Bioresource Technology 261 (2018) 104–116

Contents lists available at ScienceDirect

Bioresource Technology

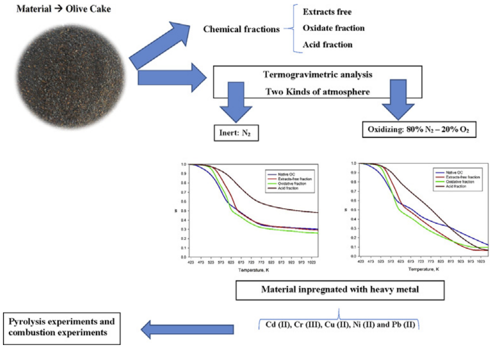
journal homepage: www.elsevier.com/locate/biortech

Kinetic study of thermal degradation of olive cake based on a scheme of fractionation and its behavior impregnated of metals

L. Quesada, A. Pérez*, M. Calero, G. Blázquez, M.A. Martín-Lara

Department of Chemical Engineering, Avenida Fuentenueva, s/n, University of Granada, 18071 Granada, Spain

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Olive cake
Biosorption
Heavy metals
Kinetics
Reaction schemes
Thermal decomposition

ABSTRACT

This research aims to provide a better knowledge of the thermal decomposition of the olive cake as well as this lignocellulosic material loaded, in a previous stage of biosorption, with heavy metals for its use in processes of energy recovery.

Firstly, isolation of constituents of the olive cake was carried out. Then, experiments were performed by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) under inert and oxidative atmosphere at a heating rate of 15 K/min for each isolated fraction. Next, adequate reactions schemes were proposed to find kinetic parameters. Validation of these schemes were verified by the goodness of fitting between experimental and simulated data. Also, some important combustion characteristics such as ignition and burnout temperatures were determined.

With regard to the effect of metals, cadmium, copper, chromium, nickel and lead present in metal-loaded olive cake did not modify values of kinetic parameters which described the thermal decomposition processes.

1. Introduction

The olive oil sector, in a broad sense, from agricultural production to industry, is a very important economic activity in Spain and, in general, in the countries of the Mediterranean area, having a deep cultural, social and environmental significance.

The difficulty of managing solid wastes with high humidity, such as the olive pomace generated by the continuous two-phase system, has stimulated the search for feasible solutions for their valorization (Agencia Andaluza de la Energia, 2016; Buratti et al., 2016.). The oil extraction factories have adapted to the reception of this solid and take advantage of their remaining oil either through a new centrifugation or

---

* Corresponding author.
E-mail address: aperezm@ugr.es (A. Pérez).

https://doi.org/10.1016/j.biortech.2018.04.014
Received 6 February 2018; Received in revised form 2 April 2018; Accepted 3 April 2018

through their chemical extraction with solvents. This oil extracted, according to European legislation, is the olive pomace oil. After the extraction of the exploitable oil, the remainder of defatted olive pomace (olive cake) is still usable using energy cogeneration techniques or composting for its use as an organic fertilizer. Olive cake has a moisture content that varies between 9% and 12%, and a calorific value of approximately 4200 kcal/kg on a dry basis.

For every ton of processed olives, approximately 0.27 tons of olive oil and 0.73 tons of fatty pomace are produced. Then, from each ton of fatty pomace 0.27 tons of olive cake is produced. In Spain, an average campaign generates around 3,000,000 tons/year of fatty pomace with an approximate humidity of 60–65% and around 810,000 tons/year of olive cake. Although, there are some energy plants that use olive cake as fuel, new proposal of valorization of this solid are being investigating.

In this context, the proposal of using this solid waste as adsorbent has gain attention and therefore, investigations about heavy metal removal by olive pomace and/or olive cake have been previously published (Martín-Lara et al., 2008, 2009, 2011, Blázquez et al., 2010, Menichi et al., 2015, Gök and Mesutoğlu, 2017, Nuhoglu and Malkoc, 2009). However, treatment and/or disposal of the metal-contaminated solid require new research for finding new industrial applications. Now, solid waste treatment techniques such as thermal treatment with energy recovery could be applied as an alternative for the final disposal of the contaminated solid. Previously, some authors as Lievens et al. (2008), Mayer et al. (2012), Al Chami et al. (2014), Martín-Lara et al. (2016) or Almendros et al. (2017) have investigated the thermal degradation of different metal contaminated solids. However, no published papers evaluated the thermal degradation of solid wastes from olive oil industry previously used as adsorbents. In addition, the majority of published works related to thermal decomposition of olive oil industry wastes has been focused on the decomposition mechanisms and kinetics of the pyrolysis process (Blázquez et al., 2014; Özveren and Özdogan, 2013; Garcia-Maraver et al., 2015; Ghouma et al., 2017). Only Buratti et al. (2016) presented a study of combustion of the olive oil production chain residues.

On the other hand, the chemical fractionation of olive cake could allow the obtaining of solid fractions with high calorific value. Those fractions could be very suitable for combustion, pyrolysis and/or gasification, showing a good performance in all cases. Thus, a chemical fractionation of olive cake in a scheme of biorefinery has been proposed previously by other authors (López et al., 2010; Pérez et al., 2018; Ronda et al., 2017).

The fundamental objective of this work is to study the thermal decomposition of the olive cake and its different solid fractions obtained by chemical treatment. Mechanistic kinetic models of correlation for each solid, with the consequent calculation of kinetic parameters, in an inert atmosphere of nitrogen and in an atmosphere of 20% O_2–80% N_2, were elaborated. Also, a complete analysis of the effect of the presence of heavy metals previously loaded by adsorption was developed.

2. Materials and methods

2.1. Raw material

The olive cake (OC) was obtained from a company in Linares-Baeza (Jaen, Spain).

The sample was prepared for subsequent fractionation by being screened for a size smaller than 1 mm.

2.2. Physico-chemical characterization of OC

2.2.1. Determination of proximate analysis

Moisture content of OC was determined by difference in weight between the wet sample and after drying in an oven (at 378 K) until constant weight (UNE-EN ISO 18134-2:2016).

Volatile matter content was calculated according to standard UNE-EN ISO 18123:2016. A sample without contact with ambient air was heated to 1173 K for 7 min. Percentage of volatile matter was calculated from mass loss of the test sample minus mass loss due to moisture. Ash content was determined by calculation from the mass of residue remaining after the sample was heated in air for at least 60 min at a temperature of 823 K according to standard UNE-EN ISO 18122:2016. Fixed carbon content was calculated by difference until 100%.

2.2.2. Chemical analysis

Firstly, removal of soluble hot water extractives was performed according to the TAPPI T 257. Then, ethanol–benzene extractable was determined according to TAPPI T 204. Finally, lignin and holocellulose were determined by quantitative acid hydrolysis with 5 mL of 72% sulfuric acid for an hour (Tappi T-248-em-85), Tappi (2017), and quantitative posthydrolysis was performed with 4% sulfuric acid (adding water until 148.67 g) at 394 K and 2 atm during 60 min in order to ensure quantitative conversion of oligomers into monomers (Garrote, 2001). Before HPLC analysis, the solid residue from posthydrolysis process was recovered by filtration and considered as Klason lignin. The monosaccharides contained were determined by HPLC in order to estimate the contents of samples in cellulose (as glucose) and hemicelluloses (as xylose). Moisture of raw material was considered as water in the material balances. Chromatographic determination was performed using a Metrohm 940 professional IC Vario equipped with Metrosep Carb 2 250/4.0 column under the following conditions: mobile phase, 100 mM NaOH and 10 mM NaAc; flow rate, 0.500 mL/s; and column temperature, 303 K.

2.2.3. Elemental analysis

Elemental analysis of dried OC sample was accomplished by combustion analysis using an Elemental Fison's Instruments EA 1108 CHNS.

2.2.4. Calorific value

Calorific value is the amount of heat that is emitted during the combustion process of a certain fuel. This was done by a calorimetric pump (Phywe LEC-02) according to the UNE-EN 14918:2011.

2.3. Impregnation of the OC with heavy metals

Impregnation of the OC with heavy metals was carried out by biosorption. A quantity of 20 g of solid was kept in contact with 2 L of heavy metal solution with a concentration of 200 mg/L in a batch reactor. It was kept under magnetic agitation and at a constant temperature of 298 K, until equilibrium was reached (approximately 120 min).

The metal salts used for preparing the metal solutions were nitrate salts of different heavy metals (Cd (II), Cr (III), Cu (II), Ni (II) and Pb (II)) purchased to Panreac, S.A. (Spain).

Once equilibrium between solid and liquid phases was reached, the samples were centrifuged and filtered. Solid phase was washed with deionized water (to remove any of the ions which were not bound to the material) and dried in an oven at 313 K for 24 h. Liquid phase was analyzed (to determine metal concentration) by atomic absorption spectrophotometry using a Perkin-Elmer AAnalyst 200 spectrophotometer.

Determination of the amount of metal retained in solid (mg of metal per g of solid), q, was determined according to the following mass balance:

$$Q = (C_i - C_f)\cdot m \tag{1}$$

where C_i and C_f are the initial and final concentrations of metal in the solution (mg/L) and m is the ratio between volume of metal solution and mass of solid (L/g).