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Selection of the best pretreatment for hydrogen and bioethanol production from olive oil waste products

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ABSTRACT

Bioethanol is one of the most promising renewable energy sources, and it can be used as an alternative to petroleum-derived products. Agro-food residues are the substrates most frequently used for bioethanol production through anaerobic fermentation. The cultivation of olive trees and olive oil production are important economic activities throughout all Mediterranean countries. The wastes derived from olive oil production include a liquid waste, known as Olive Mill Wastewater (OMW), and a semi-solid waste, called Olive Pomace (OP), which is rich is lignin and cellulose materials. The aim of this work is to evaluate the quantity of hydrogen and bioethanol that could be extracted from an OMW-OP mixture after *Saccharomyces cerevisiae* anaerobic fermentation. In addition, different pretreatments (ultrasonic pretreatment, basic pretreatment, and calcium carbonate addition) have been tested to increase the glucose concentration and, consequently, the bioethanol and hydrogen production in the reaction medium and to decrease the content of inhibiting polyphenols which are mainly present in the OMW. All of the pretreatments were shown to have improved the hydrogen and bioethanol concentration at the end of the fermentation. The basic and ultrasonic pretreatments resulted in the best bioethanol and hydrogen production. These two pretreatments contributed to the hydrolysis of the lignin and cellulose and to increasing the soluble sugars (in particular glucose) content in the reaction mixture. Calcium carbonate addition decreased the polyphenol concentration; the polyphenols inhibit the fermentation mediated by *S. cerevisiae*.

1. Introduction

Over the last few decades, the global warming that has resulted from the increase in greenhouse gas emissions and the simultaneous depletion of fossil fuels has necessitated the research of alternative and clean energy sources. Among the available renewable fuels, interest in bioethanol has been increasing. The increase in global bioethanol production between 2000 and 2013 is shown in Fig. 1 [1]. In 2011, bioethanol production reached 3.5 Mm^3 [2].

The production of biofuels, such as bioethanol, usually involves starches and simple sugars derived from sources such as sugar cane and corn. The fermentation of these substrates is highly efficient, but at the same time it is expensive and non-sustainable because of the concurrent use of these substrates as essential components of the food–feed chain [3].

Agro-food residues are the main substrates used as an alternative for bioethanol production. In the USA and in Brazil, over 87% of bioethanol is obtained from maize and sugar cane feedstocks, respectively [4], whereas in China, rice straw is the major substrate used for ethanol production [5]. These substrates contain high contents of lignin and cellulose, which show great potential for ethanol production [6]. Cellulose is a biopolymer that consists of thousands of glucose units, whereas lignin is a polymer that displays high molecular weight, insolubility, and chains of complex carbohydrates [7]. Many studies have focused on using cellulose and lignin hydrolysates to obtain biofuels, and in particular bioethanol [8,9]. The monomers of the glucose contained in the lignin and cellulose structures can be converted into glycerol through anaerobic fermentation [10]. Park et al. [11] studied the optimal concentration of glucose and performed tests with *Saccharomyces cerevisiae* batch fermenting glucose contents ranging from 30 to 120 g/L. The optimal glucose concentration for ethanol production was found to be in the 40–70 g/L range, which corresponds to an ethanol concentration of 6.9% *v*/*v* and an ethanol yield of 88.3%. An

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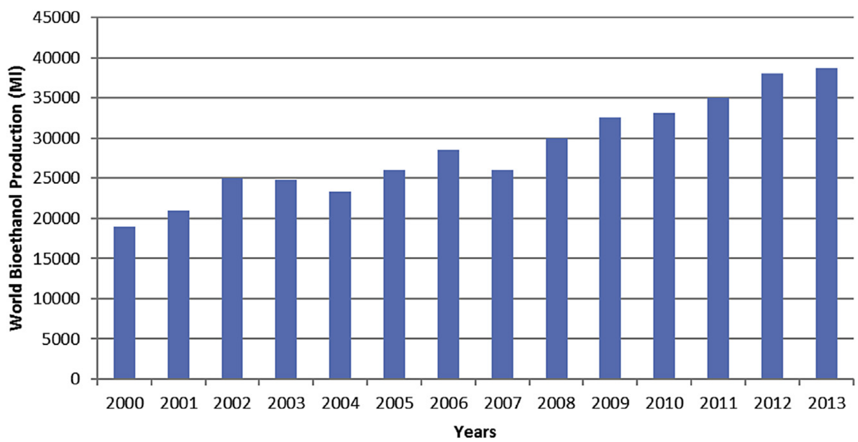

Fig. 1. Bioethanol production (Ml) between 2000 and 2013 [1,2].

abundant agricultural residue with high contents of lignin and cellulosic is Olive Pomace (OP), which (along with Olive Mill Wastewaters (OMW)) is derived from olive oil production. OP is the solid residue that remains after solvent extraction of cold pressed olives. The physical features of OP depend on the technology used during the olive oil production process, i.e., three or two phase centrifugation. In the first case, the OP has a lower water content (50% *w/w* olive) than in the second case (75% *w/w* olive). Dry OP is comprised of lignin (37% *w/w*), cellulose and hemicellulose (49.5% *w/w*), the olive oil retained in the pulp (7.5% *w/w*) and mineral components (6% *w/w*) [12,13]. OMW is the aqueous effluent that is derived from olive oil production processes and is comprised of the water contained in the olive pulp as well as the water used for the washing operations of the drupes and the machinery used for olive oil extraction. A typical OMW is comprised of 90% *w/w* water, 8.5% *w/w* organic compounds and 0.4–2.5% *w/w* mineral salts [14]. OP and OMW are rich in phenolic compounds [15], which limit the activity of microorganisms because of biostatic effects and, consequently, limit bioethanol production [16]. The bioethanol obtained from the fermentation of lignocellulosic wastes, such as olive oil production wastes, is cheaper to produce than bioethanol obtained from the fermentation of traditional feedstocks such as cassava, wheat, and corn. Additionally, these wastes display good yields when they are previously have previously been pretreated [3]. The fermentation of ligno-cellulosic materials releases hydrogen as a by-product, which is an additional biofuel used in industry [2,4,5].

Several tests on OP have been conducted to produce bioethanol. Asli and Qatibi [17] treated OP with 1.75 *w/v* sulphuric acid and heated it at 140 °C for 10 min to increase the solubility of the ligno-cellulosic material. The OP was fermented by *Escherichia coli* FBR5, and 0.81 g/L of ethanol was obtained. However, if the pretreatment temperature is increased to 180 °C, the fermentation will fail because of the higher concentration of inhibiting components released during the heating. Tayed et al. [18] isolated different yeast strains in an attempt to determine the best strain, in terms of ethanol production, from olive oil production wastes. *Issatchenkia orientalis* was the strain that displayed the highest ethanol yield (5 g of ethanol/100 g of raw material). Sarris et al. [19] evaluated the capacity of *S. cerevisiae* to ferment an OP and OMW mixture under aerobic and anaerobic conditions. The ethanol production was similar in two cases: 48.2 g of ethanol/L was obtained under aerobic conditions, while 52.4 of ethanol g/L was obtained under anaerobic conditions.

The aim of this study was to investigate the simultaneous production of bioethanol and hydrogen using OP and OMW through *S. cerevisiae* mediated anaerobic batch fermentation. Ethanol fermentation had previously been conducted at elevated temperatures (50 °C) to permit a more efficient saccharification and to increase the solubility of the substrates in order to improve volumetric productivity. High temperature fermentation requires a substantial amount of energy [20]. The present work represents an alternative to thermal fermentation as it tests some chemical and physical pretreatment methods to increase the soluble sugars in the reaction medium, to decrease the polyphenol concentration and, consequently, to optimize hydrogen and bioethanol production from olive oil production residues.

2. Materials and methods

2.1. OP, OMW and characteristics of the inoculum

The OP and OMW both originated from Melendugno, a town located near Lecce in the southern part of Italy. The OP was derived from olive production operations, which included a three phase centrifugation which was used to separate the solid phase from the oil phase and aqueous phase; the OMW originated from the same production processes. Table 1 summarizes the main characteristics of the OP and OMW.

A *S. cerevisiae* strain (24860 ATCC) was used for the fermentation of the biomasses. The inoculum was maintained at 4 °C on agar slants containing: 20 g of glucose, 5 g of peptone, and 3 g of *S. cerevisiae* ATCC 24860 (per litre).

S. cerevisiae yeast was considered for the ethanol production from lignocellulosic materials because of its successful exploitation in the fermentation industry, its proven ability to produce high ethanol concentrations and its high level of resistance against the inhibitors found in lignocellulose hydrolysates [11,21,22].

Table 1
Chemical and physical characteristics of the tested OP and OMW.

	OP	OMW
Density (kg/m^3)	969.5 ± 41.2	989.4 ± 5.31
pH	6.75 ± 0.05	4.86 ± 0.01
Content of TS (g/L)	331.33 ± 6.81	12.04 ± 0.02
Content of VS (g/L)	305.6 ± 6.18	7.49 ± 0.21
Low Heat Value (kJ/kg)	25,503.9 ± 51.61	nd
Polyphenols Content (mg gallic acid/L)	nd	237,58 ± 5,21