CHARACTERIZATION OF PORE STRUCTURE OF TURKISH COALS AND THEIR CHARS OBTAINED BY CARBONIZATION AND CO_2 ACTIVATION

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INTRODUCTION

Any cheap material with a high carbon content can be used as a raw material for the production of activated carbon. In recent years, several investigations were conducted to determine the suitability of coal to be transformed into a quality adsorbent material and a number of production processes have already been established and even some of them have been commercialized [1,2]. At present, because of the availability and cheapness of coal, 42% of the 360,000 tons/year of the activated carbon production are coal based carbons [3].

Turkey has considerable amount of coal reserves of which lignites constitutes major portion with a reserve of 8.05×10^6 tons [4] and mainly utilized conventionally for power production and heating purposes. Since also the pore structure is one of the main factors influencing the behavior of coal in various applications; The present study was undertaken to characterize the pore structure of representative Turkish coals and also to explore the possibility of the production of adsorbent materials from them.

EXPERIMENTAL

Characterization of the porous structure of twelve Turkish coals with carbon contents varying between 61-84% (daf) was carried out [5]. After initial screening, four promising coals were selected for investigating the possibility of obtaining high surface area materials. These coals were heated; at a heating rate of 10 °C/min to the final carbonization temperatures in the range of 750° to 1125°C. The total carbonization time was kept constant at two hours. Carbonized coals were activated in CO_2 atmosphere at the final carbonization temperature for an additional one hour.

The pore structures of original coals and their chars obtained were determined as follows: The volume and area of macropores which are in the pore diameter range of 8180-50 nm were determined by mercury intrusion porosimetry. Mesopore (in the range of 50-2 nm) volumes were determined by N_2 gas adsorption technique at 77 K, BET surface area of the samples were also determined in the relative pressure range of 0.05 to 0.02. The pore volume and area of the micropores which are less than 2 nm in diameter were determined by CO_2 adsorption measurements at 298 K by the application of Dubinin-Radushkevich [6] equation, in the relative pressure range of 1×10^{-4} to 1×10^{-2}.

RESULTS AND DISCUSSION

Pore volumes of the coals were varied between the minimum and maximum values of 0.04 and 0.135 cc/g for macropores corresponding to Mengen and Zonguldak coals; 0.0008 and 0.01 cc/g for mesopores corresponding to Bursa and Soma lignites; and 0.0052 and 0.028 cc/g for micropores, in Konya and Amasra coals, respectively. True and Apparent densities showed parobolic trends with the increasing rank, exhibiting a minimum at around 74% carbon content of the coals. Beypazari and Mengen lignites with their high ash contents of 49.5 and 45.3 % on dry basis gave correspondingly higher values of true densities as 1.65 and 1.70 g/cc and apparent densities, as 1.53 and 1.59 g/cc, respectively. Among the twelve coals studied, Tunçbilek coal was found to have the maximum N_2 (BET) surface area as 33.64 m^2/g while the corresponding values for rest of the coals were less than 7.4 m^2/g. CO_2 (D-R) surface areas of the mentioned coals varied in the range of 18.68-115.44 m^2/g. These two values were observed for Konya and Soma lignites, respectively.

After the carbonization step the microporosity developed significantly, mesoporosity developed moderately and macroporosity remained almost the same in comparison to the corresponding porosities of the parent coal. A significant increase in all range of pores is observed after the activation step. Eventhough contribution of the

macropores to the total pore volume was found to be greater than those of mesopores and micropores, the development in meso and micropores upon activation, in comparison to carbonized and original coals were more significant than that of macropores (Figure 1). BET and D-R surface area values of the products obtained after carbonization of the four coals varied from 4.01 to 201 m^2/g and from 42.03 to 403 m^2/g, respectively. Upon activation, these values increased considerably. BET values of these products varied from 32 to 360 m^2/g and D-R values from 88.04 to 657 m^2/g. CO_2 reactivities of the coals which were evaluated from the TGA studies under the identical conditions with the carbonization and activation experiments indicated that Elbistan lignite has the lowest and Tunçbilek the highest apparent activation energy values; as 32.38 and 71.94 kJ/mol, exhibiting the highest and lowest reactivities, respectively. Highest reactivity of Elbistan coal can be explained by the high CaO content in the starting material and the presence of considerable amount of feeder (macro and meso) pores prior to activation (both in its original state and also after carbonization) which developed significantly upon activation.

CONCLUSIONS

Adsorption isotherms and porosimetry measurements show that Turkish coals have a certain degree of porosity, located in macro, meso and micro size of pores, in various proportions, regardless of the coal rank.

Apparent and true density of these coals show parabolic trends with increasing rank, medium rank of coals are found to have lower densities. Although, there were significant differences in the manner by which burn-off affected the development of porosity, pore volume and surface area pass through a maximum value. The initial increase was due to the opening of closed pores, formation of new pores and widening of existing pores. Longer and high temperature treatments brought a decrease in the pores, presumably due to pore shrinkage, pore swelling and pore coalescence. Chars which exhibited the lower apparent activation energy and higher reactivities are found to be derived mainly from the higher CaO containing precursors. Chars which contain large proportion of macro and meso (feeder) pores are highly reactive since the ability of CO_2 gas to diffuse into the internal surface is enhanced.

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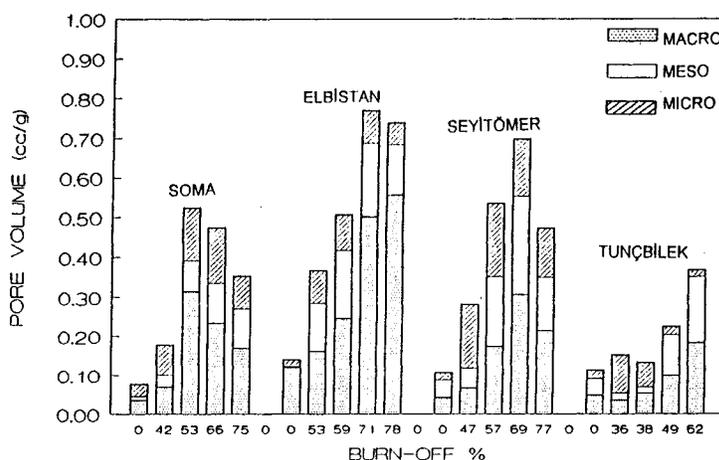Figure 1. Pore Volume of Coals upon CO_2 Activation