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Autohydrolysis Treatment of Olive Cake to Extract Fructose and Sucrose

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Abstract**—**The production of olive oil is considered as one of the most important agri-food industries. However, some of the by-products generated in the process are potential pollutants and cause environmental problems. Consequently, the management of these by-products is currently considered as a challenge for the olive oil industry. In this context, several technologies have been developed and tested. In this sense, the autohydrolysis of these by-products could be considered as a promising technique. Therefore, this study focused on autohydrolysis treatments of a solid residue from the olive oil industry denominated olive cake. This one comes from the olive pomace extraction with hexane. Firstly, a water washing was carried out to eliminate the water soluble compounds. Then, an experimental design was developed for the autohydrolysis experiments carried out in the hydrothermal pressure reactor. The studied variables were temperature (30, 60 and 90 ºC) and time (30, 60, 90 min). On the other hand, aliquots of liquid obtained fractions were analysed by HPLC to determine the fructose and sucrose contents present in the liquid fraction. Finally, the obtained results of sugars contents and the yields of the different experiments were fitted to a neuro-fuzzy and to a polynomial model.

Keywords**—**ANFIS, olive cake, polyols, saccharides.

I. Introduction

SPAIN is the world leader in olive oil production. In fact, an area of 1,500,000 hectares is occupied by olive trees in Andalucía. Therefore, the average production of virgin olive oil in Andalucía represents about 80% of national total amount [1], [2]. As a consequence, a high amount of by-products are generated. One of the most abundant wastes generated by this sector is the olive cake, which represents a 40.2% of the total amount of residues [3].

Olive cake is the solid residue that remains after the extraction of the olive oil from the olive pomace by a chemical process using hexane as solvent [3], [4].

Olive cake is composed of olive stone (30-45%), peel (15-30%) and fine solids of pulp (30-50%), expressed in dry basis. Furthermore, olive cake also presents contents in holocellulose (53 ∓ 10%), cellulose (26 ∓ 5%), hemicellulose (33.2 ∓ 0.8%), and lignin (40 ∓ 1%), as well as other by-products. Its moisture content varies between 9% and 12%, whereas its heating value is about 4,100 kcal/kg on dry basis, which is a high value for this kind of material [5], [6].

Olive cake is currently used to obtain heat for drying the olive pomace. In other cases, it is sold for power generation or cogeneration in biomass plants, thermal applications in industries and exportation [3]. However, the use of olive cake for energy purposes has the disadvantage of emitting a large amount of particles that exceed the established limits. Moreover, it generates benzopyrenes as a result of the high temperatures which are reached in combustion processes [5]. Consequently, due to its high potential of contamination, this study focused on the autohydrolysis treatment of olive cake. This treatment has a double objective: obtaining a solid with better properties than the initial one and extracting the value-added products [7].

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II. Methods and Materials

A. Raw Material

The material used in this study is olive cake with an average particle diameter of 0.96 mm. It was obtained in a company located in Jaén (Spain).

The previous characterization was carried out by Quesada et al. [9] and was based on Moreno et al. [8]. Afterwards, olive cake was treated by washing at 30ºC and for 1 h in order to perform the pressure autohydrolysis extraction. In this way, a solid with better properties than the initial one would be obtained because the heating value would be increased.

B. Hydrothermal Extraction in the High Pressure Reactor

Based on the previous results of the researching group, a design of experiments with different operating times and temperatures was carried out in a hydrothermal pressure reactor. The water/olive cake ratio was 20% so that to ensure an efficient mixing in the reactor. The reactor where the experiments were carried out was a high pressure reactor RS series model equipped with a turbine impeller with two double blades.

The obtained olive cake after of pressure autohydrolysis treatments was recovered by filtration to determine the gravimetric yield. On the other hand, aliquots of both autohydrolysis extractions were taken in order to obtain the value-added content by HPLC.

C. Sugars Determination

The chromatographic determination was carried out using an equipment HPLC Metrohm 940 professional IC Vario equipped with a column MetrosepCarb 2 250/4,0 under the following conditions: mobile phase, 100 mM of NaOH and 10 mM of NaAc; flow rate, 0.500 ml/s; and column temperature, 30ºC.

Sugar content was presented as the percentage of dissolved components with respect to total dissolved solids in the liquid (S %), (1):

$$S(\%)=\frac{[S]\cdot V\cdot F_h}{(1\text{-}R)\cdot M_t}\cdot 100 \quad (1)$$

where [S] is the dissolved saccharide concentration in the solution in mg/L, V is the total volume used in each experiment and F_h is the hydration factor, which is 162/180 for fructose and 324/342 for sucrose. R represents the gravimetric yield, which is expressed in rate per one and Mt is the total mass of olive cake used in each experiment.

D. Mathematical Models

A second factorial design was used with three levels because the operating conditions were: time (30, 60 and 90 minutes) and temperature (120, 140 and 160°C). This analysis required performing nine experiments with the objective of elucidating the influence of the two operational variables. The relationship between the dependent variables (% yield, fructose S% and sucrose S%) and the operational variables was established by using a neural-fuzzy model and a polynomial model [10].

E. Neural-Fuzzy Model

Neural-fuzzy model combines the advantages of fuzzy logic system and neural networks, and provides a powerful predictive tool based on (2) [11]-[13].

$$y_e=\frac{\sum_{l=1}^{m} y^l\cdot\left[\prod_{i=1}^{n}\mu_{F_i}^{l}\left(x_i,\theta_i^l\right)\right]}{\sum_{l=1}^{m}\left[\prod_{i=1}^{n}\mu_{F_i}^{l}\left(x_i,\theta_i^l\right)\right]} \quad (2)$$

where y_e is the estimated value of the property to be modelled, y^l is a constant, μ is a fuzzy rule, which is composed of Gaussian membership and a geometric criterion θ and x_i denotes the values of temperature and time. Gaussian membership function was used with three levels, low, medium and high, which are calculated using (3)-(5), respectively, for the two studied variables. Taking into account everything, the numerator and denominator would contain nine terms, respectively.

$$\mu(\text{low})=\exp\left(-0.5\cdot\left(\frac{x-x_{low}}{L}\right)^2\right) \quad (3)$$

$$\mu(\text{medium})=\exp\left(-0.5\cdot\left(\frac{x-x_{medium}}{L}\right)^2\right) \quad (4)$$

$$\mu(\text{high})=\exp\left(-0.5\cdot\left(\frac{x-x_{high}}{L}\right)^2\right) \quad (5)$$

where x is the absolute value of variable and L is the width of the Gaussian distribution. The parameters and constants in the previous equations were estimated by using the ANFIS (Adaptive Neural Fuzzy Inference System) edit tool in MATLAB software suite. ANFIS is a class of adaptive network, which is functionally equivalent to a diffuse inference system, whose principal objective is the optimization and prediction of the system behaviour [14].

F. Polynomial Model

On the other hand, a polynomial fitting was carried out with the values obtained in the nine experiments using Statgraphics software.

Experimental data were fitted to the following second-order polynomial (6):

$$Y=Y_0+Y_1T+Y_2t+Y_3T^2+Y_4t^2+Y_5Tt \quad (6)$$

where Y symbolizes variables of response (% yield, % fructose extract and % sucrose extract), T y t represent the normalized values of the independent variables (temperature and time) and Y_0-Y_5 are constants estimated by the model.

The independent variables values were normalized with values of -1, 0 and +1 applying the expression below (7):

$$X_n=2\,\frac{X-\bar{X}}{X_{max}-X_{min}} \quad (7)$$

where X_n is the normalized value of temperature and time, X is the absolute experimental value of the studied variable; x_{max} y x_{min} are the maximum and minimum values of the selected variable respectively and $\bar{x}$ is the average of x_{max} and x_{min}.

III. Results and Discussion

A. Fitting Carried Out by Mathematical Models

Table I presents the results of neural-fuzzy fitting for the yield, fructose and sucrose contents.

The S% was used in the case of sugar fittings because the concentration does not have a direct relationship with the operational variables. That parameter was calculated according to (1).

Table I shows that the experimental yield percentage and the calculated yield percentage by neural-fuzzy model is almost the same. The same tendency was observed in the case of the experimental and calculated fructose and sucrose percentages.

Table I shows that as the temperature increased the yield percentage decreased. The maximum yield percentage was obtained at a temperature of 120ºC and 60 minutes. However, this yield was too high in practical terms since it means that value-added products extraction was scarce. Nevertheless, for higher times the yield percentages were lower.

With regard to fructose percentages, the tendency was the same than the one obtained for the yield. The maximum S% was obtained at 120ºC and 60 minutes. Nonetheless, when temperature and time increased the S% of fructose decreased.

With respect to sucrose S%, the maximum extraction was obtained at 160ºC and 90 minutes. This indicated that the sucrose extraction was different compared to the yield and fructose percentages. Table I shows that in this case the S% was lower for temperatures and times littler than the above mentioned.

This is possibly due to the fact that sucrose is a disaccharide that contains fructose. For that reason, the behaviour changed compared to the sugars that are monosaccharides.

Figs. 1 and 2 show the surface plots of neural-fuzzy and polynomial fitting, respectively. Both surfaces have similar tendencies. However, (10)1 shows that the data fitted better to neuro-fuzzy model than to polynomial model. This is due to the fact that, polynomial model curves ((10)2) were more rigid. In addition, in both Figs. 1 and 2 was observed that the maximum yield was achieved at 120ºC and 60 minutes.

TABLE I
RESULTS OF EXPERIMENTAL AND CALCULATED (CALC.) VALUES BY NEURAL-FUZZY MODEL

T, (ºC)	T, (MIN)	% YIELD	$YIELD_{CALC.}$	S % FRUCTOSE	$FRUCTOSE_{CALC.}$	S% SUCROSE	$SUCROSE_{CALC.}$
120	30	92,90	92,90	1,69	1,69	1,18	1,18
140	30	90,05	90,05	1,29	1,29	0,68	0,68
160	30	81,97	81,97	0,49	0,49	0,61	0,61
120	60	95,41	95,41	1,95	1,95	1,35	1,35
140	60	90,59	90,59	0,74	0,74	0,54	0,54
160	60	77,59	77,59	0,27	0,27	0,73	0,73
120	90	91,72	91,72	1,29	1,29	0,84	0,84
140	90	87,63	87,63	0,80	0,80	0,37	0,37
160	90	74,53	74,53	0,56	0,56	1,87	1,87

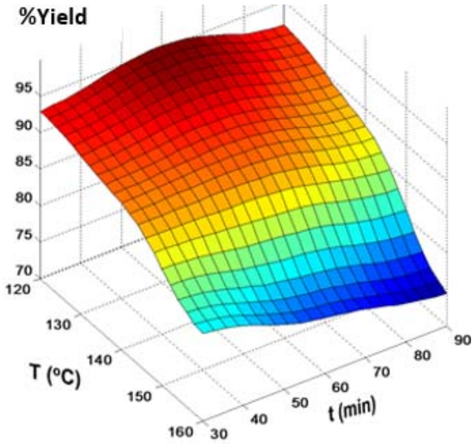

Fig. 1 Surface plot of Neural-Fuzzy fitting yield

Equation (8) corresponds to the expression to calculate the yield using the polynomial fitting:

$$Yield = 90.35-7.66*T-1.84*t-3.74*T^2-1.56*T*t-1.39 \quad (8)$$

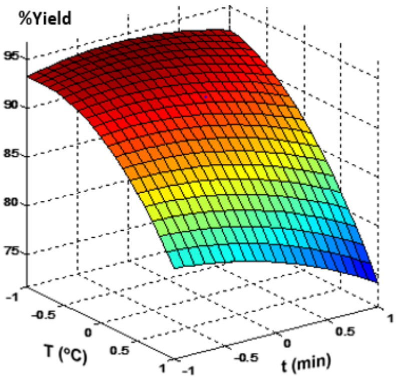

Fig. 2 Surface plot of Polynomial fitting of yield

Figs. 3 and 4 present surface plots of fructose S% fittings. Polynomial model (Fig. 4) did not fit well to the data for the same reason mentioned above. Both surface plots show that the maximum extraction of fructose was achieved at 120 ºC and 30 minutes. Fig. 3 shows a similar tendency to yield but in this case, the curves were more pronounced.

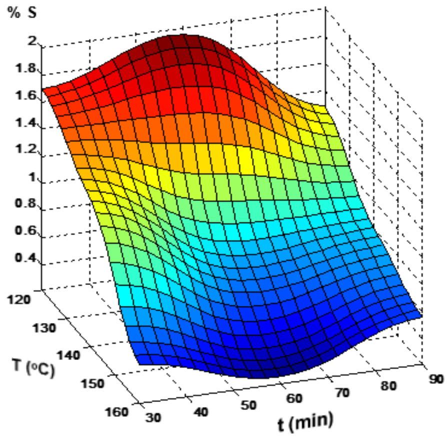

Fig. 3 Surface plot of Neural-Fuzzy fitting of fructose

Equation (9) shows the polynomial fitting equation of fructose:

$$Fructose = 0.92-0.60*T+0.09*T^2+0.12*T*t+0.03*t^2 \quad (9)$$

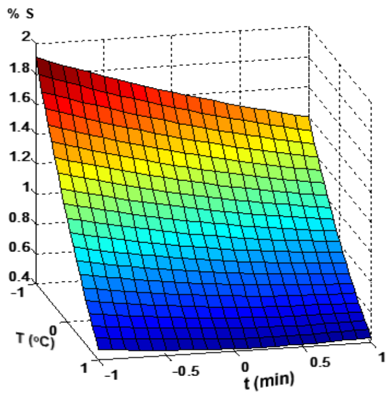

Fig. 4 Surface plot of Polynomial fitting of fructose

Figs. 5 and 6 present the surface plots of sucrose S%

fittings. Fig. 5 shows that the maximum sucrose S% obtained was at 160ºC and 90 minutes. It was observed that the behaviour of this parameter was very different with respect to fructose S% and yield %.

Fig. 6 shows the results of polynomial fitting. The curve was so rigid and sucrose S% data did not fit as well as in the other cases.

Polynomial fitting equation of sucrose is showed in (10):

$$\text{Sucrose} = 0.50-0.03*T+0.10*t+0.57*T^2+0.40*T*t+0.05*t^2 \quad (10)$$

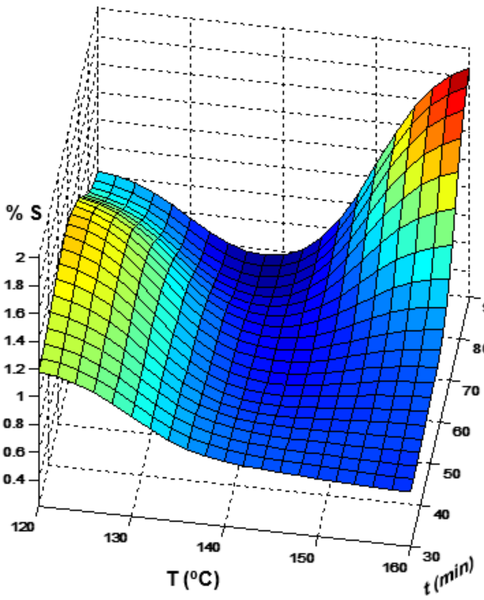

Fig. 5 Surface plot of Neural-Fuzzy fitting of sucrose

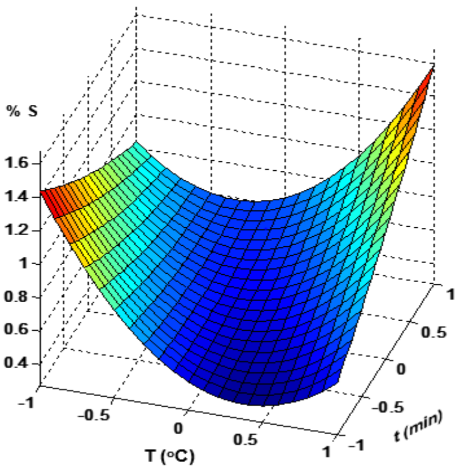

Fig. 6 Surface plot of Polynomial fitting of sucrose

This study presented the results of the most significant saccharides (fructose and sucrose). Nevertheless, other saccharides and polyalcohols were analysed too, as well as polyphenols and furfural.

IV. Conclusion

In relative terms, experimental data obtained in pressure autohydrolysis extractions were fitted to a neural-fuzzy and a polynomial model quiet well. On the one hand, the residual solid was more suitable for its use in cogeneration and as a fuel after the autohydrolysis extractions. On the other hand, liquid fractions showed to be rich in saccharides such as fructose and sucrose. Furthermore, they presented other value-added products too.

In conclusion, the treated olive cake could be applied in future studies of pyrolysis, gasification and combustion for its right exploitation.

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