Production of activated carbon from rice husk Vietnam

V V Korobochkin[1], N V Tu[2], N M Hieu[3]

[1, 3]Department of Chemical Engineering, Tomsk Polytechnic University, Tomsk
[2]School of Materials Science and Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi, Viet Nam
E-mail: [1]vkorobochkin@tpu.ru, [2] tu.nguyenvan@hust.edu.vn,[3]kqhak@yandex.ru

Abstract. This work is dedicated to the production of activated carbon from rice husk from Delta of the Red River in Viet Nam. At the first stage, carbonization of a rice husk was carried out to obtain material containing 43.1% carbon and 25 % silica with a specific surface area of 51.5 m^2/g. After separating of silica (the second stage), the specific surface area of the product increased to 204 m^2/g and the silica content decreased to 1.23% by weight as well. The most important stage in the formation of the porous structure of the material is the activation. The products with the high specific surface area in the range of 800-1345 m^2/g were obtained by activation of carbonized product with water vapour or carbon dioxide at temperatures of 700 °C and 850 °C, with varying the flow rate of the activating agent and activation time. The best results were achieved by activation of carbon material with water vapour at the flow rate of 0.08 dm^3/min per 500 g of material and the temperature of 850 °C.

1. Introduction

Recently the use of activated carbon as an adsorbent has increased rapidly. Resources base of activated carbon is quite varied, from crop waste to lignite and coal. Activated carbons obtained from these resources have high ash content and low mechanical strength. In addition, the inventories of these raw materials are reduced over time. Therefore, finding the alternative sources of raw materials for the production of activated carbon is an actual problem. However, using rice husk to produce activated carbon is significantly cheaper than other precursors, such as synthetic polymers and brown coals.

In 2014, the rice production in Viet Nam was 45 million Tons, and this continued to increase as a result of application of more advanced technologies in the process of cultivation of rice [1]. During the processing of rice, a huge amount of rice husk were formed, these waste products must be utilized. Combining Observance of environmental norms with the possibility of obtaining valuable products from rice husk is an actual task. According to [2], rice husk consists of a large amount of carbon in the composition of the natural polymer - cellulose and lignin. Besides carbon, these polymers contain sufficient amounts of hydrogen and oxygen which contribute to receiving activated carbon with the developed porous structure.

An efficient processing of rice husk into products (silica, activated carbon) is based on thermal decompression including washing, drying, pyrolysis of raw material, condensing the vapour mixture and obtaining a solid residue, followed by activation.

Production of activated carbon from rice husk has been the subject of many studies [3–5], which shows that it is possible to obtain activated carbon from rice husk with a high specific surface area.

However, these studies failed to demonstrate the efficient way to utilize a significant amount of amorphous silica dioxide, which is contained in the ashes.

The technology of processing includes the following three basic steps; First, carbonization of rice husks with an optimum temperature to remove moisture and volatile organic substances, and for the prior formation of porous structure; secondly, leaching of carbonized rice husk using sodium hydroxide is followed by precipitation of silica and filtration and third, activation of carbon material. The study in the field of thermal treatment of rice husk using pyrolysis and combustion present an interesting process. In these processes, different amount of the evolved gasses and vapors is generated, which affects the yield of carbon residue.

The purpose of this work: is to investigate the effect of heat treatment methods on the content of carbon and silica in the carbonized products in order to predict the composition of precursor for next activation stage and to carried out the process of activation of carbon residue.

2. Experimental

The rice husk from the Red River Delta in Viet Nam was used as the object of study. The process of carbonization of a rice husk was carried out in the Flow Reactor with a volume capacity of 500 cm^3 at 600 °C. Aprioristic information about the process was obtained by Differential Thermal Analysis, which is conducted on the device STD Q600 V8.1, in a stream of air or argon. The elemental composition of initial raw material, products of carbonization, products after separation of silica, products of activation and electron micrographs were obtained with the device Scanning Electron Microscope (SEM)-JED-2300 Analysis Station (JEOL). Characteristics of the porous structure (specific surface area, pore volume, pore size) were determined by nitrogen adsorption isotherms (BET method) at 77 K on the device NOVA Station, 2.11. Before measurements, the samples were maintained in the environment of nitrogen within 17 hours at a temperature of 150 °C.

3. Results and discussion

The elemental composition of rice husk, products of carbonization at 600 °C and products after separation of SiO_2 were shown in Table 1.

Table 1. The elemental composition of rice husk, products of carbonization and products after separation of SiO_2

Material	Content,% wt.								
	C	H	O	N	K	Si	Ca	Mg	Al
Rice husk	39,20	5,40	46,00	0,38	1,27	7,00	0,28	0,15	0,06
Products of the carbonization	43,10	0,01	29,33	0,03	1,57	25,00	0,39	0,29	0,08
Products after separation of silica	70,74	0,01	25,30	0,03	0,58	1,23	1,68	0,35	0,12

During carbonization stage, the decomposition and synthesis reaction of the organic part with recombination of removing gasses and vapors occur, which as a result lead to accumulation of flat formations of hexagons – precursors of graphene. Carbonization temperature is a key parameter, which affects the properties of the resulting carbons.

Differential Thermal Analysis (DTA) was conducted to determine the pre-carbonization conditions rice husk in an air flow and an inert gas (Argon). As shown in Figure 1, at a temperature below 200 °C in air flow, decomposition of a hemicellulose and removal of adsorbed moisture were observed. In the range of 280–540 °C there is a decomposition of cellulose, lignin, and other organic compounds with releasing of water and carbon dioxide. Consequencely, at up to 1000 °C a significant amount of carbon (total mass of weight loss. 89.3%) was burned.

For obtaining information about the process of decomposition of rice husk by pyrolysis, DTA in an inert gas flow (Argon) has been carried out. Results of DTA are shown in Figure 2.
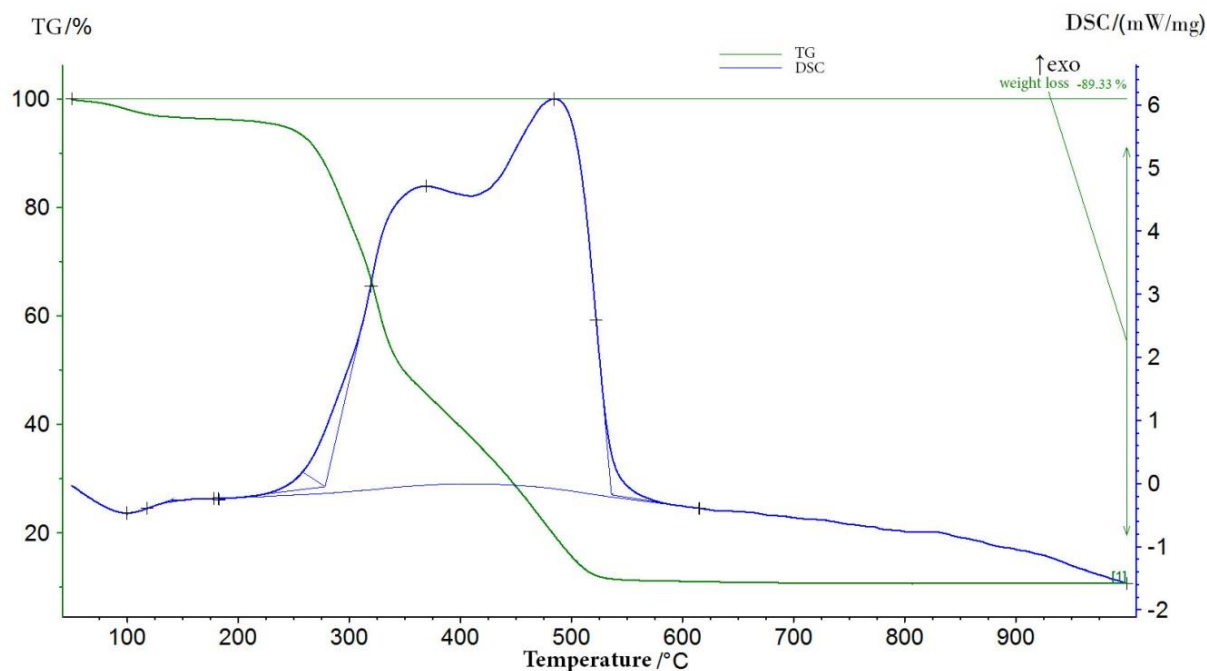
Figure 1. The results of DTA of rice husk in an Air flow
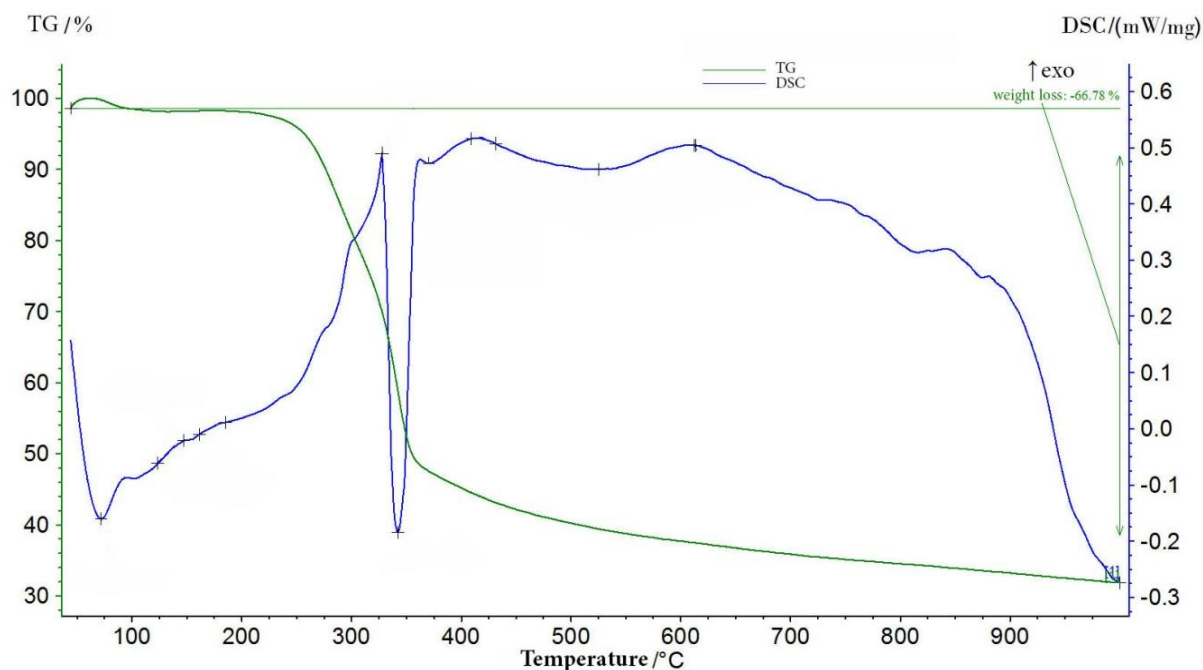

Figure 2. The results of DTA of rice husk in a flow of Argon

As shown in Figure 2, during pyrolysis, an intensive decomposition of cellulose and lignin with preferential releasing of H_2O, CO and CO_2 were observed in the temperature range of 320-380 °C. When temperature of heating upon to 1000 °C, the weight loses is 66.8%. After the temperature of 650 °C, the processes of interaction of H_2O and CO_2 with formed active carbon has begun occurred by following reactions:

$$CO_2 + C = 2CO, \qquad (1)$$
$$H_2O + C = CO + H_2. \qquad (2)$$
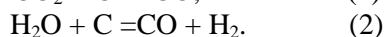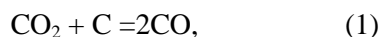
This interaction is evidenced by the DSC curve and a slight weight loss (4.8%) at temperatures above 650 °C. The reaction between carbon and carbon dioxide is a reversible reaction. Entropy factor provides the reaction moves to the right while enthalpy factor provides the reaction moves to the left. At temperatures below 400 °C, the equilibrium is almost completely shifted to the left and at a temperature above 1000 °C to the right (towards the formation of CO) [6].

Results of study [7] have shown that, at a temperature of carbonization above 850 °C the part of a pore space of the obtained carbon material is lost due to condensation of resinous substances in pores. Therefore, carbonization is recommended to be carried out at temperatures of 500-550 °C.

Carbonized material is exposed to leaching by sodium hydroxide to create favorable conditions for the formation of pores in the next stages of activation, as well as for the separation of silica dioxide [8].

Textural characteristics of products of carbonization of a rice husk and products after separation of SiO_2 are provided in Table 2.

Table 2. Pore Structure Characterization of products of processing rice husk

Material	S_{BET}, m^2/g	V_{Σ}, cm^3/g	V_{μ}, cm^3/g	Pore Diameter, nm	$S_{BET,\mu}$, m^2/g
After carbonization at 600 °C	51,5	0,0062	0,007	4,8	10,9
After separation of SiO_2	204,4	0,2248	0,057	4,4	97,8

Table 2 shows that the carbonized product has a small specific surface area and a low pore volume. However, after removing the SiO_2 significantly increases the specific surface area (up to 204 m^2/g) and an adsorption capacity. At that, in the leaching process, the carbonaceous matrix is formed with a high content of micropores, which accounts for 50% of a specific surface area of material.

Research Results by BET well illustrate micrographs of the obtained materials (Figure 3)
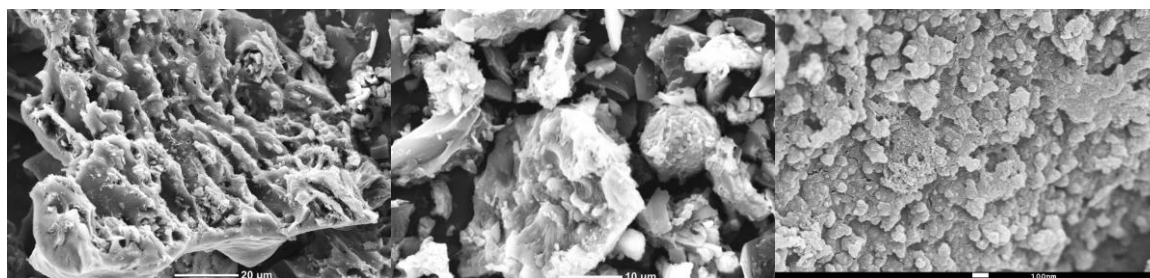
a)   b)   c)

Figure 3. Micrographs of materials obtained after carbonization (a) separation of SiO_2 (b) and activation (c)

Micrographs revealed that the structure of a product after separation SiO_2 has changed. The particles have a form of aggregates composed of laminated structures, their size decreases. This result is due to the process of leaching of silica.

Material after separating of SiO_2 contains more than 70% carbon and has the specific surface area more than 200 m^2/g. For improvement of the adsorptive properties, the product was exposed to activation.

There are two main groups of methods of activation of carbon materials: namely, physical activation and chemical activation [9]. In this work, the physical activation using carbon dioxide and water vapor was carried out. The process of activation is described by reactions (1) and (2). During

experiments, the effect of temperature, gas (water vapor) flow rate, and the activation time on the value of the specific surface area has been investigated.

In order to reduce loss of the carbon material, activation was carried out in the Flow Reactor without access of air with external electric heating. The mass of loaded material was 500g. The results of experiments are given in Table 3.

Table 3. Results of Activation of carbon obtained from rice husk

T, °C	Flow rate of H_2O, dm^3/min	S_{BET}, m^2/g	T, °C	Flow rate of CO_2, dm^3/min	S_{BET}, m^2/g
Activation time 1h					
700	0.08	1113	700	0.1	891
850	0.08	1345	850	0.1	1054
700	0.16	1089	700	0.5	924
850	0.16	1239	850	0.5	1097
Activation Time 5h					
700	0.08	1092	700	0.1	780
850	0.08	1198	850	0.1	1023
700	0.16	1198	700	0.5	816
850	0.16	1102	850	0.5	1064

The table shows that for same activation time and close value of gas (water vapor) flow rate, the maximum effect of activation is observed at a temperature of 850 °C. The specific surface area of material prepared with water vapor is higher than the one prepared with carbon dioxide. Increasing the activation time up to 5 hours, as well as increasing the values of gas (water vapor) flow rate is not effective. The best results are achieved by activation of carbon material using water vapor at the flow rate of 0.08 dm^3/min and the temperature of 850 °C.

Conclusion

Production of activated carbon from rice husk from Delta of the Red River in Viet Nam is carried out in three steps: carbonization of a rice husk, leaching of silica from carbonized material and depositing it in the form of SiO_2; activation a carbonaceous material using water vapor or carbon dioxide.

During carbonization, the material with a carbon content of 43.3% by weight and silica content of 25.9% by weight is generated. The material has a small (51.5 m^2/g) specific surface area. After separation of silica, the carbon material contains 70.74 % by weight carbon and only 1.23 % silica. The specific surface area of material significantly increases up to 204.4 m^2/g due to the formation of micropores with a diameter less than 2 nm. Micropores accounts for a half (97.8 m^2/g) of the total specific surface area.

Activation by water vapor and carbon dioxide at temperatures of 700 and 850 °C allows obtaining a material with a specific surface area in the range of 800–1345 m^2/g. The best results are achieved by activation of carbon material with water vapor at the flow rate of 0.08 dm^3 /min per 500 g of material and at the temperature of 850 °C.

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