 wt%) as binder. These authors attributed the high
51 reactivity of the resultant biocoke to the combined effect of an increase in the interfacial
52 reaction area (i.e. higher surface area) due to the presence of charcoal and the promotion
53 of gasification reactions by the alkali and alkaline earth metals in charcoal. The higher
54 reactivity created voids and caused coalescence of pores in the biocoke, resulting in
55 lower mechanical strength. Therefore, production of biocoke with suitable mechanical
56 stability and reactivity for the blast furnace operation is still a challenging task.

57

58 Kraft lignin is a renewable polymer that is obtained as a by-product in the pulping
59 industry. In a recent work, Suopajarvi et al. [3] studied the effect of Kraft lignin
60 addition on coke compression strength and reactivity. Addition of Kraft lignin reduced
61 the biocoke mechanical strength (2.5 wt% addition lowered the strength by 26.3%) and
62 increased its reactivity compared to the reference coke. The reduction in mechanical
63 strength of the biocoke could be partly attributed to the evolution of volatiles from
64 lignin (>50 wt%) that may cause the shrinkage of the solid particles and lead to the
65 development of fissures, cracks and new pores.

66

67 The possible conversion of Kraft lignin into biocoke through hydrothermal
68 carbonization was investigated by our research group [4]. The hydrochars obtained at
69 350 °C for 6 h using 30 mL of water from pine Kraft lignin, torrefied lignin and a 50:50
70 wt/wt blend of pristine and torrefied lignins yielded less ash than a good coking coal
71 (i.e. <2 wt% cf. 10 wt%). However, the reactivity of the biocokes obtained after
72 carbonization was excessively high compared to that of the coke from the good coking
73 coal (>45% cf. 10%) and the mechanical strength of the biocokes was much lower than
74 that of the coke. The high total porosity of the biocokes (>39%) and their high
75 microporous surface areas (>400 m²/g) compared to those for the coke (27% and 145
76 m²/g) together with the high alkalinity indexes of pristine and torrefied lignins
77 compared to that of coal (>27% cf. 0.6%) were considered the main factors that dictated
78 the fast degradation of the biocokes under typical reaction conditions in the blast
79 furnace (>1000 °C, CO₂ atmosphere). Another factor that could lead to the low
80 mechanical strength of the biocoke in blast furnaces could be the smaller graphitization

81 degree of the carbonized hydrochar compared to coke, as it was suggested for
82 carbonized brown coal [5].

83

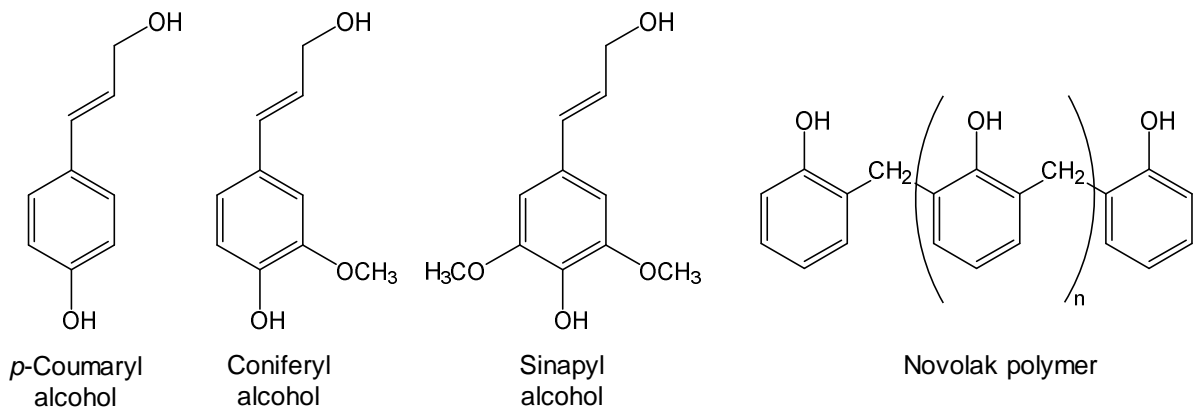
84 The mineral matter in biomass could be reduced through acid washing. De-ashing pre-
85 treatment of barks of white pine, white spruce and white birch decreased both
86 hydrothermal liquefaction conversion and bio-crude yields, leading to an increase in
87 hydrochar yield [6]. It could be argued that a similar demineralization methodology
88 could be used with lignin in order to increase the hydrochar yield after hydrothermal
89 conversion. The removal of alkaline and alkali earth metals after de-ashing would also
90 lower the reactivity of the resulting biocoke towards CO₂. In industrial coke plants,
91 lignin demineralization could be performed on-site using the sulfuric acid (H₂SO₄)
92 obtained after catalytic conversion of hydrogen sulfide (H₂S), which is recovered in the
93 coke oven gas (COG) treatment plant.

94

95 The primary monomers for lignification are *p*-coumaryl alcohol, coniferyl alcohol and
96 sinapyl alcohol. In the lignin polymer, *p*-coumaryl, coniferyl and sinapyl alcohols
97 produce respectively *p*-hydroxyphenyl, guaiacyl and syringyl units [7]. Lignin has a
98 polyphenolic structure that is very similar to that of phenolic resins (Fig. 1). Phenolic
99 resins are synthetic thermosetting polymers with excellent ablative properties and
100 structural integrity [8]. Phenolic resins are synthesized from phenol and formaldehyde
101 using an acid catalyst (novolak type) or a base catalyst (resole type) [9]. The cost of
102 commercial phenolic resins is in the order of \$900–\$1200/ton depending on resin
103 properties and applications [10]. In comparison, the cost of low-grade to high-grade
104 lignins varies from about \$60–\$1350/ton [11] and the cost of premium coking coal has

105 been in the range of \$200–\$250/ton in 2018. It has been suggested that lignin could be
106 used as a phenol substitute in phenol-formaldehyde resole resins [12], making the cost
107 of phenolic resins competitive if low-value lignins are employed. Indeed, about 50% of
108 Kraft lignin replaced phenol in the synthesis of phenol-formaldehyde resins without
109 substantially modifying the binding properties of the final product [13].

110



111

112 Fig. 1. Chemical structures of primary lignin monomers and novolak polymer [14,15].

113

114 The addition of air blown coal tar pitch and phenolic resins (50:50 wt/wt) as binder to
115 coke breeze and anthracite have produced briquettes with high tensile strength even at
116 950 °C [16,17]. Collin et al. [18] carried out co-carbonization of coal with pitches and
117 waste plastics, including a phenol formaldehyde resin, and it was found that the highest
118 yield of non-volatile compounds was obtained with the reactive pitch containing
119 phenolic resin. In another work, commercial novolak and resole phenol-formaldehyde
120 resins were blended with a coal-tar pitch in order to assess the behavior of the single
121 components and blends upon pyrolysis up to 1000 °C and their reactivity towards CO₂
122 [19]. These authors found that the burn-off in CO₂ at 1000 °C of the char from resole
123 resin was much higher than that of the char from novolak resin, despite the former

124 having higher coking value at 550 °C (51.9% cf. 40.8%) and higher carbon yield at
125 1000 °C (52.1% cf. 32.5%) than the latter. Therefore, the type of phenolic resin can
126 also influence the pyrolysis behavior of the coking blend.

127

128 The two main aims of this work are to elucidate whether biocoke can be produced from:

129 i) the hydrochar obtained after hydrothermal carbonization of demineralized lignin, and

130 ii) blends containing lignin, a low rank (high swelling) poor coking coal and novolak

131 phenolic resin as binding agent.

132

133 **2. Materials and methods**

134 2.1 Materials

135 A pine Kraft lignin (L) from the production of cellulose was used in this study. The
136 pine Kraft lignin (also referred to as pristine lignin hereafter) was obtained from Mead-
137 Westvaco (USA) and supplied as a dark brown powder (>99.5% lignin). A commercial
138 novolak phenolic resin patented by Tata Steel Limited and supplied as a yellow powder
139 was used as binding agent. A low rank, high swelling, poor coking bituminous coal
140 (coal A) was selected to prepare blends with lignin and phenolic resin. The ash and
141 volatile matter yields on a dry weight basis of coal A are respectively 9.6 wt% and 33.0
142 wt%. The coke from coal A was used as reference to evaluate the biocokes from
143 demineralized lignin and blends containing coal A, lignin and phenolic resin.

144

145 2.2 Demineralization and torrefaction

146 The pine Kraft lignin was demineralized in batches using a similar methodology to that
147 used by Fierro et al. [20]. For each batch, 2 L of deionized water was added to 100 g of

148 lignin, which led to a suspension of pH around 6.8. Afterwards, H₂SO₄ (Acros
149 Organics, 95% solution in water) was gradually added to the lignin suspension until the
150 pH decreased to 1.0. The precipitate was washed gently with deionized water until the
151 pH of the rinse remained constant and close to 6.0. The demineralized lignin (DL) was
152 removed from the suspension by filtration using a Büchner funnel and was dried
153 overnight at 105 °C.

154

155 Pristine and demineralized pine Kraft lignins were torrefied at 300 °C under N₂ for 1 h.
156 Torrefaction was carried out by pelletizing approximately 4 g of sample to produce
157 discs of 25 mm in diameter. Eight sample discs were placed inside a ceramic boat and
158 the boat was introduced in the quartz tube reactor of a horizontal tube furnace. A
159 heating rate of 3 °C/min was used from room temperature to the final temperature and a
160 constant N₂ flow of 100 mL/min was used throughout the test. The torrefied lignin (TL)
161 and torrefied demineralized lignin (TDL) were cooled down in N₂ and crushed to
162 particles < 1 mm to prepare the blends for carbonization tests.

163

164 2.3 Hydrothermal and standard carbonization tests

165 Hydrothermal carbonization (HTC) tests have been described in detail in our previous
166 work [4]. Briefly, the equipment comprised of a Parr 4740 series stainless steel 75 mL
167 cylindrical pressure vessel connected to a pressure gauge rated to 690 bar. Heat was
168 applied by means of a fluidized sand bath and the temperature was monitored by means
169 of a K-type thermocouple connected externally to a computer that recorded the
170 temperature every 10 s. Each experiment was conducted with 15 g of demineralized
171 lignin at 350 °C for 6 h using 30 mL of water (biomass/water=0.5 wt/wt). The reactor

172 was flushed with N₂ to remove the O₂ in the system. The gas generated and the liquid
173 product were discarded and the hydrochar from demineralized lignin (HDL) was
174 recovered and transferred to a vacuum oven where it was dried for 3–4 h at 40 °C.

175

176 Standard carbonization tests were carried out in a sole heated oven with the hydrochar
177 from demineralized lignin (HDL) and with blends containing the low rank coking coal
178 A, phenolic resin (PR) and either torrefied lignin (TL) or torrefied demineralized lignin
179 (TDL). For each test, a sample of 80 g with particles <1 mm was compacted in a
180 stainless steel crucible, which was covered with a perforated ceramic top to allow the
181 release of volatiles. The sole in the oven was pre-heated to 1050 °C, and then, the
182 stainless steel crucible configuration containing the sample was placed inside the oven.
183 The sample was heated from the sole at 1050 °C for 2 h. The tests were carried out in
184 inert atmosphere as the volatiles generated by the sample impeded the contact with air.

185

186 2.4 Proximate and ultimate analyses

187 Proximate analysis was carried out following the standard procedures ISO562 and ISO
188 1171 for humidity, ash and volatile matter determinations. For ultimate analysis, the
189 standard procedures ASTM D5016-98 and ASTM D5373-02 were used for the
190 determination of C, H, N and S using LECO CHN-2000 and LECO S-144DR
191 instruments.

192

193 2.5 Solid-state ¹³C nuclear magnetic resonance (NMR)

194 Cross polarization (CP) coupled with magic angle spinning (MAS) solid-state ¹³C NMR
195 analyses were performed in a Bruker Avance 200 spectrometer at a field strength of 4.7

196 T, which corresponds to resonance frequencies of 50 MHz for ^{13}C and 200 MHz for ^1H .
197 The samples were packed tightly into a zirconia rotor with a Kel-F rotor-cap and spun at
198 the magic angle ($54^\circ 44'$) with a spinning frequency of approximately 5 kHz. A contact
199 time of 1 millisecond was used during the Hartmann-Hahn condition. The acquisition
200 time was 1.5 s and the spectra were obtained after 2500 scans. The free induction decay
201 (FID) was processed using a line broadening factor of 50 Hz.

202 Tetrakis(trimethylsilyl)silane (TKS), which displays a single peak at 3.5 ppm, was used
203 as internal standard to calibrate the position of the sample peaks.

204

205 2.6 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

206 DRIFTS spectra were measured using a Nicolet Magna-IR560 spectrometer with a
207 diffuse reflectance accessory. A mercury-cadmium-telluride array (MCT-A) detector
208 that operates at sub-ambient temperature was used. The samples were dried overnight
209 before analysis and the data were collected in the range between $650\text{--}4000\text{ cm}^{-1}$ at a
210 resolution of 4 cm^{-1} . Semi-quantitative analyses were carried out using the integrated
211 area of the absorption bands to calculate selected indices.

212

213 2.7 Thermal gravimetric analysis (TGA/DTG)

214 TGA/DTG of the materials were carried out using a TA Instruments SDT Q600
215 thermoanalyser. 10–15 mg of sample with particle sizes $<0.212\text{ mm}$ were heated to
216 $1000\text{ }^\circ\text{C}$ at a rate of $3\text{ }^\circ\text{C}/\text{min}$ under a N_2 flow of $100\text{ mL}/\text{min}$. From the data obtained,
217 the volatile matter evolved up to a specific temperature (VMT) and in a specific
218 temperature range ($\text{VMT}_1\text{--T}_2$) and normalized to 100% were calculated. The
219 temperature at 5% conversion (T_i), the temperature at 95% conversion (T_f) and the

220 temperature of maximum volatile matter evolution (T_{max}) were also obtained from the
221 TGA/DTG curves.

222

223 2.8 Small amplitude oscillatory shear (SAOS) rheometry

224 High-temperature SAOS rheometry measurements were performed using a Rheometrics
225 RDA-III high-torque controlled-strain rheometer. The amount of material used for each
226 analysis was 1.5 g. The samples were compacted with a manual hydraulic press under 5
227 tons of force to form discs of 25 mm in diameter (i.e. around 100 MPa of pressure).

228 The tests involved placing the sample disc between two 25 mm parallel plates, which
229 had serrated surfaces to reduce slippage. Single samples and blends were heated from
230 50 °C to 500 °C at 3 °C/min. The furnace surrounding the sample was purged with a
231 constant flow of N₂ to transfer heat to the sample and remove the volatiles. The sample
232 temperature was monitored using a thermocouple inside the furnace. A continuous
233 sinusoidal varying strain with amplitude of 0.1% and frequency of 1 Hz (6.28 rad/s) was
234 applied to the sample from the bottom plate throughout the heating period. The stress
235 response on the top plate was measured to obtain the complex viscosity (η^*), which
236 measures the resistance to deformation and flow of the material. The complex viscosity
237 is calculated using Eq. (1), where G' is the storage or elastic modulus, G'' is the loss or
238 viscous modulus and ω is the frequency [21].

239

$$240 \quad \eta^*(Pa.s) = \frac{\sqrt{(G')^2 + (G'')^2}}{\omega} \quad (1)$$

241

242 2.9 Determination of micro-strength, reactivity and porosity of the biocokes

243 The micro-strength of the biocokes was determined with the method used by Ragan and
244 Marsh [22]. Briefly, two charges of biocoke (2 g, particle sizes 0.60–1.18 mm) were
245 placed into two separate cylinders of 25.4 mm internal diameter and 305 mm length and
246 sealed by steel dust caps. Each cylinder contained 12 steel ball-bearings of 8 mm in
247 diameter. The samples were subjected to 800 rotations at a speed of 25 rpm. Three
248 indices were derived after sieving: R_1 (>0.6 mm), R_2 (0.6–0.212 mm) and R_3 (<0.212
249 mm). The higher the value of R_2 and the lower the value of R_3 the higher the micro-
250 strength of the biocoke. At least duplicate tests were performed on each sample.

251

252 The reactivity was measured following the ECE-INCAR method [23], which briefly
253 consists of subjecting 7 g of biocoke of particle sizes between 1–3 mm to a CO₂ flow of
254 120 mL/min at 1000 °C. The reactivity is expressed as the mass loss in percentage
255 terms after 1 h of reaction.

256

257 Physical adsorption of CO₂ at 0 °C (273 K) was carried out in a Nova 4200e
258 Quantachrome Instruments to determine the microporous surface area of the biocokes.
259 Degassing was performed in vacuum for 24 h at 200 °C prior to adsorption. The
260 Dubinin-Radushkevich equation was applied to the CO₂ adsorption isotherms in order
261 to obtain the volume of micropores (W_0) and the characteristic adsorption energy (E_0).
262 Following Stoeckli's procedure [24], E_0 was used to calculate the average width of the
263 micropores (L), and then, W_0 and L were used to calculate the surface area of the
264 micropores (S_{mi}) by means of the following empirical equations:

265

$$266 \quad L \text{ (nm)} = \frac{10.8}{E_0 \text{ (kJ/mol)} - 11.4} \quad (2)$$

267

$$268 \quad S_{mi} (m^2/g) = \frac{2000 \times W_0 (cm^3/g)}{L (nm)} \quad (3)$$

269

270 **3. Results and discussion**

271 3.1 Characterization of single materials and blends

272 Fig. 2 presents the solid-state CP/MAS ^{13}C NMR spectra of pristine pine Kraft lignin
273 (L), pristine lignin demineralized with H_2SO_4 (DL), pristine lignin torrefied in nitrogen
274 at $300\text{ }^\circ\text{C}$ for 1 h (TL), demineralized lignin torrefied in nitrogen at $300\text{ }^\circ\text{C}$ for 1 h
275 (TDL), demineralized lignin after hydrothermal carbonization (HDL), phenolic resin
276 (PR) and the low rank coking coal (A).

277

278 Hagaman and Lee [25] observed that the main differences between the spectra of
279 pristine and demineralized lignins was a loss of the aliphatic signal area centered at
280 $87\text{--}70$ ppm and an equivalent gain in the area centered at $50\text{--}35$ ppm in the spectrum of
281 the demineralized lignin. The signal loss was attributed to the spectral region assigned
282 to alcohol functionality ($80\text{--}70$ ppm) and the corresponding gain occurs in the region of
283 highly substituted aliphatic carbon centers. However, the spectra in Fig. 2 do not show
284 significant differences in the peak intensities of pristine and demineralized lignins. The
285 large peak in pristine lignin at around 55 ppm corresponds to methoxyl carbons whereas
286 the large peak at around 147 ppm corresponds to aromatic carbons bonded to methoxy
287 groups [26]. Assuming that the heights of the peaks are directly proportional to their
288 areas, the ratio of aromatic carbons bonded to methoxy groups (Ar–O) to methoxyl
289 carbons ($-\text{OCH}_3$) is 1.3, which is similar to that of demineralized lignin (1.4) but lower
290 than those of both torrefied lignins (1.9).

291

292 Torrefaction causes significant changes in the chemical structure of pristine lignin. In
293 our previous work [4], it was found that torrefaction causes complete degradation of
294 aliphatic C–C and C–O groups, polysaccharides, carbonyl and carboxylic acid
295 structures, which were very similar to the modifications caused by hydrothermal
296 carbonization of lignin at 350 °C for 6 h using 30 mL of water. Torrefaction of
297 demineralized lignin greatly reduces the intensity of the peak at around 147 ppm, which
298 corresponds to aromatic carbons bonded to methoxy groups. This leads to a lower ratio
299 of these carbon groups relative to the aromatic C–C and C–H groups positioned at
300 around 130 ppm, which contrasts with the higher ratios in pristine, torrefied or
301 demineralized lignins. From these findings, it can be inferred that demineralization of
302 lignin facilitates the removal of methoxy groups attached to aromatic carbon during
303 torrefaction.

304

305 Hydrothermal carbonization of demineralized lignin (350 °C for 6 h using 30 mL of
306 water) completely destroys the methoxy groups in aliphatic structures (55 ppm) and
307 almost destroys all methoxy groups attached to aromatic carbons (147 ppm). The
308 spectrum for the hydrochar (HDL) resembles that of the low rank coal A, although the
309 coal possesses more aliphatic carbon that is evidenced by its lower aromaticity (0.71 cf.
310 0.85, Table 1).

311

312 The spectrum of phenolic resin (PR) is characterized by well-defined peaks and
313 spinning side bands originating from two different aromatic carbons. The peak seen in
314 the 40–30 ppm region originates from carbon in methylene bridges (–CH₂–). However,

315 this peak overlaps the spinning side band originating from aromatic carbon (C–C and
316 C–H) at 130 ppm. The peak at 130 ppm also produces another spinning side band at
317 around 230 ppm. The peak at around 152 ppm corresponds to phenol-ring carbon
318 bearing a hydroxyl group (Ar–OH) and the 122–113 ppm region displays unsubstituted
319 phenol rings (ortho and para) carbons [8,27]. The peak at 152 ppm generates two small
320 spinning side bands, one at around 250 ppm and the other at around 54 ppm. Unlike
321 pine Kraft lignin, the novolak phenolic resin does not show a peak at 55 ppm (i.e. no
322 methoxyl carbons).

323

324 The aromatic and aliphatic carbon peaks in all samples were integrated to calculate the
325 fraction of carbon that is aromatic (Table 1). PR has an aromaticity value of 0.91,
326 which is much higher than those of L, DL, TL and TDL (0.67–0.81). Table 1 also
327 shows that the oxygen content in these five samples varies in a similar manner. It was
328 found that there is an inverse linear correlation between aromaticity values and oxygen
329 content, with coefficient of determination $R^2=0.96$, when the data from DL is omitted.
330 The inclusion of the data from DL reduces the coefficient of determination because
331 demineralization only reduces the oxygen content by 0.4% but increases the aromaticity
332 of lignin from 0.67 to 0.72.

333

334 Fig. 3 shows the DRIFTS spectra of the same samples characterized through solid-state
335 ^{13}C NMR. A series of absorption bands can be appreciated in the spectra. The range
336 between 3700 cm^{-1} and 3100 cm^{-1} is associated to the hydroxyl stretching region.
337 Aromatic and aliphatic stretching C–H appears in the region $3100\text{--}2990\text{ cm}^{-1}$ and
338 $2990\text{--}2795\text{ cm}^{-1}$, respectively. C=O and C=C groups produce peaks in the range

339 between 1700 cm^{-1} and 1600 cm^{-1} . In addition, peaks at around 1600 cm^{-1} (1), 1510
340 cm^{-1} (2), 1465 cm^{-1} (3) and 1430 cm^{-1} (4) indicate the existence of aromatic rings and
341 C–H bonds. In the case of lignin samples, the presence of syringyl and guaiacyl groups
342 is evident from the bands at 1370 cm^{-1} (5), and 1270 cm^{-1} (6), respectively. C–O from
343 methoxy groups appears at $1120\text{--}1050\text{ cm}^{-1}$ (7–10). The $900\text{--}700\text{ cm}^{-1}$ range
344 corresponds to out-of-plane vibrations of aromatic C–H [28,29]. Three semi-
345 quantitative indices were calculated to evaluate the chemical changes observed in the
346 infrared spectra of different samples: (i) C=O/C=C index, based on the ratio of the
347 oxygen-containing structures to the aromatic carbon content; (ii) C=O/Hal, ratio of the
348 carbonyl region intensity compared to the aliphatic C–H stretch region intensity; and
349 (iii) H700-900/Hal, ratio of the C–H700-900 out-of-plane deformation compared to the
350 aliphatic C–H stretch region intensity [30].

351

352 Fierro et al. [20] found through Fourier transform infrared (FTIR) spectroscopy data
353 analysis that lignin demineralization decreases carbonates (1585 cm^{-1}) and hydroxyl
354 groups ($3600\text{--}3100\text{ cm}^{-1}$) and increases C=O groups (i.e. ketones, aldehydes and
355 carboxyl) not associated with aromatic rings (1729 cm^{-1}). The C=O/C=C index,
356 calculated for L and DL, is in accordance with this observation (0.83 cf. 1.52).

357

358 Previous work by our group [4] indicated that lignin torrefaction reduces the intensity of
359 peaks associated to aromatic rings, guaiacyl groups and methoxy groups ($1600\text{--}900$
360 cm^{-1}). Torrefaction of either pristine lignin or demineralized lignin produces similar
361 structural changes, as indicated by the almost identical spectra for TL and TDL. The
362 lower amount of aromatic carbons bonded to methoxy groups at 147 ppm in TDL

363 compared to TL evidenced by solid-state ^{13}C NMR in Fig. 2 could be related to the
364 reduction in C–O from methoxy groups at 1160 cm^{-1} in Fig. 3.

365

366 Hydrothermal carbonization of demineralized lignin reduces the amount of hydroxyl
367 groups, aliphatic C–H, $-\text{CH}_2-$ and $-\text{CH}_3$, and increases C=O, aromatic C=C and out-of-
368 plane aromatic C–H. These observations were confirmed by means of the C=O/Hal
369 index (0.85 for L and 1.46 for HDL) and the H700-900/Hal index (0.58 for L and 1.75
370 for HDL).

371

372 From a quantitative point of view and in comparison with all lignin samples, PR is
373 characterized by higher amounts of hydroxyl groups and out-of-plane aromatic C–H
374 and lower amounts of C=O and aliphatic C–H. Low rank coal A possesses less
375 hydroxyl groups, more aromatic and aliphatic C–H, less C=O and more out-of-plane
376 aromatic C–H than the lignin samples. Indeed, the C=O/Hal index of coal A is the
377 lowest (0.29) compared to those calculated for the lignin samples.

378

379 Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) results are
380 presented in Fig. 4. Lignin demineralization decreases the char yield through an
381 enhancement in lignin devolatilization, which is in agreement with previous findings
382 [20,26]. These authors attributed the increase in lignin devolatilization to the removal
383 of sodium and potassium. The derivative curves for TL and TDL overlap throughout
384 the temperature range studied, indicating that torrefaction leads to similar products
385 regardless of whether lignin is in pristine or demineralized form. This is in agreement
386 with DRIFTS results (Fig. 3). However, solid-state ^{13}C NMR results showed that TL

387 and TDL have different distributions of aromatic carbons bonded to methoxy groups
388 (Fig. 2). Therefore, it could be argued that these methoxy groups degrade into light
389 gases (CH_4 , CO_2 , CO) without causing a significant impact on the devolatilization
390 behavior of the torrefied lignins [31].

391

392 The temperature of maximum devolatilization increases in the order: L ($215\text{ }^\circ\text{C}$) < DL
393 ($358\text{ }^\circ\text{C}$) < TL ~ DTL ($407\text{ }^\circ\text{C}$) < coal A ($446\text{ }^\circ\text{C}$) < PR ~ HDL ($511\text{ }^\circ\text{C}$). TL yields
394 higher amount of char at $1000\text{ }^\circ\text{C}$ than PR (63% cf. 57% on a dry and ash free weight
395 basis, Table 1), despite the fact that TL has higher oxygen content (19 wt% cf. 11 wt%)
396 and lower aromaticity (0.79 cf. 0.91) than PR. Table 1 also shows that all lignin
397 samples and PR evolve more volatiles below $400\text{ }^\circ\text{C}$ than coal A. L and DL evolve the
398 highest proportion of volatiles (>65%) below $400\text{ }^\circ\text{C}$. Demineralization of lignin causes
399 a shift in the temperature at 5% conversion (T_i), temperature of maximum volatile
400 release (T_{max}) and temperature at 95% conversion (T_f) to higher values. This results in
401 a lower proportion of volatiles released by DL below $400\text{ }^\circ\text{C}$. As expected from the
402 TGA/DTG curves in Fig. 4, TL and TDL show identical temperatures at 5% and 95%
403 conversions and evolve almost identical amounts of volatiles in the three temperature
404 ranges studied. HDL and PR have similar temperature of maximum volatile release (ca.
405 $511\text{ }^\circ\text{C}$). However, HDL has the lowest temperature at 5% conversion ($175\text{ }^\circ\text{C}$), has the
406 highest temperature at 95% conversion ($845\text{ }^\circ\text{C}$) and produces the highest coke yield in
407 the whole series (69%). PR evolves most volatiles (45%) between $500\text{--}750\text{ }^\circ\text{C}$. In
408 contrast, coal A evolves the highest proportion of volatiles (57%) between $400\text{--}500\text{ }^\circ\text{C}$.
409

410 L, DL, TL and TDL were characterized through high-temperature rheometry to
411 elucidate their viscoelastic properties. Fig. 5 shows the variation in complex viscosity
412 (η^*) of the different lignins as a function of temperature. PR is not presented in this
413 figure because the complex viscosity dropped below the detection limit of the
414 instrument once the temperature reached 100 °C, which forced the instrument to abort
415 the test. L shows two minima in complex viscosity (η^*_{\min}), one at around 225 °C and
416 the other at around 350 °C. Demineralization of lignin does not affect the generation of
417 fluid entities at 225 °C but increases the fluidity at 350 °C, as indicated by the lower
418 minimum complex viscosity value for DL. Torrefaction destroys the fluid entities
419 regardless of whether lignin is in pristine form (TL) or demineralized form (TDL).
420

421 Blends of pristine or torrefied lignin with phenolic resin were also characterized through
422 high-temperature rheometry (Fig. 5). Blends of L and PR show that the viscoelastic
423 behavior of the blend is controlled by lignin. PR interacts with L above 200 °C and
424 causes an exponential reduction in maximum fluidity at 225 °C with coefficient of
425 determination $R^2 > 0.99$. A reduction in the maximum fluidity at 350 °C is also observed
426 but the exponential correlation has lower coefficient of determination ($R^2 = 0.92$).

427 Blends of TL and PR do not develop fluidity since the complex viscosity increases and
428 remains above 10^6 Pa.s above 150 °C, which is characteristic of predominantly solid-
429 like materials. Usually, the higher the amount of phenolic resin in the blend the higher
430 the complex viscosity values. At 300–550 °C, condensation reactions involving
431 methylene and hydroxyl functional groups dominate during phenolic resin pyrolysis,
432 which lead to carbon-hydrogen crosslinks [32]. These crosslinks will increase the
433 viscosity of PR, and thus, the viscosity of the blend with TL. It was observed that the

434 semichars obtained at the end of the rheometry tests with both blends (L-PR and TL-
435 PR) presented good cohesion when the concentration of L in the blend was ≤ 60 wt%
436 and the concentration of TL in the blend was ≤ 80 wt%. Since TL possesses higher
437 porosity than L, it is thought that the higher contact area between TL and PR particles
438 favors higher cohesion, allowing for higher amounts of TL in the blend than with L.
439 Therefore, more lignin can be included in blends with PR if lignin is in torrefied form
440 (up to 80 wt%). It has to be noted that semichars are intermediate products and this
441 work is mainly focusing on the final biocoke product. For this reason, no attempt was
442 made to determine the mechanical strength of the different semichars obtained.

443

444 3.2 Characterization of the hydrochar and biocoke from demineralized lignin

445 The composition and yield of the hydrochar obtained from demineralized lignin after
446 hydrothermal carbonization at 350 °C for 6 h using 30 mL of water (HDL) are presented
447 in Table 2. Data for the hydrochars from pristine lignin (HL) and torrefied lignin (HTL)
448 are also shown for comparison purposes. Our previous work [4] found that the biocoke
449 produced from HTL did not agglomerate, contrary to the behavior of biocokes produced
450 at 1050 °C from HL and a 50:50 wt/wt blend of HL and HTL. In the case of the
451 hydrochar obtained here from demineralized lignin, it was found that the biocoke
452 obtained showed agglomeration. Compared to HL, HDL yields lower ash (0.4 wt% cf.
453 1.0 wt%) and has lower nitrogen (0.6 wt% cf. 1.1 wt%) and oxygen (10.6 wt% cf. 11.5
454 wt%) contents. Moreover, the hydrochar yield from DL (57%) is lower than that from
455 L (61%). Ash promotes hydrochar formation and the reduction in ash yield from DL
456 might be responsible for the lower hydrochar yield. The biocoke yields obtained from
457 HL and HDL are fairly similar but lower than the biocoke yield obtained from HTL (ca.

458 68% cf. 73%). The overall biocoke yields from pristine, demineralized and torrefied
459 lignins, taking into account the yields from hydrothermal carbonization (HL, HDL and
460 HTL), are around 41%, 39% and 62%, respectively. Therefore, demineralization does
461 not have a significant impact on biocoke yield and will preserve biocoke agglomeration.

462

463 The micro-strength indices (R_1 , R_2 and R_3) and reactivity of the biocokes derived from
464 HL and HDL are presented in Table 3. The values for HTL are not presented because
465 its biocoke did not agglomerate. The value of R_1 (percentage of particles >0.6 mm) is
466 comparable in both biocokes but R_2 (percentage of particles between 0.6–0.212 mm) is
467 higher and R_3 (percentage of particles <0.212 mm) is lower in the biocoke from HDL.
468 These results indicate that the biocoke derived from HDL has higher mechanical
469 strength than the biocoke from HL. However, the mechanical strength of the biocoke
470 from HDL is lower than that of the coke from coal A, as indicated by the higher value
471 of R_3 (46.0% cf. 39.7%).

472

473 In addition, the reactivity of the biocoke derived from HDL is 20% lower than the
474 reactivity of the biocoke derived from HL. This contrasts with the higher microporous
475 surface area of the biocoke from HDL compared to that of the biocoke from HL (477
476 m^2/g cf. $414 \text{ m}^2/\text{g}$, Table 3). Still, the reactivity of the biocoke from HDL (25.5%) is
477 significantly high compared to the reactivity of the coke from coal A (11.2%).

478 Therefore, demineralization of lignin improves the reactivity of the biocoke but this
479 improvement is not enough for blast furnace utilization.

480

481 3.3 Characterization of biocokes from blends containing coal, lignin and phenolic resin

482 As previously mentioned, more lignin can be blended with phenolic resin if it is in
483 torrefied form (up to 80 wt%). Moreover, the char yield of torrefied lignin is higher
484 than that of pristine lignin (63% cf. 37%, Table 1). Therefore, torrefied lignin (TL) and
485 phenolic resin (PR) were combined with the low rank, high swelling, poor coking coal
486 (A) in order to formulate a blend that can perform like a good coking coal during
487 carbonization.

488

489 The use of the phenolic resin as a binder in the blend must be minimized due to its
490 elevated cost. Therefore, the ratio of torrefied lignin to phenolic resin should be kept at
491 4:1 wt/wt in order to achieve good cohesion of the semichar, as previously determined.
492 Lower amounts of phenolic resin (i.e. < 20 wt%) would lead to poor cohesion with
493 torrefied lignin and produce brittle semichars and biocokes.

494

495 In addition, the amount of coal A must be tailored to achieve a suitable level of fluidity
496 in the blend since phenolic resin and torrefied lignin will reduce the amount of fluid
497 material evolving from the coal. If the amount of coal A in the blend is too high, the
498 resulting high fluidity of the blend will lead to excessive porosity that will impact the
499 mechanical strength of the biocoke. If the amount of coal A in the blend is too low,
500 torrefied lignin and phenolic resin will completely destroy fluidity development in the
501 coal and the biocoke will not possess sufficient porosity to allow gas permeability inside
502 the blast furnace.

503

504 In order to determine the optimum composition of this ternary blend (coal, phenolic
505 resin and torrefied lignin), the viscoelastic and expansion/collapse behaviors of coal A

506 and two blends with different compositions were characterized through high-
507 temperature SAOS rheometry (Fig. 5). The results show that coal A develops a
508 minimum in complex viscosity of about 600 Pa.s at 430 °C. Simultaneously, the coal
509 mass undergoes expansion and significant collapse, which represent 6% and 92% of
510 initial disc thickness, respectively. The addition of PR and TL to coal A causes a
511 reduction in fluidity (i.e. increase in minimum complex viscosity) and also an increase
512 in the temperature of maximum fluidity to 440–445 °C. Indeed, the blend containing 75
513 wt% of coal A shows expansion and significant collapse (8% and 75% of initial disc
514 thickness, respectively) that resembles the behavior of coal A alone. The
515 expansion/collapse behavior is directly related to the high fluidity of this blend, as
516 indicated by its low η^*_{\min} value of 3×10^3 Pa.s (high fluidity coking coals develop η^*_{\min}
517 values around 10^3 Pa.s). The blend produced a highly porous and brittle semicoke at
518 500 °C, which was glued to the parallel plates of the rheometer. In contrast, the blend
519 containing 70 wt% of coal A develops fluidity at around 445 °C ($\eta^*_{\min}=10^5$ Pa.s), does
520 not expand and collapses slightly (only 15% of initial disc thickness). It was also found
521 that the semicoke obtained at 500 °C showed good cohesion and was easily removed
522 from the parallel plates of the rheometer, which are typical features of semicokes
523 derived from good coking coals. No attempt was made to determine the mechanical
524 strength of these semicokes since they are intermediate products. Based on these
525 results, the blend containing 70 wt% of coal A was chosen for a carbonization test at
526 1050 °C in the sole heated oven. The mechanical strength, reactivity and microporous
527 surface area of the resulting biocoke was determined and the results are presented in
528 Table 3. The fraction of fines (R_3) generated by the biocoke (27.2%) is lower than that
529 generated by the coke from the coal A (39.7%). Moreover, the value of R_2 is higher in

530 the biocoke than in the coke (70.2% cf. 50.0%). Therefore, these results indicate that
531 the biocoke has higher mechanical strength than the coke. However, the reactivity of
532 the biocoke (20.8%) is much higher than that of the coke (11.2%). Table 3 also shows
533 that replacement of torrefied lignin (TL) with torrefied demineralized lignin (TDL) does
534 not affect the mechanical strength of the biocoke but lowers its reactivity from 20.8% to
535 16.7% and increases the microporous surface area by 35 m²/g. These results indicate
536 that there is no evident relationship between the microporous surface area of the
537 biocoke and biocoke reactivity. The biocoke yield of the A/PR/TDL blend was
538 calculated using the coke yields in Table 1 for each component. The biocoke yield of
539 the blend (66%) is comparable to the coke yield of coal A (68%).

540

541 Arguably, the partial replacement of the coal A with a petroleum coke with low
542 reactivity [33] could further reduce the reactivity of the biocoke. Obviously, the
543 addition of this carbonaceous additive will impact fluidity development, and thus, the
544 combined percentage of TDL and PR must be reduced below 30 wt% to preserve the
545 fluid properties of the blend. Further research would be necessary to demonstrate
546 whether the addition of petroleum coke could reduce the reactivity of the blend to levels
547 suitable for blast furnace operation and to evaluate the economic viability of producing
548 such blends.

549

550 **4. Conclusions**

551 The biocoke obtained after carbonization at 1000 °C from the hydrochar of
552 demineralized lignin had much higher reactivity than the coke obtained from a low rank
553 coking coal (26% cf. 11%), proving that lignin demineralization cannot improve the

554 biocoke quality to levels that fulfil blast furnace requirements. In another approach,
555 blends of high swelling coal (70 wt%), torrefied lignin before or after demineralization
556 (24 wt%) and phenolic resin (6 wt%) produced biocokes with suitable mechanical
557 strength for handling but still showed excessive reactivity (>16%) compared to the coke
558 from the low rank coal (11%). No obvious relationship between biocoke reactivity and
559 its microporous surface area was found.

560

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566

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673 Table 1. Proximate analysis, ultimate analysis, aromaticity and parameters derived from
 674 thermogravimetric analysis of pine Kraft lignin (L), demineralized lignin (DL), torrefied
 675 lignin (TL), torrefied demineralized lignin (TDL), hydrochar from demineralized lignin
 676 (HDL), phenolic resin (PR) and low rank coking coal (A). Weight percentages are
 677 expressed either on a dry basis (db) or on a dry ash-free basis (daf).

678

Parameter	L	DL	TL	TDL	HDL	PR	A
Ash (wt%, db)	2.5	0.6 ^a	3.1	0.9	0.4	0.0 ^a	9.6
VM (wt%, db)	64.0	60.9 ^a	38.7	36.2	30.2	44.3 ^a	33.0
C (wt%, db)	64.7	66.6	73.5	76.2	83.2	78.5	78.5
H (wt%, db)	5.7	5.8	4.8	4.7	4.5	5.9	5.0
N (wt%, db)	0.9	0.5	0.7	0.6	0.6	4.6	1.6
S (wt%, db)	1.5	1.2	1.1	0.7	0.7	0.0	1.1
O ^b (wt%, db)	26.3	25.3	19.0	16.9	10.6	11.0	4.2
Aromaticity ^c	0.67	0.72	0.79	0.81	0.85	0.91	0.71
Ti (°C)	187	211	290	292	175	199	319
Tf (°C)	628	669	814	815	845	722	761
Tf–Ti (°C)	441	458	524	523	670	523	442
VM400 (%)	74.1	66.8	26.5	26.1	37.0	29.0	16.3
VM400–500 (%)	13.3	17.0	31.1	31.3	18.4	25.9	57.4
VM500–750 (%)	10.5	13.4	34.1	34.4	35.1	41.3	20.8
DTGmax (%/min)	0.89	1.08	0.43	0.43	0.21	0.66	0.85
Tmax (°C)	215	358	407	405	510	512	446
Coke yield (% , daf)	37.0	36.2	63.0	63.4	69.0	57.3	68.1

^a Thermogravimetric data.

^b By difference.

^c Error of ± 1 in absolute values.

680 Table 2. Proximate analysis, ultimate analysis, mean hydrochar yield and standard
 681 deviation values calculated from different hydrothermal carbonization tests, and biocoke
 682 yield of the hydrochars from pine Kraft lignin (HL), demineralized lignin (HDL) and
 683 torrefied lignin (HTL). Weight percentages are expressed on a dry basis (db).
 684

Parameter	HL	HDL	HTL
Ash (wt%, db)	1.0	0.4	1.7
VM (wt%, db)	31.2	30.2	25.8
C (wt%, db)	82.0	83.2	81.6
H (wt%, db)	4.6	4.5	4.1
N (wt%, db)	1.1	0.6	0.9
S (wt%, db)	0.8	0.7	0.9
O ^a (wt%, db)	11.5	10.6	12.5
Hydrochar yield, mean (%)	60.7	56.5	84.3
Standard deviation	3.3	1.4	1.3
Number of HTC tests	14	12	16
Biocoke yield (%)	67	69	73

685 ^a By difference.

686

687

688

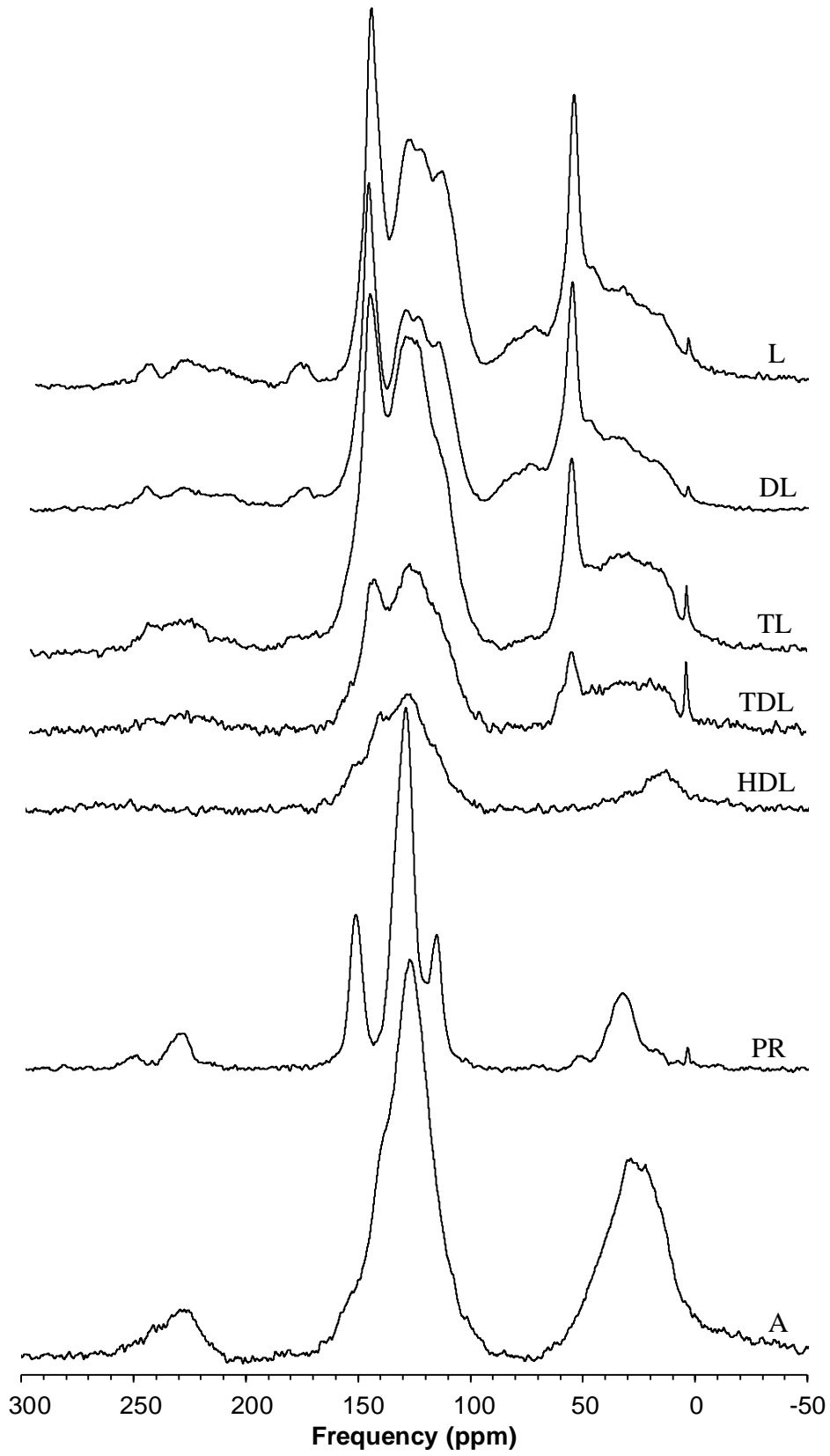
689 Table 3. Micro-strength indices, reactivity values and microporous surface areas of the
690 biocokes obtained from the hydrochars from pristine lignin (HL) and demineralized
691 lignin (HDL), two blends containing 70 wt% low rank coal (A), 24 wt% torrefied lignin
692 (TL) or torrefied demineralized lignin (TDL) and 6 wt% phenolic resin (PR) and the
693 coke from the low rank coking coal (A).

694

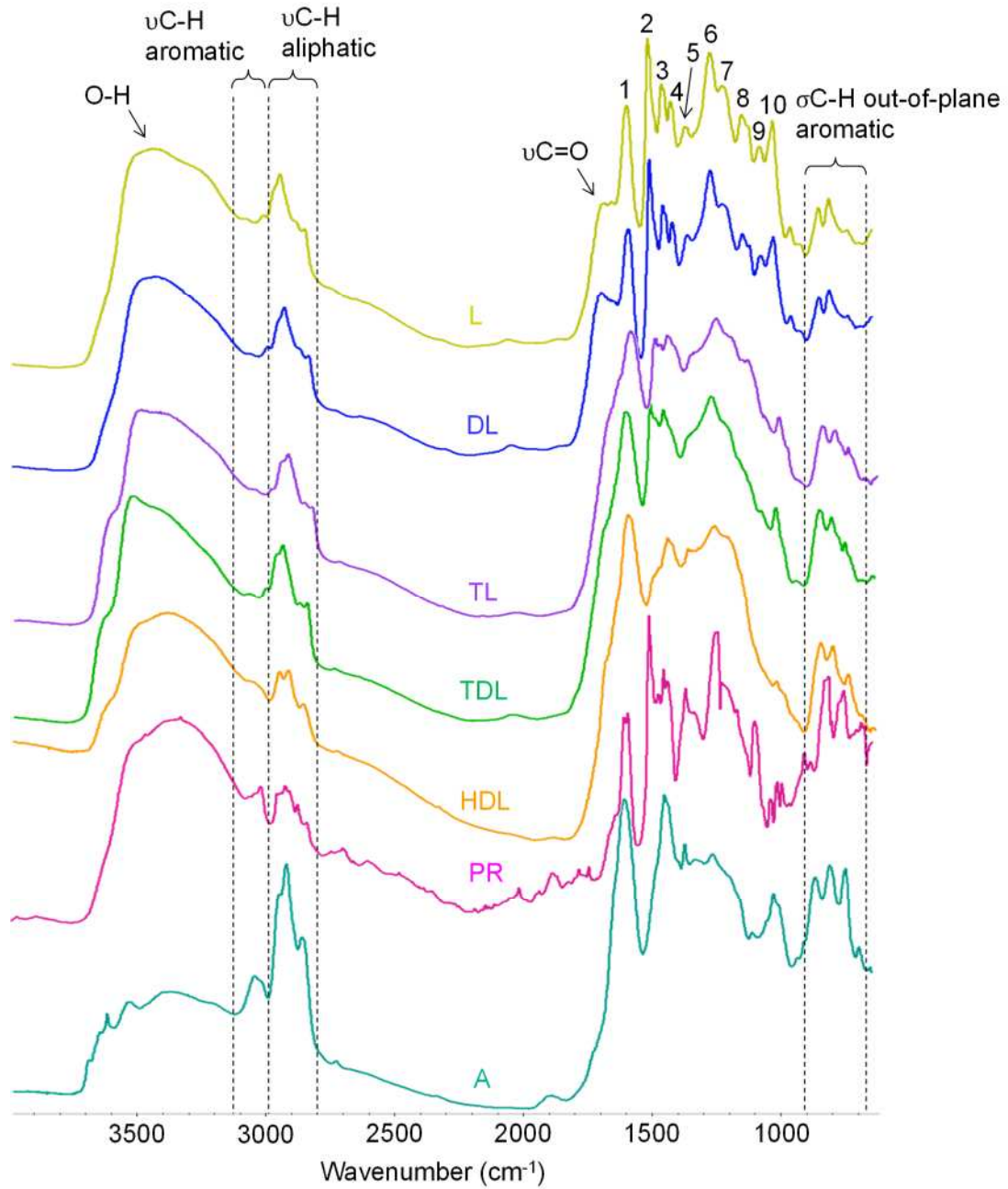
Parameter	Biocoke (HL)	Biocoke (HDL)	Biocoke (A/PR/TL)	Biocoke (A/PR/TDL)	Coke (A)
R ₁ (%)	0.4	0.3	2.6	3.3	10.4
R ₂ (%)	30.6	53.7	70.2	69.4	50.0
R ₃ (%)	69.0	46.0	27.2	27.3	39.7
Reactivity (%)	45.1	25.5	20.8	16.7	11.2
S _{mi} (m ² /g)	414	477	115	150	20

695 The standard deviation for the values of R₁, R₂, R₃ and reactivity are respectively 0.9,
696 2.8, 2.0 and 0.3.

697



699 Fig. 2. CP/MAS ^{13}C NMR spectra of pine Kraft lignin (L), demineralized lignin (DL),
700 torrefied lignin (TL), torrefied demineralized lignin (TDL), hydrochar from
701 demineralized lignin (HDL), phenolic resin (PR) and low rank coking coal (A). The
702 peak at 3.5 ppm corresponds to the internal standard tetrakis(trimethylsilyl)silane
703 (TKS).
704



706

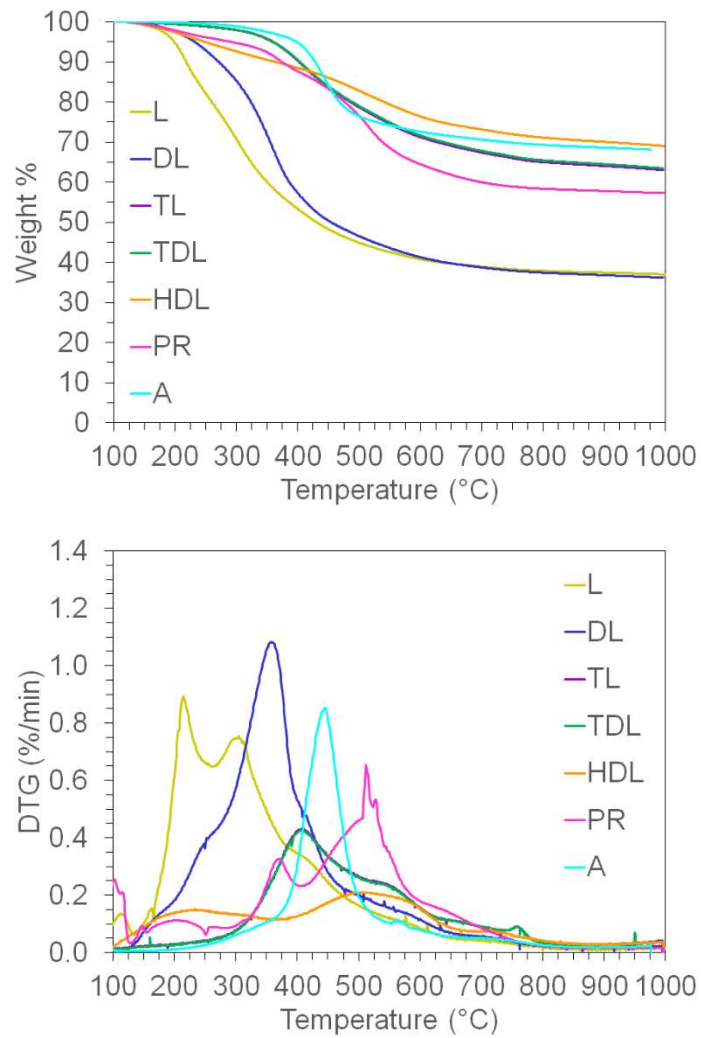
707 Fig. 3. DRIFTS spectra of pine Kraft lignin (L), demineralized lignin (DL), torrefied
 708 lignin (TL), torrefied demineralized lignin (TDL), hydrochar from demineralized lignin
 709 (HDL), phenolic resin (PR) and low rank coking coal (A).

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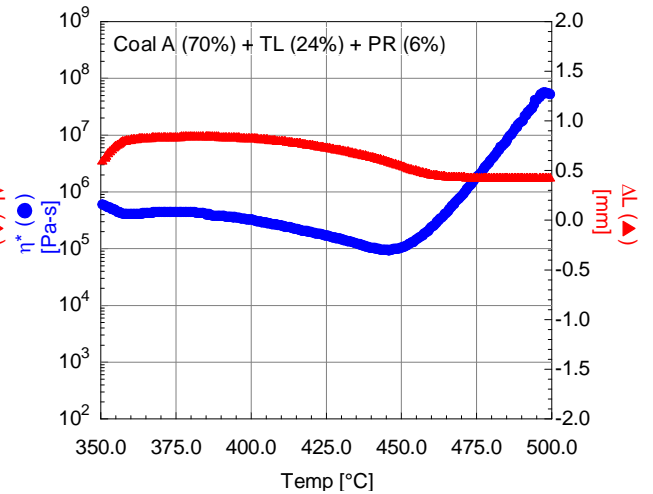
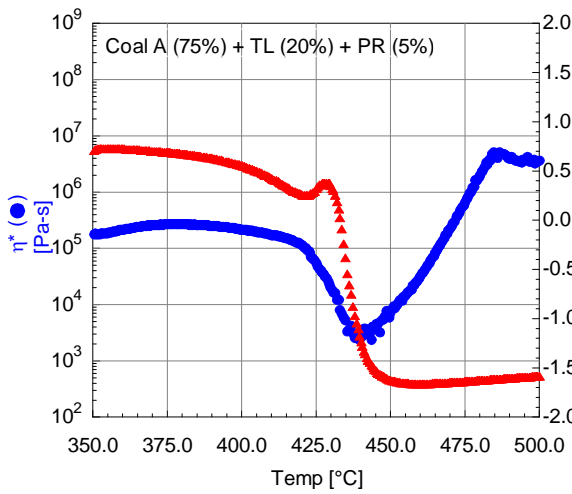
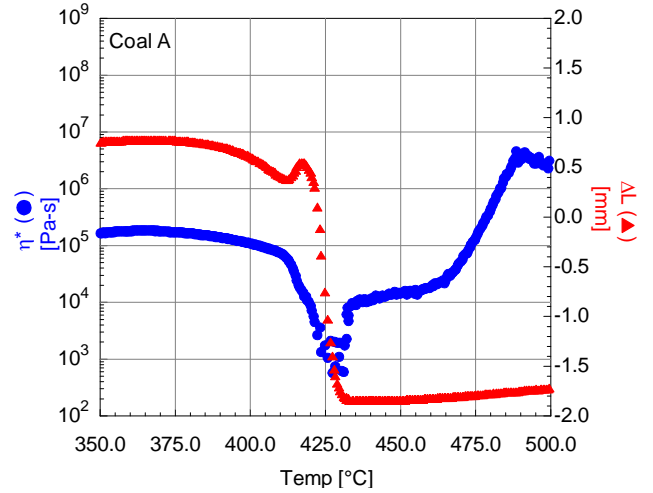
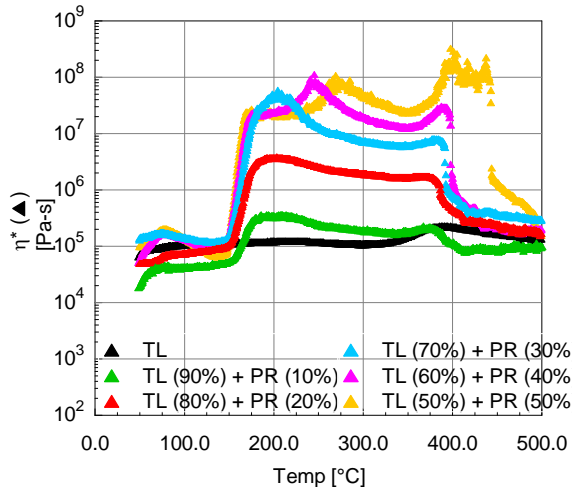
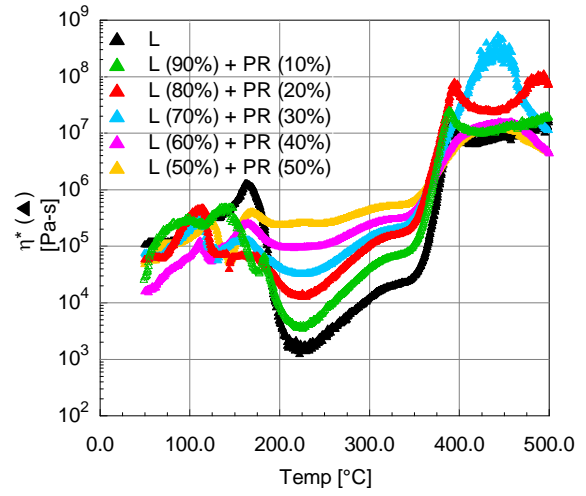
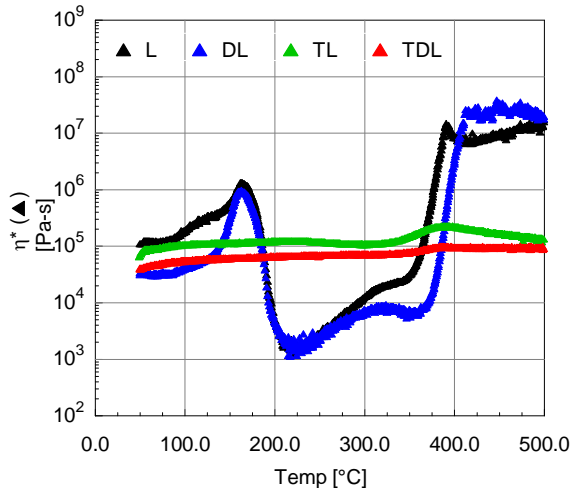


714

715 Fig. 4. Weight percentage and derivative of weight percentage as a function of
716 temperature for pine Kraft lignin (L), demineralized lignin (DL), torrefied lignin (TL),
717 torrefied demineralized lignin (TDL), hydrochar from demineralized lignin (HDL),
718 phenolic resin (PR) and low rank coking coal (A).

719

720



723 Fig. 5. Complex viscosity (η^*) as a function of temperature for pine Kraft lignin (L),
724 demineralized lignin (DL), torrefied lignin (TL), torrefied demineralized lignin (TDL)
725 and blends of pristine and torrefied lignins with phenolic resin (PR) of different weight
726 compositions, and complex viscosity (η^*) and plate gap (ΔL) as a function of
727 temperature for low rank coking coal A and two blends of coal A, TL and PR of
728 different weight compositions.