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A Predictive Model for the Anisotropy Index of Semi-Coke Derived from the Properties of Colombia's Eastern Cordillera Coals

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Abstract

This study developed a theoretical model for the determination of the Coke Anisotropy Quotient (CAQ) of semi-coke from the properties of its precursor coal. This is an useful parameter to define the resistance and reactivity of semi-coke in the blast furnace. For 36 semi-coke samples, a textural analysis was performed alongside a fluidity test to determine the real CAQ. The main textures observed were: isotropic and circular for high volatile bituminous coals (HVB); lenticular and fine ribbons for the medium volatile bituminous coals (MVB); and medium and thick ribbons for the low volatile bituminous coals (LVB). The CAQ varied in a range from 1 to 11. A principal component analysis (PCA) and multiple regression to discriminate the importance of certain coal properties, in determining the CAQ to be recognized and to estimate parameters of the mathematical model. The statistical analysis suggested that CAQ can be best predicted from the fluidity, volatile matter, and Ro of the parent coals. The veracity of this model result was then tested using a second dataset from Poland. This work optimizes the usefulness of standard datasets in the prediction of CAQ's offering a means of quality control that could be implemented in Colombian coke production.

Keywords: Coal; coke anisotropy quotient (CAQ); semi-coke; Principal Component Analysis (PCA); textural component; Colombia Eastern Cordillera.

Modelo predictivo del índice de anisotropía del semicoque a partir de las propiedades de los carbones de la Cordillera Oriental de Colombia

Resumen

En esta investigación se desarrolló un modelo teórico para la determinación del Cociente de Anisotropía del Coque (CAQ) del semicoque a partir de las propiedades de su carbón precursor. El CAQ permite definir la resistencia y la reactividad del semicoque en el alto horno. Usando material residual de las pruebas de fluidez se realizó un análisis textural para determinar el CAQ real sobre 36 muestras de semicoque. Las principales texturas observadas para los carbones bituminosos fueron: isotrópicas y circulares para los de alta volatilidad (HVB); cintas lenticulares y finas para los de media volatilidad (MVB); y cintas medias y gruesas para los de baja volatilidad (LVB). El CAQ varió en un rango de 1 a 11. Análisis de componentes principales (PCA) y regresión múltiple permitieron reconocer la importancia de ciertas propiedades del carbón para determinar el CAQ. El análisis estadístico sugirió que el CAQ puede predecirse mejor a partir de la fluidez, la materia volátil y el Ro de los carbones precursores. Este modelo fue validado a través de la comparación con datos reales de carbones de Polonia. Este trabajo proporciona un medio de control de calidad que podría implementarse en la producción de coque colombiano.

Palabras clave: Carbones; Coeficiente de anisotropía del coque (CAQ); semicoque; componentes texturales; Cordillera Oriental de Colombia.

1 Introduction

Coke is the main product of the thermal treatment (heat flow) of bituminous coals, brought about by the destructive distillation or pyrolysis of organic matter in an oven or in some specific natural geological conditions [1],[2]. As coal is a naturally heterogeneous material, it is necessary to determine its physical-chemical and optical properties to define potential uses and to predict its technological behavior [3],[4]. Coke is used in different industries due to its high calorific value, carbon content, fusible macerals (reactive organic matter), and high degree of purity [5]. Steel manufacturing requires coke with high-quality standards, for example, in order to provide heat, a reducing environment and a permeable agent in the blast furnace during the steel production, coke with a Resistance after Reaction with CO2 (CSR) values $> 65\%$ [5],[6], and a Reactivity Index (CRI) between 20 and 30%, is required [7]. According to [7] these coke quality indexes are dependent on the precursor coal (on 70%), the preparation of the sample and the furnace operating conditions during coke production (the remaining 30%). Given that, in Colombia, the value of coal and coke exports in the second quarter of 2017 contributed 1,549.81 million dollars FOB (Free On Board) to the country's budget, according to the Ministry of Mines and Energy, it is necessary to carry out studies to improve the quality of Colombian coke and so that international standards can be met.

Textural coke analysis is an optical technique used internationally to determine coke quality from the rank, coal type, rheologic properties and blend composition of the parent coals as well as the temperature and time of coalification in the furnace (e.g. [1],[3],[8],[9],[10],[11],[12],[13], among others). The description of the optical textures, defined in the ASTM D5061-19 Standard for metallurgical coke, is based on the shape, size, and optical birefringence and is used to determine the CAQ, an indicator of coke reactivity [14]. The sample preparation and analysis of optic textures, however, is an expensive and long process that could be optimized with the use of a theoretical model. The CAQ is calculated with Equation (1), as proposed by [15], and is commonly used to quantify the relationship between coal rank and coke anisotropy. The CAQ allows a quantitative value to be assigned to qualitative properties determined from the optical description of coke textures. It's an accepted fact that resistance and reactivity of globally-recognized CRI and CSR quality indices which characterize coke behavior in a blast furnace [14],[16]. The description of morphological texture has also allowed the development of predictive models associated with the fibrous index (Wx), from the linear relation between the CSR and the Wx/Ro ratio [13]. Furthermore, previous studies have demonstrated that coke reactivity has an inverse relation with CAQ values, while their resistance has a directly proportional relation [14].

Hower and Lloyd [17] suggest that it is possible to produce semi-coke using the product of the Gieseler plastometry test. They find that flow textured developed in high volatile bituminous coals (HVB), indicating that the temperature and exposure time of heat increases the anisotropy of the semi-coke. Similar optical textures of coke are produced at a temperature of about 500 °C in the plastometer (semi-coke) and could be used to the petrographic description under reflected light [18]. For this reason, we use the plastometry test to determine the rheological properties of coal according to the ASTM D2639 / D2639M-19 Standard (fluidity) (using a Gieseler plastometer) and obtain semi-coke samples. In this test, the coal is subjected to a maximum temperature of 600°C and leaves a solid residue, considered here as semi-coke. The semi-coke material is a viable resource for the purpose of research and development on a laboratory scale given that the conditions required for the observation of optical textures are readily achievable [18],[19]. Currently, there is not enough scientific data on firstly, the optical textures of coke and semi-coke produced from Colombian coals and secondly, on how these textures are related to both the final coke quality and other variables used during the coking process.

This study aimed to develop a predictive mathematical model for the CAQ of semi-coke using the textural characteristics of semi-coke and several physical-chemical variables of its parent coal. The parent coal utilized here is used in blends for coke production in the Eastern Cordillera of Colombia. Our model is defined from the results of a multivariate statistical technique known as a Principal Components Analysis (PCA) and multiple linear regressions. This method generates an Equation to predict CAQ from coal characterization tests by comparing theoretical results with real values obtained from the textural description of semi-coke samples. This provides the first predictive mathematical model for Colombian coke and semi-coke that can be used as a tool for quality control, improving the cost-effectiveness and efficiency of industrial production.

2 Materials and methods

This work comprises an analysis of 36 Colombian unitary coals extracted from central Colombia within different sections of the Eastern Cordillera (6 samples from Norte de Santander, 19 samples from Cundinamarca, and the remaining 11 samples from Boyacá state; Figure 1). These samples were taken predominantly from bituminous coals of the Cretaceous Guaduas and Catatumbo formations, commonly used in the coke production. They were provided by COQUECOL S.A. and due to confidentiality reasons, the exact location of the samples cannot be disclosed, though their approximate locations are given in Figure 1. The unitary coals have been characterized and classified by their rank, according to the volatile matter (dry and mineral-matter free), following the ASTM D388-19a standard.

Before the evaluation of the textural components of the semi-coke samples, the parent unitary coals were characterized to identify the relationship between their texture and the quality of the coals used in coking industries. The tests follow the ASTM standard procedures, including the proximate analysis, total sulfur content, mean reflectance of vitrinite (Ro), maceral composition, and plastometry (fluidity) (Table 1). These tests are conventionally used in the coal and coke industries as they are a quick and cost-effective way to define the technological behavior of these materials. After obtaining the semi-coke, through heating the coal to a temperature of approximately 500°C (i.e. a plastometry test), the specimens were prepared for textural analysis by making a polished probe that can be analyzed with an optical microscope. For the sample preparation, we follow the ASTM D2797 / D2797M-11a standard, except for the crushing process, where instead material was passed through sieve number 6, taking care to preserve the optical textures of the samples.

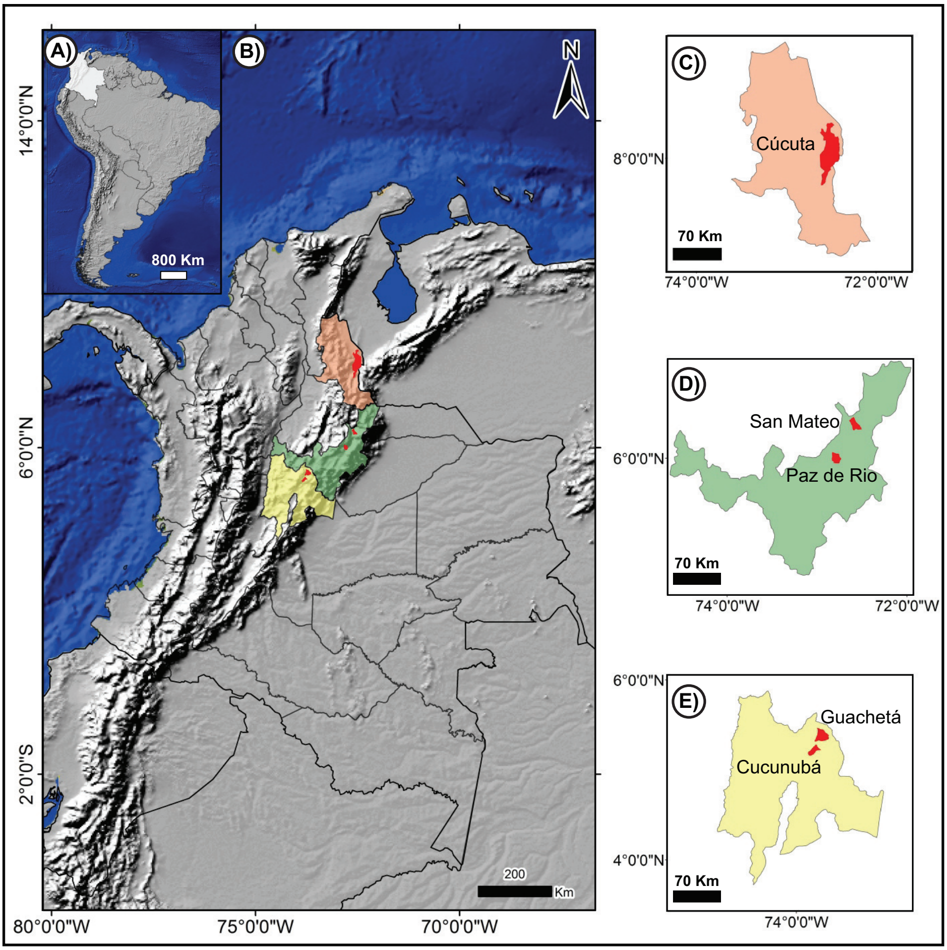

Figure 1: Approximate location of the studied coal samples in the Eastern Cordillera. A) General map of South America highlighting Colombia. B) General map of Colombia with Norte de Santander, Boyacá and Cundinamarca states. C) Norte de Santander, D) Boyacá, E) Cundinamarca; showing the municipalities where coals were extracted.

Table 1: Standard methods used for laboratory testing of coal. A: Proximate analysis + total sulfur (moisture, ash, volatile matter, fixed carbon, total sulfur). B: Samples preparation, estimation of losses due to air drying, crushing, homogenization, quartering, elaboration of polished sections. C: Mean reflectance of vitrinite under a microscope with photometer, identification of coal quality and mixtures quantification by reflectograms. D: Discrimination of the maceral composition of the coal. E: Plastometry of unitary coals in order to determine the fluidity of the coal and semi-coke using the Gieseler plastometer.

Test	Standard reference (ASTM)
A	D3173 / D3173M-17a; D374-12(2018); D3175-20; D3172-13; D4239-18e1
B	D2797/D2797M-11a
C	D2787-20
D	D2799-13
E	D2639/D2639M-19

The textural component analysis of the semi-coke followed the ASTM D506119 standard (1). A microscopic point-count analysis of the textural components was conducted under reflected light conditions using polarized light and a mineral plate to produce interference colors (gypsum plate). A total of 1000 count points were used to calculate the CAQ using the Equation proposed by [15] (Equation (1)). From the description of these textures, i.e. their shape, optical birefringence, and size, the relation between the reactive/non-reactive components of coal and the operating conditions in the furnace during the coke production, can be determined.

$$CAQ = (a + 2b + 3c + 4d + \cdots + nm)/(a + b + c + d + \cdots + m) \qquad (1)$$

In this equation: a, b, c, d,. . . , nm represent, in percentages, the observed coke textures. a: isotropic, b: incipiently anisotropic, c, d, and e: anisotropic textures in fine, medium, and coarse circular. f, g, h: anisotropic textures in fine, medium, and coarse lenticular shapes, and i, j, k anisotropic texture in fine, medium, and coarse ribbons, respectively, thus transferring qualitative optical characteristics to a single quantitative value.

We applied the PCA, this statistical technique allow us to reduce the dimensionality of the input dataset using the information contained in their respective covariance or correlation matrix [20]. Thus, is possible to identify the dominant parameters that produce the most variance within the dataset. This allows to generate a new system of coordinates generated through linear transformations applied on the original dataset. In this new system, the largest variance (or total variance) is resolved by the first, second-third component and so on [21]. The PCA let us to reduce the number of dimensions of a high-dimensional dataset where the variance of the original dataset is preserved. Components derived from the PCA are useful to detect input variables that exhibit more relations with the variable to be calculated. These input variables are used as predictors using multiple linear regression methods. Thus, finally the PCA was carried out using R programming language [22] on the physical-chemical properties of the precursory coal (Table 2): residual moisture (Mr), ash content (A), sulfur (S), volatile matter (Vm), mean reflectance of the vitrinite (Ro), log(fluidity), and the CAQ defined with the textural description.

This method has been successfully used to define geological factors related to environmental pollution [23], depositional environments and sediment supply [20], improvement of accuracy in geodetic data [24], and geochemical prospection [25]. However, for Colombian coals and cokes is the first time that this methodology is applied. Scatterplot matrix and/or correlograms are useful to show variables highly correlated with the CAQ including Volatile matter, fixed carbon, log(fluidity) and Ro. The presence of these highly correlated variables is technically called multicollinearity and it can cause problems in the estimation of the coefficients, residuals and predictions of the multiple linear regression model.

According [26], the previously mentioned problems in the multiple linear regression approach can be solved using the PCA. The goal of this last is to define a new set of variables from linear combinations of the original set such that the variance of the original set is preserved and the correlation between the new variables is minimized [21]. Computationally, the PCA defines the new set of variables using the eigenvectors and eigenvalues of the spectral decomposition of the covariance matrix of the original dataset [21].

Table 2: Percentage ranges derived from coal characterization and real CAQ for semi-coke. M: moisture, A: ash, Vm: volatile matter, C: fixed carbon, S: total sulfur, Fm: maximum fluidity, DDPM: dial revolutions, Ro: reflectance of vitrinite, R: reactive macerals, NR: non-reactive, CAQ: quotient of anisotropy, AD: as determined basis, D: dry basis, Dmmf: dry mineral matter free basis.

Code	M(AD)	A(D)	Vm(Dmmf)	C(D)	S(D)	Fm(DDPM)	log(Fm)	Ro	R	NR	CAQ
101	0.55	2.67	18.61	78.9	0.47	41	1.61	1.64	76.65	23.35	10.13
201	0.47	6.46	22.15	72.22	0.72	41	1.61	1.47	72.94	27.06	9.21
102	0.48	7.05	24.61	69.5	0.55	1334	3.13	1.3	74.22	25.78	8.54
103	0.65	9.32	36.32	57.03	1.18	43998	4.64	0.89	65.28	34.72	4.87
104	0.75	4.69	23.31	72.69	0.46	518	2.71	1.46	71.61	28.39	8.17
105	0.8	10.44	27.86	63.89	0.51	21443	4.33	1.29	71.2	28.8	8
106	1.22	3.71	26.24	70.69	0.46	2549	3.41	1.31	68.32	31.68	7.1
107	1.15	5.2	33.69	62.49	0.45	17199	4.24	1	73.76	26.24	6.54
202	0.9	3.56	36.01	61.4	0.66	43757	4.64	0.95	73.52	26.48	6.02
203	0.87	5.81	31.96	63.61	0.7	37702	4.58	1.08	65.34	34.66	7.61
301	0.53	5.94	21.65	73.2	0.44	197	2.29	1.57	72.48	27.52	6.98
302	0.67	8.39	31.48	62.08	0.98	6247	3.8	1.13	77.06	22.94	6.48
204	0.79	5.93	22.56	72.34	0.52	111	2.05	1.37	81.73	18.27	8.95
108	0.79	2.91	32.87	64.91	0.51	19356	4.29	1.03	75.9	24.1	7.66
109	0.83	8.67	36.67	57.21	0.98	35972	4.56	0.94	71.7	28.3	5.25
110	0.85	5.55	37.47	58.66	0.61	21789	4.34	0.88	76.4	23.6	4.52
111	1.03	8.52	20.87	71.71	0.5	193	2.29	1.61	77.6	22.4	8.76
112	0.64	8.68	23.35	69.34	0.46	1097	3.04	1.47	77.4	22.6	9.18
113	0.35	6.8	33.66	61.33	0.63	7246	3.86	0.94	72.5	27.5	4.2
114	0.17	5.74	15.22	79.36	0.54	0	0	1.82	73.5	26.5	10.02
115	0.69	9.99	18.68	72.37	0.58	0	0	1.5	73.0	27.0	10.16
205	0.17	8.05	20.24	72.62	0.73	28	1.45	1.57	72.8	27.2	9.18
206	0.53	8.11	30.97	62.63	1.55	21711	4.34	1.06	81.5	18.5	7.51
207	0.56	6.59	36.47	58.81	0.95	37110	4.57	0.91	76.3	23.7	7
208	0.57	6.97	25.43	68.59	1.4	1398	3.15	1.26	79.5	20.5	7.77
303	1.8	3.58	36.03	61.33	0.84	4133	3.62	0.85	76.6	23.4	4.27
304	1.68	5.91	41.93	54.23	0.79	45031	4.65	0.373	80.2	19.8	2.73
305	2.92	4.11	44.85	52.63	0.45	48588	4.69	0.61	79.8	20.2	1.06
306	1.21	8.05	35.81	58.46	0.72	43769	4.64	0.91	78.5	21.5	5.93
116	0.78	8.09	24.32	68.9	0.65	1133	3.05	1.37	77.6	22.4	7.58
117	1.03	11.31	21.5	68.65	0.91	100	2	1.51	69.5	30.5	9.4
118	0.92	10.47	25.00	66.37	0.54	841	2.92	1.25	79.5	20.5	7.42
119	1.06	9.18	24.4	67.88	0.84	708	2.85	1.31	69.6	30.4	7.13
209	0.99	6.4	25.26	69.38	0.76	357	2.55	1.15	73.8	26.2	7.43
210	0.63	5.81	23.38	71.55	0.94	346	2.54	1.14	75.9	24.1	7.55
211	0.79	6.54	20.64	73.56	0.71	16.00	1.20	1.21	76.65	23.35	9.11

3 Results

3.1 Coal characterization

The studied coals varied from high volatile bituminous (HVB) coals to low volatile bituminous (LVB) coals according to the ASTM D388-19a standard. M contents ranged from 0.17 to 2.92%, A from 2.67 to 11.31%, Vm from 15.22 to 44.85%, C from 52.63 to 79.36%, S from 0.44 to 1.55, log(fluidity) from 0 to 2.29 and Ro from 0.60 to 1.89 (Table 2), which together indicate variations in coal rank. These samples were predominantly composed of macerals of the vitrinite group, with lesser abundances of the inertinite group and the liptinite group (Figures 2A,B). Variations in mineral content were also observed, notably in clay minerals, quartz and pyrite, as is frequent in Colombian Cretaceous coals [27],[28],[29],[30],[31]. The reactive macerals, which are of interest here as they generate the optical textures for defining CAQ, included vitrinite, liptinite, and $\sim 1/3$ of the semifusinite present in the samples (65.28 to 81.73%). The non-reactive components present were inertinite, mineral matter, and the remaining $2/3$ of the semifusinite, which kept its original shape through the coking process (18.27 to 34.72%). The presence of significant amounts of macerals of the inertinite group could be related to the generation of a coke with maximum strength and stability [4], however, the CAQ value depends only on the textures formed from the reactive macerals.

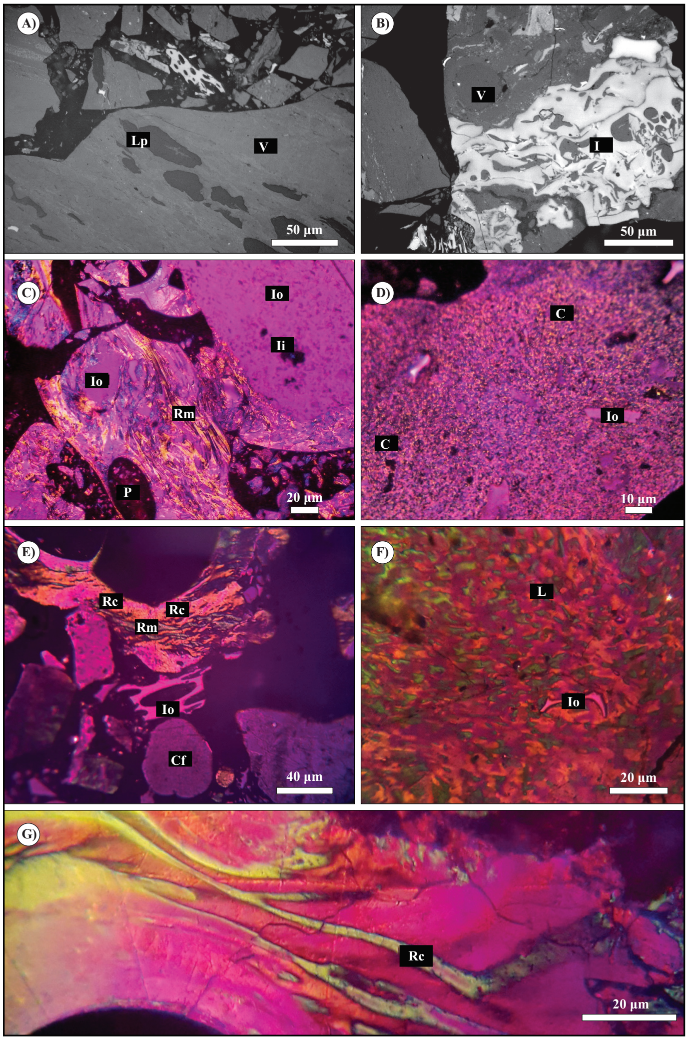

Figure 2: Maceral composition of coal and semi-coke textures. A) HVB coal with macerals of the liptinite group (dark gray) in a vitric matrix (medium gray). B) MVB coal with macerals of the inertinite group (white to light gray). C) Development of isotropic texture, medium ribbons, and pores. D) Fine circular texture. E) Development of medium to coarse ribbons and organic inerts (conserving the original texture from coal). F) Lenticular texture. G) Development of coarse ribbons. V: vitrinite, Lp: liptinite, I: inertinite, C: Circular, Cf: fine circular, Lt: lenticular, Io: organic inert, Ii: inorganic inert, P: pore, Rm: medium ribbon, Rc: coarse ribbon.

Petrographic descriptions are a conventional tool for identifying coal blends and are especially useful for identifying differences between samples with similar physicochemical parameters, such as M, Vm, and A. These parameters have different technological behaviors during the coke production [4]. For the preparation of coal blends, typically low quantities of coke fines, anthracite, and petroleum coke are introduced to improve the final coke resistance [32]. However, in this case, the Ro values and the maceral composition corroborated the presence of unitary coals with a single Gaussian curve in their reflectograms as well as the absence of external material in all coal samples. This highlight that organic petrography is the most reliable technique for defining the coal rank and type.

The mean values for each type of coal are presented in Table 3. It can be noted that across samples, properties related to coal rank have similar values (i.e. Vm, C, fluidity, and Ro), while A, S, reactive, and non-reactive properties show greater variability between samples. This indicates that these latter properties are influenced by the depositional environment of the parent coal and are relatively independent of the coalification process. It therefore evident that CAQ depends predominantly on properties that are indicative of coal rank. Fluidity changes with coal oxidation, however, indicate that the length of time and conditions of parent coal storage can influence the final quality of the coke, modifying the CAQ values and reducing their resistance [33]. The classification results show that there are 8 samples of unitary LVB, 14 samples of MVB, and 14 samples HVB coals.

Table 3: Summary of properties according to the coal classification. M: moisture, A: ash, Vm: volatile matter, C: fixed carbon, S: total sulfur, Ro: reflectance of vitrinite, R: reactive macerals, NR: non-reactive macerals, AD: as determined basis, D: dry basis, Dmmf: dry mineral matter free basis.

Type	M(AD)	A(D)	Vm(Dmmf)	C(D)	S(D)	log(Fm)	Ro	R	NR
LVB	0.17-1.03	2.67-11.31	15.22-21.65	68.65-79.36	0.44-0.91	0-2.29	1.21-1.89	65.34-77.6	22.4-34.66
MVB	0.47-1.22	3.71-10.47	22.15-30.97	62.63-72.69	0.46-1.55	0.46-1.55	1.06-1.46	65.28-79.5	20.5-34.72
HVB	0.35-2.92	2.91-9.32	31.48-44.85	52.63-64.91	0.45-1.18	0.45-1.18	0.60-1.13	68.32-81.73	18.27-31.68

3.2 Semi-coke textures

A number of features were identified through the optical texture analysis of the semi-cokes. Isotropic textures show in the 98.8% of the HVB coals specimens with 44.85% of Vm (Dmmf basis; Figure 2C), whereas fine, medium and coarse circular textures in the 79.5% of the HVB samples with 33.66% of the Vm (Dmmf basis; Figures 2D,E). Fine, medium, and coarse lenticular textures were identified in 94% of the MVB samples with 21.65% of Vm (Dmmf basis; Figure 2F). Fine, medium and coarse ribbon textures exist in 93.3% of the LVB samples, with percentages of Vm of 15.22% (Dmmf basis; Figure 2G). The presence of organic inert reflects the high amounts of macerals of the inertinite group and oxidized vitrinite, however, these components are not related with the development of optical textures and therefore were not taken into account in the anisotropy evaluation [3]. The percentages of each texture allowed the calculation of the CAQ value, where samples of parent coals with low volatile content produced semi-cokes with elongated and fluid ribbon textures (Figures 2E,G), characterized by a CAQ greater than 8.5. Samples from precursor coals with intermediate volatile content produced semi-cokes with interlaced and lenticular textures with a smaller size than the ribbon ones produced for the LVB samples (Figure 2F). In this case, the CAQ values were between 6.5 and 8.5. Finally, parent coals with a high volatile matter content produced semi-cokes with dispersed and isolated circular textures with sizes less than 2 microns. These samples were less anisotropic and had values of CAQ less than 6.5. The observed variation in CAQ, according to the coal rank, is consistent with other studies where increased anisotropy was found in high-rank coals used in coke production. This suggests anisotropy is useful for the characterization of product quality in the coke production line [34].

3.3 Statistical model

The biplot in Figure 3 represents the two-dimensional projection of all samples analyzed, along with a set of arrows representing the contribution of each variable. The length and position of these arrows provide useful information about the correlation and association between the input variables, including the CAQ. A biplot shows two variables, the dots in this plot represent the principal component scores of samples, while the vectors represent the loadings of variables. The further away these vectors are from origin, they have more influence on those components. Vector angles also hint at how variables correlate with one another: a small angle implies positive correlation, a large one suggests negative correlation, and a 90° angle indicates no correlation between two variables.

The correlation between the i-th input variable and the first and second components depends on the proximity of the arrows to the corresponding component axis. The variables associated with the first component are mostly are aligned to the horizontal axis. All tests performed in this study are included as variables in the PCA, except for the maceral composition. The latter variable is excluded because firstly, it is not a conventional analysis in the coking industry and secondly, while it provides information on the proportion of reactive and non-reactive components, is not associated with the capacity for generating textures in semi-cokes during combustion.

From visual inspection of the biplot, the variables related to component 1 are the CAQ, C, Ro, Vm, and log(fluidity); whereas M does not show a clear correlation with the component axes. The importance of M on the CAQ is not very clear, probably owing to the fact that this parameter does not depend exclusively on the coalification process and that some geological factors, such as fracturing, faulting, and migration of groundwater, can also alter this value. The A and S contents are associated with component 2, implying that these variables are not as related to the CAQ. This is likely due to the dependency of this variable on the coal rank [3]. Both S and A content are influenced by the depositional environment of coal and they do not develop optical textures during the coking process.

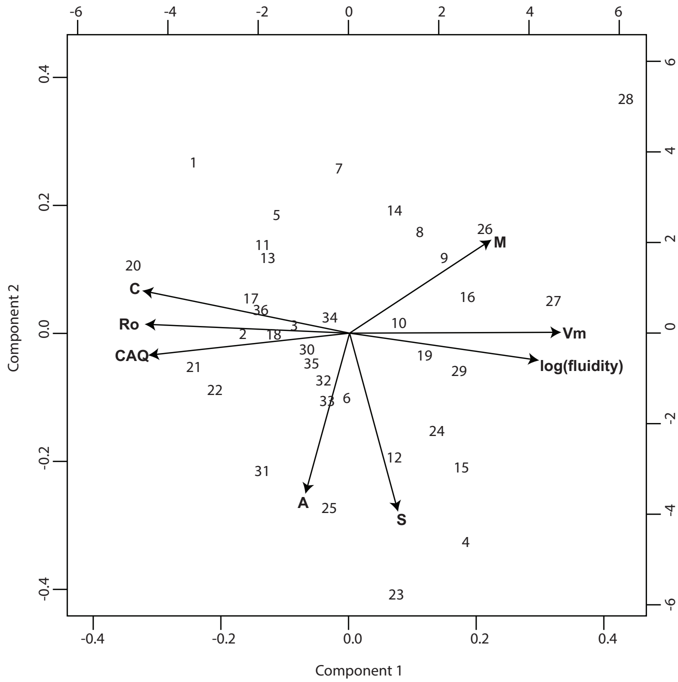

Figure 3: Biplot graph for the PCA of coal properties and semi-coke (CAQ). The data are projected into a coordinate system whereby the horizontal and vertical axes of the biplot are the components that capture the most variation in the data, components 1 and 2, respectively. The length of arrows indicates the importance of that variable for the respective component.

As CAQ is the interest parameter, it is necessary to define which variables will be considered for the formulation of the mathematical model. From the correlogram (Figure 4), it is clear that there is a directly proportional relationship between CAQ and Ro and CAQ and C content, whereas there is a inversely proportional relationship between CAQ and Vm and between CAQ and log(fluidity), suggesting a dependency of CAQ on these variables. The width of the ellipses in the correlogram also show a great degree of dispersion between CAQ versus M, CAQ versus S, and CAQ versus A, indicating a lack of dependence of CAQ on these input variables. The variables that do not show a strong dependency on CAQ are not considered in the mathematical model.

3.4 Mathematical model

Mathematical methods for predicting coke quality have been implemented from coal blend characterization using Gaussian functions [35], additive law [36] and the random forest method [37]. Conclusive findings, however, are not yet available to determine the CAQ employing coal properties. The PCA and the correlogram showed that the Vm, C, log(fluidity), and Ro are parameters that exhibit good correlation with CAQ and, therefore, they should be the variables to consider in the definition of a predictive mathematical model. These findings are in agreement with Morga *et al.* [38], who found the coke micro-raman spectra has a linear relation with the Vm, C and Ro.

The Vm and C are complementary variables that consequently provide the same information about the precursory coal. As such, only Vm data is utilized in the model. This parameter is selected as it is calculated directly from a lab test and does not depend on other parameters (e.g. A, S and M), unlike the C. The correlation values between the Vm and Ro also suggest that these two variables provide similar data about the coal (Figure 4). The Ro, however, is attained from a petrographical analysis and its variation depends only on the organic matter's thermal maturity during coalification. Ro is therefore the more reliable test for coal rank determination and the only method that allows the existence of unitary coals or coal blends to be realized. The same level of accuracy is not attained with Vm as this parameter could also integrate an inorganic volatile product of some mineral phases, due to the high temperatures during the test.

Multiple linear regressions allowed the dependence of CAQ on the parent coal properties to be theoretically modelled (Equation (2)). These properties include Vm, log(fluidity), and Ro. To define this mathematical model, each variable is accompanied by a coefficient that quantifies the importance of every independent variable in the definition of the CAQt (theoretical model, Equation ((2))).

$$CAQ_T = 14.216 - 0.320Vm + 0.490log(fluidity) + 0.389Ro \qquad (2)$$

where CAQ_T is the theoretical CAQ index, Vm is the volatile matter (dry mineral matter free) and Ro is the average reflectance of vitrinite.

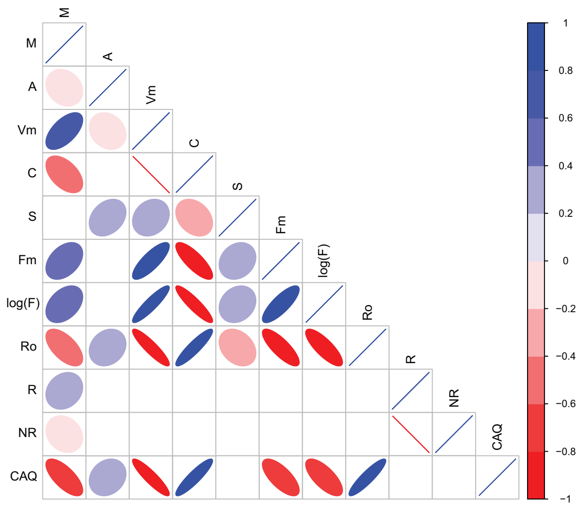

Figure 4: Chart of correlation statistics showing relations among variables.

4 Discussion

This research supported the hypothesis that the formation of the coke optical textures occurs at a temperature as low as 500°C, as proposed by [18]. The optical properties of semi-coke, attained at lower temperatures and shorter heating times in a laboratory, could therefore be equally useful for fluidity analysis in unitary bituminous Colombian coals. Organic petrography is a methodology applied in the coking industry for predicting coke strength and reactivity as well as reconstructing the coal blend, burnt coke, among others [39]. While these experimental findings are important for recognizing the potential of semi-cokes for textural analysis, it should be recognized that some maceral properties only develop in temperatures between 500 and 700 °C, causing some properties, such as Ro, to vary through the heating process [34]. Isotropic and circular textures, however, are already formed at low temperatures, ∼400°C, allowing the CAQ to be determined [40]. This preliminary investigation into the viability of semi-coke as a CAQ indicator is the starting point for further research into methods for optimizing scarce resources in the assessment of coke quality. Furthermore, it opens up the possibility of testing new coke production procedures and optimizing coke quality and coal blending schemes in the lab before moving to an industrial scale [35].

The PCA and the proposed model (Equation (2)), demonstrate that the parent coal variables that influence the development of texture are the Vm, log(fluidity) and Ro. There is statistical evidence that variables such as M, A and S, do not affect the development of semi-coke textures and do not determine the behavior of the anisotropy index (CAQ). Similarly, the maceral content does not reflect variations in the CAQ as this property is sensitive only to the proportions of reactive and non-reactive macerals, therefore controlling only the quantity of reactions in the furnace but not the type of coke textures that develop. These results most likely indicate that CAQ is dependent on coal properties that relate to the coalification processes (coal rank) [3]. The thermal history of the precursor coals must therefore be the main factor that controls the quality of its derived coke.

A comparison between the theoretical and observed CAQ (Figure 5) demonstrates that the proposed model captures most of the variation in the CAQ dataset, and therefore can be used for predictive purposes. The variation between the theoretical and observed statistical values was not higher than 1, which means the theoretical model fits the data well with a significance of 95%, reflecting the accuracy of this mathematical model.

Due to a confidentially agreement enforced by the private coal and coke companies that supplied the data, a number of factors associated with sample location could not be investigated. These included the tectonic and burial history of the samples, their stratigraphic position and proximity to magmatic activity. Likewise, the storage time of the coal is unknown, generating uncertainty in the degree of oxidation the samples had experienced, which affects the fluidity and optical textures of the produced coke, as demonstrated by [33]. However, this does not detract from the significance of the results in determining coke quality for industrial purposes. The results of [16],[19],[41], and [42], suggest that there is a relationship between the CAQ, the resistance and reactivity indexes of coke and the parent coal, though additional factors could also be considered, such as plasticity tests and the chemical composition of the residual ashes [43].

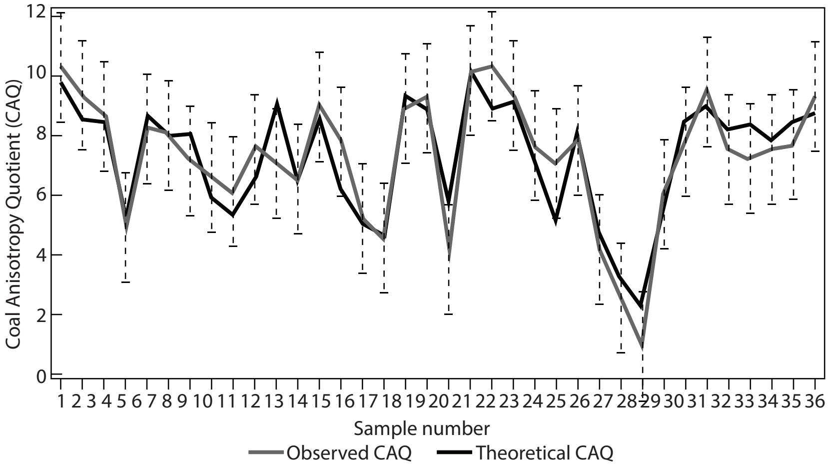

Figure 5: Comparison between observed and theoretical CAQ for the Colombian semi-cokes. The trend indicates that the mathematical model fits the data using a significance level of 95%

In order for a theoretical model to be validated, it needs to be tested against other datasets. A unique dataset of coal characteristics and CAQ values was published by [33]. Originally the data was used by the authors previously mentioned to discriminate anisotropy of coke due to the effect of weathering in 4 samples for three different phases. The information of fresh samples belongs to [33] was used in this study for validating the CAQ model. Figure 6 exhibits the relationship between the observed CAQ for the Polish samples and the CAQ value calculated with the theoretical model from this study. The mathematical model estimates CAQ values for the Polish dataset that are within one standard deviation of their true values. The differences between the modelled CAQ, based on the Colombian dataset, and the observed Polish data could be explained by several factors: e.g. due to differences in coal properties and geological history or due to variations in the operating conditions and weathering during storage. While the model does a good fit at predicting the dataset, there is a possibility for improvement with the addition of new datasets.

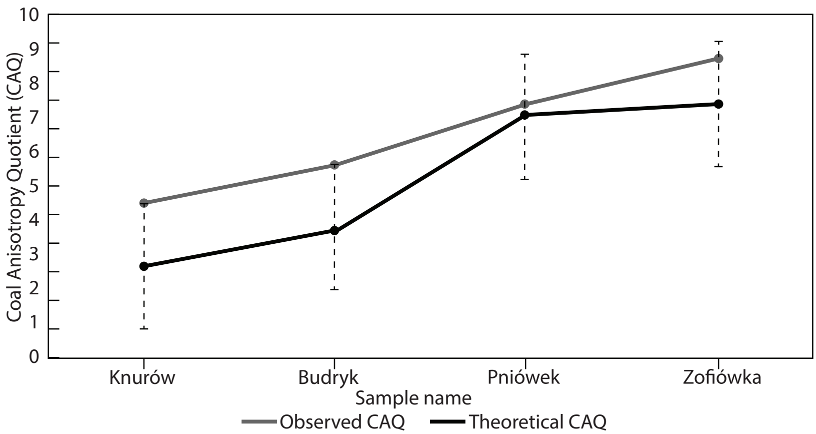

Figure 6: Comparison between observed and theoretical CAQ for Polish cokes. The trend indicates that the mathematical model predicts these data within one standard deviation (vertical line).

5 Conclusions

The residuals of a fluidity test allow us to identify coke optical textures at low-temperature ranges in a controlled laboratory environment [18]. The anisotropy index CAQ, determined from optical textures of coke/semi-coke [15] depend on several physical-chemical properties of the parent coal. Utilizing a methodology for giving quantification to otherwise qualitative data, allows comparison of optical texture with, for example, reactivity and resistance indices. The proposed mathematical predictive model of the CAQt depends on the values of the Vm, log(fluidity), and Ro (Equation (2)); indicating that CAQ depends mainly on the coal rank. The scatter of the CAQ with other parameters such as: M, A, S, and maceral content reflects the minimal significance of these parameters in the formation of the coke and semi-coke textures.

Our results show the success of the CAQ model in fitting the Polish data that indicates the veracity of the model and its more universal application in the coal, coke, and steel industry. This mathematical model was successful in predicting CAQ in a Polish dataset that was not used for model calibration, highlighting the possibility for the model's applicability for coals and semi-cokes in other localities. It is recommended that future works should investigate the properties of industrially-produced coke to determine the anisotropy, resistance and reactivity indexes under different temperature and heating-time conditions so that the textures obtained with coke and semi-coke can be compared and used to corroborate the reliability of this model for industrial use. The work also provides a useful method for determining the relationship between resistance and the anisotropy index, which could be used in the design of the coal blends during the coking process.

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