CARBONACEOUS MATERIALS OBTAINED FROM SUNFLOWER HUSKS FOR NO_2 REMOVAL

Angelika Rutkowska, Piotr Nowicki, Robert Pietrzak

Laboratory of Coal Chemistry and Technology,
Faculty of Chemistry, A. Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland

Introduction

Growing interest in the sorption materials has been a result of development of new industrial technologies and the necessity of satisfying increasing demands on the protection of the natural environment. From among products used for this purpose, of greatest importance are the adsorbents made of carboniferous materials. Carbon sorbents occur as a wide range of materials (activated carbons, activated carbon fibers, nanotubes, carbon molecular sieves) characterised by different surface area development, depending on the type of the raw material. Of greatest application are active carbons used for adsorption of pollution from liquid and gas phase, in catalysis as well as in electrochemistry or for gas storage [1-3].

Active carbon can be produced from various precursors such as peat, lignin, wood, fruit stones and certain waste materials, however, their most important precursors are all types of fossil coals of different degree of coalification, from brown coals to anthracites [4-5]. From the ecological point of view, adsorbents obtained from waste materials such as sawdust, plastics or agricultural wastes make an excellent alternative to those produced from fossil fuels. It is a very interesting method of utilisation of wastes and their conversion into valuable products.

For this reason the objective of this paper was to obtain the series of adsorbents from sunflower husks and to characterise its sorption performance towards NO_2.

Experimental

The starting sunflower husks (SF) were cleaned with distilled water and dried at 110 ºC for 24 h. Then they were ground with a roller mill and sieved to a size range of 1.5–2.5 mm. Next the crushed sunflower husks were subjected to carbonisation. The carbonisation (C) was carried out in a horizontal furnace under argon with a flow rate of 170 mL/min. The sample was heated (5 ºC/min) from room temperature to the final carbonisation temperature of 600 (C6), 700 (C7), 800 (C8) and 900 ºC (C9), respectively. In the final temperature, samples were kept 60 min and then cooled in inert atmosphere.

The elemental analysis of the starting sunflower husks and chars were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

The content of surface oxygen functional groups were determined by the Boehm method [6].

The pH of active carbons was measured using the following procedure: a portion of 0.4 g the sample of dry active carbon powder was added to 20 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then pH of the suspension was measured.

Evaluation of NO_2 sorption capacity: Samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 3 cm^3). Dry or wet air (75% humidity) with 0.1% of NO_2 was passed through the column of adsorbent at 0.450 L/min. The breakthrough of NO_2 was monitored using electrochemical sensor. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of mg of NO_2 per g of adsorbent were calculated by integration of the area above the breakthrough curves, and from the NO_2 concentration in the inlet gas, flow rate, breakthrough time, and mass of adsorbent [7].

Results and Discussion

According to the data presented in Table 1, carbonisation of sunflower husks led to important changes in the elementary composition of the precursor. The content of carbon increased by 36.0-40.9 % accompanied by a decrease in the content of hydrogen and especially oxygen by 33.2-36.4 %. The content of nitrogen increases insignificant, which suggests that the sunflower husks contain nitrogen in the form of thermally stable functional groups. Changes in the elementary composition of the precursor are mainly a result of high temperature. On heating, the least stable fragments of the structure (e.g. methylene and oxygen bridges) undergo decomposition leading to formation of the side products of carbonisation rich in hydrogen and oxygen, such as water and simple hydrocarbons.

Table 1. Characteristics of Raw Sunflower Husks and Chars Obtained at 600, 700, 800 and 900ºC (wt.%).

Sample	Ash^d	C^{daf}	H^{daf}	N^{daf}	O^{daf*}
SF	2.5	44.0	5.6	1.4	49.0
SFC6	10.6	80.0	2.2	2.0	15.8
SFC7	10.2	83.4	1.5	2.4	12.7
SFC8	10.8	84.1	1.2	2.5	12.2
SFC9	10.8	84.9	0.6	1.9	12.6

* by difference

To establish the acid–base properties of the materials obtained, the content of the oxygen functional groups of acidic and basic character was determined. Analysis of the data collected in Table 2 has shown that the chars obtained are characterised by different content of surface oxides; from 1.04 to 2.03 mmol/g. All samples show distinctly basic character of the surface. The content and type of the surface oxygen groups is determined mainly by the temperature of carbonisation. An increase in the temperature of carbonisation from 600 ºC to 900 ºC leads to a decrease in the amount of groups of acidic

Table 2. Acid-Base Properties of Chars Obtained.

Sample	pH	Acidic groups [mmol/g]	Basic groups [mmol/g]	Total content [mmol/g]
SFC6	10.4	0.12	0.92	1.04
SFC7	10.5	0.08	1.43	1.51
SFC8	10.3	0.05	1.62	1.67
SFC9	10.9	0.00	2.03	2.03

character and an significant increase in the number of basic groups. The greatest content of the surface oxygen groups of over 2 mmol per 1g of sorbent was found in SFC9 sample, containing only basic groups, while the lowest content of the surface oxides of 1.04 mmol/g was determined in SFC6 sample, carbonised at 600 ºC.

All the samples produced were tested for the NO_2 adsorption in dry and wet conditions. The calculated breakthrough capacities for the chars obtained presents Table 3.

Table 3. NO_2 Breakthrough Capacities of the Chars Obtained.

Sample	NO_2 breakthrough capacity [mg/g$_{ads}$]	
	Dry conditions	Wet conditions
SFC6	2.5	19.1
SFC7	6.6	26.4
SFC8	10.5	32.4
SFC9	9.0	26.3
Norit® SX2	11.5	2.8
Norit® RKD-3	24.0	27.1

According to the data shown in Table 3, the chars obtained from sunflower husks are characterised by diverse sorption capacities of NO_2. The results indicate that the sorption ability of the chars obtained, both in dry and wet conditions, increases with increasing temperature of carbonisation, reaching a maximum at 800 ºC. The highest NO_2 sorption capacity of 32.1 mg/g was obtained for sample SFC8 in wet conditions, while the lowest of 2.5 mg/g for sample SFC6 in dry conditions. It should be noted that some of the chars obtained showed better or comparable sorption capacities (especially in wet conditions) with those of the commercially available activated carbons such as: Norit® RKD-3 or Norit® SX-2.

All the samples studied in our experiments showed much better sorption abilities in wet conditions. This difference was particularly pronounced for sample SFC6, which sorption capacity in wet conditions was almost 8 times greater than that in dry conditions. Greater sorption capacities in wet conditions most probably follow from a different mechanism of NO_2 adsorption. According to Jeguirim [8], the presence of water in the reaction environment can be responsible for the changed mechanism of adsorption. In the wet conditions the reaction between NO_2 and H_2O can lead to formation of a mixture HNO_2 and HNO_3 acids and the nitric(V) acid formed can react with the carbon surface, according to the equation:

$$-C^* + HNO_3 \rightarrow C(ONO_2).$$

Conclusions

The above-discussed results have shown that the sunflower husks may be suitable precursor for obtaining cheap adsorbents characterized by good sorption properties from gas phase. The adsorptive properties of these materials against NO_2 increase with increasing temperature of carbonization and reach a maximum for the samples obtained at 800 ºC. The NO_2 breakthrough capacities obtained in dry and wet condition prove that the presence of water increases the NO_2 breakthrough capacity.

Acknowledgments. This work was supported by The Polish Ministry of Science and Higher Education project No. N N204 277537.

References

[1] Bagreev A, Menendez JA, Dukhno I, Tarasenko Y, Bandosz T J. Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide Carbon 2004;42:469-476.

[2] Jasińska E, Krzyżyńska B, Kozłowski M. Activated carbon modified with different chemical agents as a catalyst in the dehydratation and dehydrogenation of isopropanol. Catalysis Letters 2008;125:145-153.

[3] Jurewicz K. Pietrzak R, Nowicki P, Wachowska H. Capacitance behaviour of brown coal based active carbon modified through chemical reaction with urea. Electrochimica Acta 2008;53:5469-5475.

[4] Nowicki P, Pietrzak R, Wachowska H. Comparison of physicochemical properties of nitrogen-enriched activated carbons prepared by physical and chemical activation of brown coal. Energy Fuels 2008;22:4133-4138.

[5] Nowicki P, Pietrzak R, Wachowska H. Siberian anthracite as a precursor material for microporous activated carbons. Fuel 2008;87:2037-2040.

[6] Boehm HP, Diehl E, Heck W, Sappok R. Surface oxides of carbon. Angewandte Chemie. Int. Edit in English 1964;3:669-677.

[7] Pietrzak R. Active carbons obtained from bituminous coal for NO_2 removal under dry and wet conditions at room temperature. Energy Fuels 2009;23:3617-3624.

[8] Jeguirim M, Tschamber V, Brilhac JF, Ehrburger P. Oxidation mechanism of carbon black by NO_2: Effect of water vapour. Fuel 2005;84:1949-1956.