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Selection of coals of different maturities for CO₂ Storage by modelling of CH₄ and CO₂ adsorption isotherms

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Abstract

CO₂ injection in unmineable coal seams could be one interesting option for both storage and methane recovery processes. The objective of this study is to compare and model pure gas sorption isotherms (CO₂ and CH₄) for well-characterised coals of different maturities to determine the most suitable coal for CO₂ storage. Carbon dioxide and methane adsorption on several coals have been investigated using a gravimetric adsorption method. The experiments were carried out using both CO₂ and CH₄ pure gases at 25 °C from 0.1 to 5 MPa (1 to 50 bar). The experimental results were fitted using Temkin's approach but also with the corrected Langmuir's and the corrected Tóth's equations. The two last approaches are more accurate from a thermodynamical point of view, and have the advantage of taking into account the fact that experimental data (isotherms) correspond to excess adsorption capacities. These approaches allow better quantification of the adsorbed gas. Determined CO₂ adsorption capacities are from 0.5 to 2 mmol/g of dry coal. Modelling provides also the affinity parameters of the two gases for the different coals. We have shown these parameters determined with adsorption models could be used for classification and first selection of coals for CO₂ storage. The affinity ratio ranges from a value close to 1 for immature coals to 41 for high rank coals like anthracites. This ratio allows selecting coals having high CO₂ adsorption capacities. In our case, the modelling study of a significant number of coals from various ranks shows that anthracites seem to have the highest CO₂ storage capacities. Our study provides high quality affinity parameters and values of CO₂ and CH₄ adsorption capacities on various coals for the future modelling of CO₂ injection in coal seams.

Keywords: CO₂ storage; Coals; Methane and carbon dioxide adsorption; Modelling isotherms

1. Introduction

CO₂ is a greenhouse gas and is naturally present in the atmosphere. Its concentration has been influenced by human activities since industrial revolutions, when fossil fuels were used extensively and CO₂ emissions increased. Between 1800 and 2010, the atmospheric concentration of CO₂ increased from 280 to 379 ppm (IPCC, 2007). Over the last few decades, one way envisaged by researchers to reduce the quantity of greenhouse gases in the atmosphere is the geologic storage of CO₂. It would, in the medium timescale, allow for the

creation of a sink for CO₂ to reduce the risks of climatic disorder. The carbon dioxide (CO₂) is captured from flue gases originating from sources such as coal-fired or gasification power plants. It is then transported, typically by pipeline, to a storage site where it is injected into deep geologic formations to remain for thousands of years and, it is hoped, never back to the surface. (Mangal, 2010). The IPCC rapport (IPCC, 2005) about carbon dioxide capture and storage indicates that the capacity of unmineable coal is estimated from 3 up to 200 GtCO₂ therefore CO₂ storage in coal seams is one of the potential types of storage under study.

If the first advantage is adsorption capacity, the second advantage of CO₂ storage can be, in some cases, the possibility of methane recovery through Enhanced Coal Bed Methane (ECBM) operations (Ozdemir, 2009). For [Bachu, 2000] , [Bachu, 2002] , [Srivastava and Harpalani, 2004] , [White et al., 2003] and [White et al., 2005] , the concept of CO₂ sequestration combined with ECBM recovery is considered to provide good synergy for economic and environmental long-term benefits. One of the main parameters needed to select the storage site is the evaluation of the sorption capacity of CO₂ adsorption and CH₄ desorption (Gensterblum et al., 2009; Goodman et al., 2004, 2007). To determine this parameter, isotherm's models can be used. The other important parameters are affinity, swelling (Day et al., 2008), effects of stress ([Hol et al., 2011] and [Karacan, 2003]), permeability ([Mazumder and Wolf, 2008] and [Siriwardane et al., 2009]), etc. As the swelling capacity of the coal is a key issue for the CO₂ injectivity into coal seams, the mechanical properties of the coal have been measured.

The research program CHARCO supported by the French National Research Agency aims at developing methods and analyses in order to determine the main parameters defining coal seams that could be favourable to CO₂ storage purposes. An effort has been made to study a panel of coals with a large extension of their maturities, from the lignite to the meta-anthracite. However, on our coal collection, only two were sufficiently hard to be cored. So, an alternative approach has been developed to assess coal mechanical properties but this will be described in another paper.

Thus we have focused on experimental investigations of gas sorption (carbon dioxide and methane) on various coals having very different maturities using a gravimetric method. For this method, inter-laboratory studies on CO₂ sorption on coal ([Goodman et al., 2004] and [Goodman et al., 2007]) have revealed the difficulty to obtain good reproducible isotherms. In order to elucidate the impact of the density error on the adsorption measurements (Pini et al., 2006), to minimise heterogeneity effect and to optimize the experimental procedures (Gensterblum et al., 2009) the system CO₂ on activated carbon was analyzed. The recent paper of Gensterblum et al. 2010 using natural coals of various rank to study the influence of heterogeneities and varying starting conditions on the CO₂ sorption properties showed excellent agreement (< 5% deviation) among the participating laboratories with good repeatability.

The aim of this article is to estimate relative performances of different models (Langmuir, Tóth, Temkin, BET, etc.) present in the literature. Using the experimental data, the best models for CH₄ and CO₂ isotherms will be selected. These models lead to determine the gas sorption capacity on studied coals in order to classify them and determine the best candidate.

2. Sorption isotherm models

Three isotherm models were applied for their ability to describe the experimental results and for their complementarities: Langmuir's (L), Tóth's (T) and Temkin's (Tem) isotherms.

2.1. Langmuir's Model

Langmuir's isotherm (Langmuir, 1918) assumes that surfaces are homogeneous. The adsorption is local, specific and is made on a limited number of sites under a monolayer of adsorbat. This adsorption is reversible: at an equilibrium pressure P , the rate of adsorption and desorption from the solid is equal.

$$k_{ads}PS(1-\theta) = k_{des}S\theta$$

where q is the adsorbed quantity at equilibrium pressure P and q_m is the maximum adsorbed quantity.

The Langmuir constant α_L depends on the temperature according to the relation of van't Hoff:

$$\alpha_L = \alpha_{0L} \exp(-\Delta H_{ads}/RT)$$

with R is the ideal gas constant ($8.314 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$). α_{0L} is a constant described by Goodman et al. (2005) as depending on the molecular area (0.22 nm^2 for CO_2 and 0.19 nm^2 for CH_4) (Suzuki et al., 1995) and on the molecular weight of adsorbat. ΔH_{ads} is the adsorption enthalpy.

2.2. Tóth's Model

Tóth formulated a three-parameter equation. While the use of the Langmuir's isotherm implies a homogeneous surface, the choice of the isotherm of Tóth (1962) suggests a heterogeneous surface if $n \neq 1$ ($0 < n \leq 1$).

$$\frac{q}{q_m} = \frac{\alpha_T P}{[1 + (\alpha_T P)^n]^{1/n}}$$

where α_T and n are the Tóth's constants.

2.3. Temkin's Model

Temkin's isotherm contains a factor that explicitly takes into account the adsorbent–adsorbate interactions. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin's isotherm is expressed as:

$$\frac{q}{q_m} = \frac{RT}{Q} \ln(K_0 P)$$

R is the ideal gas constant ($8.314 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature (K), Q is related to heat of adsorption (equivalent to $-\Delta H_{ads}$) and K_0 the equilibrium binding constant.

$$K_0 = k_0 \exp(Q_0/RT)$$

Q_0 is the lowest characteristic heat of adsorption and k_0 is a constant.

This isotherm cannot be used for very small quantities of sorbed gas because the limit of the $q(P)$ function when P tends to 0 is:

$$\lim_{P \rightarrow 0} q = \lim_{P \rightarrow 0} q_m \frac{RT}{Q} \ln(K_0 P) = -\infty$$

This equation (*cf.* Eq. 7) shows that the isotherm has no physical sense for very low pressure. Furthermore, when the heterogeneity of surface decreases and when Q/RT reaches zero, the equation of Temkin also loses any physical meaning because q approaches infinity at any value of the pressure (Asnin et al., 2001).

3. Materials and methods

3.1. Origin and characteristics of coal

Coal samples from different coal basins were used for this study. Some indicative compositions are given in Table 1. A large panel of coal maturities has been chosen: from lignite to meta-anthracite. Details can be found in Gaucher et al. (2011).

Table 1. Some characteristics of samples.

	CO04 -HVB	CO02 -HVB	CO01 -SB	BHL01 -HVB	ES02 - MVB	ES01 - HVB	GR02 -MVB	AL02 - MVB	AL01 - MVB	JER01 -MA	CO03 -A
Volumic mass on dry coal (g/cm ³)	1.361	1.335	1.348	1.363	1.427	1.424	1.422	1.664	1.382	1.586	1.449
Aches on dry coal (%)	22.05	0.5	0.3	5.2	15.7	10.9	8.4	31.7	3.9	4.5	2.2
Volatile mater on dry and pure coal (%)	46.4	37.4	34.4	32.1	30.4	28.6	20.3	18.2	14.0	10.7	7.3
W% ^(a)	0.35	0.89	0.22	0.92	0.30	0.46	1.32	2.63	0.59	1.40	1.13
S _{BET N2} (m ² /g)	1.2	2.8	5.3	1.9	1.6	1.6	2.0	3.8	2.0	6.8	1.1
S _μ	121	121	118	268	99	110	118	91	119	218	175

	CO04 -HVB	CO02 -HVB	CO01 -SB	BHL01 -HVB	ES02 - MVB	ES01 - HVB	GR02 -MVB	AL02 - MVB	AL01 - MVB	JER01 -MA	CO03 -A
(m ² /g) (b)											
R ₀ ^(c)	0.76	0.75	0.49	0.74	1.24	0.98	1.42	1.44	1.16	3.65	2.54
Rank ^(d)	HVB	HVB	SB	HVB	MVB	HVB	MVB	MVB	MVB	MA	A

(a) Percentage of water.

(b) Microporous specific surface.

(c) Vitrinite reflectance.

(d) US classification of coals: SB (Sub Bituminous coal), HVB (High Volatile Bituminous coal), MVB (Medium Volatile Bituminous coal), LVB (Low Volatile Bituminous coal), MA (Meta-Anthracite), A (Anthracite).

3.2. Determination of adsorption isotherms

Laboratory adsorption experiments were performed using gravimetric technique with a magnetic suspension balance (Rubotherm, Germany). Details of used experimental method can be found in some previous publications ([Charrière et al., 2010] and [Gensterblum et al., 2009]). The capacity of sorption by coal of CO₂ and CH₄ were established at pressures ranging from 0.1 to 5 MPa and at a temperature of 298 K (25 °C). The usual particle size used for the tests is 50–200 µm or 0.5 to 1 mm depending on the case. According to previous studies, this difference of coal particles size has no significant influence on the determination of the adsorption capacities ([Beckman, 1954] and [Moffat and Weale, 1955]). The validity of this observation on the used experimental device have been beforehand verified (Charrière, 2009).

4. Results and discussion

4.1. CO₂ sorption

CO₂ excess sorption isotherms obtained at 298 K on dry coal samples are shown in Fig. 1. For all studied coals, isotherm behaviour is of type I (as defined by the IUPAC classification) which characterizes microporous adsorbent (monolayer adsorption). This corroborates results already obtained by several other authors ([Gunther, 1965] , Lason, 1990 and [Yu et al., 2008]). The shape of the isotherm imposes certain limitation in the choice of the models. Indeed the model hypotheses have to take into account this monolayer adsorption. For example, BET model cannot be used with this isotherm type. Main differences between the samples are concavity of the isotherm curves at low pressure and also the amount of CO₂ adsorbed at saturation. To classify the studied coals from the point of view of the CO₂ storage efficiency, models previously discussed have been used. In Fig. 2, the fitted results obtained on coal AL02-MVB are given. The Langmuir's model slightly overestimates the CO₂ adsorption for pressure values below 3 MPa. The same remark can be made for all the studied coals: calculated q_m values are higher than experimental data. It is necessary to keep in mind that in case of adsorption at high pressures, experimental results are excess adsorption capacities. On the contrary, Tóth's and Langmuir's isotherms present hereafter are absolute isotherms. According to Tóth “they neglect the differences between the densities of gas phase and the adsorbed gas. This negligence leads to contradictions, especially at high equilibrium pressure when the classic equations calculate the total adsorption capacity by extrapolation of

the equilibrium pressure to infinity” and “[they] are, from a thermodynamic standpoint, incorrect”. The correction of this equation is explained by Tóth in several papers ([Tóth, 1995] , [Tóth, 1997a] and [Tóth, 1997b]). The introduction of one constant χ allows taking into account the excess quantities:

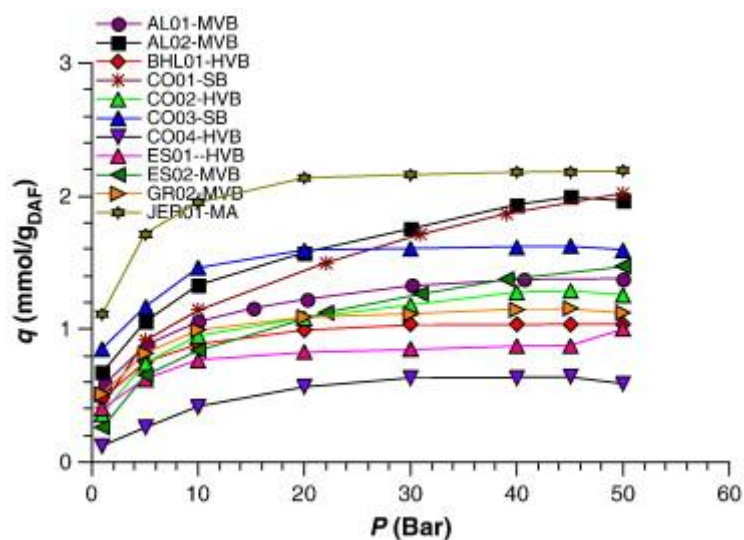


Fig. 1. : CO₂ sorption isotherms for all coals (DAF: dry and ash-free) at a temperature of 298 K. The error bar of the excess sorption measurements is estimated at 5% of the sorption.

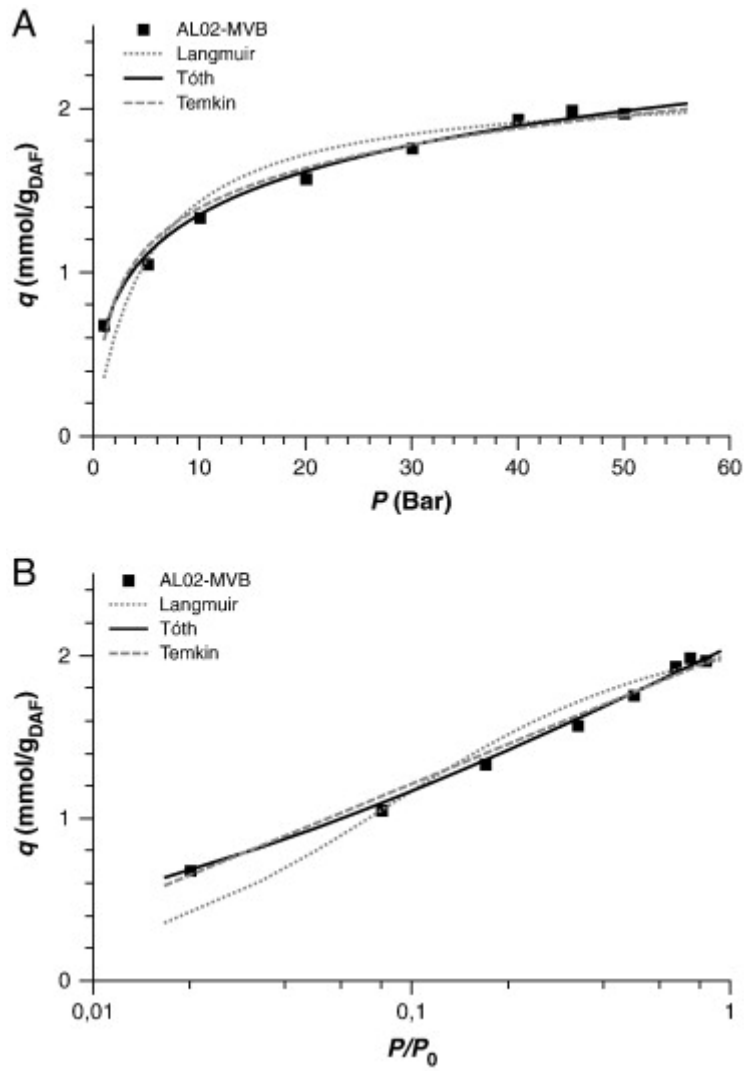


Fig. 2. : CO₂ sorption isotherms for AL02-MVB with the fit results obtained with Langmuir's, Tóth's and Temkin's equations; (A) with linear abscise and (B) in logarithmic of P/P_0 form.

For Langmuir, χ equals:

$$\chi L = 1/\alpha L P_0 + 1$$

giving the corrected form:

$$\theta = \frac{q}{q_{mc}} = \frac{\chi_L \alpha_L P}{1 + \alpha_L P}$$

where q_{mc} is the corrected maximum adsorbed quantity.

For Tóth χ equals:

$$\chi T = 1/(\alpha T P_0)^{n+1}$$

The equation of Tóth becomes:

$$\frac{q}{q_{mc}} = \frac{\chi_T^{1/n} \alpha_T P}{[1 + (\alpha_T P)^n]^{1/n}}$$

The constant χ is always strictly inferior to 1 so monolayer adsorption capacities of the modified equation are always below those calculated by the absolute isotherm. Yet, whatever the model chosen,

$$q_{mc} = q_m / \chi^{1/n}$$

q_{mc} , the corrected monolayer capacity, is always lower than q_m that is the uncorrected value. So, when n is small, the error on q_m is significant. This induces a misestimating in the calculation of the specific surfaces.

This correction was applied on all isotherms and an example is given on Fig. 3. The fitted parameters are summarized in Table 2. Note that this correction does not change other parameters (α_L for Langmuir's and α_T and n for Tóth's models). For samples AL02-MVB or ES01-HVB having lowest n values (and thus heterogeneous internal coal surfaces), the differences between q_m and q_{mc} are great. The correction is negligible with Langmuir's model (for $n = 1$) but much significant with Tóth's equation (especially when n is small). The obtained q_{mc} values predicted from the Langmuir's and Tóth's models are equivalent and fit well with experimental data.

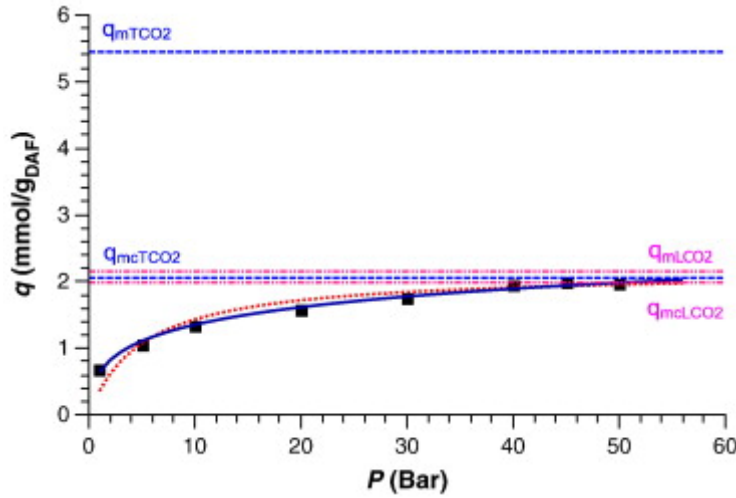


Fig. 3. : Example of corrected CO₂ isotherm on AL02-MVB for Tóth's and Langmuir's isotherms.

Table 2. Parameters for CO₂ for models: Langmuir (L), Tóth (T) and Temkin (Tem).

		CO04-HVB	CO02-HVB	CO01-SB	BHL01-HVB	ES02-MVB	ES01-HVB	GR02-MVB	AL02-MVB	AL01-MVB	JER01-MA	CO03-A
L	α_L (Bar ⁻¹)	0.17	0.24	0.12	0.57	0.11	0.36	0.58	0.20	0.30	0.79	0.77
	q_m (mmol/g _{DAF})	0.71	1.38	2.26	1.08	1.68	0.97	1.18	2.15	1.47	2.25	1.66
	q_{mc} (mmol/g _{DAF})	0.64	1.28	1.97	1.05	1.46	0.93	1.15	1.98	1.39	2.20	1.62
T	n	1.00	0.50	0.31	1.00	0.52	0.20	0.69	0.23	0.34	1.00	1.00
	α_T (Bar ⁻¹)	0.17	0.71	0.37	0.57	0.2	126.9	1.24	7.42	4.31	0.79	0.77
	q_m (mmol/g _{DAF})	0.71	1.76	5.80	1.08	2.52	2.03	1.25	5.45	2.17	2.25	1.66
	q_{mc} (mmol/g _{DAF})	0.64	1.31	2.07	1.05	1.52	0.96	1.16	2.05	1.44	2.20	1.62
Tem	RT/Q	0.22	0.18	0.21	0.14	0.22	0.14	0.14	0.17	0.16	0.12	0.12
	K_0	2.01	4.75	1.76	33.19	1.51	22.82	30.63	5.31	11.13	91.41	83.49

Using the q_{mc} values given in Table 2, a classification of coals depending on their adsorption capacities can be done:

$$\begin{aligned}
 &\text{JER01 - MA} > \text{CO01 - SB} = \text{AL02 - MVB} > \text{CO03 - A} > \text{ES02} \\
 &\quad - \text{MVB} > \text{AL01 - MVB} > \text{CO02 - HVB} > \text{GR02 - MVB} > \text{BHL01} \\
 &\quad - \text{HVB} > \text{ES01 - HVB} > \text{CO04 - HVB}.
 \end{aligned}$$

X > Y means that adsorption capacity of X is greater than the adsorption capacity of Y

X = Y means that adsorption capacity of X equals the adsorption capacity of Y

The adsorption capacity of coal JER01-MA is the greatest ($q_{mc} = 2.2$ mmol/g) and the one of coal CO04-HVB the lowest ($q_{mc} = 0.64$ mmol/g).

Fig. 4 represents microporous surface *versus* the amount adsorbed at saturation (q_{mc}). A linear relation is found if we exclude the coals with high percents of ashes (superior at 15%). The type and amount of ashes are important for CO₂ adsorption. Another coal was excluded: BHL01-HVB. It presents a microporosity twice to three times superior to the other coals and 5% of ashes.

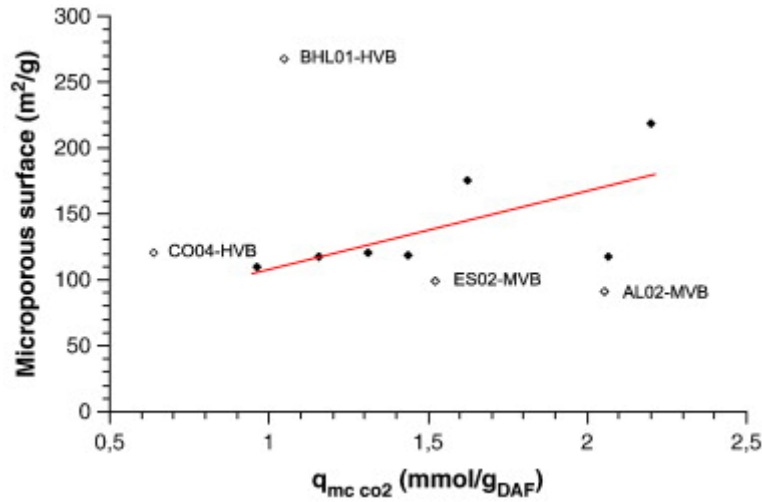


Fig. 4. : Microporous surface versus the corrected maximum adsorbed quantity of CO₂ (q_{mc}). The excluded coals are CO04-HVB, ES02-MVB, AL02-MVB and BHL01-HVB.

To apply the Temkin's model, the q_{mc} value determined with the Tóth's model is used. Both Temkin's and Tóth's equations fit well with CO₂ experimental data. These models provide information about surface heterogeneity and heat of adsorption. The n parameter from Tóth's model, which reflects heterogeneity of coal surface, is often different from 1 except for BHL01-HVB, CO03-A, CO04-HVB and JER01-MA. Except the four previously quoted coals, other seven samples have a heterogeneous surface at low pressure with CO₂ molecule, but it is currently difficult to determine the nature of these heterogeneities.

The Langmuir coefficient α_L is the highest (around 0.78) for the JER01-MA (meta-anthracite coal) and CO03-A (anthracite coal) and the lowest (0.12) for CO01-SB (lignite, low rank coal). This parameter is proportional to the maturity of the coal. Similar results were obtained by other authors (Busch et al., 2003).

K_0 values determined with Temkin's equation provide information about CO₂ adsorption affinity. Higher is the value, better is the affinity. In this case, five coals ($K_0 > 20$) have a good affinity for CO₂: JER01-MA, CO03-A, GR02-MVB, BHL01-HVB and ES01-HVB. Except JER01-MA sample, these coals have not the greatest adsorption capacities. Note that K_0 values are not linked to maximum adsorption quantities but forced the shape of the isotherm curves in the domain of low pressures. Samples that have the highest K_0 values are those that have the highest CO₂ adsorption capacities at low pressures (Fig. 1). However, there is a relation between K_0 and the rate of volatile matter (Fig. 5). This relation is not linear but exponential: more the rate of volatile matter is weak more are affinity for the CO₂ is strong. The adsorption is strongest with a high-rank coal. The coal BHL01-HVB was excluded from this relation. It presents a microporosity twice to three times superior to the other coals.

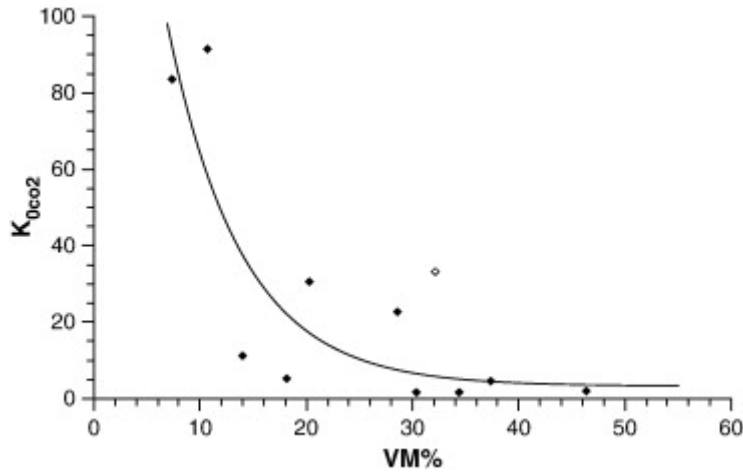


Fig. 5. : K_0 versus the volatile matter. The excluded coal is BHL01-HVB which is the coal with the biggest microporous specific surface of our panel.

4.2. CH_4 sorption

CH_4 adsorption isotherms have the same shape than those determined for CO_2 : they are all isotherms of type I according to the IUPAC classification (Fig. 6). Thus the same models and corrections for maximum adsorption capacities q_m are used. All values for parameters from Langmuir's, Tóth's and Temkin's models are shown in Table 3. As for CO_2 , a classification of coals can be done using q_{mc} values (Table 3):

JER01 – MA > AL02 – MVB > CO03 – A > CO01 – SB > GR02 – MVB $\approx$ ES02 – MVB $\approx$ CO02 – HVB > BHL01 – HVB $\approx$ ES01 – HVB > CO04 – HVB.

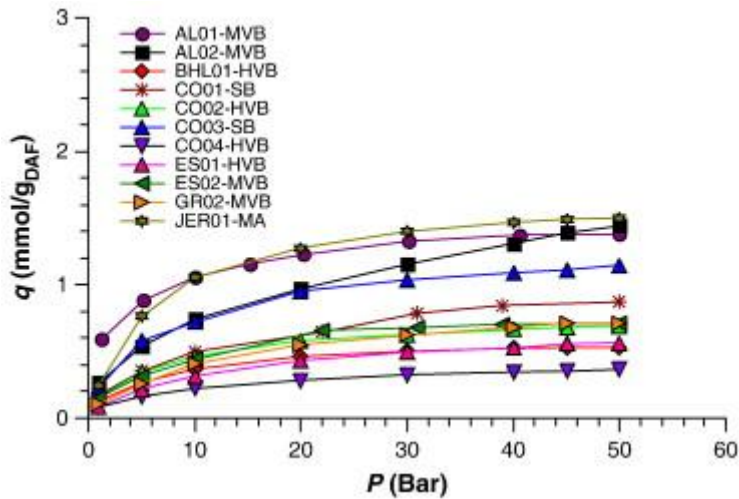


Fig. 6. : CH_4 sorption isotherms for all coals (DAF: dry and ash-free) at a temperature of 298 K. The error bar of the excess sorption measurements is estimated at 5% of the sorption.

Table 3. Parameters for CH₄ for models: Langmuir (L). Tóth (T). Temkin (Tem).

		CO04-HVB	CO02-HVB	CO01-SB	BHL01-HVB	ES02-MVB	ES01-HVB	GR02-MVB	AL02-MVB	AL01-MVB	JER01-MA	CO03-A
L	α_L (Bar ⁻¹)	0.15	0.18	0.11	0.20	0.11	0.15	0.10	0.10	0.22	0.17	0.17
	q_m (mmol/g _{DAF})	0.41	0.76	1.02	0.59	0.66	0.82	0.85	1.67	0.69	1.68	1.26
	q_{mc} (mmol/g _{DAF})	0.37	0.70	0.89	0.54	0.57	0.74	0.73	1.42	0.64	1.53	1.15
T	n	1.00	0.55	0.29	0.58	0.45	1.00	0.48	0.34	0.56	1.00	0.56
	α_T (Bar ⁻¹)	0.15	0.34	0.27	0.36	0.16	0.15	0.14	0.24	0.49	0.17	0.30
	q_m (mmol/g _{DAF})	0.41	0.99	3.27	0.72	1.18	0.82	1.46	3.96	0.83	1.68	1.64
	q_{mc} (mmol/g _{DAF})	0.37	0.72	0.95	0.56	0.60	0.74	0.77	1.47	0.65	1.53	1.18
Tem	RT/Q	0.21	0.20	0.21	0.20	0.21	0.22	0.22	0.21	0.19	0.21	0.20
	K_0	2.39	2.71	1.52	3.03	1.50	1.82	1.41	1.59	3.77	2.23	2.47

This classification is more or less the same as the one obtained for CO₂. JER01-MA is the coal with the highest CH₄ adsorption capacity and coal CO04-HVB has the lowest CH₄ adsorption capacity. As with CO₂ sorption, a linear relation is found between microporous surface and q_{mc} (Fig. 7). In this case, only two samples with the highest ashes percentage (CO04-HBV and AL02-MVB with 22.05% and 31.7% of ashes respectively) were excluded. For CH₄ adsorption, the ashes influence is less important than for CO₂ adsorption. The same remark can be made with BHL01-HVB coal.

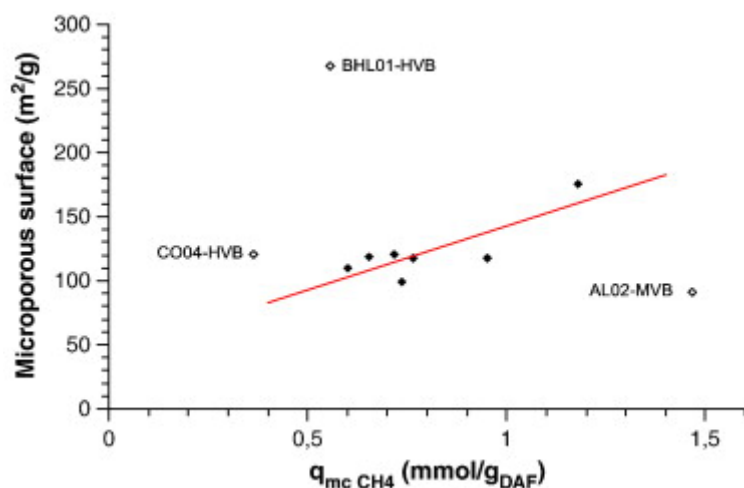


Fig. 7. : Microporous surface *versus* the corrected maximum adsorbed quantity of methane (q_{mc}). The excluded coals (empty points) are CO04-HVB, AL02-MVB and BHL01-HVB.

Langmuir's coefficient α_L is very small for all samples and thus it is difficult to make a good interpretation.

The K_0 constant determined through Temkin's model gives information about coal affinity for CH₄. All studied coals show very low affinities for CH₄ ($K_0 < 3.03$). Once again coal JER01-

MA is the one which adsorbs the greatest quantity of CH₄ but for this molecule, the K_0 parameter is still very low, reflecting low affinity of studied coals for CH₄. The n parameter obtained with Tóth's model is often different from 1 except for CO04-HVB, ES02-MVB, JER01-MA.

4.3. Comparison of CO₂ and CH₄ sorption

The q_{mc} parameters determined with Tóth's or Langmuir's models show that monolayer adsorbed CH₄ quantity is always below the one determined for CO₂ on the same coal (Fig. 8). This trend is well-known and reported by numerous authors in the literature ([Borowski, 1975] , [Ettinger et al., 1967] , [Li et al., 2010] and [Wang et al., 2009]). Ratios between the q_{mc} sorption capacities for pure CO₂ and CH₄ among the panel of studied coal samples vary between 1.4 for high rank coals (AL02-MVB, CO03-A and JER01-MA) and 2.2 for low rank coals (CO01-SB and AL01-MVB) (Table 4) with an average of 1.7 ± 0.3 .

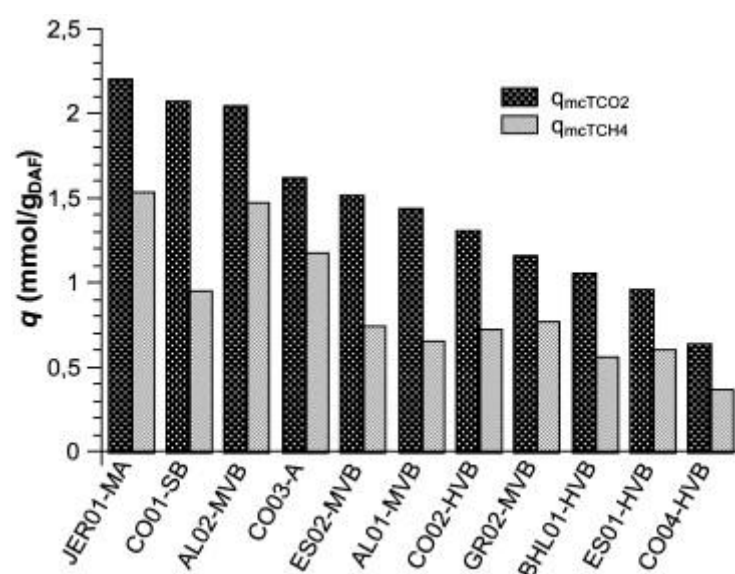


Fig. 8. : Classification on coals according their adsorption capacity.

Table 4. Comparison of CH₄ and CO₂ parameters obtained with Langmuir's and Temkin's models.

	CO04-HVB	CO02-HVB	CO01-SB	BHL01-HVB	ES02-MVB	ES01-HVB	GR02-MVB	AL02-MVB	AL01-MVB	JER01-MA	CO03-A
q_{mcCO_2} / q_{mcCH_4}	1.73	1.83	2.21	1.94	1.97	1.63	1.57	1.39	2.17	1.44	1.41
K_{0CO_2} / K_{0CH_4}	0.84	1.75	1.16	10.95	0.83	15.21	21.72	3.34	2.95	40.99	33.80

For the Langmuir's coefficient α_L , values obtained for CO₂ are always higher than those determined for CH₄. Relative affinities of the coals for the two molecules can be determined from the K_{0CO_2}/K_{0CH_4} ratios (Table 4). Coal JER01-MA shows the largest difference in affinities, with an affinity 41-time greater for CO₂. Coal samples CO04-HVB and ES02-MVB distinguish themselves from other coals because the same ratio is inferior to 1 ($K_{0CO_2}/K_{0CH_4} \approx 0.8$). This means that these two coals show a greater affinity for CH₄ than for CO₂.

5. Conclusions

This study provides experimental data for methane and carbon dioxide adsorption on coal samples from different countries. Adsorption experiments were conducted using a gravimetric method. Experimental results were analyzed through Langmuir's, Tóth's and Temkin's sorption isotherm model equations which lead to estimate relative performances of these models, describe the experimental results, quantify the gas sorption on coals and classify them.

Our experimental isotherms have an evident character of type I (Langmuir type), reflecting adsorption in a microporous adsorbant with a good affinity with CO₂ and CH₄. So, the adsorption could be considered as reversible, local and limited to a monolayer and the Langmuir equation fits reasonably well with experimental data. Tóth's and Temkin's models appear to be more accurate due to the corrected forms suggested by Tóth. Parameters obtained with these two models were used to classify samples for CO₂ storage efficiency.

In order to accurate estimation of the maximum sorption capacities of coals at high pressure, a correction of the parameter q_m has to be made, especially for heterogeneous coals. Indeed, the calculated q_m values are higher than the experimental data. It is necessary to keep in mind that in case of high pressure adsorption, the adsorption quantities found from experiments are excess adsorption values. This is very important when isotherm curves are used to determine specific surface area for example. The q_m values must be estimated precisely not to over-estimated the site's storage capacity.

The comparison between the adsorption affinity (K_0 values determined with Temkin's equation) and the rate of volatile matter shows an exponential relation indicating that the adsorption is strongest with a high-rank coal which reinforce the interest of the use of high rank coals for CO₂ storage. Nevertheless, it is not the only parameter to take into account. For samples with lower ashes percentage, maximum adsorption capacities for CO₂ and CH₄ are proportional to the microporous volume but the presence of ashes disturbs this relationship. The composition, the percentage and the nature of ashes in a coal are important to select the storage site. For all samples maximum adsorption capacities determined for CO₂ are higher than the ones determined for CH₄. Ratios between CO₂ and CH₄ adsorption capacities vary from 1.4 for high rank coals to 2.2 for low rank coals. These relative affinities of coals for CO₂ and CH₄ can be compared through $K_{0\text{CO}_2}/K_{0\text{CH}_4}$ ratios. This emphasizes coals having a higher affinity for CO₂ than for CH₄, and enables to select coals showing the largest differences of affinity for CO₂ and thus permits to identify the most effective coals for CO₂ storage by adsorption.

The total amount of CO₂ that can be adsorbed in coal seams depends on porosity, ashes but also on coal affinity for this molecule. Thus, several parameters must be determined from adsorption isotherm curves: q_{mc} , as the corrected monolayer capacity, α_L as the Langmuir constant, the K_0 constant of Temkin's model and the $K_{0\text{CO}_2}/K_{0\text{CH}_4}$ ratio. These parameters can be used to classify coals from different maturities and to do a first selection regarding CO₂ storage efficiency. In our case, the modelling study of a significant number of coals from various ranks shows that anthracites seem to be the coal type with the highest capacity. Further studies focusing on other parameters will detail nature of coal that best suits to CO₂ storage purposes.

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