Effective thermal properties and proximate analysis of coke-coal fines mixtures

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Abstract. We report the effective thermal properties at room temperature and proximate analysis of three mixtures of coke and carbon fines formed by uniaxial pressing at 30 MPa. Using differential scanning calorimetry and thermogravimetry, the thermal behavior of the carbon samples was determined. The KD2 Pro® system was used to measure the effective thermal properties, while the proximate analysis was carried out applying the ASTM D 3172-89 standard. It was found for coke fines that in the range between 40.00 °C and 293.94 °C there is a loss in weight of 3.2%, which corresponds to the degradation of low molecular weight volatiles, another degradation was also observed between 90.07 °C and 336.21 °C, and the maximum devolatilization temperature was 579 °C, finally from 700 °C the melting process begins, which corresponds to the formation of coke. It was also observed that the thermal conductivity increases with increasing coke concentration in the sample, and that the mixture with the highest thermal diffusivity was the one formed with 80% coke fines and 20% carbon fines. According to the thermal properties of the samples can be to be used efficiently as fuel.

1. Introduction
From the industrial revolution between 1760 and 1840, coal became a fuel that allowed industrial and social transformations, giving the global economy a step towards industrialization, inventions such as the steam engine caused a world transformation, allowing the development of humanity. It is estimated that in the future the use of coal is uncertain, and its use will decrease, due to environmental regulations, however, this fuel is one of the primary sources of energy with a participation of 26.5% in the world [1]; for Höök, et al. [2], even though there are large coal reserves in the world, what matters is recoverable coal, which is easy to exploit, transform and supply. According to [3], the use of coal for power generation will continue to increase, especially in developing countries.

The thermal properties of coals were mainly reported during the year 2000 [4], but due to the new technological applications that use this fuel, and especially the heat transfer process, the thermo-physical properties, thermal conductivity (λ), thermal diffusivity (α) and volumetric heat capacity (pc); they are important during pyrolysis and advanced oxidation, as well as in gas recovery, geothermal coal utilization, and underground gasification [5]. Likewise, these thermal properties depend on the type of coal, humidity, temperature, ash, fixed carbon, porosity, and volatile matter present in the sample [6,7], also on the anisotropic orientation in the geological formation of the coal, where it has been reported
that heat is preferentially transported in a direction parallel to the stratification planes, increasing thermal conductivity in this direction [5].

Three main stages are described in the coke manufacturing process, the first between 350 °C and 550 °C in which the volatilization of gases increases, the second that goes up to 700 °C in which the semi-coke appears, and the latter, on average, ends at 1300 °C, where coke is formed [8], and the slaking process begins with water, then it is taken to screening for the selection of the sizes that are commercially demanded. In this process, coke fines appear, which particles with a size are smaller than 5 mm [9], representing approximately 5% of production, which has a low commercial value, and generates additional costs, causing losses in financial operations of the company.

Therefore, and to give added value to coke fines, it is intended to produce briquettes with mixtures of coal fines, formed by uniaxial pressing at 30 MPa, and study their thermal behavior as a function on the proximate analysis.

2. Methodology and materials

Cylindrical briquettes were produced by uniaxial pressing at 30 MPa, for three blends (90%-10%; 80%-20%; 70%-30%) made in weight percentage from mixtures of coke fines and coal fines, where the majority phase is coke. The proximate analyses (moisture, ash, volatile matter, fixed carbon, sulfur, and calorific value) were carried out according to ASTM D3172-89 [10]. The thermal behavior of the coal fines was studied by differential scanning calorimetry (DSC) and thermogravimetry (TGA), while the thermal properties of the briquettes (λ, α, and ρc) were measured using the SH-1 dual sensor of the KD2 Pro® system, which operates on the physical principle of transient linear heat flow. In Figure 1, an image of the SH-1 sensor is presented, as well as an explanatory diagram that allows explaining the physical principle of transient linear heat flow, which according to Xiaoli, et al. [11], when a transient heat flux (Q) in J/m² is applied for a given time (tₜ), and the temperature is measured at a distance (r) during the heating and later in the cooling period, the variation of temperature over time is described by Equation (1).

\[ ΔT = \frac{-Q}{4\pi\lambda} E_1\left(\frac{r^2}{4\alpha t}\right); 0 < t ≤ tₜ, \]

where \( λ \) (W/mK) is the effective thermal conductivity, \( α \) (m²/s) is the thermal diffusivity of the medium, and \( E_1 \) is the exponential integral over time [12].

Figure 1. (a) SH-1 dual sensor, from the KD2 Pro system; (b) diagram explaining linear transient heat flow theory.
It should be noted that for the SH-1 sensor, \( r = 6 \text{ mm} \), which is the separation between the two needles (see Figure 1(b)). The temperatures are then processed by subtracting the ambient temperature, multiplying by \( 4\pi \) and dividing by \( Q \) in Equation (1). The resulting data are fitted using a nonlinear least squares procedure by the following Equation (2) and Equation (3) [13].

\[
T^* = b_0 + b_1 \left( E_i \left( \frac{b_2}{t} \right) - E_i \left( \frac{b_2}{t_{H_{\text{b}}}} \right) \right) \approx b_0 + b_1 E_i \left( \frac{b_2}{t_{H_{\text{b}}}} \right),
\]

\[
T^* = \frac{4\pi(T - T_{\text{a}})}{Q},
\]

where \( b_0, b_1 \) and \( b_2 \) are adjustment parameters, \( T_0 \) is the temperature at the beginning of the measurement and \( Q \) is the heat input. Equation (2) applies during the first few seconds, while heat is applied, and Equation (3) applies when the heat source is turned off or during cooling. The effective thermal conductivity of the medium (sample) is calculated using Equation (4). While thermal diffusivity is determined by Equation (5). On the other hand, once \( \lambda \) and \( \alpha \) are known, the specific heat per unit volume and thermal effusivity \( (\varepsilon) \) are calculated using Equation (6) and Equation (7) [12].

\[
\lambda = \frac{1}{b_1},
\]

\[
\alpha = \frac{r^2}{4b_2},
\]

\[
\rho c = \frac{\lambda}{\alpha},
\]

\[
\varepsilon = \frac{1}{\lambda \alpha^2}.
\]

3. Results and discussion

Figure 2 shows the graph of the DSC-TGA data of the coal fines sample, for the TGA it is observed that between 40.00 °C and 293.94 °C there is an approximate weight loss of 3.2% due to the degradation of the low molecular weight volatile compounds, There is also another degradation of about 90.07% between 336.21 °C and 634.47 °C, on the other hand, a maximum devolatilization temperature was found around 579 °C, and from 700 °C onwards, the melting process occurs, which is associated with the formation of semi-coke [14]. For the DSC, no endothermic peak is observed between 40 °C and 600 °C two exothermic peaks are observed, which are associated with oxidative degradation processes of the volatile matter (\(-35\%\), see Table 1) which were described in the TGA; on the other hand, between 700 °C and 1,110 °C, an endothermic peak occurs, corroborating what was described in the TGA, which is associated with a melting process. It is also observed that the peak is quite wide, possibly indicating very little structural homogeneity of the sample [14].

Table 1 shows the results of the proximate analysis of the coke and coal fines, in which it is observed that the free swelling index (FSI) of the coal fines is within the high coking range classifying it as bituminous [15], which will provide the briquette with a high degree of compaction or union of the particles during agglutination [16]. Likewise, when comparing the values in Table 1 with Table 2, which correspond to the proximate analyses of the briquettes for the three mixtures, M1 (90%-10%), M2 (80%-20%), M3 (70%-30%), as the concentration of coke fines increases humidity increases slightly, while the volatile matter decreases. It can also be seen that the calorific value of the briquettes increases as the concentration of coal fines increases.

The values of the thermal properties at room temperature of the briquettes are presented in Table 3. From these \( \lambda \) increases up to 15% as the concentration of coal fines decreases, reporting the highest
value for M3, which corresponds to the sample with the highest calorific value (see Table 2), which was to be expected since, having the highest concentration of coke fines, it has structurally the highest concentration of graphite crystals [17]. On the other hand, the sample that reported the highest capacity to store or yield energy was M1, which has the highest concentration of coke fines, moisture, and heat exchange capacity ($\varepsilon$). It should be noted that the heat transport phenomenon in the samples is via phonons, which for the samples correspond to the vibrations of the poly-condensed aromatic rings and the aliphatic bridges between them, which allow the continuity of the phonons contributing to the transport of energy [6].

![Figure 2. DSC-TGA data of the coal powder.](image)

**Table 1.** Coke and coal fines proximate analysis.

| Parameters                  | Fines Coke | Coal Fines |
|-----------------------------|------------|------------|
| Moisture (%w/w)             | 12.24      | 8.54       |
| Dry ashes (%w/w)            | 22.98      | 8.04       |
| Volatile matter (%w/w)      | 4.78       | 35.58      |
| Fixed carbon (%w/w)         | 72.24      | 56.38      |
| Free- Swelling Index (FSI)  | -          | 8          |
| Sulfur (%w/w)               | 0.634      | 0.86       |
| Calorific value (Btu)       | 11101      | 14330      |

**Table 2.** Proximate analysis of the briquettes.

| Samples | Moisture (%w/w) | Dry ashes (%w/w) | Volatile matter (%w/w) | Fixed carbon (%w/w) | Calorific value (Btu) |
|---------|-----------------|------------------|------------------------|---------------------|----------------------|
| M1      | 9.07            | 18.6             | 12.05                  | 69.35               | 11496                |
| M2      | 8.35            | 18.8             | 13                     | 68.19               | 11489                |
| M3      | 7.81            | 17.72            | 16.53                  | 65.74               | 11779                |

**Table 3.** Thermal properties at room temperature of the briquettes.

| Samples | $\lambda$ (W/mK) | $\alpha$ (m$^2$/s) x 10$^{-6}$ | $\rho c$ (J/m$^3$K) x 10$^6$ | $\varepsilon$ (W$^{1/2}$/m K$^{1/2}$) |
|---------|------------------|-------------------------------|-------------------------------|--------------------------------------|
| M1      | 0.335 ± 0.011    | 0.202 ± 0.001                 | 1.657 ± 0.030                 | 746.103 ± 4.155                      |
| M2      | 0.310 ± 0.001    | 0.324 ± 0.011                 | 0.956 ± 0.003                 | 545.199 ± 1.503                      |
| M3      | 0.284 ± 0.002    | 0.231 ± 0.015                 | 1.227 ± 0.008                 | 590.259 ± 2.239                      |
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