

# Activated Carbons from Molasses as CO<sub>2</sub> Sorbents

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Aim of this research is to obtain effective, molasses based activated carbon, which would adsorb big amounts of CO<sub>2</sub>. Molasses was mixed with KOH. Weight ratio of dry materials was 1:1 (AC1, AC3) and 1:2 (only AC2). Homogeneous mixture was obtained. Material was left for 3 h at 25 °C. Drying lasted for 12 h at 200 °C, and the material was grounded. The mixture was pyrolysed at 750 °C, under constant flow (18 dm<sup>3</sup>/min) of nitrogen. The material was grounded again. Then, powder was washed with water, until filtrate was neutral, which took about 5 dm<sup>3</sup> of water. AC3 was washed with 1 dm<sup>3</sup> of water. After drying, materials were soaked in HCl (0.1 mol/dm<sup>3</sup>) for 19 h, and washed with water, until filtrate was neutral. CO<sub>2</sub> adsorption was performed under high pressure up to 40 atm, at 40 °C. Specific surface area (according to the Brunauer–Emmett–Teller equation) was calculated for AC1, AC2 and AC3 and it is respectively 1985, 1967, and 2026 m<sup>2</sup>/g, micropore volume — 0.714, 0.707, and 0.728 cm<sup>3</sup>/g and it was between 75% and 89% of total pore volume. The excess uptake at 40 atm pressure was as follows: AC1 — 14.02 mmol/g, AC2 — 12.75 mmol/g, and AC3 — 15.79 mmol/g.

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## 1. Introduction

CO<sub>2</sub> is considered as one of the biggest precursor of greenhouse effect [1, 2]. Therefore there is a necessity to decrease the emission of this gas into the atmosphere. CO<sub>2</sub> is one of the main component of post-combustion gases. Lots of different techniques was studied over the years, for example CO<sub>2</sub> conversion to useful products [3]. One of the most popular is carbon capture and storage (CCS). Capturing of CO<sub>2</sub> can be performed in pre-combustion or post-combustion stage of process. Nowadays it is the last one that is widely used. This process requires effective sorbent and reactor to perform the adsorption. One of the best gas-adsorbing materials is activated carbon (AC). Vast surface area and porosity makes ACs potential highly impressive [4, 5]. It is plausible to produce AC materials from almost every organic material, with relatively high content of carbon. Choosing the right material is actually crucial factor determining ACs adsorbing abilities and its surface properties [6, 7]. In recent years huge attention is turned to residual wastes and agricultural products. It would be expected that the material will be efficient, cheap and within fairly easy reach. Plenty of raw materials were tested as such source e.g. residual wastes and agricultural products: straw, corn straw, corn cob and hulls, eucalyptus maculata, wheat birch wood, almond shells, nut shells, sunflower shells, peanut hulls, rice hulks, husks and straw, peach pits, cherry pits, apricot pits, olive pits and residues, pine cones and needles, rapeseed, miscanthus, sugarcane

bagasse [6–10]. Using such unusual material is a challenge, because preparation procedure, activating agent, physical and chemical properties of starting materials can influence the textural properties of ACs [11].

Great example of such underestimate material is molasses, which is residue from sugar producing process. Up until now, molasses has been considered as such carbon source just twice [6, 12], and it has been proven as very promising material to study. Results of this study was AC able to adsorb 11.76 mmol/g of CH<sub>4</sub> at 40 °C and 40 atm pressure, which at that time was considered as one of the most effective sorbents of that gas ever produced.

Aim of this research is to obtain molasses based activated carbon, which would be highly effective in CO<sub>2</sub> adsorption. Results of CH<sub>4</sub> adsorption are very promising. ACs produced from molasses, presented in this study, are according to our knowledge one of the most effective CO<sub>2</sub> sorbents. We will also use solid state of KOH, which can improve the textural properties of AC materials produced from molasses.

## 2. Materials and methods

Dense liquid, molasses, has been mixed with solid KOH, which is an activating agent. Weight ratio, calculated for dry materials mass, was as follows: AC1 — 1:1, AC2 — 1:1.2 and AC3 — 1:1. Mixing has been continued until homogeneous mixture was obtained. Material was left for 3 h at 25 °C. Drying was provided for 12 h at 200 °C. Then, after grounding, the mixture was moved to quartz boat, and pyrolysis was performed. Temperature was 750 °C, at constant flow (18 dm<sup>3</sup>/min) of nitrogen. Material was grounded again. Then, powder was washed with water till filtrate pH was neutral which took about

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5 dm<sup>3</sup> of water. AC3 was washed with 1 dm<sup>3</sup> only during the first washing. After drying, materials were soaked in HCl in concentration of 0.1 mol/dm<sup>3</sup> for 19 h, and washed with water again to neutral pH of filtrate. In AC3 dish during soaking exothermal reaction was noticed.

Adsorption and desorption of liquid nitrogen at -196 °C was performed. Surface area ( $S_{BET}$ ) was calculated on the basis of the Brunauer–Emmett–Teller (BET) equation. Micropore volume were calculated with density functional theory (DFT) method. CO<sub>2</sub> adsorption was provided at pressure up to 40 atm, at temperature of 40 °C. Although these materials are designed as post-combustion sorbents of CO<sub>2</sub>, so the most interesting for us was their CO<sub>2</sub> uptake at 1 atm pressure.

### 3. Results and discussion

The textural properties of obtained ACs are presented in Table I. Specific surface area of produced sorbents reaches 2000 m<sup>2</sup>/g, total pore volume (TPV) reaches up to 0.95 cm<sup>3</sup>/g. Furthermore, it is noticeable that all materials have high micropore volume (MP) to total pore volume ratios higher than 75% (AC1 — 75.7%; AC2 — 89.1%; AC3 — 76.8%).

TABLE I

Activated carbons surface properties.

sample	$S_{BET}$ [m <sup>2</sup> /g]	TPV [cm <sup>3</sup> /g]	MV [cm <sup>3</sup> /g]
AC1	1985	0.9424	0.7138
AC2	1967	0.794	0.7075
AC3	2026	0.9481	0.7283

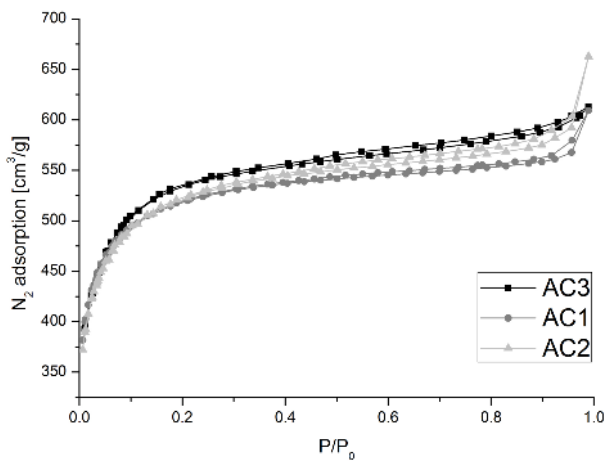


Fig. 1. Nitrogen adsorption and desorption isotherms.

Figure 1 shows isotherms of ACs, with hysteresis loops. Considering high uptake at low pressure, these are recognizable as type I isotherms, at high pressure though it is closer to type IV. Hysteresis loops, especially AC1 and AC2 are examples of mixed type H3 and H4 loops. Combined with isotherm these are exhibited, confirming

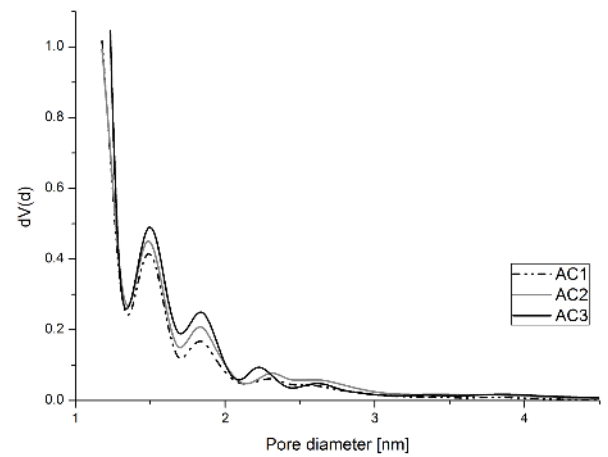


Fig. 2. Pore size distribution curve, calculated by DFT method.

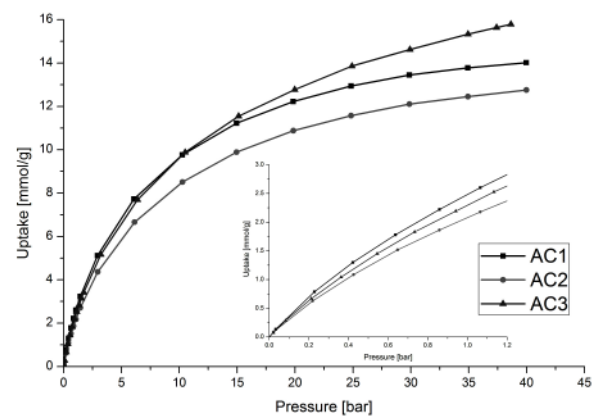


Fig. 3. Uptake of CO<sub>2</sub> at pressure up to 40 bar.

that obtained structures are in fact microporous. It also suggests that there is no limited adsorption on these materials.

Figure 2 presents pore size distribution (PSD). Over 4.5 nm of diameter there was no pores found. On the basis of Fig. 2, it was found that obtained materials contain mostly micropores and small amount of mesopores of very low diameter. Pore diameter range is similar in each AC. AC3 developed the most microporous structure, which is probably a result of exothermal reaction noticed during the soaking with HCl. This proves also information gathered in Table I. Considering AC1 and AC2, applying higher concentration of KOH increased the micropore volume.

Figure 3 reveals that at 1 atm, uptake of CO<sub>2</sub> was as follows: AC1 — 2.54 mmol/g, AC2 — 2.07 mmol/g, AC3 — 2.47 mmol/g. Considering pressure up to 10 atm, sorbents effectiveness was settled in certain order: AC1 > AC3 > AC2. At about 11 atm pressure AC1 and AC3 adsorb the same amount of CO<sub>2</sub> (about 9.97 mmol/g). Over 11 atm of pressure effectiveness of sorbents was as

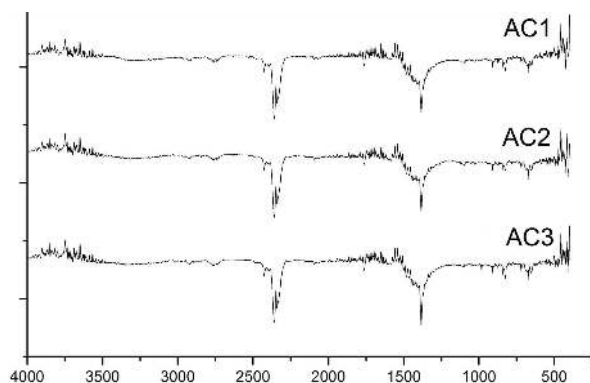


Fig. 4. FTIR results ( $2380\text{ cm}^{-1}$  KBr).

follows:  $AC3 > AC1 > AC2$ . AC1 and AC3 are affected by the pressure of  $\text{CO}_2$  in very predictable matter. Such phenomenon can be explained by different surface structure of researched materials. Considering AC1 and AC2 we found that higher KOH/C ratio decreases amount of adsorbed  $\text{CO}_2$  [7].

Figure 4 shows results of IR spectrum. At about  $1380\text{ cm}^{-1}$  there is a band, which comes from bonds between aryl group and hydroxide group. At  $2600\text{--}2950\text{ cm}^{-1}$  there are weak, but noticeable bands, which come from unsaturated bonds between carbon atoms. These are also noticeable at about  $750\text{--}900\text{ cm}^{-1}$ .

#### 4. Conclusions

Chemical activation of molasses with solid KOH allows one to obtain high surface area activated carbons with a predominantly microporous structure. The  $\text{CO}_2$  uptakes reached  $2.5\text{ mmol/g}$  at  $40^\circ\text{C}$  (AC1 and AC3). Such high  $\text{CO}_2$  adsorption was ascribable to the presence of high micropores content (89%).

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