Importance of biomass and binder selection for coking briquette preparation. Their effect on coal thermoplastic properties.

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Abstract

Blends consisting of a high volatile bituminous coal, biomass and binder that were used in the preparation of briquettes were analyzed in order to select the best components from the viewpoint of their influence on the coal's thermoplastic properties. The raw materials were studied by means of thermogravimetry, high-temperature rheometry, high-temperature proton nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopy. In addition, the fluidity of the blends was determined with the standard Gieseler plastometer test method (ASTM D 2639-74). Various parameters derived from these different techniques were used to explain the effects of biomass and binder on the fluidity of the blends with coal. It was found that the deleterious effect of biomass was mainly related to its physical properties, whereas the effect of the binder was controlled by its chemical composition. Coal tar, coal tar sludge, pine sawdust and a bio-coal derived from hydrothermally treated waste biomass obtained from pruning were the best materials for the preparation of briquettes for cokemaking.

Keywords

Biomass, coal, binder, briquettes, fluidity.

1. Introduction

The use of additives has been common practice for many years in the cokemaking industry as a means to reduce costs, widen the range of raw materials that can be introduced into blends used for the preparation of metallurgical coke and recycle wastes produced in-situ and ex situ.[1–6]

In recent years, the use of biomass as an additive to coal blends, in order to produce metallurgical coke, has been envisaged as a possible solution for reducing the generation of non-renewable CO_2 emissions by the steel industry and for promoting the use of low-cost raw materials to replace expensive prime coking coals.[7–9] The direct addition of sawdust to industrial coal blends has been investigated but the resultant decrease in bulk density diminishes the quality of the coke.[7] It was also found that biomass produces a decrease in the fluidity of coal even at low addition levels of 0.75 wt%.

It has been proposed that the decrease in bulk density caused by the introduction of biomass in coal blends can be overcome with the use of briquettes. The quality of the coke produced from blends containing briquettes has been compared with the direct addition of un-briquetted components, with favorable results towards the use of briquettes.[10]

The use of coal tar as binder in the briquettes can compensate to some extent for the decrease in fluidity produced by the biomass. However, coal tar also leads to the formation of a large amount of polycyclic aromatic hydrocarbons (PAHs) during carbonization,[11] which are considered to be dangerous to human health by the US Environmental Protection Agency (EPA). Hence, in the present research work other

binders that are less pollutant, such as paraffin,[12] have been studied and compared with coal tar. Moreover, the thermoplastic properties of blends containing coal and biomass differ depending on the type of biomass used.[13] Therefore, four different biomass samples have been selected in this study in order to obtain a more comprehensive understanding of the mechanisms that control fluidity development in the blends.

Due to the importance of the coal plastic stage in the formation of the structure of coke, several conventional methods are currently used to measure coal thermoplasticity. Among these methods, the Gieseler[14] and Brabender[15] plastometers provide information about the softening, maximum fluidity and resolidification stages of coal. Novel techniques such as proton magnetic resonance thermal analysis (PMRTA)[16] and high-temperature ^{1}H NMR[17] have been used to measure the concentration and mobility of fluid hydrogen of carbonaceous materials during pyrolysis. High-temperature small-amplitude oscillatory-shear (SAOS) rheometry is another technique that can provide direct information about the viscoelastic properties of the bulk mass of coals in their thermoplastic temperature range.[18]

The aim of the present work is to determine the combination of biomass and binder that has the least deleterious effect on the thermoplastic properties of a low rank bituminous coal, and whenever possible, to correlate the results with the properties of the raw materials.

2. Materials and Methods

2.1. Materials

An American low rank bituminous coking coal with high volatile matter content (ca. 31.5 wt%) and high Gieseler maximum fluidity (ca. 26000 ddpm) was used to prepare binary and ternary blends using eight different additives, namely four biomass wastes and four binders. The biomass samples were a pine sawdust obtained as waste from the timber industry (SP), the pine sawdust torrefied in a rotary oven of 95 mm diameter at 300 °C for half an hour under a 250 ml/min N_2 flow (SPT), pine Kraft lignin from the production of cellulose (Lg), and a commercial bio-coal derived from hydrothermally-treated waste biomass obtained from pruning (BIOC). The binders used included molasses from the sugar industry (Mol), paraffin (Par), coal tar (T) and coal tar sludge (CTS). T, CTS and Mol are liquids and Par is solid at room temperature. The bituminous binders T and CTS were obtained as by-products in an industrial coke plant. T was separated from the raw coke oven gas in the by-products plant and CTS was collected at the sole of the tar decanter. CTS not only contains tar and water but also fine particles of coal and coke, which are drawn away and deposited at the bottom of the tar decanter. Mol and CTS can be considered as waste materials while Par and T are commercial products. All these materials were characterized through proximate and ultimate analysis. Proximate analysis was carried out following the standard ISO 562 and ISO 1171 procedures for humidity, ash and volatile matter, respectively. Ultimate analysis was performed using the standard method ASTM D 5373-02 for the determination of C, H and N using a LECO CHN-2000 instrument and the standard method ASTM D 5016-98 for the determination of S using a LECO S-144 DR instrument. The characteristics of the materials are presented in Table 1. The maceral composition of the bituminous coal is as follows: 77.9% vitrinite, 8.4% liptinite, 8.0% semifusinite, 2.0% fusinite and 3.7% inertinite.

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT 2960 thermobalance. Approximately 10 mg of sample with a particle size < 0.212 mm were heated under a N_2 flow of 100 ml/min from room temperature to 1000 °C at a rate of 3 °C/min.[19]

2.3. Fourier transform infrared

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-IR560 spectrometer equipped with a multi-bond ZnSe crystal attenuated total reflection (ATR) accessory and a DTGS detector. The spectra were collected over 128 scans at a resolution of 4 cm^{-1} in the 4000–500 cm^{-1} range. In order to facilitate comparison of the spectra, two semi-quantitative indices were defined (Table 2). The degree of aromaticity can be calculated by dividing the area of aromatic C–H groups (A_{ar}) by the sum of the areas of aromatic and aliphatic C–H groups ($A_{ar} + A_{al}$). However, some biomass samples did not present a visible peak for aromatic C–H groups (i.e. $A_{ar} \approx 0$). Thus, the area of aromatic C=C groups ($A_{C=C}$) divided by the area of aliphatic C–H groups (A_{al}) was used instead to determine the degree of aromaticity of the samples.

2.4. High-temperature ^{1}H nuclear magnetic resonance

A Doty 200 MHz ^{1}H nuclear magnetic resonance (NMR) probe was used in conjunction with a Bruker MSL300 instrument to determine the development of fluidity in the raw materials. A detailed description of this technique has been published elsewhere.[20] Approximately 140−150 mg of sample (63−212 μm) was loosely packed inside a boron nitride container, and 100 scans were accumulated using a recycle delay of 0.3 s. All samples were analyzed at a heating rate of 3 °C/min. Spectra were acquired from 25 °C to 400 °C for the biomass samples, from 25 °C to 500 °C for the binders and from 360 °C

to 500 °C for the coal. The spectra were deconvoluted into Gaussian and Lorentzian distribution functions. The area of the Lorentzian peak multiplied by 100 and divided by the total area of the NMR signal represents the concentration of fluid H in the sample, and the width of the Lorentzian peak at half height is inversely proportional to the mobility of the fluid H or spin-spin relaxation time (T2L).

2.5. High-temperature SAOS rheometry

High-temperature small-amplitude oscillatory shear (SAOS) measurements were performed using a Rheometrics RDA-III high-torque controlled-strain rheometer[21]. Approximately 1.5 g of sample with a particle size of 63−212 μm were compacted with a hydraulic press under a 5-ton force to form discs of 25 mm in diameter. The biomass and coal samples, as well as the 95:5 wt/wt blends of coal with biomass and coal with binder were analyzed. Also, blends of coal pre-heated in N_2 to 466 °C (C466) with binder in the same ratio (95:5 wt/wt) were tested in order to assess the degree of viscosity of the binder. The coal was pre-heated to reduce its volatile matter content, which causes scattering of the data, and to make clear the influence of the binder on the complex viscosity of the blend. The pre-heating of the coal was conducted following fast heating at 40 °C min^{-1} from room temperature to 520°C. In this process the coal temperature was monitored using a thermocouple inside the furnace, the final temperature detected for the sample was 466 ± 2 °C. During the experiments, the biomass samples were heated from 50 °C to 400 °C at 3 °C/min. The coking coal and the blends of coal with binders or biomass samples were heated from room temperature to 330 °C at around 85 °C/min and from 330 °C to 500 °C at 3 °C/min. The complex viscosity was calculated using Eq. (1), where G' is the storage or elastic modulus, G" is the loss or viscous modulus and ω is the frequency.[21]

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

2.6. Briquette preparation

In order to optimize the composition of the briquettes, various trial runs were carried out in a briquetting press under a constant pressure of 100 bar. The briquettes were cylindrical in shape with 40 mm in diameter. The coal content in the briquette was always 70 wt%. The amount of biomass was kept at 15 wt% except when molasses were used as binder, in which case 20 wt% was the quantity employed. The briquettes also contained 15 wt% of binder except in the case of briquettes containing molasses, for which 10 wt% was used. Different amounts of binder were tested in the preparation of the briquettes but the total percentage of biomass plus binder was kept constant in order to compare the individual effects of these components. None of the liquid binders drained during pressing. The nomenclature used was, for example, T-Lg for a briquette prepared with coal, lignin and coal tar as binder and T/CTS-BIOC for a briquette prepared with coal, BIOC and a 1:1 wt/wt blend of coal tar and coal tar sludge.

2.7. Gieseler fluidity of briquette mixtures

The thermoplastic properties of the mixtures that made up the briquettes were measured by means of the Gieseler test (ASTM D2639-74).[22–24] The samples (5 g), with a particle size < 0.425 mm, were heated at a rate of 3 °C/min up to a final temperature of 550 °C, while constantly applying a torque to the stirrer inside the crucible containing the sample. The parameters derived from this test were: (i) softening temperature, Ts; (ii) temperature of maximum fluidity, Tf; (iii) resolidification temperature, Tr; (iv) plastic range, Tr-Ts; and (v) maximum fluidity, MF, expressed as dial divisions per minute (ddpm).

175

176 ## 3. Results and Discussion

177 ### 3.1. Thermogravimetric analysis of raw materials

178 The TGA curves corresponding to the mass loss and the derivative of the mass loss curves
179 of the briquette components are shown in Figure 1. The plots are presented in wet basis. The
180 vertical dash line in the plots represents the temperature of maximum fluidity or minimum
181 viscosity of coal (435 °C), calculated as the average of Gieseler plastometry (440 °C) and
182 rheometry (430 °C) results. The curves for the variation of mass loss of the biomass with
183 temperature indicate that, at 435 °C, the highest char yield corresponds to Lg (55 wt%),
184 followed by BIOC and SPT (43 wt% and 40 wt%, respectively) and by SP (21 wt%), which
185 is in agreement with the carbon contents (Table 1). With regard to the binders, the highest
186 coke yield at 435 °C corresponds to T (38 wt%), followed by CTS and Mol (28 wt% and 24
187 wt%, respectively) and Par (0.2 wt%), with the latter almost volatilizing completely at 400
188 °C. The maximum devolatilization rate occurs at around 450 °C in the coal, 330 °C in SP,
189 SPT, BIOC and Lg, 300 °C in Par and 200 °C in Mol. T and CTS do not show a clear
190 maximum in the devolatilization rate.

191

192 ### 3.2. Infrared spectroscopy of raw materials

193 The chemical composition of the additives is important as it might influence coal fluidity.
194 Tsubouchi et al.[25] reported that the Gieseler maximum fluidity (MF) values tend to decrease
195 with the increase in the total amount of evolved oxygenated species during carbonization
196 (mainly CO, CO_2 and H_2O). These authors attributed the release of these species to the
197 presence of carboxyl and acid anhydride groups. On the other hand, another study on the
198 development of fluidity in biomass and coal blends[18] reported that the higher the carbonyl
199 groups and the lower the aromatic carbon in biomass, the lower the detrimental effect on

200 coal fluidity. Aromaticity has also been reported to be an important factor in the
201 enhancement of fluidity. Polycondensed aromatics can provide a pathway for the transfer
202 of hydrogen to radical sites in bituminous coals, and thereby, act as intermediates in the
203 transformation of coal to coke.[26,27] Sharma et al.[28] also emphasized the importance of the
204 C/H atomic ratio of the binder because it has a decisive effect on the strength of the briquettes
205 under differing thermo-chemical conditions of curing and carbonization. These authors
206 indicated that binders with C/H ratios above 1 are preferable for the production of briquettes.

207

208 Table 1 shows that Mol has the highest oxygen content (55.9 wt%), followed by SP (44.7
209 wt%). As expected, the heat-treated sample SPT has lower amounts of oxygen than SP (35.5
210 wt% cf. 44.7 wt%). The oxygen content in Lg (26.3 wt%) is comparable to that in BIOC
211 (25.5 wt%). T and CTS have lower oxygen contents than those in the biomass samples (3.0
212 wt% and 8.2 wt%, respectively). The oxygen content in paraffin is almost insignificant (0.3
213 wt%). Regarding the C/H ratio (Table 1), both bituminous binders have a ratio between
214 1.3−1.6, which is desirable (i.e. > 1). In the case of the other two binders the ratios are lower
215 (< 0.5), being the lowest C/H ratio that of Mol (0.3).

216

217 Figures 2 and 3 display the FTIR spectra of the biomass samples and the binders,
218 respectively. The FTIR spectrum of the bituminous coal is also presented in Figure 3 for
219 comparison purposes. Several bands can be observed in the ATR infrared spectra of the
220 biomass samples (Figure 2). The broad and intense peak around 3300 cm^{-1} is attributed to
221 the stretching of the O–H group due to inter and intramolecular hydrogen bonding of
222 cellulosic compounds, such as alcohols and phenols.[29] The range between 2990 cm^{-1} and
223 2765 cm^{-1} is assigned to the aliphatic stretching of C–H, the 1770−1650 cm^{-1} range

originates from C=O bonds and the 1600 cm^{-1} band is assigned to C=C stretching vibrations of the aromatic rings.[12] The absorption bands at around 1230 cm^{-1} and 1060 cm^{-1} correspond to C–O stretching, and at 1027 cm^{-1} there is a strong C–O bond attributed to the ether group of cellulose.[29,30] The spectra for SP and SPT are fairly similar. Mol, BIOC and Lg possess higher concentrations of C=O groups (1770−1650 cm^{-1}) and C=C bonds of aromatic rings (1600 cm^{-1}) than SP and SPT. Mol presents the highest content of O–H groups (3300 cm^{-1}).

Figure 3 shows the ATR infrared spectra of the low rank coal, paraffin, coal tar and coal tar sludge. The aromatic and aliphatic C–H stretching modes appear at 3100−2990 cm^{-1} and 2990−2765 cm^{-1}, respectively.[12] The C=O band appears between 1800−1633 cm^{-1} and C=C stretching modes appear between 1633−1538 cm^{-1}.[12] Flexions in methylene and methyl groups are observed at 1450 cm^{-1} and 1375 cm^{-1}, respectively. The 900−700 cm^{-1} range corresponds to the out-of-plane aromatic C–H vibration modes and reveals differences in the substitution patterns of the aromatic structures.[31] The strong peak in the spectrum of paraffin at 720 cm^{-1} has been ascribed to the in-plane rocking vibration of the $–CH_2$ group.[32] The spectra of T and CTS are fairly similar and very different to those of Par and the bituminous coal. Par is mainly constituted by aliphatic C–H groups whereas T and CTS mainly contain aromatic C–H groups.

Table 3 presents the semi-quantitative indices previously defined in Table 2. The $A_{OH}/A_{C=O}$ index, which gives information about the distribution of oxygen functionalities, decreases in the following order for the biomass samples: SP (23.82) >> Mol (13.40) >> BIOC (8.37) ≈ SPT (7.45) = Lg (7.45). Most of the oxygen species present in SP are O–H groups. Mol shows a large amount of both O–H and C=O groups, which is in agreement with the results from other authors.[30] The heat-treated biomass samples SPT and BIOC have lower

proportions of the O–H bond as indicated by the low $A_{OH}/A_{C=O}$ index values (< 9). This index was not calculated for the coal, due to the interference of mineral matter, or for the bituminous binders and Par, as the band due to O–H is not apparent in the spectra (Figure 3).

The $A_{C=C}/A_{al}$ index was calculated to determine semi-quantitatively the degree of aromaticity of the samples. Mol and BIOC are the most aromatic biomass samples (0.43 and 0.46), whereas SP has the lowest value (0.33). The highest aromaticity corresponds to T (0.74) and CTS (0.63). Coal has a lower $A_{C=C}/A_{al}$ ratio (0.35) than some biomass samples due to the large amount of aliphatic hydrogen in the coal used due to its rank.[33] This index was not calculated for paraffin because it does not show a band at 1600 cm^{-1}.

3.3. High-temperature ^{1}H NMR of raw materials

3.3.1. Changes in the concentration of fluid H

Figure 4 shows the development of fluid H as a function of temperature for the raw materials. Mol, T and CTS have not been included in the graph because they remain liquid (i.e. 100% fluid H) throughout the test. The fluid H profiles of BIOC, SP and SPT are very similar and show two maxima: one at around 100 °C, mainly due to the evaporation of water, and the other one at around 300 °C. The maximum percentages of fluid H and the temperatures of maximum fluid H for BIOC, SP and SPT are similar to those of miscanthus (i.e. 25% fluid H and 330 °C).[20] Lignin develops fluidity between 200−400 °C and reaches a maximum of 80% fluid H at around 300 °C. The fluid phase development of coal takes place at higher temperatures (375−500 °C), reaching a maximum of 90% fluid H at 460 °C, in agreement with results from the literature.[34] Paraffin becomes completely fluid at 75 °C, and remains fluid until it completely devolatilizes at around 400 °C.

3.3.2. Changes in the mobility of the fluid H

Figures 5a and 5b show the changes in the spin-spin relaxation time (T2L), or mobility of the fluid H, as a function of temperature for the raw materials. Similarly to the development of fluid H, SP, SPT and BIOC display similar mobility profiles (Figure 5a). These biomass samples have three maxima: the first one at around 75 °C; the second one depends on the biomass (SPT at 150 °C and SP and BIOC at 200 °C); and the third one at 325 °C. Lg only has two maxima, one at around 75 °C and the other at around 300 °C. These changes in mobility seem to be related to the evaporation of water (75 °C) and the decomposition of hemicellulose, cellulose and lignin constituents. A previous study[35] has shown that the T2L of cellulose reaches a maximum of 300 μs at 150 °C. The same authors found that xylan, which represents 90% of the hemicellulose, reaches the maximum T2L of 450 μs at a higher temperature than cellulose (around 175 °C cf. 150 °C) and that Lg maintains a T2L value of around 200 μs between 250−350 °C. In light of this, the maximum T2L at 150 °C of SPT could be related to the mobility of cellulose, whereas the wide T2L peak of SP at 200 °C could be due to the combination of cellulose and hemicellulose mobilities. The changes in mobility of the fluid H in the case of miscanthus[35] are similar to the results for SP reported in the present research work. The maximum T2L of 200 µs at around 300 °C could be associated with the aromatic structures in biomass (i.e. lignin).

The development of T2L for the low rank bituminous coal takes place between 400−500 °C, reaching a maximum of 150 μs at around 450 °C (Figure 5b). Among the binders, molasses develops the lowest maximum T2L (ca. 115 μs). Paraffin exhibits a maximum T2L of 276 μs at 75 °C, but also reaches mobilities of 220 μs between 300−400 °C. T presents a maximum T2L of 286 μs at 100 °C. The T2L profiles of T and CTS are very similar from

200 °C onwards, remaining constant at around 160 μs and 150 μs, respectively. Out of all these additives, only coal tar and coal tar sludge develop mobility of fluid H that is equal to or higher than the mobility of fluid H in the coal during its plastic stage (80−150 μs).

3.4. High-Temperature Rheometry

Figure 6a shows the variation in complex viscosity as a function of temperature for the biomass samples and the coal. SP and SPT display a small decrease in complex viscosity, which reaches a minimum of 1 $\times 10^6$ Pa.s at around 343 °C. The development of viscosity for sawdust and miscanthus follows a similar trend,[18] in line with the similarities previously mentioned for the fluid phase and mobility developments of these samples. The complex viscosity of lignin is very similar to the elastic and viscous moduli described in the literature.[20] Lignin shows a lower minimum in complex viscosity (1 $\times 10^4$ Pa.s) that the other biomass samples. In contrast, BIOC did not experience any decrease in viscosity during the thermal treatment, although it showed fluid H and T2L development. This finding suggests that the fluid H in BIOC is not able to alter the viscoelastic properties of the bulk material. Coal reached a minimum of 6 $\times 10^3$ Pa.s at 427 °C, in agreement with the results found for other coals with high volatile matter.[36]

The rheometry analyses of the high volatile coal and its blends with the additives (5 wt%) are shown in the Supplementary Material section (Figure SM1). Only a few noteworthy changes were observed. Biomass samples cause a slight shift of the softening and minimum viscosity temperatures of the coal to higher temperatures and the resolidification of the blend containing SP is the slowest in the series.

323 The coal was pre-heated to reduce data scattering and to clearly elucidate the influence of
324 the binders on the viscosity of the blends. Figure 6b shows the complex viscosity analysis
325 of blends made up of 5 wt% binder and 95 wt% pre-heated coal (C466). Under these
326 conditions, coal tar and coal tar sludge cause a remarkable decrease in the softening
327 temperature range and the minimum viscosity temperature (413 °C vs. 423 °C), in agreement
328 with data from the literature.[37] Par also causes a reduction in the softening temperature range
329 (360−385 °C) but additional heating does not entail any significant change compared to that
330 of the pre-heated coal up to the temperature of minimum viscosity (423 °C). Melendi et al.[38]
331 showed that polyolefins and hydrocarbon oil are weaker modifiers of coal's rheological
332 properties, which is in agreement with our results for Par. Finally, the softening and
333 minimum viscosity temperatures of the blend with molasses rise (435 °C vs. 423 °C). A
334 previous research work focusing on the effect of biomass (i.e. pine wood, sugar beet,
335 miscanthus) on fluidity development in coking blends did not show this effect for blends
336 with a coal of moderate VM content (25.2 wt% daf) and a Gieseler fluidity of 817 ddpm.[18]
337 However, similar results were obtained by these authors through rheometry analysis of a
338 high volatile bituminous coal (31.9 wt% db) mixed with miscanthus. This effect has also
339 been reported during the analyses of blends of a bituminous coal (VM, 25.2 wt% db) with
340 charcoal, wood and other additives.[34] The addition of coal tar sludge or paraffin causes a
341 decrease in the resolidification temperature. On the contrary, the resolidification stage takes
342 place at a higher temperature when molasses are added. The values of the minimum complex
343 viscosity for C466 and its blends is about 1.5×10^4 Pa.s, except with molasses, which is less
344 viscous (3×10^4 Pa.s).
345
346 **3.5. Thermoplastic properties of ternary blends constituting the briquettes**

347 The results of the Gieseler fluidity tests in this work are shown in Table 4 and Figure 7. The
348 high volatile, high fluidity bituminous coal (26000 ddpm) was chosen in this work to prepare
349 the briquettes taking into consideration the deleterious effect of biomass on the plastic
350 properties of coal. It is envisaged that the resultant briquettes should be capable of
351 developing suitable levels of fluidity.[8,18,39] The importance of this feature cannot be
352 underestimated since the lack of fluidity can affect the integration of briquettes into the coke
353 matrix, which would increase the possibility of fissures, affecting the quality of the final
354 coke product.[40] The components of a coal blend soften independently and, as a consequence,
355 the plastic range of a blend may be wider than that of the base coal. It is also necessary to
356 bear in mind that the properties of the softened mass may be influenced by interactions
357 between the softened and inert components of the blend.[37] In the present research work, the
358 blends used were complex and made up of products that, when individually added to the
359 coal, can have opposite effects. In summary, biomass has been found to decrease fluidity
360 and move the plastic stage to higher temperatures, T and CTS produce a decrease in the
361 softening range of the coal, and Par has very little effect on coal fluidity.
362
363 The softening, maximum fluidity and resolidification temperatures of the ternary blends
364 are displayed in Table 4. No systematic trend can be observed for the softening
365 temperature of the blends containing T and CTS compared with blends containing Par.
366 On the other hand, blends with Mol show the highest softening temperatures. However,
367 examination of the temperature of maximum fluidity (Tf) and the Gieseler curves in
368 Figure 7 shows lower Tf values for blends with aromatic binders than with Par. In fact,
369 the maximum fluidity temperatures of blends containing Par and Mol are very close to
370 each other. Mol also produces resolidification at the lowest temperatures. As a result, their
371 blends have the narrowest plastic range, which is defined by the difference between the

372 resolidification and softening temperatures (Tr-Ts). This finding is in agreement with the
373 rheometry results (Figure 6b). The Gieseler plastometer results in Table 4 also indicate
374 that the Tr of coal is always equal to or higher than the Tr of the blends.
375
376 For the same binder, the following order of increasing deleterious effect of the biomass
377 upon the thermoplastic properties of the coal has been established:
378
379 $$SP < BIOC < SPT < Lg$$
380
381 Although there are some exceptions, SP and BIOC develop similar MF with T/CTS as
382 binder, as in the case of SPT and BIOC with blends containing Par. A previous research
383 work established that torrefied sawdust produced a slightly greater reduction in Gieseler
384 maximum fluidity than sawdust that had not been heat-treated.[8] It would appear that this
385 result is related to the char yield of the biomass, as shown in Figure 8a. BIOC is an
386 exception to this correlation because it produces only a small deleterious effect in blends
387 with bituminous binders. For this reason, these blends have not been taken into account
388 when calculating the correlation coefficients.
389 There is some debate as to the influence of the oxygen content on fluidity. Previous
390 studies by Tsubouchi et al.[25] have shown that oxygen species can have a deleterious
391 effect. Whereas, other authors have shown using ^{13}C NMR that, the aromatic carbon in the
392 biomass could have a detrimental effect and/or the carboxyl groups from hemicellulose
393 could have a beneficial effect on coal fluidity[18]. Our results show that an increase in oxygen
394 species is accompanied by smaller loss in MF (Figure 8b). However, there is also an inverse
395 linear relationship between the coke yield and the oxygen content of biomass ($R^2 = 0.82$).
396 The oxygen species are highly reactive compounds that reduce the char yield from biomass.

As a result, the contact area between the evolving char and the fluid material of coal decreases and the impairment in coal fluidity is reduced by reducing the amount of biomass char, which might act as a sink for the fluid entities evolving in the coal.

Although it might appear that oxygen content has a positive effect, if two biomass samples with a similar char yield are compared, such as BIOC and SPT that produce char yields of around 42%, the less deleterious effect is caused by the biomass with lower oxygen content (i.e. BIOC, with 25.5% cf. 35.5% of SPT, Table 1). These results prove that oxygen species in biomass have a negative effect on coal fluidity.

The results in Figures 8a and 8b for blends containing the same biomass sample indicate that the binders cause a greater increase in fluidity in the following order:

$$T > T/CTS > Par > Mol$$

These results do not seem to be related to the coke or char yields of the binders. Mol and CTS yield similar amounts of solid residue at the temperature of maximum fluidity of the coal, but they have completely opposite effects on the fluidity of the coal. However, a relationship has been found between the effect of the binders on the coal plastic properties and their C/H atomic ratio (Figure 9). In the case of Lg, the factor discussed above does not appear to be very significant, as can be seen by the low value of the correlation coefficient (R^2 = 0.672), which suggests that the effect of this biomass constituent is predominant over that of the binder.

These results also confirm that the greater the char yield of the biomass, the greater the reduction in blend fluidity. Furthermore, the effect is even more pronounced in the case of the binders that have a greater C/H atomic ratio, and consequently, a greater effect on

422 the plastic properties of the coal. A combination of physical and chemical effects explains
423 these results. On the one hand, the inert additives that are blended with the softening coal
424 possibly reduce fluidity by adsorbing the primary decomposition compounds responsible
425 for the development of fluidity.[41,42] On the other hand, the binders with higher C/H values
426 are able to supply aromatic compounds that serve as stabilizers of the radicals formed
427 during coal decomposition, compensating for the deleterious effect of chars present in the
428 reaction system. Polycondensed aromatics can provide a pathway for the transfer of
429 hydrogen to radical sites in bituminous coals, and thereby, act as intermediates in the
430 transformation of coal to coke.[26,27] For any particular biomass, the least deleterious effect
431 is produced if an aromatic binder is used.
432
433 Therefore, the biomass samples studied in this work that are more suitable for the
434 preparation of the briquettes, considering their effect on the thermoplastic properties of
435 coal, are SP and BIOC. In the case of the binders, T and CTS are the binders that best
436 compensate for the deleterious effect of biomass on coal fluidity.
437
438 **4. Conclusions**
439 Four biomass samples and four binders have been blended with a low rank bituminous coal
440 to determine their effect on the thermoplastic properties of the coal. The biomass samples
441 comprised of pine sawdust (SP), torrefied pine sawdust (SPT), pine Kraft lignin (Lg) and a
442 bio-coal derived from hydrothermally treated waste biomass obtained from pruning (BIOC).
443 The binders included molasses (Mol), paraffin (Par), coal tar (T) and coal tar sludge (CTS).
444 The analysis of blends composed of coal, biomass and binder using the Gieseler plastometer
445 has shown that the binder's effects, as identified by rheometry analysis, are sometimes
446 modified by interaction with biomass. For the same binder, the following order of

447 increasing deleterious effect of the biomass upon the maximum fluidity of the coal has
448 been established: SP < BIOC < SPT < Lg. It can also be deduced that for the same biomass
449 the order of increasing deleterious effect of the binder on the coal maximum fluidity is as
450 follows: T < T/CTS < Par < Mol. The coke yields of the biomass samples together with the
451 chemical composition of the binders help to explain the fluidity of the blends.
452
453 The oxygen species in biomass have a negative effect on coal fluidity, these species are
454 associated to highly reactive compounds that reduce the char yield from biomass. As a result,
455 the contact area between the char from biomass and the fluid material of coal decreases and
456 the impairment in coal fluidity is reduced.
457
458 Coal tar, coal tar sludge, pine sawdust and BIOC appear to be the best briquette components.
459 Nevertheless, paraffin can be considered as a good alternative to bituminous binders because
460 it does not cause any significant impairment of the thermoplastic properties of coal and it is
461 less polluting. Future work must address other important factors such as optimum
462 concentrations of biomass and binder in the briquettes and the impact of coal rank and coal
463 blend composition in order to preserve coke quality and safeguard coke oven operation.
464

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469

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595

596 Table 1. Proximate and ultimate analysis of the briquette components.

	Coal	SP	SPT	BIOC	Lg	Mol	T	CTS	Par
Ash (wt% db)[a]	7.3	0.2	0.4	6.1	2.5	2.8[c]	0.4[c]	1.7[c]	0.1[c]
VM (wt% db)[a,b]	31.5	84.3	71.1	68.0	64.0	94.4[c]	65.9[c]	71.1[c]	99.6[c]
C (wt% db)[a]	81.2	50.9	59.8	59.8	64.7	26.5	90.3	84.2	85.1
H (wt% db)[a]	5.0	6.2	5.7	6.0	5.7	8.0	4.7	5.3	14.5
N (wt% db)[a]	1.6	0.3	0.3	1.2	0.9	1.7	0.8	1.3	0.2
S (wt% db)[a]	1.03	< 0.05	<0.05	0.15	1.52	0.18	0.40	0.60	<0.05
O (wt% db)[a]	4.8	44.7	35.5	25.5	26.3	55.9	3.0	8.2	0.3
C/H[d]	1.35	0.68	0.87	0.83	0.95	0.28	1.60	1.32	0.49

597

598 a: dry basis; b: volatile matter; c: determined in a thermobalance; d: atomic ratio

599 Table 2. Definition of the semi-quantitative indices derived from ATR infrared spectra.

Index	Description	Band region (cm^{-1})
Aromaticity ($A_{C=C/}A_{al}$)	ν C=C/ν C-H aliphatic	A1600/A(3000−2800)
Oxygen distribution ($A_{OH/}A_{C=O}$)	ν OH/ ν C=O	A3000/A(1770−1650)

600 ν: stretching vibration; σ: bending vibration

601

602

Table 3. Values for the semi-quantitative indices of the briquette components.

	Coal	SP	SPT	BIOC	Lg	Mol	T	CTS	Par
$A_{OH}/A_{C=O}$	-	23.82	7.45	8.37	7.45	13.40	-	-	-
$A_{C=C/}A_{al}$	0.35	0.33	0.39	0.46	0.36	0.43	0.74	0.63	0.00

Table 4. Parameters derived from the Gieseler fluidity test of the coal and briquettes.

Sample	Ts (°C)	Tf (°C)	Tr (°C)	Tr-Ts (°C)	MF (ddpm)	MF loss (%)
Coal	382	439	484	102	26055	-
T-BIOC	386	434	479	93	2268	91.3
T/CTS-BIOC	384	433	481	97	2125	91.8
Mol-BIOC	404	443	466	62	69	99.7
Par-BIOC	384	444	479	95	395	98.5
T-Lg	342	433	475	133	389	98.5
T/CTS-Lg	342	436	475	133	340	98.7
Mol-Lg	-	-	-	-	-	100
Par-Lg	412	448	481	69	284	98.9
T-SP	387	432	483	96	3173	87.8
T/CTS-SP	392	434	482	90	2046	92.1
Mol-SP	403	442	475	72	242	99.1
Par-SP	378	441	486	108	922	96.5
T-SPT	394	438	481	87	962	96.3
T/CTS-SPT	389	440	476	87	999	96.2
Mol-SPT	416	446	467	51	11	99.9
Par-SPT	382	442	484	102	526	98.0

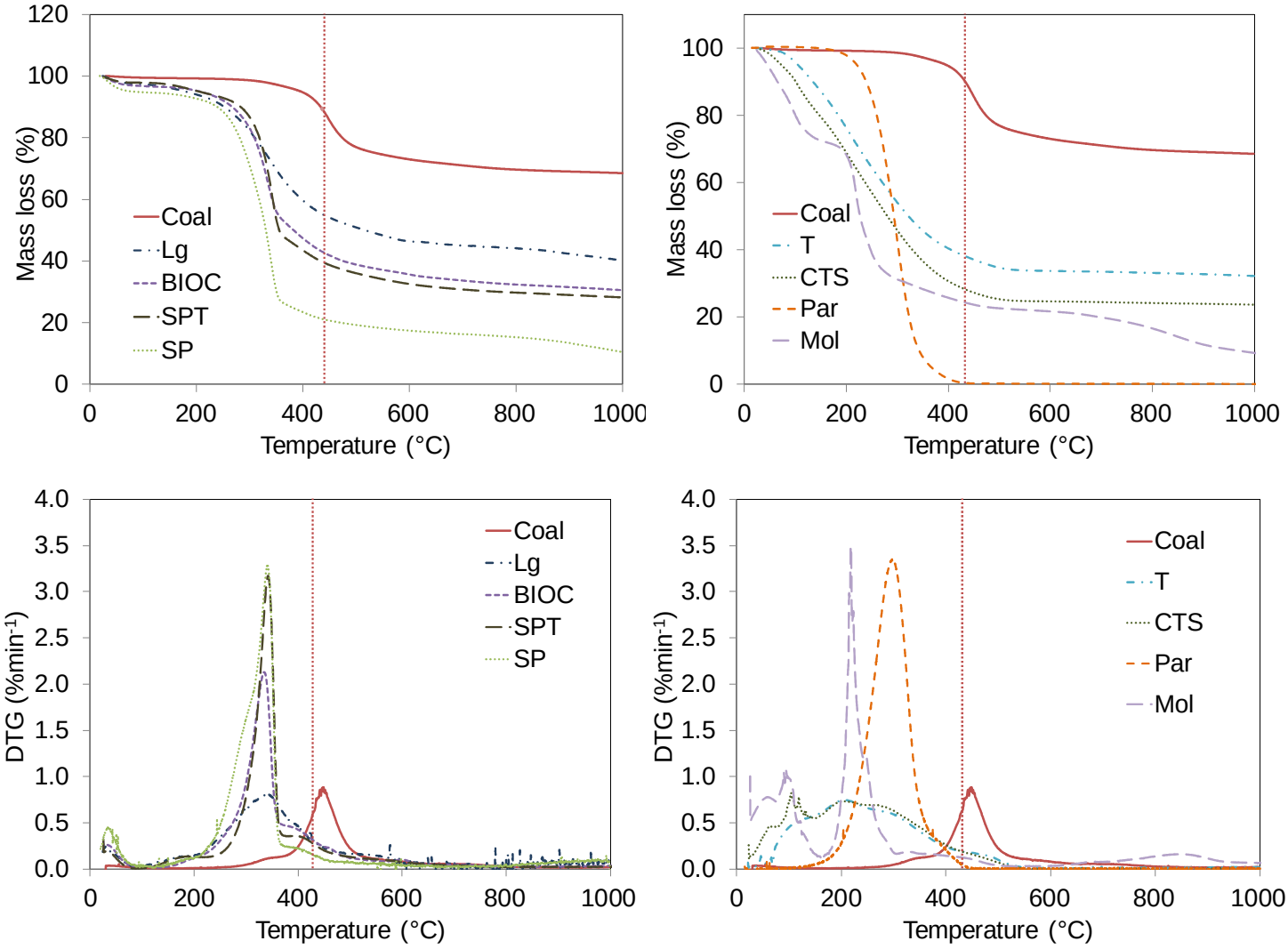

Figure 1. Mass loss of the raw materials as a function of temperature.

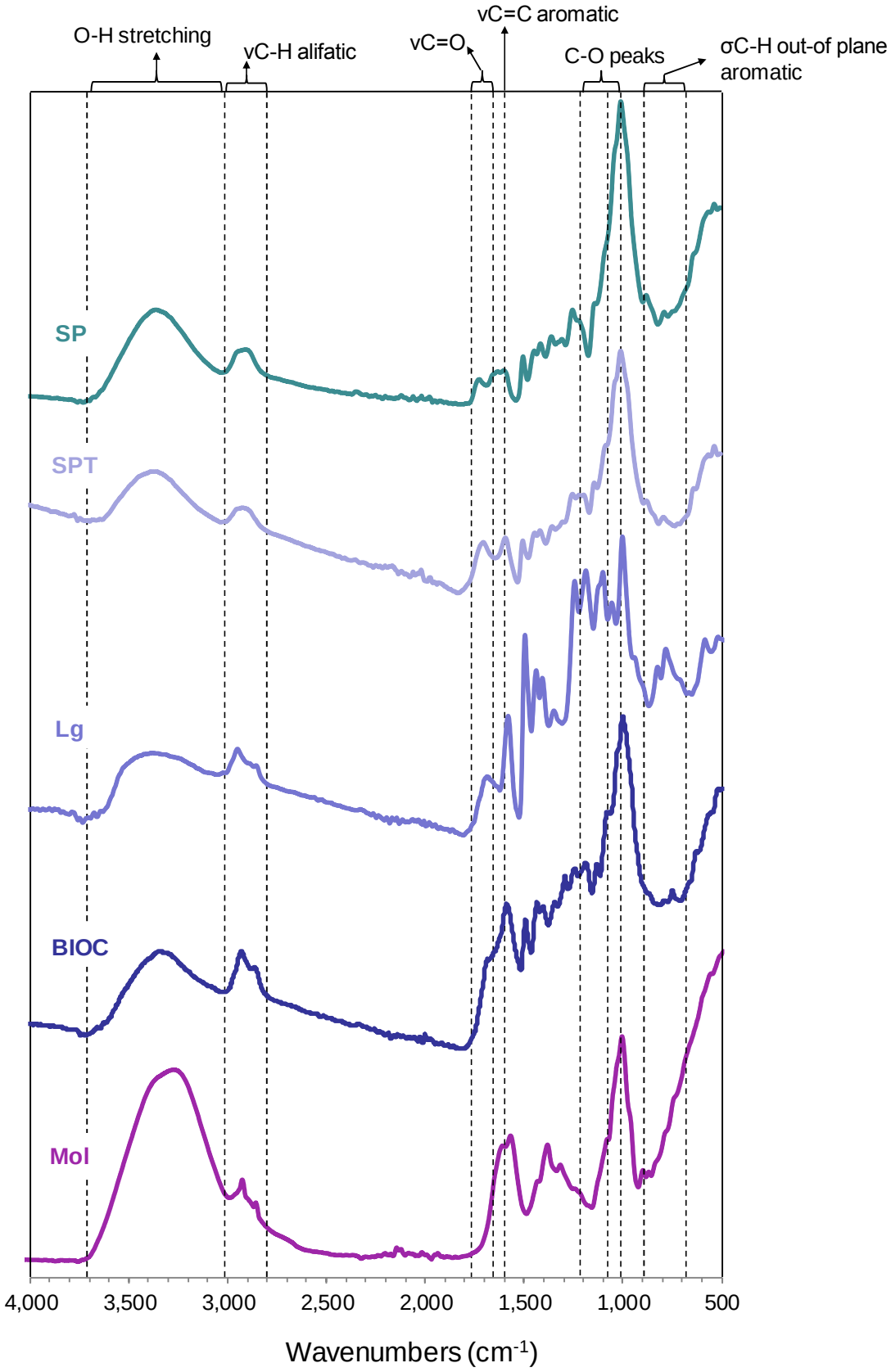

Figure 2. Infrared spectra of SP, SPT, Lg, BIOC and Mol.

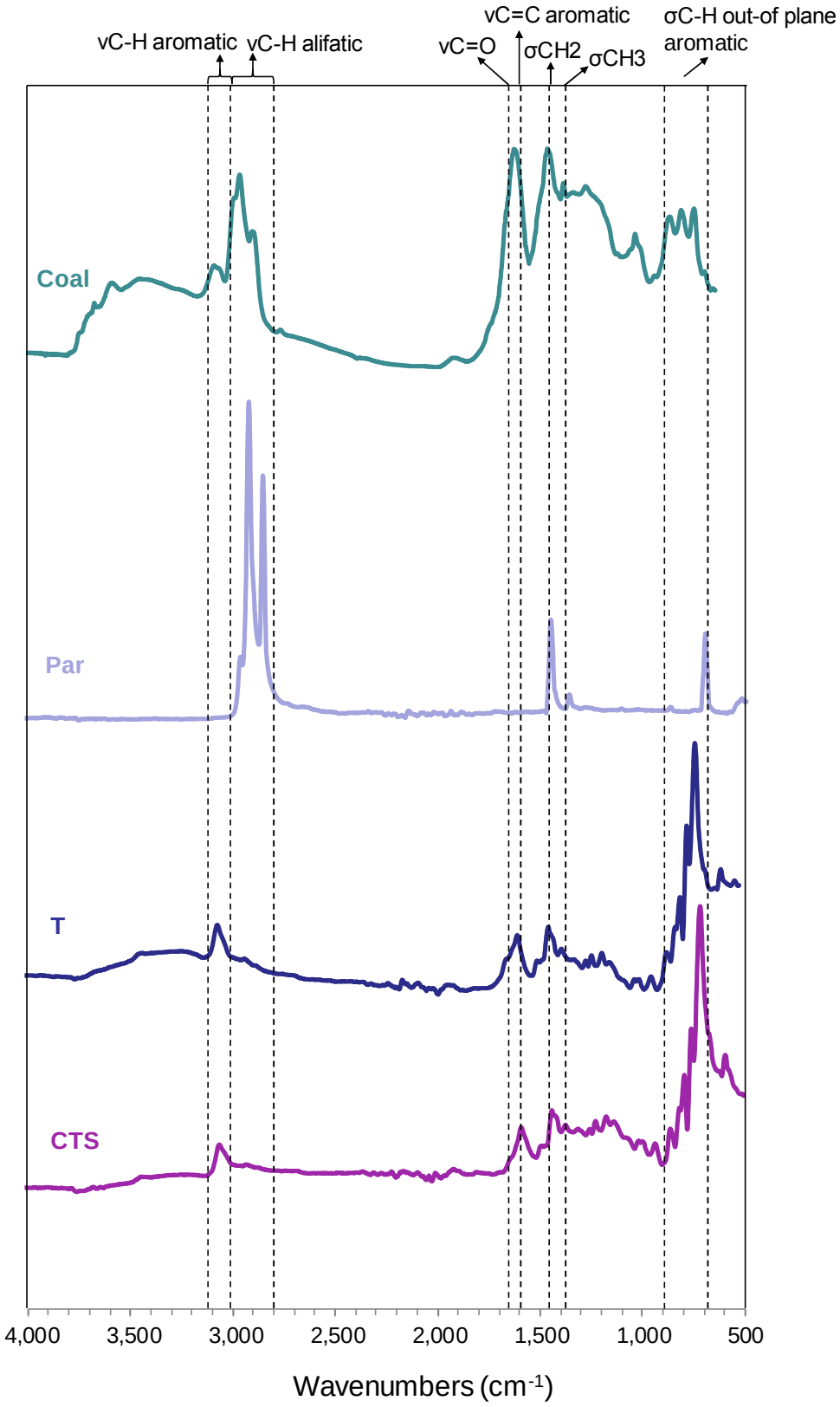

Figure 3. Infrared spectra of coal, Par, T and CTS.

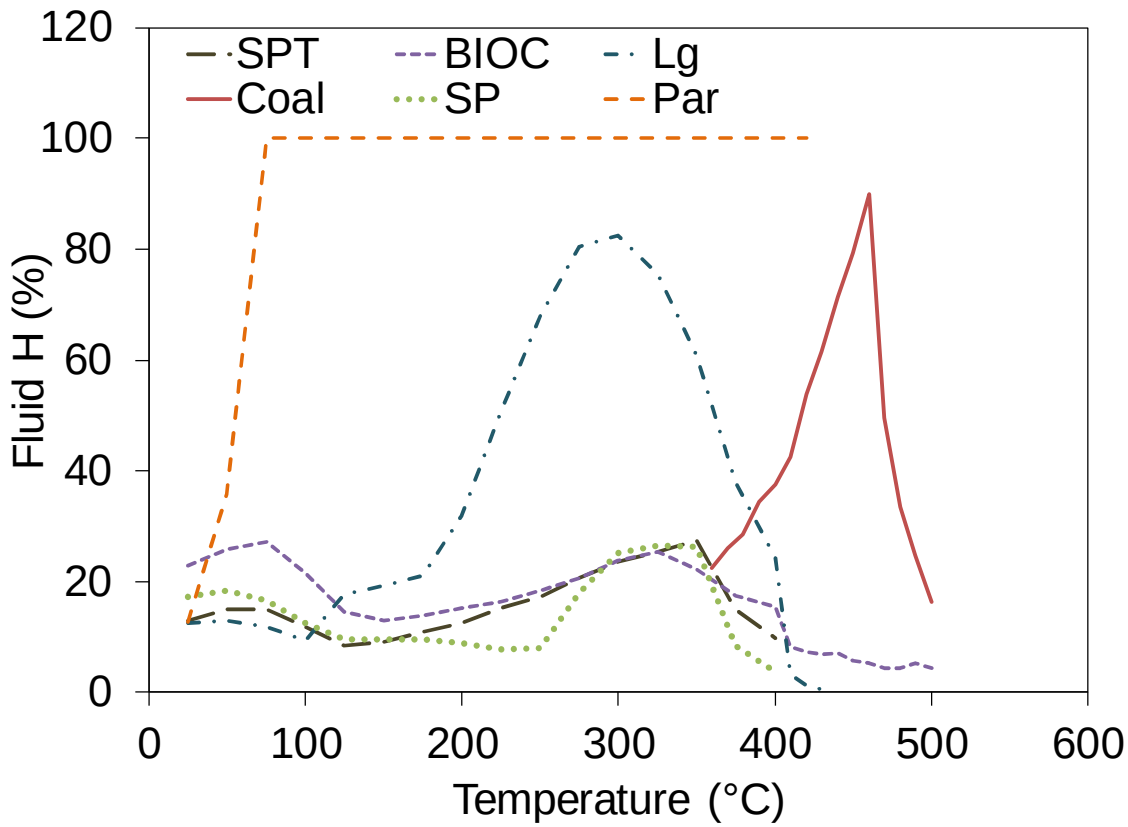

Figure 4. Fluid H development as a function of temperature.

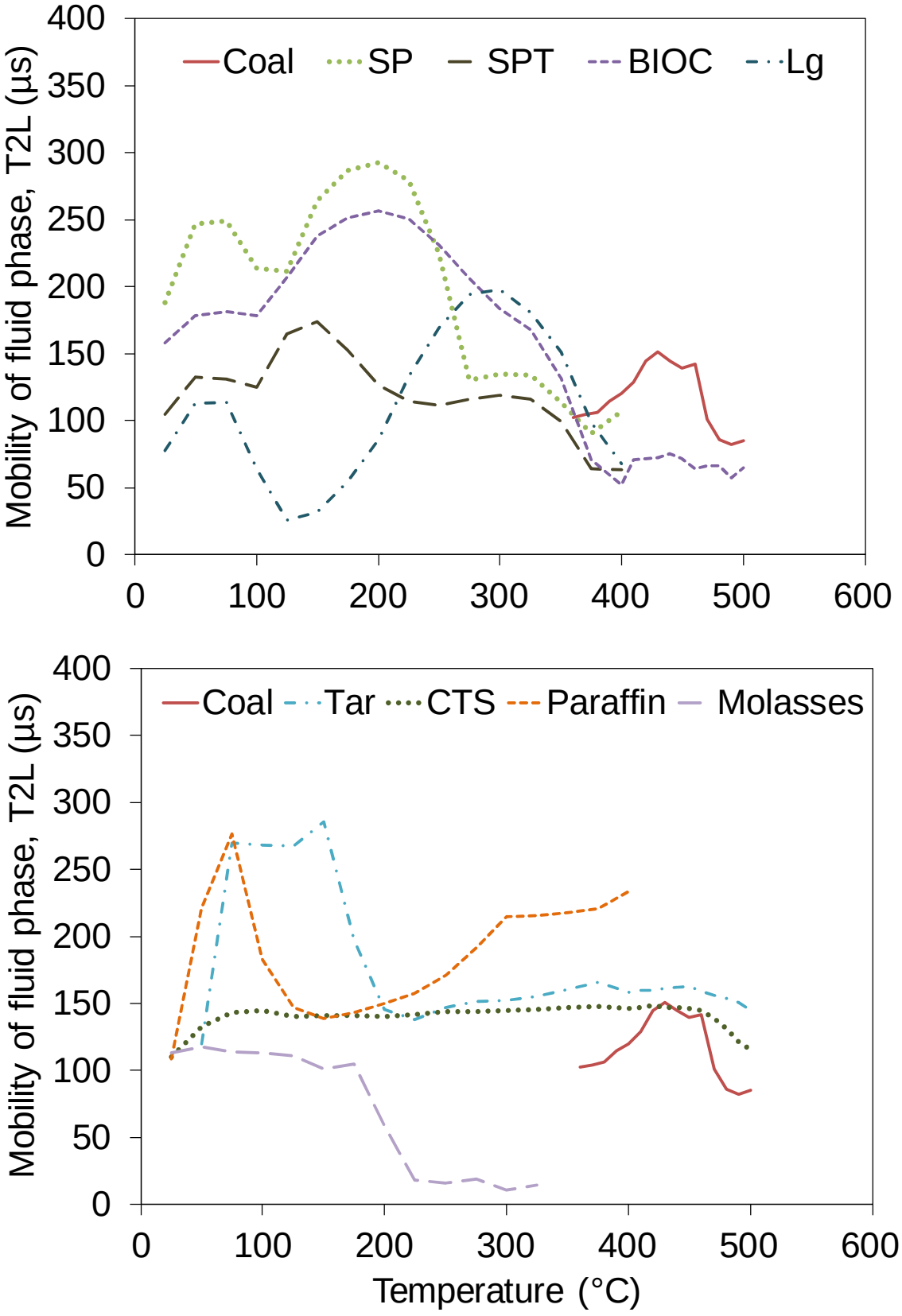

Figure 5. Changes in the mobility of fluid phase (T2L) as a function of temperature.

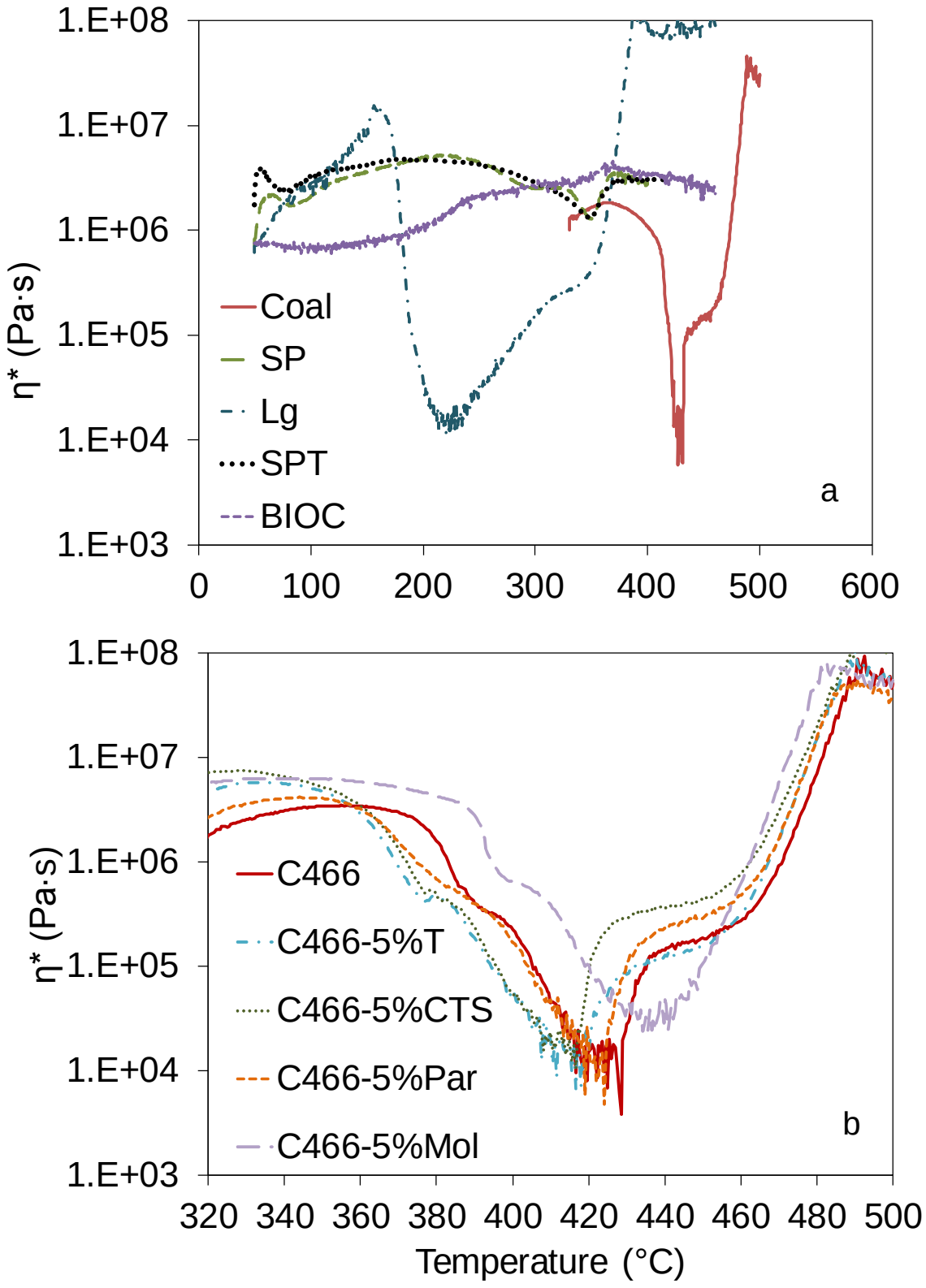

Figure 6. Complex viscosity as a function of temperature for a) coal and biomass samples and b) blends of coal pre-heated up to 466 °C with binders.

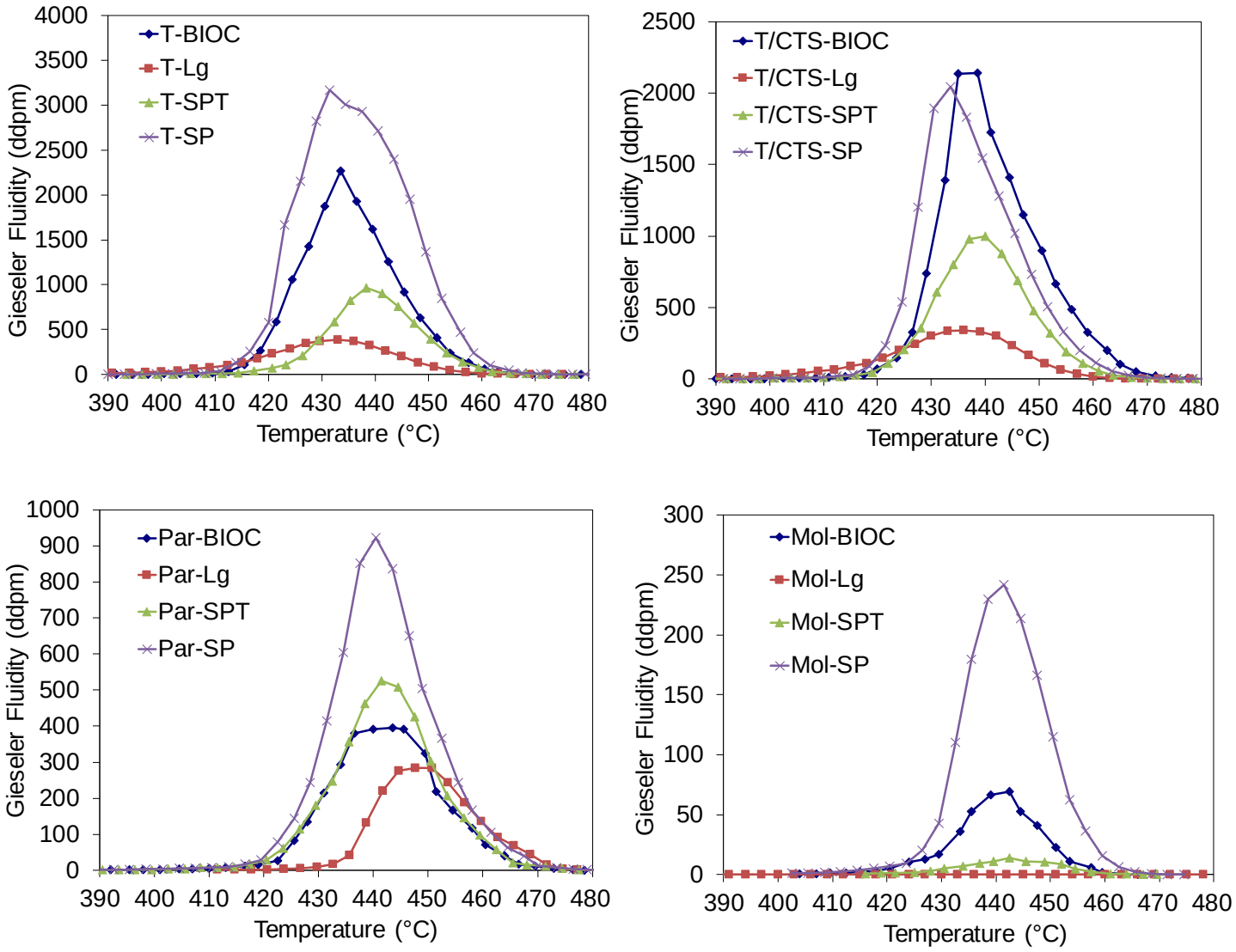

Figure 7. Gieseler fluidity curves as a function of temperature for the briquette blends.

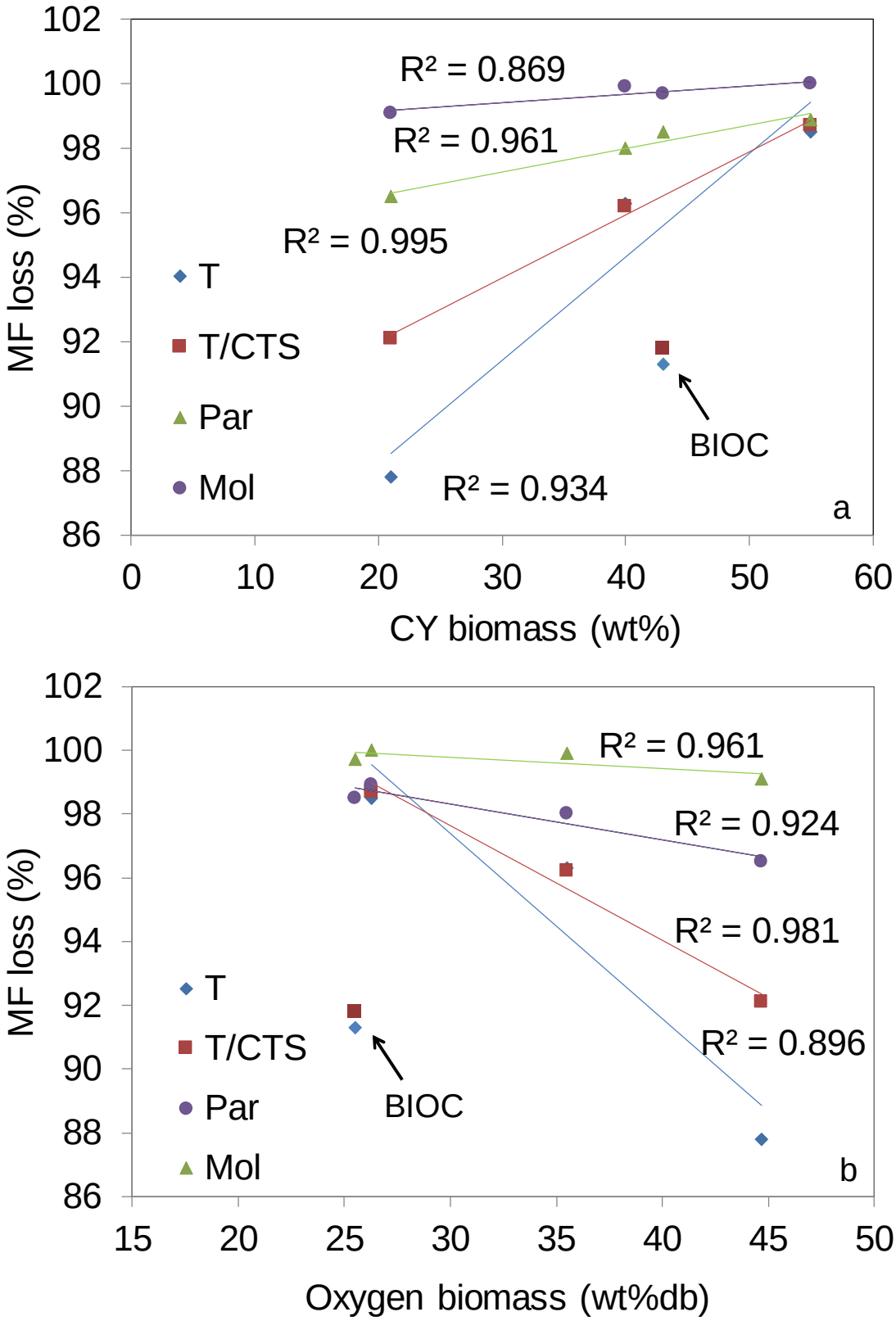

Figure 8. Variation of maximum fluidity loss with a) biomass char yield, from left to right SP, SPT, BIOC and Lg and b) oxygen content of the biomass samples, from left to right BIOC, Lg, SPT and SP.

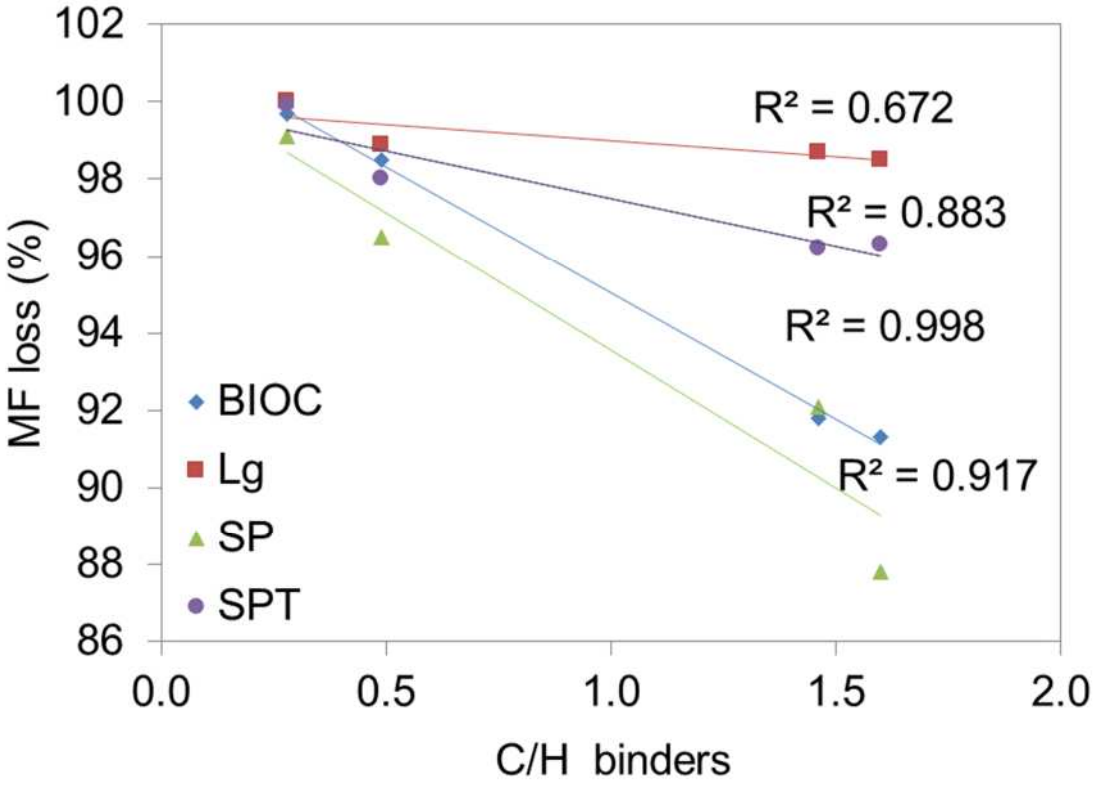

Figure 9. Relationship between the MF loss and the C/H atomic ratio of the binders. Binders from left to right: Mol, Par, T/CTS and T.