COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 28 ANNÉE : 1982

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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The Determination of the Micropore Volumes of Turkish Coals and Cokes by Gas Adsorption

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Abstract

Adsorption of carbon dioxide at 195, 273, 298, 323 K by Seyitömer lignite and its cokes which have been obtained at 300, 400, 500, 600°C has been studied. Adsorption of nitrogen at 77 K and 195 K by the same adsorbents has also been investigated. The adsorption isotherms of carbon dioxide and nitrogen at these temperatures were examined by using the Dubinin theory to give micropore volume. The change in pore-structure of coal during carbonization has also been criticized.

Introduction

An extensive study has been reported[1,2,3] of the evolution of internal porosity during carbonization of coals. Many years have been spent for the selection of suitable adsorption temperatures and theories for interpretation of the adsorption phenomenon on coals and their cokes. No method has so far been described which can be applied to all coals without some degree of critism.

Coals and cokes are microporous materials with their internal volumes contained within pores less than 25 A° in diameter; in fact many have the property of ultramicroporosity possessing pores of molecular dimensions (i.e. about 5 to 10 A°diameter)[4]. Dubinin[5], Spencer and Bond[6] pointed out that, it is questionable to use the BET equation to interpret isotherms for microporous materials, because micropore-filling by adsorbate occurs before monolayer formation and in a pore of molecular dimensions, one adsorbate molecule is possibly shared by several surfaces. According to Dubinin[5] the application of the BET

or Langmuir theories or any modification of them to give a monolayer coverage is purposeless. Therefore the Dubinin theory is used in order to interpret the adsorption isotherms in terms of micropore limit volumes.

The aim of this study is to apply the Dubinin theory to a Turkish lignite from Seyitömer and its cokes in order to increase our knowledge of the carbonization process.

Experimental

A Turkish lignite from Seyitömer and its carbonization products have been examined. Carbonization of this coal were carried out in nitrogen atmosphere at the temperatures of 300, 400, 500, 600°C.

Adsorption of carbon dioxide and nitrogen were measured by using conventional volumetric apparatus. This apparatus and experimental procedures have been described in detail elsewhere[7]. The adsorbents were activated by heating at 110°C, and under about 10^{-3} mm Hg pressure for 4 hours.

Adsorption of carbon dioxide on coal and cokes was studied at temperatures of 195, 273, 298, 323 K at pressures up to 800 mm Hg. For the same adsorbents adsorption of nitrogen was also carried out at 77 K and 195 K.

The Dubinin-Polanyi equation to describe adsorption in microporous adsorbents is:

$$\log V = \log V_o - D \log^2(P/P_o) \quad (1)$$

A plot of log V against $\log^2(P/P_o)$ is linear. The slope is equal to to D where

$$D = 2.303\ R^2T^2k/\beta^2 \quad (2)$$

V is the volume adsorbed in the adsorbed state per gramme of coal at relative pressure P/P_o, V_o is the limiting micropore volume per gramme of coal, β is the affinity coefficient of adsorbate relative to nitrogen, k is a constant characterizing the micropore size, and R is the gas constant.

The volume in adsorbed state, V, which can be obtained from the volume in the gaseous state, v (cm^3/g STP), is

$$V = \frac{v \cdot M}{22400 \cdot \rho_t} \tag{3}$$

where ρ_t(g/cm^3) is the density of adsorbate in adsorbed state at T K. The density of adsorbate in adsorbed state is expressed as,

$$\rho_t = \rho_b - \frac{\rho_b - \rho_{cr}}{T_{cr} - T_b} (T - T_b) \tag{4}$$

where ρ_{cr} and ρ_b are the densities for the critical temperature (T_{cr}) and for the boiling temperature (T_b).

The filled volumes of adsorption space for gases are expressed as:

$$V = n.b \tag{5}$$

where n is the amount of adsorption in moles and b is the van der Waals constant.

The filling of pores by adsorption in the micropore range may be described by the potential theory. According to Polanyi[8] the adsorption potential expresses the work of temperature independent dispersion forces. The change in free energy when one mole of adsorbate is transferred from vapour state to the adsorbed state is

$$\Delta G = -\epsilon = 2.303\ RT \log (P/P_o) \tag{6}$$

A plot of the volume of the filled adsorption space, V, against the adsorption potential, ϵ, gives the characteristic curve which is independent of temperature. The Dubinin approach to describe adsorption potential of gases is given by the following equation

$$\epsilon = 2{,}303\ RT \log (P_{cr}\tau^2/P) \tag{7}$$

where τ is the reduced temperature and P_{cr} is the critical pressure. P_o is empirically equated to

$$P_o = P_{cr} \cdot (T^2/T^2_{cr}) \tag{8}$$

Table. 1 shows the saturation vapour pressure of carbon dioxide[9] and the densities in the adsorbed state calculated from equation (4) by using M = 44 g/mol, ρ_b= 1.176 g/cm^3, T_b= 216.4 K, b = 42.8 cm^3/mol.

The following values are used for adsorption isotherms of nitrogen:

b = 39.1 cm^3/mol, ρ = 0.808 g/cm^3(at 77 K)

Table. 1 Vapour Pressure and Densities of Carbon dioxide

Temperature (K)	Saturation vapour pressure (mm Hg)	Density in adsorbed state (g/cm³)
195	1414	1.360
273	26140	1.080
298	48300	1.038

Results and Discussion

The experimental carbon dioxide isotherms were obtained at 298 K for the Seyitömer lignite and for its cokes are given in Figure 1, the nitrogen isotherms at 195 K in Figure 3 and the Dubinin-Polanyi isotherms of adsorption of carbon dioxide and nitrogen are given in Figures 2 and 4.

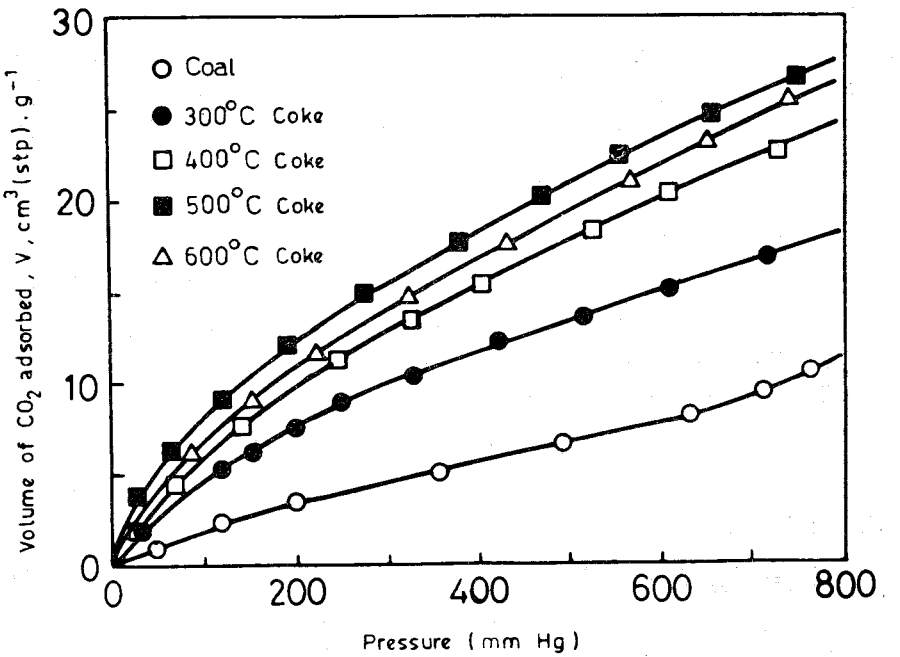

Fig.1 Adsorption of carbon dioxide at 298 K on carbonizated Seyitömer Lignite (Isotherms)

The extent of carbon dioxide adsorption for different cokes are shown in Figure 1. The enhanced adsorptive capacity with increasing

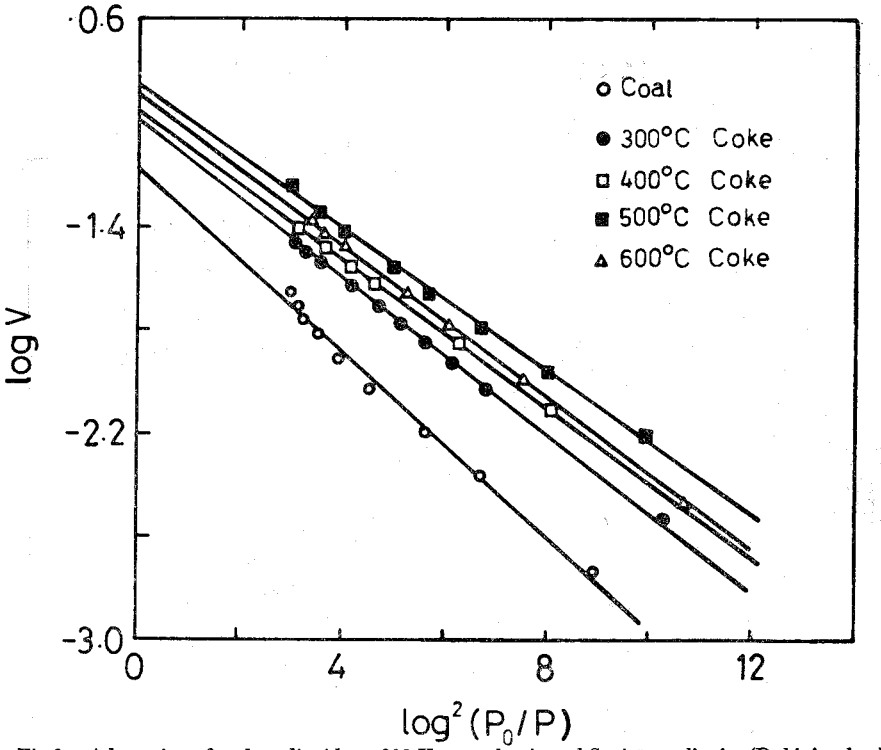

Fig.2 Adsorption of carbon dioxide at 298 K on carbonizated Seyitömer lignite (Dubinin plots)

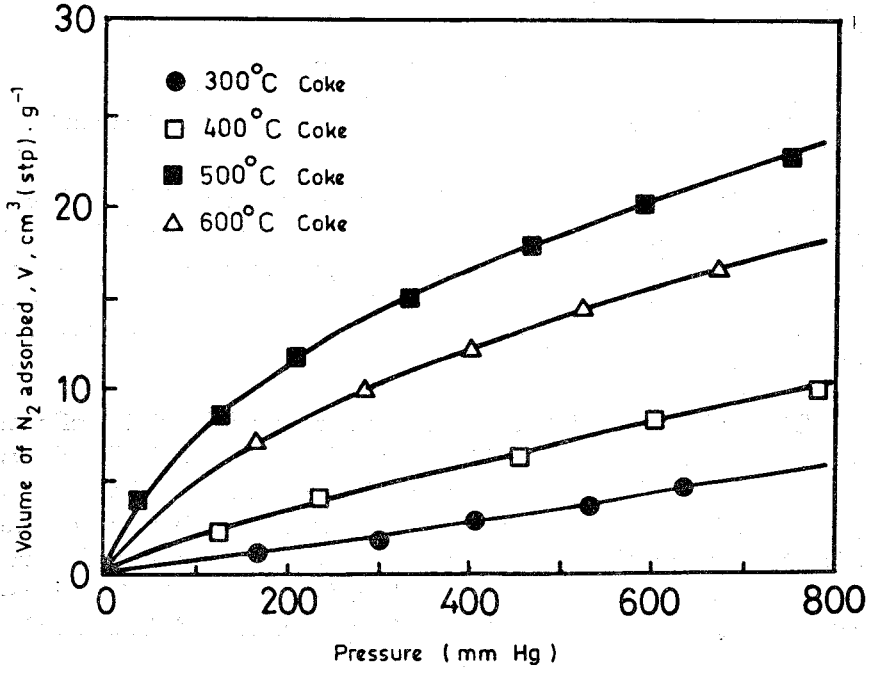

Fig.3 Adsorption of nitrogen at 195 K on carbonizated Seyitömer lignite (Isotherms)

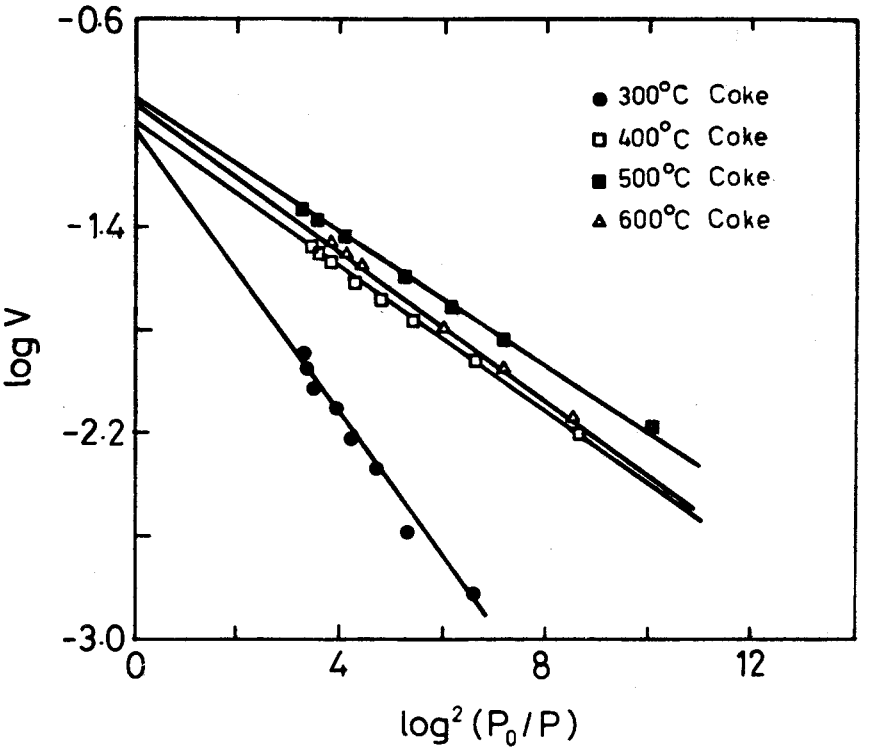

Fig.4 Adsorption of nitrogen at 195 K on carbonizated Seyitömer lignite (Dubinin plots)

carbonization temperature up to 500°C has been observed. The adsorptive capacity of 500°C coke is maximum and a decrease at 600°C coke was also observed. The change of adsorptive capacity shows a progressive development of new pores during carbonization. Above 500°C, contraction or sintering can take place within the coal, and this causes decrease in adsorptive capacity.

The equilibrium points of different adsorbents fell satisfactorily on a single straight line of the Dubinin plots (Figures 2 and 4). This shows that the Dubinin-Polanyi equation is suitable to explain adsorption of carbon dioxide and nitrogen on coals and cokes. The micropore volume of coal and cokes, V_0, and D factors can be obtained respectively from the intercepts and slopes of Dubinin plots. As the carbonization temperature is increased up to 500°C, the micropore volume of the cokes also

increased. This effect can be seen on both of adsorption of carbon dioxide and nitrogen.

The Seyitömer lignite and its cokes have adsorbed more nitrogen at 195 K then at 77 K. Coals and some cokes have micro-and submicropores. Because the submicropores are of the same order of magnitude as the molecular diameters of the gaseous or vaporous adsorbates, the penetration of adsorbates into the pores is difficult. For the submicropores the phenomenon of activated diffusion of adsorbates is observed[10,11], which is characterized by the exponentially rising adsorption rate with temperature. Another reason can probable be the contraction of pores at lower temperatures.

The adsorption isotherms of carbon dioxide on 500°C Seyitömer coke at 195, 273, 298, 323 K are shown in Figure 5. The characteristic curve of adsorption (i.e. a plot of V against ϵ, where V is the volume

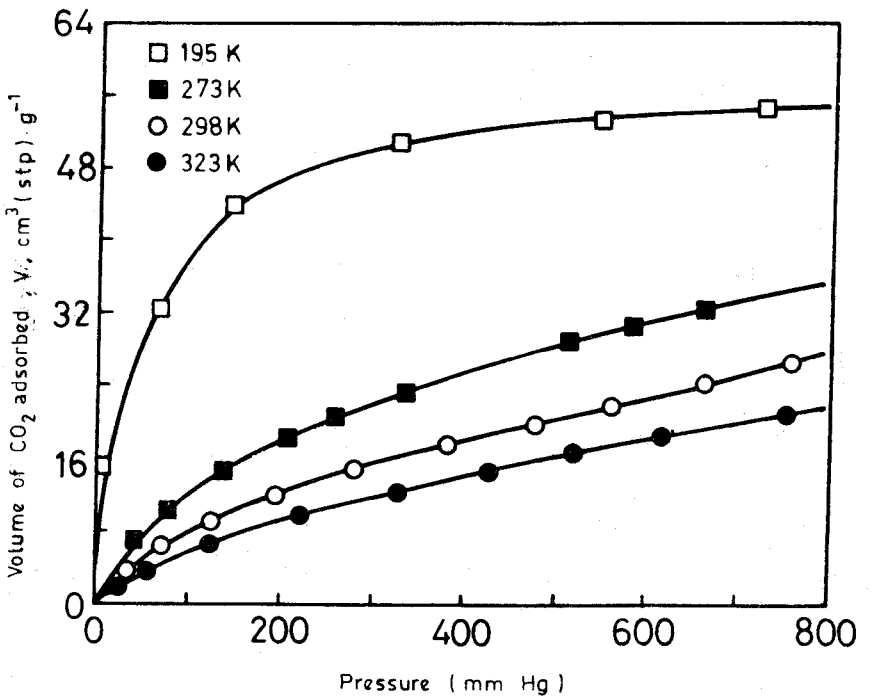

Fig.5 The adsorption isotherms of carbon dioxide on 500°C Seyitömer coke at 195, 273, 298, 323 K

adsorbed in the adsorbed state and ϵ is the adsorption potential) is temperature independent (Figure 6). The non-agreement of 195 K isotherm is the result of inability to establish the thermodynamic equilibrium because of the slow rates of adsorption.

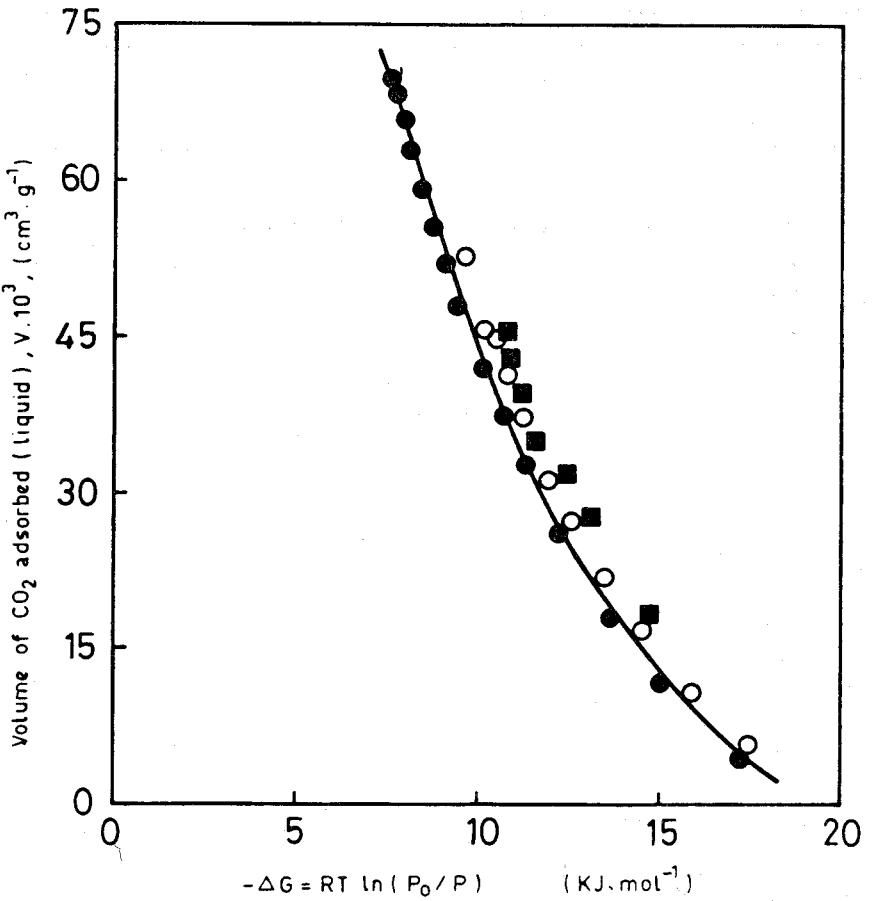

Fig.6 The characteristic curve of 500°C Seyitömer coke for the carbon dioxide adsorption at 273 K (●), 298 K (○), 323 K (■)

The amount of adsorbed carbon dioxide at 298 K and average micropore volume of adsorbents against the carbonization temperature is shown in Figure 7. The gradients of Dubinin plots of isotherm at

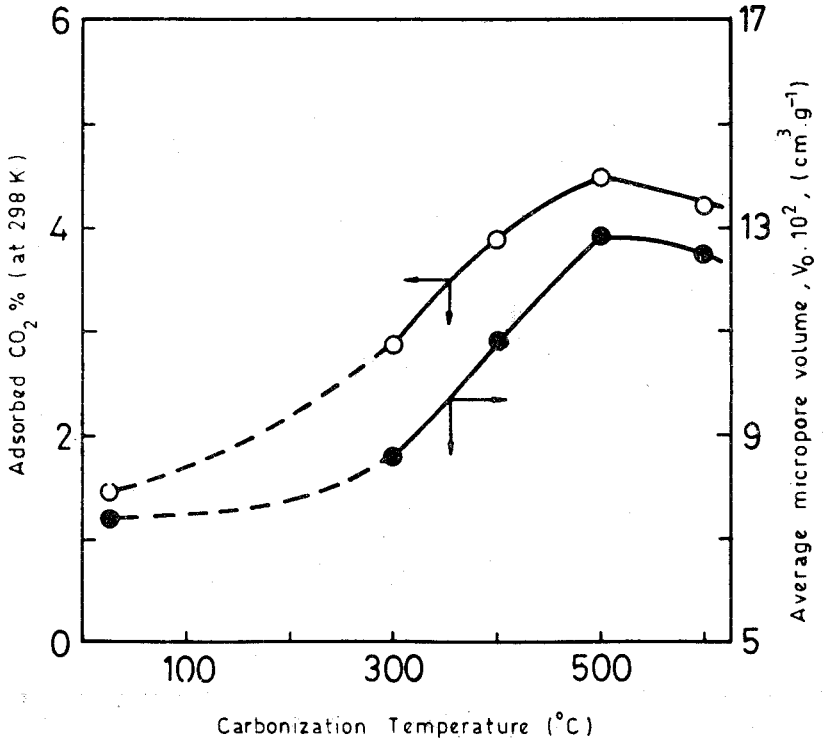

Fig.7 The amount of adsorbed carbon dioxide at 298 K and average micropore volume of adsorbents against the carbonization temperature

298 K and the adsorption potentials at a definite adsorbed amount against the carbonization temperature are also shown in Figure 8. As the carbonization temperature is progressively increased to 500°C, an increase in micropore volume of adsorbents and a decrease in D values may be interpreted as a progressive narrowing of average pore diameter, which is also supported with the increase of the adsorption potentials (Figure 8). An explanation of this is that during the carbonization process of coal, the material is decomposed and new pores with smaller diameters are produced and the accessibility into the micropores is increased.

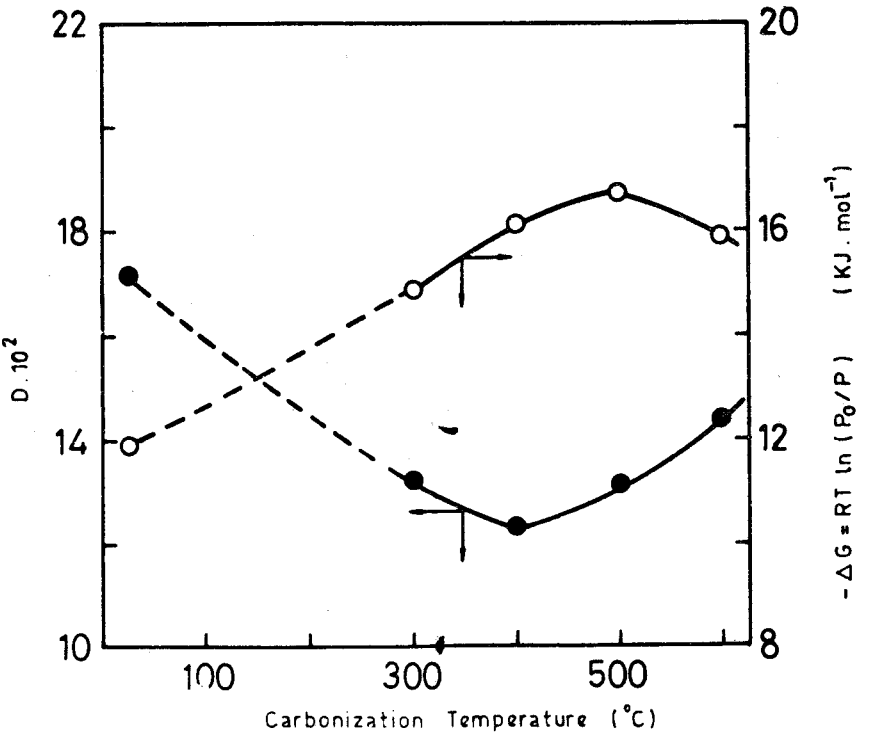

Fig.8 The gradients of Dubinin plots of isotherms at 298 K and the adsorption potentials at a definite adsorbed amount against the carbonization temperature

ÖZET

Seyitömer linyiti ve bu linyitin 300, 400, 500, ve 600°C da koklaştırılmasından elde edilen koklar üzerinde geniş bir sıcaklık aralığında karbondioksit ve azotun adsorpsiyonları incelenmiştir. Adsorpsiyon izotermlerine Dubinin'in hacim dolma kuramının uygulanması oldukça iyi sonuçlar vermiştir. Dubinin eğrilerinin eğimlerinden adsorplayıcının gözenek açıklığı hakkında bilgi edinilmiş, kaymalarından ise mikrogözenek sınır hacimleri bulunmuştur. Ayrıca herbir örnek için karakteristik eğriler çizilerek, adsorplanan miktarla adsorpsiyon potansiyelinin değişimi gözlenmiştir. Buna göre koklaşma sıcaklığının artması yeni gözeneklerin oluşumunu sağladığı gibi, gözeneklerin daralmasına da neden olmaktadır.

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