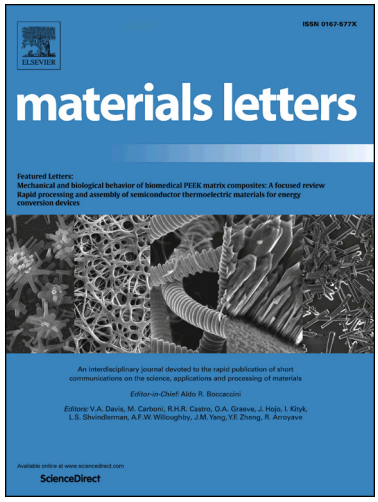

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PII: S0167-577X(17)30118-0
DOI: http://dx.doi.org/10.1016/j.matlet.2017.01.100
Reference: MLBLUE 22053

To appear in: *Materials Letters*

Received Date: 9 November 2016
Revised Date: 10 January 2017
Accepted Date: 21 January 2017

Please cite this article as: S.H. Zein, B. Asenso, V.K. Skoulou, Nanocarbons from Acid pretreated Waste Coffee Grounds using Microwave Radiation., *Materials Letters* (2017), doi: http://dx.doi.org/10.1016/j.matlet.2017.01.100

Nanocarbons from Acid pretreated Waste Coffee Grounds using Microwave Radiation.

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Abstract

This study investigates the use of microwave radiation to produce nanocarbons from Waste Coffee Grounds (WCG). It is first step to demonstrate the potential of integrating the microwave power to conventional methods of carbonaceous materials and nanocarbons production, aiming to overcome their high production cost. The process parameters and interactions investigated were: microwave radiation power (W), temperature (^oC) and residence time (min). Results obtained from the lab-scale experiments indicated the optimum conditions for maximizing the nanocarbons yield (wt%) from the H_2SO_4 acid pretreated WCG at 200 °C, 850 for 60min resulting in a 87.6 wt% char yield which ranged between the average size of 100-140 nm and lower. Moreover, the optimum conditions to achieve the maximum yield of nanocarbons (wt%) where: same temperature (200 °C), lower microwave power (650W) and residence time (45min). Then a yield of 60 wt% nanocarbons of average sizes 60nm were produced, indicating the potential of this method to produce value-added biomaterials (spherical shaped nanocarbons) applicable for future scientific breakthroughs.

Keywords: biomass; carbonaceous; waste; microwave; pre-treatment; biomaterials

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1. Introduction

A significant amount of lignocellulosic-residues emerging from agriculture, due to both pre and post-harvest losses, as well as food processing industry are still being classified as waste [1]. The total amount of paper, wood, food and garden waste produced in EU reaches 900,000,000 tons/yr [2]. Some of these waste is recycled and re-used, while the total lignocellulosic waste sent for landfilling reaches 220,000,000 tons/yr. A 55% of such waste is crop residues, 35% forest, food and garden waste and 10% emerges from paper-wood processing industries. This indicates an attractive opportunity to produce new value added products from waste on an industrial scale [2], helping to eliminate problems related to use of inorganic synthetic based materials (plastics), which are non-renewable, non-biodegradable, consume large amounts of energy during manufacture and pose health risks.

Coffee is a popular beverage with its worldwide consumption reaching 400 billion cups/yr [3], producing approximately 8,000 ton/yr of WCG, as a cup produces ~20 gr of WCG. Moreover WCG logistics is cost effective and applied easily from coffee-shop vendors. As WCG is still considered as a waste, disposed for landfilling even though it is phytotoxic and takes longer time to decompose compared to other waste [3].

One of the routes of upgrading WCG to a value added feedstock is to convert it to char or better to nanocarbon particles, Nanocarbons find use in a wide range of high-tech applications from display panels, fibre-reinforced composites, energy storage [4], catalyst support [5-7], orthopaedics, sports equipment, dielectric electromagnetic absorbers to automotive and aerospace related products [8-10]. Nanocarbons performance and number of potential applications can be increased by combining them with functional materials.

Generally, nanocarbon synthesis involve high temperature, vacuum and inert gases [11]. Lignocellulosic waste to produce carbonaceous materials via the thermochemical route i.e. pyrolysis and/or slow oxidative carbonization at T> 350^{o}C have been reported [12-13]. However, those processes are energy intensive, present high activation energies and result in high costs. We believe microwave will reduce the energy consumption and thus nanocarbons-biomaterials can be produced efficiently, with an overall reduced operational cost and offer a marketable product of considerable value in future. Furthermore, to the best of our knowledge, the use of the microwave in converting WCG to nanocarbon particles has not yet been investigated.

2. Experimental methods

2.1 Statistical optimisation methods

The experimental conditions matrix was designed using analysis of variance (ANOVA) software as given in detail in our previous work [14] using Surface Response Methodology (SRM) coupled with Central Composite Design (CCD). This experimental design strategy enables embodiment of advantages of performing a specific number of experiments, targeting at identification of the optimum results, save time, manpower and resources from performing unnecessary experiments. It fully considers the multivariate nature of any novel process parameters (factors) and the definite interactions between process conditions and impact on the response yield (char or nanocarbons-yield, wt%). The parameters studied were: temperature, microwave power and acid pre-treatment time.

The optimum experimental runs designed by setting the upper and lower process parameter limits as: a) T= 150, 200^{0}C; b) t= 30, 60 min; microwave power P=450, 850W. A total number of 30 best experimental runs- suited process conditions-highly possible to lead to an optimum result (maximization of the char and nanocarbons-yield) were obtained based on different combinations of the process parameters (factors) with one (1) response being the char and nanocarbons-yield (wt%).

2.2 Materials and Lab scale reactor

WCG obtained from the UoH coffee shop. Low amount of H_2SO_4 used for WCG pre-treatment. Char and nanocarbons production was carried out in a Milestone microwave laboratory system (Ethos EX, 1200 W) with a rotary vessels reactor system; the chamber hosted the WCG at a maximum working temperature of 200°C. The reaction temperature was continuously measured by a ATC-FO-Fiber-Optic automatic temperature control system and control of a reference vessel. The microwave heating controlled using a PID algorithm. For each experiment two 200ml cylindrical PTFE reactor-vessels were microwaved to the desired temperature, while the residence time of products varied between 30-60min under an acid atmosphere. More details of the experimental system can be found elsewhere [15]. After acid pretreatment and microwave irradiation of WCG a rich carbonaceous product obtained. The SEM images (SEM, Hitachi TM 1000) of untreated and pre-treated WCG products were taken and revealed the surface morphology of the char and nanocarbons produced.

3. Results and Discussion

Table 1 depicts the matrix of 30 optimum conditions determined from experimental design and the char and nanocarbons yield from experiments performed in lab.

Table 1. Optimum microwave process parameters, char and nanocarbons- yield (shaded cells) (wt%) results.

Run No.#	Microwave Power (W)	Temperature (°C)	Time (min)	Char, nanocarbons-yield (wt%)
#1	**850**	**200**	**60**	**Max char-yield: 87.61**
12	850	200	60	85.99
4	850	150	60	85.60
5	850	200	45	79.90
3	850	175	60	75.13
7	650	200	60	68.00
#8	**650**	**200**	**45**	**Nanocarbons: 68.00**
32	750	200	45	63.70
28	650	200	60	56.71
26	850	150	60	53.00
23	850	150	60	52.98
15	750	200	45	52.69
20	450	200	60	52.69

Run No.#	Microwave Power (W)	Temperature (°C)	Time (min)	Char, nanocarbons-yield (wt%)
22	850	150	30	52.07
25	550	150	60	52.00
24	850	150	30	49.99
31	850	200	30	49.77
14	450	200	60	48.71
16	750	100	30	48.70
6	850	150	30	47.87
2	450	200	30	45.62
#17	**550**	**200**	**60**	**Nanocarbons:44.00**
30	450	200	60	42.99
13	450	200	60	41.19
19	450	150	60	40.09
21	450	150	30	39.33
11	650	175	45	36.00
9	450	200	30	25.57
27	450	150	30	21.68
29	450	150	30	21.23
10	450	150	60	21.12
18	450	150	30	20.01

SEM analysis of untreated and acid-treated WCG products was carried out based on their qualitative and quantitative characteristics namely, colour and char-yield. The sample produced the highest char yield obtained at: 200 ^{o}C, 850W, 60min, [run 1]. The intermediate to least desirable yielded chars were analysed, too. The parameters for the other representative samples were: 550W, 60 min and 200 ^{o}C and 200^{o}C, 650W, 45 min ([run 17] and [run 8], respectively).

Figure 1a depicts the surface morphology of untreated WCG and revealed pores around and within the existing lignocellulosic-matrix (as a result of the fresh coffee-grounds water leaching) and a "sponge-puff" like appearance. At magnification of 10,000 times, pores were around and within existing pores, which are comparatively smaller. The pattern is shown around and at 3,500 times magnification, the smaller pores on the treated surface appear along with the already existing pores. The analysis of the acid-pretreated WCG (**Fig.1b**) showed a rough "ridged" surface with more developed porosity.The pattern is at 3,500 -20,000 times magnification and shows the appearance of these smaller along regular developed bigger pores. The smaller pores are regularly shaped whereas bigger ones are random. Porous network of smaller pores can be seen to develop around existing pore surface. This seems promising for increasing porosity of the pre-treated WCG.

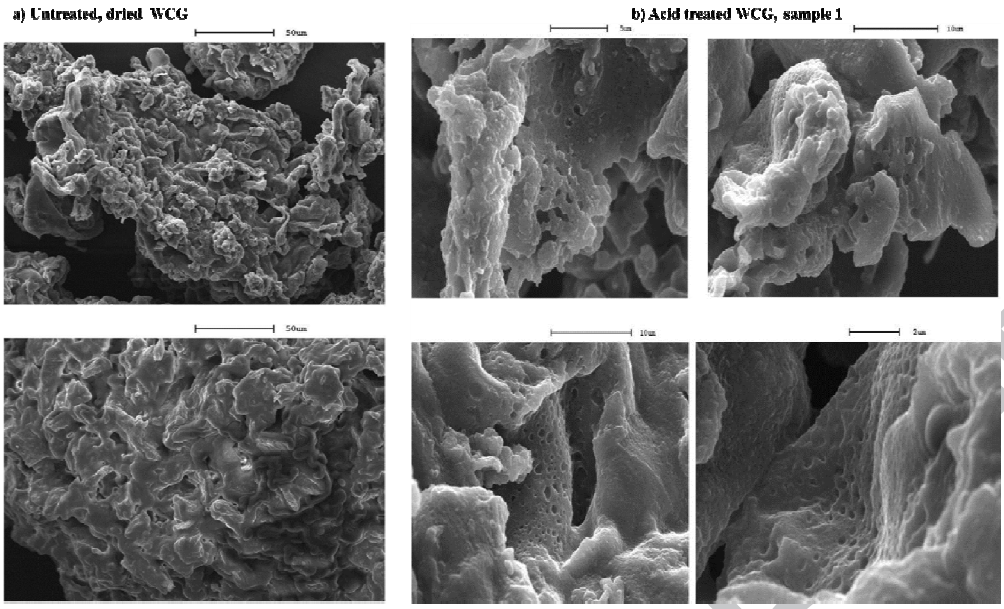

Fig. 1. Surface morphology of: a) untreated and b) acid pre-treated WCG-char sample from [run 1]: 850W, 200 ^{o}C 60min.

The analysis of carbonaceous sample [run 17]: 550W, 200^{o}C, 60min, and [run 8]: 650W, 45min, 200 ^{o}C indicated some surprising surface features: instead of the expected pore formation, spherical particles were formed. This surface morphology could be an indication of carbon nanoparticles formation and this pattern is widespread and repeated across the surface of sample.

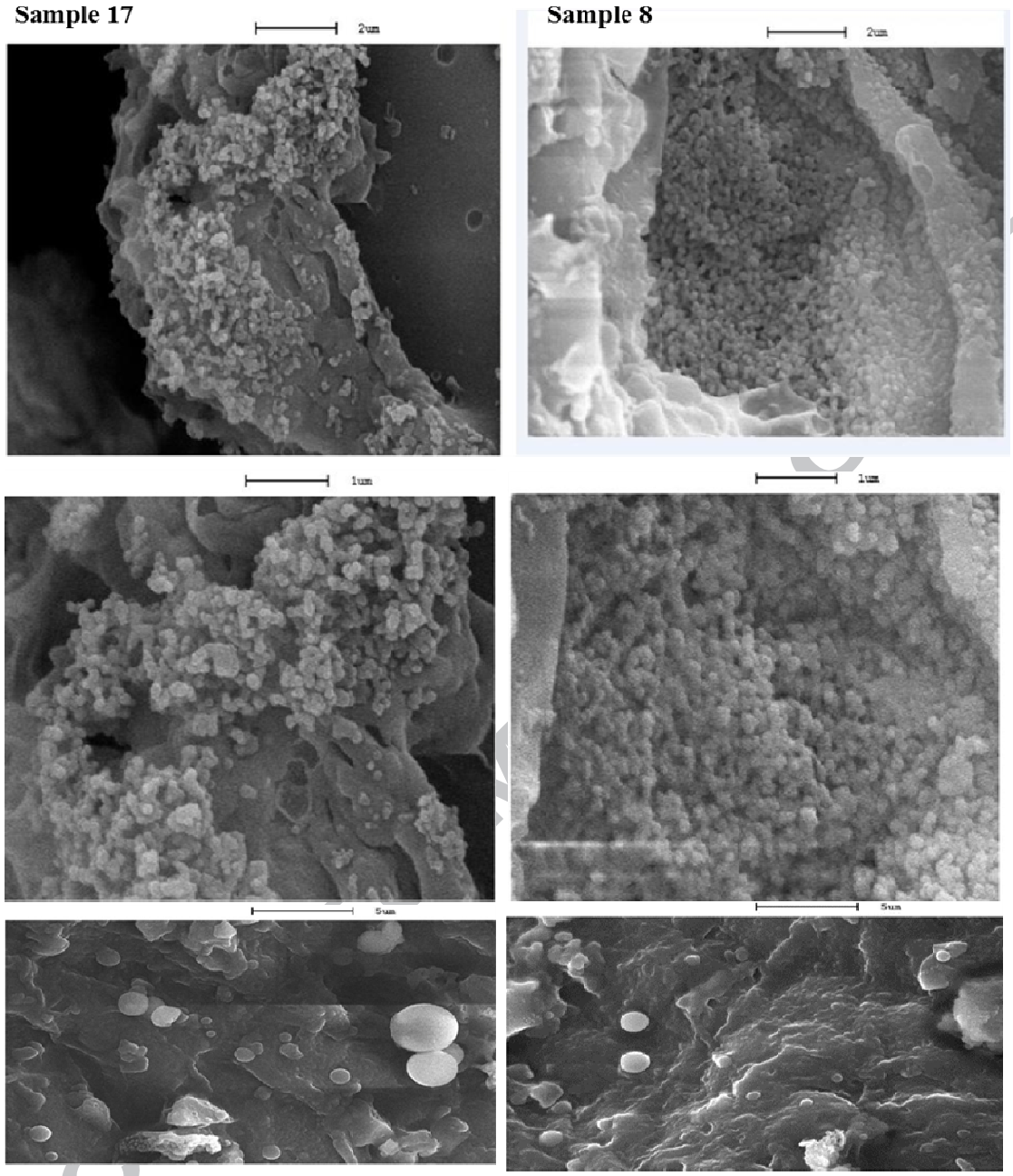

Fig. 2. Formation of nanocarbons in products from [run 17] and [run 8], alongside their random size distribution.

Particles on sample [Run 17] are well formed and regularly shaped with size range of 100-140nm, whereas the ones on [Run 8] vary in size and are non-uniform. However, smaller than the average measured diameters (100-140 nm) were still noticed in the SEM images. Examinations of samples of [run 8] revealed a mixture of pores and microspheres, but particles have a random size distribution. The size ranges between 500nm - 3.24 micron, with the relatively smaller particles not exceeding 1.04μ. A number of surface examinations revealed a trend of repeating features of nanocarbons (**Fig.2**).

Further analysis with Energy Dispersive X-ray (EDX) can conclusively determine if those spherical morphologies are carbon-based. The composition indicated by the spectrum obtained from particles investigation justified that they are C **(Fig.3)** and production of spherical WCG nanocarbons. The most influential parameters for nanocarbons production were the microwave treatment time (min) and the irradiation power (W).

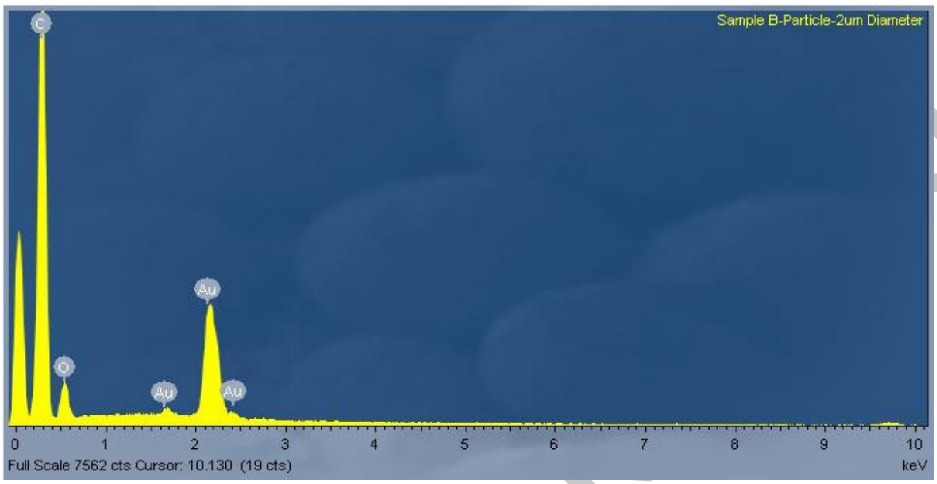

Fig. 3 EDX analysis of nanocarbons.

Conclusion

Careful selection of process parameters of the microwave acid- pretreated WCG lead to char and nanocarbons production. Lab scale experiments indicated that 850W, 200°C, 60min ([run 1]) yielded the maximum char residue (87.6 wt%). More interestingly, at lower irradiation power (550W), same temperature and residence time ([run 17]), as well as at medium power and lower time (Run 8:650W, 45min, 200^{o}C) nanocarbons of different yields ([run8]: 45 wt% and [run 17]: 60 wt%) were produced. A wider range of process parameters and interactions are currently under investigation in order to establish the appropriate relationship-interactions of process parameters which will lead to the desired nanocarbon sizes. Application of these nanocarbons as reinforcement material is also in process, and could be also of interest in materials research.

Acknowledgement

We thank Mr G.Robinson for his assistance with SEM measurements. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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Highlights

- The use of microwave radiation to produce nanocarbons from Waste Coffee grounds (WCG).
- 87.6 wt% of char yield from acid-pretreated WCG at 200 °C, 850W, and 60min
- 60 wt% of nanocarbon yield from acid –pretreated WCG at same temperature (200 °C), lower microwave power (650 W) and residence time (45min).