

Study on Mechanism of Microwave Aided Co-Carbonization of Coal with Waste PET Plastic

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Abstract: The co-carbonized materials of coal and PET were prepared by microwave heating. The mechanism of co-carbonization is presented by thermogravimetric analysis and pyrolysis chromatography, combining with chemical changes of coal pyrolysis at lower temperature. The results show that the cracking reaction is dominated in synergistic carbonization prophase, while polycondensation in the late. Carbonization cracking of PET can promote carbonization of coal and formation of pore structure. The infrared adsorption peaks of -OH, O-H, -COOH and N-H disappear, the vibration intensity of N-H descends and the adsorption peaks of aromatic enhance, which prove the reactions of side chains break, decarboxylation reaction and oxygen-containing functional groups remove have taken place. The XRD analysis of co-carbonized materials shows that the materials take on disordered state in whole and microcrystalline graphite exists in part. The d (002) is large which results in the increase of the value of methylene blue and iodine sorption. It can provide theoretical foundation of the directional preparation of cheap and high performance activated carbon materials.

Keywords: Coal-based Activated Carbon; PET; Co-carbonization; Microwave Heating; Synergistic Effect

1 Introduction

In recent years, the problems of environmental pollution brought by plastic products are becoming more and more severe. According to statistics, the amount of waste plastics in China broke though 2010 Million tons but the recovery percent is less than 30%. How to solve the serious problems of "white pollution" is the one of great subject in contemporary. [1-4].

On the theoretical basis of the co-coking of coal/waste plastic to prepare the carbon materials, on the one hand, it could make full use of the structural characteristics of coal and, on the other hand, it could make use the synergistic effect of coal/waste plastics to improve the coking property of coal and the performance of co-carbonization materials. Using coal and PET as raw materials and microwave aided has prepared the high performance active carbon and application for patent at present, this indicated that it is feasible to produce the high performance active carbon using the great synergistic effect of coal/PET, but now there is no report for the mature and practicable co-carbonization mechanism.

2 Experimental

2.1 Raw materials pretreatment and analysis

The coal sample of Shenfu was grinded using the vi-

bration ball-milled system, and the particle size measured by laser Sizer was $d_{50} \leq 10 \mu m$.

PET raw materials: Several abandoned colorless PET beverage bottles were eliminated covers, tips and bottoms of non-PET component. And then they were sheared into very small pieces, washed clean and dried. Caustic soda as chemical coating elimination agent was used to do surface cleaning, in order to remove of the pollutants adhering to surface of PET bottles. Subsequently, the materials were cleaned, dried and comminuted, as well as screening the particle with the size of less than 180 meshes.

The comminuted coal samples were dried in a vacuum drying oven at 105°C for 4h to remove the water. About 2.5g cleaned samples were taken out to determine the its content of C, H, N and S on the elemental analyzer (Elementar, Vario ELIII), with the instrumental standard deviation $CHN < 0.1\%$ abs. The results of proximate and ultimate analysis were shown in Table 1 and Table 2.

Table 1 Ultimate analysis for raw shenfu coal

M_{ad}	V_{daf}	A_d	FC_d^a
7.29	36.42	4.27	63.58

Table 2 Proximate analysis for raw shenfu coal

C_{daf}	H_{daf}	O_{daf}^b	N_{daf}	$S_{t,d}$
81.75	4.79	11.95	1.10	0.38

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2.2 Preparation of material of microwave- assisted co-carbonization of coal/PET

Experimental group I : 1.00g Shenfu coal; Experimental group II : 0.40g PET; Experimental group III: mix Shenfu coal (1.00g) with PET in a 1:0.4 proportion; Experimental group IV: mix Shenfu coal (1.00g) with KOH in a 1:3 proportion; Experimental group V : mix 0.40g Shenfu coal with 3.00g KOH; Experimental group VI: Mix Shenfu coal (1.00g), PET and KOH in a 1:0.4:3 proportions.

Cover up the coal in the pot into ceramic container with insulation material. And then the ceramic container was put into microwave oven (Glanz, Model NO. G80F23CN2L-A9, microwave frequency 2450MHz) and carbonized for 6.5min at the 450W power setting.

After cooling the products was treated by grind, acid cleaning (dilute hydrochloric acid; diluted the concentrated hydrochloric acid with water in 1:9 ratio), distilled water cleaning and drying, and then the products will be analyzed ulteriorly. The carbonization products of all experimental group are marked successively as AC I , AC II , ACIII, ACIV, ACV and ACVI. The methylene blue adsorption value is an essential parameter of characterization of adsorption of active carbon adsorbing material which can be measured expediently. This paper measured the methylene blue adsorption value in GB/T 7702.7-2008.

2.3 Carbonization process and product analytical methods

The thermal stabilities of samples were carried out using a thermogravimetric analyzer (TA, SDT Q600). The samples were heated from 35 to 85°C at a rate of 20 °C min⁻¹ under the protection of nitrogen flow 100cm³/min.

Chromatography: Thermal desorption (TP-2020)/GC900A.

Fourier transform infrared (FTIR) spectra of the samples were obtained by using a spectrophotometer (PE, Spectrum GX, wave-numbers 400–4000 cm⁻¹) at a scanning number of 32 with the KBr sampling method.

X-ray diffraction analysis was conducted on an X-ray diffractometer (Rigaku, D/MAX-2400) with Cu-Ka radiation ($\lambda = 1.5406$ nm,) at a voltage and current of 46 kV and 100 mA.

3 Results and Discussion

3.1 Preparation and methylene blue adsorption of charring materials

The results of methylene blue adsorption experiments

for all carbonization products as followed:

I .59 mg•g⁻¹; II . 45 mg•g⁻¹; III.74 mg•g⁻¹; IV.207 mg•g⁻¹; V . 89 mg•g⁻¹; VI. 344 mg•g⁻¹.

The adsorption capacity of methylene blue of ACIV and ACVI is great higher than that others's, this illustrated that shenfu coal could be made into active carbon with the higher activities by potassium hydroxide. Further analysis, the adsorption capacity of methylene blue of ACVI is higher than that ACIV, this shows that shenfu coal and PET exists the great co-carbonization synergistic effect.

3.2 Mechanism analysis of co-carbonization of shenfu coal and PET

The TG curve of experimental group VI are showed in Figure 1, that have the number of significant regional rapid weight loss between 50 °C~800 °C, in which the weight loss of around 100 °C was mainly adsorbed on the samples of the physical pore structure of adsorbed water removal of the weight loss. It is worth noting that: PET alone pyrolysis weight loss starting temperature is 360 °C, PET and co-pyrolysis of coal is not the phenomenon of weightlessness near the temperature, it may be due to: Shenfu coal is lower rank bituminous coal, beginning to softening in 350 °C, the product of cracking was absorbed by softening coal, significantly reduces the weight loss rate of PET, in Figure 1, there can be seen from the weight loss curve of the experimental group I , II , III that the weight loss rate of PET and co-pyrolysis of coal were significantly reduced; another reason may be that: the KOH begin to melt under this temperature which absorbed the product of PET pyrolysis, all of that were formed by the experimental group II and V . This shows that Shenfu coal and KOH may also lead PET to significantly reduced weight loss, products of PET pyrolysis may be completely absorbed, and participate in aromatic polycondensation reaction., pyrolysis gas chromatography analysis in experimental group II showed that PET pyrolysis have five main product as the table shown in Figure 2, the peak intensity is proportional to the amount generated.

Samples of the FT-IR analysis showed that the carbonyl groups and oxygen-containing heterocyclic broke off and created a large number of CO during charring , aliphatic side chains and low-molecular-weight compounds which based on fat structure cracked and generated gaseous hydrocarbon (such as CH₄, C₂H₆ and C₂H₄, etc.), which explained the phenomenon of macro-weightlessness of samples at 450 °C. In this temperature range the bridge-bond in the structure of unit coal such as -CH₂- , -CH₂-CH₂- , -CH₂-O- , -O- , -S- and so on generated free radicals fragment due to heating[5].

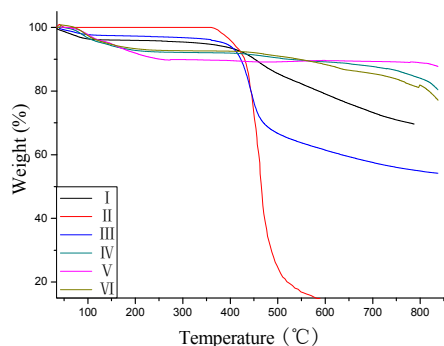


Figure 1 Thermogravimetric analysis curve

I - AC I; II - AC II; - AC III; IV - AC IV; V - AC V; VI - AC VI

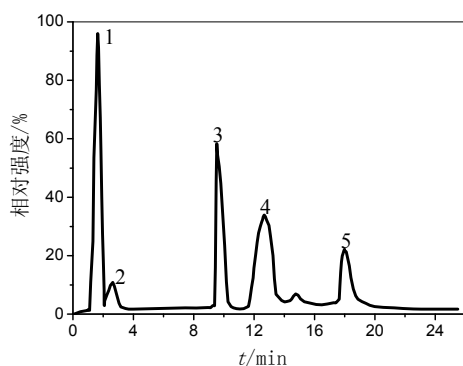


Figure 2 Pyrolysis gas chromatography analysis for PET and the structural formula of products corresponding to the chromatographic peak

1- $\text{CH}_2=\text{CH}_2$, CH_3CHO ; 2- C_6H_6 ; 3- $\text{C}_6\text{H}_5\text{COOH}=\text{CH}$; 4- $\text{C}_6\text{H}_5\text{COOH}$; 5- $\text{CH}_2=\text{CH}-\text{OOH}-\text{C}_6\text{H}_4-\text{COOCH}=\text{CH}_2$

The cracking products of PET were absorbed by carbonization system, and the main gases were only CO_2 , CO , H_2 , CH_4 during the carbonization process (shown in Figure 3), which showed that the cracking products of PET were attacked by thermal alkali and free radicals, and occurred second-cracking and generated CO_2 , CO , H_2 , CH_4 , C_2H_4 and C_6H_6 . The analysis of main gas component showed that substantial amount of C_2H_4 and C_6H_6 were not released, both of which contained weaker π bond and occurred easily electrocyclic reaction under heating, indicating that C_2H_4 and C_6H_6 molecules may be captured by coal structure, and participated in the reaction of dehydrogenation and polycondensation in the aromatic structure of coal, the reaction as follows in figure 4.

Figure 5 is the XRD analysis of ACVI that do not any treatment after carbonization. The results show that the main potassium compound formed in the activation process is potassium carbonate, hydrated potash and a spot of potassium oxide and potassium super-oxide. The

study of Lozano-Castello D [6-8] shows that potassium carbonate formation does not only take place on the carbon surface to forming a shell that surrounding the carbon particles, but also has molten potassium hydroxide congregate in the pore and holes of carbon. Potassium ion has the strong effect of electron donating and, in the higher temperature, can form the complex salt ' CO-K^+ ' that caused the break of carbon bond, then form the ' CO-K^+ ' to repeat the catalytic reaction of 'open-loop-bond breaking-open-loop'. In the condition of above 873K, potassium ion is reduced to atomic state by carbon atoms on the primary formed pore wall and then form the micropore structure after carbon atom released [9-11]. The XRD analysis as Figure 4 also detects that the atomic state of potassium exists.

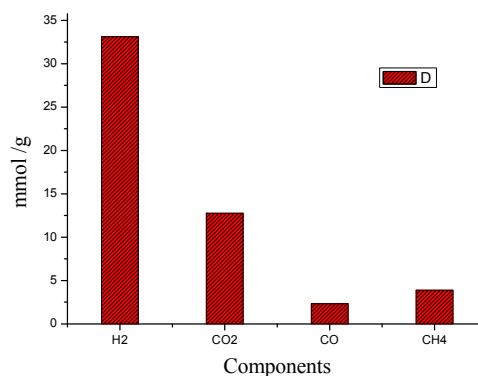


Figure 3 The analysis of the main gas elements in the carbonization process

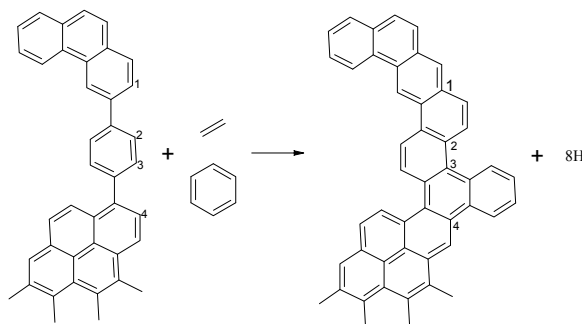


Figure 4 The reaction of dehydrogenation and polycondensation in the aromatic structure of coal

The peaks of (002) and (004) due to aromatic ring carbon net synusia in space arrangement degree of orientation. That is, the synusia packing height (L_c); The peaks of (100) and (110) due to the condensation degree of aromatic ring, that is the size of the aromatic carbon net synusia (L_a); The packing number of aromatic plane is about 3 or 4 based on the microcrystalline parameters $L_c = 1.16\text{nm}$ calculated from formula for Bragg; $L_a = 2.38\text{nm}$, $d(002) = 0.4133\text{nm}$ as a measuring index of

graphitization degree, $d(002)$ is smaller, the degree of graphite will be higher (the limit is $d(002)$ of graphite = 0.3354nm). Studies show that, the $d(002)$ of microcrystalline is higher, the adsorption properties of its production will be better, which explains the high product of methylene blue, as well as provides a micro-structural basis of a good carbonization collaborative effect of coal and PET plastic.

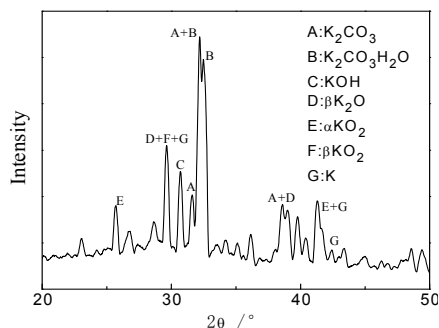


Figure 5 Shenfu coal/PET Co-carbonization material XRD analyse

4 Conclusions

1) The carbonization cracking of PET can promote the carbonization of shenfu coal and formation of pore structure. The cracking products of PET were attacked by thermal alkali and free radicals occurred by second-cracking; the products occur the electrocyclic reaction with coal macromolecule. Shenfu coal and PET exists the great co-carbonization synergistic effect.

2) The materials take on disordered state in whole and exist microcrystalline graphite in part. The $d(002)$ is large which results in the increase of the value of methylene blue.

It can provide theoretical foundation of the directional preparation of cheap and high performance activated carbon materials and an effective way for the comprehensive treatment of white pollution, meanwhile, play an active driving role for development and utilization of the high additional value of our national coal resources.

References

- [1] Liao H J, Qian K, Liu J, et al. The method of co-coking between waste plastics with coal. [P] CN 1465656. 2004-01-07.
- [2] Wei W. The novel carbonation technology of waste wood [J]. Resource environment strategy, 1999, 36 (6):10-12.
- [3] Tian F J, Li B J, Li W. Study on co-carbonization of coal with waste plastics II The heat behavior of coal with waste plastics in co-pyrolysis [J]. Journal of fuel chemistry an technology, 1999,2:27(2)
- [4] Wisner W H, Hill G R, Kertamus N J. Kinetic Study of the Pyrolysis of a High-Volatile Bituminous Coal [J]. Ind. Eng. Chem., Process Des. Dev., 1967, 6(133)
- [5] Lozano-Castello D, Lillo-Rodenas M A, Cazorla-Amoros D, et al. Preparation of activated carbons from Spanish anthracite I. Activation by KOH [J]. Carbon, 2001, 39(6): 741~749
- [6] Lillo Rodenas M A, LozanóCastello D, Cazorla-Amoros D. Preparation of activated carbons from Spanish anthracite II. Activation by NaOH [J]. Carbon, 2001, 39(5): 751~759
- [7] Lillo-Ródenas M A, Marco-Lozar J P, Cazorla-Amorós D, et al. Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide [J]. Journal of Analytical and Applied Pyrolysis, 2007, 80(1): 166~174
- [8] Yang Z Y. Mechanism, Kinetics and Application of Ultra-fine Coal Powder in Photo-oxidation [M]. Xi'an: Shaanxi Science and Technology Press, 2007, 10: 32~34