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Energy and autohydrolysis by-products from industrial crops

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Abstract

The world is experiencing a growing shortage of raw materials which is especially severe in the energy sector and being worsened by the unfavorable environmental impact of a consumerist culture revolving around the exploitation of non-renewable resources.

In this work, the calorific value and chemical composition of liquors resulting from the autohydrolysis of six different lignocellulosic materials was determined (*Eucalyptus globulus, Arundo donax, Leucaena diversifolia, Paulownia fortunei*, Sunflower stalks and *Chamaecytisus proliferus* –tagasaste-) and was assesed for the obtainment of energy, sugars and other chemical products by using of integral fractionation based on autohydrolisys.

Autohydrolysis processes have been considered interesting in the case of timber species studied compared with herbaceous species with variations in the extraction of the xylan fraction at 180 ° C and 200 ° C.

Keywords

Autohydrolysis, biomass, energy, biorefinery, industrial crops.

1. Introduction

The world is experiencing a growing shortage of raw materials which is especially severe in the energy sector and being worsened by the unfavorable environmental impact of a consumerist culture revolving around the exploitation of non-renewable resources. Accomplishing sustainable development and renewability entails finding and using new resources and chemical and consumer products where lignocellulosic biomass constitutes a "necessary" source of raw materials on account of its ubiquity, availability and low polluting power. In fact, lignocellulosic biomass has been widely acknowledged as the largest source of renewable energy available in the world to respond to the decline in fossil fuel sources [1].

Using biomass from forest or agrarian "crops" to extract energy or chemical products provides additional advantages such as a reduction in the use of fossil fuels, the release of no additional CO_2 into the atmosphere ─in fact, any CO_2 produced is previously captured from it─ and the ability to convert crops into net carbon sinks by increasing the amount of carbon accumulating in the soil via organic matter, dead leaves, roots, *etc.* Also, using resprouting plants and harvesting their aerial portion only ─thus leaving roots and shoots intact─ reduces the need for machine tillage ─and hence energy use─ for as long as the plants retain their regrowing ability.

Incorporating the hydrolysis of hemicelluloses into a more general process involving the integral fractionation of the raw material can be easier if the use of chemical reagents other than those strictly needed for separation is minimized. This can be especially easy with autohydrolysis. At high temperatures, acetyl groups in the lignocellulosic material give acetic acid (really, the lignocellulosic material give acetic acid at any temperature but the dissociation equilibrium and the process are slower), which catalyses the solubilization of hemicelluloses [2].

2. Material and Methods

A. *Analysis of Raw Material.*

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The six raw materials used (*Eucalyptus globulus*, *Leucaena diversifolia*, Sunflower stalks, *Chamaecitysus proliferus* -tagasaste-, *Paulownia fortunei* and *Arundo donax)* were characterized chemically in the following parameters: Klason lignin (Tappi T 222 om-98) and holocellulose [3] contents. All treatments in this study were in a completely randomized design with five replications (variation coefficient less than 1% for holocellulose contents).

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% H_2SO_4 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 30ºC, mobile phase, H_2SO_4 0.05 M; flow, 0.6 ml/min. Ashes were determined by calcinations (T-244-om-93).

The superiors calorific values (constant volume) were determinate according "CEN/TS 14918:2005 (E) Solid biofuels—Method for the determination of calorific value" and UNE 164001 EX standards by using a Parr 6300 Automatic Isoperibol Calorimeter.

B. Hydrothermal Processing of Different Samples.

The different raw materials and water were mixed in the desired proportions and treated in a 600 cm^3 stainless steel reactor (Parr Instruments Company, Moline, IL) using a liquid/solid ratio of 8 kg water kg raw material^{-1}, and 10 kg water kg raw material^{-1} for *Paulownia fortunei*, on a dry basis (the moisture content of the material was considered to be water). Previous works demonstrated that the influence of the variation of the liquid/solid ratio is practically negligible [4,5]. The reactor was fitted with four blade turbine impellers, heated by an external fabric mantle, and cooled by cool water circulating through an internal loop. A total of 12 experiments were carried out at temperatures of 180 and 200 °C.

3. Main Contributions

In this work, the calorific value and chemical composition of liquors resulting from the autohydrolysis of six different lignocellulosic materials was determined (*Eucalyptus globulus, Arundo donax, Leucaena diversifolia, Paulownia fortunei*, Sunflower stalks and *Chamaecytisus proliferus* –tagasaste-) and was assesed for the obtainment of energy, sugars and other chemical products by using of integral fractionation based on autohydrolisys.

Table 2. Percentage of different monomers on the quantity of each compound present in the original raw material or polymer derived.

	Eucalyptus globulus	*Leucaena diversifolia*	*Paulownia fortunei*	*Arundo donax*	**Sunflower stalks**	*Chamaecytisus proliferus*
Glucan, %	44.3	38.0	34.2	34.8	33.8	38.9
Klason lignin %	27.1	24.8	27.2	23.0	19.9	19.8
Holocellulose %	66.7	76.3	56.9	64.5	74.2	80.3
Xylan %	18.0	15.7	18.3	19.4	23.9	19.9
Araban %	1.1	1.50	1.1	1.5	0.4	0.7
Acetyl groups %	3.3	3.3	3.3	3.4	4.3	4.4
Superior calorific value (Constant volume) J/g. Over dry basis	19324.0	19148.0	19843.3	19161.0	17259.4	19564.0
Superior calorific value (Constant volume) J/g.	17555.7	17262.4	17997.3	16958.7	15413.0	17649.9
Lignocellulosic materials 180º (Constant volume) J/g. Over dry basis	19363.5	19294.6	19812.4	19163.9	19044.4	19451.8
Lignocellulosic materials 200º Constant volume) J/g. Over dry basis	19731.8	19856.4	20487.3	19363.7	19047.5	19902.3

Table 1 shows the results of chemical composition and calorific value of the six lignocellulosic materials studied. The calorific value at constant volume in dry basis only vary by a margin of 3.5% with the exception of sunflower stalks that they show a 13% lower value on *Paulownia fortune*. That is the material that has a higher value calorific value at constant volume. The relationship between calorific constant volume is similar in wet basis, but there was a relative decrease in the amount of energy that could be derived from timber materials compared to woody.

It highlights the interesting result of increased calorific value, at constant volume on a dry basis, of the solid fraction post-autohydrolysis going from 180 ° C to 200 ° C for the same raw material, between 1.2% for *Arundo donax* (presents a behavior similar to sunflower stalks) and 6.7% for *Leucaena diversifolia* (3.4% for *Paulownia fortunei* between 2.2% for *Eucaliptus globulus*).

Table 2. Percentage of different monomers on the quantity of each compound present in the original raw material or polymer derived.

	Glucose, %	Xylose, %	Arabinose, %	Acetyl Groups, %
***Eucaliptus Globulus* 180º**	0,4	3,8	23,1	6,8
***Eucaliptus Globulus* 200º**	0,7	14,9	56,4	26,5
Sunflower stalks 180º	1,6	3,9	43,2	15,7
Sunflower stalks 200º	1,1	4,1	68,3	33,9
***Leucaena diversifolia* 180º**	3,0	1,8	17,1	8,1
***Leucaena diversifolia* 200º**	2,0	5,8	25,5	24,8
***Paulownia fortunei* 180º**	1,3	4,0	22,2	5,00
***Paulownia fortunei* 200º**	2,3	10,9	37,2	16,0
***Arundox donax* 180º**	4,7	10,8	33,7	23,0
***Arundox donax* 200º**	5,0	11,4	37,3	28,0
***Chamaecytisus proliferus* 180º**	1,3	2,1	42,2	6,9
***Chamaecytisus proliferus* 200º**	1,3	5,0	75,2	18,5

% sugars dissolved of initial fraction

	Yield, %	Glucan, %	Xylan, %	Arabana, %
***Eucaliptus Globulus* 180º**	90,7	1,3	19,7	35,6
***Eucaliptus Globulus* 200º**	74,7	2,6	71,2	71,1
Sunflower stalks 180º	74,6	2,3	12,3	81,3
Sunflower stalks 200º	64,2	2,5	35,6	92,4
***Leucaena diversifolia* 180º**	90,3	4,3	36,8	48,7
***Leucaena diversifolia* 200º**	76,2	4,2	62,2	35,3
***Paulownia fortunei* 180º**	90,6	3,9	22,8	39,6
***Paulownia fortunei* 200º**	76,6	9,2	57,9	45,2
***Arundox donax* 180º**	82,5	6,2	25,5	53,7
***Arundox donax* 200º**	78,2	7,0	35,3	67,1
***Chamaecytisus proliferus* 180º**	87,2	7,5	32,4	56,8
***Chamaecytisus proliferus* 200º**	71,0	11,5	79,1	86,9

Table 2 shows the results of the characterization of the liquid phases of the six lignocellulosic raw materials used after autohydrolysis processing (non-isotherma conditions up to 180 ºC and 200 ° C). Also, table 2 shows percentage contents of individual monomers, oligomers and acetyl groups in the liquid phases of hydrolysis respect to the quantity present of each compound in the original raw material or polymer derived. It also appears the result of the process performance of autohydrolysis is understood as solid fraction yield regard to the raw material used in the trial. All results are expressed on a dry basis.

The yield of extraction in the liquid phase at 180 ° C varies between 25.4% for sunflower stalks and 9.3% for *Eucalyptus globulus*, although with similar values for wood materials. The high yields of sunflower stalks are attributable to the high ash content, and equally to the other herbaceous species used (*Arundo donax*). Naturally, the yield of extraction of autohydrolysis process substantially increases to 200 °C between 35.8% for sunflower stalks and 21.8% for *Arundo donax*, again with very similar results for woody species with values between 29.0% and 23.4%.The results are similar to previous works [6,7]. The extraction percentage increases in the liquid phase of the process between 180 ° C and

200 ° C show a distinction between the two non wood materials (4.4 and 10.4%) and wood (14 and 16.2%). It can be concluded with the observation of a higher predisposition to higher yields at elevated temperatures timber materials against the woody tested.

4. Conclusion

Autohydrolysis processes have been considered interesting in the case of timber species studied compared with herbaceous species with variations in the extraction of the xylan fraction at 180 ° C between 19.68% for *Eucalyptus globulus* and 36.79% for *Leucaena diversifolia* and 200 ° C between 57.86% for *Paulownia fortunei* and 79.13 for *Chamaecytisus proliferus*.

In general, all materials show a solid fraction "more energy" from the hydrolysis to 200ºC than 180ºC and raw materials. It is interesting as the potential economy valuation of the liquid fractions of the hydrolysis, the solid waste recovery present more energetic profitability.

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