

Production of eco-materials from organic wastes by pyrolysis process

Elena David*

Institute of Cryogenics & Isotopic Technologies, Rm. Valcea, P.B. 10, Code 240050, Romania

Received 18 September 2006; received in revised form 10 January 2007; accepted 23 January 2007

Available online 12 March 2007

Abstract

The research objective of this work was to develop eco-materials which can be used in environment depollution. The activated carbons considered as eco-materials have been prepared from rape seeds after the extraction of oil by a slow pyrolysis process. The optimum conditions were an activation temperature of 650 °C, an activation time of 3 h and a nitrogen flow rate of 30 l/h, using steam as activating agent. The prepared activated carbons had a specific surface area of 700–1500 m²/g and a grain bulk density of 0.4–0.8 g/cm³. The physico-chemical characteristics of the carbon active samples were determined using adsorption methods. The carbon adsorbents were chemically modified to have base sites on their surfaces and to investigate the adsorption characteristics of carbon dioxide. Strong interaction between carbon dioxide and base sites enhanced the adsorption of carbon dioxide at temperatures up to 250 °C.

© 2007 Published by Elsevier B.V.

Keywords: Amorphous materials; Gas–solid reactions; Thermochemistry

1. Introduction

The development of materials that can reduce the environmental impact is important to protecting the earth's natural environment. Activated carbons (AC) can be considered as eco-materials because they are widely used as adsorbents in gas and liquid-phase separation processes, purification of products, air and water cleaning operations. The preparation of activated carbons involves, frequently, two steps: carbonization of the raw material in absence of oxygen, and activation of the carbonized product with water vapour or carbon dioxide [1–3]. The activation can be carried out under well-controlled conditions to a desired conversion. The pores thus produced in the char give the activated carbon its high surface area and adsorptive properties. A simple one-step method for the production of activated carbons by pyrolysis of solid fuels in the presence of steam has also been developed [4,5]. Another method for the production of activated carbons is through chemical activation. In this method, the precursor material is impregnated with a dehydrating and stabilizing chemical reactant in order to enhance the develop-

ment of a porous structure upon heat treatment [6]. Preparation method, type of used reactor, employed conditions and selected precursor material influence the properties of the obtained activated carbons [1–7]. Physical activation with steam or CO₂ has resulted in carbons with a pore structure consisting mainly of narrow micropores and wide macropores [8–13]. In the present work the biomass samples were carbonized and activated in a one-step treatment involving pyrolysis in a flow of steam. The almost simultaneous pyrolysis and gasification favoured the high reactivity of the solid material and at milder treatment conditions its conversion into activated carbon with a well-developed porous structure and good adsorption capacity [9,10]. The quick removal of the volatiles and the stabilization of the radicals in the presence of steam results in increased yields of volatiles and the formation of solid products with a highly developed active surface free from organic compounds.

The objectives of this investigation were to develop environmental materials and to find optimum conditions to obtain AC by one-step pyrolysis and steam activation, to study the physical and chemical properties of the product AC and to chemically modify these adsorbents to become selective materials. These modified carbon adsorbents were investigated as CO₂ adsorbing eco-materials which can be used in many applications such as gas separation and purification and vehicle exhaust emission

* Tel.: +40 250 732744; fax: +40 250 732746.

E-mail address: david@icsi.ro.

control, because of their high specific pore surface area, adequate pore size distribution and relatively high mechanical strength.

2. Experimental

The experiment used rape seeds for the production of AC by pyrolysis and steam activation in one stage. First, the oil was extracted from rape seeds and then the resulting residue was extruded, without binder addition in extrudates of 4 mm in diameter. Then the residue was dried in air at room temperature for 24 h. The experimental system used for the preparation is presented in Fig. 1. It included a fixed bed reactor of a length of 1.2 m and an inner diameter of 0.055 m, recipients with pressured gases, a steam generator, an equipment for removal of the liquid products and a gas meter. The reactor tube was heated by an electric heater. The liquid products were collected in a receiver. The water was pumped to the steam generator by a peristaltic pump. The steam temperature was around 105 °C. The volatiles were cooled down in a water-cooled condenser. The gas composition was analyzed by a gas chromatograph (type Varian) for CO₂, H₂, CO, N₂, CH₄ and hydrocarbons up to C₇. The gas chromatograph was equipped with three columns. A Porapak Q 80/100 (3 mm in diameter and 2 m in length) produced a good separation of CO₂ and hydrocarbons such as C₂H₄, C₂H₆, C₂H₂. A molecular sieve column (MS5 60/80, 3 mm in diameter and 2 m in length) was used for separation of H₂, O₂, N₂, CH₄ and CO. Both columns used helium as carrier gas and were connected to a thermal conductivity detector. A Megabore column (bonded phase: DB-1, 0.9 mm in diameter and 16 m in length) was used for the separation of hydrocarbons such as C₆H₆ and C₇H₈. The column used nitrogen as carrier gas and was connected to a flame-ionization detector.

In each experiment 600 g of biomass was subjected to pyrolysis in presence of water steam at atmospheric pressure. The steam flow was varied from 18 to 30 l/h. The steam was introduced into the reactor when the temperature in the reactor was 150 °C. The reactor was heated at constant rate 3–5 °C/min) to the selected final temperature (550, 600 and 650 °C). The sample was kept at the final temperature for 1, 2 or 3 h and then the electrical heater was switched off. After the treatment the samples were left to cool down and the steam flow was interrupted at a temperature of 250–300 °C. Before each experiment nitrogen was led through the system to empty it from air. After each experiment nitrogen was also led through the system to rinse it from volatile products. The collected char was measured and characterized. Product distribution and ash content of the obtained activated carbons are shown in Table 1. The surface area (S_{BET} , m²/g) was determined using the Brunauer–Emmett–Teller equation (BET equation for multilayer adsorption of gas molecules on a solid

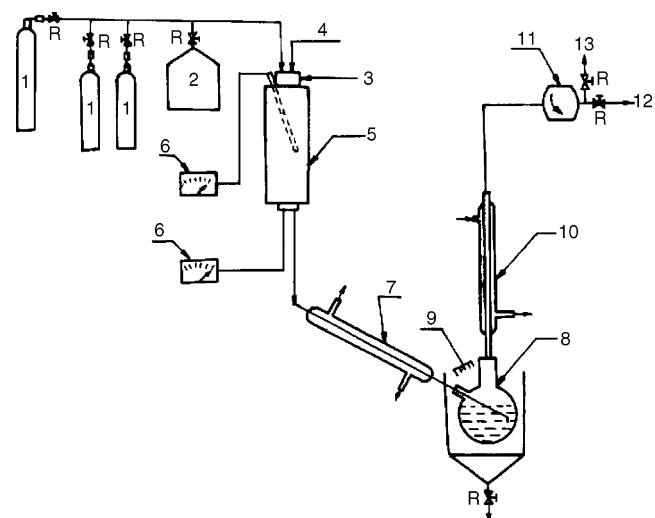


Fig. 1. Experimental system with stationary reactor for pyrolysis of biomass in presence of steam: (1) pressure gas vessels; (2) steam generator; (3) feeder; (4) stationary reactor; (5) oven; (6) thermocouple; (7) cooler; (8) receiver; (9) water cooling; (10) cooler; (11) gas counter; (12 and 13) gas product evacuation.

surface). S_{BET} was calculated from nitrogen adsorption/desorption isotherms according to the ASTM D 4820. The surface area was also determined by the adsorption capacity towards iodine [14]. The iodine number of the prepared AC was determined according to the ASTM D 4607-94 (1999) specification. The samples AC were then chemically modified to have base sites on their surfaces. For this purpose calcium acetate monohydrate was used, which was dissolved in deionized water for 4 h with agitation. A saturated solution was obtained by removing undissolved salt by vacuum filtration. The samples were impregnated with this solution for 2 h at room temperature. Vacuum drying for 8 h at 120 °C followed and finally the impregnated materials were calcined at 700 °C, for 3 h in nitrogen flowing at 30 l/min. The chemically modified carbon adsorbents were designated AC(Ca). The microstructure of these adsorbents were analyzed from the nitrogen adsorption isotherms at –196 °C. The surface morphologies of carbon adsorbents before and after chemical modification were observed using a scanning electron microscope (Phillips, SEM 515). The liquid products were extracted from the receiver (Fig. 1) for their characterization.

Table 1
Product distributions at different temperatures and times (pyrolysis with steam at a flow of 30 l/h, rape seeds extrudates of 4 mm in diameter)

Selected conditions			Product distributions		
T (°C)	t (h)	Carbon yield (wt.%, maf)	Gas yield (wt.%, maf)	Tar, water losses (wt.%, maf)	Ash (wt.%, mf)
500	1	33.4	34.2	32.4	4.7
	2	30.9	31.6	37.5	4.7
	3	29.5	30.4	40.1	4.9
550	1	33.1	34.7	32.2	4.7
	2	30.7	31.8	37.5	4.8
	3	29.2	30.9	39.9	5.4
600	1	32.8	33.7	33.5	5.1
	2	28.1	30.1	41.8	5.3
	3	24.4	27.5	48.1	5.8
650	1	32.4	33.1	34.5	5.5
	2	27.6	29.5	42.9	5.7
	3	22.5	23.7	53.8	6.5

mf: moisture free; maf: moisture and ash free.

3. Results and discussion

3.1. The optimum temperature for pyrolysis and steam activation

The biomass samples selected for this study included the waste formed from rape seeds after the oil was extracted. When the temperature was kept at 550–650 °C for 1, 2 and 3 h, a decrease of yield could be observed (Table 1 and Fig. 2). This decrease (from 32.4% down to 22.5% at 1 h) could be attributed a first removal of light volatile matter followed by big molecules with the increase of temperature.

In order to characterize the gaseous effluents and tars the tables of Evans and Milne were used [12] which offer a classification of the chemical compounds produced during the pyrolysis process. Fig. 3 presents the evolution of gas composition from 350 to 650 °C. The primary compounds were predominant on the whole temperature range. They decreased after 400 °C as secondary compounds increased. Tertiary compounds were quite stable from 450 to 650 °C.

Fig. 4 presents the evolution of the tar composition from 350 to 650 °C. The maximum for primary compounds was situated at 450 °C. Then, as the temperature increased, the proportion of primary compounds decreased. They were not yet the majority compounds. The maximum of secondary compounds was reached at 550 °C and remained quite constant at 650 °C. The tertiary compounds increased from 450 to 650 °C and were the less representative.

When the temperature increased from 600 to 650 °C, the iodine number increased.

From these results, the optimum temperature was 650 °C, since the iodine number of the activated carbon was the highest in value (Table 2).

In the experiments at 650 °C, the AC yield was about 32.4% for 1 h treatment time. Rape seeds had a high reactivity in the pyrolysis process. The increase of the temperature from 500 to 650 °C resulted in higher yields of gaseous products and lower yields of tar and water due the increased cracking. The ash contents of the solid products depended on the chemical composition of the raw materials and the degree of carbonization. Rape seeds had undergone deep carbonization and the process was accompanied by the removal of large amounts of volatile compounds. The composition of the gaseous product is shown in Table 3.

Increase of the temperature from 500 to 650 °C favoured the cracking of the hydrocarbons into gaseous products and thus increased the yield of hydrogen. It has also decreased the content of CO₂ and CO in the gases. Aromatic hydrocarbons (benzene, toluene) were products of secondary reactions at higher temper-

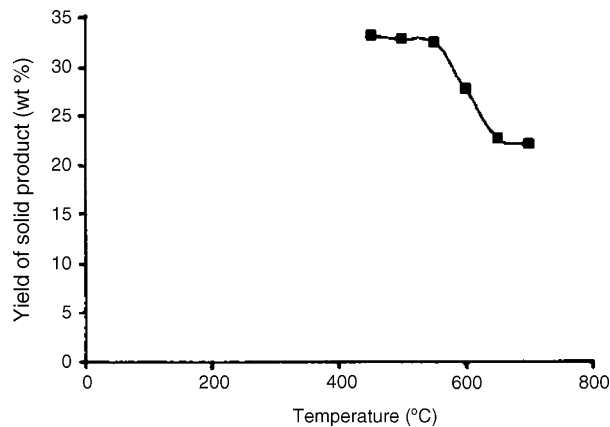


Fig. 2. Effect of temperature on % yield at different times (extrudates of 4 mm in diameter, 30 l/h steam flow).

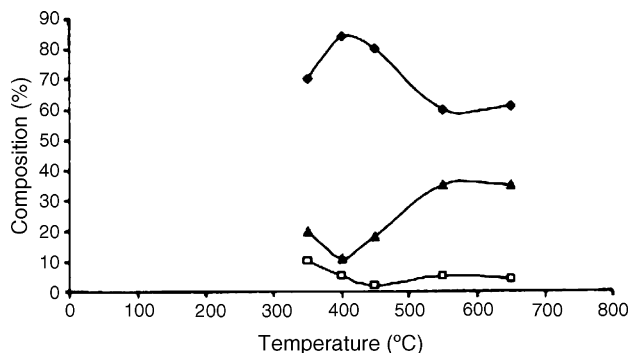


Fig. 3. Average composition of gaseous emissions during rape seeds waste pyrolysis at 350–650 °C: (◆) primary compound; (▲) secondary compound; (□) tertiary compound.

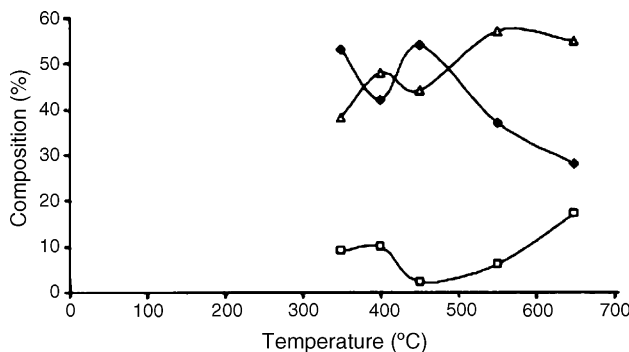


Fig. 4. Average composition of tars of rape seeds waste pyrolysis: (◆) primary compound; (△) secondary compound; (□) tertiary compound.

Table 2
Influence of treatment time on the yield of AC and iodine number at a temperature of 650 °C

Biomass	Treatment time (h)	Y (yield) (wt.%)	IA (iodine number) (mg/g)
Extrudates (rape seeds of 4 mm in diameter)	1	32.4	790
	2	27.6	875
	3	22.5	1020

Table 3

Composition of the gaseous product at different temperatures (pyrolysis with steam at a flow of 30 l/h, activation time of 3 h)

Biomass	T (°C)	H ₂ (vol.%)	CH ₄ (vol.%)	C ₂ (vol.%)	CO (vol.%)	N ₂ (vol.%)	CO ₂ (vol.%)	C ₆ H ₆ (vol.%)
Extrudates (rape seeds of 4 mm in diameter)	500	35.2	8.2	3.6	10.8	25.1	16.7	0.4
	550	38.2	7.4	3.5	4.8	29.4	16.4	0.3
	600	39.7	6.8	3.8	7.2	29.7	16.3	0.2
	650	41.2	5.4	3.4	1.4	32.3	16.1	0.2

atures. Further increase of the temperature above 650 °C had not affected significantly the composition of the produced gas.

The steam flow influenced the product distribution. The yield of liquid products was reduced from 50 to 25 wt.%, the gas yield was increased from 33 to 69 wt.% and the solid product was decreased from 32.4 to 22.5 wt.% when the steam flow was reduced from 30 to 18 l/h.

Increasing the heating rate from 3 to 10 °C/min had not significant influence on product distribution, AC surface area and gas composition. The heating rate played much less role when the pyrolysis was performed in a steam atmosphere instead of inert gas.

At the selected experimental conditions the increase of the duration of treatment from 1 to 2 or 3 h resulted in a decrease of the yield of the solid residues and in an improvement of the adsorption capacities (Table 2).

A further increase of the temperature decreased the yield of the solid product without any improvement in the adsorption capacity. The high adsorption capacities of the solid products towards iodine (specific surface area) obtained in presence of the activating agents suggested the possibilities of using the solid products as adsorbents.

Fig. 5 shows the change in the % burn-off and in the BET surface area as a function of the activation temperature, using data from pyrolysis performed with nitrogen for 30 min without the steam activation section. While the % burn-off increased, the BET surface area reached a maximum at 650 °C and then decreased. This observed behaviour of the BET surface area at large burn-off is well known and was attributed to the transformation of micropores into mesopores by a burn-off mechanism in the internal wall of the micropores [14].

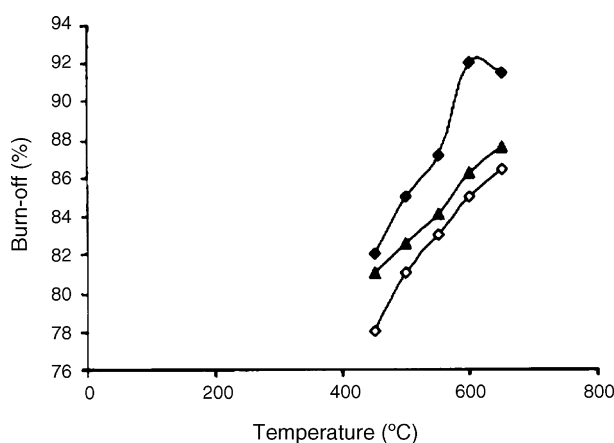


Fig. 5. Correlation between % burn-off and the activation temperature (activation time: □ 1 h, ▲ 2 h, ◆ 3 h).

3.2. Morphology of adsorbents

Microstructures of the pure and chemically modified carbon adsorbents were examined through nitrogen adsorption. Carbon adsorbents which experienced only thermal treatment at 650 °C for 3 h in inert atmosphere gave the same morphological characteristics as unmodified adsorbents which were not treated thermally. That is, thermal treatment alone does not make a considerable change in the microstructures of carbon adsorbents. Therefore, the morphology of carbon adsorbents was changed mainly by chemical modification with calcium acetate monohydrate. The calcium oxide (CaO) load was 27.45 wt.%. The effects of the chemical modification on the morphology could be investigated by comparing the modified adsorbents with unmodified ones.

The isotherms from Fig. 6 with no hysteresis were obtained with AC and AC(Ca) adsorbents. These forms of isotherms correspond at type I (after BET isotherm classification) and characterize microporous materials [14]. Consequently, AC and AC(Ca) adsorbents have a microporous structure. Surface area and pore size distributions were calculated from these isotherms. The characteristics of the prepared AC had a specific surface area of 700–1500 m²/g, a grain bulk density of 0.4–0.8 g/cm³, a packing density of 0.30–0.70 g/cm³, ash content of 1.0% or less, and a tensile strength of activated carbon grains of about 30 kg/cm². It was shown that chemical modification led to decreases in pore volume and surface area of AC(Ca) adsorbents. The total volume of pores was determined to be 1.6 cm³/g for AC and 0.98 cm³/g for AC(Ca). However the average pore radius of activated carbons increased a little after the modification (i.e. for AC the average radius was 10 Å and for AC(Ca) it was 12 Å, see Table 4).

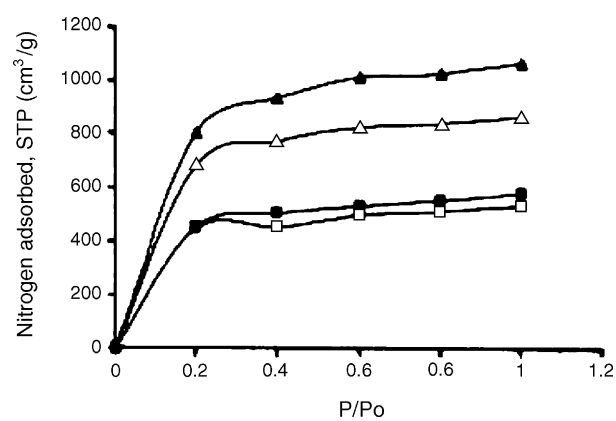


Fig. 6. Adsorption of nitrogen on the carbon adsorbents at -196 °C: (□, ■) AC and (△, ▲) AC(Ca). The filled symbols and the open symbols were obtained from the adsorption and the desorption experiments, respectively.

Table 4
Microstructure of the carbon adsorbents (temperature of activation 650 °C, time 3 h, 30 l/h steam flow)

Carbon adsorbent	Surface area, S_{BET} (m ² /g)	Total volume of pores, V_{tot} (cm ³ /g)	Average radius, r_{avg} (Å)	CaO load (wt.%)
AC	1485	1.6	10	–
AC(Ca)	760	0.98	12	27.45

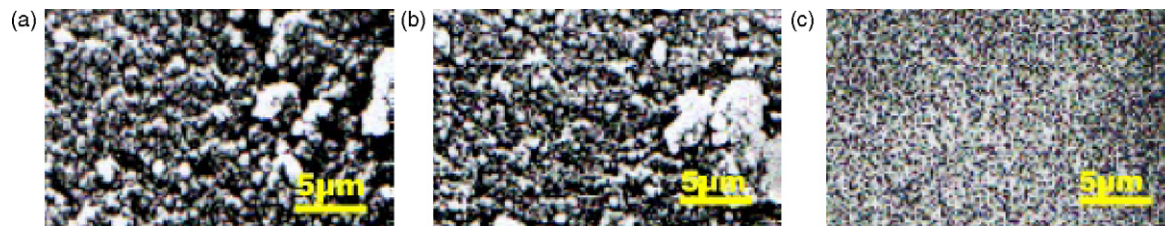


Fig. 7. Surface morphologies of AC and AC(Ca): (a) SEM photography of AC (30,000×); (b) SEM photography of AC(Ca) (30,000×); (c) X-ray map of Ca (10,000×).

The increase in the average pore radius is due to the removal of pores smaller than the average pore radius in carbon adsorbents due to the impregnation of salts. Activated carbon adsorbents are included in this case since they are microporous. Surface morphologies of the chemically modified adsorbents are shown in the SEM photographs of Fig. 7.

Also included in these figure are X-ray maps of calcium atoms distributed on the surfaces. A uniform distribution of calcium and thus of calcium oxide is obvious from this figure.

3.3. Adsorption of carbon dioxide on activated carbons

Separation of gases based on adsorption requires a reversibility of adsorption and desorption processes. The chemically modified carbon adsorbents prepared in these experiments had highly irreversible surfaces due to strong chemisorption. This irreversibility, however, can be circumvented by pretreating the adsorbents with carbon dioxide. Reversible adsorption–desorption was observed after a dose of carbon dioxide adsorption in all experiments. Adsorption experiments of carbon dioxide were carried out at 25, 150 and 250 °C with AC(Ca). Similar experiments were also done with AC to investigate the effect of chemical modification on the adsorption of CO₂. Fig. 8 shows the results of adsorption experiments.

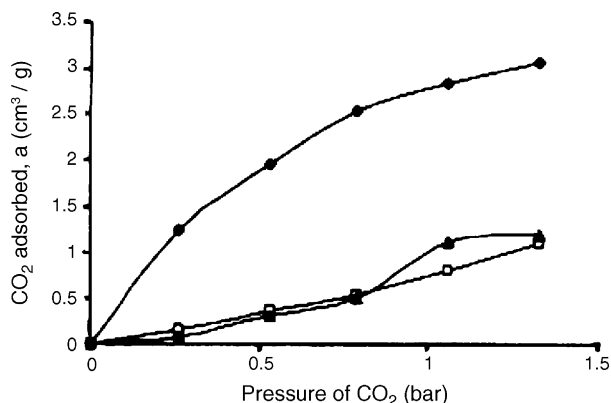


Fig. 8. Adsorption of carbon dioxide on modified carbon adsorbent AC(Ca): (◆) 25 °C; (□) 150 °C; (▲) 250 °C.

The amounts of adsorbed carbon dioxide on the carbon adsorbents decreased with increasing adsorption temperature and the same was true for the chemically modified carbon adsorbents. However, since the interaction between base site and carbon dioxide was stronger than that between carbon and carbon dioxide, a considerable amount of carbon dioxide could be adsorbed on the chemically modified carbon adsorbent at temperatures as high as 250 °C. The amount of physically adsorbed gas became proportional to the partial pressure at low relative pressures. The pure calcium oxide surface had a strong affinity for carbon dioxide, resulting in irreversible chemisorption. On the other hand, the base sites (calcium oxide with chemisorbed carbon dioxide) had an intermediate affinity for carbon dioxide. The affinity was too weak to induce chemisorption, but stronger than that of the pure carbon surface. Therefore, enhancement of adsorption at elevated temperatures could be achieved by addition of base sites on the surface of porous carbons.

4. Conclusions

The experimental results showed the possibility for the production of activated carbon with well-developed pore structure, high specific surface area and high adsorption capacity from rape seeds waste by one-step pyrolysis process and steam activation. Experimental data showed that the increase in temperature and time resulted in a better activation. However, at the higher temperature, the decrease in micropores was observed which was due to coalescence or widening of already formed pores.

The activated carbon from rape seeds waste extrudates (diameter size of 4 mm) obtained at an activation temperature of 650 °C had the highest values of iodine number and surface area. The optimum condition for the production of activated carbon from rape seed waste by one-step pyrolysis and steam activation in a fixed reactor was 650 °C for 3 h at a flow rate of 30 l/min with steam as activation agent. A high char reactivity was favoured by conditions where the volatiles were quickly removed from the particle, because some chemical rearrangement in the char structure took place.

It was shown that the surface properties of carbon adsorbents can be modified by simple chemical treatment. The base sites

thus generated have a strong affinity for carbon dioxide. Since the chemically modified carbon adsorbents adsorb considerable amounts of carbon dioxide at high temperatures, they can be used for removal of carbon dioxide directly from the effluent gas.

References

- [1] R. Bonelli, P. Della Rocca, A. Cerella, *Bioresour. Technol.* 76 (2001) 15–22.
- [2] M. Martinez-Escandell, M. Molino-Sabio, *Carbon* 39 (2000) 320–323.
- [3] P. Della Rocca, P.A. Horowitz, et al., in: A.V. Bridgwater, D.G.B. Boocock (Eds.), *Development in Thermochemical Biomass Conversion*, Blackie, London, 1997, pp. 176–190.
- [4] P. McKendry, *Bioresour. Technol.* 83 (2002) 37–63.
- [5] A. Demirbas, *Fuel* 80 (2001) 1885–1891.
- [6] P. Minkova, *Fuel Process. Technol.* 70 (2001) 53–61.
- [7] J.M. Encinar, *Fuel Process. Technol.* 75 (2002) 27–43.
- [8] H. Vernersson, *Bioresour. Technol.* 83 (2002) 95–104.
- [9] J.A. Antal, S. Allen, X. Dai, B. Shimizu, S.M. Tam, M. Gronli, *Ind. Eng. Chem. Res.* 39 (2000) 4024–4031.
- [10] V.A. Bridgwater, C.V.G. Peacocke, *Renew. Sust. Energ. Rev.* 4 (2001) 68–73.
- [11] S.M. Tam, J.M. Antal, *Ind. Eng. Chem. Res.* 40 (2001) 578–588.
- [12] R.P. Bonelli, P.A. Della Rocca, G.E. Cerella, A.L. Cukierman, *Bioresour. Technol.* 76 (2001) 15–22.
- [13] Y. Uehara, J. Hayashi, K. Muroyama, *Proceedings of Energy Engineering Symposium*, vol. 4, no. 1, Society of Chemical Engineers, Japan (SCEJ), 2005, pp. 9–12.
- [14] G.H. Findenegg, *Fundamentals of Adsorption*, Engineering Foundation, New York, 1984, pp. 207–218.