



Evaluating the gas content of coals and isolated maceral concentrates from the Paleocene Guasare Coalfield, Venezuela

L.A. Berbesi^a, G. Márquez^{b,*}, M. Martínez^a, A. Requena^b

^aInstituto de Ciencias de la Tierra, Central Universidad Central de Venezuela, Caracas, 3895 1010-A, Venezuela

^bDepartamento de Ingeniería Minera, Mecánica y Energética, Universidad de Huelva, Palos de Fra., 21819 Huelva, Spain

ARTICLE INFO

Article history:

Received 25 February 2009

Accepted 13 June 2009

Available online 18 June 2009

Editorial handling by Dr. R. Fuge

ABSTRACT

This work presents the results from evaluating the gases sorbed by coal samples extracted from the Paleocene Guasare Coalfield (Marcelina Formation, northwestern Venezuela), as well as by their distinct maceral concentrates. The aim of this work has been to obtain an initial experimental main value of the gas content per unit weight of high volatile bituminous A coal samples from the open-pit Paso Diablo mine. An additional goal was to study differences in the CH₄ storage ability of the distinct maceral groups forming part of the coal matrix. Both the coal samples and the maceral concentrates were studied by thermogravimetric analysis (TGA) in order to determine the temperature to be used in subsequent experiments. On-line analyses of hydrocarbons (C₁, C₂, C₃) and CO₂ yielded gas concentrations, plus δ¹³C values. Thermogenic gas is prevalent in the Guasare coals with vitrinite reflectance (%R_o) values from 0.65% to 0.88%. The amount of gas retained in the coals and maceral concentrates was measured with a special device that allows determination of the volume of gas sorbed by a solid sample subjected to controlled thermal treatment. The average coalbed gas concentration obtained was 0.51 cm³/g. The following list of maceral concentrates shows the relative capacity for the volume of sorbed gas per unit weight: inertinite > low-density vitrinite > liptinite ≈ high-density vitrinite. It is concluded that the gas volumes retained in the distinct maceral concentrates are not controlled by porosity but rather by their microscopic morphology.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

During the formation and maturation of coal, considerable quantities of hydrocarbons are generated, mainly methane, also called “coalbed methane” or CBM. Due to the high sorption capacity of a microporous solid such as coal, though not always (Petersen, 2006), these hydrocarbons may be retained in the pore network, it being a case where the source rock also acts as a reservoir rock (Behar et al., 1995). Various studies (e.g. Yee et al., 1993) have demonstrated that the CH₄ retention in the coal is primarily due to a reversible process of physical sorption.

The literature commonly contains references to the evaluation of the coalbed-CH₄ potential of several sequences (e.g. Ryan and Dawson, 1995; Drobnik et al., 2004; Langenberg et al., 2006). Coalbed-CH₄ is an unconventional gas whose potential in resources is enormous (Aravena et al., 2003). Coalbed gas comprises mainly CH₄ and CO₂, although it often contains variable amounts of hydrocarbon gases C₂₊ (ethane, propane, butane) and lesser amounts of N₂, H₂S, O₂, H₂ and Ar (Clayton, 1997). The generation

of coalbed gas occurs by both biogenic and thermogenic processes. Biogenic gas is produced from the decomposition of organic matter deposited in peatmarshes by micro-organisms (Whiticar et al., 1986). Thermogenic gas, in contrast, derives from the thermal cracking reactions of organic matter due to an increase in pressure and temperature in sedimentary basins (Tissot and Welte, 1984).

Although most natural gas (CH₄) retained in coal seams is of thermogenic origin, there are some cases in which a significant proportion of the gas may be associated to microbial methanogenesis (Smith and Pallasser, 1996). In fact, it has been proposed that the biogenic gas retained in coal may be generated not only during the early stages of coal formation (diagenesis), but also during the last tens to hundreds of million years (biogenic secondary gas) due to the recharging of meteoric water supplying the necessary nutrients for bacterial growth (Kotarba and Rice, 2001).

The petrographic composition, coal rank, and the type of organic matter are just some of the main factors controlling the type and quantity of gaseous hydrocarbons generated by coal (Gürdal and Yalçın, 2000; Quick and Brill, 2002; Mastalerz et al., 2008). Coalbed gas reservoir exploration and characterization is complex due to the high grade of heterogeneity and spatial variation in maceral

* Corresponding author. Fax: +34 959217325.

E-mail address: gmarmar@us.es (G. Márquez).

composition (Chalmers and Bustin, 2007); in fact, it can vary significantly for coals located in different zones of the same basin or even within the same bed.

The identification, distribution, and evolution of the main macerals generating coalbed CH_4 plays an important role in the accurate evaluation of such properties as the hydrocarbon generation potential of coals and in the study of the generation mechanism of gaseous hydrocarbons from coal (Wei et al., 2007; Liu et al., 2007).

The Guasare Coal Basin in the northwestern sector of Zulia State (northwestern Venezuela) is the most important in the country due to both its size and the quality of its coal resources (Escobar and Martínez, 1993). The Paso Diablo mine is located in the eastern foothills of the Sierra de Perijá in the Guasare Basin, approximately 85 km NW of the city of Maracaibo (Fig. 1).

The coal collected in the mine is from the Marcelina Formation, dated as Paleocene based on palynological evidence (Kuyf et al., 1955) and on its stratigraphic position with respect to the underly-

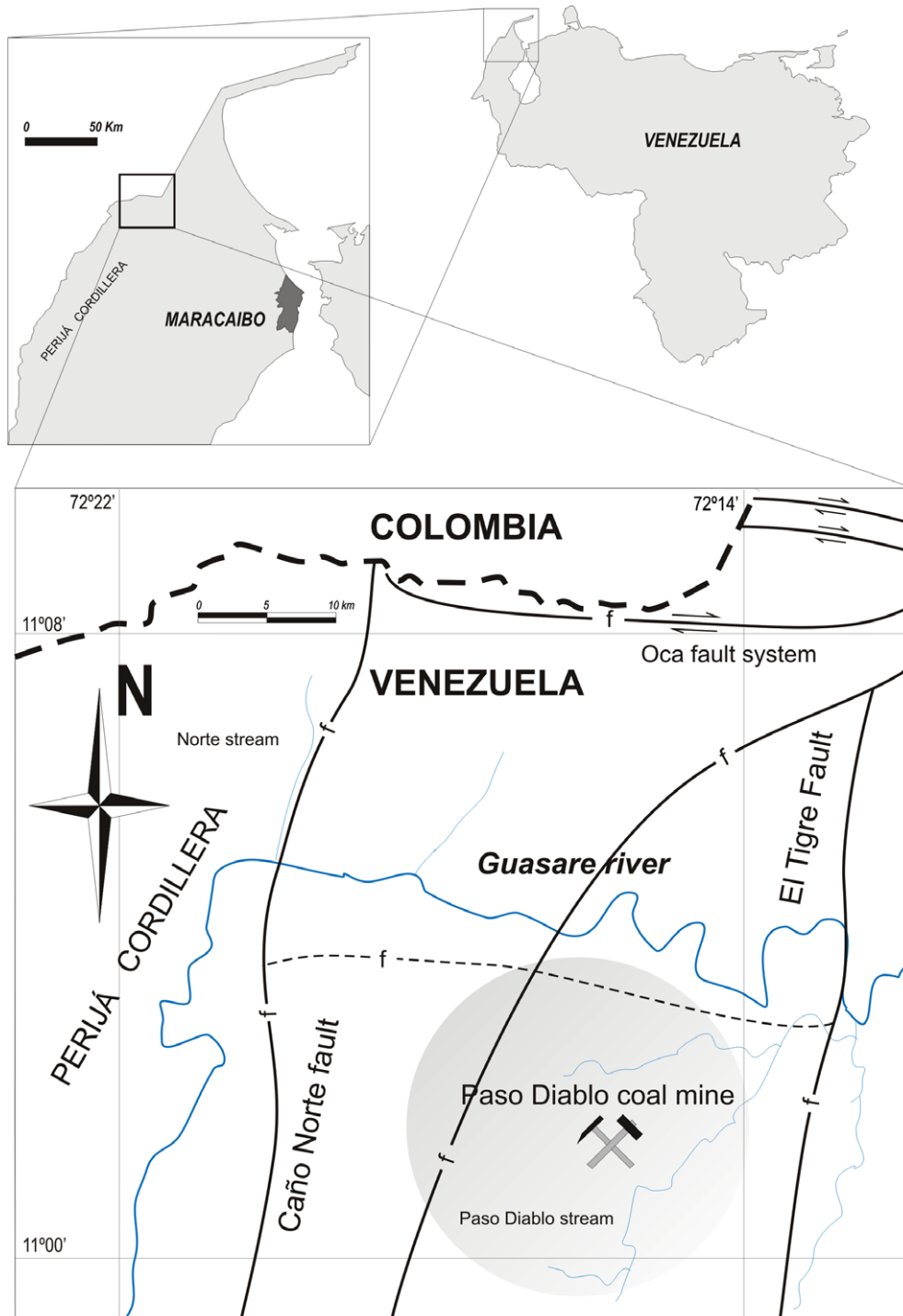


Fig. 1. Location of the Paso Diablo open-pit mine in the Guasare Basin.

ing Guasare Formation. The Marcelina Formation is about 530 m thick in the area of the Paso Diablo open-pit mine. The Marcelina Formation is limited in area, cropping out in a band approximately 50 km long and about 4 km wide.

The coals of the Marcelina Formation were formed in a foreland basin environment, where the subsidence rate was similar to the peat accumulation rate (McCabe, 1991). This depositional setting gave rise to 25–30 coal seams in this unit. The prevailing tectonic regime during deposition favoured the accumulation of many coalbeds > 2 m thick and as thick as 12 m (seam number 4), with great lateral continuity (Bailey, 1981).

Canónico (2002) made a preliminary estimate of the possible gas resources sorbed by coal seams in the Guasare Basin by applying the following formula:

$$G = 1359.7 \cdot A \cdot h \cdot G_c \cdot \rho$$

In this equation, G , A , h , G_c and ρ are gas-in-place (scf, standard cubic ft), reservoir area (acre), seam thickness (ft), average gas content at the average *in situ* coal composition (scf/tonne), and pure coal density (g/cm^3), respectively (Mavor and Nelson, 1997). The values of almost all the given variables are already available from previous studies (e.g. Canónico et al., 2004; Hackley and Martínez, 2007). However, the G_c variable was completely unknown and was estimated from various data, based on measured gas *in situ* contents from United States coal (Eddy et al., 1982).

Therefore, the objective of this work was to undertake a study of the coals in the Paso Diablo mine to evaluate the coalbed gas potential of the Guasare Basin using a novel and simple technique to evaluate, through controlled thermal treatment, the concentration of gas sorbed by coal samples and maceral concentrates.

2. Geological setting

Geologically, the Guasare Basin is located in the Manuelote syncline in the Sierra de Perijá, defined as a tectonic horst stretching NE–SW. The Misoa, Marcelina and Guasare Formations are all of Paleocene age and occur in the Manuelote syncline (González de Juana et al., 1980). In the area of the Paso Diablo mine, the Marcelina Formation is conformably overlain by the Misoa Formation, a thick (up to 5000 m) package of lower-Eocene sandstones of deltaic and shoreline origin. In the subsurface of the Maracaibo Basin, the Misoa Formation unconformably overlies the Marcelina Formation (Parnaud et al., 1995).

The lithology of the Marcelina Formation (Fig. 2) consists of grey sandstones, black mudstones, sandy shales, and coal seams (Sutton, 1946). At the bottom of the unit, the sandstones are massive, thick, light grey and locally calcareous. The sandstones fine upwards and become intercalated with grey shales. The sandstones and shales contain elongated nodules of bluish-grey sandy limestone that can be up to 3 m thick in the lower part of the unit (González de Juana et al., 1980). Coalbeds are most abundant towards the lower-central part of the Marcelina Formation.

The accumulated thickness of coal in the Marcelina sequence averages 45–50 m, with few partings. Coals from the Marcelina Formation have scant impurities comprising traces of clay and clay-ferruginous calcareous intercalations (Escobar and Martínez, 1993). The Marcelina Formation represents a swamp environment produced by a progradational delta system over the shelf margin of Guasare Formation (González de Juana et al., 1980).

The coalbeds in the Paso Diablo mine dip moderately (5–15°) ESE; to the south, the dip is greater (15–25°) and the beds are nearly vertical (Hackley and Martínez, 2007). The mine structure is dominated by the El Tigre fault and by innumerable smaller faults orientated N 45° W and spaced 60–160 m apart (see Fig. 1). To the north, the coalbeds slowly thin out to become lenses, whereas to the south, coalbed thickness increases.

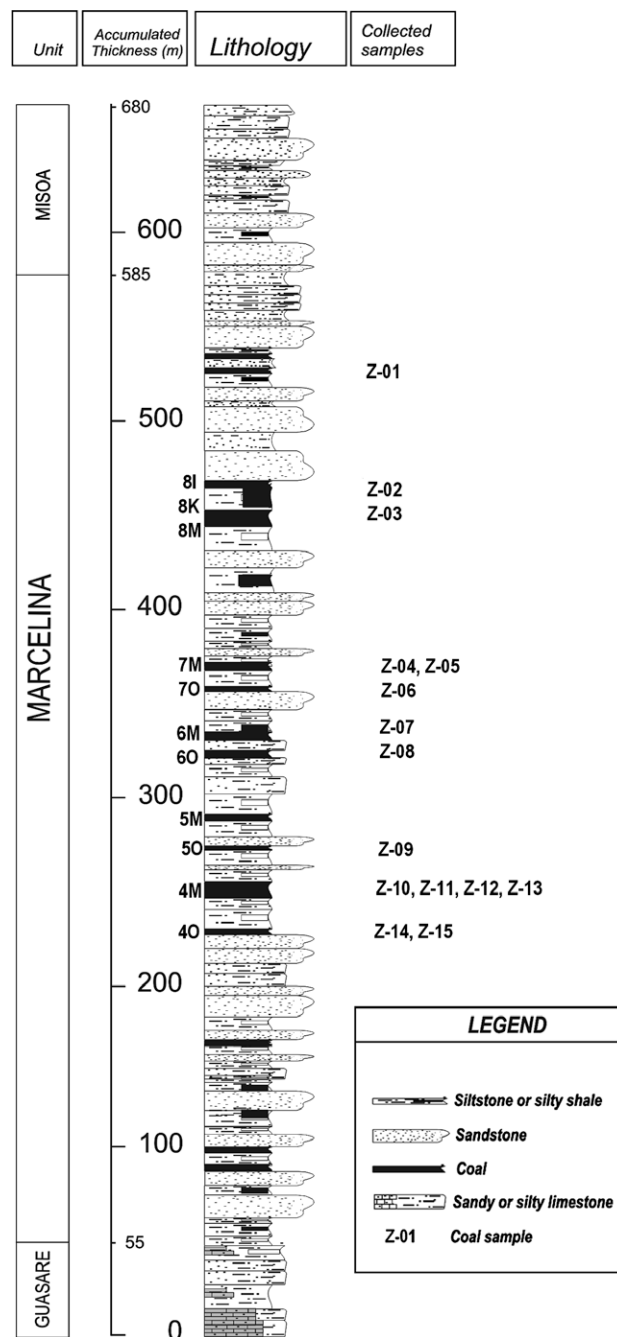


Fig. 2. Lithologic column for the area of the Paso Diablo mine showing the thickness of the Marcelina Formation, coalbed names and stratigraphic position of collected samples.

The work by Hackley and Martínez (2007) established the coalbed naming convention at the Paso Diablo mine. Coalbeds within the mine area are divided into 11 groups and the stratigraphically lowest one is Group 1, the next higher, Group 2, and so on. In each group, the stratigraphically highest coalbed is given a letter and the next lowest coalbed is assigned a letter farther along in the Latin alphabet.

3. Samples and methods

Fifteen samples of coal were collected from different coal seams (8I, 7O, 5M, among others) in the Marcelina Formation (Paso Diablo

mine) in accordance with ASTM D4596 practice (ASTM, 2007). All samples were collected from active mine faces, and approximately 5 kg of coal were collected for each channel sample.

3.1. Proximate, elemental and petrographic data

Volatile matter (average 37.5%, range 29.9–41.4%) and fixed C (average 56.8%, range 48.0–63.1%) data for the studied samples have been reported by Hackley and Martínez (2007). They also reported average values for C, H and O contents: 79.04%, 5.15%, and 8.01%, respectively. The Paso Diablo coals are also characterized by low-ash yield (average 1.9 wt.% on a dry basis, range 0.4–14.3 wt.%) and low S contents (0.7 wt.% on average, range 0.4–1.4 wt.%). Moisture contents average 3.89 wt.% and range from 1.73 to 5.64 wt.%. Calorific values (average 33.66 MJ/kg on a moist and mineral-matter-free basis, range 32.33–34.66 MJ/kg) together with the proximate and elemental analyses classify the Paso Diablo coals as high volatile bituminous type A.

The petrographic composition of the coals is characterized by a mean vitrinite content of 79 vol.% (range 67–97 vol.%) on a mineral-matter-free basis reference. Telo- and detrovitrinite are the dominant macerals of this group. The average inertinite content is 18 vol.% (range 2–33 vol.%), dominated by semifusinite. Total liptinite constitutes 2 vol.% on average in the Paso Diablo coals (range 0–3.4 vol.%). Vitrinite reflectance (% R_o) ranges between 0.65% and 0.88%. Mineral matter ranges from 0.4 to 8.3 vol.% (averaging 1.2 vol.%) and is very scarce in these coals (Hackley and Martínez, 2007).

The low amounts of inorganic matter (ash and S) in the coals suggest they were deposited in raised or ombrogenous mires in which peat accumulated as domes rising above the phreatic level. In this particular sedimentological situation, the peats were protected from any clastic supply; in contrast, rainfall tended to leach any soluble inorganic components, thereby further reducing mineral matter content (e.g. Neuzil et al., 1993). High levels of inertinite in the Paso Diablo coals corroborate the above interpretation of the depositional setting, since higher inertinite contents in the 8I coalbed may be interpreted to indicate that the peat mire was relatively more affected by oxidation–desiccation processes than other Paso Diablo coals (Hackley and Martínez, 2007).

3.2. Maceral concentrate separation

In the laboratory, the samples were manually crushed and pulverized in an agate mortar for brief periods to avoid heating the coal. Equal amounts (100 g) of each pulverized sample were sieved through 100 and 200 mesh sizes in order to optimize the separation of the maceral groups in the coal (see Poe et al., 1989). A sufficiently narrow particle size distribution (average 90 μm , RSD of 0.20) was determined by a laser diffraction method using a LS 13-320 Beckman Coulter analyzer. The distinct maceral concentrates were obtained by flotation/centrifugation using ZnBr_2 in solutions of different concentration (1.45, 1.33, 1.28, and 1.24 g/ cm^3). Peraza (2008) characterized the maceral concentrates obtained by Infrared (IR) spectroscopy, establishing by this way the efficiency of the separation procedure. In addition, good separations for over 1.28 g/mL density of high-density vitrinitic macerals (mainly telovitrinite), inertinite (fusinite and predominantly semifusinite), and low-density vitrinite (micrinite bound exinite-like material and abundant desmocollinite) were corroborated petrographically using a Leitz Leica Orthoplan Microscope according to standard techniques.

Approximately 35 g of coal were placed in a 1000 cm^3 separating funnel with 200 cm^3 of a ZnBr_2 solution with a specific gravity of 1.45 g/ cm^3 and eight drops of methanol. The resulting mixture

was shaken for 1 h and then the mineral fraction was separated. The residual (solution plus supernatant) was gently shaken and centrifuged using a Labnet Hermle Z300 instrument at 500 rpm for 20 min. The supernatant was extracted with pasteur pipettes, filtered, and placed in another separating funnel with 240 cm^3 of ZnBr_2 with a specific gravity of 1.33 g/ cm^3 and another 8 drops of methanol to repeat the separation cycle. The fraction that sank (inertinite) was filtered, washed with Milli-Q water, dried at room temperature for 72 h, and placed in a vial. Finally, the high- and low-density vitrinite concentrates were separated along with the less-dense liptinitic macerals by repeating the separation with solutions of ZnBr_2 with densities of 1.28 and 1.24 g/ cm^3 . Measurements were made with a Genec Inc., model SD-200L densimeter.

3.3. Coalbed gas analyses

Samples of approximately 10 mg were studied using a Pyris 1 thermogravimetric analyzer at a heating rate of 5 $^\circ\text{C min}^{-1}$ from 25 $^\circ\text{C}$ to 600 $^\circ\text{C}$, in an inert N_2 atmosphere. The goal was to determine the appropriate temperature range for the study in order not to quantify artificially generated thermogenic gases, and it was noted that the percentages of mass loss were comparatively small in the range of 40–240 $^\circ\text{C}$, which corresponds to the release of water vapour and sorbed gas (Das, 2000).

Gas sorption measurements were performed with the help of a novel, simple device (modified after Jerz and Rimstidt, 1999) that consists of a system with two chambers, one for coal and one for the control (quartz), linked by a manometer. This design also comprises a heater, thermal couple and an electronic controller (Fig. 3). This allowed the determination of very small amounts (in volume) of gas emitted by a solid sample compared to a reference material (clean and previously calcined at 900 $^\circ\text{C}$ quartz) subjected to exactly the same conditions and free of gases. The coal sample (2 g) is placed in a glass balloon, which is submerged in a sand bath. The covered sample then undergoes controlled thermal heating from 25 to 240 $^\circ\text{C}$ at a rate of 8 $^\circ\text{C min}^{-1}$. At the same time, the equivalent mass of reference material (quartz) is heated under the same conditions at the other end of the apparatus. The volume change in the sample due to the release of sorbed gases is quantified by the manometer. This design can measure as little as 0.1 micromoles of CH_4 . The system has two valves: one in the upper part to level off the internal pressure with atmospheric pressure between each experiment and another valve in the central part to isolate the two ends of the apparatus during measurement (or to connect them if the internal pressure must be regulated). Each analysis was performed in triplicate. The experimental error associated with these analyses was $\pm 0.10 \text{ cm}^3$.

Coalbed gas samples were stored in an inert impermeable container and analyzed for C_1 , C_2 , and C_3 composition by gas chromatography (GC). GC analyses of the gas samples were performed using a specific method (see Colman et al., 2001; Barletta et al., 2002). The analytical procedures involved the cryogenic pre-concentration of each sample with liquid N_2 ($-196 \text{ }^\circ\text{C}$). Later, CH_4 was analyzed using an HP 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID). The samples were injected into a stainless steel 0.9 m column packed with 80/100 mesh Spherocarb. The system used to analyze ethane and propane involved the vaporisation of pre-concentrated gas samples using a hot-water bath and splitting them into a stream directed to another HP 5890. The second GC was equipped with a GS-Alumina PLOT, 30 m, 0.53 mm I.D. output to an FID measuring C_2 and C_3 . Moreover, $\delta^{13}\text{C}$ isotopic analyses were performed on-line in three coalbed gas samples through a Delta Plus XP isotope mass spectrometer, an HP 6890 GC, and C reductive interfaces to generate CO_2 (Henning, 2002). These measurements utilized CH_4 and CO_2

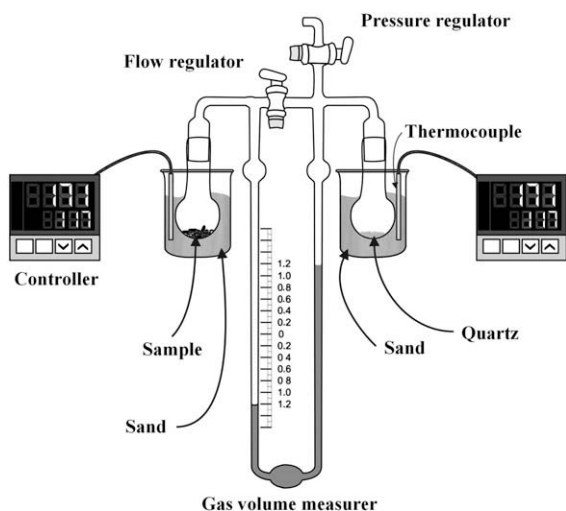


Fig. 3. Schematic diagram of the novel device to measure gas contents.

reference gases that have been previously calibrated off-line against VPDB for $\delta^{13}\text{C}$.

4. Results and discussion

4.1. Coalbed gas content and genetic type

The data for sorbed gas volume emitted by 2 g coal and maceral concentrate samples are shown as a function of the work temperature (see Table 1). The average values recorded were $0.51 \text{ cm}^3/\text{g}$ (16.39 scf/tonne) and the relative standard deviation (RSD) was 0.03, with a maximum percentage of weight loss of 2.52%. This figure is the sum of the water vapour from the coal wetness plus the sorbed gases released during the thermal treatment. In subsequent tests, a mass of water equivalent to the wetness reported for the Guasare coal was put in the apparatus, and the majority of the gases released were not water vapour. In addition, the maximum

gas storage capacity (G_{daf}) of Guasare coal was estimated by an indirect method that calculates the dry, ash-free maximum coalbed gas concentration at any depth from proximate analysis data (Kim, 1977). The average coalbed gas content measured in this study by the simple device ($0.51 \pm 0.03 \text{ cm}^3/\text{g}$) is lower than the calculated average value (G_{daf}): $0.72 \text{ cm}^3/\text{g}$ (23.22 scf/tonne). These data indicate that the Guasare coals can accommodate more gas than is present in the coals.

The value of "G" (0.12 trillion cubic feet) obtained for the Guasare Coal Basin corresponds only to the total volume of CBM sorbed on the internal surfaces (in micro- and mesopores) and not to coalbed gas retention in other forms such as: trapped gas within the matrix porosity; as free gas in cleats, fractures, and macropores of the coal; and as dissolved gas in water occupying the coal reservoir (Clarkson and Bustin, 1996). After Meissner (1984), the maximum expected thermogenic gas potential in relation to average Guasare coal maturity ($\%R_o$ of 0.73%) is about $2 \text{ cm}^3/\text{g}$ (64.51 scf/tonne). In addition, the data in the present study is necessarily an underestimation of the volume of gas sorbed by the Guasare coals due to gas loss during the time between sampling and analysis, and due to crushing and screening of the samples. It should also be taken into account that the exploitation of the natural gas retained in coal seams is determined by the relationship between six geological and geochemical criteria (Scott, 2002): coal depositional system and distribution, tectonic and structural situation, coal rank, gas *in situ* content, permeability and hydrodynamic factors. Fig. 4 shows data for sorbed gas volume/g of coal and isolated maceral concentrates.

In this study, the samples were crushed by hand in order to obtain coal fragments that were not very fine; the reasoning was to preserve most of the micropore (pore diameter $<2 \text{ nm}$) and mesopore ($<50 \text{ nm}$ in diameter) volume. Consequently, the amount of gas determined is equivalent to the residual gas fraction and to a part of the desorbed gas, as defined in the literature (Strapóć et al., 2007).

Finally, the main relative abundances of C_1 (89.1 vol.%), C_2 (6.5 vol.%), and C_3 (2.4 vol.%) and the average gas wetness ratio C_1/C_{2+3} (about 10) are indicative of a considerable contribution of thermogenic gas. These C_2 and C_3 abundances are similar to those

Table 1

Average volumes (cm^3) of gas emitted from coal and maceral concentrate samples (2 g) at different temperatures. Note: negative values appear in parentheses, but without minus signs.

Temperature (°C)	Average volume coalbed gas	Average volume inertinite	Average volume heavy vitrinite	Average volume light vitrinite	Average volume liptinite	Blank (quartz)
25	0.000	0.000	0.000	0.000	0.000	0.000
40	0.000	0.000	0.000	0.000	0.000	0.000
50	0.000	0.000	0.000	0.000	0.000	0.000
60	(0.005)	0.000	(0.010)	0.000	(0.025)	0.000
70	(0.010)	0.000	(0.025)	0.000	(0.025)	0.000
80	(0.025)	0.000	(0.050)	0.000	(0.050)	(0.010)
90	(0.025)	0.000	(0.050)	0.000	(0.050)	(0.015)
100	(0.020)	0.025	(0.050)	0.020	(0.040)	(0.010)
110	(0.010)	0.065	(0.020)	0.050	(0.025)	0.000
120	0.000	0.125	0.020	0.115	0.000	0.000
130	0.055	0.180	0.055	0.190	0.050	0.000
140	0.130	0.250	0.085	0.240	0.105	0.000
150	0.200	0.325	0.120	0.290	0.175	0.000
160	0.280	0.400	0.160	0.335	0.230	0.000
170	0.375	0.480	0.205	0.385	0.280	0.005
180	0.485	0.570	0.250	0.440	0.320	0.005
190	0.575	0.675	0.290	0.505	0.365	0.005
200	0.660	0.800	0.340	0.570	0.405	0.005
210	0.765	0.900	0.390	0.640	0.460	0.010
220	0.855	1.000	0.445	0.650	0.520	0.020
230	0.915	1.075	0.500	0.745	0.575	0.030
240	1.020	1.120	0.520	0.760	0.600	0.040

predicted by the empirical relationship between vitrinite reflectance and the expected relative abundances of the thermogenic gas components ethane and propane (Berner and Faber, 1988), namely $C_2 = 6.6$ vol.% and $C_3 = 2.7$ vol.%. Average $\delta^{13}C$ values of carbonic anhydride and CH_4 are $-49.6 \pm 1.4\text{‰}$ and $-24.5 \pm 3.6\text{‰}$, respectively. The difference (about 25‰) between these $\delta^{13}C$ values confirms that the Guasare coalbed gases are of thermogenic origin (Strapóć et al., 2007).

4.2. Methane contents of maceral concentrates

The average gas sorption capacities for the distinct maceral concentrates, the standard deviations corresponding to the observations made, and the percentages of maximum weight loss are given in Table 2. All sorbed gas concentrations are expressed in SI units; because the petroleum industry still uses Imperial units, these results are also given, in parentheses, as scf/tonne.

As pore size distribution is very closely linked to the internal surface area available in the coal for gas sorption, one would expect the inertinite concentrate, the most macroporous maceral group, to have a lower CH_4 capacity than vitrinitic macerals, which are mainly microporous and mesoporous (Beamish and Crosdale, 1995).

However, the results obtained (Table 2) suggest that the phenomena of gas sorption in coal and its macerals are not so easy to account for since inertinitic macerals show a greater ability to store CH_4 than low-density vitrinite-rich concentrates. Moreover, the high-density vitrinitic macerals, which are chemically more similar to the inertinite-rich concentrates, display a volume of sorbed gas that is nearly identical to that of the liptinitic macerals, the least macroporous group. Furthermore, the low-density vitrinite group, chemically similar to the liptinite-rich concentrates, has a greater ability to store CH_4 than expected. All this indicates that the volume of sorbed gas in the samples analyzed depends more on the pore density than on the chemical characteristics. Nevertheless, a significant influence of maceral composition for some high volatile A bituminous coals has also been reported

(Lamberson and Bustin, 1993). Levine (1993) suggested that hydrocarbons generated at this rank (R_{max} of about 0.8%) block micropores and reduce gas sorption capacity, especially that of vitrinite macerals such as telocolinite, but probably not that of inertinite. Ettinger et al. (1966) indicated that low-ash and semi-fusinite-rich coals had higher sorption capacities and desorption rates than the vitrinitic coals. Lastly, Gamson et al. (1993) reported that the density at the microscopic level, the continuity, orientation, and pore space, as well as the types of microstructures present, can influence gas behaviour within coal and its maceral concentrates. Liptinitic macerals released less gas than the inertinite and low-density vitrinite groups, possibly because the relationship between the pore space and the sample morphology at the microscopic scale is unfavourable concerning the internal surface area available for sorption.

One advantage of the technique used in this work is that it allows comparisons between the sorption capacities of sets of maceral concentrates from the same coal. In contrast, in the canister desorption technique (Chalmers and Bustin, 2007), the mechanism of gas sorption in liptinite is different than that for vitrinite and inertinite, so that the data obtained are not comparable.

5. Conclusions

The estimates obtained in this work for the sorbed gas volume per unit weight of coal allow the preliminary supposition that the Guasare coals contain significant enough quantities of CH_4 to be economically viable as a coalbed gas source. The amount of gas determined is not equivalent to the total gas capacity, but rather to the residual gas fraction and to a part of the desorbed gas fraction, which are the fractions obtained whenever the potential gas resources retained in coalbeds are determined by the standard canister desorption protocol.

The sorbed gas volumes per unit weight of samples from the different maceral concentrates indicate the following order:

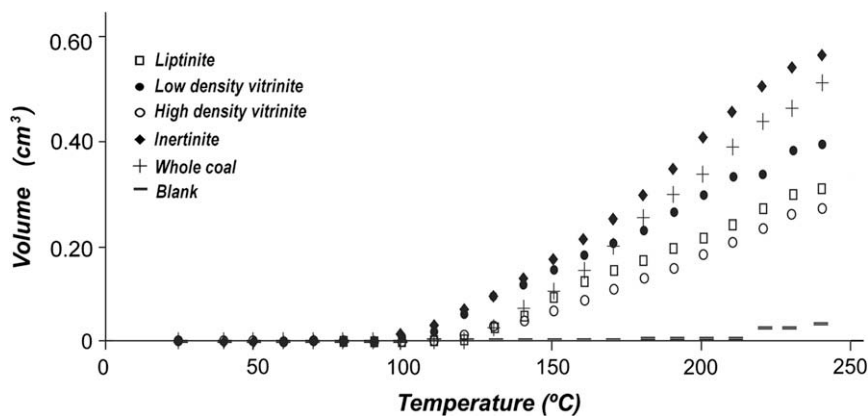


Fig. 4. Sorbed gas volumes per gram of coal and isolated maceral concentrates.

Table 2

Weight losses, average gas sorption capacities and RSDs of maceral concentrates.

	Weight loss (%)	Methane capacity in cm^3/g (scf/tonne)	RSD
Inertinite	2.38	0.56 (18.06)	0.02
High-density vitrinite	50.15	0.26 (8.39)	0.01
Low-density vitrinite	43.80	0.38 (12.26)	0.02
Liptinite	1.58	0.30 (9.68)	0.03

inertinite > low-density vitrinite > liptinite \approx high-density vitrinite. This sequence may not be controlled by the nature of the pores in each fraction (as can be seen in the analysis of high- and low-density vitrinitic macerals), but by the specific pore morphology of each maceral concentrate.

The technique employed to evaluate the sorbed gas is suitable for studies where it is crucial to maintain the organic matrix of the coal unaltered. This technique also allows the comparison of the behaviour of sets of maceral concentrates from the same coal seam. The method is extremely easy, quick, economical and reproducible; it has demonstrated its applicability for the direct evaluation of gases contained in coal. Finally, analyses of the methane, ethane and propane yielded gas concentrations and a gas wetness ratio typical of thermogenic gas. This origin of coalbed gases is also characterized by compound-specific $\delta^{13}\text{C}$ values of CH_4 and CO_2 from Guasare coalbeds.

Acknowledgments

This study was funded by the Consejo de Desarrollo Científico y Humanístico of the UCV (Project CDCH PG-03-30-4933-2002). We thank Christine Laurin for her assistance. We are also grateful to the referees (Dr. H.I. Petersen and Dr. M. Escobar) for their comments which helped to improve the original version of this work.

References

- Aravena, R., Harrison, S.M., Barker, J.F., Abercrombie, H., Rudolph, D., 2003. Origin of methane in the Elk Valley coalfield, southeastern British Columbia, Canada. *Chem. Geol.* 195, 219–227.
- ASTM, 2007. Annual Book of ASTM Standards: Petroleum Products, Lubricants, and Fossil Fuels; Gaseous Fuels; Coal and Coke, Sec. 5, v. 5.06. ASTM International, West Conshohocken, PA.
- Bailey, A., 1981. Chemical and mineralogical differences between Kittanning coals from marine-influenced versus fluvial sequences. *J. Sediment Petrol.* 51, 383–395.
- Barletta, B., Meinardi, S., Simpson, I.J., Khwaja, H.A., Blake, D.R., Rowland, F.S., 2002. Mixing ratios of volatile organic compounds – VOCs – in the atmosphere of Karachi, Pakistan. *Atmos. Environ.* 36, 3429–3443.
- Beamish, B.B., Crosdale, J.P., 1995. The influence of maceral content on the sorption of gases by coal and the association with outbursting. In: *Internat. Symp. Cum Workshop on Management and Control of High Gas Emission and Outbursts, Wollongong, 20–24 March, 1995*. Wollongong, Australia.
- Behar, F., Vandenbroucke, M., Teerman, S., Hatcher, P., Leblond, C., Lerat, O., 1995. Experimental simulation of gas generation from coals and a marine kerogen. *Chem. Geol.* 126, 247–260.
- Berner, U., Faber, E., 1988. Maturity related mixing model for methane, ethane and propane, based on carbon isotopes. *Org. Geochem.* 13, 67–72.
- Canónico, U., 2002. Evaluación de la capacidad de generación de gas de carbones del occidente de Venezuela. Trabajo especial de grado. Universidad Central de Venezuela, Escuela de Química, Caracas.
- Canónico, U., Tocco, R., Ruggiero, A., Suárez, H., 2004. Organic geochemistry and petrology of coals and carbonaceous shales from western Venezuela. *Int. J. Coal Geol.* 57, 151–165.
- Chalmers, G., Bustin, R., 2007. On the effects of petrographic composition on coalbed methane sorption. *Int. J. Coal Geol.* 69, 288–304.
- Clarkson, C.R., Bustin, R.M., 1996. Variation in micropore capacity and size distribution with composition in bituminous coal of the western Canadian sedimentary Basin. *Fuel* 75, 1483–1498.
- Clayton, J., 1997. Geochemistry of coalbed gas: a review. *Int. J. Coal Geol.* 35, 159–173.
- Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM – Tropics A & B. *Anal. Chem.* 73, 3723–3731.
- Das, T.K., 2000. Thermogravimetric characterization of maceral concentrates of Russian coking coals. *Fuel* 80, 97–106.
- Drobniak, A., Mastalerz, M., Rupp, J., Eaton, N., 2004. Evaluation of coalbed gas potential of the Seelyville Coal Member, Indiana, USA. *Int. J. Coal Geol.* 57, 265–282.
- Eddy, G.E., Rightmire, C.T., Byrer, C., 1982. Relationship of methane content of coal, rank and depth. In: *Society of Petroleum Engineers/Department of Energy Unconventional Gas Recovery Symp.*, Pittsburgh, Pennsylvania, vol. 10800. Society of Petroleum Engineers/Department of Energy, 117–122.
- Escobar, M., Martínez, M., 1993. Los depósitos de carbón en Venezuela. *Interciencia* 18, 224–229.
- Ettinger, I., Eremin, B., Zimakov, Yavovskaya, M., 1966. Natural factors influencing coal sorption properties. I: Petrography and the sorption properties of coals. *Fuel* 45, 267–275.
- Gamson, P.D., Beamish, B.B., Johnson, D.P., 1993. Coal microstructure and micropermeability and their effects on natural gas recovery. *Fuel* 72, 87–99.
- González de Juana, C., Iturralde de Arzena, J.M., Piccard, C.X., 1980. *Geología de Venezuela y de sus cuencas petrolíferas*, Tomos I y II. Ediciones Foninves, Caracas.
- Gürdal, G., Yalçın, M.N., 2000. Gas adsorption capacity of carboniferous coals in the Zonguldak Basin (NW Turkey) and its controlling factors. *Fuel* 79, 1913–1924.
- Hackley, P.C., Martínez, M., 2007. Organic petrology of Paleocene Marcelina Formation coals, Paso Diablo mine, western Venezuela: tectonic controls on coal type. *Int. J. Coal Geol.* 71, 505–526.
- Henning, M.J., 2002. Development and assessment of inlet system for stable carbon isotopic analysis of individual compounds in gas mixtures. M.Sc. Thesis, Indiana Univ., Bloomington.
- Jerz, J.K., Rimstidt, J.D., 1999. A novel reactor to determine the rate of pyrite oxidation in air. In: 9th Ann. V.M. Goldschmidt Conf., Abstract No. 7156.
- Kim, A.G., 1977. Estimating methane content of bituminous coal-beds from adsorption data. Report of investigations, United States Bureau of Mines RI 8245.
- Kotarba, M.J., Rice, D.D., 2001. Composition and origin of coalbed gases in the Lower Silesian basin, southwest Poland. *Appl. Geochem.* 16, 895–910.
- Kuyil, O.P., Muller, J., Waterbolk, H.T., 1955. The application of palynology to oil geology with reference to western Venezuela. *Geol. Mijnb. New Ser.* 17 (3), 49–76.
- Lamberson, M.N., Bustin, R.M., 1993. Coalbed methane characteristics of gates formation coals, northern British Columbia: effect of maceral composition. *Am. Assoc. Petrol. Geol. Bull.* 77, 2062–2076.
- Langenberg, C.W., Beaton, A., Berhane, H., 2006. Regional evaluation of the coalbed-methane potential of the Foothills/Mountains of Alberta, Canada. *Int. J. Coal Geol.* 65, 114–128.
- Levine, J.R., 1993. Coalification: the evolution of coal as source rock and reservoir. In: Law, B.E., Rice, D.D. (Eds.), *Hydrocarbons from Coal, Studies in Geology*, vol. 38. Am. Assoc. Petrol. Geol., pp. 39–77.
- Liu, Q., Liu, W., Dai, J., 2007. Characterization of pyrolysates from maceral components of Tarim coals in closed system experiments and implications to natural gas generation. *Org. Geochem.* 38, 921–934.
- Mastalerz, M., Drobniak, A., Strapóč, D., Solano-Acosta, W., Rupp, J., 2008. Variations in pore characteristics in high volatile bituminous coals: implications for coalbed gas contents. *Int. J. Coal Geol.* 76, 205–216.
- Mavor, M., Nelson, C.R., 1997. Coalbed reservoir gas-in-place analysis. Gas Research Institute Report No. GRI-97/0263, Chicago.
- McCabe, P.J., 1991. Tectonic controls on coal accumulation. *Bull. Soc. Geol. France* 162, 277–282.
- Meissner, F.F., 1984. Cretaceous and lower tertiary coals as sources for gas accumulations in the rocky mountain area. In: Woodward, J., Meissner, F.F., Clayton, J.L. (Eds.), *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region*. Rocky Mountain Association of Geologists, Denver, Colorado, pp. 401–430.
- Neuzil, S.G., Supardi, C.B., Cecil, C.B., Kane, J.S., Soedjono, K., 1993. Inorganic geochemistry of domed peat in Indonesia and its implication for the origin of mineral matter in coal. In: Cobb, J.C., Cecil, C.B. (Eds.), *Modern and Ancient Coal-Forming Environments*, Geol. Soc. Am. Special Paper, vol. 286, pp. 23–44.
- Parnaud, F., Gou, Y., Pascual, J.C., Capello, M.A., Truskowski, I., Passalacqua, H., 1995. Stratigraphic synthesis of western Venezuela. In: Tankard, A.J., Suárez, R.S., Welsink, H.J. (Eds.), *Petroleum Basins of South America*, Mem., vol. 62. Am. Assoc. Petrol. Geol., pp. 681–698.
- Peraza, A., 2008. Estudio termogravimétrico y espectroscópico de los macerales separados de carbones de Guasare (Formación Marcelina, Paleoceno). Trabajo especial de grado. Universidad Central de Venezuela, Escuela de Química, Caracas.
- Petersen, H.I., 2006. The petroleum generation potential and effective oil window of humid coals related to coal composition and age. *Int. J. Coal Geol.* 67, 221–248.
- Poe, S., Taulbee, D., Keogh, R., 1989. Density gradient centrifugation of less 100 mesh coal: an alternative to using micronized samples for maceral separation. *Org. Geochem.* 14, 307–313.
- Quick, J.C., Brill, T., 2002. Provincial variation of carbon emissions from bituminous coal: influence of inertinite and other factors. *Int. J. Coal Geol.* 49, 263–275.
- Ryan, B.D., Dawson, F.M., 1995. Coal and coalbed methane resource potential of the Bowser Basin, northern British Columbia. *Energy Sources* 17, 107–129.
- Scott, A.R., 2002. Hydrogeologic factors affecting gas content distribution in coal beds. *Int. J. Coal Geol.* 50, 363–387.
- Smith, J.W., Pallasser, R.J., 1996. Microbial origin of Australian coalbed methane. *Am. Assoc. Petrol. Geol. Bull.* 80, 891–897.
- Strapóč, D., Mastalerz, M., Eble, C., Schimmelmann, A., 2007. Characterization of the origin of coalbed gases in southeastern Illinois Basin by compound-specific carbon and hydrogen stable isotope ratios. *Org. Geochem.* 38, 267–287.

- Sutton, F.A., 1946. Geology of Maracaibo Basin, Venezuela. *Am. Assoc. Petrol. Geol. Bull.* 30, 1621–1741.
- Tissot, B., Welte, H., 1984. *Petroleum Formation and Occurrence*, second edition. Springer-Verlag, Berlin.
- Wei, C., Qin, Y., Wang, G., Fu, X., Jiang, B., Zhang, Z., 2007. Simulation study on evolution of coalbed methane reservoir in Qinshui basin, China. *Int. J. Coal Geol.* 72, 53–69.
- Whiticar, M., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation: isotope evidence. *Geochim. Cosmochim. Acta* 50, 693–709.
- Yee, D., Seidle, J.P., Hanson, W.B., 1993. Gas sorption on coal and measurement of gas content. In: Law, B.E., Rice, D.D. (Eds.), *Hydrocarbons from Coal, Studies in Geology*, vol. 38. *Am. Assoc. Petrol. Geol.*, pp. 203–218.