

SEMILOG COORDINATES IN PRESENTING SOME CHARACTERISTICS OF POROUS SYSTEMS

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Semilog coordinates are widely applied in presenting characteristics of porous systems. Here, two types of diagrams were considered - cumulative diagrams and diagrams of first derivatives of cumulative curves. While deriving, two kinds of increments ($d\underline{x}$ and $d\underline{\log x}$), concerning the independent variable, were taken into account. A comparative analysis of mentioned diagrams was performed. Based on the analysis, it was concluded that semilog coordinates are particularly suitable for presenting characteristics of porous systems, despite all noticeable disadvantages. As illustrative examples, pore volume and pore area of a catalyst and apparent density of a ceramic compact were used.

INTRODUCTION

Many physical parameters, obtained by measurements, take values that lie on a broad scale; that is, a same parameter of a system can have values ten-, hundred-, thousand- and more-times different among themselves. The difficulties in graphical presentation of such quantities can be solved by introducing log-log or semilog coordinates, which enable a kind of "space compaction". As everybody knows, the log scale is obtained by dividing its total length in equal subintervals-one for each decade- while the decade is divided by applying log function to the length of the subinterval. In such a way, every decade (e.g., 0.01- 0.1 or 100-1000) takes the same part in the diagram. That causes adequate changes of curve shapes and requires a careful interpretation so that errors might be avoided.

While characterizing porous systems (such as catalysts, ceramic products, adsorbents, etc.), two parameters are particularly interesting: pore volume and pore surface area; both dependent on so called porous structure. This term includes: pore size distribution, their shape, connections between pores and other characteristics. In pore size distribution measurements pore diameter is taken as a porous structure representor, while assuming that all pores are open, straight cylinders. One of the well-known methods for pore volume (and surface area) determination is the Static Low Temperature Adsorption of Nitrogen [1]. This method involves recording of cumulative $V_p(D)$ - and $S_p(D)$ curves with pore diameter as the independent variable that varies from "micro"- to "macro"-size, so that semilog coordinates are appropriate. Usually, cumulative curves are accompanied by the curves of derivatives to

illustrate more precisely the contribution of the pores of defined diameter to total pore volume and/or pore area. Here, $dV_p(D)/dD$ and $dS_p(D)/dD$ as well as $dV_p(D)/d\underline{\log D}$ and $dS_p(D)/d\underline{\log D}$ will be considered and the distinction will be pointed out.

A useful tool in characterizing the powder pressing operation is a compaction response diagram that relates the percent of the density of the compact to a series of particular compaction pressures [2, 3]. The first derivative curve, obtained by graphical or numerical derivation, illustrates the rates at which compaction is occurring at the given pressures [4]. Very often, both diagrams are presented in semilog coordinates, so that processes at low pressures can be investigated as completely as the processes at high pressures.

PORE VOLUME AND PORE AREA DIAGRAMS

Cumulative (Adsorption) Diagrams

As a typical pore volume diagram, the plot obtained by recording nitrogen adsorption inside the pores of defined size in porous catalyst sample was taken (see Figure 1). The sample was selected from the commercially available CoO-MoO₃ (Al₂O₃- catalyst, for the hydro- desulphurization of oil fractions [5, 6], which was exposed to the influence of high temperature (800 °C during 6 hours). In this way a kind of rapid aging was achieved, so that the processes similar to the real ones were simulated. Volume and area measurements were performed by using ASAP 2000, Micromeritics.

Pore area plot for the same catalyst sample is given in Figure 2.

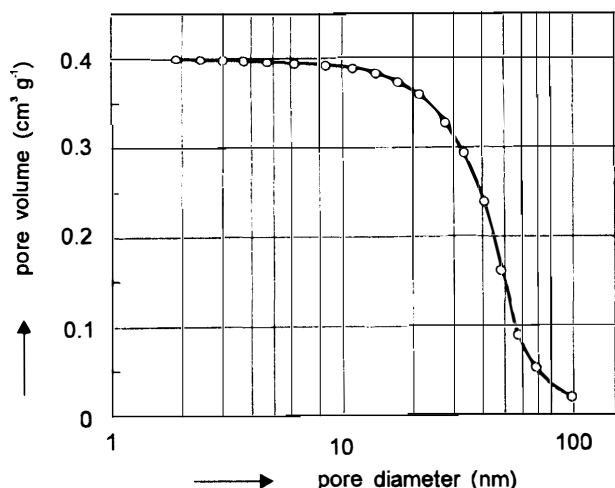


Figure 1. Cumulative pore volume diagram

Both diagrams are drawn in the semilog system whose x axis shows pore diameter values. Thereby, pores from 1 to 10 nm are given the interval as pores between 10 and 100 nm. So, a contribution of small pores (to the volume and area values) can be easily seen.

Diagrams of Derivatives

During the measurements nitrogen is injected in portions which accumulate inside the porous body. It gives cumulative $V_p(D)$ and $S_p(D)$ curves and is useful to find slopes at particular points of these curves. For this purpose, two types of D increments are applied.

dD increments

Curves drawn in Figures 3-4 present first derivatives of $V_p(D)$ and $S_p(D)$ functions in the form: $dV_p(D)/dD$ and $dS_p(D)/dD$. They show the change of V_p or S_p due to the change in the pore size. These curves can be used for quantifying the contribution of pores of particular sizes to the total pore volume (or pore area) by finding the surface below the curves, because of very obvious reason:

$$\int_{D_{\min}}^{D_{\max}} \frac{dV_p(D)}{dD} dD \approx \sum_{i=1}^n \frac{\Delta V_{p_i}(D)}{\Delta D_i} \Delta D_i = V_{p_{\text{tot}}} \quad (1)$$

and

$$\int_{D_{\min}}^{D_{\max}} \frac{dS_p(D)}{dD} dD \approx \sum_{i=1}^n \frac{\Delta S_{p_i}(D)}{\Delta D_i} \Delta D_i = S_{p_{\text{tot}}} \quad (2)$$

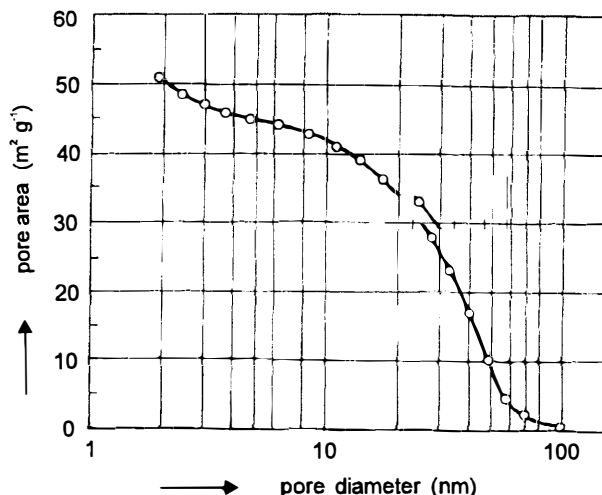


Figure 2. Cumulative pore area diagram

Non-equally distant ΔD increments have values dependent on the decade they belong to ($\Delta D = 1$ nm for the first decade, $\Delta D = 10$ nm for the second decade etc.).

After calculating the integral (Equation 1), for the curve in Figure 3, it can be concluded that the contribution of pores less than 10 nm in size to the total volume ($0.4 \text{ cm}^3 \text{ g}^{-1}$) does not exceed 2.5 % ($0.01 \text{ cm}^3 \text{ g}^{-1}$), although adequate surface (in Figure 3) seems to be large. Namely, due to the log character of x axis the surface above the interval: 10-100 nm is ten times "compacted" in comparison with the surface above the interval: 1-10.

The same can be stated for the $dS_p(D)/dD$ diagram in Figure 4. At the first glance, the contribution of pores less than 10 nm to the pore area seems very significant. However, it does not exceed 16 % of the total.

$d \log D$ increments

When the increments are taken as $d \log D$, the derivatives are obtained in the form: $dV_p(D)/d \log D$ and $dS_p(D)/d \log D$. They are in the following relation with the original derivatives:

$$\frac{dV_p}{d \log D} = 2.303 \frac{dV_p}{d \ln D} = 2.303 \frac{dV_p}{1/D dD} = 2.303D \frac{dV_p}{dD} \quad (3)$$

and:

$$\frac{dS_p}{d \log D} = 2.303D \frac{dS_p}{dD} \quad (4)$$

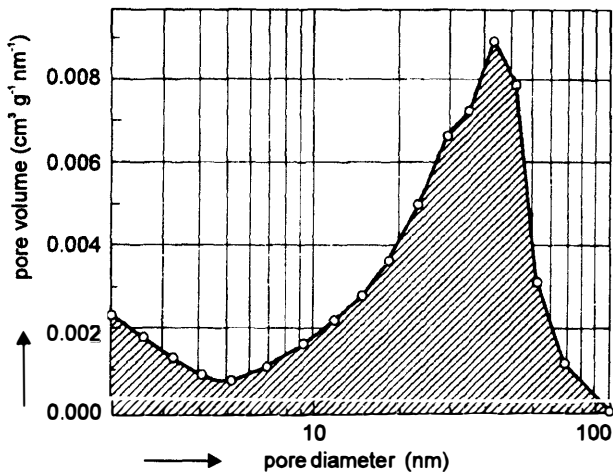


Figure 3. $dV_p(D)/dD$ versus pore diameter

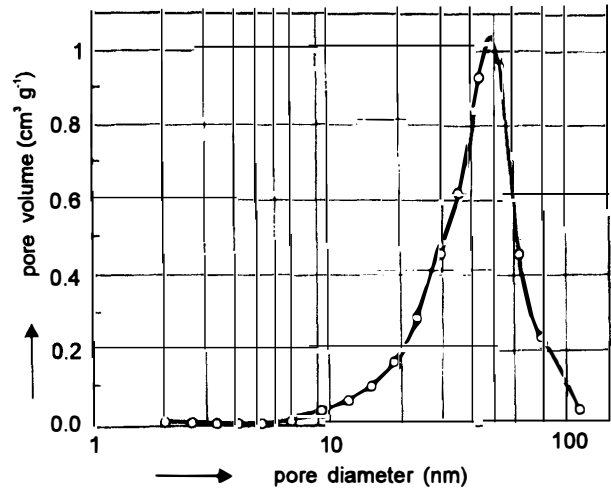


Figure 5. $dV_p(D)/d\log D$ versus pore diameter

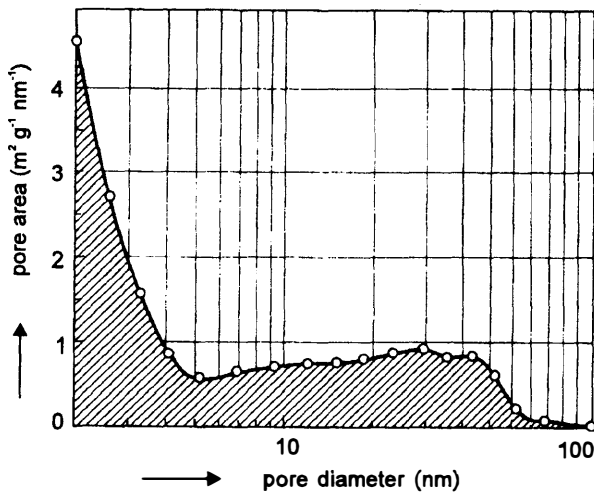


Figure 4. $dS_p(D)/dD$ versus pore diameter

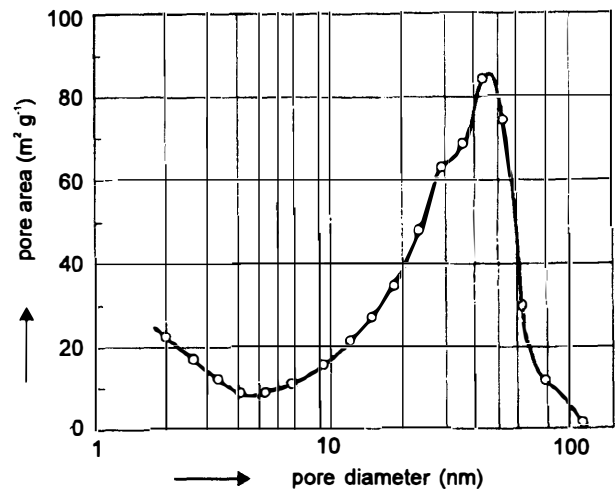


Figure 6. $dS_p(D)/d\log D$ versus pore diameter

So, curves in Figures 3-4 are related to the curves in Figures 5-6 according to Equations (3) and (4). Each $dV_p(D)/dD$ value (multiplied by adequate, average D value) corresponds to the $dV_p(D)/d\log D$ value. In this way, a suitable representor of particle size influence to the V_p and/or S_p value is obtained. Consequently, analysis of diagrams 5 and 6 shows that the greatest influence on the $V_{p_{tot}}$ and $S_{p_{tot}}$ can be associated with pores whose diameters are 45-50 nm.

COMPACTION DIAGRAMS

Compaction Response Diagrams

Behaviour of any powder, exposed to the influence of pressures, can be investigated by analysis of its com-

paction response diagram. As for its character, the diagram belongs to the class of cumulative curves. Here, the compaction characteristics of a spray-dried ceramic powder (whose particles were 0.09-0.2 mm in size) were investigated [7]. The powder was extracted from the industrial raw material batch (for roof tile production) and then compacted by using INSTRON- press 1122 (die dimensions: $d = 7$ mm and $h = 5.5$ mm). The function presented in Figure 7 was obtained.

Compaction Rate Diagrams

After finding first derivatives at particular points of the curve in Figure 7, a compaction rate diagram appears (as presented in Figure 8). Its shape as well as the magnitude and location of peaks contains important infor-

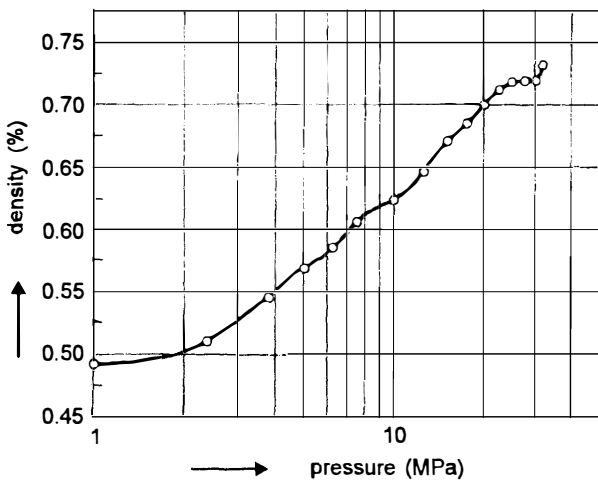


Figure 7. Compaction response diagram

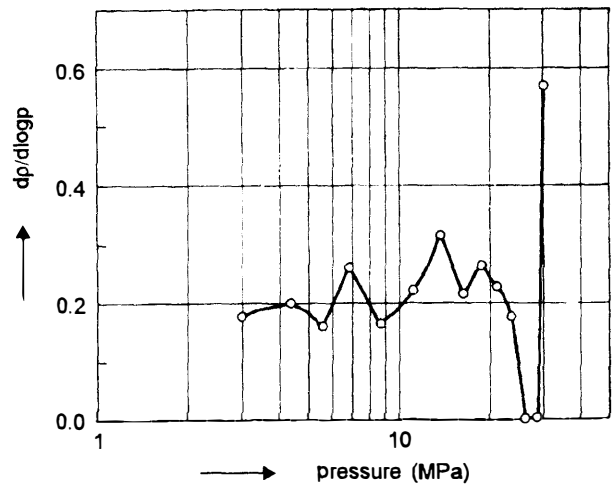


Figure 8. Compaction rate diagram

mation about the compaction process. Namely, the pressure necessary to effect the breakup of agglomerates of particles occurs at the maximum of the compaction rate [4]. From Figure 8 it is obvious that several breakpoints characterize the investigated ceramic powder; the most effective pressure seems to be 30 MPa, less effective is 13 MPa and so on, quite in accordance with the magnitude of adequate \underline{y} values in the $\underline{dp}/\underline{dlogp}$ diagram.

CONCLUSION

This short analysis of application of semilog diagrams in characterizing porous materials (illustrated by a few examples) leads to the following conclusions:

- Semilog coordinates are very suitable for presenting both integral (cumulative) curves and their derivatives.
- An integral curve presents \underline{y} values cumulatively, i.e. at the particular point it gives a sum of \underline{Y} 's for all \underline{X} 's up to the chosen point; at the last point it gives \underline{y}_{tot} .
- First derivative of cumulative curve can be given alternatively; when choosing \underline{dx} or \underline{dlogx} as the increment.
- Graphically presented derivatives show changes of function due to changes of independent variable and are usually called: rate diagrams.
- An integral curve and its $\underline{dy}/\underline{dx}$ derivatives are related as follows:

$$\int_{x_1}^{x_2} \frac{dy}{dx} dx \approx \sum_{i=1}^n \frac{\Delta y_i}{\Delta x_i} \quad \text{---} \quad \Delta x_i = y_{tot}$$

whereby the areas obtained by integration, located at different parts (decades) of the diagram, have different values.

- $\underline{dy}/\underline{dx}$ curve and $\underline{dy}/\underline{dlogx}$ curve are connected by a simple relation:

$$\frac{dy}{dlogx} = 2.303x \frac{dy}{dx}$$

which proved that $\underline{dy}/\underline{dlogx}$ adequately represents the \underline{x} influence on function changes by taking into account the magnitude of the particular \underline{X} 's.

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POUŽÍVÁNÍ SEMILOGARITMICKÝCH SOUŘADNIC
PŘI POPISU NĚKTERÝCH CHARAKTERISTIK
PÓRÉZNÍCH SYSTÉMŮ

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Semilogaritmické souřadnice se používají v široké míře při popisu charakteristických vlastností póréních systémů. Logaritmická stupnice se získá rozdělením její celé délky do stejných intervalů, jednoho na každou dekádu, a každá dekáda se rozdělí logaritmováním délky příslušného podružného intervalu. Z toho důvodu hraje každá dekáda v diagramu stejnou úlohu, což vede k odpovídajícím změnám ve tvarech křivek, a vyžaduje pečlivou interpretaci. V této práci jsou analyzovány kumulativní křivky a rovněž dvě varianty jejich derivací, a pojednává se o příslušných rozdílech. Měřenými charakteristickými vlastnostmi jsou objem pórů a plocha povrchu pórů určitého vzorku katalyzátoru, a rovněž objemová hmotnost lisované keramické směsi.

Jako typické (semilogaritmické) diagramy objemu pórů a plochy povrchu pórů byly zvoleny záznamy absorpce dusíku uvnitř pórů vzorku katalyzátoru. Katalyzátor byl typu $\text{Co}/\text{Al}_2\text{O}_3$, používaný pro hydrodesulfurizaci těžkých ropných frakcí. Během měření se dusík nastříkuje po dávkách, které se adsorbují uvnitř póréního vzorku. Tím vznikají kumulativní křivky $V_p(D)$ a $S_p(D)$, jejichž směrnice v určitých bodech lze snadno zjistit. Za

tímto účelem byly zvoleny dva typy přírůstků D : dD a $d\log D$. Bylo prokázáno, že křivky představující první derivace funkcí $V_p(D)$ a $S_p(D)$ ve tvaru $dV_p(D)/dD$ a $dS_p(D)/dD$ lze použít pro kvantifikaci podílu pórů určité velikosti v celkovém objemu pórů (nebo v celkové ploše povrchu pórů), a to podle velikosti plochy pod křivkami. Je však nutná opatrnost při stanovování podílu určitých částí povrchu, nacházejících se v různých dekáдах.

Pokud se přírůstky stanoví jako $d\log D$, derivace se získají ve formě $dV_p(D)/d\log D$ a $dS_p(D)/d\log D$. S původními derivacemi jsou v následujícím vztahu:

$$\frac{dV_p}{d\log D} = 2,303D \frac{dV_p}{dD} \quad \text{a} \quad \frac{dS_p}{d\log D} = 2,303D \frac{dS_p}{dD}$$

Tímto způsobem se získá vhodný parametr vlivu velikosti částic na hodnotu V_p a S_p . Tento parametr je přímo úměrný průměru pórů.

Charakteristiky zhutňování (lisování) práškových hmot lze studovat pomocí analýzy reakčního diagramu zhutňování. V našem případě jsme uvažovali charakteristické vlastnosti keramického práškového materiálu sušeného ve vlnosu, a to pomocí závislosti objemové hmotnosti na lisovacím tlaku. Rovněž uvádíme stanovení první derivace určitých bodů na křivce $\rho(p)$ a jejich grafické znázornění. Tvar (a rovněž velikost a umístění) maxim na derivačních křivkách rovněž poskytuje důležité informace o procesu zhutňování. U studovaného vzorku bylo zjištěno několik inflexních bodů, zcela v souladu s velikostí příslušných hodnot y v závislosti $dp/d\log p$.