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MICROPOROUS CARBONATE CATALYSTS FROM LIGNOCELLULAR WASTE PROCESSING SORGO (BAGASSE)

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Abstract. *New microporous carbon materials from lignocellulosic sorghum waste (bagasse) were synthesized and their structural-porous and ion-exchange characteristics were studied. A method of thermochemical modification of the surface of synthesized coals is proposed to improve the sorption and catalytic ability. The activity of the obtained carbon catalysts in the process of hydrolytic splitting of sucrose was studied.*

Keywords: *bagasse, structural-sorption properties, catalyst, hydrolysis, sucrose*

Over the past two decades, a new field of knowledge has been established and formed - the technical chemistry of carbon materials. It is in constant development, its theoretical positions are refined and enriched, and technologies for the production and application of coals are being improved [1-3]. One of the main problems of technical chemistry of carbon sorbents is the study of new types of carbon-containing compounds for the synthesis of special-purpose materials, increasing the efficiency of their use in various technologies.

In contemporary life, carbon sorbents from vegetable raw materials are widely used [2-8]. Such sorbents include carbon-containing materials obtained by pyrolysis of lignocellulose waste from the food industry, wood processing, etc. In [4-8], new methods of pyrolysis were developed, and hence new directions for the synthesis of adsorbents of various classes from lignocellulosic waste of enterprises, such as combined pyrolysis process – steam-gas activation, oxidative pyrolysis and thermochemical activation, etc. The purpose of this work was the study of some of the structural-sorption and physico-chemical properties of active coal obtained by thermal activation of lignocellulose waste formed during the processing of sugar sorghum (bagasse), the development of a method for thermochemical modification of the carbon surface to improve the sorption and catalytic ability of the samples studied and the determination of possible ways of its practical use as catalysts in the reaction of sucrose hydrolysis.

Methods of research and research results. When processing sorghum saccharatum (L.) Moench in order to obtain glucose-fructose syrups and patches, a significant amount of lignocellulosic waste bagasse is formed - the yield of which is about half of the total amount of processed raw materials. Bagasse is a valuable raw material for the synthesis of carbon adsorbents.

At the initial stage of the synthesis of the carbon material, we used a well-known method of obtaining sorbents from lignocellulosic raw materials, which involves preliminary carbonization and its subsequent vapor-gas activation according to the procedure [4,5]. The initial sample of crushed bagasse (particle size 0.2-0.5 mm) was heated in a quartz reactor, which was placed in a muffle furnace heated to the temperature of 800 ° C and kept at this temperature under an inert gas atmosphere (argon) for 1 hour. First, the removal of free and bound moisture and other volatile constituents (at 100-170 ° C) took place, and secondly, when the temperature was raised to 800 ° C, the pyrolysis products turned out to be structurally transformed, the mass of the product decreased by almost 50 %. The pyrolyzate obtained in this way was activated (at the temperature of 800 °C) in a water vapor atmosphere for 20 minutes. Such activation leads to an increase in the specific surface area of the material, the total pore volume and the static exchange capacity (Table 1). The yield of finished activated carbon is 30 - 45% of the initial mass of waste. From Table 1 it can be seen that the coal obtained by us has a mixed porous structure with predominance of mesopores.

Laboratory tests of the coal sample of obtained from bagasse conducted in accordance with generally accepted procedures [6-8] attested to its following characteristics.

Table 1.

Structural-porous and ion-exchange characteristics activated carbon from lignocellulosic sorghum waste (bagasse)

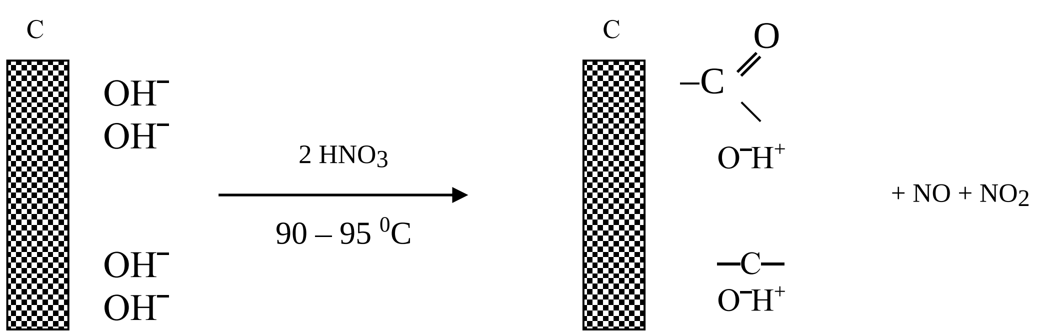
Name sample	Specific area surface, m^2 / g	Specific area of surface	Specific area surfaces micropores, m^2 / g	Total pore volume,	Microporous volume,	Average radius pore, Å	Static exchange capacity by (Na^+),	Static exchange capacity according
Coal from bagasse	1265	1147	118	0,46	0,18	5,58	0,25	0,22

Thus, the coal obtained from bagasse is a carbon material of medium activation degree with a specific surface of 1265 m2 / g, with a predominant content of mesopores of average radius is 5.58 Å.

To improve the sorption characteristics of the material, giving it greater microporosity, ion exchange and catalytic properties, the obtained sample of coal was subjected to additional treatment - washing with hot distilled water to neutral pH of aqueous extract, special oxidation in the liquid phase with 25% nitric acid by boiling in a water bath (oxidation) in order to impart to the coal the properties of effective cationic or anion exchangers [9, 10].

The process of coal oxidation with nitric acid can be schematically represented as follows:

Activated carbon Oxidized coal



Parameters of the obtained coals (Table 2) were evaluated according to the standart methods (GOST 6217-74, GOST 4453-74): the total volume of sorption pores for benzene (Ws), sample moisture, ash content, pH of aqueous extract, bulk density, anion exchange capacity - by sorption of CI ions from 0.01 N. aqueous solution of HCI and a cation exchange capacity (COE) for the sorption of Na + ions from 0.1N. solution of NaOH; The specific surface was measured by the gas-chromatographic method of thermal desorption of argon. To characterize the porous structure, the low-temperature sorption method N_2 was used [11].

Table 2

Structural-porous characteristics coal from lignocellulosic sorghum waste (baggas)

Indicators	Coal from baggas			KAU
	Initial activated	Initial washout	Oxidized	
Ws in benzene, cm^3 / g	1.1	1.16	1.12	0.9
Humidity,%	18	12	-	10
Ash content,%	10.8	9.0	-	3.0
Bulk density Δ, g / cm^3	0.78	0.37	0.25	0.36
PH of the water extractor	4.4	6.0	-	6.5
Specific area surface, m^2 / g	1265	2950	2200	1010
COE according to NaOH, meq / g	0.25	0.6	4. 6	0.1
COE according to HCI, meq / g	0. 22	0.2	0.1	0.35

From the data in Table 2 it can be seen that the coals from bagasse studied in their structural and sorption characteristics are not inferior to known granular sorbents (for example, coal from natural stone fruit raw materials of KAU). The presence of microporous structure in the studied samples is confirmed by the results of studies of the structural-sorption characteristics of N_2 samples obtained with the use of high-speed gas sorption analyzer NOVA-2300. It was established that the coal obtained during the acid modification had a high specific surface area of 2200-2950 m^2 / g, and large volume of sorption space (Ws = 1-1.16 cm^3 / g). Figure 2 shows the curve of the distribution of pores along radii for oxidized coal based on bagasse.

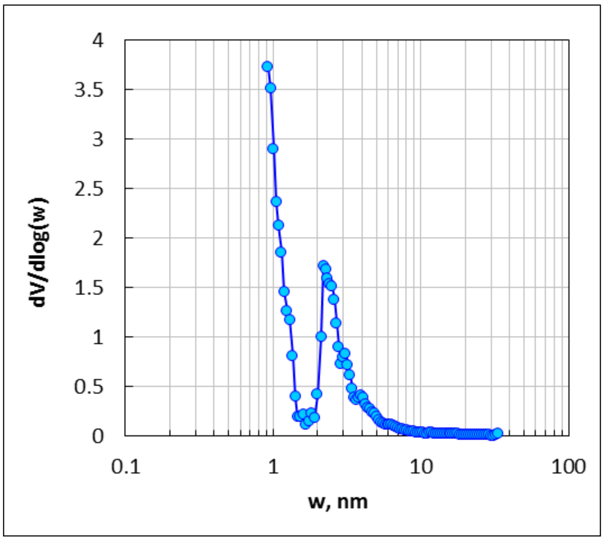


Fig.1. Pore size distribution for oxidized coal obtained from bagasse.

The sample appeared to be really uniformly microporous with pore sizes w 3-10Å, which is a valuable quality for the practical use of materials of this type. The experiments showed that the coal under investigation is easily oxidized: after 1 h of boiling in nitric acid on a water bath, it was possible to achieve a fairly high ion-exchange capacity (COE = 4.6 meq / g) with a predominant content of surface strongly acidic and phenolic groups, whereas under similar conditions, coals from the fruit bone KAU for example are oxidized to similar values of COE in only 15-20 hours [12, 13]. Probably, the catalytic effect of mineral impurities in them (ash 10%) exerts a catalytic effect on the oxidation rate of the investigated coal. Similar phenomena had been noted earlier in [14].

The chemical methods used to determine the amount of acid groups of oxidized coals from bagasse by titrating them with alkalies of different strengths allowed us to determine that 4.68 meq / g of the total exchange capacity of the coals strong carboxylic acid groups of 2.08 meq / g and phenolic 2.5 meq / g we contained.

Thus, coal produced by additional oxidation is a polyfunctional cation exchanger with a wide range of acid properties, determining responsible for the ability to ion exchange of protonogenic groups. Due to its sufficiently developed surface, such coal is a good sorbent, and thanks to microporosity it is a very suitable catalyst for liquid-phase oxidation processes.

The catalytic activity of the samples of carbon materials obtained by us was investigated in the sucrose hydrolysis reaction (inverting). The hydrolysis of sucrose was carried out at a temperature of 100 ° C in the presence of a carbon catalyst. The initial concentration of sucrose was 10% by weight, the ratio of the weight of the solid catalyst to the mass of sucrose was 1:10. In the hydrolyzate, the content of the hydrolysis products (glucose and fructose) was determined by the Knight and Allen method (ICUMSA method) [15]. The results of experiments on hydrolytic cleavage of sucrose by heterogeneous catalysis on sulfonated carbon materials are shown in Fig. 2.

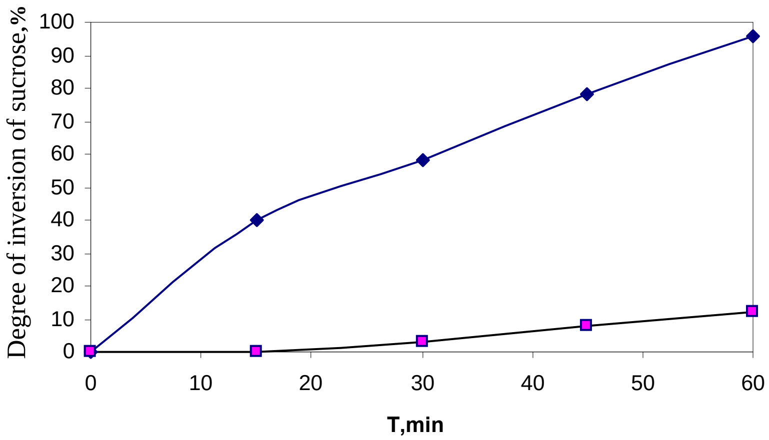


Fig.2. The kinetics of catalytic decomposition of sucrose: ■ - activated (washed), ♦ - oxidized coals from bagasse.

From the data presented, it can be seen that the catalytic activity of the obtained coals from bagasse (washed and oxidized) in the process of hydrolysis of sugar solutions is almost by an order of magnitude different for samples with a static exchange capacity of 0.6 and 4.6 meq / g. It can be assumed that the chemistry of the material surface (the presence and concentration of oxygen-containing groups) has determining effect on the kinetics of the decomposition of sucrose. The maximum decomposition of sucrose under the action of the resulting catalysts is 85-96% with a duration of hydrolysis of 60 min, which exceeds the properties of the most effective solid acid catalysts V_2O_5 / γ-Al_2O_3, Amberlite IR-120B and Amberlite IR-120H [16, 17].

Conclusions

1. New microporous carbon materials were obtained on the basis of lignocellulosic sugar sorghum (bagasse) waste, by thermal treatment and steam-gas activation. Using the modern methods of analysis, the basic structural parameters of the synthesized carbon sorbents were determined, the specific surface (~ 1200 m^2 / g), the total volume of the sorption pores (Ws ~ 1.1 cm^3 / g) were found. The prevailing presence of micropores in them is established, their radii were calculated.

2. Directional changes in the chemical nature of the surface of the coal under investigation were carried out using liquid-phase oxidation with nitric acid (catalytic properties). The catalysts, investigated by the method of low-temperature nitrogen adsorption and acid-base titration, have a rather high BET specific surface area (2200 m^2 / g), the acidity of the surface reaches 4.5-4.6 mmol / g, the predominant presence of micropores with a radius of 3- 10Å.

3. The activity of the obtained catalysts in the process of hydrolytic decomposition of sucrose was studied. It is shown that the chemistry of the material surface (concentration of oxygen-containing groups) has a determining effect on the kinetics of decomposition of sucrose. The maximum decomposition of sucrose under the action of the resulting catalysts is 85-96% with a duration of hydrolysis of 60 min, which exceeds the properties of the most effective solid acid catalysts V_2O_5 / γ-Al_2O_3, Amberlite IR-120B and Amberlite IR-120H.

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МІКРОПОРИСТІ ВУГЛЕЦЕВІ КАТАЛІЗАТОРИ З ЛІГНОЦЕЛЮЛОЗНИХ ВІДХОДІВ ПЕРЕРОБКИ СОРГО (БАГАСИ)

Л. А. Купчик, Л. И. Котинская, Н. В. Сич, Н. А. Григоренко

Анотація. *Синтезовані нові мікропористі вуглецеві матеріали з лігноцелюлозних відходів переробки сорго (багаси) і вивчені їх структурно-пористі і іонообмінні характеристики. Запропоновано спосіб термохімічного модифікування поверхні синтезованих вугілля для поліпшення сорбційної і каталітичної здатності. Досліджено активність отриманих вуглецевих каталізаторів в процесі гідролітичного розщеплення сахарози.*

Ключові слова: *багаса, структурно-сорбційні властивості, каталізатор, гідроліз, сахароза*

МИКРОПОРИСТЫЕ УГЛЕРОДНЫЕ КАТАЛИЗАТОРЫ ИЗ ЛИГНОЦЕЛЛЮЛОЗНЫХ ОТХОДОВ ПЕРЕРАБОТКИ СОРГО (БАГАСЫ)

Л. А. Купчик, Л. И. Котинская, Н. В. Сыч, Н. А. Григоренко

Аннотация. *Синтезированы новые микропористые углеродные материалы из лигноцеллюлозных отходов переработки сорго (багасы) и изучены их структурно-пористые и ионообменные характеристики. Предложен способ термохимического модифицирования поверхности синтезированных углей для улучшения сорбционной и каталитической* *способности. Исследована активность полученных углеродных катализаторов в процессе гидролитического расщепления сахарозы.*

Ключевые слова: *багаса, структурно-сорбционные свойства, катализатор, гидролиз, сахароза*