



Energy Optimization from raw materials and evaluate hemicelluloses.

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Abstract.

The aim of this study was to optimize the energetic use and extraction of hemicelluloses by hydrolysis with dilute acid of three different lignocellulosics materials from rapid growth biomass using a factorial experimental design and multiple regression models.

For that, calorific power value and chemical composition of solid phases after acid hydrolysis of three different lignocellulosic materials were determined (*Chamaecytisus proliferus or tagasaste-*, *Leucaena leucocephala*, and a dihybrid of Paulownia (fortunei and elongata). These solid phases were assessed for obtainment of energy, sugars and other by product. Superior calorific value at constant volume over dry basis and lower calorific value at constant pressure was determinated for energy purposes.

The proposed acid hydrolysis process allows increased yield and xylan under more selective extraction conditions. Also higher values of superior calorifc power values that raw materials are reported. The operational ranges are especially suitable for the extraction of xylose, which was virtually quantitative at 170 °C The selective extraction of hemicelulloses alows to have a solid part with a high content in glucan a lignin and the value of superior calorimetric is suitable for obtain energy.

Key words

Acid hydrolysis; Biorefinery; Calorific value; Energy from biomass, Forestry raw materials.

1. Introduction

The assessment of the biomass of energy crops has garnered widespread interest since renewable bioenergy may become a substantial proportion of the future energy [1].

In the biorefinery schemes, the hemicelluloses fraction, they have a high potential and they could be used in many applications, not only for liquid biofuels production, notably bioethanol, and butanol. The integrate process are the future to develope of industrial crops and forest use from raw material [2].

Biorefinery is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum [3]. The lignocellulose biorefinery will most probably be pushed through with the greatest success, due to the optimal situation for the raw material and conversion products have a good position in the traditional petrochemical as well as in the future biobased product market [4-6]. The solution is to obtain high quality competitive products and lead agriculture towards non-alimentary uses.

Therefore, using biomass from forest crops to extract energy or chemicals product provides additional advantages Lignocellulosic biomass is the most abundant renewable feed stock and low-cost raw materials. biomass can potentially be converted into different high value products including value added chemicals and energy sources. [7]

Respect to raw material selected in this work, are a very fast-growing and non-food crops for example. Leucaena species showed high biomass productivity more than 50ton hectare year under Mediterranean conditions.

Among the different pretreatment methods to enhance the extraction of carbohydrates in the process from lignocellulosic materials, hot water or weak acid hydrolysis are among the most suitable first step typically used to hydrolyze carbohydrates from lignocellulosic materials. Moreover, acid hydrolysis has proved one of the most efficient choices for this purpose in as much as it facilitates the dissolution of hemicellulose polymers. [8].

Moreover, this process can facilitate the hemicellulose polymer dissolution, which can be used to obtain oligomers, xylose, and arabinose for a variety of novel applications in the chemical, pharmaceutical, and food industries. The aim of this study was to optimize the energetic use and extraction of hemicelluloses by hydrolysis with dilute acid of three different lignocelluloses materials from rapid growth biomass using a factorial experimental design and multiple regression models.

2.Materials and Method

2.1. Characterization and storage of raw material Acid hydrolysis processing of wood samples

The three raws materials used were used (Chamaecitysus proliferus -tagasaste-, Paulownia dihibrid and Leucaena leucocephala were characterized chemically in the following parameters: Klason lignin (Tappi T 222 om-98) an holocellulose contents (Wise et al.). Aliquots of raw material were ground to a particle size < 0.5 mm and subjected to moisture and extractives determination (TAPPI T-264-om-88) and to quantitative acid hydrolysis with 72% H2SO4 following standard methods (T-249-em-85). The monosaccharides glucose, xylose, and arabinose as glucan, xylan and araban) and acetic acid contained in the hydrolysates were determined by high performance liquid chromatography (HPLC), using a column of exchange ionic Aminex HPX-87H to 30°C, mobile phase, H2SO4 0.05 M; flow, 0.6 ml/min. The superior calorific values (constant volume was determinate according "CEN/TS 14918:2005 (E) Solid biofuels-Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr6300 Automatic Isoperibol Calorimeter.

For acid hydrolysis, raw material and water were mixed in the desired proportions and treated in a 2 L stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture content of material was considered as water). The operating conditions were 130 °C, 150 °C and 170 °C temperature; 30, 45 and 60 min operating time and 0.5%, 1.25% and 2% H₂SO₄ content and a liquid/solid ratio of 8 kg water by kg raw material, on a dry basis. After treatment, solid residues were recovered by filtration, washed with water, air-dried, weighted for yield determination. Aliquots of the solid phase were analyzed and calorimetric value.

1.3. Experimental design for acid hydrolysis processes. Multiple regression models

In order to relate the dependent (yield, hemicelluloses extracted) and independent variables (temperature and acid concentration) in process with the minimum possible number of experiment, a 2^n central composite factor experimental design was used, making it possible to construct a second-order polinomial in the independent variables and the identification of statistical significance in the variables was used. independent variables were normalized by using Eq. (1).

$$X_n = \frac{X - \overline{X}}{(X_{\text{max}} - X_{\text{min}})/2}$$

Where X is the absolute value of the independent variable concern \overline{X} is the average value of the variable, and X_{max} and X_{min} are its maximum and minimum values respectively. The range of variation of independent variables was determinate according to previous work (data not shown). The number of tests required was calculated as $N = 2^n + 2 \cdot n + n_{\rm C}$, 2^n being the number of points constituting the factor design, $2 \cdot n$ that of axial point, and $n_{\rm C}$ that of central point.

The experimental results were fitted to the following secondorder polynomial

$$Y = a_o + \sum_{i=1}^n b_i X_{ni} + \sum_{i=1}^n c_i X_{ni}^2 + \sum_{i=1; j=1}^n d_i X_{ni} X_{nj} \quad (i < j)$$

The independent variables used in the equations relating the two types of variables were those having a statistically significant coefficient (*i.e.*, those not exceeding a significance level of 0.05 in Student's *t*-test and having a 95% confidence interval excluding zero). The results were assessed with STATISTICA 8.0 (StatSoft, Inc., Tulsa, OK).

3. Results and Discussion

3.1 Characteristics of the Raw Material

Table 1 Average chemical composition for the three raw materials used (tagasaste, Leucaena Leucocephala and Paulownia)

	Leucaena	Paulownia	Tagasaste	
	leucocephala	fortunei	(Present	
	(Present	(Present	study)	
	study)	study)		
Ash, %	1.4	n.d	0.7	
Ethanol	n.d	n.d	2,3	
extract., %				
Holocelulose,	72.8	56.9	80,3	
%				
Glucan, %	32.2	34.2	38,9	
Lignina,	21.5	27.2	19,8	
Klason %				
Xylan, %	15.5	18.3	19.9	
Araban, %	1.0	1.1	0.6	
Acetyl	2.1	3.3	4.4	
groups, %				
¹ Raw material percentages (100 kg dry matter)				

According with Section 1.3, to assess the relative influence of the selected independent variables (temperature and acid concentration) on each dependent variable (Superior calorific value), the polynomial mathematical models were obtained (Table 2) by substituting the values of the measured independent variables for each dependent variable, and applying a polynomial model analysis.

Each value used to obtain the equations is the average of three measurements. The differences between the experimental values and those that were estimated using the previous equations never exceeded 10% for Superior calorific value. Suitable fits with values of F-Snedecor >56 and R² greater than 0.96 in all cases have been obtained.

Table 2.	Equations	for each	dependent	variable	of superior
calorific	value.				

Equation		D 2	F-		
Equation			Snedecor		
(1)	Paulownia = 20211.25 + 220.67				
	X_{c} + 381 X_{T} + 192.08 X_{c} X_{c} - 168	0.96	56		
	$X_{c}X_{T}$				
(2)					
	$+706 X_{T} + 162.93 X_{c}X_{c} + 345.43$	0.98	112		
	X _T X _T				
(3)	Leucaena = 19220.64 + 220.17				
	X_{c} + 256.33 X_{T} - 227.29 X_{c} X_{c} +	62			
	365.21 X _T X _T				
Dep	Dependent variables: Superior calorific value. Independent				
varia	variables: X_c and X_T : concentration and temperature of				
oper	operation, respectively				
The differences between the experimental values and those					
estimated using the equations never exceeded 10% of the					
former. Independent variables are expressed in coded units					
(Eq. (1))					

In order to better envisage the influence of operational variables on extraction liquor of wood, and to compare different conditions, the surface responses were plotted. The space among three response surfaces represents the whole range of values for each dependent variable that was used at three extreme values, +1, 0, -1, of the most influential variable are temperatura and acid concentration.

As can be seen in Fig. 1 response surface from Paulownia, temperatura and acid concentartion are the most influentian variable, In that form, high concentration acid values and médium temperatura could be the optimization process where has been obtained high superior calorifc values.



Figure 1. Variation of superior calorific value from Paulownia as a function of acid concentration and temperature under acid hydrolysis process.

With respect the other materials present in this study Similar behavious has been found.as can been see in figure 2 and 3.



Fig. 2. Variation of superior calorific value from Tagasaste as a function of acid concentration and temperature under acid hydrolysis process.



Fig. 3. Variation of superior calorific value from Leucaena as a function of acid concentration and temperature under acid hydrolysis process.

Maximing superior calorific value are between 19800 and 21200 J/g.of lignocelullosics material studied. In the figure 4 show the response surface obtained of the trhree materials studied (Paulownia, Tagasaste and Leucaena) as a matter of comparison.



Figure 4 show variation of the Superior calorific value of the three species as a function of the temperature and the concentration acid.

4. Main contributions

In this work, the calorific value and chemical composition of liquors resulting from the acid hydrolysis of three different lignocellulosic materials was determined (Chamaecytisus proliferus –tagasaste-Leucaena leucocephala, Paulownia dihibrid) and was assessed for the obtainment of energy, sugars and other chemicalproducts by using of integral fractionation based on acid hydrolysis.

The normalized values of independent variables (temperature and acid concentration), the solid yield and superior calorific value phase relative to the initial (Chamaecytisus proliferus –tagasaste-Leucaena leucocephala, Paulownia dihibrid) raw material are shown in tables 3, 4 and 5 for each material respectively.

The time to reach the operating temperature in nonisothermal process between 130°C and 170°C has not been considered due to the short time heating the reactor, between both temperatures, elapsed compared to both heating from ambient temperature.

Among the obtained results, the variation ranges in solid phase:

48.9-83.3% of the solid yield and 19163-20889 J/g of the Superior calorific value for Tagasaste; 59.1-87.8 % of the solid yield and 18916-19869 J/g of the Superior calorific value for Leucaena; 37.5-72.0 % of the solid yield and 19642-21222 J/g of the Superior calorific value for Paulownia.

The error in mass balance was less than 10% in all components. It is assumed to be a considerable difference because the working hypothesis was to maximize the extraction of hemicellulose derivatives while minimizing that of cellulose derivatives to get the maximum power capacity.

It is observed the Paulownia has a calorific yield lightly superior to the other two species getting to obtain the 21222 J/g.

Table 3. Experimental design, yields on solid phase after acid hydrolysis stage and calorimetric values from Tagasaste.

Xc	X _T	Yield (%)	Superior calorific value (Constant volume) J/g. Over dry basis	Lower calorific value (constant pressure) J/g over dry basis
1	1	52.8	20889	18125
1	-1	48.9	19487	18265
-1	1	64.0	20714	19492
-1	-1	83.3	19269	18047
1	0	53.7	19905	18683
-1	0	73.1	19445	18223
0	1	56.1	20232	19010
0	-1	68.1	19163	17941
0	0	76.0	19605	18383
0	0	69.9	19604	18380

Table 4. Experimental design, yields on solid phase after acid hydrolysis stage and calorimetric values from *Leucaena leucocephala*

			Superior	
Ve			calorific value	Lower calorific
	V _	Yield	(Constant	value (constant
nu	211	(%)	volume) J/g.	pressure) J/g over
			Over dry	dry basis
			basis	
1	1	69.21	19869	18995
1	-1	87.85	19353	19005
-1	1	59.27	18995	18758
-1	-1	72.01	18916	17835
1	0	78.17	19149	17927
-1	0	65.31	19411	18189
0	1	59.13	19.873	18651
0	-1	75.17	19265	18043
0	0	65.70	19199	17977
0	0	65.73	19148	17926

Table 5. Experimental design, yields on solid phase after acid hydrolysis stage and calorimetric values from *Paulownia dihybrid*.

Xc	X _T	Yield (%)	Superior calorific value (Constant volume) J/g. Over dry basis	Lower calorific value (constant pressure)J/g over dry basis
1	1	37.5	21222	20000
1	-1	45.3	20400	18866
-1	1	44.8	20673	19451
-1	-1	54.7	19642	18420
1	0	61.8	20713	19491
-1	0	71.0	20233	19011
0	1	72.2	20784	19562
0	-1	68.8	19753	18531
0	0	65.7	20002	18780
0	0	65.7	20200	18820

In all case, a valorizable liquid phase has been obtained. The operational conditions were optimized at 170°C of temperature and 0.5% sulphuric acid concentration. A liquid phase with high contents of hemicellulose derivates was obtain. More of 70% xylose from raw material (as xylan or other hemicellulose polysaccharides) can be extracted

5. Conclusion

The proposed acid hydrolysis process allows increased yield and xylan under more selective extraction conditions .and were obtain high values of superior calorific values of lignocellulosic materials studied.

The operational ranges are especially suitable for the extraction of xylose, which was virtually quantitative at 170°C. The selective extraction of hemicelluloses allows to have a solid part with a high content in glucan a lignin and the value of superior calorimetric is suitable for obtain energy.

Paulownia has a higher calorific value than Leucaena even for lower concentrations and same temperatures and a calorific power similar to Tagasaste.

For the three species, the higher calorific power is obtained in temperatures of 170 °C and 2% acid concentration.

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