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Thermal Treatment of Charcoal for Synthesis of High-Purity Carbon Materials

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Abstract

The use of pure carbon materials in energy storage systems has the enormous potential for improvement of their performance. Among various carbon materials, natural and synthetic graphite is known to be the most widely used for batteries. Nonetheless, biomass as a good auxiliary carbon-containing material can also become a sustainable source of high-purity carbon material for this purpose. To examine these opportunities, a multistage technology comprised by pyrolysis of walnut shells and subsequent thermal purification of carbon residue at 3000 °C has been studied. As a result, high-purity carbon material has been synthesized, it can find the application in energy storage systems, for instance, lithium-ion batteries.

Keywords: *Charcoal; Pyrolysis; Thermal treatment; High-purity carbon materials; Walnut shells.*

1. Introduction

Lithium-ion batteries are the most widely used energy storage system in electric vehicles and portable electronic devices [1], due to the advantages of high energy density, self-discharge, low maintenance, cell voltage, load characteristics, no requirement for priming, and variety of types available. Manufacturers of lithium-ion batteries use heavy metals as cathode material and graphite (or other carbon materials) as anode. The ratio of heavy metals depends on production technology and can vary widely. Ordinarily, the anode material is made of graphite [2]. However, more efficient and environmentally friendly carbon materials derived from biomass can be used in anodes [3-4].

Compared to non-renewable carbon, biomass is a cheaper, environmentally friendly, readily available raw material with a low content of mineral components and sulfur. A significant advantage of biomass derived carbon is its multivariance, both in terms of biomass conversion technologies and end-use methods. Biomass has been and remains to be of a great scientific interest as it is a raw material for the production of high-purity carbon materials, which are widely used for manufacturing modern power sources, carbon-carbon products, products with special thermal, physical, physical and chemical, and sorption properties, etc. In their turn, high-purity carbon materials can be obtained, mainly, by artificial ways as a result of thermal action on carbon-containing raw materials.

A number of studies [5-13] examined the use of carbon materials including biomass as anode material of lithium-ion batteries. For instance, paper [7] reports on the anode material of charcoal obtained from rice husks. It was found that the capacity of lithium-ion batteries remained 400 mAh/g after a charge-discharge for 60 cycles.

In addition, Li *et al.* [14] carbonized corn stalks in an inert gas atmosphere with subsequent activation of KOH solution. The authors proved that this biomass waste is a feasible one for

high capacity lithium-ion batteries. The activated carbon anode retains the excellent recycling capacity of 504 mAh/g after 100 cycles at 0.2C.

Xu *et al.* [15] studied a crop stalks waste for obtaining hierarchical porous carbon composites employed in electrode materials of lithium-ion batteries. The obtained porous template is adopted for large-scale production of high-performance anode and cathode materials for lithium-ion batteries. Due to the large surface area, hierarchical porous structures and subsize of the functional particles, the electrode materials manifest excellent electrochemical performance.

The review of the studies on the use of biomass in lithium-ion batteries along with our previous research [16-19] on different types of biomass (brushwood, coniferous wood, sunflower husks, walnut shells, wheat straw, corn stalks) allow us to conclude that the most promising raw material for obtaining high-purity carbon materials is walnut shells. The main advantages of this raw material are low ash content (0.3-0.6 wt.%), almost complete absence of sulfur (less than 0.1 wt.%), high bulk density among other types of biomass (392-430 kg/m^3), and good mechanical properties ensuring material resistance to impact and abrasion.

One of the downstream methods for production of high purity carbon materials applicable for batteries is the thermal treatment of feedstock in an electro-thermal fluidized bed at temperatures 3000°C [16,20], so-called EFB technology. This technology ensures simultaneous purification and graphitization of carbon powder on industrial scale.

In this paper, we study both the conventional and the oxidative pyrolysis of walnut shells to obtain charcoal, as well as charcoal thermal treatment at 3000°C for producing high-purity carbon material to be used as anode material in lithium-ion batteries.

2. Experimental

2.1. Walnut shells characterization

Figure 1. Images of the original walnut shells

Walnut shells (*Juglans regia*) from Dnipro Region of Ukraine were taken as the raw material for the current study. After drying to the air-dry state, the initial properties of walnut shells were registered as follows, %: analytical moisture (W^a)–7.2, ash to dry mass (A^d)–0.3, volatile matter (V^d)–75.86, sulfur content (S^d)–0.2, hydrogen (H^d)–6.5, carbon (C^d)– 6.4 and nitrogen (N^d)–0.4. Additionally, the original walnut shells were characterized by the following particle size range: lengths to 30.5 mm, widths to 28.5 mm, and thicknesses of 0.3-2.8 mm; the surface area varied in the range of 3.4-1000 mm^2 while bulk density was 392.2-430.4 kg/m^3. Refer to Fig. 1 for the original walnut shells.

2.2. Conventional pyrolysis

The pyrolysis of walnut shells was carried out in an electric shaft furnace without any access to oxygen. The initial walnut shells were loaded into a cylindrical steel retort, which was loaded into a furnace preheated to a predetermined temperature. The pyrolysis was performed within the temperature range from 300 to 700°C with an interval of 100°C. The duration of the pyrolysis depended on the final temperature and holding time (15-20 min): 300°C–35 min; 400°C–40 min, 500°C–45 min, 600°C–55 min, 700°C–65 min. After the pyrolysis, the retort with charcoal was taken out of the furnace and cooled down to the room temperature.

2.3. Oxidative pyrolysis

The oxidative pyrolysis was conducted in the fixed bed of the filtration combustion condition. This process diagram is presented in Fig. 2. The source of the heat was the partial oxida-

tion reaction of the pyrolysis gases. The released heat was used for drying, heating and the pyrolysis to occur below the underlying biomass layers. The air acted as the oxidant.

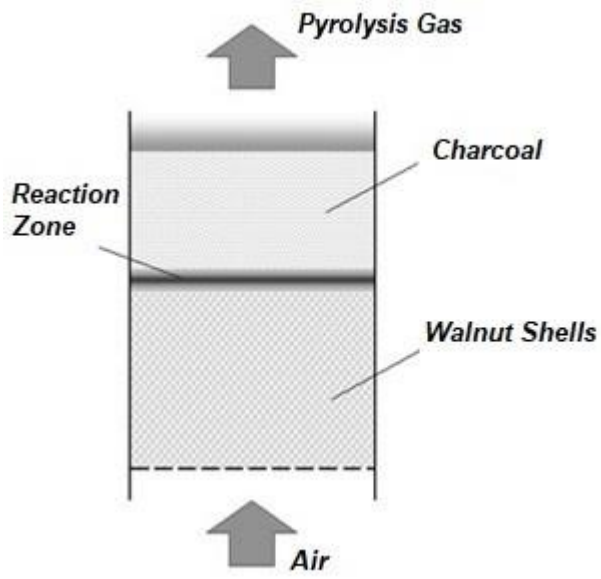

Figure 2. The Scheme of the oxidative pyrolysis process

The biomass bed was ignited from the top side, opposite to the air supply. The formed pyrolysis gases contained CO, CO_2, H_2, CH_4, N_2 and a significant amount of tar; those substances reacted with the oxygen from the air to form a reaction zone that was shifting towards the airflow. This effect is termed as "counter flow heat wave".

Heat transfer and concentration profiles occurred isomorphically. The reverse motion of the reaction zone was possible due to the high thermal conductivity of the layer and customized air flow rate. The charcoal residue was formed behind the reaction zone. The pyrolysis gases and products of their partial oxidation, moving in the same direction as the airflow did, passed through the layer of the charcoal residue. Due to high temperatures, the tar was decomposing into non-condensable gases (CO, CO_2, H_2, etc.) as the gases passed through the bed.

This scheme allows the process to be conducted without any external source of heat and is able to decrease the tar content within the pyrolysis gases. Further, by regulating the airflow it is possible to change the heat amount released from the partial oxidation of the pyrolysis gases, which is necessary for drying the biomass.

2.4. Thermal purification

Figure 3. High-temperature unit for thermal treatment of carbon materials by TMEC

To perform the thermal purification of charcoal, a laboratory high-temperature furnace was used (Fig. 3).

The reactor is intended for thermal processing of carbon materials at temperatures of up to 3000°C under inert gaseous environment. Its description is as follows:

i. the furnace with the material cell equipped with electric heaters, thermal insulation and main body;
ii. power supply source;
iii. inert gas supply source.

The principle technical features of the reactor are as given: power – 5 kW, voltage – 220/12-30V, current – 50-300A DC, maximum weight of a sample – 30 g. The type of heating system is resistive. The unit is equipped with a temperature control system. A typical cycle of thermal treatment consists of loading (5 min), drying (15 min), holding time (10 min), treatment (optional duration) and cooling down (30 min).

3. Results and discussion

3.1 Conventional pyrolysis

The results of proximate and ultimate analyses obtained after conventional charcoal pyrolysis are given in Table 1.

Table 1. Proximate and ultimate analyses of the original walnut shells and the charcoal after pyrolysis [%]

Pyrolysis final temperature, °C	W^a	A^d	V^d	FC	H^d	C^d	S^d	N^d
Original state	7.2	0.3	75.86	23.84	6.5	56.4	0.2	0.4
300	2.21	1.86	37.49	60.65	4.46	75.38	trace	0.33
400	3.25	2.02	27.15	70.83	3.92	79.48	trace	0.39
500	2.64	2.79	17.98	79.23	2.93	81.57	trace	0.32
600	1.62	2.64	11.25	85.11	2.87	88.74	trace	0.35
700	1.4	2.38	7.94	89.68	1.86	89.74	trace	0.31

With the increase in the pyrolysis temperature, the carbon content in the solid residue naturally increases while those of hydrogen and nitrogen decrease. Sulfur in is not detected in the charcoal. Furthermore, with the increase in the temperature of the walnut shells heat treatment, the yield of volatile matters decreases, the ash content and fixed carbon (FC) increase, reaching a maximum of 89.68% at a pyrolysis temperature of 700°C. The carbon content is 89.74%, V^d – 7.94%, and A^d – 2.38%.

3.2. Oxidative pyrolysis

The further studies were carried out under different technological conditions of oxidative pyrolysis (Table 2) and the process description is as follows.

Table 2. The results of the biomass oxidative pyrolysis in the closed layer

Parameters	Varieties in technological conditions		
	№ 1	№ 2	№ 3
Specific airflow rate in the pyrolysis, m^3/h	6.5	9.5	13.1
Specific gas flow rate per square meter, m^3/m^2h	27.4	40.0	55.2
Process time, min	230	180	150
The average temperature in the zone, °C	585	670	741
The filtration velocity, m/s	0.105	0.164	0.241
The average velocity of the counter flow heat wave, cm/h	11.4	15.2	18.2
The sedimentation velocity of the fuel layer, cm/h	6.52	9.67	12.40
The average temperature of the pyrolysis gases, °C	350	390	425
Proximate analysis [wt.%]			
W^a	2.0	1.5	1.3
A^d	2.2	2.5	2.91
V^d	12.4	8.5	7.0
FC	85.4	89.0	90.09
Ultimate analysis [wt.%]			
C^d	79.3	82.2	86.9
H^d	2.9	2.01	1.69
S^d		trace	
N^d	0.39	0.33	0.28
Content of the pyrolysis gases [vol.%]			
CO	5.3	5.6	6.5
H_2	8.7	9.5	10.1
CH_4	7.2	6.3	6.2
CO_2	13.8	12.7	11
N_2	56.5	57.3	57.6
O_2	8.5	8.6	8.6

The qualitative data of the process are the shape of the combustion zone and the uniformity of its movement along the reactor volume. The released gaseous substances contain CO_2, H_2, H_2O, CH_4, CO, O_2, N_2 and tar, which by reacting with the oxygen from the air provide the temperature in the combustion zone of 550-750°C. This temperature is determined by the reaction processes and heat exchange between the biomass and the gases, which, in turn, depends on the intensity of the airflow rate and the removal of the gaseous products from the reaction zone.

During the pyrolysis of the walnut shells, the deposition of the biomass bed is registered under all these technological conditions. At the same time, the higher airflow rate enables the increase in the average processing temperature for the walnut shells from 585 to 740°C, and the velocity of the thermal wave is changing within the range of 11.4 cm/h to 18.2 cm/h.

The comparative analysis of the performances per both pyrolysis technologies (Tables 1-2) has shown the close results as to the charcoal chemical composition. However, for several reasons, we consider the oxidative process to be the most feasible and suitable for industrial application. Due to the presence of the airflow, passing through of the bed of the material, there is an intensive heat and mass transfer between gaseous and solid phases. This decreases the processing time, compared to that of the indirect heating conventional process, with a possibility to maintain highly productive process in a relatively smaller reactor. Moreover, the oxidative pyrolysis is sustainable, because it can be carried out without energy consumption from any outer sources.

All the test runs made via the lab reactor have demonstrated the repeatability of the results, in terms of the final products properties. Therefore, the oxidative process is recommended not only for synthesis of pure "green" carbon, but also for heat or electricity generation based on the by-product gas with the combustible properties.

For the stage of thermal purification, we continued the study on the charcoal samples obtained under operating conditions No. 3 (Table 2) due to their highest level of carbon in the residues.

3.3. Thermal purification

Thermal purification of charcoal (particle size less than 0.2 mm) were conducted via the lab reactor at 3000°C. During the experimental study, the treatment of each sample lasted for approximately 5 minutes under steady conditions. The ultimate analysis of the mineral part of the carbon material after oxidative pyrolysis and after thermal purification are presented in the Table 3.

Table 3. Ultimate analysis of the mineral part [ppm] of the carbon material after oxidative pyrolysis and after thermal purification

Components	Charcoal after oxidative pyrolysis	Carbon after thermal purification
Total Ash [wt.%]	2.91	< 0.01
Mg	149.6	-
Al	163.3	< 2.4
Si	135.6	< 4.4
P	44.5	-
S	48.6	< 1.7
K	6347.0	< 6.7
Ca	5599.7	< 27.0
Ti	164.4	< 4.1
Mn	19.8	-
Fe	279.7	< 16.0
Cu	56.5	-

According to the obtained data, the thermal treatment technology provides fast purification of charcoal derived from walnut shells. It takes several minutes to reduce total ash content of

the material to less than 0.01%. That presents the significant advantage over Acheson conventional chemical processes. Practically, such performance indicators as the operating temperature and the treatment duration can be reached only via electro-thermal purification technology applied as based on a fluidized bed, so-called EFB Technology [20]. Therefore, the biomass producing carbon is a good source of a "green" carbon produced in an environmentally friendly way with the lowest carbon dioxide footprint.

As it follows from the chemical composition of the final product, such elements as Ca and Fe represent the challenge, as they are not easily removed from the charcoal even at 3000°C. However, it should be noticed that such a tendency for all carbon materials like natural graphite, anthracite, carbon black, etc. has been observed. This behavior is not related to the initial content of the elements, but rather to their atomic weight. Thus, the feature has to be taken into account for possible ways of pure carbon application.

Within this study, the development of the EFB lab reactor, capable of purifying the biomass intended for carbon production at continuous mode is being developed. Regarding the environmental issues, it is also important to develop a new engineering concept of an industrial purification unit based on electric supply from renewable energy sources that will significantly decrease operating costs.

4. Conclusions

Herein the technique for producing high-purity carbon materials using walnut shells as a feedstock has been studied. The results have shown that for charcoal production both the conventional and the oxidative pyrolysis to the temperatures of approximately 700°C could be applied with further thermal treatment of charcoal in an electro-thermal fluidized bed up to 3000°C.

The currently reported studies carried out at different ranges of airflow allow us to determine the parameters of the technological modes of oxidative pyrolysis. The repeatability of the process enables us to conclude that oxidative pyrolysis can be implemented on an industrial scale.

The electro-thermal purification technology applied on a fluidized bed allows charcoal high temperature treatment and obtaining high-purity carbon materials for use in energy storage systems.

Symbols

W^a	*Moisture (air dried basis);*	C^d	*Carbon (dry basis);*
A^d	*Ash (dry basis);*	N^d	*Nitrogen (dry basis);*
V^d	*Volatile Matter (dry basis);*	*FC*	*Fixed Carbon (dry basis);*
S^d	*Sulfur (dry basis);*	*LCV*	*Low calorific value*
H^d	*Hydrogen (dry basis);*		

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