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Valorization of the wast descended from the hydrodistillation of *Rosmarinus officinalis*

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Abstract

The production of essential oils from rosemary (*Rosmarinus officinalis*) result the formation of lignocellulosic waste, not easily biodegradable and involve environmental problems. In this work we developed process to produce monomeric sugars with high added value from this waste, after the treatment respectively with the vapour (10min, 205°C under 1 bar) and acid hydrolysis (sulphuric acid 0.5%).

The acid hydrolysis thereafter, improved by pretreatments (explosion by the steam of water), permits to damage all polymers recalcitrant to the acidic hydrolysis.

1. Introduction

Lignocellulosics contain sugars polymerised to cellulose and hemicellulose which can be liberated by hydrolysing the material, and then fermented to ethanol by microorganisms, e.g. *Saccharomyces cerevisiae, candida tropicalis, Pichia Stipitis* [1].

The biological ethanol can be regarded as a more environmentally friendly fuel than gasoline because it adds only little net carbon dioxide to the atmosphere. This is the main reason why large research efforts are done to find a cheap way of producing ethanol from renewable raw materials [2; 3].

The work presented in this paper was performed to elaborate treatment process on *Rosmarinus officinalis* essential oils hydrodistilation waste

2. Materials and methods

2.1. Preparation of the lignocellulosic hydrolysate

Hydrodistilation by product biomass (1Kg) of *Rosmarinus officinalis* was washed with water and filtered in filter press unit at a pressure of 10 bar. The filtrate was collected and subjected to steam pretreatment at 205 C° for 10 minutes.

The steam treated residual is diluted in sulphuric acid, and then it is maintained to the heating during 50 min.

Detoxification is achieved by increasing pH to 9 with $Ca(OH)_2$ (room temperature, magnetic stirrer for 2 h) after which the solution was filtered through a 0.45 µm Millipore filter and the pH was adjusted pH 7 with concentrated H_2S0_4.

2.2. Analysis

The phenol-sulfuric acid method was used for measuring a broad spectrum for carbohydrates, [4]. Total phenol was analyzed according to a modification of the Folin-Ciocalteau method [5].

3. Results and discussion

The experimental programme was divided chronologically into two different phases. During the first phase, the pre-treatment process of substrate was elaborated by means of primary (steam and acid hydrolysis) and secondary treatments (detoxification) to permit further ethanol bioconversion.

3.1. Treatment procedure

Various methods for the hydrolysis of lignocellulosic materials for ethanol production have recently been described [1]. In this work steam hydrolysis and dilute-acid hydrolysis will be measured.

a. high-temperature steam treatment

Prior to acid hydrolysis, the cellulose structure must be made available to the hydrolysing acids by subjecting the material to some form of pre-treatment. Wood can be pre-treated using high-temperature steam which solubilises the hemicelluloses [6].

From figure 1, we noticed that great fraction of total phenolic compounds are liberated from hydro-distilled biomass. The release of sugars is not a sufficient amount when compared to phenolic compounds.

a. Diluted acid hydrolysis

Optimal concentration of sulphuric acid (0.5%) has been added to plant biomass waste (100g). As means of measurement the liberation of the reducing sugars and phenolic compounds has been followed.

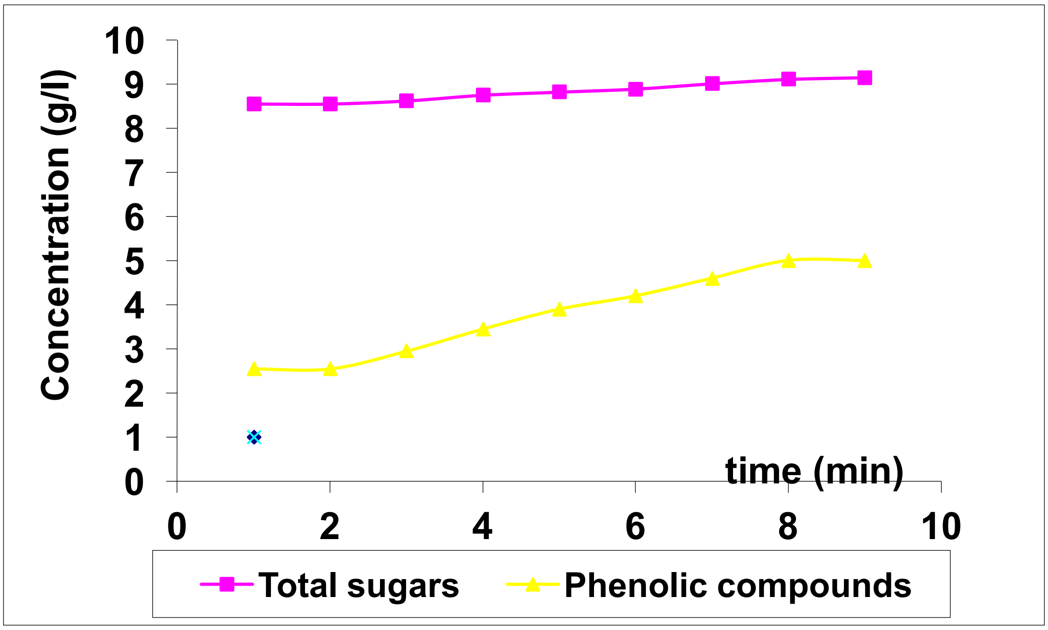

Fig 2: Liberation of total sugars and total phenolic compounds during the time of the steam pre-treatment .

Table 1: Liberation of total sugar and phenols according to the sulphuric acid concentration during 50min acidic hydrolysis.

Sulfuric acid (%)	total sugar gl^{-1}	Phenolic compounds gl^{-1}
0.1	10.85	14.25
0.5	17	14.25
1	17	14.25
2	17	14.25
5	17	14.25
10	17	14.25
20	17	14.25

From table 1 we noticed that 0.1% of acid release the totality of phenolic compounds, whereas a concentration of 0.5% is sufficient to release the majority of the monomeric sugars contained in polymeric carbohydrate in the plant waste.

Dilute-acid hydrolysis is fast and easy to perform and the ethanol yields obtained is only 30-50% of the theoretical values (unpublished results) so technical detoxification was called out to increase the yield of fermentation.

b. Detoxification

Detoxification methods can be developed for efficient removal of inhibitors prior to fermentation of strongly inhibiting hydrolysates in rosemary biomass after hydrodistilation. $Ca(OH)_2$ has been tested for its well-known precipitation characteristics with regard to acid and phenolic compounds substances, including several inhibitors of hemicellulose fermentation.

The phenolic compounds elimination was very important (60%) and fermentation was improved by 40% (unpublished results). From these results we noticed that the detoxification reduces a great part of inhibitors of the alcoholic fermentation (tab. 2).

Table 2: Evolution of Sugar composition during all the steps of *Rosmarinus officinalis* biomass testament.

Sugars	Distillation	Vapour treatment	Hydrolyse acid	Detoxification
Glucose (g/l)	6.05	6.55	9.6	9.5
Xylose (g/l)	2.02	2.25	7.33	7.2
Manose (g/l)	0.015	0.02	2.37	2.37
Galactose (g/l)	0.225	0.25	1.2	1.2
Cellulose Hemicellulose (g/l)	8.8	9.2	0	0
Total phenolic compounds (g/l)	2.5	5.1	14.25	5.8

Sugars production yields were improved gradually from distillation, steam pretreatment and acidic hydrolysis procedure. The effects are revealed in Table 2. The best results have been obtained at acidic hydrolysis. Direct acidic hydrlysis did not give the same results. This procedure resulted in an increase the yield of sugars up to 9.6 of glucose, 7.33g/l of xylose, 2.37 g/l of mannose, and 1.2g/l of galactose. These values are more important than those observed in steam treatment.

The firsts steps in the process are the distillation of essential oil, prehydrolysis (steam pre-treatment) and acidic hydrolysis (fig1 and table 1). In these steps the lignocellulose is delignified and a depolymerisation takes place. During the acid hydrolysis not only free sugars are formed (table 1), but also inhibitors, like acidic and phenolic compounds.

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