

Adaptability of Powdered Activated Carbon Production from Ground Catering Waste Pyrolysis Coke

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Abstract. Three mixture of catering waste was pyrolyzed at 650, 725 and 900 °C and the solid residue (coke) was examined for powdered activated carbon production. For this, the carbon content, iodine number, particle size distribution and scanning electron microscopic images were analysed. Based on the carbon content, these cokes are suitable for activated carbon production, which were 60-85 wt.% (depending on the base material and pyrolysis temperature). The studied cokes showed slightly porous structure with smooth surfaces. Because of this, the iodine number was mostly small (13-30). Based on the grinding experiments, 10 minutes of grinding was found to be optimal. After this grinding time, the reached iodine number of powdered activated carbon was 350-610.

Keywords: activated carbon, catering waste, pyrolysis, pyrolysis coke

Introduction

Carbonaceous material produced from raw materials under high temperature reactions that have high internal surface area and highly developed porous structure is referred to as activated carbon (AC) [1]. AC can be produced by such thermochemical conversion methods of carbonaceous feedstock as pyrolysis or carbonization. In many cases, the required porous structure cannot be achieved with these processes alone, therefore, different types of activation methods can be used. These methods may be physical or chemical processes. During physical activation, the first step is carbonization to eliminate the volatile matters from the base material. The next step is the activation which usually occurs above 800 °C in steam, nitrogen, argon or carbon dioxide media. For chemical activation, first, the base material is impregnated by a dehydrating chemical agent and next, the chemical activation and carbonization take place in one step at lower temperature than during physical activation [2].

AC can be in powdered, granular or extruded form for different applications. During our experiments, powdered activated carbon (PAC) was made by grinding after the pyrolysis of the raw material. According to the European Council [3], "PAC is defined as consisting of at least 90 % by weight

(weight%) of particles with a size less than 0.5 mm” and the requirement of the ASTM D5158 standard [4] is that the PAC particles pass through an 80 mesh sieve (below 0.177 mm). PAC can be used for various purposes, for example mercury vapour capture [5], organic micropollutants removal during wastewater treatment [6], odour removal of drinking water [7] or dioxin adsorption in flue gas [8].

AC can be produced from any carbonaceous material (fossil, waste or renewable), therefore food waste can also be used. According to the latest study carried out in the EU member states, [9] on average, 11.6% of the food produced in the EU becomes waste. In case of the USA [10], the ratio rises to approximately 31%. According to a 2012 study [11], 56% of the food waste is catering waste, which according to the Commission Regulation (EU) No 142/2011 means “*all waste food, including used cooking oil originating in restaurants, catering facilities and kitchens, including central kitchens and household kitchens*” [12].

During pyrolysis, the carbonaceous material can be transformed into gaseous (pyrolysis gas or synthesis gas) and liquid products (pyrolysis oil), and solid material (pyrolysis coke) with high carbon content remains in the reactor. The gas can be used as chemical raw material beside the energetic application, the liquid is suitable for combustion or different chemicals can be extracted from it. The main users of the solid residue are the metallurgical and energy industry, but it has high importance as a soil conditioner or activated carbon [13]. Pyrolysis can be a good way to utilize food waste, including catering waste too [14]. The literature of this topic is minimal. Only one significant publication-deals with activated carbon production. Krithiga et al. [15] used cooked rice as the base material of activated carbon production via chemical activation. The BET specific surface area of the produced activated carbon were 306.83 and 539.78 m²/g, depending on the activation agent. Furthermore, when producing activated carbon from food waste, most researches focus on using base materials like agricultural by-products [16] or wastes generated during food production, for example potato peels [17], orange peels [18], olive stones [19], etc.

During our experiments, catering waste was modelled by three mixture. One of the mixtures contained foods of plant origin, the other one contained foods of animal origin and the last one consisted of foods with plant and animal origin. These were pyrolyzed at three temperatures: 650, 725 and 900 °C. These temperatures are commonly used for the pyrolysis of biomass [20]. After the pyrolysis, the change of specific surface area (based on iodine number) of pyrolysis cokes was measured as a function of the type of base material and the pyrolysis temperature. In case of the mixture of animal and plant origin food, the effect of coke grinding time was examined, as well.

1. Materials and methods

Canteen waste was modelled with three type of food mixture, which can be found in a regular Hungarian canteen. A mixture of vegetable food (1:1 mass ratio of cooked rice and French fries), a mixture of food of animal origin (1:1 mass ratio of breaded pork and roast chicken breasts) and a mixture, which contains food with animal and plant origin (1:1 mass ratio of cooked rice and breaded pork) were prepared. The examined properties of the mixtures are summarized in Table 1.

The lab-scale pyrolyzing system can be seen in Figure 1. As the furnace is turned on, the reactor is heated to 650, 725 or 900 °C with 20 °C/min heating rate, then the holding time lasts for 70 minutes which is necessary for the gas production to decrease below 1 l/h.

		Parameter	Cooked rice and French fries in 1:1 mass ratio (CRFF)	Cooked rice and breaded pork in 1:1 mass ratio (CRBP)	Breaded pork and roast chicken breasts in 1:1 mass ratio (BPRC)
Dry matter	wt. %	Nitrogen	1.78	9.87	11.57
		Carbon	49.86	53.84	54.84
		Hydrogen	6.93	7.51	7.49
		Sulphur	1.06	1.37	0.77
		Oxygen	38.50	24.89	22.14
		Ash	1.87	2.52	3.20
Moisture content of original matter		wt. %	41.29	46.88	51.10

Table 1. Ultimate and proximate analysis of base materials.

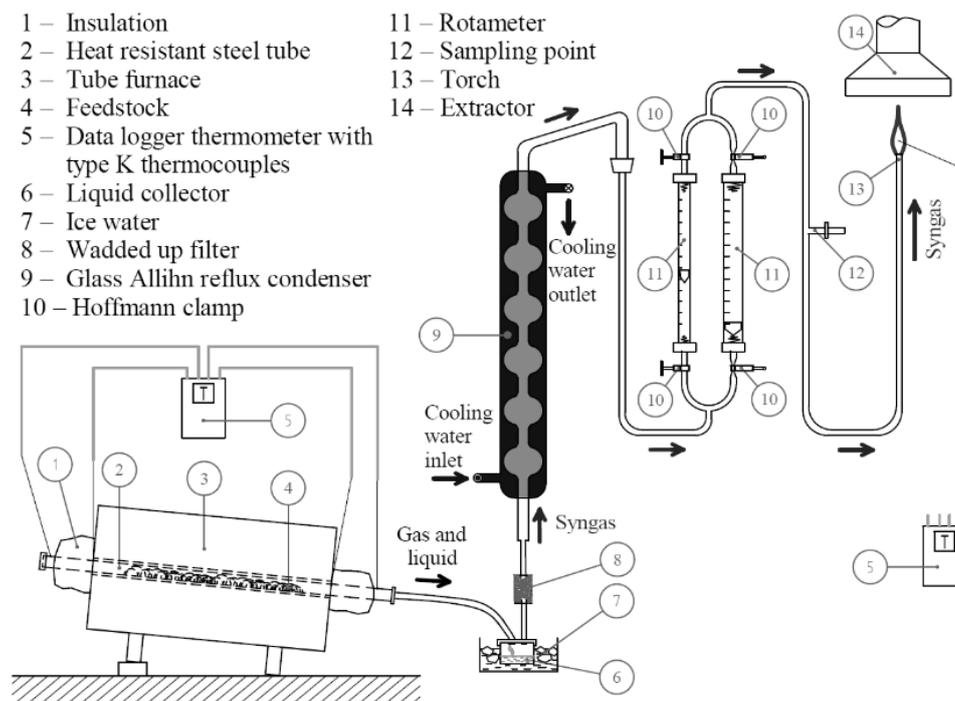


Figure 1. Schematic illustration of the lab-scale pyrolyzing system.

The coke was crushed in a mortar to reduce the particle size under 1 mm, then milled for 5, 10 and 15 minutes with 300 revolutions per minute in a Fritsch Pulverisette 6 planetary ball mill. The carbon content of the samples was determined with a Carlo Erba EA 1108 elemental analyzer. The analysis of specific surface area was carried out according to “D 4607 - 94: Standard Test Method for Determination of Iodine Number of Activated Carbon” standard. Even though gas adsorption methods are the most commonly used for specific surface area determination, the resulting BET specific surface value has a good correlation with the iodometric titration results, as well [21]. Thus, latter was used for the determination of specific surface area. The particle size distributions of the crushed and ground

samples were determined with a Horiba LA 950-V2 laser diffraction particle size analyzer, and these samples were observed with a Hitachi TM 1000 scanning electron microscope (SEM).

2. Results

During pyrolysis, the <1 cm base material loosely filled in the reactor is vitrified, and a loose-textured porous solid residue remains in the reactor. A piece of coke after an experiment (CRBP-725°C) can be seen in Figure 2. The amount of solid residues and their carbon content after pyrolysis can be seen in Table 2.

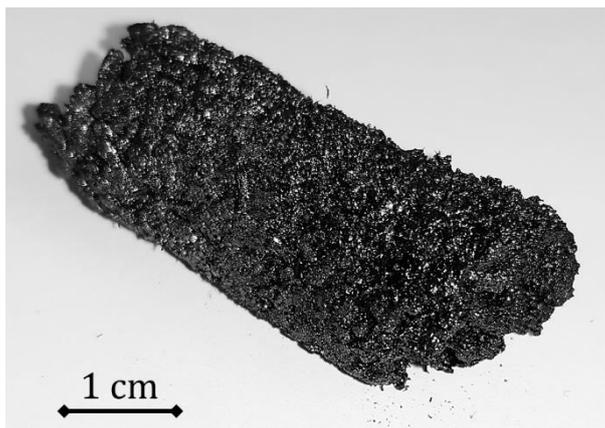


Figure 2. Charred residue of CRBP-725 °C.

Base material	Temperature of pyrolysis, °C	Solid residue, wt.%	Carbon content of solid residue, wt.%
CRFF	900	8.8	84.79
	725	11.6	81.31
	650	21.2	69.01
CRBP	900	8.0	81.10
	725	9.0	80.04
	650	15.2	60.66
BPRC	900	8.5	70.11
	725	10.1	69.22
	650	15.0	63.77

Table 2. Amount of solid residues and their carbon contents.

According to the data of Table 2, as the maximum temperature of pyrolysis is increasing, the amount of coke is decreasing. In parallel, the carbon content of samples is decreasing because as temperature increase, more gas is released from the base material. The carbon content of cokes was 60-85 wt.%, therefore, these cokes can be a good base material to use as activated carbon.

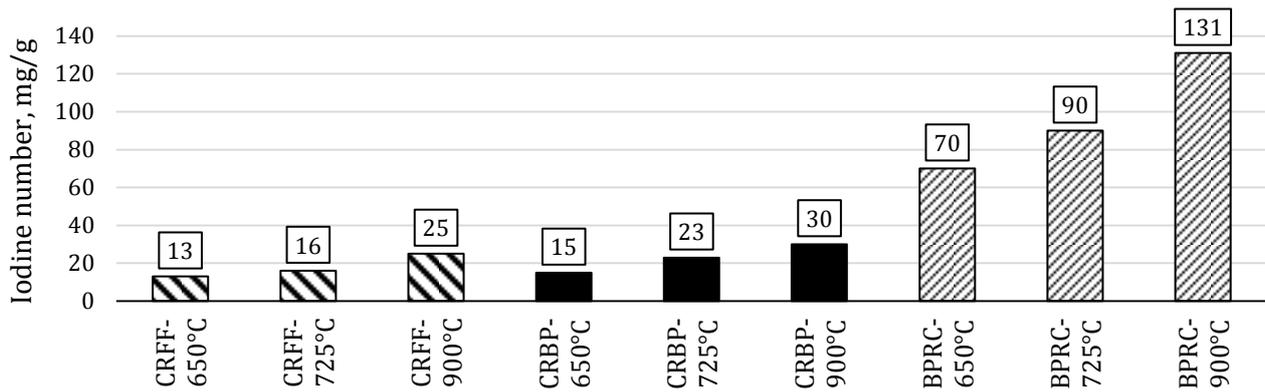


Figure 3. Iodine number of solid residues from pyrolysis at different temperatures.

It can be observed for all three base materials (Figure 3.), that as the temperature increased, the iodine number increased, as well. *CRFF* and *CRBP* samples resulted in cokes with small iodine number (15-30) at all pyrolysis temperatures. Coke with much larger iodine number can be produced from the pyrolysis of mixture which contains only food of animal origin (*BPRC*).

As plant and animal origin catering wastes are not separated in practice, the *CRBP* mixture was used for the further milling experiments. Figure 4. shows the change in iodine number as a function of the milling time. The behaviour of cokes from all three pyrolysis experiments was similar. 5-minutes grinding resulted in a slightly increased iodine number, however, an additional 5-minute grinding resulted in a 6-11-fold increase in iodine number, compared to the 5-minutes ground samples. The highest iodine number was measured for the coke of 900°C pyrolysis. After 15-minutes grinding, the iodine number decreased in all cases compared to the 10-minutes grinding.

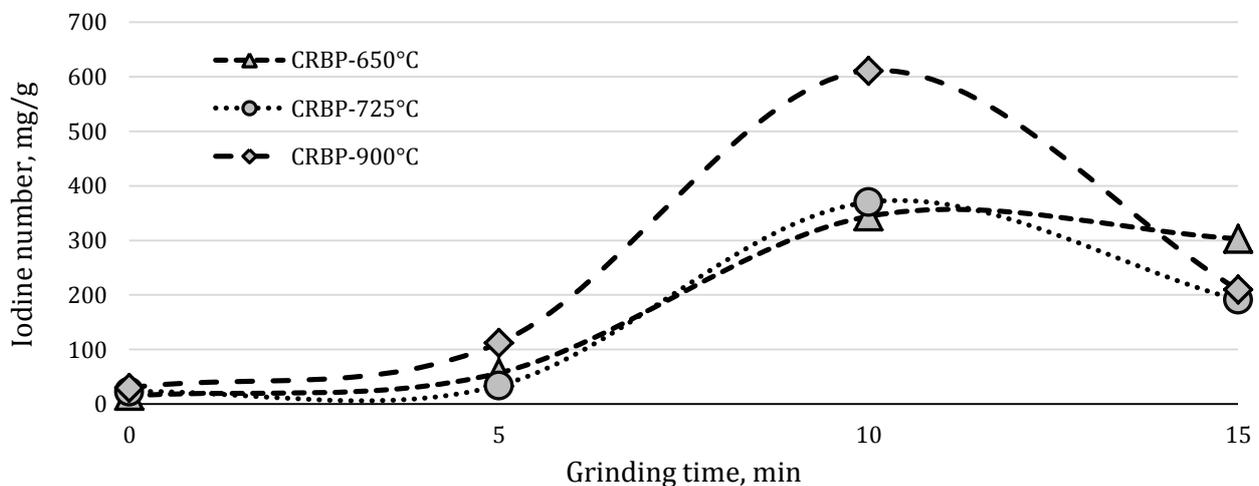


Figure 4. The dependence of iodine number from grinding time.

In order to obtain further information on the decrease in iodine number after 15 minutes of grinding, SEM images were taken, and particle size analyses were performed. The SEM micrographs of samples can be seen in Figure 5.

In the micrograph of crushed *CRBP-900°C* sample (Figure 5/a) the surface of particles is contiguous, smooth and slightly porous. Large, smooth cavities are visible on the fracture surface. These were

formed by released volatiles in the softened material during pyrolysis. The fracture surface of the crushed sample clearly shows a brittle-type fracture, which is more observable on the micrographs of the 5-minutes ground sample (Figure 5/b). During grinding, the particle size decreased, and fragmentation occurred mainly along pores and cavities. As a result, flat angular particles were formed. After another 5-minutes grinding (Figure 5/c) smaller amounts of larger particles are visible, and the shape of the particles is similar to the 5-minutes ground samples. In addition, agglomeration can be observed at 1500x magnification on some larger particles. On the SEM images of 15-minutes ground samples (Figure 5/d), a slight decrease in particle size and an increase in the agglomeration of the finer particles can be observed.

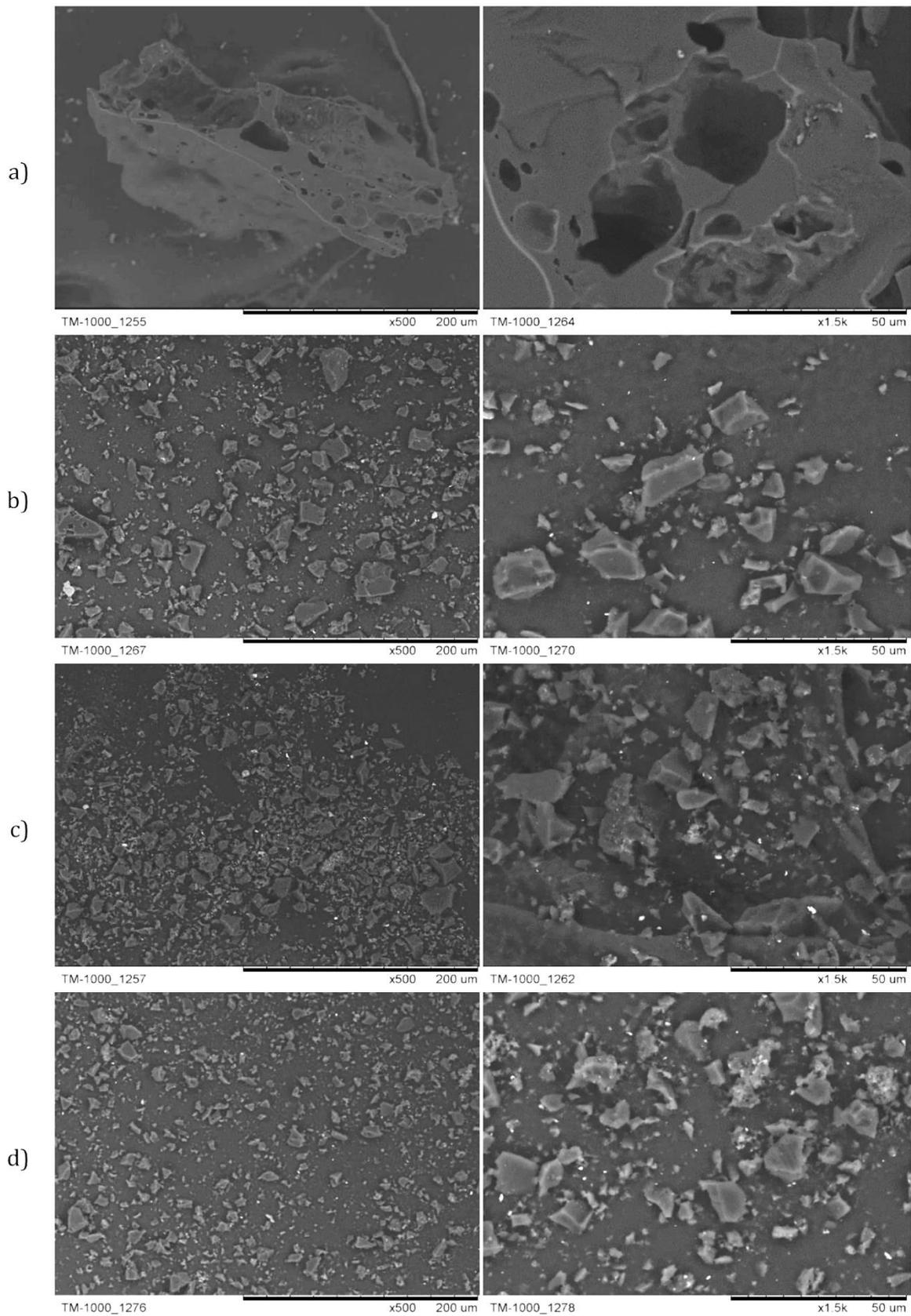


Figure 5. SEM micrographs of crushed (a) and ground CRBP-900°C sample after 5 min (b), 10 min (c) and 15 min(d) at 500x and 1500x magnification.

The characteristic particle sizes of the ground CRBP-900°C samples are summarized in Table 3.

Characteristic particle size	Crushed coke	After 5 min grinding	After 10 min grinding	After 15 min grinding
X_{10} , μm	39	5	5	4
X_{50} (median size), μm	188	11	8	7
X_{90} , μm	761	22	13	11

Table 3. Characteristic particle sizes of the crushed and ground coke of CRBP-900°C samples.

According to the particle size analysis, the characteristic particle sizes (X_{10} , X_{50} and X_{90}) of the samples decreased in relation to increased grinding time. Thus, the drastic decrease of specific surface cannot be explained with the agglomeration of particles due to the longer grinding time. However, as there was no significant decrease in the particle size after 10- and 15-minutes grinding, the completion of size reduction can be assumed, which could explain the turning point in the specific surface values [22].

3. Conclusion

Different catering wastes were pyrolysed at 650, 725 and 900 °C, and the suitability of the solid residues as activated carbon was examined.

The resulting 60-85 wt.% carbon content can provide a good basis for activated carbon production, but the iodine number (therefore the specific surface area) of the crushed samples were small. The particle size was significantly decreased by 5-minutes grinding, but the iodine number only slightly increased. However, 10-minutes grinding had remarkable effect on the iodine number, but no significant decrease was observed in the particle size. After 15-minutes grinding, the fragmentation was not notable, but based on the SEM images, the agglomeration of the finer particles intensified. Because of this, the iodine number was decreased.

Overall, the cokes had small specific surface area and the SEM images showed slight porosity even in case of crushed cokes, therefore these cokes are considered charred intermediate products rather than activated carbon. Further chemical or physical activation processes are required to achieve the proper structure. Moreover, the optimisation of grinding time is necessary to find the turning point, at which grinding has negative effect on the specific surface area.

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