Identification of porous coal structure using of Multiple Sorption Model

M Wójcik1,*, G S Jodłowski1
1AGH University of Science and Technology, Al. A.Mickiewicza 30, 30-059 Krakow, Poland
E-mail: mwojcik@agh.edu.pl

Abstract. This paper presents a review of the investigation into coal sorption properties carried out on set of coal samples ranging from lignite up to anthracites using the Multiple Sorption Model. The coexistence of three phenomena, absorption, expansion and adsorption, is the basis of sorption modelling together with the copolymeric model of coal structure. Decreasing volumetric ratio of molecular phase and increasing macromolecular phase parameter tendencies versus coal rank are stated. Parameters describing sorption have no regular trends, depending on the character of the sorbate. The biggest surface area and adsorption is indicated by H2O and it has a decreasing tendency with coal rank. CH4 and CO2 show a slightly increasing trend in adsorption capacity vs. coalification degree. For the three above stated sorbates, absorption plays a different role in the whole sorption process, and its influence on the adsorption sub-process is indicated.

1. Introduction
Coal as a fossil organic substance has been of interest to technology for hundreds of years. Yet its structure and predictable properties for any given sample are not fully recognised and describable by the common theory. Some scientists investigating coal properties regarded the material from different perspectives, for example as an organic rock, a solid fuel [1], a substrate for chemical reactions/processes such as transformation to syngas or liquid fuel [2-5], or as a cheap sorbent [6-9]. In every purpose, coal properties such as its geometric/porous structure, petrographic composition, energetic properties and interaction with other chemicals play an important role in developing and controlling the technological process. This paper aims to investigate the porous structure properties of coal components and their interactions with small molecule substances. Many models of coal structure are elaborated, taking into account its composition and properties as well as its behaviour in different processes. It seems that the co-polymeric model of coal structure is the most suitable for the description of the geometric and energetic properties of different kinds of coal. This approach to defining coal matter is the basis for the elaborated Multiple Sorption Model (MSM) in the statistical point of view, including a broad spectrum of coals from lignite, sub-bituminous and bituminous up to anthracites and active coals.

Sorption isotherms of different small molecule substances on samples of hard coals were used for the thermodynamic analysis of the properties of pore structure, for rough analysis of specific interactions, and for the investigation of energetic interactions between coal substance and sorbate molecules. Many investigations result in a database of analyses of the sorption of different substances
on different kinds of coal samples. The idea of simultaneous analysis of different sorbates on the same coal sample is introduced to the study (the unchangeable parameter of the sorption system – monolayer capacity) for more adequate estimation of many parameters introduced to the model. This paper presents a set of such analyses and summary thereof.

2. Fundamentals of the Multiple Sorption Model (MSM)

The copolymer model of coal structure is taken as the basis for thermodynamic dissertations resulting in the set of formulas composing MSM.

2.1 Copolymer model of coal structure

This point of view on coal structure assumes the presence of main groups of components such as:

- Macromolecular phase – set of aliphatic, alicyclic or heterocyclic compounds connected to each other and to arene domains, constructing a rigid network for the whole coal substance.
- Arene domains – different size forms constructed by plates of condensed benzene rings connected to each other forming the spatial arrangement. Very rigid and not attainable by any penetrants – forming a hole in the model network from the point of view of entropy. This component is also a part of macromolecular network, but it is specially indicated because of its importance in thermodynamic analysis.
- Molecular phase – composed of aliphatic, alicyclic and heterocyclic chains of organic compound not connected each other. The average length and partition in coal mass depend on degree of coalification. Its state is semi-elastic in the mass of coal, and moreover it could flow very slowly in the interior of the rigid macromolecular phase.
- Pores – empty spaces in the coal mass, which generally remain after desorption of natural gas, methane, carbon dioxide and water.
- Mineral admixtures – small particles of inorganic substances such as sulphates, pyrite, carbonates, and so on. Rigid, but with a negligible influence on the sorption processes in comparison to coal mass. [10, 11]

![Figure 1. Visualisation of the structure of coal within the copolymer model.](image)
place that is occupied by another segment of the components. In the case of pores, the model assumes that the same position is simultaneously accessible for the segment of pore and the sorbate molecule.

The name “copolymer model” means that there are many monomers repeated in the structure without any easy describable order. Therefore, the model space for sorption phenomena is described from the statistical point of view, without reference to the particular location in the coal substance. Coal is a composition of different objects from five main groups of components (Figure 1).

2.2 Construction of the Multiple Sorption Model

The physicochemical space structure of coal as outlined above is a basis for thermodynamic dissertation which effects the set of formulas describing the entropy of mixing and enthalpy of interactions of all the segments of every component of the sorption system. The formulas take into account the complex structure: the distribution of pores, inaccessibility of space taken by the arene domains (decreasing entropy of mixing and its insulation effects for sorbate molecule interaction), and the effect of the presence of the elastic part of the coal substance (absorption, swelling and contraction). Finally, analysis results in formulas describing three phenomena: absorption (location of sorbate molecule – penetrant – in the place taken earlier by the segments of the molecular phase), adsorption (location of sorbate molecule – adsorbate – on the free surface of the coal matter, including in pores) and expansion, which is a sub-process between absorption and adsorption (location of sorbate molecules in the pores smaller than its diameter which need to be expanded – sub-micropore) [10].

Expansion and swelling should not be confused with each other. Swelling of coal mass is the effect of the expansion and contraction of pores. Part of the pores could be narrowed or completely disappear due to stress resulting from expansion; this is contraction, and usually results in swelling to a lesser degree than expansion[12].

Absorption is possible because of enthalpy consumed to overcome the cohesion forces of the coal material. Normally, molecules of every physical substance are in continuous movement (oscillation) and momentary changes of location of the segments in the model space represent the natural movements of molecules. Adsorption is a physicochemical process with a dynamic balance, which also generates energy (enthalpy) as an effect of molecules interacting by the use of adhesion forces, in accordance with the Berthelot Rule [13]. Expansion involves both types of interaction (cohesion and adhesion).

The system of pores is divided into 11 virtual sub-systems for mathematical reasons, in order to obtain the pore distribution, but the thermodynamic description of whole phenomena and whole pore sizes is continuous. The first sub-system is assigned to pore radius R=0 (R - is pore radius relative to molecule size, unitless), which means that absorption is a phenomenon that is estimated and only cohesion forces take place, but that interaction with sorbate molecules from other sub-systems is possible. The next nine sub-systems are assigned to the pores in the range 0>R>1, constructing normal distribution spread around the average pore radius Rsr. The final sub-system is assigned to pores with radius R>1, which means the whole adsorption process involving adhesion forces. Adsorption, playing the most important role in the whole sorption process, is a very complex phenomenon because of the heterogeneity of the surface. Therefore, this part of the process is described by the most developed part of model, called the LBET model (and by the family of successive models) [13-15].

MSM gives a complex description of coal structure by:

- Volume partitions of unconnected chains (UFC) cross-linked chains (UCC), arene domains (UAD) and pores (UH).
- Geometric factors of coal as a sorbent: volume of sub-micropores (Vh) in cm³/g, total capacity of pores (mht) in mmol/g, adsorption capacity (mhad) in mmol/g, and real adsorption (ads) in mmol/g (all relative to the mass of coal).
- Geometric factors of molecule contacts with coal matter: ZA - quality of contacts in smaller sub-micropores (below Rsr), ZB - quality of contacts in bigger sub-micropores (exceeding Rsr), ahb - average surface area of sub-micropore relative to the size of sorbate molecule.
Energetic factors of sorption: $Q_{abs}$ - enthalpy of absorption, $Q_{ads}$ - enthalpy of adsorption, $\delta C$ - cohesion density parameter.

The above list does not present all parameters of models which could be calculated within the model. Based on the fundamental parameter some additional information such as the partition of absorption in whole sorption process ($abs/sorp$) and partition of expansion ($exp/sorp$) could be obtained. The most informative functions of the model are calculated distributions of molecules in different sub-systems.

Selected parameters are set at the beginning of the simulation based on the literature [19] and previous optimization studies. These parameters are the percentage mass shares of arene domains, unconnected chains and cross-linked chains as well as pores. However, during simulation they may change, in particular the share of pores. These changes can only be of limited range so as not to exceed the framework available for coal with a given degree of coalification.

3. Investigated samples of coal

All samples were investigated under laboratory conditions. Every sample was homogenised after grinding and sieving to the appropriate grain size (usually in the range 0.1-2 mm). A small portion of sample was introduced to the measurement vessel (usually about 2g, but in some cases -B80 and AK - 200 - 300g). The mass of the sample has no influence on the parameters given in values relative to coal mass, so could be disregarded. Samples were purified in a $10^3$ Pa vacuum before measurements were taken. Sorption isotherms were measured with the micro burette apparatus for liquid sorbates (water, methanol, and small organic compounds such as hexane, benzene etc.) or with the use of manostate apparatus, which involves the volumetric method of measurement. Consecutive points of isotherms were obtained by the dosage of the next portion of the sorbate to the measurement space. This space was in thermostatic conditions (298 K). It is important to take the measurement with enough time to obtain the thermodynamic balance. This means that a measurement of a separate point of isotherm takes three to five days, and even a whole week in the case of CO$_2$. This situation is caused by the very slow-going phenomenon of absorption. Too quick measurements of consecutive points of sorption isotherm prolong the absorption process to the next measured point and lead to a constant error in the measured curve.

Properties of the selected samples are presented in Table 1.

| Sample | $d_{He}$ [g/cm$^3$] | $d_{Hg}$ [g/cm$^3$] | Proximate Analysis | Ultimate Analysis | (O+N)$_{daf}$ |
|--------|---------------------|---------------------|--------------------|------------------|---------------|
|        |                     |                     | $A^a$ $W^a$ $V^{daf}$ $C^{daf}$ $H^{daf}$ $S^{daf}$ |                  |               |
| W31B   | 1.617               | 1.343               | 1.7 n.a. 36.50     | 73.5 n.a. n.a. n.a. | 19.28         |
| W31J   | n.a.                | n.a.                | 2.6 8.75 39.20     | 75.16 5.56 0.62(a) | 11.51         |
| B80    | 1.387               | 1.230               | 15.50 1.65 40.90   | 79.60 5.00 0.71   | 14.69         |
| B82*   | 1.36                | 1.255               | 2.48 3.76 40.80(a) | 80.88 5.26 0.62(a) | 13.14         |
| W32    | 1.473               | 1.328               | 8.8 2.5 36.3       | 82.4 5.16 0.86(a) | 11.51         |
| W33    | 1.403               | 1.336               | 2.00 2.03 30.30    | 83.31 5.1 0.30(a) | 8.60          |
| AK     | 1.35                | 1.23                | 6.15 1.55 29.20    | 86.40 4.9 0.8     | 1.7(N$^{daf}$) |
| Th**   | 1.37                | 1.305               | 7.89 1.13 29.30    | 86.40 4.65 b.d.   | 8.37          |
| K87*   | 1.36                | 1.306               | 16.64 1.32 32.68(a) | 86.55 5.22 0.90(a) | 7.37          |
| Vi**   | 1.4                 | 1.30                | 7.78 1.25 27.90    | 87.60 4.88 b.d.   | 6.41          |
| Wa**   | 1.44                | 1.35                | 8.92 0.90 16.40    | 89.10 3.47 b.d.   | 5.94          |
| M510   | 1.29                | 1.26                | 2.27 b.d. 22.43    | 90.08 4.76 b.d.   | 4.13          |
| W42    | 1.434               | 1.357               | 3.6 n.a. 13.1      | 91.2 n.a. n.a. n.a. |               |
| W      | 1.45                | 1.30                | 9.10 0.77 9.46     | 92.13 2.95 b.d.   | 3.76          |
| M85*   | 1.43                | 1.357               | 3.70 0.81 6.09(a)  | 92.41 3.02 0.46(a) | 4.09          |
| A      | 1.97                | 0.84                | 23.50 2.80 0.80    | 97.00 0.9 0.75 b.d. |               |

*index daf means dry and ash-free state of parameter*
(a) - in some cases, value of parameter is calculated in analytic state

Symbols of contents: A - ash, W - humidity, V - volatile matter, C - carbon, H - hydrogen, S - sulfur, O - oxygen, N - nitrogen; all in %

* - isotherms and sample analyses taken from [16]

** - isotherms and sample analyses taken from [17, 18]

Selected samples cover the range of lignites, sub-bituminous and bituminous coals up to anthracites.

The sorption isotherm, containing a small number of points, is transformed mathematically to the curve containing about 30 points with the aim of representing the shape of the isotherm well. Original points of isotherms introduced to the MSM calculation packet are automatically transformed to a form usable in the model space.

The next step is simulation of the sorption isotherm using structural and geometrical parameters for which tendencies versus coalification degree are known [19, 20]. The programme calculates energetic parameters of molecules in sub-systems and parameters of sorption systems (theoretical isotherms), finally adding all phenomena to give the theoretical isotherm of total sorption, which is checked for fitting with the empirical one. The process of computation of the next set of system parameters is repeated until the satisfactory fitting of theoretical and empirical sorption isotherm is reached.

4. Results of Multiple Sorption Model computation

For the purposes of precise estimation of the sorption system parameter, the procedure employed several sorbates elaborated in parallel on the same coal sample. In this case, some structural parameters of coal are the same for all sorbates and the surface geometry and sorbate interactions are match made only. If necessary, selected structure parameters are changed, but for all sorption systems worked out together and with respect to common known tendencies. Exemplary results of the calculations are presented graphically in Figures 2-4.

![Figure 2: Sorption isotherms in physical sub-systems for K87 sample: green - absorption, blue - expansion, red - monolayer adsorption, purple dashed – poly-layer adsorption, black solid - total sorption, circles - empirical sorption.](image)
Figures 2 and 3 illustrate estimates of sorption systems of the K87 coal sample with water, carbon dioxide and methane. Figure 2 presents multiple isotherms in sub-systems. Only sorption of water vapour shows poly-layer adsorption (purple dashed line), which is an effect of the specific interaction of the polar sorbate with the surface active group. This situation is taken into account in the LBET description of adsorption. The remaining sorption systems presented (with CO₂ and CH₄) contain monolayer adsorption. On the other hand, sorption of water vapour and carbon dioxide contains a significant absorption sub-system contrary absorption of methane, for which it is very small. Such a tendency for absorption of methane is observed for all coal samples. Expansion is present in sorption for nearly all samples, but the presented one (K87) shows only dual character (adsorption-absorption) without expansion (see Figure 3 - middle chart). The remaining sorption systems have expanded sorption isotherm distribution to the sub-systems with a mound in the range of pores 0.5<R<1. This distribution is well observable in Figure 4. The curve plotted in R=0 is the absorption isotherm (Figure 3), and in R=1 it is the adsorption isotherm. Remain isotherms plotted in the sub-systems (in the range 0<R<1) are expansion-like and summarise to the expansion curve presented in Figure 2.

Charts presented in Figure 4 present the summarised isotherm from the sets shown in Figure 3. Distribution of sub-micropore capacity is constructed in such a way. The dotted line on the charts shows the value of radius for maximum distribution of sub-micropores (Rₐ). Simultaneously occurring is a parameter dividing zones of correction factors of contact geometry for smaller and bigger pores.
5. Summary of Multiple Sorption Model investigations

Results of several investigations of different coal samples and different sorbates allow us to state some tendencies for coal. Selected results are presented in Figures 5 - 8. Tendencies of structure parameters versus coalification degree are displayed in Figure 5. The starting parameters of the simulation are changed if manipulation of other parameters (sorption system characterisation) do not lead to successful fitting.

Volumetric partitions of components building the macromolecular phase (connected chains and arene domains in Figure 5) increase with increasing carbon content. Conversely, partitions of unconnected chains and pores decrease with increasing carbon content. However, the tendency of pore partition is not very clear. These tendencies are in agreement with commonly known trends in coals, but pore partition should slightly increase for anthracites.

![Graphs: a) connected chains, b) arene domains, c) unconnected chains, d) pores]

**Figure 5.** Volumetric partition of components of coal matter (y-axis description is volumetric partition of selected coal component given in caption above the chart).

A better picture of the surface properties of different coal samples is obtained from a review of selected adsorption parameters calculated in the model (given in mmol/g): total volume of pores nht,
including bigger pores such as meso and macropores, pores accessible for pure adsorption sub-process nhad and real adsorption capacity in pores nads without specific interactions (Figure 6). One could state on the basis of the charts presented in Figure 6 that carbon dioxide molecules cover all the adsorptive pores in the monolayer, especially for lower rank coal samples. This is probably caused by the origin of pores which are empty spaces after desorption of occluded natural gases such as carbon dioxide and methane. For higher rank coal samples, a small discrepancy with this tendency is observed. Theorem on pore origin is also supported by the course of the graph nhad and nads for methane, which are the same, but in which a small shift appears. This shift is probably the effect of small partition of absorption in the whole sorption process, during which some inaccessible pores remain free from methane. A big difference between estimated total pore capacity nht and its usage by sorbate molecules nads for both gases is caused by the lack of condensation in pores or specific interactions. In the case of water vapour sorption, however, specific interactions and condensation in mesopores cause a greater usage ratio for all coal samples. However, the trend of adsorption changes course for higher rank coals, which is caused by the lower content of surface oxygen groups in coking coals and anthracites [21-25], thus adsorption decreases because of the lack of specific interactions.

**Figure 6.** Changes in adsorptive properties of coal samples vs. water vapour, carbon dioxide and methane, capacities in millimoles per gram of coal: nht - total pores, nhad - pure adsorption pores, nads - pores filled in adsorption way.
6. Conclusions
The Multiple Sorption Model, together with the poly-layer adsorption model class LBET, allows fine identification of coal structure and sorption properties despite its complex structure and complicated thermodynamic description. One could precisely estimate the parameters of the system using simultaneous (or parallel) analysis of sorption systems containing many sorbates and the same coal sample, because some of the structure and sorption factors are the same for all sorption systems measured on the same coal sample.

Some clear tendencies are proved under investigation. These include the volumetric partition of coal substance compounds, and some such as sub-micropores, big absorption partition in sorption of CO₂, smaller for H₂O and insignificant for CH₄ can be stated.

The obtained estimates could be used for predictions of coal behaviour under technical processes such as methane storage or carbon dioxide sequestration [26, 27].

Acknowledgement
This work was carried out with the financial support of AGH University of Science and Technology Statutory Research No. 11.11.210.373.

References
[1] Cao W, Cao W, Peng Y, Qiu S, Miao N and Pan F 2015 Powder Technology 283 p 512–518
[2] Feng J, Li J and Li W 2013 Fuel Processing Technology 109 p 19–26
[3] Lin X, Wang C, Ideta K, Miyawaki J, Nishiyama Y, Wang Y, Yoon S and Mochida I 2014 Fuel 118 p 257–264
[4] Yu J, Tahmasebi A, Han Y, Yin F and Li X 2013 Fuel Processing Technology 106 p 9–20
[5] Czerski G, Dziok T, Strugała A and Porada S 2014 Przemysł Chemiczny 93 (8)
[6] Charrière D and Behra Ph 2010 Journal of Colloid and Interface Science 344 p 460–467
[7] Nishino J 2001 Fuel 80 p 757-764
[8] Švábová M, Weishauptová Z, Pribyl O 2011 Fuel 90 p 1892–1899
[9] Simatea G S, Maledi N, Ochieng A,, Ndlovu S, Zhang J and Walubit L F 2016 Journal of Environmental Chemical Engineering, 4 (2) p 2291-2312
[10] Jodłowski GS, Baran P, Wojcik M, Nodzenski A, Porada St and Milewska-Duda J 2007 Applied Surface Science 253 p 5732–5735
[11] Milewska-Duda J, Duda J, Nodzeński A and Lakatos J 2000 Langmuir 16 (12) p 5458-5466
[12] Pan Z 2012Frontiers of Chemical Science and Engineering 6 (1) p 94-103
[13] Milewska-Duda J, Duda J T, Jodłowski G and Kwiatkowski M 2000 Langmuir 16 (18) p 7294–7303
[14] Duda J T and Milewska-Duda J 2002Langmuir 18 (20) p 7503–7514
[15] Milewska-Duda J and Duda J T 2002Colloids and Surfaces A: Physicochemical and Engineering Aspects 208 p 71–81
[16] Ceglarska-Stefańska G 1990 Współzależność procesów sorpcyjnych i dylatometrycznych zachodzących w układach: węgle kamiennie - para wodna, dwutlenek węgla, metan, Zeszyty Naukowe AGH, Chemia 16, Kraków 1990
[17] Ceglarska-Stefańska G, Nodzeński A and Holden S 2007 Mineral Resources Management 23 (3), p 51-59
[18] Nodzenski A 1996 Adsorption Science & Technology 13 (2)p 71–84
[19] Van Krevelen D W 1965 Fuel 44 p 229
[20] van Heek K H 2000 Fuel 79 (1) p1-26
[21] Chen Y, Mastalerz M and Schimmelmann A 2012 International Journal of Coal Geology 104 p 22–33
[22] Huang X, Chua W, Sun W, Jiang C, Feng Y and Xue Y 2014 Applied Surface Science 299 p 162–169
[23] Liu X, Feng L, Wang X, Zhang Y and Tang H 2015 *Chinese Journal of Chemical Engineering* 23 p 456–460

[24] Zhou G, Xu C, Cheng W, Zhang Q and Nie W 2015 *Journal of Analytical Methods in Chemistry*

[25] Zhou F, Liu S, Pang Y, Li J and Xin H 2015 *Energy Fuels* 29 (3) p 1550–1557

[26] Perera M S A, Ranjith P G and Choi S K 2011 *Environ Earth Sci* 64 p 223–235

[27] Staša P, Chovancová K, Kebo V, Chovanec J and Kodym O 2013 *Procedia Earth and Planetary Science* 6 p 14 – 23