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Utilization of Carbonaceous Materials To Restore the Coking Properties of Weathered Coals

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ABSTRACT: Coking coals with different rank and maceral compositions have been weathered, and their fluidity has been determined through high-temperature rheometry. The pristine and weathered coals were blended with carbonaceous additives comprised of coal tar, diesel fuel, high-density polyethylene, sugar beet roots, lignin, and bio-oil in order to produce blends with optimum fluid characteristics. The addition of only 3 wt % coal tar to a high-rank coal weathered for 6 months completely restored its fluid properties, and the addition of 3 wt % diesel fuel was able to restore the fluidity of the coal but only after shorter weathering periods (4 months). However, the strength parameter R1 (particles > 0.6 mm) of the semicokes obtained from these blends at 700 °C was lower than that of the pristine coal by 3%. Biomass additives such as sugar beet roots and lignin were found to reduce the fluidity of a weathered coal with medium-volatile-matter content (25 wt % dry ash free (daf)) to levels similar to those encountered in good coking coals. Although sugar beet roots reduced the strength of the semicoke obtained from the blend, the blend with lignin produced a semicoke with strength similar to that of the pristine coal. The lower volatility matter content in lignin compared to sugar beet roots and its high oxygen content (~25 wt %) could limit fissure formation in the semicoke and facilitate the cohesion with the oxidized coal matrix, respectively.

1. INTRODUCTION

Coal weathering decreases the thermoplastic capability of coking coals, which in turn modifies coal behavior during the coking process affecting coke structure and properties. Chemical reagents have been used in the past to restore the caking properties of oxidized coals. For instance, a high-volatility, high Gieseler fluidity bituminous coal that was oxidized under mild conditions recovered its fluidity and dilatation properties after treatment with barium hydroxide or barium acetate solutions.¹ Co-carbonizations of oxidized coking and caking coals with decacyclene have also been found to be effective in removing the effects of mild oxidation.^{2,3}

Carbonaceous additives, such as coal tar pitch that develop highly condensed aromatic structures during the plastic temperature range of coal (400–600 °C) can contribute to the development of fluidity as these entities can stabilize the free radicals formed in coal.⁴ The addition of cheaper carbonaceous materials such as waste plastics and biomass usually cause a reduction in Gieseler maximum fluidity. However, different plastics or biomass types cause different effects on coal fluidity. For instance, the deleterious effect of high-density polyethylene (HDPE) on coal fluidity is less pronounced compared to other plastics such as polystyrene or polypropylene.^{5–11} Regarding biomass materials, lignin has a less deleterious effect on coal fluidity than cellulose or raw biomass¹² and bio-oil causes a less pronounced reduction in Gieseler maximum fluidity than porous char.¹³ Low concentrations of lignin (2 wt %) were found to have an effect similar to that of water-insoluble tar whereas higher concentrations of lignin (5–10 wt %) were found to have an effect similar to that of charcoal.¹² This was explained by the partial volatilization and condensation of lignin that produces as a phenolic tar with

a similar composition to that of the water-insoluble tar and the partial transformation of lignin into a char during pyrolysis. Exceptions where biomass was able to preserve the fluid characteristics of coals with volatile-matter contents of 23–25 wt % dry ash free (daf) were found when adding 5 wt % xylan¹² and 5 wt % sugar beet.¹⁴

The principal aim of this work is to restore the fluid characteristics of weathered coals through the use of relatively cheap carbonaceous additives. The selected additives are comprised of liquid and solid carbonaceous materials with plasticizing properties such as coal tar and waste plastics. Biomass materials will also be tested as they can reduce nonrenewable carbon emissions from coke ovens. High-temperature, high-torque, small-amplitude oscillatory shear (SAOS) rheometry will be used to determine the viscoelastic behavior and the expansion/collapse of the coals, additives, and blends as a function of temperature. Microstrength tests will also be carried out to determine the strength of the semicokes obtained from the blends. This study expands on an ongoing work that considers blending weathered coals with pristine coals to produce optimum coking blends and, therefore, represents another approach to beneficiate weathered coking coals.

2. EXPERIMENTAL SECTION

2.1. Materials. The characteristics of the five coals studied in this work are given in Table 1. These pristine coals were stored in open bags and placed outdoors at locations in France (coals C1, C2, and

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Table 1. Coal Characteristics and Coking Properties

	C1	C2	C6	C7	C8
origin	AUS	AUS	USA	POL	POL
ash (% db)	9.3	8.7	7.6	8.5	6.6
VM (% daf)	22.3	25.4	32.7	22.1	33.4
vitritine (%)	81.3	84.4	73.2	48.6	62.6
liptinite (%)	0	0.2	9.2	3.8	9.0
inertinite (%)	13.2	10.4	13.2	40.0	21.9
inertodetrinite (%)	5.2	3.7	5.2	17.9	10.8
fusinite (%)	0.9	1.7	1.7	7.6	8.0
semifusinite (%)	7.1	5.0	6.3	14.5	3.1
mineral matter (%)	5.5	5.1	4.4	7.6	6.5
R ₀ (%)	1.32	1.23	0.98	1.22	0.93
log K (log m ²)	−10.4	−10.3	−10.2	−9.7	−9.6
Gieseler max fluidity (ddpm)	137	720	21654	272	4232
T _{softening} (°C)	418	404	384	410	393
T _{maximum} (°C)	463	461	445	462	443
T _{resolidification} (°C)	493	498	488	498	481
free swelling index	9	9	8	7.5	8
CSR (%)	74.3	72.0	62.1	56.8	40.6
CRI (%)	16.2	17.5	28.2	33.0	43.3
internal gas pressure (mbar)	36	52	20	40	22

C6) and Poland (coals C7 and C8), and samples were collected after weathering periods of 2, 4, and 6 months.

Six liquid and solid carbonaceous additives were used to restore the fluidity of weathered coals. These additives are coal tar, diesel fuel, high-density polyethylene (HDPE), sugar beet roots (SBR), lignin, and bio-oil. The coal tar was obtained from SADIM-Asturias S.A. in Langreo, Spain. The diesel fuel was obtained from Instituto Nacional del Carbón (INCAR-CSIC) in Oviedo, Spain. HDPE was obtained from waste plastic bottles, which were cut to small pieces to produce needle-shaped particles < 2 mm in length and < 0.5 mm in width. The sugar beet roots were supplied by British Sugar Plc (Peterborough, U.K.) and were washed to remove any residual soil, cut into small pieces, and dried overnight at 100 °C. The lignin was obtained from the Kraft pulping process and supplied in powder form by CPL Industries (Sheffield, U.K.). The bio-oil was supplied by BP Plc (London, U.K.) and was obtained from flash pyrolysis of wood.

2.2. Experimental Methods. SAOS measurements were performed using a Rheometrics RDA-III high-torque controlled-strain rheometer. The amount of coal or blend used for each analysis was 1.5 g, and the amount of solid additive was approximately 1 g. The blends were prepared using either 3 or 5 wt % additive. The samples were compacted with a hydraulic press under 5 tons of force in a 25 mm die to form coal discs with a thickness of approximately 2.6 mm and additive discs of around 2.0 mm. The tests involved placing the sample disc between two 25 mm parallel plates which had serrated surfaces to reduce slippage. The coals and blends were heated from room temperature to 330 °C at 85 °C/min and from 330 to 520 °C at 3 °C/min. The solid additives were heated from room temperature to 400 °C at 3 °C/min. The furnace surrounding the sample was purged with a constant flow of nitrogen 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 an 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. A constant normal force of 200 g was applied through the top plate, which allowed the plate gap to change. 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. Moreover, the change in plate gap from the initial position (ΔL), which is a measure of the expansion and collapse of the coal mass, was recorded as a function of temperature. The complex viscosity is calculated using eq 1, where G' is the storage or elastic modulus, G'' is the loss or viscous modulus, and ω is the frequency.¹⁵ For a

completely elastic solid (or Hookean solid), there is no viscous dissipation of energy and $G'' = 0$ whereas for a completely Newtonian liquid the material does not store energy and $G' = 0$. Therefore, the complex viscosity is a measure of overall resistance to flow as a function of frequency.

$$\eta^* = \{(G')^2 + (G'')^2\}^{1/2}/\omega \quad (1)$$

Microstrength tests of semicokes prepared with 80 g of sample and obtained at 700 °C were determined according to the Ragan and Marsh method.¹⁶ Briefly, two charges of semicoke (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 semicokes were subjected to 800 rotations at a speed of 25 rpm to measure three different particle size fractions: >0.6 mm (R1), 0.6–0.212 mm (R2), and <0.212 mm (R3). The R indices were obtained from duplicate tests.

3. RESULTS AND DISCUSSION

Figure 1 presents the complex viscosity of three solid carbonaceous additives as a function of temperature. Coal tar,

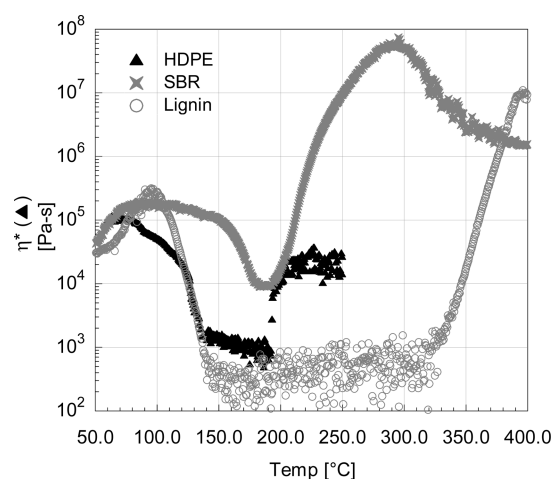


Figure 1. Complex viscosity as a function of temperature for the carbonaceous additives.

diesel fuel, and bio-oil were not characterized using high-temperature SAOS rheometry since they develop complex viscosity values below 10² Pa·s (or 10⁵ cP) upon heating. The increase in fluidity follows the order sugar beet roots < high-density polyethylene < lignin. SBR show a minimum in complex viscosity at around 185 °C, which could mainly be attributable to the degradation of molasses.¹⁷ HDPE and lignin do not show a clear minimum in complex viscosity as the values fall below the detection limits of the instrument. However, it could be said that HDPE remains highly fluid between 140 and 190 °C whereas lignin remains highly fluid between 140 and 330 °C. SBR and lignin do not contain a fluid phase above 400 °C, and thus, no contribution to fluidity development is expected from these two materials when blended with coking coals. HDPE could still contribute to fluidity development in the thermoplastic range of coal as it shows a peak in devolatilization rate at around 460 °C.⁶

In order to ascertain the effect of the carbonaceous additives on coal fluidity, two low-volatility coals and two high-volatility coals in pristine form were chosen to prepare blends with 3 wt % additive. The minimum complex viscosity (η^*_{\min}) values of the coals and blends are shown in Figure 2. Low minimum

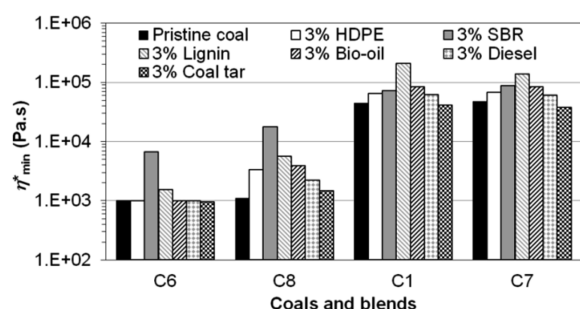


Figure 2. Minimum complex viscosity of four pristine coals and blends with 3 wt % additive.

complex viscosity values in coal are associated with high Gieseler maximum fluidity values and *vice versa* (Table 1), which agrees with previous findings by Yoshida et al.¹⁸ for maximum $\tan \delta$ (inversely proportional to minimum complex viscosity) and Gieseler maximum fluidity. The results indicate that the interactions between the coal and additive not only depend on the chemical/physical characteristics of the additive but also on the chemical properties of the coal. This is clearly seen in coals C6 and C8, which develop the same amount of fluid material but there is more interaction between the fluid material in coal C8 and the additives, causing a significant reduction in fluidity or increase in complex viscosity regardless of the additive used. In the case of the blends with coal C6, only SBR and lignin have deleterious effects on coal fluidity. Furthermore, SBR are the most deleterious additive for the fluidity of high-volatility matter, high-fluidity coals C6 and C8 (η^*_{\min} of the blend is 3–5 times higher with SBR than with lignin), whereas lignin is the most deleterious additive for the fluidity of low-volatility matter, low-fluidity coals C1 and C7 (η^*_{\min} of the blend is 1.5–3 times lower with SBR than with lignin). This corroborates the hypothesis that the chemical properties of the coal play an important role in the capability of the additives to destroy the fluid phase of coal. The high amounts of fluid material evolving from lignin could interact with the small amounts of fluid material in low-fluidity coals. On the other hand, the formation of a char in SBR at low temperatures (~ 300 °C, Figure 1) could act as a sink for the high amounts of fluid constituents evolving from high-volatile-matter coals.

Taking into consideration these findings, Figure 3 illustrates the effect of the plasticizing additives HDPE, diesel fuel, and

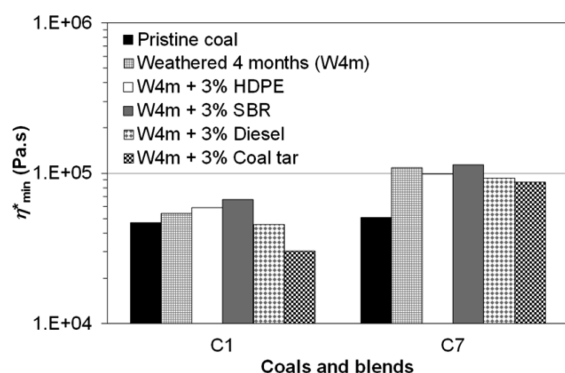


Figure 3. Minimum complex viscosity of the pristine coals C1 and C7, the coals after weathering for 4 months, and the blends of the weathered samples with 3 wt % additive.

coal tar together with the deleterious additive SBR on the fluidity of good coking coals C1 and C7 before and after weathering for 4 months. The fluid characteristics of the weathered coal C1 can be restored through the use of diesel fuel and coal tar since coal weathering did not cause a significant reduction in fluidity development. On the contrary, coal C7 losses fluidity to a great extent after weathering for 4 months, which is not easily recovered through the addition of 3 wt % additive. Indeed, significant amounts of diesel fuel or coal tar (>20 wt %) would be required to reduce the minimum complex viscosity of the blend, that in turn could impair the strength of the resulting coke.

The effect of additive concentration on the minimum complex viscosity of the coking blend with the weathered coal C1 has also been ascertained (Figure 4). These binary

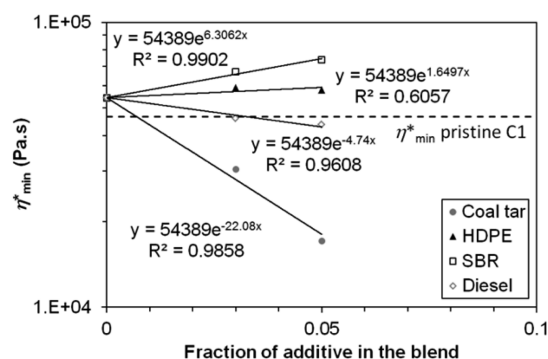


Figure 4. Minimum complex viscosity of coal C1 after weathering for 4 months and the blends with different additives.

blends follow the polymer blend rule,¹⁹ whereby the minimum complex viscosity of the blend can be calculated from the minimum complex viscosity values of the individual components. Coal tar increases the amount of fluid material in the blend with the weathered coal to higher levels than that of the pristine coal when added in concentrations of 5 wt %. The addition of 5 wt % diesel fuel restores the fluid properties of the weathered coal, HDPE does not seem to affect fluidity development within experimental error, and an increase in SBR concentration in the blend causes a further reduction in fluidity.

The expansion and contraction behavior of the blend must replicate that of the pristine coking coal to validate the formulation of optimum coking blends. Figure 5 proves that the blends of coal C1 after weathering for 4 months with 3 wt % diesel fuel and coal C1 after weathering for 6 months with 3 wt % coal tar are able to mimic the viscoelastic and expansion/contraction behaviors of the unweathered coal C1.

The microstrength indices of the semicokes obtained at 700 °C with the blends of weathered coal C1 and coal tar or diesel fuel are listed in Table 2. The higher the R1 value (>0.6 mm particles) and the lower the R3 value (<0.212 mm particles) the higher is the strength of the semicoke. The results indicate that the addition of diesel fuel and coal tar to weathered coal C1 is not able to recover the semicoke strength of the pristine coal, probably due to the high fluid character of the additives that promotes the formation of a highly porous semicoke structure as previously suggested.^{8,20} Coal tar has a more beneficial effect on semicoke strength than diesel fuel, as indicated by the higher R1 value (by 0.6%) and lower R3 value (by 2.5%) of the blend with coal tar. However, it has to be noted that the blend with

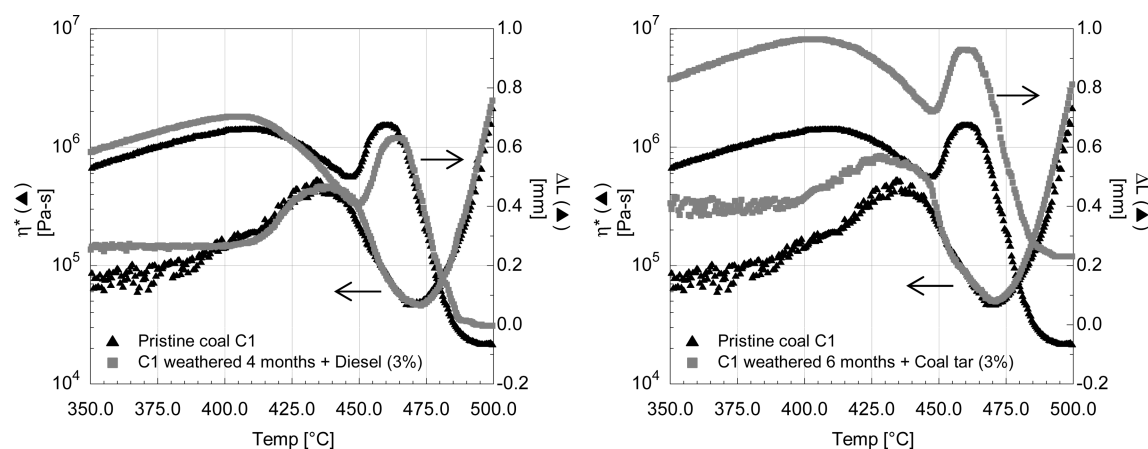


Figure 5. Complex viscosity and change in plate gap as a function of temperature for pristine coal C1, blend of coal C1 after weathering for 4 months with diesel fuel (3 wt %), and blend of coal C1 weathered for 6 months with coal tar (3 wt %).

Table 2. Microstrength Indices of the Semicokes Obtained at 700 °C from Pristine Coal C1 and Blends of Weathered Coal C1 with Diesel Fuel and Coal Tar (3 wt %)

	R1 (%)	R2 (%)	R3 (%)
pristine coal C1	5.7	43.8	50.6
C1 weathered for 4 months + diesel fuel (3 wt %)	2.3	38.9	58.8
C1 weathered for 6 months + coal tar (3 wt %)	2.9	40.8	56.3

coal tar contains coal C1 after weathering for 6 months rather than 4 months, and thus, coal tar could potentially be used with this coal over shorter weathering times (≤ 4 months) without impairing the semicoke strength significantly. Intuitively, the lower strength of the semicoke obtained from the blend with diesel fuel compared to that of the blend with coal tar (even with a greater extent of coal weathering) could be due to the higher devolatilization rate of diesel fuel during pyrolysis that would promote the formation of a more porous semicoke structure. This porous structure would be characterized by thinner pore walls that reduce its mechanical strength.

On the other hand, biomass derived additives could be used to further reduce the fluidity of weathered coking coals with medium or high-volatile-matter contents in order to produce blends that possess viscoelastic properties similar to those of pristine good coking coals. Figure 6 shows that the medium-volatile-matter (25.4 wt % daf) coal C2 develops a minimum complex viscosity of approximately 6×10^3 Pa·s when weathered for 4 months. The additions of sugar beet roots, lignin, and bio-oil further decrease the fluidity of this weathered

coal, wherein the lignin has the most deleterious effect on fluidity and bio-oil the least deleterious effect. The calculated amounts of additive in the blend to achieve minimum complex viscosity values similar to those of good coking coals ($\sim 5 \times 10^4$ Pa·s) are 4 wt % for lignin, 6 wt % for SBR and 22 wt % for bio-oil. Therefore, only lignin and SBR could potentially be blended with this coal without significantly impairing the coke strength. This methodology not only would reduce the amounts of nonrenewable carbon emissions by the introduction of biomass in the blend but also would add value to weathered coking coals.

Figure 7 indicates that the temperature of maximum fluidity of the blend of the weathered coal C2 with lignin (5 wt %) is identical to that of the pristine coal C7. Moreover, the expansion behavior of the blend is similar to that of coal C7, but the extent of collapse in the blend is significantly lower. On the contrary, the temperature of maximum fluidity in the blend with 5 wt % SBR is lower than that of the pristine coal C7, and although this blend does not expand during softening, the extent of collapse is fairly similar to that of coal C7.

Table 3 shows that the microstrength parameter R3 (< 0.212 mm particles) for the blend of weathered coal C2 with 5 wt % lignin is similar to that of the pristine coal C2 (i.e., 51%). However, this parameter increases by 4% when SBR are added in similar amounts to coal C2 weathered for 4 months, which indicates a deterioration in semicoke quality. These results suggest that lignin could be used to reduce the fluidity of weathered coking coals with volatile-matter contents around 25 wt % daf to produce blends with optimum fluidity properties and obtain semicokes with good strength. A possible explanation by which lignin is able to preserve or even improve the semicoke strength would be due to the fact that (i) it forms the most char compared to other biomass additives and hence the lowest amounts of volatiles,^{12,21} limiting the formation, propagation, and coalescence of pores that eventually cause fissuring; (ii) it is highly fluid and aromatic in character with high oxygen content (~ 25 wt %),²² which will facilitate the

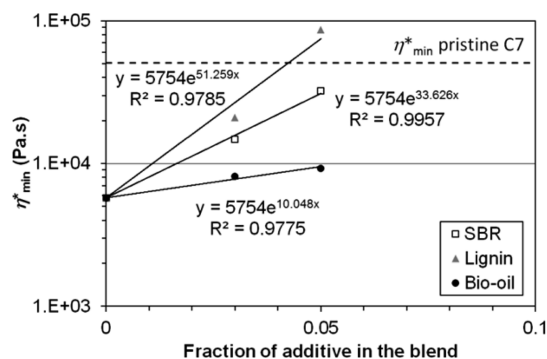


Figure 6. Minimum complex viscosity of coal C2 after weathering for 4 months and the blends with additives derived from biomass.

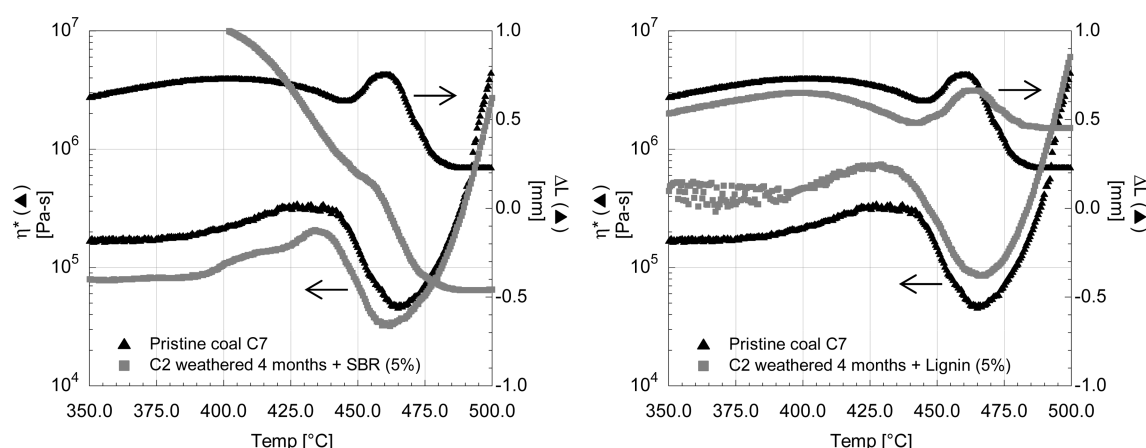


Figure 7. Complex viscosity and change in plate gap as a function of temperature for pristine coal C7 and blends of coal C2 after weathering for 4 months with SBR (5 wt %) and with lignin (5 wt %).

Table 3. Microstrength Indices Obtained for the Semicokes of Coal C2 before and after Weathering for 4 Months and the Blends of Weathered Coal C2 with Sugar Beet Roots (SBR) and Lignin (5 wt %)

	R1 (%)	R2 (%)	R3 (%)
pristine coal C2	5.3	43.4	51.3
C2 weathered for 4 months	5.4	42.6	52.0
C2 weathered for 4 months + SBR (5 wt %)	3.1	41.5	55.4
C2 weathered for 4 months + lignin (5 wt %)	6.5	42.1	51.4

cohesion with the oxidized coal matrix. Indeed, polymers bearing polar groups such as polyesters establish a much more compatible interface with lignin than nonpolar macromolecules resulting in strong adhesion.²³

4. CONCLUSIONS

Coal tar, diesel fuel, and high-density polyethylene (HDPE) can increase or preserve the fluid characteristics of pristine coals, whereas sugar beet roots, bio-oil, and lignin reduce coal fluidity to different extents. The reduction in fluidity caused by sugar beet roots is higher than that caused by lignin in high-volatile-matter coals (>30 wt % daf), and the opposite is true for low-volatile-matter coals (<23 wt % daf). This finding suggests that the chemical properties of coal play an important role in the interactions with biomass. The high amounts of fluid material evolving from lignin could interact with the small amounts of fluid material in high-rank coals whereas the early formation of a char in SBR could act as sink for the high amounts of fluid constituents evolving from low-rank coals.

The addition of 3 wt % diesel fuel and coal tar restored the fluid characteristics and expansion/collapse behaviors of a high-rank coal weathered for 4 and 6 months, respectively. However, the semicoke strength was reduced in both cases, probably due to the high fluid character of the additives that promotes the formation of a highly porous structure. HDPE was not able to restore the fluid characteristics of weathered coals, and the biomass materials destroyed fluidity to different extents. In this manner, sugar beet roots and lignin were added in concentrations of 5 wt % to a high-fluidity, medium-volatile-matter coal (ca. 25 wt % daf) to produce blends with viscoelastic behavior similar to that of low-volatile-matter, good coking coals. Although sugar beet roots reduced the strength of the semicoke obtained from the blend, the blend with lignin produced a semicoke with strength similar to that of the pristine coal. A possible explanation for this finding is that

lignin could limit fissure formation in the semicoke due to the lower formation of volatiles, and its high oxygen content (~25 wt %) and aromatic character would facilitate the reactivity and cohesion with the oxygenated functional groups of the weathered coal.

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Notes

The authors declare no competing financial interest.

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