

## Article

# Raman Spectroscopy of Lignite Gasification Char Morphotypes

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**Abstract:** The purpose of this study is to characterize and compare the microstructural features of the main morphotypes occurring in the char obtained at 850–950 °C by fluidized bed gasification of lignite from the “Szczerców” deposit (Central Poland), and to bring new insights into the knowledge on the origin of these morphotypes. Optical microscopy and Raman spectroscopy were used. The char is composed mostly of crassinetwork and inertoid, accompanied by tenuinetwork and small amounts of fusinoid. Tenuinetwork originates mainly from textinite, crassinetwork is formed from attrinite, while inertoid results from transformation of strongly gelified macerals such as densinite and ulminite. Similarities in the microstructure of tenuinetwork and crassinetwork as well as inertoid and fusinoid are observed. Inertoid and fusinoid are composed of larger aromatic systems, with lower amount of alkyl-aryl structures, and their microstructure is better organized compared to tenuinetwork and crassinetwork. Inertoid and fusinoid differ in microscopic appearance and were formed from different starting materials, but their microstructural properties converged during gasification. Different morphological features of the network morphotypes (tenuinetwork, crassinetwork) are not reflected in the differences in their microstructural characteristics.

**Keywords:** lignite; gasification; char; morphotypes; Raman spectroscopy



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## 1. Introduction

Poland is one of the few European countries where power generation is still largely based on domestically mined bituminous coal and lignite. The possibility of using coal in processes other than direct combustion was investigated due to the abundance of lignite reserves in Poland. The main focus was on clean coal technologies and in particular the gasification process in gasifiers. Research on various aspects of coal gasification technology has been conducted for many years [1–14]. Recently, due to the urgent need to mitigate climate changes and in connection with the rise in oil and gas prices this issue has taken on particular significance. Lignite is mined on a large scale in many countries, mainly in Germany, China, Russia, United States, and Poland. The development of local coal gasification projects is also essential in order to meet the needs of individual countries, which simultaneously translates into energy security and independence from external suppliers. Lignite usability for gasification was confirmed in several studies, usually conducted on coal from China, Japan, Canada, Russia, and the USA [10,11,15–19].

Previous works demonstrated the importance of petrographic examination in determining the suitability of coal for gasification and in predicting its behavior during the process. Furthermore, the importance and role of individual macerals in the gasification process was highlighted [5,12,20–24]. The petrographic features of chars obtained by the gasification process were also investigated [12,24–31]. The evolution of char structure can be characterized by coal petrography, in particular, the percentage char determination [27].

The structure of char was found to be one of the key factors affecting its reactivity during gasification [14,32]. To characterize the chemical-structural evolution of coals during

gasification, and to determine the properties of the resulting chars Raman spectroscopy was frequently used [14,27,33–47]. It was found that with increasing temperature the amount of large aromatic structures increased at the cost of smaller systems (<6 fused aromatic rings) and amorphous carbon [14,27,33–35,42,43]. The concentration of active sites ( $sp^2$ – $sp^3$  bonding) initially increased in lower temperature, and decreased above 800 °C [27]. The course of structural changes depends also on the gasifying agent [37,38].

However, these studies focused on bulk samples, and almost no attention was paid to the individual petrographic components of chars [48]. Therefore, structural properties of the morphotypes that may affect char reactivity remain unknown. It has also not been known whether the differences in morphological features, which are the basis for identification of the char morphotypes [26], are related to different microstructural characteristics of these components.

The purpose of this study was to characterize and compare the microstructural features of the main morphotypes occurring in the char produced by fluidized bed gasification of lignite from the “Szczerców” deposit (Central Poland), and to bring new insights into the knowledge on the origin of these morphotypes. The Raman characteristics of lignite macerals before gasification were obtained previously [49].

## 2. Materials and Methods

### 2.1. Gasification

The tested material is the residue from the gasification of lignite from the “Szczerców” deposit. The deposit is situated in the southern part of the Middle Polish synclinorium, within the Kleszczów Graben in Central Poland. The gasified coal is of the Miocene age. The physico-chemical parameters of the gasified lignite from the “Szczerców” deposit are shown in Table 1, whereas its petrographic composition is given in Table 2.

**Table 1.** Physico-chemical parameters of lignite from the “Szczerców” deposit [50].

| Parameter                                 | Norm                | Lignite |
|-------------------------------------------|---------------------|---------|
| As received                               |                     |         |
| Total moisture content $M_t^{ar}$ [%]     | ISO 589:2008 [51]   | 50.3    |
| Ash content $A^{ar}$ [%]                  | ISO 1171:2010 [52]  | 11.6    |
| Total sulfur content $S_t^{ar}$ [%]       | ISO 19579:2006 [53] | 0.46    |
| Net Calorific Value $NCV^{ar}$ [kJ/kg]    | ISO 1928:2020 [54]  | 8159    |
| Air-dried                                 |                     |         |
| Moisture content $M^{ad}$ [%]             | ISO 589:2008 [51]   | 8.5     |
| Ash content $A^{ad}$ [%]                  | ISO 1171:2010 [52]  | 20.1    |
| Volatile matter content $V^{ad}$ [%]      | ISO 562:2010 [55]   | 41.13   |
| Net Calorific Value $NCV^{ad}$ [kJ/kg]    | ISO 1928:2020 [54]  | 17,075  |
| Carbon content $C_t^{ad}$ [%]             | ISO 29541:2010 [56] | 46.40   |
| Hydrogen content $H_t^{ad}$ [%]           | ISO 29541:2010 [56] | 3.75    |
| Nitrogen content $N_t^{ad}$ [%]           | ISO 29541:2010 [56] | 0.52    |
| Total sulphur content $S_t^{ad}$ [%]      | ISO 19579:2006 [53] | 0.84    |
| Dry basis                                 |                     |         |
| Ash content $A^{db}$ [%]                  | ISO 1171:2010 [52]  | 23.2    |
| Total sulphur content $S_t^{db}$ [%]      | ISO 19579:2006 [53] | 0.92    |
| Volatile matter content $V^{daf}$ [%]     | ISO 562:2010 [55]   | 58.59   |
| Gross Calorific Value $GCV^{daf}$ [kJ/kg] | ISO 1928:2020 [54]  | 18,099  |

The lignite was gasified at the Institute for Chemical Processing of Coal in Zabrze, Poland, in a pilot circulating fluidized bed reactor using CO<sub>2</sub> as the gasification agent. The other components of the gasification mixture were nitrogen and oxygen. The temperature was between 856 °C and 952 °C. The process used 97 kg of coal, which yielded 21.5 kg of char [56].

**Table 2.** Petrographic composition of lignite from the “Szczerców” deposit [49].

|          |                | Component       | Content [% vol.] |
|----------|----------------|-----------------|------------------|
| Macerals | Huminite       | Textinite       | 11.7             |
|          |                | Uminite         | 12.1             |
|          |                | Attrinite       | 29.9             |
|          |                | Densinite       | 23.9             |
|          |                | Corpohuminite   | 1.6              |
|          |                | Gelinite        | 1.5              |
|          | Liptinite      | Sporinite       | 0.6              |
|          |                | Cutinite        | 0.1              |
|          |                | Resinite        | 1.1              |
|          |                | Suberinite      | 0.2              |
|          |                | Alginite        | 0.1              |
|          |                | Liptodetrinite  | 3.6              |
|          | Inertinite     | Fusinite        | 1.0              |
|          |                | Semifusinite    | 0.2              |
|          |                | Funginite       | 0.1              |
|          |                | Micrinite       | 0.0              |
|          |                | Inertodetrinite | 1.8              |
| Minerals | Pyrite         |                 | 0.8              |
|          | Carbonates     |                 | 0.5              |
|          | Quartz + Clays |                 | 9.2              |

The gasification parameters and the content of combustible components in the process gases are presented in Table 3. The entire system was discussed by [56]. Table 4 shows the physical parameters and chemical composition of the resulting char. A representative channel sample of char was collected to make preparations for microscopic and spectroscopic examinations.

**Table 3.** Gasification process parameters and the content of combustible components in the process gases [50].

| Parameter                                             | Value     |
|-------------------------------------------------------|-----------|
| Gasification temperature [°C]                         | 856–952   |
| Carbon flow rate [kg/h]                               | 83–130    |
| Air flow rate [m <sup>3</sup> /h] [m <sup>3</sup> /h] | 40–120    |
| CO <sub>2</sub> flow rate [m <sup>3</sup> /h]         | 0–65      |
| O <sub>2</sub> flow rate [m <sup>3</sup> /h]          | 0–19      |
| Hydrogen [% vol.]                                     | 9.1–13.2  |
| Methane [% vol.]                                      | 2.3–4.6   |
| Carbon monoxide [% vol.]                              | 12.3–20.1 |

**Table 4.** Physico-chemical parameters of the studied char [50].

| Parameter                              | Norm                | Char   |
|----------------------------------------|---------------------|--------|
| As received                            |                     |        |
| Total moisture content $M_t^{ar}$ [%]  | ISO 589:2008 [51]   | 0.4    |
| Ash content $A^{ar}$ [%]               | ISO 1171:2010 [52]  | 29.1   |
| Total sulphur content $S_t^{ar}$ [%]   | ISO 19579:2006 [53] | 1.18   |
| Net Calorific Value $NCV^{ar}$ [kJ/kg] | ISO 1928:2020 [54]  | 22,337 |
| Air-dried                              |                     |        |
| Moisture content $M^{ad}$ [%]          | ISO 589:2008 [51]   | 1.6    |
| Ash content $A^{ad}$ [%]               | ISO 1171:2010 [52]  | 28.7   |
| Volatile matter content $V^{ad}$ [%]   | ISO 562:2010 [55]   | 7.8    |
| Net Calorific Value $NCV^{ad}$ [kJ/kg] | ISO 1928:2020 [54]  | 22,039 |

Table 4. Cont.

| Parameter                                        | Norm                | Char   |
|--------------------------------------------------|---------------------|--------|
| Carbon content $C_t^{ad}$ [%]                    | ISO 29541:2010 [56] | 64.7   |
| Hydrogen content $H_t^{ad}$ [%]                  | ISO 29541:2010 [56] | 0.88   |
| Nitrogen content $N_t^{ad}$ [%]                  | ISO 29541:2010 [56] | 1.01   |
| Total sulphur content $S_t^{ad}$ [%]             | ISO 19579:2006 [53] | 1.17   |
| Dry basis                                        |                     |        |
| Ash content $A^{db}$ [%]                         | ISO 1171:2010 [52]  | 29.2   |
| Total sulphur content $S_t^{db}$ [%]             | ISO 19579:2006 [53] | 1.19   |
| Volatile matter content $V^{daf}$ [%]            | ISO 562:2010 [55]   | 8.0    |
| Gross Calorific Value GCV <sup>daf</sup> [kJ/kg] | ISO 1928:2020 [54]  | 22,270 |

## 2.2. Petrographic Analysis

The petrographic analysis of chars was based on the procedure used to develop a coal char classification [26]. It was performed with the use of 500 equally spaced points on the surface of the polished sections, prepared following the ISO standard 7404-2:2009 [57].

## 2.3. Raman Spectroscopy

Raman spectroscopy investigation was carried out on polished sections, allowing for identification of char morphotypes. This was done following the previous studies [27,48]. However, based on the recommendations of Lünsdorf [58], the final polishing (with the finest slurry of 0.5  $\mu\text{m}$ ) was omitted to exclude the possible effect of polishing on the Raman spectra. Vitrinites are unaffected by polishing up to maximum reflectance value of 7% [58].

The Raman measurements were performed on 22 (fusinoid) to 32 (inertoid) randomly chosen spots, with a Thermo Scientific DXR Raman microscope with a 900 grooves/mm grating and a CCD detector. The smaller number of analyses executed on fusinoid, in comparison to other morphotypes, was due to low proportion of this component. The Olympus 10 $\times$  (NA 0.25) objectives (spot sizes 2.1  $\mu\text{m}$  and 1.1  $\mu\text{m}$ , respectively) were used. Excitation was activated with a 532 nm diode laser with a maximum power of 10 mW. Measurements were conducted in a spectral range of 400–3500  $\text{cm}^{-1}$ , at a spectral resolution of 1  $\text{cm}^{-1}$ , and an area of 1  $\mu\text{m}^2$ . The laser power was set at 1–2 mW. The spectrometer was calibrated using a polystyrene standard. The accumulated measurement time was 30 s for each spectrum. The spectra were analyzed by peak-fitting performed in the range of 1000–1800  $\text{cm}^{-1}$  using GRAMS32, based on the previous Raman studies of chars and related carbon materials [39,40,59–62]. The second derivative of the spectra was also considered to find the initial positions of the bands. Four bands (D2, G, D1, and D4) were fitted by Lorentzian curves and one (D3 band) by the Gaussian curve. The goodness of fit was checked by the  $\chi^2$  test. The  $I_{D1}/I_G$  ratio was determined from the D1 and G band intensities (heights). Furthermore, the  $A_{D1}/A_{ALL}$ ,  $A_{D3}/A_{ALL}$ , and  $A_{D4}/A_{ALL}$  ratios were calculated from the band areas, where “ $A_{ALL}$ ” denotes the sum of all band areas in a spectrum. The final Raman results given below are the arithmetic means of the values obtained from the individual spectra. The standard deviations were also calculated.

## 2.4. Statistical Analysis

To assess the statistical significance of the differences in the spectral parameters between the morphotypes, the analysis of variance ANOVA and the Tukey’s HSD multiple comparison test were performed. This was preceded by checking the normality of distribution by the Shapiro-Wilk test and assessing the equality of variances by the Levene test. All statistical analyses were carried out using the Statistica 13.3. software (TIBCO Software Inc., Palo Alto, CA, USA).

### 3. Results and Discussion

#### 3.1. Petrographic Composition of the Char

The petrographic composition of the char is dominated by inertoid (35.44% vol.) (Table 5, Figure 1C,D) and crassinetwork particles (31.59% vol.) (Table 5, Figure 1B,F). Inertoids are dense with porosities between 5 and 40% [26]. In the tested samples it can be either fused or unfused. On the other hand, commonly observed crassinetwork chars are particles with internal network structure, where most of wall area  $>3\ \mu\text{m}$ , and the porosity is greater than 40%. However, it should be noted that, in total, chars with several types of pores formed by degassing (tenuinetwork, crassinetwork, tenuisphere, crassisphere, mixed porous) account for 52.33% by volume of all components (Table 5).

**Table 5.** Petrographic composition of chars. Reprinted with permission from [29] 2016 Elsevier.

| Component      | Content [% vol.] |
|----------------|------------------|
| Tenuisphere    | 1.92             |
| Crassisphere   | 1.92             |
| Tenuinetwork   | 12.64            |
| Crassinetwork  | 31.59            |
| Mixed Porous   | 4.26             |
| Mixed Dense    | 2.34             |
| Inertoid       | 35.44            |
| Fusinoid/Solid | 1.79             |
| Mineroid       | 8.10             |

Tenuinetwork, such as crassinetwork have internal network structure, but their porosity is over 70%. In contrast to crassinetwork, in the case of tenuinetwork more than 50% of wall area is thinner than  $3\ \mu\text{m}$ . Sphere-type grains, tenuisphere and crassisphere, which are spherical to angular in shape and have porosity higher than 60%, are less commonly observed in the gasification residue.

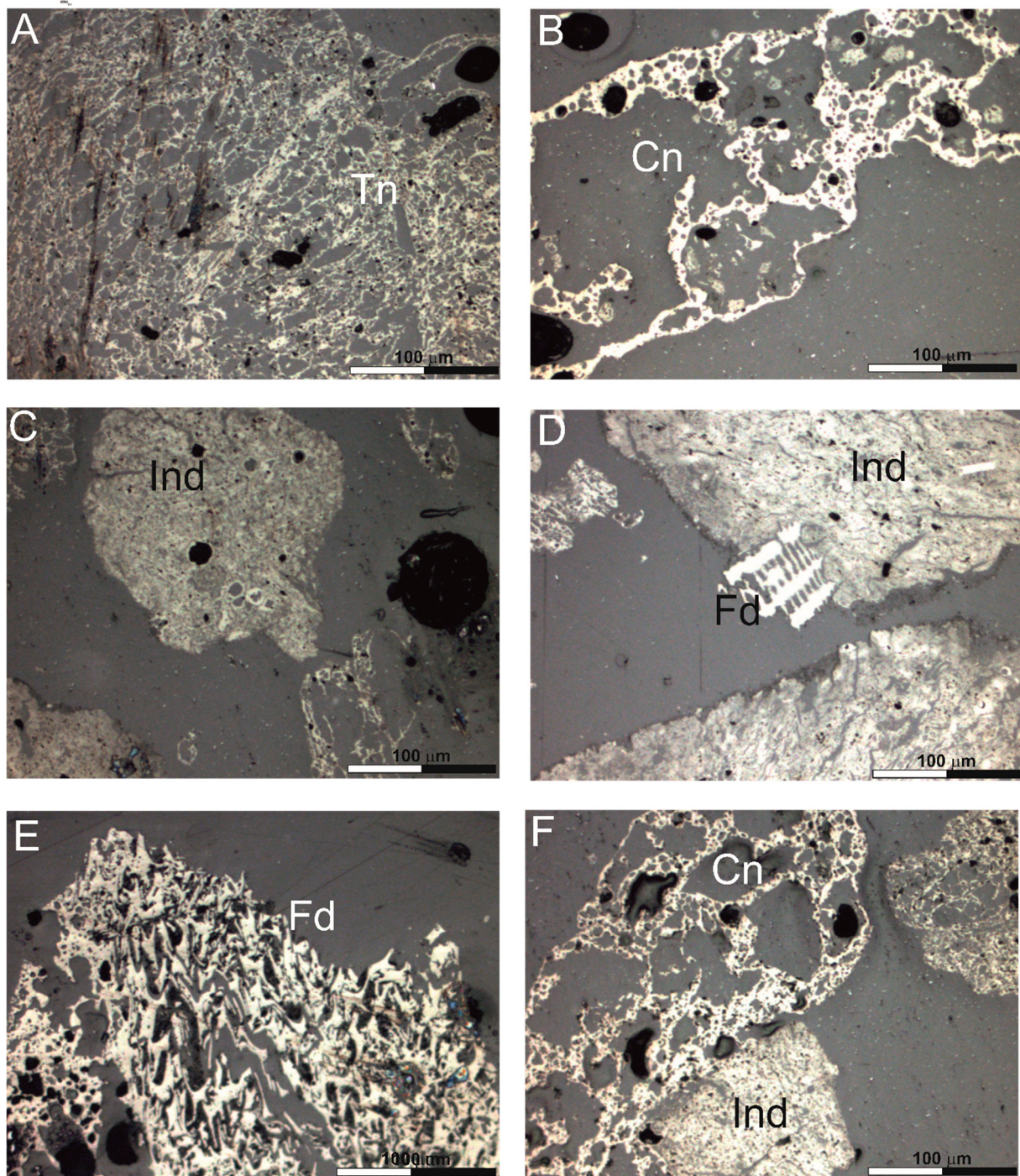
In tenuisphere chars over 50% of wall area is below  $3\ \mu\text{m}$ , for crassisphere chars over 50% of wall area is below  $3\ \mu\text{m}$ . The share of fusinoid, which is characterized by inherited cellular fusinite structure, or solid particle with  $<5\%$  porosity, in the tested chars is 1.70% vol., (Figure 1D,E). The inertinite group macerals almost do not change during the gasification process.

Gasification produces char that contains mineral matter. These are products of the thermal decomposition of the original mineral matter. The minerals in lignite are dominated by quartz and clay minerals (Table 2). The output coal from the “Szczerców” deposit also contains calcite and, to some extent, aragonite. Calcite, occurring in the form of lacustrine chalk in deposits, forms layers and spherical aggregates in the seam. Pyrite occurs as framboidal pyrite, but also as regular crystals and in the form of veins. The process produces loose, glassy or crystalline mixtures of silicates and aluminosilicates, and small amounts of complex mixtures of metal oxides and metalloids. Some minerals, such as pyrite, quartz, dolomite, and siderite, retain their original form during gasification. Clay minerals are also present in inertoids.

#### 3.2. Raman Spectroscopy of the Char Morphotypes

The Raman spectra of the studied morphotypes (Figure 2) show the occurrence of five bands: D2, G, D3, D1, and D4 (Figure 3). The G band ( $\sim 1585\ \text{cm}^{-1}$ ) corresponds to the graphitic lattice vibration ( $E_{2g}$  mode) or aromatic ring breathing [34,63,64]. The D2 band ( $\sim 1612\ \text{cm}^{-1}$ ) makes a shoulder on the G band, and it is also assigned to the  $E_{2g}$  mode [65,66]. Its intensity decreases with increasing degree of organization [67]. The D3 band ( $\sim 1510\text{--}1525\ \text{cm}^{-1}$ ) originates due to interstitial defects outside the plane of aromatic layers [68,69]. It is attributed to the occurrence of small aromatic systems composed of 3–5 rings, organic molecules or functional groups forming “amorphous” carbon phase [59,66,70]. Sometimes two [48] or three [34] bands are detected within the

D3 band region. The D1 band ( $\sim 1340\text{ cm}^{-1}$ ) is related to vibration mode  $A_{1g}$  of graphitic lattice and assigned to in-plane defects, and the occurrence of heteroatoms [62,63,68,69] as well as aromatics with six or more fused rings [34]. The D4 band ( $\sim 1180\text{--}1200\text{ cm}^{-1}$ ) is attributed to  $sp^3$  or  $sp^2\text{--}sp^3$  carbons such as alkyl-aryl C–C structures, which have been suggested as the location of active sites [33,34,59,71–73]. Such sites are mostly positioned at the edges of aromatic structures [72–74]. Three bands within the D4 band region were also proposed [34]. The extracted spectral parameters are given in Tables 6 and 7.



**Figure 1.** Char morphotypes: (A)—tenuinetwork, (B)—crassinetwork, (C)—inertoid, (D)—inertoid and fusinoid, (E)—fusinoid, (F)—crassinetwork and inertoid. Explanations: Tn—tenuinetwork, Cn—crassinetwork, Ind—inertoid, Fd—fusinoid.

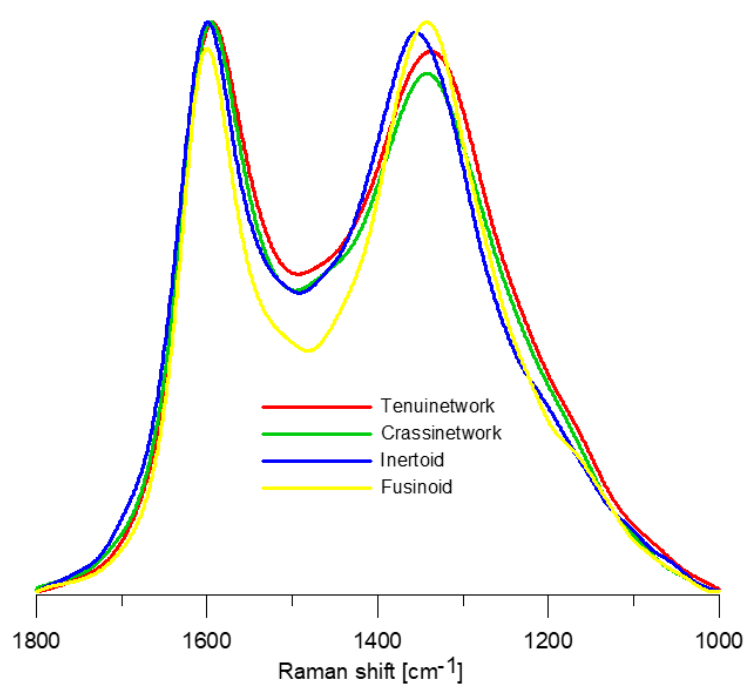


Figure 2. Representative Raman spectra of the investigated morphotypes.

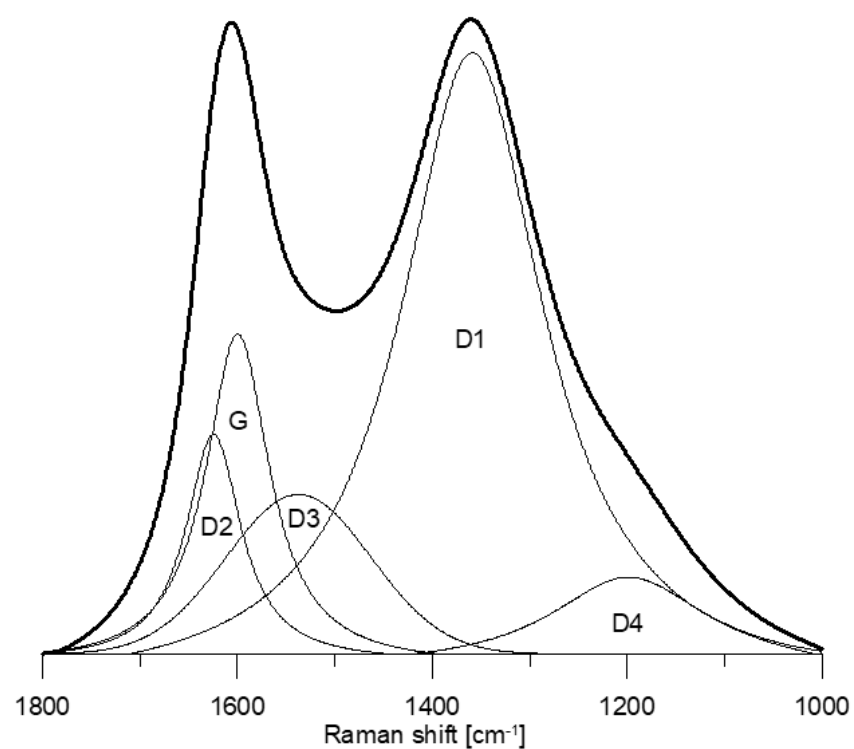


Figure 3. Curve-fitting of a representative inertoid spectrum.

**Table 6.** Position and full width at half maximum (FWHM) of the Raman bands in the spectra of the studied morphotypes.

| Morphotype | D2<br>$\omega$<br>[cm <sup>-1</sup> ] | G<br>$\omega$<br>[cm <sup>-1</sup> ] | G<br>FWHM<br>[cm <sup>-1</sup> ] | D3<br>$\omega$<br>[cm <sup>-1</sup> ] | D1<br>$\omega$<br>[cm <sup>-1</sup> ] | D1<br>FWHM<br>[cm <sup>-1</sup> ] | D4<br>$\omega$<br>[cm <sup>-1</sup> ] |
|------------|---------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|---------------------------------------|-----------------------------------|---------------------------------------|
| Tn         | 1611.4<br>(2.2)                       | 1584.6<br>(2.8)                      | 79.3<br>(5.5)                    | 1510.6<br>(11.1)                      | 1340.4<br>(2.7)                       | 200.3<br>(11.6)                   | 1200.3<br>(12.0)                      |
| Cn         | 1612.2<br>(2.2)                       | 1585.9<br>(3.4)                      | 80.2<br>(5.8)                    | 1509.9<br>(15.0)                      | 1344.3<br>(2.7)                       | 201.2<br>(8.2)                    | 1202.4<br>(10.5)                      |
| Ind        | 1612.3<br>(1.9)                       | 1585.8<br>(3.3)                      | 75.0<br>(4.5)                    | 1523.4<br>(7.8)                       | 1341.3<br>(3.8)                       | 207.9<br>(11.3)                   | 1188.3<br>(9.0)                       |
| Fd         | 1613.6<br>(1.1)                       | 1588.4<br>(1.7)                      | 71.3<br>(4.0)                    | 1525.1<br>(6.5)                       | 1341.1<br>(1.1)                       | 195.1<br>(10.9)                   | 1179.8<br>(7.9)                       |

Explanations:  $\omega$ —position of the Raman band, FWHM—full width at half maximum; the standard deviation is given in the brackets.

**Table 7.** Raman spectral ratios for the studied morphotypes.

| Morphotype | I <sub>D1</sub> /I <sub>G</sub> | A <sub>D3</sub> /A <sub>ALL</sub> | A <sub>D1</sub> /A <sub>ALL</sub> | A <sub>D4</sub> /A <sub>ALL</sub> |
|------------|---------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Tn         | 1.83<br>(0.21)                  | 0.09<br>(0.02)                    | 0.58<br>(0.05)                    | 0.09<br>(0.03)                    |
| Cn         | 1.85<br>(0.26)                  | 0.10<br>(0.02)                    | 0.56<br>(0.05)                    | 0.10<br>(0.03)                    |
| Ind        | 2.08<br>(0.18)                  | 0.10<br>(0.01)                    | 0.64<br>(0.04)                    | 0.04<br>(0.03)                    |
| Fd         | 1.99<br>(0.12)                  | 0.09<br>(0.01)                    | 0.64<br>(0.02)                    | 0.05<br>(0.01)                    |

Explanations: I<sub>D1</sub>/I<sub>G</sub>—relative intensity (height) of the D1 and G bands; A<sub>X</sub>/A<sub>ALL</sub>—the relative intensity of the band (D3, D1, or D4) and the sum of intensities of all bands (D2, G, D3, D1, and D4); the standard deviation is given in the brackets.

The spectra, taking the occurrence of the D3 and D4 bands, and overlapping D2 and G bands, are typical for poorly organized carbonaceous material (“crystallinity” level 1 [75]).

To assess the significance of the differences in the spectral parameters between the morphotypes, the statistical analysis was performed. The Shapiro–Wilk test demonstrates that all sets of results obtained for the G band position and FWHM, D1 band FWHM, and I<sub>D1</sub>/I<sub>G</sub>, A<sub>D1</sub>/A<sub>ALL</sub> and A<sub>D4</sub>/A<sub>ALL</sub> ratios, for the morphotypes analyzed (tenuinetwork, crassinetwork, inertoid and fusinoid) have normal distribution, and the Levene test shows that variances are equal. Considering this, the ANOVA analysis of variance was conducted. It indicates that in all six sets of the above mentioned spectral parameters at least one mean value significantly differs from the others. This was checked by the Tukey’s HSD multiple comparison test, results of which are summarized in Tables 8–12.

**Table 8.** Results of the Tukey’s HSD multiple comparison test for the G band position.

| Morphotype    | G Band Position |                |                |                |
|---------------|-----------------|----------------|----------------|----------------|
|               | Fusinoid        | Inertoid       | Tenuinetwork   | Crassinetwork  |
| Fusinoid      |                 | <u>0.02234</u> | <u>0.00042</u> | <u>0.03551</u> |
| Inertoid      |                 |                | 0.48539        | 0.99801        |
| Tenuinetwork  |                 |                |                | 0.14469        |
| Crassinetwork |                 |                |                |                |

Note: Significant differences ( $p < 0.05$ ) are underlined.

**Table 9.** Results of the Tukey's HSD multiple comparison test for the G band FWHM.

| Morphotype    | G Band FWHM |          |                |                |
|---------------|-------------|----------|----------------|----------------|
|               | Fusinoid    | Inertoid | Tenuinetwork   | Crassinetwork  |
| Fusinoid      |             | 0.07111  | <u>0.00014</u> | <u>0.00014</u> |
| Inertoid      |             |          | <u>0.01064</u> | <u>0.00229</u> |
| Tenuinetwork  |             |          |                | 0.92636        |
| Crassinetwork |             |          |                |                |

Note: Significant differences ( $p < 0.05$ ) are underlined.

**Table 10.** Results of the Tukey's HSD multiple comparison test for the  $I_{D1}/I_G$  ratio.

| Morphotype    | $I_{D1}/I_G$ Ratio |          |                |                |
|---------------|--------------------|----------|----------------|----------------|
|               | Fusinoid           | Inertoid | Tenuinetwork   | Crassinetwork  |
| Fusinoid      |                    | 0.49077  | <u>0.02942</u> | 0.07602        |
| Inertoid      |                    |          | <u>0.00021</u> | <u>0.00073</u> |
| Tenuinetwork  |                    |          |                | 0.97940        |
| Crassinetwork |                    |          |                |                |

Note: Significant differences ( $p < 0.05$ ) are underlined.

**Table 11.** Results of the Tukey's HSD multiple comparison test for the  $A_{D1}/A_{ALL}$  ratio.

| Morphotype    | $A_{D1}/A_{ALL}$ Ratio |          |                |                |
|---------------|------------------------|----------|----------------|----------------|
|               | Fusinoid               | Inertoid | Tenuinetwork   | Crassinetwork  |
| Fusinoid      |                        | 0.99982  | <u>0.00015</u> | <u>0.00014</u> |
| Inertoid      |                        |          | <u>0.00014</u> | <u>0.00014</u> |
| Tenuinetwork  |                        |          |                | 0.39791        |
| Crassinetwork |                        |          |                |                |

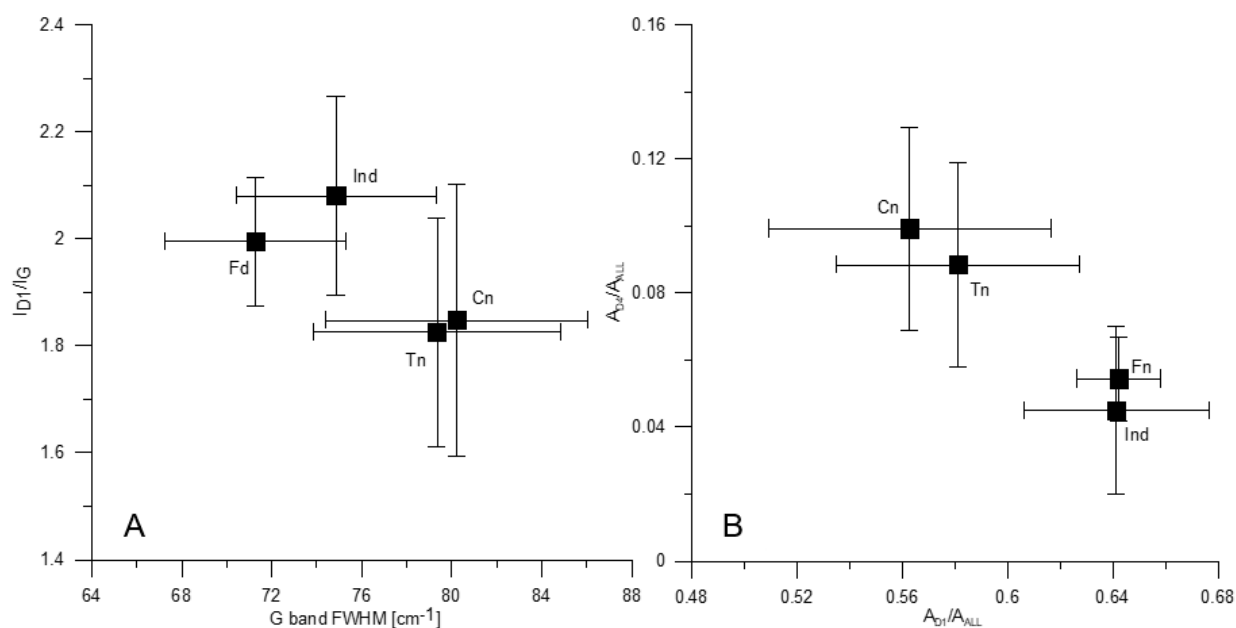
Note: Significant differences ( $p < 0.05$ ) are underlined.

**Table 12.** Results of the Tukey's HSD multiple comparison test for the  $A_{D4}/A_{ALL}$  ratio.

| Morphotype    | $A_{D4}/A_{ALL}$ Ratio |          |                |                |
|---------------|------------------------|----------|----------------|----------------|
|               | Fusinoid               | Inertoid | Tenuinetwork   | Crassinetwork  |
| Fusinoid      |                        | 0.62918  | <u>0.00031</u> | <u>0.00014</u> |
| Inertoid      |                        |          | <u>0.00014</u> | <u>0.00014</u> |
| Tenuinetwork  |                        |          |                | 0.47441        |
| Crassinetwork |                        |          |                |                |

Note: Significant differences ( $p < 0.05$ ) are underlined.

The G band position in the spectra of the tested morphotypes falls in a narrow range of 1585–1588  $\text{cm}^{-1}$  (Table 6). The mean value is highest for fusinoid and differs significantly compared to the other components (Table 8). The FWHM of the G band is smaller in fusinoid (ca. 71  $\text{cm}^{-1}$ ) and inertoid (ca. 75  $\text{cm}^{-1}$ ) spectra than those of tenuinetwork and crassinetwork (ca. 79  $\text{cm}^{-1}$  and 80  $\text{cm}^{-1}$ , respectively) (Tables 6 and 9, Figure 4A), which indicates higher structural ordering of the first pair of the morphotypes [67]. Similar G band half-width as determined herein for fusinoid and inertoid was previously found in the spectra of chars from low rank coals [48], inertinite-rich coals [27,33], and inertinite concentrate chars [61,76]. Similar to what is observed in this study, lower G band FWHM in the spectra of fusinoid and dense char (inertinite-derived) than the fused char (vitrinite-derived) was communicated [27,48].



**Figure 4.** The full width at half maximum (FWHM) of the G band vs.  $I_{D1}/I_G$  ratio (A) and the  $A_{D1}/A_{ALL}$  vs.  $A_{D4}/A_{ALL}$  ratio (B) for the tested morphotypes. Explanations as in Figure 1.

The D1 peak is centered at  $1340\text{--}1344\text{ cm}^{-1}$ , and its FWHM ranges from  $195\text{ cm}^{-1}$  to  $208\text{ cm}^{-1}$  (Table 6), which means that the size distribution of aromatic clusters does not differ much between the morphotypes studied [77]. In fusinoid, however, it is less varied than in inertoid (lower D1 band half-width), as the Tukey's HSD test confirms ( $p < 0.05$ ). Compared to this study, lower D1 band FWHM values (ca.  $160\text{--}170\text{ cm}^{-1}$ ) were found both for the vitrinite-derived and inertinite-derived chars [27]. On the other hand, higher values were communicated for the bituminous coal chars [33]. The RBS value (i.e., the distance between the G and D1 peak) is highest in the case of fusinoid ( $247\text{ cm}^{-1}$ ).

The  $I_{D1}/I_G$  ratio is higher in the inertoid than in the tenuinetwork and crassinetwork spectra (Tables 7 and 10, Figure 4A). The fusinoid spectra reveal higher  $I_{D1}/I_G$  ratio than those of tenuinetwork (Tables 7 and 10, Figure 4A). As previously discussed [77–80], when the diameter of coherent domains (“crystallites”) ( $L_a$ ) in carbonaceous materials is below 2 nm, increase in  $L_a$  corresponds to increasing  $I_{D1}/I_G$  ratio, contrary to the equation introduced by Tuinstra and Koenig [63]. When domains are larger than 2 nm, the increase in  $L_a$  is reflected by the decreasing  $I_{D1}/I_G$  ratio value. The studied char was obtained at  $850\text{--}950\text{ }^\circ\text{C}$ . As it is known from numerous studies, the size of coherent domains in chars and similar carbonaceous materials, formed at approximately the same temperature, does not exceed 2 nm [81–87]. Therefore, the higher value of the ratio is indicative for morphotypes with a larger  $L_a$ . An increase in  $I_{D1}/I_G$  ratio of various carbonaceous materials with temperature increasing up to  $900^\circ$ , and its subsequent decrease at higher temperature was previously observed [27,33,34,41,48,61,73,76,78–80,88,89]. This change was directly correlated with an increase in  $L_a$  [76,80]. The increase in the size of coherent domains results mainly from the dehydrogenation of hydroaromatics [34]. A higher  $I_{D1}/I_G$  ratio was found for fusinoid [48] and the inertinite-derived char [27] than for the vitrinite-derived char [27,48].

The higher  $A_{D1}/A_{ALL}$  ratio for fusinoid and inertoid (Tables 7 and 11, Figure 4B) indicates that they are more abundant in larger aromatic structures (composed of at least 6 aromatic rings) than tenuinetwork and crassinetwork. On the other hand, lower  $A_{D4}/A_{ALL}$  ratio in fusinoid and inertoid spectra (Tables 7 and 12, Figure 4B) shows that  $sp^3$  or  $sp^2\text{--}sp^3$  bonding (active sites) is less frequent in these components than in the other two. This is because concentration of active sites decreases as the size of coherent domains increases [27,42,74]. The content of small aromatic units (3–5 rings) and amorphous carbon

does not vary between the morphotypes, as it can be concluded from the  $A_{D3}/A_{ALL}$  ratio values (Table 7).

Considering the above findings, morphotypes tested can be divided into two groups. The first includes inertoid and fusinoid, and the second comprises tenuinetwork and crassinetwork. In general, these two groups differ by the G band FWHM, and the  $I_{D1}/I_G$ ,  $A_{D1}/A_{ALL}$  and  $A_{D4}/A_{ALL}$  ratios (Tables 6–12, Figure 4A,B). Inertoid and fusinoid and are composed of larger aromatic structures, forming larger coherent domains, with lower amount of alkyl-aryl structures. Their microstructure is better organized compared to the network morphotypes. Raman characteristics of the morphotypes within each pair do not differ significantly. The fusinoid spectra compared to those of inertoid are distinguished by the G band peak positioned at higher values. The highest standard deviations of most spectral parameters found for crassinetwork (Tables 6 and 7) indicate that it is the most heterogeneous of all morphotypes examined.

Tenuinetwork, which has the highest porosity (>70%, [26]) of all morphotypes tested, accounts for 12.64% vol. (Table 5) of the char, and it is mainly derived from textinite (11.70% vol.) (Table 2). Textinite is a porous maceral, which contains varied amounts of humins, cellulose, and lignin as well as resins and waxes, depending on a variety (textinite A or B) [29,90,91]. During gasification it acts as a reactive component and produces substantial amounts of tar and gas, while its porosity increases [16]. Textinite belongs to the macerals, which are most heavily altered [31] but its primary cellular structure is frequently preserved [29]. Therefore, mostly thin-walled network (i.e., tenuinetwork) comes into being.

Crassinetwork constitutes 31.59% vol. (Table 5) of the char, and its porosity varies between 40% and 70% [26], whereas inertoid accounts for 35.44% vol., and its porosity is below 40%. Given the petrographic composition of the parent coal and the char (Tables 2 and 5), and the chemical properties of lignite constituents, the explanation of the origin of these two morphotypes leads primarily to the other macerals of the huminite group, which are: attrinite (29.90% vol.), and densinite and ulminite, which together comprise 36% vol. of the char (Table 2). Attrinite, densinite, and ulminite, which are the main components of the parent coal, differ by their content of small aromatic units (3–5 rings), amorphous phase and  $sp^2$ – $sp^3$ -bonded carbon, increasing from attrinite to ulminite [49]. These differences are related to the degree of gelification, as aromaticity increases with increasing gelification [90,92–94]. They may also result from different origin of the plant material, as attrinite may come from the soft tissues (i.e., cellulose-rich), while ulminite—from the lignin-rich (and though more aromatic) xylem [95]. Attrinite, due to its low aromaticity, is the most reactive of these three macerals. Moreover, it is often accompanied by various liptinite macerals, such as resinite or sporinite, which are abundant in aliphatic hydrocarbons, further increasing its reactivity [96]. Lignite chars obtained at 500 °C contain cavities resulting from complete decomposition of liptinite group macerals, whose shapes are similar to the morphology of these macerals [24]. Such cavities retain their shape even after heating at 950 °C [24]. These are the reasons for the formation of still very porous but a thick-walled network (i.e., crassinetwork) from attrinite. Densinite, and, especially, ulminite are more abundant in small aromatic systems [49]. They are also less porous, which makes the process of gasification more difficult, even though they are richer in active sites than attrinite [49]. Technological properties of the former maceral depend on the degree of homogenization and gelification, and worsen as gelification increases [97,98]. Densinite does not have coking properties. Ulminite produces greater amount of char than textinite during carbonization [97,98]. It accounts for the largest part of unchanged macerals during gasification [31]. Moreover, ulminite does not change its shape, and its porosity does not increase substantially [29]. This explains the transformation of densinite and ulminite into inertoid. It is usually observed that dense chars are produced from inertinite-rich coals [27,89,98]. However, inertinite content (deducting fusinite, which contributes to the formation of fusinoid) is about 2% vol., being incomparably lower than inertinoid content in the char (ca. 35% vol.). This indicates that the other macerals must have played a significant

role in the formation of inertoid, with inertodetrinite (1.80% vol.) (Table 2) making only a minor contribution.

Morphotypes constituting the studied char are typical products of lignite gasification, as lignite usually generates network-type to solid char structure [31,89]. Morphology of the chars derived from the low rank coals closely reflects coal maceral composition [24]. This results from the limited thermoplasticity of such coals. An increase in heating temperature increases the proportion of the more reacted network-type morphotypes due to further chemical-structural changes [23,24,89,99].

Compared to the corresponding macerals from the parent coal [49], the huminite-derived char morphotypes are characterized by a higher content of large aromatic systems ( $\geq 6$  fused rings), and the occurrence of larger coherent domains (higher  $I_{D1}/I_G$  ratio). The amount of small aromatics and amorphous carbon decreased. Regarding various types of chars (bulk samples), such changes were previously reported [14,27,33,34,42,43]. Crassinetwork and tenuinetwork are still rich in alkyl-aryl C-C structures that are not easily removed [34].

Fusinoid (1.79%), porosity of which is below 5% [26] emerges mainly from fusinite (1.0%). Alteration of chemical structure of fusinite requires high activation energy and has more limited range, which reflects inert nature of this maceral, resulting from highly cross-linked structure and low content of mobile phase [61,74,76,100]. However, in comparison to the fusinite in the parent coal [49], the content of large aromatic systems in fusinoid increased, and the amount of amorphous carbons and small aromatics decreased. The  $sp^2$ – $sp^3$  bonds in fusinoid are scarce and therefore concentration of active sites is low, as in inertoid, which is due to the presence of relatively large coherent domains, as evidenced by the  $I_{D1}/I_G$  ratio (Tables 7 and 10, Figure 4A). These observations are consistent with the results of previous works on the microstructural alteration of fusinite under heat-treatment [48,61,76].

The Raman characteristics of inertoid and fusinoid are remarkably similar, although these morphotypes differ in morphology and they are derived from macerals having different properties. During gasification, the chemical-structural features of both morphotypes converged. Similar phenomenon was previously observed by Guedes et al. [48] who studied Raman properties of a fused char and fusinoid after heat treatment at 800 °C. In addition, chars generated at 800–1000 °C from inertinite- and vitrinite-rich coals had similar structure, differing mainly in  $L_a$  size, which was larger in the former char [27,42].

#### 4. Conclusions

The studied lignite char is composed mainly of crassinetwork and inertoid, accompanied by tenuinetwork and small amounts of fusinoid. Tenuinetwork originates mostly from textinite, crassinetwork is formed from attrinite, while inertoid results from transformation of strongly gelified macerals such as densinite and ulminite. Similarities in the microstructure of tenuinetwork and crassinetwork as well as inertoid and fusinoid are observed. Inertoid and fusinoid are composed of larger aromatic systems, with lower amount of alkyl-aryl structures, and their microstructure is better organized compared to tenuinetwork and crassinetwork. Inertoid and fusinoid differ in microscopic appearance and were formed from different starting materials, but their microstructural properties converged during gasification. Different morphological features of the network morphotypes (tenuinetwork, crassinetwork) are not reflected in the differences in their microstructural characteristics.

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