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Technical note

Evaluation of the effect of the dilute acid hydrolysis on sugars release from olive prunings

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ABSTRACT

Olive prunings are considered a potential lignocellulosic raw material for production of energy (fuel-ethanol, pellets...) and other value-added products as an alternative to starch-containing feedstock. From an economic point of view, it is particularly important to recover sugars from hemicellulose. The use of dilute acid can lead to rapid hydrolysis conditions, providing hydrolysates rich in D-glucose and D-xylose that do not require further treatment. The effect of the residence time, temperature and sulphuric acid concentration on the formation of D-glucose and D-xylose was estimated by response surface methodology. Batch hydrolysis was carried out at very low temperatures (70–90 °C) and H_2SO_4 concentrations from 0 to 1 N, sampling at different times from 0 to 300 min. According to statistical analysis, all of the three parameters had significant interaction effects on sugars production. Results illustrated that the highest concentrations of D-glucose and D-xylose were found at the highest levels of temperature, acid concentration and residence time assayed. In these conditions, the maximum predicted yields expressed as g of sugar per 100 g of dry matter fed were 0.13 in D-glucose (about 40% of maximum attainable) and 0.10 in D-xylose (about 60% of the potential yield).

1. Introduction

Second generation bioethanol is obtained from non-food crops or inedible waste products. The production of fuel-ethanol from lignocellulose materials is of growing interest around the world because of its advantages over conventional fossil fuels, most notably a reduction in greenhouse-gas emissions. However, its comparatively higher production cost compared to gasoline (1.3 dollars/dm^3) and its lower heating value (26,700 kJ/kg at room temperature) are still hindrances in bioethanol becoming an alternative fuel [1].

One of the sources for second generation bioethanol production could be the pruning debris from olive tree, which area currently under cultivation in Mediterranean countries covers approximately 5.4×10^6 ha and produces about 1.6×10^{10} kg of olive-pruning debris in the European Union per year [2,3]. At present, the conversion of biomass to ethanol includes four steps: pretreatment, hydrolysis of polysaccharides and oligosaccharides into monomer sugars, fermentation of sugars to ethanol and, finally, ethanol concentration to absolute alcohol. From a techno-economic point of view, it is necessary to consume the pentoses from hemicellulose, employing microorganisms capable of fermenting them. D-xylose is produced in the hydrolysis stage as the main sugar from hemicellulose. Its fermentation to ethanol or xylitol, a value-added product with high sweetening properties, could enhance the feasibility of an industrial scheme.

Dilute acid hydrolysis, based on its low economic cost and high hydrolysis rate compared to enzymatic hydrolysis, have been comprehensively studied and widely employed. Applied to olive prunings, it has been verified that dilute acid hydrolysis does not degrade lignin and subsequent phenolic compounds are not released [2,4], which are considered yeast inhibitors. Its main drawback is that sugars are also degraded rapidly under acidic conditions to compounds that can inhibit the subsequent fermentation, including furfural, a product of dehydration of pentoses, and 5-(hydroxymethyl)furfural, a product of the dehydration of hexoses [5]. Sulphuric acid is usually used instead of hydrochloric acid because of its low volatility, lower corrosion on equipment and more reduced cost. Nevertheless, it was found lower D-xylose concentrations under H_2SO_4 hydrolysis than under HCl hydrolysis in some lignocellulosic raw materials such as sugarcane bagasse, which means that HCl could break hemicellulosic chains better than H_2SO_4 [6].

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The dilute sulphuric acid hydrolysis of olive prunings and a proposed kinetic equation for total reducing sugar generation ($r_0 - (r_0)_0 = k\ C_A^n$), based on the calculation of the initial hydrolysis rates (r_0), was elaborated in a previous work [2], however, it only evaluated one factor at a time, the interactional effects between each factor has as yet not been investigated.

In the present work, mathematical model was employed to study the combined influence of temperature, sulphuric acid concentration and residence time in the generation of not only reducing sugars, but also of the two main monomeric sugars in hemicellulose: D-glucose and D-xylose. Since some authors have pointed out that acid concentration is the most important parameter affecting sugar yields whereas temperature is mainly responsible for sugar degradation [7], the range of temperatures chosen was very low.

The objective of this work is thus to analyse the influence of the three factors using response surface methodology, to determine the most favourable conditions in order to attain high D-glucose and D-xylose yields by dilute acid hydrolysis. Those conditions could complete the available information on the utilization of olive-pruning debris for ethanol or xylitol production regarding a future scale-up of the laboratory research.

2. Materials and methods

2.1. Raw material

Olive prunings were collected on-site after the 2004 harvesting from ‘Picual’ olive trees.

Leaves were eliminated from the debris by means of a densimeter table, and the resulting ground residue (thin branches of diameter ≤ 5 cm) was air-dried at room temperature in the laboratory, milled and screened. The size of the fraction selected was between 30 and 40 mesh (0.425–0.600 mm), according to ASTM E11-09 specification, which was then homogenized in a single lot and stored until used. Essential data of the same debris lot previously published [8]: moisture 8.3%, ash 2.3%, cellulose 36.4%, hemicellulose 21.5%, lignin 17.1%, extractives 14.4%; C 46.1%, H 6.4%, N 0.4%, S 0.0% and O 47.2%. As it can be observed, olive tree pruning is a sulphur-free lignocellulosic raw material.

2.2. Acid hydrolysis

The whole dilute acid hydrolysis processes were carried out in a 1-L discontinuous stirred tank reactor at atmospheric pressure provided with agitation and temperature control. The solid:liquid ratio was set to 1:20 (w/v) in all experiments. Temperature ranged between 70 and 90 °C and sulphuric acid concentration was modified from 0 to 1 N. The stirring was kept at 250 rpm and hydrolysis time was set to 5 h. The evolution of the hydrolysis was studied by sampling at different times according to the factorial design; 5-mL samples were centrifuged and their sugars contents were measured. The concentration of total reducing sugars was determined using the dinitrosalicylic acid (DNS) method [9]. D-glucose and D-xylose were quantified by a Dionex Biolc DX300 HPLIC system equipped with a pulsed amperometer detector (gold electrode). Chromatography was performed on a CarboPac PA1 anion-exchange column (4.6 mm × 250.0 mm) equipped with a guard column using NaOH gradient elution from 0 to 1 mol/L with a flow rate of 1 mL/min at 20–22 °C. The sample volume injected was 25 μL. Analyse was completed in a run time of 50 min and post-run time of 15 min.

2.3. Response fitting

We adjusted the data of reducing sugars, D-glucose and D-xylose concentrations obtained at different temperatures, sulphuric acid concentrations and treatment times to a 3-level factorial design (Table 1). Response surface methodology was employed to predict the yields of main sugars in olive-pruning debris during the whole dilute acid hydrolysis processes. To be specific, the three independent variables were temperature (T), sulphuric acid concentration

Table 1
3-Level factorial design arrangement and responses.

Run	T (°C)	C_A (N)	Time (min)	Reducing sugars (g/L)		D-glucose (g/L)		D-xylose (g/L)	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
1	70	0.0	0	0.82	0.96	0.05	0.55	0.00	0.45
2	80	0.0	0	0.77	0.65	0.05	−0.40	0.00	−0.16
3	90	0.0	0	1.41	−0.04	0.05	−0.51	0.00	−0.77
4	70	0.5	0	2.85	2.65	0.31	0.46	0.00	−0.16
5	80	0.5	0	2.76	3.31	0.45	0.26	0.00	−0.06
6	90	0.5	0	2.01	3.59	0.08	0.91	0.01	0.04
7	70	1.0	0	1.64	0.61	0.42	−0.13	0.00	−0.77
8	80	1.0	0	1.84	2.24	0.52	0.43	0.00	0.04
9	90	1.0	0	3.36	3.49	1.47	1.83	0.01	0.85
10	70	0.5	150	6.36	7.44	1.33	1.47	0.03	−0.11
11	80	0.5	150	8.79	9.22	1.70	1.88	0.18	0.64
12	90	0.5	150	12.44	10.61	3.55	3.12	1.71	1.39
13	70	1.0	150	8.13	8.32	1.70	1.66	0.09	−0.11
14	80	1.0	150	13.50	11.07	2.62	2.81	1.14	1.34
15	90	1.0	150	13.02	13.44	5.38	4.81	3.99	2.80
16	70	0.0	300	1.27	0.12	0.17	−0.19	0.00	−0.66
17	80	0.0	300	1.36	2.04	0.17	0.06	0.00	0.03
18	90	0.0	300	1.68	3.58	0.16	1.15	0.00	0.72
19	70	0.5	300	7.98	7.65	1.47	1.25	0.75	−0.06
20	80	0.5	300	11.86	10.54	2.37	2.26	0.75	1.34
21	90	0.5	300	15.16	13.05	5.03	4.10	3.88	2.74
22	70	1.0	300	10.16	11.45	1.79	2.20	0.02	0.54
23	80	1.0	300	15.64	15.32	3.93	3.96	2.54	2.65
24	90	1.0	300	17.43	18.80	6.25	6.55	4.70	4.76
25	80	0.5	150	8.80	9.22	1.76	1.88	0.17	0.64
26	80	0.5	150	8.81	9.22	1.80	1.88	0.17	0.64
27	80	0.5	150	8.79	9.22	1.80	1.88	0.16	0.64
28	80	0.5	150	8.80	9.22	1.73	1.88	0.18	0.64
29	80	0.5	150	8.76	9.22	1.74	1.88	0.19	0.64