CO_2 activation of char from argan nutshells pyrolysis: a preliminary study

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Abstract

CO_2 physical activation was performed to produce activated carbons from pyrolysis char. The process was fed by char produced in the pyrolysis of argan nutshells. This unexplored feedstock is a residue of argan oil production. This preliminary study showed that the activated carbons obtained in this process are characterized by a large surface area and a great capacity to retain contaminants.

Introduction

Developing sustainable technologies in energy production as well as finding a clean feedstock has become a primary worldwide challenge. There is an excellent potential to achieve significant reductions in emissions if biomass is well used and valorized. Many pathways are developed to valorize biomass from different origins, not only as a source of energy but also in the production of chemicals and products with noticeable economical add-value, where fossil derivatives had been traditionally the unique suppliers. In this field, thermochemical processes have proven to be effective and efficient in biomass valorization into valuable products due to their diversity and broader technology choice. Pyrolysis is a thermochemical decomposition of organic matter in the absence of oxygen [1], occurring in the temperature range between 350 and 600 °C [2]. Pyrolysis appears as a promising valorization process because of its high-value products: bio-oil, bio-char and gas [2]. Bio-char, or in other words, the pyrolyzed solid, is a carbonaceous residue composed mainly of elemental carbon and ash coming from the original raw material (dirties or mineral content). Bio-char is a prime candidate as a solid biofuel because of its essential higher heating value and energy density, homogeneity, hydrophobicity, and easier pulverization [2]is also valuable as a soil amendment or as a precursor for preparing activated carbons (AC). This latter further expands bio-char applications as contaminants adsorbent for cleaning gas and liquids or electrode materials or catalyst supports.

The scope of this study reports the production of activated carbon from an unexplored agricultural waste named argan nutshells (residue from argan oil production). In addition, sustainable applications and end-uses of this product, such as contaminants retention, have been tested.

Materials and methods

Argan nutshells (AS) was supplied by a Moroccan rural cooperative in the region of Essaouira (southwest of Morocco). AS characterization in terms of ultimate and proximate analyses, higher heating value (HHV) and extractives, hemicellulose, cellulose and lignin contents can be found in previous work [3]. Char from AS was obtained by pyrolysis in a lab-scale plant. The pyrolysis was performed in a fixed-bed reactor at a temperature of 450 ºC under inert N_2 atmosphere. The produced char (ArC) was characterized, as well as the original material. In a second step, ArC has been activated physically using CO_2 in a horizontal fixed-bed reactor. During the activation process, the reactor was heated from room temperature until 900 °C at 15 °C/min under N_2 atmosphere; then, when the temperature rose the setpoint, the N_2 flow was substituted by a flow of CO_2. The experiments were carried out at three different activation times: t_1=90 min, t_2=120 min and t_3=150 min, thus producing three different activated carbons (AC90, AC120 and AC150, respectively). Specifically, this study focuses on the impact of the activation time on some of the activated carbon characteristics. Once the time finished, the reactor left cooling until room temperature under an inert atmosphere of N_2. Some experiments (at t_1 and t_2) were repeated twice in order to evaluate the reproducibility.

The recuperated activated carbon from each experiment was characterized in terms of elemental composition, ash content, textural properties, pH and functional groups in the surface (Boehm titration). The analytical standards or the devices used in the characterization are shown in Table 1, together with the results.

Finally, four aqueous solutions were prepared with an initial concentration of 125 mg/l of methylene blue (MB) and 50 mg/l of phenol, 50 mg/l of vanillin and 50 mg/l of catechol to test the activated carbons aptness to adsorb contaminants. A small amount of each AC prepared was added to each aqueous solution (250 mg of each AC was added to MB solution and 50 mg to phenolic solutions). The tests were carried out under continuous stirring at 700 rpm with a magnetic stirrer at room temperature. UV-Visible absorbance measurements at each correspondent wavelength (665, 270, 275, and 280 nm for MB, phenol, catechol, and vanillin, respectively) were used to follow the evolution of each component retention. Aliquots from each solution were taken after different contact times with the activated carbon. The contaminant retention percentage was calculated according to:

$$Retention\ (\%) = \frac{C_{initial} - C_t}{C_{initial}} \cdot 100$$

Results and discussion

- Products yields

Char product from the pyrolysis step yielded up to 30 wt.% with respect to the raw AS fed. On the other hand, the yields obtained after the activation step ranged between 68 and 38 wt.% with respect to the ArC fed into this second step. Accordingly, a yield of 20, 16 and 11 wt.% (at t_1,t_2 and t_3, respectively) of AS could be converted to activated carbon.

- Char and activated carbons characterization

Table 1 summarizes the results of the chars characterization before and after the activation step at the three different treatment times. As could be seen, the carbon content in the char after activation increased from 88.5 wt.% to around 95 wt.% in the activated one, regardless of the treatment time, and the hydrogen content in the activated carbons was up to 0.5 wt.% instead of 3 wt.% in the ArC. Ash content ranged between 1.3 wt.% and 2 wt.%.

Textural characterization of the activated carbons, as well as AS and ArC, was investigated using N_2 (measured at 77 K). BET equation was applied to the resulting isotherms to obtain BET surface area (S_{BET}). A significant improvement of this parameter was already observed when comparing the original surface area in the non-activated ArC (286 m^2/g) with any AC.

Figure 1 shows the evolution of BET surface area as a function of the char activation time. The activation time positively affects the BET surface area, obtaining a maximal value of 1544 m^2/g after 150 min.

The pH of the produced activated carbon ranged between 7.8 and 8. Furthermore, the Bohem titration showed that the total amount of acid sites on the surface was almost the same as the total alkaline sites (up to 4100 µmol/g). The acid sites identified were mainly lactones (up to 935 µmol/g), carboxyls (up to 2340 µmol/g) and phenolics (up to 830 µmol/g).

- Adsorbance tests

Figures 2 shows the results of the contaminants retention capacity of the produced AC. Generally, all the activated carbons showed an excellent retention capacity of contaminants. Almost the totality of MB was removed from the aqueous solution after 24 h of contact with any of the AC. Regarding phenolic compounds, phenol and vanillin were totally adsorbed after 24 h, while 95 wt.% of the initial amount of catechol was retained after the same contact time. It is to highlight that the performance of AC150, which was obtained after the longest treatment time, seems to be greater thanks to its largest surface area.

Conclusions

As the main result of this preliminary study, it could be stated that pyrolysis char from Argan nutshells could be a brilliant candidate to produce high-quality activated carbons. After physical activation with CO_2, the obtained carbons were characterized by high carbon content, low ash content and an important BET surface area (up to 1500 m^2/g) in addition to a relatively neutral surface. These characteristics make this residue a potential feedstock for interesting end-uses.

REFERENCES

[1]. KOPPEJAN, J. S.V.L., The Handbook of Biomass Combustion and Co-firing. *Edition, s.2007, London: Routledge. 464.*

[2]. ADHIKARI, S., NAM, H. and CHAKRABORTY, J.P., Chapter 8 - Conversion of Solid Wastes to Fuels and Chemicals Through Pyrolysis, in Waste Biorefinery, *Bhaskar, T., et al., Editors. 2018, Elsevier. p. 239-263.*

[3]. AFAILAL, Z. GIL-LALAGUNA, N. TORRIJOS, M T. GONZALO, A. ARAUZO, J. SÁNCHEZ, J L. (2021) Antioxidant Additives Produced from Argan Shell Lignin Depolymerization. Energy & Fuels.

FIGURES / TABLE

Table 1: Chars characterization before and after the CO_2 activation at different treatment times.

	ArC	AC90	AC120	AC150	Analytical standard/equipment
Ultimate analysis (wt.% ar. basis)					
C	88.5 ± 0.2	95.1 ± 0.2	94.9 ± 0.3	94.3 ± 0.1	LECO CHN628
H	3.3 ± 0.1	0.7 ± 0.1	0.55 ± 0.04	0.505 ± 0.004	LECO CHN628
N	0.6 ± 0.1	1.02 ± 0.03	1.0 ± 0.1	1.12 ± 0.02	LECO CHN628
S	<0.05	<0.05	<0.05	<0.05	LECO CHN628- 628-S add-on
O[a]	6.1 ± 0.5	1.9 ± 0.1	2.0 ± 0.1	1.9 ± 0.2	By difference
Ash (wt.%)	0.93 ± 0.04	1.3 ± 0.1	1.5 ± 0.2	2.1 ± 0.3	EN 14775:2010

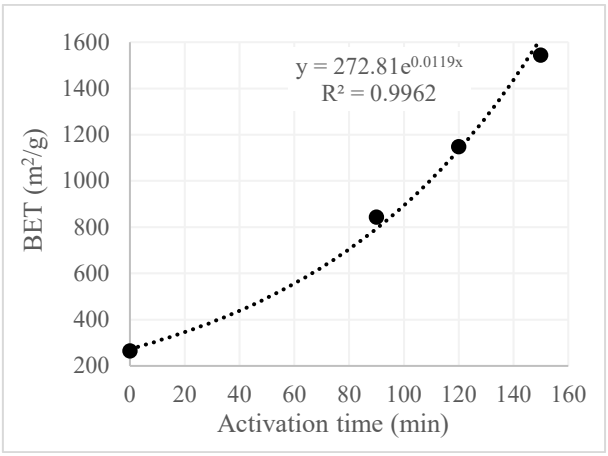

Figure 1: Evolution of BET surface area as a function of char activation time.

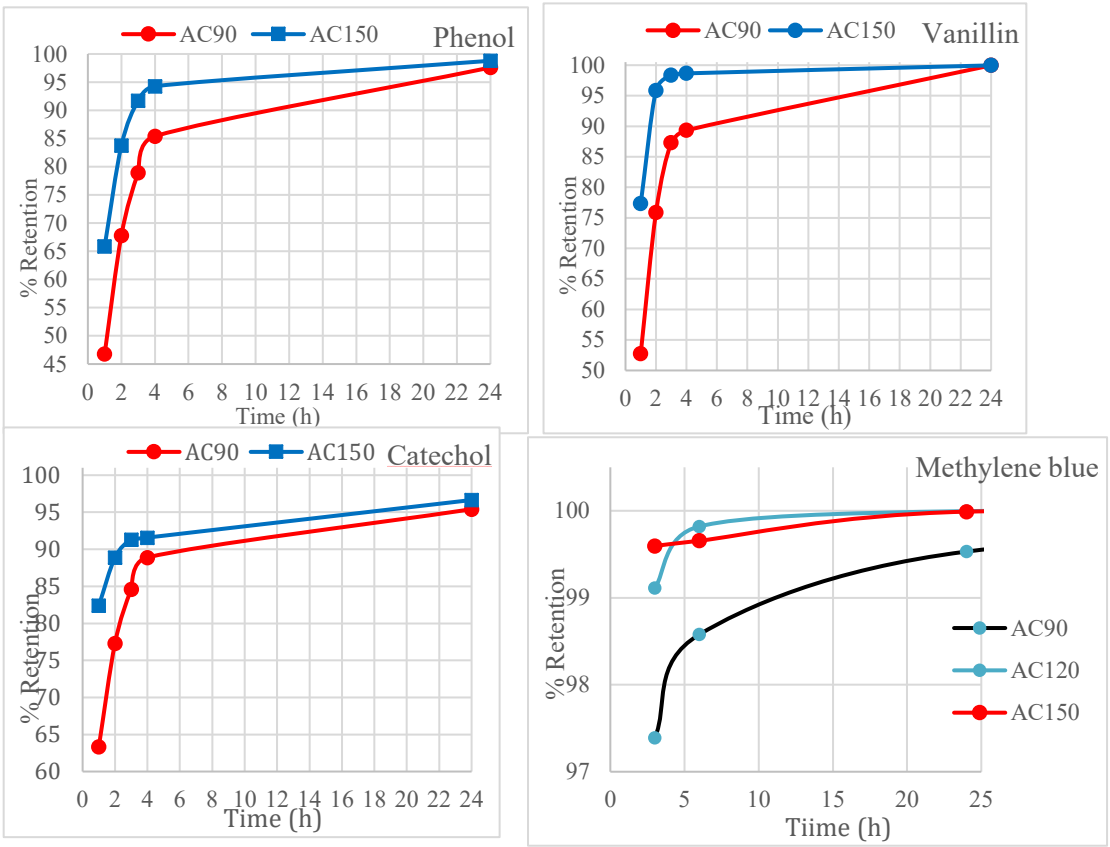

Figure 2: Contaminants retention capacity of the produced AC.