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Ferulic Acid Production from Agroindustrial Waste of Barley Malting Process

Cantillo-Pérez, N.[1], Villarraga-Palencia, F[1], González Delgado, A.[1], Ojeda Delgado, K.[1*], Sánchez Tuiran, E.[1], Paz Astudillo, I[2]

[1]University of Cartagena, Chemical Engineering Department, Cartagena, Colombia, Avenida del Consulado Calle 30 No. 48 – 152
[2]Faculty of Agronomic Engineering, University of Tolima, Ibagué, Colombia

Abstract : The wastes generated by agroindustry represents a great opportunity to obtain high value products, such is the case of ferulic acid extraction from barley grain. In this work, the yield of this process from the residue generated in the malting barley by alkaline hydrolysis was evaluated, based on an experimental design which contemplated the variation of sodium hydroxide concentration and temperature of the hydrolysis process. Furthermore, the acid amount obtained was quantified using spectrophotometric methods. With best experimental results obtained, a simulation of the process using specialized software was made in order to evaluate process scaling feasibility and, finally, an economic analysis was performed. Results shows that at a hydroxide concentration of 1.5% and hydrolysis temperature of 100°C allow achieving a yield of 0.075%. In addition, the economic analysis revealed that due to the low production rate of ferulic acid extracted from the process, a high selling price is required to surpass the investment costs.
Keywords : Agroindustry, Waste valorization, Bioproducts, Antioxidant production, Alkaline hydrolysis.

Introduction

Agricultural wastes are defined as the secondary product during the crops production whether during the harvest or the preparation processes for marketing or manufacturing of those crops[1]. However, given the increasing number of agroindustrial residues that are produced worldwide[2] as a result that this activity is a backbone for national economy[3], it is important to seek alternatives for the integral use of biomass through their transformation into organic fertilizers, food for man or clean energy and develop sustainable biorefineries. The types of biomass used as raw material in yellow and green biorefineries, such as cereal straw, grains[4] and green leaves of grass, represent an available, economical, and promising source for biotechnological processing[5,6.] Based on this, Zhang et al. (2010)[7] notes that although these waste materials have high potential to become value-added products, in most cases, the sector that generates does not know these attractions. Due to its composition, the residue generated in the barley malting process is considered a potential source for the production of value-added components, such as ferulic acid. This acid is used in the pharmaceutical industry for its anti-inflammatory properties[8], and due to its antioxidant properties may offer beneficial effects against chronic diseases, cardiovascular and cerebral ischemia[9, 10, 11]. For its extraction, Ndolo et al. (2013)[8] reported the use of NaOH solutions taking into account variables such as extraction time, concentration and temperature, showed that after the process optimization, the percentage of ferulic acid can improve from 0.518 % to 0.817 %. Zhao et al. (2014)[12] obtained ferulic acid from the corn bran by membrane separation of the treated hydrolyzate, using an alkaline aqueous ethanol solution. Corn bran was extracted using 0.25 mol/L NaOH in a 50 % aqueous ethanol solution at 75 °C for 2 h to obtain 8.47 g of ferulic acid/kg of corn bran with 84.45 % purity. Likewise, Arabi et al. (2015)[13] extracted ferulic acid from the sugar beet pulp using three solvents: 0.5 and 1 M NaOH, 2 M methanol and a mixture thereof. The acid amount was quantified by the HPLC method, where the effects of solvent type, concentration and reaction time on the solubilization of ferulic acid were evaluated. Results showed that a minimum amount of acid was obtained from the alcoholic extract, while a concentration of 957.4 mg/L was obtained with the highest concentration of NaOH and a reaction time of 12 h.

This paper presents an evaluation of ferulic acid extraction potential by alkaline hydrolysis from the agroindustrial residue of the barley malting process. Based on the results obtained, a mathematical model was established to predict the behavior of the process in function of the studied variables, the simulation of the process was carried out to assess its performance on an industrial scale and estimate the economic viability.

Experimental

Agroindustrial residue characterization and acid pretreatment

The barley grain was purchased from the residue generated at the Maltería Tropical malting barley plant in Mamonal, Cartagena, Colombia. This residue was stored in a refrigerator and washed with distilled water to neutralize the pH, dried to 10% moisture and subjected to a grinding and sieving process to obtain particle sizes in the range of 1 mm - 0.15 mm. The dry material was pre-treated with 2% w/w diluted sulfuric acid in a solid: liquid mass ratio of 1:8, at 118 °C for 60 min. Based on procedure reported by Xiros et al. (2008)[9], Yang et al. (2013)[14] and Panagiotopoulos et al. (2012)[15], after reaction completion, the mixture was subjected to a filtration process to remove the two phases, washed with distilled water to neutralize the pH and dried at 50 °C for 12 h until a moisture content of 50% was reached. Finally, the amount of hemicellulose, cellulose and lignin present in the barley malting residue was determined before and after pretreatment.

Alkaline hydrolysis

For the alkaline hydrolysis process an experimental design 2^2 plus 1 central point with a replica at the end points and two replicas at the central point was developed, for a total of 11 tests where temperature and NaOH concentration were varied. Table 1 presents the levels for these two variables, where (+), (-) and (0) mean the highest, lowest and center value used in experiments.

Table 1. Factorial design for ferulic acid extraction process

Factor name	Level	Simbol
Temperature	130 °C	+
	120 °C	0
	100 °C	-
NaOH concentration	2.5 %w/v	+
	2.0 %w/v	0
	1.5 %w/v	-

Ferulic acid content was determined using a standard calibration curve made from an acid stock solution (1 mg/mL). From the solution obtained (100 mg/mL), aliquots of 0.1 to 0.8 mL were taken and deposited in different flasks of 10 mL, each being added 2 mL of 15 % sodium carbonate and 0.5 mL of diluted Folin-Ciocalteu in distilled water in a ratio of 1:2. Then, the volume was filled to the physical capacity with distilled water in order to obtain concentrations of 1 μg/mL to 8 μg/mL of ferulic acid. The absorbance was measured on a UV-Vis spectrophotometer at a wavelength of 718 nm against a blank of reagents, which were plotted against their corresponding concentration. Finally, according to the methodology proposed by Jadhav et al. (2012)[16], a least squares linear regression was performed in order to have the equation describing the calibration curve.

On the other hand, the alkaline hydrolysis was performed in a batch system, where the solid obtained from the pre-treatment was contacted with NaOH in a solid:liquid mass ratio of 1:20. The NaOH concentrations and the temperature were varied in a reaction time of 60 min, as presented by Mussatto et al. (2007)[17]. The solution was cooled in an ice bath, filtered with polyester and the obtained liquor was analyzed for the determination of ferulic acid concentrations. Finally, 1 mL aliquots were transferred to a 10 mL volumetric flask, the sodium carbonate and Folin-Ciocalteu were added in the same ratio and concentration used for the calibration, and the volume was completed with distilled water. The solution was homogenized for 1 h at room temperature, 1 mL of the prepared solution was diluted with 4 mL of distilled water and its absorbance was measured against a blank of reagents at a wavelength of 718 nm.

Statistical analysis of ferulic acid extraction process

For the statistical analysis, Statgraphics was used and based on the results of the experimental tests with their respective replicas, the individual and joint influence of the independent variables on the ferulic acid extraction yield. In addition, the statistical model represented by Equation (1) was established to describe the behavior of ferulic acid (Y) extraction yields mathematically when there is a change in the independent variables. Where, a_o is a constant that indicates the relation with the model error, the coefficients $a_{1,}$ $a_{2,}$ a_3 represent the effect of temperature, NaOH concentration and temperature-concentration, respectively, and X_1, X_2 corresponds to the variables temperature and concentration, respectively.

$$Y=a_0+a_1*X1+a_2*X2+a_3(X1*X2) \quad (1)$$

Finally, the optimum value of sodium hydroxide (NaOH) concentration and the temperature that allowed to reach the maximum ferulic acid extraction yield were obtained within the conditions and limits established in the factorial design.

Simulation and economic evaluation of ferulic acid extraction

The simulation and the economic evaluation were carried out using a commercial process simulation software with 40 tonnes per month as a basis of calculation, which it is equivalent to the production capacity of Maltería Tropical company. The pilot scale process was evaluated taking into account the yield experimentally obtained and the yields for the subsequent stages based on the bibliographic review. For the economic assessment, a study of energy requirements and service fluids was carried out using economic parameters such as raw material cost, product sale price, electricity, drinking water cost and minimum wage under Colombian conditions.

Results and Discussion

Characterization of the agroindustrial residue of the barley malting process

Table 2 shows the results obtained by gravimetric methods for characterizing the residue of the barley matting process before and after pretreatment. When comparing the data obtained for grain imported from Argentina and the Netherlands with the results of similar cases carried out in Brazil and Mexico, differences are observed between the concentrations of the components, which can be attributed to factors that affect the chemical composition of the grain, such as cultivation field, the malting process which were subjected, the climatic conditions of cultivation, transport and storage, as well as to the non-standardization of determination methods of these components.

Table 2. Characterization of the agroindustrial residue of the barley malting process

<table>
<tr><th rowspan="2">Parameters</th><th colspan="3">Before the Pre-treatment</th><th>After the Pre-treatment</th></tr>
<tr><th>Agroindustrial waste, %</th><th>Mussatto et al. (2007), % [17]</th><th>Rojas-León et al. (2014), % [21]</th><th>Agroindustrial waste, %</th></tr>
<tr><td>Cellulose</td><td>9.7</td><td>16.8</td><td>58</td><td>27.7</td></tr>
<tr><td>Hemicellulose</td><td>17.9</td><td>28.4</td><td>6.6</td><td>21.2</td></tr>
<tr><td>Lignin</td><td>4.0</td><td>27.8</td><td>14.7</td><td>18.9</td></tr>
<tr><td>Ash</td><td>0.63</td><td rowspan="2">27</td><td rowspan="2">20. 7</td><td>1.68</td></tr>
<tr><td>Removable material</td><td>67.77</td><td>30.52</td></tr>
</table>

As for the residue composition after the pretreatment, a significant increase in the amount of lignin of 4.0 to 18.9 % is evidenced, which allows to infer that this process can favor the rate of ferulic acid extraction because of the acid is present mainly in this fraction of the lignocellulosic material[18]. On the other hand, this pre-treatment was carried out to solubilize the hemicellulose in order to increase the porosity of the material facilitating the subsequent diffusion and impregnation of the sodium hydroxide in the biomass. This is confirmed by comparing the hemicellulose and cellulose fractions before and after pretreatment. Initially, the hemicellulose constitutes one of the fractions of greater representation within the material, however, after the pre-treatment the greater proportion is given by the cellulose.

Extraction of ferulic acid by alkaline hydrolysis

The results of the average amount of ferulic acid extracted based on the experimental design are presented in Table 3. It is observed that the highest amount ($1.12x10^{-2}$ g) was extracted at low temperatures and dilute concentrations. Also, the maximum extraction yield obtained of 0.074 % is higher than that reported by Mussatto et al. (2007)[17], which was 0.029 %.

Table 3. Average yield of ferulic acid extraction

Sample	Temperature, °C	NaOH concentration, %	AF extracted $x10^{-2}$, g	Average yield, %
1	100	1.5	1.12	0.0749 ± 0.0006
2	130	1.5	0.97	0.0644 ± 0.0062
3	120	2.0	0.90	0.0603 ± 0.0042
4	100	2.5	0.80	0.0533 ± 0.0018
5	130	2.5	0.85	0.0564 ± 0.0021

Statistical analysis of ferulic acid extraction process

The variance analysis of the ferulic acid extraction yield was performed, which is represented graphically by the standardized Pareto diagram of Figure 1, where the vertical line can be used to identify the statistically significant effects, according to the level of confidence used of 95 %.

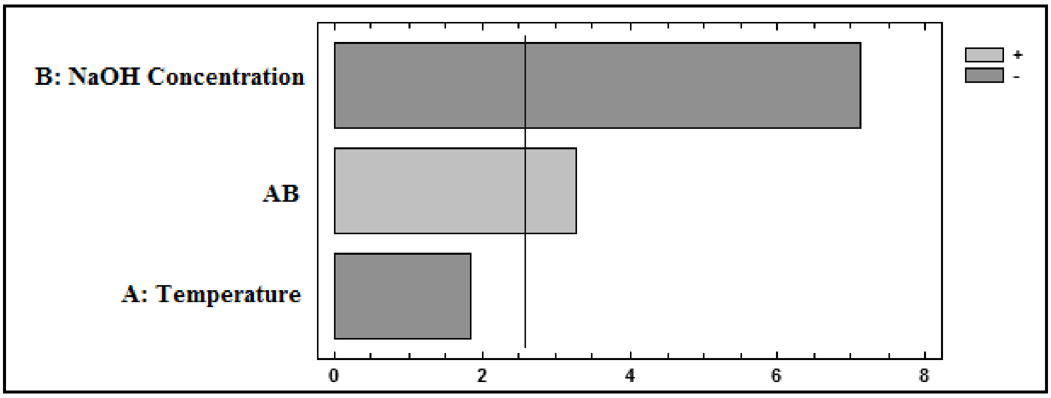

Figure 1. Standardized Pareto diagram for the yield of ferulic acid extraction

The diagram shows each of the estimated effects in order of importance. Any effect that exceeds the vertical line is considered significant for the process, likewise, the signs (+) and (-) for the effects represent a direct and inversely relation proportional to the response variable, respectively. Thus, it was observed that lower concentrations of NaOH have a greater effect on the yield of ferulic acid extraction. On the other hand, the behavior of ferulic acid extraction as a function of temperature (A) and NaOH (B) concentration was analyzed from a multiple regression, which allowed to adjust the results and obtain the following coefficients: 0.21 (constant), -0.00103 (A), -0.0668 (B) and 0.000452 (AB). With these values, Equation (2) was proposed to estimate the yield of ferulic acid extraction, having data of operation temperature and NaOH concentration. The values of the polynomial variables are specified in their original units.

$$\% \text{ yield} = 0{,}21\text{-}1{,}03\text{x}10^{-3}\text{T} - 6{,}68\text{x}10^{-2}\text{C} + 4{,}52\text{x}10^{-4}\text{TC} \qquad (2)$$

The mathematical model developed by multiple regression allowed obtaining an optimum value of ferulic acid extraction yield of 0.075 % within the conditions and limits established in the factorial design. The temperature conditions influencing the yield are 100, 100 and 130 °C; and 1.5, 1.5 and 2.5 % of NaOH concentration, these being the minimum, optimal and maximum values, respectively, for both variables.

Simulation and economic assessment of acid ferulic extraction process

After performing the experimental process and based on the results of the statistical analysis, the simulation was carried out giving a detailed view of the ferulic acid extraction process from the residue of the barley malting process as it is shown in Figure 2.

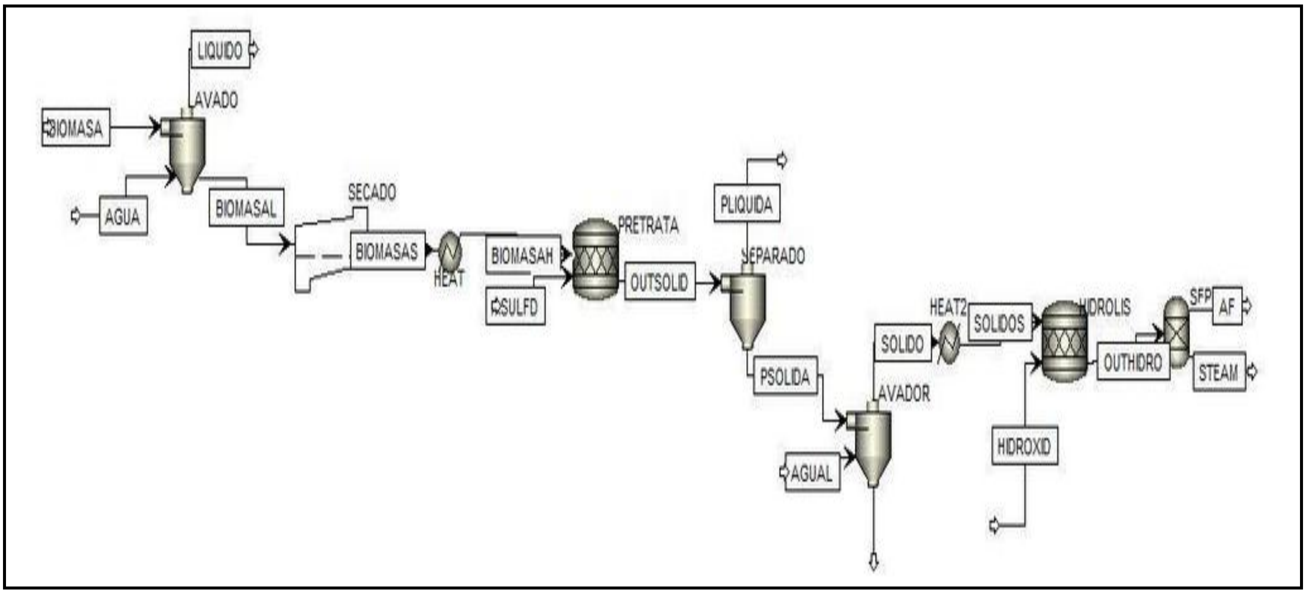

Figure 2. Scheme of the ferulic acid extraction process from the residue of the barley malting process

The simulation starts with a washing and drying stage, where 400 g of barley/h are brought into contact with 100 L/h of water at 29 °C in order to remove pollutants and neutralize the pH, then the biomass is dried 70 °C to 10 % moisture. Then, it enters to a heat exchanger until to reach a temperature of 120 °C, which is necessary to carry out the pretreatment in a reactor type CST. A stream of 3.2 L of sulfuric acid/min is fed into this reactor and another is sent to a separator in which the liquid phase, composed mainly of sulfuric acid and solubilized hemicellulose, is separated from the solid phase composed of cellulose, lignin and hemicellulose that were not solubilized.

The solid phase is washed with water entering at 30 L/min to keep the pH controlled and to preserve the integrity of the equipment. This solid at 29 °C enters to a heat exchanger where its temperature rises to 100 °C and then is fed to a hydrolysis reactor. The output stream of this latter process reaches a separator of components where, finally, the ferulic acid is separated from all the impurities, achieving a flow of 0.016 kg of ferulic acid/h, corresponding to an extraction yield of 4 %. The simulation allowed an extraction efficiency of 8.5 %, that is, a production of 20.24 kg of ferulic acid/h or 177.311 kg/year obtained from 238.09 kg of agroindustrial residue/h, an amount required for companies dedicated to the manufacture of cosmetics located in Cartagena city.

The economic evaluation was made based on the US dollar currency over a 20-year period with a linear depreciation of 15 %, as explained by Baca (2001)[19], without including costs of civil works, purchase and adaptation of land. Table 4 shows the criteria taken into account at the time of the analysis of the operating costs, in order to obtain the price per liter of ferulic acid, which was considered as a relevant indicator to analyze the economic viability of the process giving an idea about the risk of process execution.

Table 4. Economic variables used in the ferulic acid extraction process

	Variable	Value
Economic parameters	Annual interest rate [22]	4 %
	TIR	20 %
	Increase in production	10 % annual
	Increase in operating cost	3 % annual
Raw material and inputs costs	Barley[23]	US$ 0.1/kg
	Sulfuric acid[21]	US$ 0.094/mL
	Sodium hydroxide[21]	US$ 0.06/mL
	Water[24]	US$ 0.0037/kg

The cost of raw materials, operating costs and total cost of the project amounted to US $ 363,234/year, US $ 1,051,590/year and US $ 1,414,824/year, respectively. The total of the project includes all the expenses generated by the operation of the plant.

In order to offset the investment costs and thus maintain the profitability of the business, the sale price of the acid must be US $ 5,300/L, which is higher than the US $ 145/L commercial delivered at Alibaba (2016)[20], which makes the process not economically viable. However, the extraction efficiency obtained from 4% based on 400 g is higher than some obtained with similar methodologies for raw materials such as corn bran of 8.47 g/kg or 0.85 % or *Angelica sinensis* de 0.6 mg/g or 0.06 % reported by Zhao et al.,(2014)[12] and Salleh et al., (2011)[10], respectively.

Conclusions

Taking into account the conditions considered in this work, it is concluded that execution of ferulic acid extraction process is acceptable if the price of acid reaches a more competitive value than the one currently in the market, in order to guarantee a capital gain or recovery during the project life. To do so, it is necessary to reduce investment costs or evaluate other ferulic acid extraction conditions that increase the yield of the process, improve the competitiveness of the product in the market and favor its implementation at the industrial level as an alternative for the utilization of by-products of the malting process.

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