TOTAL USE OF OLIVE TREE PRUNINGS BY MEANS OF HYDROTHERMAL AND COMBUSTION PROCESSES

Ana Requejo,[a] Manuel Javier Feria,[b] Fátima Vargas,[a] and Alejandro Rodríguez *,[a]

The aim of this work is to chemically characterize olive tree prunings and use the material in hydrothermal and combustion processes. The influence of the hydrothermal treatment conditions, with and without acid catalyst, of the main fraction of olive tree prunings (stems with a diameter > 1 cm) (temperature 150 to 190ºC, time 0 to 20 minutes after reaching the operation temperature, liquid/solid ratio 6 to 8, and sulphuric acid concentration -0.1 to 0.5%), on the composition of resulting liquid fraction and on the solid yield of resulting solid fraction were studied. A polynomial model was found to reproduce the glucose and arabinose concentration, as well as the experimental results for solid yield with errors less than 20% at worst (< 10-12% in 90-95% of all cases). Good content values of glucose (5.33%) and arabinose (2.76%), and an acceptable value of the solid fraction yield (57.96%) were obtained operating with following values of temperature, time, liquid/solid ratio, and sulfuric acid concentration: 186ºC, 18 min, 7:1, and 0.1%, respectively. With these values are saved, with respect to the use of higher values for operating variables, 2.1% energy, 80% sulfuric acid, and more than 10% of capital facilities. Residual fraction of olive tree prunings (leaves and stems with a diameter < 1 cm) had a heating value of 18699 kJ/kg, a flame temperature of 1207-2234 ºC, and a dew point temperature of combustion gasses of 45-53 ºC.

Keywords: Biorefinery; Olive tree prunings; Hydrothermal treatment; Hemicellulose; Sugars; Combustion

*Contact information: a: Chemical Engineering Department, Campus de Rabanales, Building Marie Curie (C-3), University of Córdoba, 14071 Córdoba, Spain; b: Chemical Engineering Department. University of Huelva, Spain. * Corresponding author: a.rodriguez@uco.es*

INTRODUCTION

The utilization of the main components of the lignocellulosic materials can be implemented by following various procedures commonly associated with the concept of "biorefinery" (Thorp 2005; Yawalata and Paszner 2006; Van Heinigen 2006; Kelley 2007; Towers et al. 2007; Sjoede et al. 2007; Larson et al. 2008). The biorefinery or fractionation of agricultural residues is especially interesting, since it endows an added value and provides an environmental benefit derived from the suppression of a polluting source (Sasaki et al. 2003; Garrote et al. 2007a; Sakaki et al. 2006; Caparrós et al. 2008a; Jiménez et al. 2008; Kadam et al. 2008). Fractionating agricultural residues such as olive tree prunings would be highly attractive in olive-producing countries such as Spain, especially if one considers that the resulting residues have traditionally been eliminated by on-site ashing, and this practice has recently been banned.

The amount of this residue in Spain is more than 5.7 million tons per year (Jiménez and Rodríguez 2010). The price is low and represents only the cost of collection and transport, making it potentially attractive for use in processes for the use of its components.

One potentially effective alternative fractionation procedure involves treating the target materials hydrothermally in order to depolymerise hemicelluloses by autohydrolysis. This produces an aqueous fraction essentially containing hemicellulose sugars consisting of xylo-oligosacharides and monosaccharides (xylose, glucose, arabinose), which can be used for various purposes (Focher *et al.* 1998; García-Jaldón *et al.* 1998; Sakaki *et al.* 2006; Vázquez *et al.* 2007; Jiménez *et al.* 2008; Gullon *et al.* 2008). In addition it produces a solid fraction composed largely of lignin and cellulose, and potentially amenable to pulping or to produce bioethanol through the process of saccharification and fermentation (Sasaki et al. 2003; Garrote et al. 2003; López et al. 2004; Caparrós et al. 2008a; Jiménez et al. 2008; Kadam et al. 2008; Sjoede et al. 2007).

Hydrothermal treatments can be conducted over wide ranges of operating conditions (Garrote *et al.* 2007*b*; Vegas *et al.* 2008). In a weakly acidic media, they cause ether bonds in lignin to break above 160–180 °C; the treatment time can also vary widely (from a few seconds to several hours); the liquid/solid ratio from 2 to 40 g water/g material; the pH has a strong influence on cellulose degradation; and particle size ranges from 0.5 to 10 mm in laboratory tests (Jiménez et al. 2008; Sundqvist et al. 2006; Jiménez 2008).

Many non-wood raw materials contain fractions unsuitable for the production of sugars and/or pulp, such as those formed by leaves, bark, pith, and young stems, which contain relatively little α-cellulose content. However, these fractions, which can be called waste, can be exploited through the application of physical-chemical or biochemical processes, for the conversion of chemical energy into other forms that are simpler and easier to use (Rodriguez et al. 2010). The use of all fractions of a lignocellulosic material can be also called biomass biorefinery, which uses all the raw material (Towers et al. 2007; Kelley 2007).

The easiest physical-chemical process for the exploitation of lignocellulosic materials is combustion. The residual biomass of forests and agricultural waste (straw, stalks, stems, leaves, etc.) has been widely used as fuel for producing heat for heating or for producing steam or electricity in small industrial plants. These waste materials are at present still interesting as energy sources, using them in combustion processes (Nieblas et al. 1990; Rey et al. 1993; Arvelakis and Kouki 2020; Ozturk and Bascetinlik 2006; Overend and Wright 2008).

The aim of this study was to evaluate the optimal use of olive tree prunings, separating it into two parts: a main one, consisting of wood, and a residual one, formed by the leaves and young stems. The main fraction was subjected to a hydrothermal treatment, with and without acid catalyst, studying the influence of operating variables (viz. temperature, time and liquid/solid ratio or sulphuric acid concentration) on the composition of the resulting liquid fraction (glucose, xylose, arabinose and acetic acid) and solid yield of solid fraction. The residual fraction was used as fuel, determining the heating values, flame temperature, and dew point temperature of the combustion gases.

EXPERIMENTAL

Material

Olive tree prunings, directly from an olive tree forest, were separated into two fractions, with the following characteristics: a) main fraction, consisting of woody stems above 1 cm diameter, and b) residual fraction, consisting of leaves and stems with diameter less than 1 cm. Wood chips were used with a 30 x 3 mm size

Characterization of Olive Tree Prunings

The two fractions of the olive tree prunings were characterized chemically in accordance with the following procedures: holocellulose (TAPPI T9m-54), lignin (TAPPI T13m-59), ethanol-benzene extractives (TAPPI T6m-59), ash (TAPPI T15m-58), volatile components (UNE-32019), and fixed carbon (difference between 100 and the sum of ashes plus volatiles). Elemental analysis was made using the Dumas method with a Eurovector EA 3000. The raw material was subjected to extraction and quantitative acid hydrolysis (TAPPI T249-cm-85) to determine the sugar content, using a refractive index detector and an Aminex HPX-87H column, eluted with 0.01 mol L^{-1} H_2SO_4 at a flow rate of 0.6 mL min^{-1}.

Hydrothermal Treatment

The amounts of main fraction of olive tree prunings and water required to obtain an appropriate liquid/solid ratio was placed in a 15 L batch reactor that was heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating the reaction vessel via a motor connected through a rotary axle to a control unit including the required instruments for measurement and control of pressure and temperature. Once the mixture was heated at the selected temperature for the indicated time, the reactor was depressurized, and the liquid and solid fractions were separated for subsequent treatment or analysis.

Characterization of the Fractions of the Hydrothermal Treatment

The glucose, xylose, arabinose, and acetic acid contents of the liquid fraction provided by the hydrothermal treatment were determined as follows: an amount of 10 to 20 g of liquid fraction was placed in a 100 mL ISO bottle and supplied with sulphuric acid to a 4 % concentration by weight. Then, the bottle was autoclaved at 121 °C for 20 min, and cooled to room temperature with water, and its contents analysed by HPLC.

Pulp yield was determined by weighing, after removing the uncooked material.

Experimental Design

In the study of hydrothermal treatment, using three independent variables [*viz.* temperature (*T*), time (*t*), and liquid/solid ratio (*R*) or sulphuric acid concentration (*S*)], it was used a central composite factorial design, which places the experiments (points) in a cube: one in the center, 8 vertices and 6 faces (Montgomery 1991). The total number of tests required for the three independent variables studied was found to be 15.

The values of the independent variables were normalized by using the following equation in order to facilitate direct comparison of coefficients and expose the individual effects of the independent variables on each dependent variable,

$$X_n = 2 \frac{X - \bar{X}}{X_{max} - X_{min}} \quad (1)$$

where X_n is the normalized value of T, t, R, or S; X is the absolute experimental value of the variable concerned; $\bar{X}$ is the mean of the extreme values of X; and X_{max} and X_{min} are its maximum and minimum value, respectively. The normalized values used are presented in Tables 2 and 3.

Experimental data were fitted to a second-order polynomial, which relates each dependent variable (glucose, xylose, arabinose, acetic acid, and solid yield) with the operational variables (temperature, time and liquid/solid ratio or sulphuric acid concentration).

Heating Value

The calorific values were determined according to EN/TS 14918:2005 (E) Solid biofuels method, and UNE 164001 EX standards by using a Parr 6200 Isoperibol Calorimeter.

RESULTS AND DISCUSSION

Raw Material Characterization

Table 1 shows the results of elemental analysis and analysis of the main components of the main and residual fractions of olive tree pruning. The carbon content of the main fraction was higher than those of other agricultural residues (from 42.5 to 46.2% for sunflower stalks, cotton stalks, wheat straw, and vine shoots). By contrast, the content of carbon for the residual fraction was lower than those of the considered agricultural residues, except in the case of sunflower. The hydrogen content of both fractions was higher than those of sunflower stalks (5.9%) and similar to those of other agricultural residues considered (6.1 to 6.4%). The nitrogen content of the main fraction was less than the mentioned agricultural residues (0.5 to 1.3%); for the residual fraction the nitrogen content was similar to that of wheat straw (0.5%) and lower than those of other agricultural wastes considered. Finally, the sulfur content was low, as in the agricultural residues studied (Jimenez et al. 1991)

The holocellulose content of the olive tree prunings was higher than those agricultural residues considered (60.8 to 64.1%), higher than for agro-industrial residues (60.3 and 64.1% for sunflower seed husk and olive marc), higher than those of eucalyptus residues (61.8%), and similar to olive stones (67.6%) and holm oak residues (66.4%). The lignin contents were similar to those of cotton stalks (18.3%), eucalyptus residues (17.9%), sunflower seed husk (17.3%), and olive stones (19.1%); higher than those of wheat straw (14.5%), sunflower stalks (14.1%), olive marc (13.3%), and holm oak

residues (13.9%); and lower than those of vine shoots (21.6%). Extractable contents were lower than those of the materials considered (13.4 to 17.9%), except in the case of olive stones (12.2%) which is similar to the fraction from olive tree pruning. The ash content was lower than those of most of the materials considered (3.7 to 9.5%) and the order of olive stones, holm oak and eucalyptus residues (1.1 to 2.4%). The volatile contents were similar to those of holm oak residues (80.6%) and higher than those of other materials considered (69.5 to 75.5%). Finally, the fixed carbon content of the main fraction was similar to wheat straw (18.6%), cotton stalks (20.3%), and seed husk sunflower (19.3%), higher than those from sunflower stalks (15.9%) and holm oak residues (17.6%), and lower than those of the other materials considered (21.5 to 25.8%). In the case of the residual fraction, the fixed carbon was less than the materials considered (Jiménez and González 1991).

Results obtained for glucan, xylan, and arabinan content (33.8 %, 16.6% and 2.01%, respectively) were in agreement with reported results (Cara et al. 2008).

Table 1. Elemental Analysis and Components Analysis of Olive Tree Prunings

Parameter	Main fraction	Residual fraction
Carbon, %	50.11	44.18
Hydrogen, %	6.66	6.25
Nitrogen, %	0.19	0.51
Sulfur, %	0.04	0.03
Holocellulose, %	69.23	66.11
Lignin, %	19.51	17.53
Extractives, %	9.00	12.49
Ash, %	1.18	3.59
Volatile, %	79.91	81.42
Fixed carbon, %	18.91	14.99

Hydrothermal Treatment Without Catalyst

The main fraction of olive tree pruning was used. The values of the operational variables used in the 15 tests required by the experimental design used were as follows: 150 to 190 °C for temperature (4.5 to 15.5 atm), 0 to 20 min treatment time (as the time elapsed after the operating temperature was reached (heating rate is 10ºC / min), and 6-8 as liquid/solid ratio. The values of the independent variables and their respective normalized values are shown in Table 2. The choice of the values of operating variables was done considering the values used for similar materials: paulownia (Caparrós et al. 2008b), corn stalks (Tortosa et al. 1995), wheat straw (Kubikova 1996), vine shoots (Jiménez et al. 2006), *Arundo donax* (Caparrós et al. 2007), sunflower stalks (Caparrós et al. 2008a), legumes (Alfaro et al. 2009) *Sabastian grandiflora* (Yañez et al. 2009), bagasse from sugar cane (Boussarsar 2009), rice straw (Rodríguez et al. 2009), and *Hesperaloe funifera* (Sánchez et al. 2011).

Table 2 also shows the results of the tests as the averages of three determinations per dependent variables related to the liquid fraction and solid yield of solid fraction obtained in each test. The values found are in the range of those published by the authors mentioned above. Carrying out an acid hydrolysis step makes it possible to obtain a liquid fraction rich in sugars that can be used in the pharmaceutical and/or alimentary industry at the same time getting a solid fraction rich in cellulose that can be used later to obtain cellulosic fibers or to produce bioethanol

A multiple regression analysis of the experimental results with selection of the statistically significant terms in the polynomial model used (viz. those having a Snedecor F-value greater than 2) provided the following equations,

$$GL = 1.57 + 1.05X_T + 0.54X_t + 1.20\,X_T^2 + 0.27X_R^2 - 0.32X_TX_R - 0.31X_tX_R \quad (R^2 = 0.98;\ F > 4.12;\ p < 0.0769;\ t > 2.03) \quad (2)$$

$$AR = 1.00 + 0.68X_T + 0.52X_t - 0.08X_R + 0.34X_T^2 + 0.27X_t^2 + 0.35X_R^2 - 0.43X_TX_t \quad (R^2 = 0.99;\ F > 4.57;\ p < 0.0698;\ t > 2.14) \quad (3)$$

$$YI = 72.16 - 8.21X_T - 5.64X_t - 4.18X_R \quad (R^2 = 0.84;\ F > 8.89;\ p < 0.0125;\ t > 2.98) \quad (4)$$

where GL is the glucose concentration, AR the arabinose concentration, YI the solid yield (including uncooked material), and X_T, X_t, and X_R the normalized values of the temperature, time process and liquid/solid ratio, respectively. These equations reproduced the experimental values for the glucose concentration, arabinose concentration, and solid yield with errors less than 18, 15, and 10%, respectively. It was found that for the glucose and arabinose concentration, 90% of the results had an error less than 12%. For cases of xylose concentration and acetic acid concentration, the obtained equations reproduced the experimental results with very high errors, so those results were not suitable for the simulation of values of these dependent variables during the hydrothermal treatment of the main fraction of the olive tree pruning

The polynomial models derived for the glucose and arabinose concentration and solid yield were similar to those previously obtained for eucalyptus, tagasaste, sunflower stalks, and rice straw (Gilarranz et al. 2000; Garrote et al. 2003; López et al. 2004; Caparrós et al. 2008; Rodríguez et al. 2009).

By using equations 1 to 3 we can to identify the values of the independent variables leading to the maximum possible values of the dependent variables. It was found that obtaining high values of glucose concentration and arabinose concentration entailed using high values of operational variables. On the other hand, ensuring high solid yield required using low values of operational variables.

By using Eqs. 2 to 4 we identified that the operational variable most strongly influencing the dependent variables was the temperature; the liquid/solid ratio was the least influencing in the cases of glucose concentration and solid yield, and the time the least influencing in the arabinose concentration.

On the other hand, the influence that temperature has on the xylose and acetic acid concentration also can be observed (Table 2), by comparison the values of experiments performed under identical conditions of time and liquid/solid but a different temperature. It is apparent that the concentrations of xylose and acetic acid increased with increasing temperature (compare data of xylose and acetic acid concentration from the experiments 3 and 2; 7 and 6; 9 and 8; 5 and 4; 15 and 14; and 15 and 1). Also note in Table 2, comparing experiments to the temperature and liquid/solid identical, but at different times, that the concentrations of xylose and acetic acid increased with increasing time (compare data the experiments 6 and 2; 7 and 3; 8 and 4; 9 and 5; 11 and 10; and 11 and 1). When comparing experiments performed under identical conditions of temperature and time but with different liquid/solid ratio, it was found that the xylose and acetic acid concentration decreased with increasing liquid/solid ratio (compare data from the experiments 4 and 2; 5 and 3; 8 and 6; 9 and 7; 13 and 12; and 13 and 1); this is logical for the highest dilution of the liquid fractions resulting from hydrothermal treatment.

It follows that it is required operate with high values of operation variables to obtain high values of the concentrations of xylose and acetic acid. Also from the above comparisons it can be deduced that the most influential variable in acetic acid and xylose concentration was the temperature and that the liquid/solid ratio had less influence.

Table 2. Composition of Liquid Fraction and Solid Yield of Solid Fraction Resulting from Hydrothermal Treatment without Catalyst

X_T, X_t, X_R	T, t, R,	Glucose, g/L	Xylose, g/L	Arabinose, g/L	Acetic acid, g/L	Solid yield, %
0, 0, 0	170,10,7	1.64	1.15	1.17	0.19	71.10
1, 1, 1	190,20,8	4.11	8.14	2.72	1.13	58.52
-1, 1, 1	150,20,8	2.42	2.13	2.19	0.32	65.15
1, 1, -1	190,20,6	5.54	9.60	2.82	1.33	59.27
-1, 1, -1	150,20,6	2.49	3.21	2.35	0.42	75.75
1, -1, 1	190,0,8	3.43	5.93	2.42	0.52	59.70
-1, -1, 1	150,0,8	2.01	0.17	0.22	0.03	79.43
1, -1, -1	190,0,6	3.54	6.67	2.60	0.76	71.22
-1, -1, -1	150,0,6	0.93	0.25	0.40	0.05	88.78
0, 1, 0	170,20,7	2.01	1.20	1.59	0.29	67.04
0, -1, 0	170,0,7	1.25	0.41	0.85	0.10	82.97
0, 0, 1	170,10,8	1.56	0.82	1.21	0.10	70.19
0, 0, -1	170,10,6	1.90	1.16	1.40	0.21	79.80
1, 0, 0	190,10,7	3.51	1.84	1.98	0.29	65.90
-1, 0, 0	150,10,7	1.82	0.37	0.60	0.09	87.59

X_T, X_t, X_R = Normalized values of temperature, time and liquid/solid ratio, respectively
T,t,R = values of temperature (ºC), time (minutes) and liquid/solid ratio (g/g), respectively

Hydrothermal Treatment with Acid Catalyst

Table 3 shows the operating conditions of the 15 experiments in the experimental factorial design applied to main fraction of olive tree prunings hydrothermal treatment using sulfuric acid as catalyst (0.1 to 0.5% odm), and with a value of 7 for the liquid/solid ratio. Also shown in Table 3 are the experimental results obtained in the characterization of liquid fraction and solid yield of solid fraction resulting from the application of hydrothermal treatments. As happened in the study of main fraction of olive tree prunings

hydrothermal treatment without catalyst, in this case the polynomial model did not provide adequate equations to reproduce the experimental values of the xylose and acetic acid concentration. For the remaining dependent variables the following equations were obtained,

$$GLs = 2.55 + 1.64\ X_T + 1.10X_t + 0.78X_S + 1.03X_t^2 + 0.71X_S^2 \quad (R^2 = 0.92;\ F > 2.84;\ p < 0.1264;\ t > 1.68) \quad (5)$$

$$ARs = 1.77 + 0.59X_T + 0.65X_t + 0.48X_S + 0.65X_T^2 + 0.10X_TX_t \quad (R^2 = 0.97;\ F > 2.21;\ p < 0.1714;\ t > 1.49) \quad (6)$$

$$YIs = 62.29 - 5.32X_T - 4.44X_t - 3.48X_S \quad (R^2 = 0.81;\ F > 9.49;\ p < 0.0105;\ t > 3.08) \quad (7)$$

where GLs is the glucose concentration, ARs the arabinose concentration, YIs the solid yield, and X_T, X_t, and X_S are the normalized values of the temperature, time of processing, and sulfuric acid concentration, respectively. These equations reproduced the experimental values for the glucose concentration, arabinose concentration, and solid yield with errors less than 20, 18, and 10%, respectively. It was found for arabinose concentration that 95% of the results had an error less than 10%.

Table 3. Composition of Liquid Fraction and Solid Yield of Solid Fraction Resulting from Hydrothermal Treatment with Catalyst

X_T, X_t, X_S	T, t, S	Glucose, g/L	Xylose, g/L	Arabinose, g/L	Acetic acid, g/L	Solid yield, %
0, 0, 0	170,10,0.3	3.19	2.24	1.86	0.19	62.65
1, 1, 1	190,10,0.5	7.01	11.33	4.44	1.25	51.78
-1, 1, 1	150,20,0.5	5.03	6.80	2.75	0.63	54.39
1, 1, -1	190,20,0.1	6.95	11.22	3.30	1.18	52.12
-1, 1, -1	150,20,0.1	3.13	1.46	1.92	0.14	66.74
1, -1, 1	190,0,0.5	6.68	11.10	2.76	0.82	53.58
-1, -1, 1	150,0,0.5	2.21	0.71	1.77	0.09	67.20
1, -1, -1	190,0,0.1	3.39	2.11	1.98	0.17	65.68
-1, -1, -1	150,0,0.1	0.86	0.27	0.72	0.02	71.99
0, 1, 0	170,20,0.3	4.10	2.97	2.36	0.31	59.50
0, -1, 0	170,0,0.3	2.09	0.46	1.06	0.04	70.48
0, 0, 1	170,10,0.5	3.40	2.68	2.29	0.24	62.63
0, 0, -1	170,10,0.1	2.16	0.66	1.27	0.06	67.82
1, 0, 0	190,10,0.3	4.50	6.25	2.55	0.48	55.89
-1, 0, 0	150,10,0.3	0.91	0.51	1.95	0.02	71.93

X_T, X_t, X_S = Normalized values of temperature, time and sulphuric acid concentration, respectively
T, t, S = values of temperature (ºC), time (minutes) and sulphuric acid concentration (%), respectively

By a similar procedure for the experiments performed before in the hydrothermal treatment without catalyst, in the case of hydrothermal treatment with acid catalyst it can be deduced that to achieve high values of glucose, xylose, arabinose, and acetic acid concentrations one should operate with high values of operating variables. On the other hand, if a high yield value is required, is necessary to operate with low values of

operating variables. The most influential variable over the composition of the liquid fraction and the yield of the solid fraction was the temperature, and the least was the sulfuric acid concentration.

Selection of Operating Conditions

Comparing Eqs. 2 to 4 with Eqs. 5 to 7, and the xylose concentration values from the Tables 1 and 2, corresponding to the results of composition of liquid and solid fractions of hydrothermal treatment with and without catalyst, respectively, one can deduce that by using sulfuric acid as catalyst:

a) The maximum level of glucose increased by 48.5%: from 5.26% to 7.81%.
b) The maximum levels of xylose increased by 18.0%: from 9.60% to 11.33%.
c) The maximum levels of arabinose increased by 50.9%%: from 2.81% to 4.24%.
d) The maximum yields decreased from 90.19% to 75.53%: a 16.3% change.
e) The minimum yields decreased from 54.13% to 49.05%: a 9.4% change.

These results suggest that it is appropriate to use sulfuric acid, because the sugars content of the liquid fraction obtained in the hydrothermal treatment were considerably higher than when the acid was not added. But the yield of the solid fraction decreased and thus the possible production of cellulosic pulp or ethanol also would be reduced, if this was the purpose for the solid fraction

In order to find the best possible compromise between efficient use of the raw material (viz. a good solid yield for the solid fraction) and rich composition of the liquid fraction, the next procedures were followed: Eqs. 5 to 7 were used to simulate different cases, as presented in Table 4 (cases C to K). The first two cases in Table 4 represent operating without sulfuric acid: in the A case it is operated to achieve maximum values of sugars, and in B for maximum yield of the solid fraction.

The operating conditions of the cases C to K were chosen so as to obtain glucose and arabinose concentrations near to the possible maximum without using acid catalyst (case A) and values of the yield of the solid fraction not too low. These operating conditions represent not very high values of temperature, time, liquid/solid ratio, and sulfuric acid concentration. The goal of using these moderate values is to save energy for heating, sulfuric acid and capital facilities, with respect to the case of using the highest values of operating variables.

An interesting case may be E, because it operates with values of temperature (186 º C) and time (18 min) lower than the maximum (190 º C and 20 min, respectively), a liquid/solid ratio (7:1), and low sulfuric acid concentration (0.1%), getting good values for the sugars contents and an acceptable value of solid fraction yield. With these values are saved, with respect to the use of higher values for operating variables, 2.1% energy, 80% sulfuric acid, and more than 10% of capital facilities.

Comparing the results of cases E and G shows that an increase in the sulfuric acid concentration produced an increase in sugars concentration, but a decrease in yield.

Moreover, operating with values of temperature and time lower than those used in case C made it possible to obtain lower values of sugars contents, and the values of yield did not increase too much (cases I to K).

Table 4. Simulation of Composition of Liquid Fraction and Solid Yield of Solid Fraction in the Hydrothermal Treatment from Olive Tree Prunings

Cases	Glucose,g/L	Arabinose, g/L	Solid yield, %
A: Maximum concentration of sugars without catalyst (Eqs. 1 y 2) $X_T = 1$; $X_t = 1$; $X_R = -1$	5.25	2.81	62.49
B: Maximum value of solid yield without catalyst (Eq. 3) $X_T = -1$; $X_t = -1$; $X_R = -1$	0.82	0.41	90.19
C: Eqs 4 to 6 $X_T = 1$; $X_t = 0.75$; $X_R = 0$; $X_S = -1$	5.52	3.09	57.12
D: Eqs. 4 to 6 $X_T = 0.75$; $X_t = 1$; $X_R = 0$; $X_S = -1$	5.84	2.82	57.34
E: Eqs 4 to 6 $X_T = 0.80$; $X_t = 0.80$; $X_R = 0$; $X_S = -1$	5.33	2.76	57.96
F: Eqs 4 to $X_T = 0.75$; $X_t = 0.75$; $X_R = 0$; $X_S = -1$	5.11	2.64	58.45
G: Eqs 4 to 6 $X_T = 0.80$; $X_t = 0.80$; $X_R = 0$; $X_S = 0$	5.40	3.24	54.48
H: Eqs 4 to 6 $X_T = 0.75$; $X_t = 0.75$; $X_R = 0$; $X_S = 0$	5.18	3.12	54.97
I: Eqs. 4 to 6 $X_T = 0.75$; $X_t = 0.5$; $X_R = 0$; $X_S = -1$	4.52	2.46	59.56
J: Eqs. 4 to 6 $X_T = 0.5$; $X_t = 0.75$; $X_R = 0$; $X_S = -1$	4.70	2.27	59.78
K: Eqs 4 to 6 $X_T = 0.50$; $X_t = 0.50$; $X_R = 0$; $X_S = -1$	4.11	2.10	60.89

Combustion Process

Heating values

Table 5 presents the experimental results of the heating values of the two factions of the olive tree prunings. These values are of the same magnitude as those found in the literature (Jiménez et al. 1991; Jiménez and González 1991) for different lignocellulosic materials (wheat straw, sunflower stalks, vine shoots, cotton stalks, olive stones, olive marc, holm oak residues, and eucalyptus residues).

In the literature (Jiménez et al. 1991, Jiménez and González 1991) empirical equations are found that predict the heating values (HV, kJ/kg) of lignocellulosic materials,

$$HV = 393.81\ C + 230.22 \quad (8)$$

$$HV = 436.66\ C - 305.51 \quad (9)$$

$$HV = 173.89\ Ce + 266.29\ L + 321.87\ E \quad (10)$$

$$HV = 173.89\ Ce + 266.29\ (100\text{-}Ce') \quad (11)$$

$$HV = (1 - A/(Ce + L + E))\ (173.89\ Ce + 266.29\ L + 321.87\ E) \quad (12)$$

$$HV = 339.82\ T - 14308.93 \quad (13)$$

$$HV = 313.30\ T - 10814.08 \quad (14)$$

where C is the total carbon content (%), Ce, L, E, and Z are the contents of cellulose, lignin, extractives, and ash (all in%), Ce' is the cellulose content on free base of extractives (%), and T is the sum of the contents of volatile and fixed carbon.

Table 5. Heating Values of the Fractions of Olive Tree Prunings Determined Experimentally and by Equations 8 to 14; Errors Compared to Recent Experiments

Heating values, KJ/Kg	Main Fraction	Residual Fraction
Experimental	19110	18699
Calculated Eq.8	19964 (4.47%)	17629 (5.72%)
Calculated Eq.9	21576 (12.90%)	18986 (1.54%)
Calculated Eq.10	20131 (5.34%)	20184 (7.94%)
Calculated Eq.11	18408 (3.67%)	18007 (3.70%)
Calculated Eq.12	19888 (4.07%)	19430 (3.91%)
Calculated Eq.13	18766 (1.80%)	17947 (4.02%)
Calculated Eq.14	20146 (5.42%)	19391 (3.70%)

By applying the experimental data of Table 1 in Equations 8 to 14, the values of the heating values presented in Table 5 were obtained, also showing the values of the errors in these estimates for the experimental values.

As noted, Eqs. 11-13 are the ones that best reproduced the values of the heating values of the olive tree prunings (with errors less than 4%).

Flame temperature and dew point temperature

Using the elemental analysis of the orange tree pruning (Table 1) and following the estimation techniques described in the literature (Jiménez et al. 1991) the values of flame temperature (1094 to 2234 ºC) (Table 6) and dew point temperature (45 to 53 ºC) (Table 7) were determined for different values of excess air used in combustion (10 to 50%). The values of the flame temperature and dew point were of the same magnitude as those of other lignocellulosic materials (wheat straw, sunflower stalks, vine shoots and cotton stalks) (Jiménez et al. 1991).

The high values of flame temperature, for all materials considered, demonstrate the possibility of using these materials in the production of steam.

The dew point was low for combustion gases of all materials tested, thus avoiding condensation in chimneys and flue pipes, preventing corrosion that could cause condensation; anyway, in the event of such condensation, the phenomenon is expected not to be very serious given the low sulfur content of the material considered. This is an additional advantage associated with the clean nature of these fuels.

Comparison of cost of the heat units obtained by combustion

Table 8 compares the heating values, unit cost of the fuel and cost of the heat units obtained by combustion of the different fuels. As can be seen, the MkJ of energy obtained by combustion of olive tree prunings is cheaper than that obtained from mineral coal and much cheaper than that obtained from liquid fossil fuels. Moreover, we should emphasize some of the advantages of the lignocellulosic residues studies: they are renewable and release very small amounts of sulfur dioxide in combustion gases and smaller amounts of ash than the solid fossil fuel. Such attributes mean that lignocellulosic residues tend to be good competitors with fossil fuels for non-transportation applications.

Table 6. Values of Flame Temperature in Combustion of Orange Tree Pruning

Heat loss %	Excess air in the combustion, %	Main Fraction T, ºC	Residual Fraction T, ºC
10	10	2013	2234
	20	1910	2122
	30	1818	2023
	40	1737	1934
	50	1664	1854
20	10	1840	2040
	20	1747	1938
	30	1664	1849
	40	1591	1768
	50	1525	1696
30	10	1664	1842
	20	1581	1752
	30	1508	1672
	40	1442	1600
	50	1384	1536
40	10	1485	1641
	20	1413	1562
	30	1349	1492
	40	1292	1429
	50	1240	1373
50	10	1303	1436
	20	1241	1368
	30	1186	1309
	40	1138	1255
	50	1094	1207

Table 7. Values of Dew Point Temperature in Combustion of Orange Tree Pruning

Excess air in the combustion, %	Main Fraction T, ºC	Residual Fraction T, ºC
10	50.6	52.6
15	49.8	51.8
20	49	51.1
25	48.3	50.4
30	47.5	49.7
35	46.9	49
40	46.3	48.4
45	45.6	47.8
50	45	47.2

Table 8. Comparison of Heating Values and Energy Costs Obtained by Combustion of Various Fuels

Fuel	Heating values, MkJ/t*	Cost of fuel, €/t	Cost of the unit of heat, €/MkJ
Main fraction of olive tree prunings	19.11	60	3.14
Residual fraction of olive tree prunings	18.70	60	3.20
Coal	25.94	100	3.86
Heating oil	37.67	800	21.24
Commercial propane	43.89	1650	37.59

*millions of kJ/t

CONCLUSIONS

Polynomial equations were found reproduce the composition of the liquid fraction (glucose and arabinose) and solid yields of solid fractions obtained by hydrothermal treatment of main fraction of olive tree prunings with errors less than 20%, in all cases (10-12% lower in 90-95% of cases).

The highest possible glucose, xylose, arabinose, and acetic acid concentrations in liquid fraction were obtained by using 190ºC, 20 minutes, a liquid/solid ratio of 9, and 0.5% of sulphuric acid concentration. On the other hand, to obtain high yield of solid fraction requires the use of low values of operational variables (150ºC, 0 min, liquid/solid ratio of 6:1, and 0.1% sulphuric acid concentration).

Based on the polynomial equations found to simulate the hydrothermal treatment of main fraction of olive tree prunings, it was concluded that by operating with values of temperature (186 ºC) and time (18 min) lower than the maximum (190 ºC and 20 min, respectively), a liquid/solid ratio (7:1) and low sulfuric acid concentration (0.1%), it is possible to obtain good values for the glucose and arabinose content (5.33% and 2.76%, respectively) and an acceptable value of solid fraction yield (57.96%) saving, with respect to the use of higher values for operating variables, 2.1% energy, 80% sulfuric acid, and more than 10% of capital facilities.

The residual fraction of olive tree prunings had a heating values of 18699 kJ/kg, a flame temperature of 1207 to 2234 ºC, and a dew point temperature of combustion gasses of 45 to 53 ºC (considering different heat losses and various excess air in the combustion). On the other hand, the price of kJ obtained by combustion of this residual fraction is less than that of coal and much lower than those of liquid fossil fuels.

ACKNOWLEDGMENTS

The authors are grateful to Ecopapel, S.L. (Écija, Sevilla, Spain) and ENCE (Huelva, Spain) for their support, to Spain's DGICyT and Junta de Andalucía for funding this research within the framework of the Projects CTQ 2010-19844-C02-01, TEP-6261 and TRA-2009_0064.

REFERENCES CITED

Alfaro, A., Rivera, A., Pérez, A., Yáñez, R., García, J. C., and López, F. (2009). "Integral valorization of two legumes by authohydrolysis and organosolv delignification," *Bioresource Technol*. 100(1), 440-445.

Arvelakis, S., and Koukios, E. G. (2002). "Physicochemical upgrading of agroresidues as feedstocks for energy production via thermochemical conversion methods," *Biomass Bioenerg.* 22(5), 331-348.

Boussarsar, H., Rogé, B., and Mathlouthi, M. (2009). "Optimization of sugarcane bagasse conversión by hydrothermal treatment for the recovery of xylose," *Bioresource Technol*. 100(24), 6537-6542.

Caparrós, S., Ariza, J., López, F., and Díaz, M. J. (2007). "Optimizing cellulosic paper obtained from *Arundo donax* under hydrothermal treatment," *J. Ind. Eng. Chem*. 13(3), 465-473.

Caparrós, S., Ariza, J., López, F., Nacimiento, J.A., Garrote, G., and Jiménez, L. (2008a). "Hydrothermal treatment and ethanol pulping of sunflower stalks," *Bioresource Technol.* 99, 5, 1368-1372.

Caparrós, S., Díaz, M. J., Ariza, J., López, F., and Jiménez, L. (2008b). "New perspectives for *Paulownia fortunei* L. Valorisation of the autohydrolysis and pulping processes," *Bioresource Technol*. 99 (4), 741-749.

Cara, C., Ruíz, E., Oliva, J. M., Sáez, F., and Castro, E. (2008). "Conversion of olive tree biomass into fermentable sugars by dilute acid pretreatment and enzymatic saccharification," *Bioresource Technol.* 99, 1869-1876.

Focher, B., Marzetti, A., Beltrame, P. L., and Aella, M. (1998). "Steam exploded biomass for the preparation of conventional and advanced biopolymer-based materials," *Biomass Bioenerg* 14, 187-194.

García-Jaldon, C., Dupeyre, D., and Vignon, M. R. (1998). "Fibres from semi-retted hemp bundles by steam explosion treatment," *Biomass Bioenerg* 14, 251-260.

Garrote, G., Eugenio, E., Díaz, M. J., Ariza, J., and López, F. (2003). "Hydrothermal and pulp processing of eucalyptus," *Bioresource Technol.* 88(1), 61-68.

Garrote, G., Falque, E., Domínguez, H., and Parajó, J. C. (2007a). "Autohydrolysis of agricultural residues: Study of reaction byproducts," *Bioresource Technol.* 98, 1951-1957.

Garrote, G., Kabel, M. A., Schols, H. A., Falque, E., Domínguez, H., and Parajó, J. C. (2007b). "Effects of *Eucalyptus globulus* wood autohydrolysis conditions on the reaction products," *J. Agr. Food. Chem.* 55(22), 9006-9013.

Gilarranz, A., Rodríguez, F., and Oliet, M. (2000). "Lignin behavior during the autocatalyzed methanol pulping of *Eucalyptus globules*," *Holzforschung* 54, 373-380.

Gullón, P., González-Muñoz, M. J., Domínguez, H., and Parajó, J. C. (2008). "Membrane processing of liquors from *Eucalyptus globulus* autohydrolysis," *J. Food. Eng.* 87(2), 257-265.

Jiménez, L., Angulo, V., de la Torre, M. J., Ramos, E., Caparrós, S., and Pérez, A. (2006). "Simulation of the hydrothermal treatment applied to the vine shoots, like previous stage in the cellulose pulp production," *Afinidad* 63(524), 277-285.

Jiménez, L., Bonilla, J. L., and González, F. (1991). "Physical and chemical characterization of agricultural wastes," *Afinidad* 48(431), 39-44.

Jiménez, L., Caparrós, S., and Ariza, J. (2008). "Autohydrolysis of hemicelluloses in the fabrication of pulp for paper," *Ingeniería Química* 462, 178-193.

Jiménez, L., and González, F. (1991). "Study of the physical and chemical properties of lignocellulosic residues with a view to the production of fuels," *Fuel* 70(8), 947-950.

Jiménez, L., and Rodríguez, A. (2010). "Valorization of agricultural residues by fractionation of their components," *The Open Agriculture Journal*, 4, 125-134.

Kadam, K. L., Chin, Ch. Y., and Brown, L.W. (2008). "Flexible biorefinery for producing fermentation sugars, lignin and pulp from corn stover," *J. Ind. Microbiol. Biot.* 35(5), 331-341.

Kelley, S. S. (2007). "Lignocellulosic biorefineries: Reality, hype or in between," *ACS Symposium Series* 954, 31-47.

Kubikova, J., Zemann, A., Krkosva, P., and Bobleter, O. (1996). "Hydrothermal pretreatment of wheat straw for the production of pulp and paper," *Tappi J*. 79(7), 163-169.

Larson, E. D., Consoni, S., Katofsky, R. E., Kristiina, L., and James, F. W. (2008). "An assessment of gasification-based biorefining at Kraft pulp and paper mills in the United States, Part A: Background and assumptions," *Tappi J.* 7(11), 8-14.

López, F., Alfaro, A., García, M. M., Díaz, M. J., Calero, A. M., and Ariza, J. (2004). "Pulp and paper from tagasaste (*Chamaecytisus proliferus L.F. ssp. palmensis*)," *Chem. Eng. Res. Des.* 82(A8), 1029-1036.

Montgomery, D. C. (1991). *Diseño y Análisis de Experimentos*, Grupo Editorial Iberoamericana, Mexico.

Nieblas, R., Rubio, A., Mendoza, V., and Bladimir, H. (1990). "Charaterization of sugarcane wastes as fuel," *Centro Azúcar* 17(3), 16-20.

Overend, R. P., and Wright, L. L. (2008). "Biomass energy," *Energy Conversion* 3(1/3), 18.

Ozturk, H. H., and Bascetinlik, A. (2006). "Energy, exploitation of agricultural biomass potential in Turkey," *Energ. Explor. Exploit.* 24(4), 313-330.

Rey, F. J., Martín, J., Villamanan, M. A., and San José, J. (1993). "Thermal analysis of agricultural residues with application to production of fuels," *J. Therm Anal.* 40(1), 239-247.

Rodríguez, A., Rosal, A., and Jiménez, L. (2010). "Biorefinery of agricultural residues by fractionation of their components through hidrotermal and organosolv processes," *Afinidad* 67(545), 14-19.

Rodríguez, A., Moral, A., Sánchez, R., and Jiménez, L. (2009). "Use of diethanolamine to obtain cellulosics pulps from solid fraction of hydrothermal treatment of rice straw," *Afinidad* 66(539), 60-66.

Sakaki, T., Yamada, N., Kumagai, S., Uehara, R., and Genta, M. (2006). "Hydothermolysis of agricultural waste," *AIChE Annual Meeting Conference Proceeding*, San Francisco, CA. United States, 11, 12-17.

Sánchez, R., Rodríguez, A., García, J. C., Rosal, A., and Jiménez, L. (2011). "Exploitation of hemicellulose, cellulose and lignin from *Hesperaloe funifera*," *Bioresource Technol.* 102, 1308-1315.

Sasaki, M., Adschiri, T., and Arai, K. (2003). "Fraction of sugarcane bagasse by hydrothermal treatment," *Bioresource Technol.* 86(3), 301-304.

Sjoede, A., Alriksson, B., Jaensson, L., and Nilvebrant, N. O. (2007). "The potential in bioethanol production from waste fiber sludges in pulp mill-based biorefineries," *Appl. Biochem. Biotech.* 137-140, 327-337.

Sundqvist, B., Westermark, U., and Erikkson, G. (2006). "Cellulose degradation during hydrothermal treatment of birch wood (*Betula pubescens* Ehrh.)," *Cell. Chem. Technol.* 40(3-4), 217-221.

Thorp, B. (2005). "Biorefinery offers industry leaders business model for major change," *Pulp and Paper* 79(11), 35-39.

Tortosa, J. F., Rubio, M., and Soler, A. (1995). "Auto-hydrolysis of corn stalks in aqueous medium," *Afinidad* 52(457), 305-311.

Towers, M., Browne, T., Kerekes, R., Paris, J., and Tran, H. (2007). "Biorefinery opportunities for Canadian pulp and paper industry," *Pulp and Paper Canada* 108(6), 26-29.

Van Heiningen, A. (2006). "Converting a Kraft pulp mill into an integrated forest biorefinery," *Pulp and Paper Canada* 107(6), 38-43.

Vázquez, M. J., Alonso, J. L., Domínguez, H., and Parajó, J. C. (2007). "Production and refining of soluble products from *Eucalyptus globulus* glucoronoxylan," *Collection of Czechoslovak Chemical Communications* 72(3), 307-320.

Vegas, R., Kabel, M., Schols, H. A, Alonso, J. L., and Parajó, J. C. (2008). "Hydrothermal processing of rice husks: Effects of severity of product distribution," *J. Chem. Technol. Biotechnol.* 83(7), 965-972.

Yáñez, R., Garrote, G., and Díez, M. J. (2009). "Valorisation of a leguminous specie, *Sebatia grandiflora*, by means of hydrothermal fractionation," *Bioresource Technol*. 100(24), 6514-6523.

Yawalata, D., and Paszner, L. (2006). "Characteristics of NAEM salt-catalyzed alcohol organosolv pulping as biorefinery," *Holzforschung* 60(3), 239-244.

Article submitted: September 22, 2011; Peer review completed: October 31, 2011; Revised version received and accepted: November 4, 2011; Published: November 7, 2011.