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Study of variables in energy densification of olive stone by hydrothermal carbonization

A. Álvarez-Murillo*, S. Román, B. Ledesma, E. Sabio

Departamento de Física Aplicada, Escuela de Ingenierías Industriales, Universidad de Extremadura. Avda. Elvas s/n, Badajoz 06006, Spain

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ABSTRACT

The influence of the variables biomass/water ratio (1.1–12.3%), temperature (150–250 °C) and residence time (3.2–36.8 h) on the hydrothermal carbonization of olive stone has been studied. The implementation of a design of experiments – response surface methodology approach allowed the process to be optimized in terms of reactivity (solid yield) and energy densification (increase in higher heating value), and the importance of each variable in the process to be identified. Solid yield ranged between 30.95% and 55.75% and HHV from 22.2 to 29.59 MJ kg^{-1}. Interactions between the different variables involved were investigated to provide more precise control of the overall process so as to satisfy any given energy densification requirement of the final hydrochar.

1. Introduction

There is an increasing awareness on the unsuitability of current energy consumption scheme, based mainly on the use of fossil fuels. Emissions coming from fossil fuels combustion lead to problems such as global warming, climate change and environmental pollution. Also, fossil fuel reserves are rapidly depleting, while energy consumption is dramatically increasing. As a result, the necessity of renewable and clean energy resources to replace fossil fuels is widely recognized.

Within this frame, there is a growing interest in the development of alternative sources for clean renewable energy production sources such as biomass. Besides, in general terms, biomass does not contribute to global warming since it recycles carbon dioxide from the atmosphere.

The olive oil sector has a significant role in the economy of the European Union (EU). In particular, the EU is the largest world olive oil producer, contributing with 80% of world production, and consumer, 70% of it. EU average production of olive oil in recent seasons was 2.2 million tonnes, of which about 62% corresponded to Spain, making it by far the first community producer [1]. Olive industry presents a high potential for solid biofuel production because of the residues generated from olive groves and those by olive oil industries. Olive stone is one of the most important residues generated in this sector and could be an interesting renewable energy source. According to González et al. [2] this residue is constituted by cellulose (30.8%), hemicellulose (17.1%) and lignine (32.6%). This lignocellulosic material is mainly used as solid biofuel to thermal power generation [3].

Several forms of pre-treatment can be considered in order to improve the physicochemical characteristics of lignocellulosic biomass for its subsequent combustion. These include drying [4], pelleting [5], ultrasonication [6], washing with chemicals [7], torrefaction [8], etc. In this context, it is interesting to remark that hydrothermal carbonization (HTC) of biomass has gained great relevance during the last few years due to its simplicity and low cost [4,9]. HTC involves heating biomass in water under autogenous conditions, in some cases in the presence of chemicals, to enhance energy densification by yielding a carbonaceous fraction called hydrochar (HC), which is more stable and has higher C content than the raw matter. Previous works in this line have examined the use of biomassic materials such as grass cuttings [10], algae [11], maize [12], invasive aquatic plants [13], and sewage sludge [14]. To the best of the authors' knowledge, no study has considered HTC of the olive stones yet.

Given this context, the objective of the present work was to provide added value to olive stone, a sub-product of the olive oil industry, potentially suitable as a hydrochar precursor. In

Abbreviations: *R*, biomass/water ratio; *R*–*t*, biomass/water ratio–residence time; *R*–*T*, biomass/water ratio–temperature; CCD, central composite design; DoE/RSM, design of experiments/response surface methodology; HHV, higher heating value; HTC, hydrothermal carbonization; *t*, residence time; *t*–*R*, residence time–biomass/water ratio; SY, solid yield; SPSS, statistical software package; *T*, temperature; *T*–*R*, temperature–biomass/water ratio; *T*–*t*, temperature–residence time.

* Corresponding author. Tel.: +34 924289600; fax: +34 924289601.
E-mail address: andalvarez@unex.es (A. Álvarez-Murillo).

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particular, an HTC process was tested, studying the influence of three processing variables: temperature, residence time, and biomass/water ratio. To gain deeper insight into the HTC process and a more realistic interpretation of the results, a DoE/RSM (design of experiments/response surface methodology) approach was used. This is a particularly useful strategy for investigating interactions between variables, which would be hard to verify by a classical 'one variable at a time' approach.

2. Experiments

2.1. Materials

The raw material was olive stone, produced in a company located in Valdetorres (Extremadura, Spain), producing mainly olive oil. After the olive oil extraction, and like a by-product, the olive stone mixed with the olive pulp appears. The olive stone used, was separated from the pulp, and it was grounded and sieved to a particle size of 0.4–2.0 mm. Then, the sample was dried overnight at 100 °C and stored in a closed flask placed in a desiccator until further analysis.

2.2. HTC processes and hydrochar characterization

The HTC processes were performed in a stainless steel autoclave (Berghof, Germany). In a 0.2 L teflon vessel (unstirred), an appropriate amount of sample (5–18.4 g) and 150 mL of deionised water at room temperature were added, in order to obtain the targeted biomass/water ratio, R (1.1–12.3%). Then, the teflon vessel was sealed and placed into the autoclave and the system remained overnight at room temperature. Thereafter, the system was heated up in an electric furnace at selected temperatures (150–250 °C), during a chosen processing time (3.2–36.8 h). When the reaction time was reached, the autoclave was removed from the oven and subsequently placed in a cold-water bath and allowed to cool down up to room temperature. After cooling, solid was separated from liquid by vacuum filtration and subsequently dried at 80 °C to remove residual moisture. The dried hydrochar was stored in closed flasks placed into a desiccator until further analysis. The experiments were carried out under autogeneous pressure in an autoclave without possibility of measuring interior conditions, but according to our studies the pressure inside the vessel corresponds with that of the water at saturated conditions.

The hydrochars were characterized in terms of their solid yield, higher heating value (HHV, MJ kg^{-1} dry basis), which was determined experimentally by a bomb calorimeter (Parr) [15]. Elemental analysis for carbon, hydrogen, nitrogen, and oxygen were carried out with an elementary analyzer (Eurovector EA 3000), according to the norm CEN/TS 15104 (for determining the content of C, H and N) and CEN/TS 15289 (for S) (CEN/TS 335 Biomass standards, 2004). The surface chemistry was studied by FTIR spectroscopy. FTIR spectra were recorded with a PerkinElmer model Paragon 1000PC spectrophotometer, using the KBr disc method, with a resolution of 4 cm^{-1} and 100 scans.

2.3. DoE/RSM procedures

The DoE/RSM approach has proven to be a very useful tool to investigate the influence of several variables on a given magnitude (the output function) [16,17]. This technique allows the optimal processing conditions to be identified by taking into account the interactions between the different variables involved, unlike the case of classical step-by-step analyses. Moreover, fewer independent runs are required for this optimization.

A central composite design (CCD) is useful in RSM to implement the DoE approach because it provides an even distribution of the experimental points. It involves the use of a two-level factorial design with 2^k points combined with $2k$ axial points and n centre runs, with k being the number of factors. With k factors, the total number of experiments, N, is:

$$N = 2^k + 2k + n \quad (1)$$

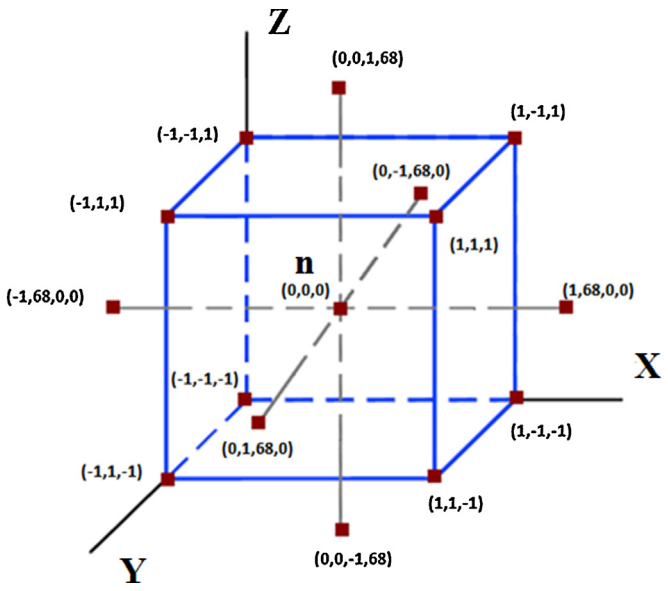

Fig. 1. Representation of the CCD points for 3 factors.

The plot of the CCD for 3 factors is presented in Fig. 1. It can be observed that this experimental design gives a spherical distribution. This homogeneous distribution facilitates the further statistical analysis.

As noted above, the present work involved the analysis of the influence of three variables: temperature (T), residence time (t), and biomass/water ratio (R). Thus the number of factors was $k = 3$, and, according to Eq. (1) and taking $n = 4$, the total number of experiments to conduct was 18. The runs were made randomly in order to avoid hidden effects. A second-order model was used as the equation defining the target function (the response, Y):

$$Y = A_0 + A_1R + A_2T + A_3t + A_4RT + A_5Rt + A_6tT + A_7R^2 + A_8T^2 + A_9t^2 \quad (2)$$

Eq. (2) was fitted to the experimental results using IBM SPSS statistical software package, and the resulting equations were plotted using Wolfram Mathematica 8 software.

3. Results and discussion

As was detailed in Section 2.3, prior to experimentation, a CCD was used in order to define the experimental conditions to test (operating temperature, residence time, and biomass/water ratio). Based on the results of previous experiments [18], the ranges used for these three parameters were 150–250 °C, 3.2–36.8 h, and 1.1–12.3%, respectively. The values of SY and the corresponding HHVs obtained for each run are listed in Table 1. These results will be discussed in Sections 3.1 and 3.2, respectively.

The Levenberg–Marquardt algorithm was applied to fit the model to the experimental data, using the SPSS software package. The model fits well both SY and HHV data as the high values of R^2 indicate (0.8468 and 0.9031, respectively), thus endowing the further analysis carried out with validity in providing a true picture of the HTC process.

The values of the normalized coefficients (A0–A9) fitting the target function (Y, Eq. (2)), in accordance with the defined model are presented in Table 2.

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