

Preparation of Activated Carbons from Mongolian Lignite and Sub-Bituminous Coal by a Physical Method

Uugantsetseg Gombojav, Irekhubayar Jambal, Enkhsaruul Byambajav

Laboratory of Clean Energy Technology Development, Department of Chemistry, National University of Mongolia, Ulaanbaatar, Mongolia

Email: enkhsaruul_b@num.edu.mn

How to cite this paper: Gombojav, U., Jambal, I. and Byambajav, E. (2020) Preparation of Activated Carbons from Mongolian Lignite and Sub-Bituminous Coal by a Physical Method *Journal of Minerals and Materials Characterization and Engineering*, 8, 97-106.
<https://doi.org/10.4236/jmmce.2020.83007>

Received: March 10, 2020

Accepted: April 18, 2020

Published: April 21, 2020

Copyright © 2020 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Preparation of activated carbons by a physical activation technique is performed using the methods of coal pyrolysis and gasification at different temperatures. As increasing pyrolysis temperature from 520°C to 700°C, the yield of activated carbons from the Khuut (KH) sub-bituminous coal is lowered, and amount of micropores increases gradually; however there is no development of mesopores by the KH coal pyrolysis. When the KH coal has a small loss during its physical activation due to difficulty and inactivity of its macrostructure decomposition, the smaller porosity is developed in the resulting carbons. The Aduunchuluun (AD) lignite is activated by pyrolysis and gasification at the highest temperature of 700°C in the present study. It is identified that the gasification of AD lignite develops well a porous structure with the highest surface area of 522 m²/g which is three times larger than that (155 m²/g) of the activated carbon produced by pyrolysis of the same lignite. The IR and SEM analysis confirm a significant difference in chemical and structural changes between the AD, KH raw coals and corresponding carbon samples in the physical activation processes.

Keywords

Coal-Based Activated Carbon, Porous Structure, Physical Activation, Micropores, Mesopores

1. Introduction

Activated carbon has recently received much attention as adsorbent material because of its adsorptive capacity and as a catalyst support for several chemical processes, since it has high surface area, good resistance to coke deposition, rela-

tively ready control of pore structures [1]-[15]. Consequently, the need of activated carbon is increasing continuously. However, activated carbon is high-priced that restrained its bulk-scale production. Due to cost effective concept, coal is considered as a promising resource for adsorbent preparation processes. Generally, activated carbons can be produced by physical and chemical activation processes. Every method has its own advantages and disadvantages. Yong Zou and Bu-Xing Han reported that three Chinese coals are proven to be suitable raw materials for activated carbons prepared by chemical activation, and anthracite coal gives the high-surface-area activated carbon [2]. Nakamura and Fujimoto have physically prepared the activated carbon using CO₂ gasification of an Australian Yallourn coal, and its porosity is higher compared to that of commercial activated carbon [3]. Also H. Teng *et al.* have demonstrated the phosphoric acid is a suitable activating agent for the preparation of high porosity carbon from bituminous coal [4].

Mongolia has a rich source of coal, the amount of which is accounted geologically by 173 billion tons. Type of most coal resource is an energy and non-coking coal. Therefore, it is economically desirable to prepare valuable adsorbent materials from the non-coking coal besides its energy application. In the present study, we aim to determine a possibility to prepare activated carbons from Mongolian coals by their pyrolysis in inert atmosphere and also gasification with a steam. In order to make a clear effect of coal type, the samples of lignite and sub-bituminous coal are selected in this research. Due to sustainable and eco-friendly production concepts, the physical methods of pyrolysis and steam gasification without strong acid and alkaline usage are examined for the preparation of coal-based activated carbons from Aduunchuluun lignite and Khuut subbituminous coal, in this research work.

2. Experimental Methods

2.1. Samples

The Aduunchuluun lignite (coded as AD) deposit is located near to Choibalsan city of Dornod province, and its reserve is estimated at approximately 300 million tons. The sub-bituminous Khuut coal (coded as KH) deposit is far of 26 km from Bayanjargalan village of Dognogovi province, and its reserve is similar to that of previous one. The coal samples are ground and sieved to produce batch with particle sizes of 0.074 - 0.15 mm. Proximate and ultimate analysis of the coal samples are summarized in **Table 1**.

Table 1. Proximate and ultimate analysis of research raw materials.

Coal code	Proximate analysis, wt%				Ultimate analysis, wt% (daf)			
	M, wt% (a.r)	A, wt% (d)	V, wt% (d)	Q, kcal/kg (daf)	C	H	N	O ¹⁾
KH	13.1	16.7	43.4	4747	75.4	5.0	1.0	18.6
AD	38.7	9.9	45.8	3203	66.0	4.1	0.8	29.5

¹⁾By difference.

2.2. Preparation of Activated Carbon from Coal Samples—Pyrolysis and Steam Gasification

Preparation of activated carbons by physical activation technique is performed using two methods: pyrolysis and gasification. Pyrolysis of a coal sample is performed in a Fischer retort. 50 g of coal sample is heated at a rate of 17°C/min up to temperature of 520°C, 600°C or 700°C, and hold at that temperature for 30 minutes.

Activation by steam gasification is carried out in a stainless vertical fixed bed reactor. About 500 mg of coal sample is first heated up with a heating rate of 25°C/min to temperature of 700°C in a stream of argon inert gas, then hold for 10 min to remove preliminarily coal volatiles, and finally exposed to 50 vol% H₂O in argon carrier gas to gasify in situ the resulting solid residue for development of porous structure in the carbon at the temperature of 700°C for 30 minutes.

The obtained activated carbons are named as coal code with corresponding activation temperature as follows: KH520°C-P, KH600°C-P, KH700°C-P, AD700°C-P and KH520°C-G, KH600°C-G, KH700°C-G, AD700°C-G. **Figure 1** shows a total scheme of this research method.

2.3. Characterization of Activated Carbons

Methylene blue adsorption. Adsorption of activated carbon is tested in terms of methylene blue for determination of meso-sized pore formation [16]. Analysis procedure is followed through steps: 0.1 g of activated carbon sample is added to 5 ml of the methylene blue test solution, then shake this solution until decoloring occurs. Addition of methylene blue test solution in 1 ml portions is repeated till decoloring within five minutes. The entire volume of test solution decolorized by the activated carbon is calculated in every sample.

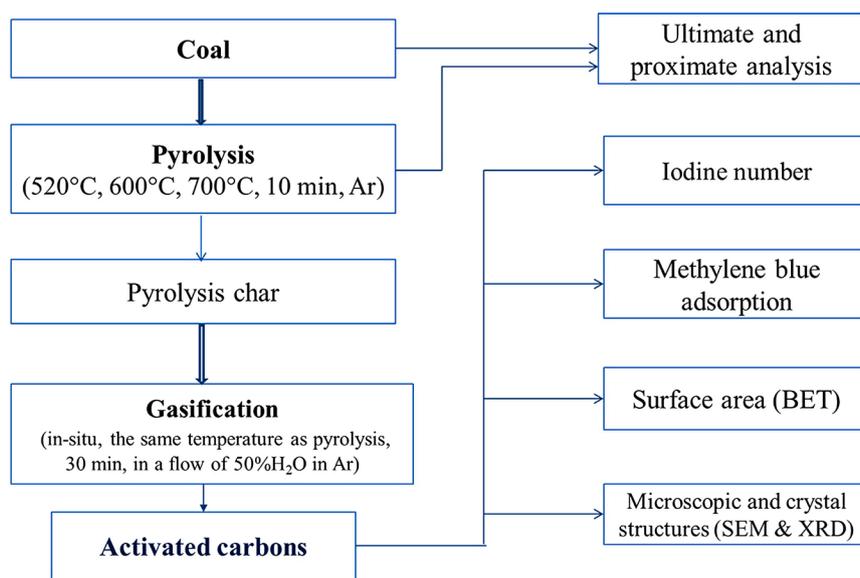


Figure 1. A total scheme of the research method.

Iodine number determination. 50 ml iodine solution with concentration of 0.1 N is added to 1 g of activated carbon sample. After 15-minute shaking, the solution is kept for 5 minutes to separate the phases of activated carbon and iodine solution. The 10 ml iodine solution is titrated by 0.1 N solution of $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of a starch indicator until disappearing the blue color. Iodine number is calculated as follows:

$$X\% = \frac{(V_0 - V_1) * 0.0127 * 100 * 50}{m * 10}$$

V_1 —consumed amount of 0.1N $\text{Na}_2\text{S}_2\text{O}_3$, ml;

V_0 —consumed amount of 0.1N $\text{Na}_2\text{S}_2\text{O}_3$, ml in blank test;

m —weight of activated carbon, g;

50—volume of 0.1 N iodine solution, ml;

0.0127—amount of iodine contained in 1 ml of 0.1 N iodine, g.

Porous and crystal structure determination. X-ray diffraction patterns of raw coals and activated carbon samples are recorded using a diffractometer (XRD mini Flex 600) employing with Cu $K\alpha$ radiation (40 kV, 30 mA). The diffraction angle is selected from 5° to 70° with a scan rate of $5^\circ/\text{min}$ and step size of 0.01° . BET surface area is measured using the Flowsorb III 2305/2310. Nitrogen adsorption is done at the temperature of 77 K in N_2 flow with a flow rate of 53 ml/min. SEM measurement of activated carbon is performed by the JEOL JSM 7001F model to show carbon micro textural structure.

3. Results and Discussions

3.1. Effect of Coal Types on Porous Structure Development in Activated Carbons

Figure 2 shows activation temperature and weight loss corresponding to the activation method and coal type. It is found that the weight loss of KH coal sample

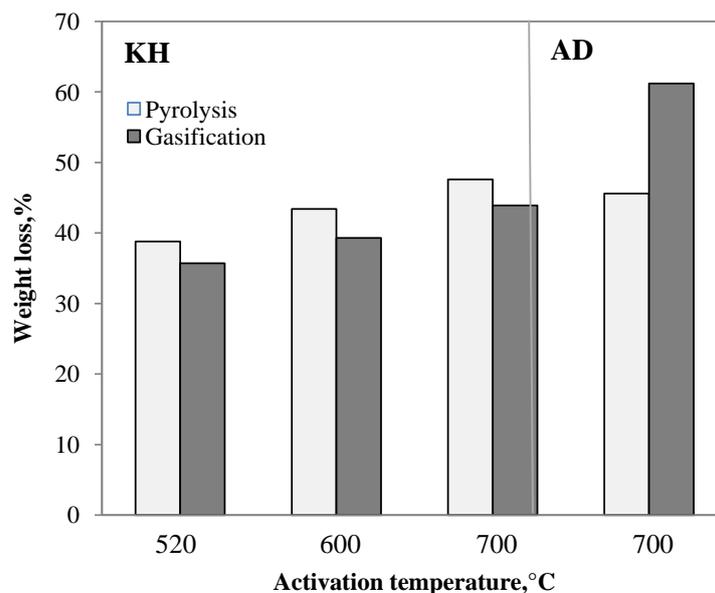


Figure 2. Weight losses depending on coal type, activation method and temperature.

is increased gradually with increasing temperature in both cases of pyrolysis and gasification.

The AD coal sample is activated at only 700°C by all activation methods. Pyrolysis of KH and AD coal samples at 700°C give almost similar weight losses of 47.6% and 45.6%, respectively. However, as can be seen in **Figure 2**, the increments of weight losses as increasing the gasification temperature of the KH sample is not so high compared to the weight losses from its pyrolysis. For the AD coal sample, the gasification gives a high weight loss of 61.2% in comparison with the weight losses from the AD lignite pyrolysis at 700°C and from gasification of KH coal sample at 700°C, respectively.

Activated carbon yields and their porosities after physical activation at different temperatures are described in **Table 2**. As shown here, activated carbon yield decreases with increase of activation temperature in both cases of pyrolysis and gasification. Due to removal of coal volatiles and burn-off of carbons, the iodine number which represents a micropore content with the sizes of 0 - 2 nm increases with increasing the activation temperature of KH coal sample. It is interesting that the methylene blue number, which represents a microporosity (>1.5 nm) and a mesoporosity (2 - 50 nm), is identified only for the activated carbons prepared by the activation processes of the AD lignite sample. Moreover, it can be seen that the AD700°C-G contains the highest amounts of micropores and mesopores formed by the steam gasification of the AD lignite.

BET surface area is an important value for the determination of surface capacity of adsorbent materials [17] [18] [19]. It is determined that the physical activation by steam gasification of AD lignite develops well a porous structure with the highest surface area of 522 m²/g which is three times larger than that (155 m²/g) of the activated carbon produced by pyrolysis of the same lignite. It could be concluded that coal gasification is the most suitable method to prepare a porous material from coal sample. In case of KH coal, BET surface area (214 m²/g) of the KH700°C-G is still two times smaller than the value with the AD700°C-G sample perhaps due to lower reactivity of KH sub-bituminous coal with a steam even at high temperature.

Table 2. Obtained yields and porosities of activated carbons after physical activation at different temperatures.

AC code	AC Yield, wt%	Iodine number %	Methylene blue number mg/g	BET Surface Area, (m ² /g)
KH520°C-P	61.2	20.6	0	5.80
KH600°C-P	56.6	22.2	0	17.9
KH700°C-P	52.4	33.7	0	68.8
AD700°C-P	54.4	21.8	6	155
KH520°C-G	64.3	23.1	0	-
KH600°C-G	60.7	18.4	0	18.4
KH700°C-G	56.1	32.5	0	214
AD700°C-G	38.8	89.6	36	522

3.2. Characterization of Coal and Activated Carbon Samples

Porosity analysis and weight loss obtained by the physical activation of the coal samples show that the high temperature processes influence effectively the creation of pore structure in the activated carbons. Changes in the coal samples by activation processes at 700°C are checked by FT-IR analysis. In **Figure 3**, as the peak in the range of 3200 - 3550 cm⁻¹ represents the presence of alcohols/phenols in the activated carbons, and the peak at 2926 cm⁻¹ is corresponding to the C-H stretching vibration of aliphatic chains. Therefore, it is revealed that the thermal processes of the KH coal sample cracked some alkyl side groups; however the phenolic compounds cannot be decomposed due to condensed macromolecular structure of the sub-bituminous coal. During pyrolysis and gasification of the KH coal sample, aromatization and condensation of coal fragments occur, consequently the peak intensity of aromatic C-H bending at 803 cm⁻¹ increased, and porosity cannot be developed sufficiently compared to that from the AD sample. On the contrary, the peaks attributed to the alcoholic/phenolic -OH functional groups are almost disappeared by the thermal treatments of the AD lignite sample at 700°C. This result is also confirmed by very small absorbance of the peaks at 1158 cm⁻¹, which is attributed to C-O bending of alcohol/phenolic compounds, in the AD activated carbons.

For both coal samples, the peak at 1607 cm⁻¹ attributed to C=O carbonyl group is disappeared by the thermal activation treatments. It might be related to hydrogenation similar chances in hydrogen-rich atmosphere during coal cracking and gasification reaction for the KH sub-bituminous coal and AD lignite. The small peaks at 2324 - 2328 cm⁻¹ are observed in the samples probably due to adsorbed carbon dioxide in measurement atmosphere.

XRD patterns for both series of samples indicate gradual changes according to the progress in activation. **Figure 4** shows the diffraction profiles of the raw coal samples and activated carbons prepared by pyrolysis and gasification at 700°C.

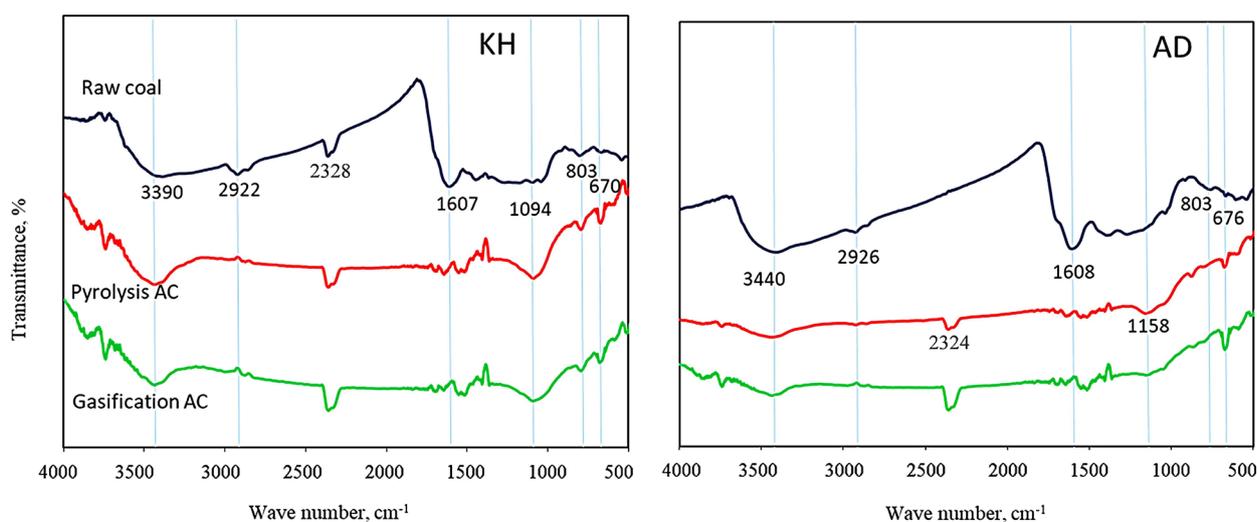


Figure 3. FT-IR spectra of raw coals, pyrolysis and gasification AC-s prepared from KH sub-bituminous coal and AD lignite at 700°C.

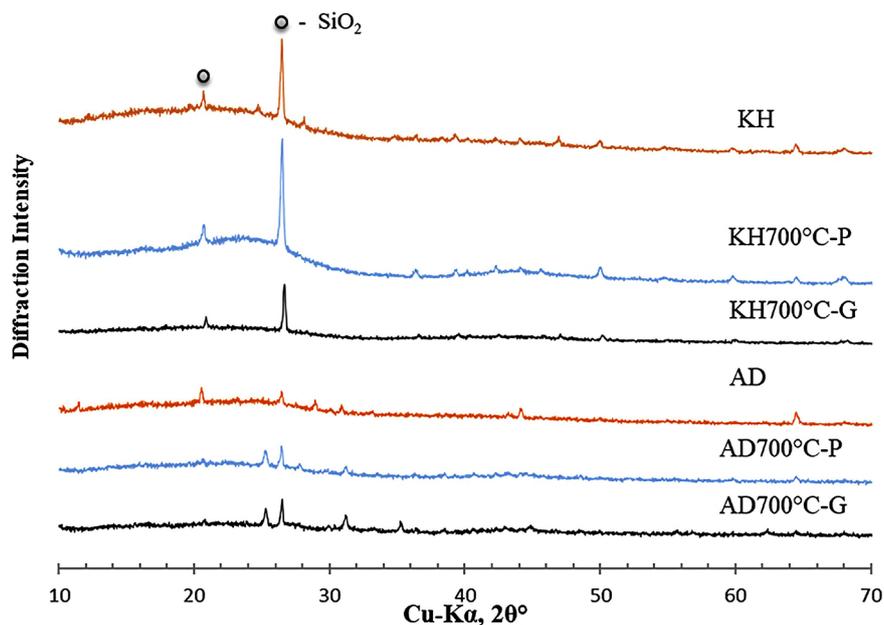


Figure 4. XRD profiles of the raw coal samples and activated carbons prepared by pyrolysis and gasification at 700°C.

In **Figure 4**, for both series of the samples, broad peak around $2\theta = 20^\circ - 25^\circ$ corresponds to (002) reflection of carbon because of the stacking structure of coal aromatic structure. Broadening of the 002 peak can be interpreted in terms of non-crystallinity of carbon structure [20] [21]. Burn-off of coal samples by the thermal treatments has been corresponded to decrease of the 002 carbon peak intensity, as shown in **Figure 4**. As shown in **Table 1**, ash contents of the KH and AD coal samples are 16.7 wt% and 9.9 wt% (on dry base), respectively. These data suggest that the feed coal samples contain their inherent minerals species. Moreover, it can be seen in **Figure 4**, that the samples contain mainly quartz species before and after physical activation. In case of KH coal sample, there are several unknown peaks of its inherent minerals, and the peaks are almost not changed after the treatments. However, some changes are observed after thermal treatments of the AD coal exhibiting decomposition of the inherent minerals during its activation processes.

SEM images with the same zooming scale of the activated carbons which are prepared by pyrolysis and gasification at 700°C are shown in **Figure 5** and **Figure 6**. As shown in **Figure 5(A)**, **Figure 5(B)**, although there are some cracks and crevices in external surface of the KH700°C-P and the KH700°C-G, it seems that holes and porous structure are not observed in micrographs of the activated carbons prepared from KH sub-bituminous coal. However, as shown in **Figure 6(A)**, **Figure 6(B)**, the holes and porous structure are described clearly on external surface of the AD700°C-G sample.

It can be concluded from SEM images taken during tests performed at the physical activations at 700°C that porous structure is well developed because of the large removal of volatiles and carbons and the high reactivity of the AD lignite

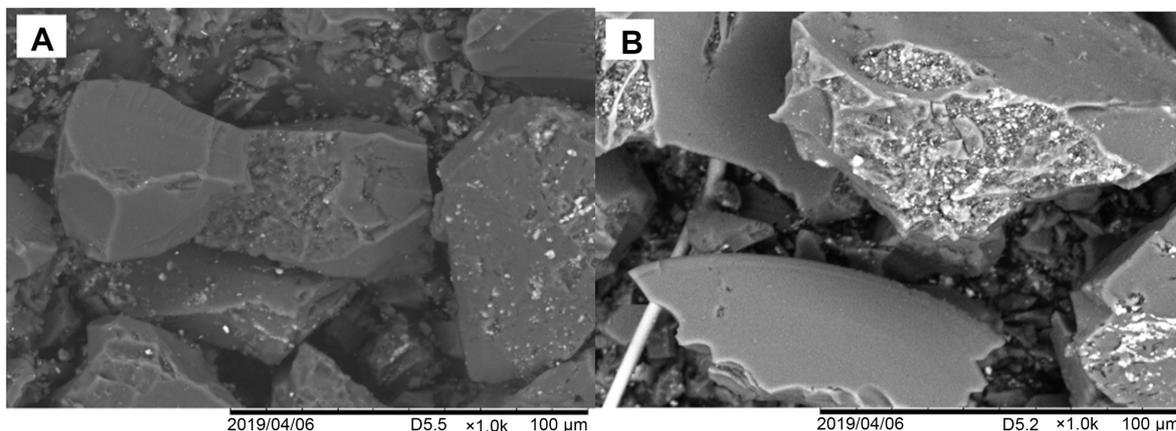


Figure 5. SEM images of the activated carbons prepared from KH sub-bituminous coal. (A) Activated carbon—KH700°C-P; (B) Activated carbon—KH700°C-G.

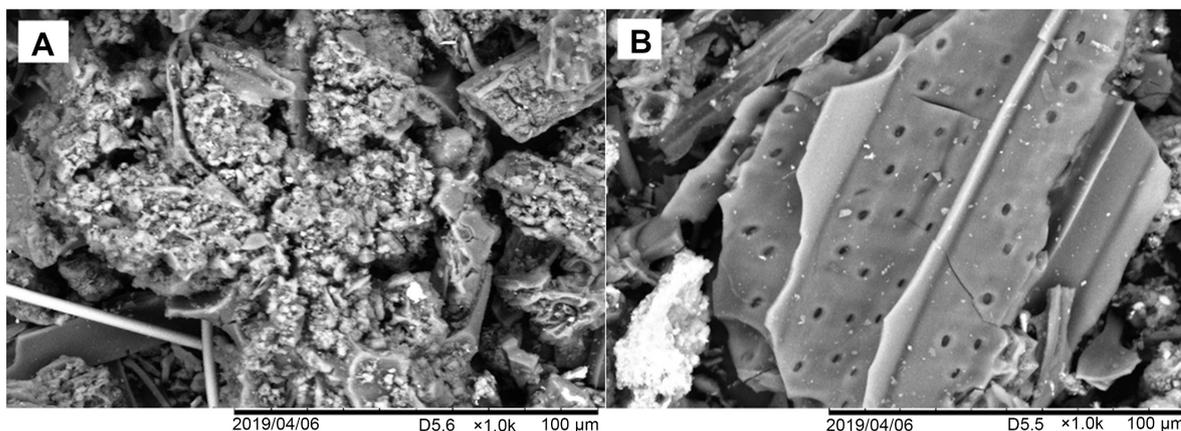


Figure 6. SEM images of the activated carbons prepared from AD lignite. (A) Activated carbon—AD700°C-P; (B) Activated carbon—AD700°C-G.

with a steam. Moreover, pyrolysis and gasification of KH sub-bituminous coal cannot occur through whole mass of coal aromatic condensed macromolecule skeleton, nevertheless coal small parts joined with the macromolecule by weak and single bonds are cracked during its activation.

4. Conclusions

Activation process of coal pyrolysis has a different tendency on porosity development for the KH sub-bituminous coal and the AD lignite samples. As increasing pyrolysis temperature, the yield of activated carbons from the KH coal is lowered, and the amount of micropores increases gradually; however there is no development of mesopores by the pyrolysis. The KH sub-bituminous coal has a small loss during physical activation due to difficulty and inactivity of its macrostructure decomposition; the smaller porosity is developed in the resulting carbons.

It is identified that the physical activation by gasification of AD lignite develops well a porous structure with the highest surface area of 522 m²/g which is

three times larger than that (155 m²/g) of the activated carbon produced by pyrolysis of the same lignite. The IR and SEM analysis confirm a difference in chemical and structural changes between the raw coals and corresponding carbon samples.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Lee, J., Kim, J. and Hyeon, T. (2006) Recent Progress in the Synthesis of Porous Carbon Materials. *Advanced Materials*, **18**, 2073-2094. <https://doi.org/10.1002/adma.200501576>
- [2] Zou, Y. and Han, B.-X. (2001) High-Surface-Area Activated Carbon from Chinese Coal. *Energy & Fuels*, **15**, 1383-1386. <https://doi.org/10.1021/ef0002851>
- [3] Fujimoto Kaoru, N.I. (1988) Activation of Coal with CO₂ and Its Utilization. *Proceeding of the 25th Coal Science Conference*, 20-25.
- [4] Teng, H., Yeh, T.-S. and Hsu, L.-Y. (1998) Preparation of Activated Carbon from Sub-Bituminous Coal with Phosphoric Acid Activation. PII: S0008-6223(98)00127-4, 1387-1395. [https://doi.org/10.1016/S0008-6223\(98\)00127-4](https://doi.org/10.1016/S0008-6223(98)00127-4)
- [5] Byambajav, E., Paysepar, H., Nazari, L. and Xu, C. (2018) Co-Pyrolysis of Lignin and Low Rank Coal for the Production of Aromatic Oils. *Fuel Processing Technology*, **181**, 1-7. <https://doi.org/10.1016/j.fuproc.2018.09.008>
- [6] Naoto, T., Yuuki, M., Enkhsaruul, B., Yuu, H., Takemitsu, K. and Yasuo, O. (2017) Steam Gasification of Low-Rank Coals with Ion-Exchanged Sodium Catalysts Prepared Using Natural Soda Ash. *Energy & Fuels*, **31**, 2565-2571. <https://doi.org/10.1021/acs.energyfuels.6b02905>
- [7] Byambajav, E., Hachiyama, Y., Kudo, S., Norinaga, K. and Hayashi, J. (2016) Kinetics and Mechanism of CO₂ Gasification of Chars from Mongolian 11 Lignites. *Energy & Fuels*, **30**, 1636-1646. <https://doi.org/10.1021/acs.energyfuels.5b02262>
- [8] Byambajav, E. and Ohtsuka, Y. (2004) Novel Utilization of Mesoporous Molecular Sieves as Supports of Metal Catalysts for Hydrocracking of Asphaltene. In: *Heavy Hydrocarbon Resources*, Chapter 15, Springer, Berlin, 205. <https://doi.org/10.1021/bk-2005-0895.ch015>
- [9] Byambajav, E. and Ohtsuka, Y. (2003) Cracking Behavior of Asphaltene in the Presence of Iron Catalysts Supported on Mesoporous Molecular Sieve with Different Pore Diameters. *Fuel*, **82**, 1571. [https://doi.org/10.1016/S0016-2361\(03\)00094-2](https://doi.org/10.1016/S0016-2361(03)00094-2)
- [10] Reimerink, W.M.T.M. (1999) The Use of Activated Carbon as Catalyst and Catalyst Carrier in Industrial Applications. *Studies in Surface Science and Catalysis*, **120A**, 751-769. [https://doi.org/10.1016/S0167-2991\(99\)80571-0](https://doi.org/10.1016/S0167-2991(99)80571-0)
- [11] Dabrowski, A. (2001) Adsorption from Theory to Practice. *Advances in Colloid and Interface Science*, **93**, 135-224. [https://doi.org/10.1016/S0001-8686\(00\)00082-8](https://doi.org/10.1016/S0001-8686(00)00082-8)
- [12] Ahmadpour, A. and Do, D.D. (1996) The Preparation of Active Carbons from Coal by Chemical and Physical Activation. *Carbon*, **34**, 471-479. [https://doi.org/10.1016/0008-6223\(95\)00204-9](https://doi.org/10.1016/0008-6223(95)00204-9)
- [13] Walker, P.L., Shelef, M. and Anderson, R.A. (1968) Catalysis of Carbon Gasification. In: Walker Jr., P.L., Ed., *Chemistry and Physics of Carbon*, Volume 4, Marcel

Dekker, New York, 287-383.

- [14] Verheyen, V., Rathbone, R., Jagtoyen, M. and Derbyshire, F. (1995) Activated Extrudates by Oxidation and KOH Activation of Sub-Bituminous Coal. *Carbon*, **33**, 763-772. [https://doi.org/10.1016/0008-6223\(95\)00010-B](https://doi.org/10.1016/0008-6223(95)00010-B)
- [15] Tsai, W.T., Chang, C.Y., Wang, S.Y., Chang, C.F., Chien, S.F. and Sun, H.F. (2001) Preparation of Activated Carbons from Corn Cob Catalyzed by Potassium Salts and Subsequent Gasification with CO₂. *Bioresource Technology*, **78**, 203-208. [https://doi.org/10.1016/S0960-8524\(00\)00111-5](https://doi.org/10.1016/S0960-8524(00)00111-5)
- [16] Shrestha, R.M. (2016) Effect of Preparation Parameters on Methylene Blue Number of Activated Carbons Prepared from a Locally Available Material. *Journal of the Institute of Engineering*, **12**, 169-174. <https://doi.org/10.3126/jie.v12i1.16900>
- [17] Hidayu, A.R., Mohamad, N.F., Matali, S. and Sharifah, A.S.A.K. (2013) Characterization of Activated Carbon Prepared from Oil Palm Empty Fruit Bunch Using BET and FT-IR Techniques. *Procedia Engineering*, **68**, 379-384. <https://doi.org/10.1016/j.proeng.2013.12.195>
- [18] Gomez-Serrano, V., Pastor-Villegas, J., Perez-Florindo, A., Duran-Valle, C. and Valenzuela-Calahorra, C. (1995) FT-IR Study of Rockrose and of Char and Activated Carbon. *Journal of Analytical and Applied Pyrolysis*, **36**, 71-80. [https://doi.org/10.1016/0165-2370\(95\)00921-3](https://doi.org/10.1016/0165-2370(95)00921-3)
- [19] Saka, C. (2012) BET, TG-DTG, FT-IR, SEM, Iodine Number Analysis and Preparation of Activated Carbon from Acorn Shell by Chemical Activation with ZnCl₂. *Journal of Analytical and Applied Pyrolysis*, **95**, 21-24. <https://doi.org/10.1016/j.jaap.2011.12.020>
- [20] Hung, Y.T., Lo, H.H., Wang, L.K., Taricska, J.R. and Li, K.H. (2005) Granular Activated Carbon Adsorption. In: Wang, L.K., Hung, Y.T. and Shammas, N.K., Eds., *Handbook of Environmental Engineering*, Volume 3, Humana Press, Totowa, NJ, 573-634. <https://doi.org/10.1385/1-59259-820-x:573>
- [21] Yoshizawa, N., Maruyama, K., Yamada, Y. and Zielinska-Blajet, M. (2000) XRD Evaluation of CO₂ Activation Process of Coal- and Coconut Shell-Based Carbons. *Fuel*, **79**, 1461-1466. [https://doi.org/10.1016/S0016-2361\(00\)00011-9](https://doi.org/10.1016/S0016-2361(00)00011-9)