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Evolution of the metal and metalloid content along the bioethanol production process

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ABSTRACT

Metal and metalloid concentration has been determined through inductively coupled plasma - mass spectrometry (ICP-MS) in bioethanol samples, raw materials employed to obtain this biofuel and samples taken from different critical points of the manufacture method. In this way, it was possible to study the evolution of the metal and metalloid content all along the bioethanol production process, allowing to establish the origin of the elements determined in the final samples. Moreover, the steps of the production process where they were either removed from the biomass or accumulated in the biofuel were successfully identified.

Four different acid assisted protocols were compared through the analysis of two biomass certified reference materials (CRMs). The results revealed that, for the most suitable method (nitric acid assisted MW digestion), recoveries for the analytes of interest went from 90% to 110%. Furthermore, good short-term and long-term precision and acceptable limits of detection (LODs) were obtained.

Two different production lines were studied, and our results show that slight differences in terms of the minor elements concentration (Cd, Co, Sb, Pb and V) were identified. The most important source of metals and metalloids in the whole process can be attributed to the raw material. Meanwhile the distillation step caused 1000 to 10,000 times decrease in elemental concentration in the final bioethanol as compared to the initial biomass.

1. Introduction

Recently, biofuels have been considered as an effective alternative energy source due to the health and potential environmental concerns that it may be caused by fossil fuels together with the increasing demands for energy and the depletion of petroleum conventional reserves [1–3].

Bioethanol is one of the most promising biofuel, because its use may reduce by up to 75% the emission of greenhouse gases (GHG), such as CO_2, CH_4 and N_2O, as compared with fossil fuels [1–5]. Consequently, its production and consumption have grown exponentially during the last two decades [6].

Bioethanol can be used in its pure form within modified spark-ignition engines or blended with petroleum distillates, this blend is known as ethanol-fuel. Although 1 L of ethanol contains 66% of the energy provided by a liter of petroleum fuel, it acts as a very efficient octane-boosting agent, thereby replacing other chemical additives such as methyl ter-buthyl ether (MTBE) [1,3,7].

Although the synthesis of bioethanol process depends strongly on the raw material, the production of bioethanol generally includes the following steps: (*i*) preparation of the feedstock to achieve maximum sugar extraction yield; (*ii*) hydrolysis of the feedstock and extraction of the sugars; (*iii*) production of solutions with high sugar concentrations (syrups); (*iv*) fermentation to convert sugars into ethanol; (*v*) distillation, which is one of the most important process in terms of other organic compounds and water removal; and, (*vi*) dehydration, that is carried out to obtain the ethanol concentration required (anhydrous ethanol or hydrated ethanol) [2,4].

Several industrial processes have been developed for bioethanol production, leading to different generations of this fuel. The first-generation bioethanol is the alcoholic product generated from sugars (sugar cane, sugar beet, *etc.*), seeds or starch (potato, corn, wheat, *etc.*) using microorganisms. Generally, the yeasts convert sugars into ethanol by fermentation and, after that, the distillation and the dehydration are carried out [7,8]. Although the process is simple and efficient due to its relatively ease of converting sugars and starch into ethanol, only a reduced fraction of the plant is efficiently transformed into bioethanol. This leads to the unwanted fuel-food competition phenomenon [1,7,8,9]. The second-generation bioethanol appears to overcome this problem and its production involves a previous enzymatic hydrolysis of

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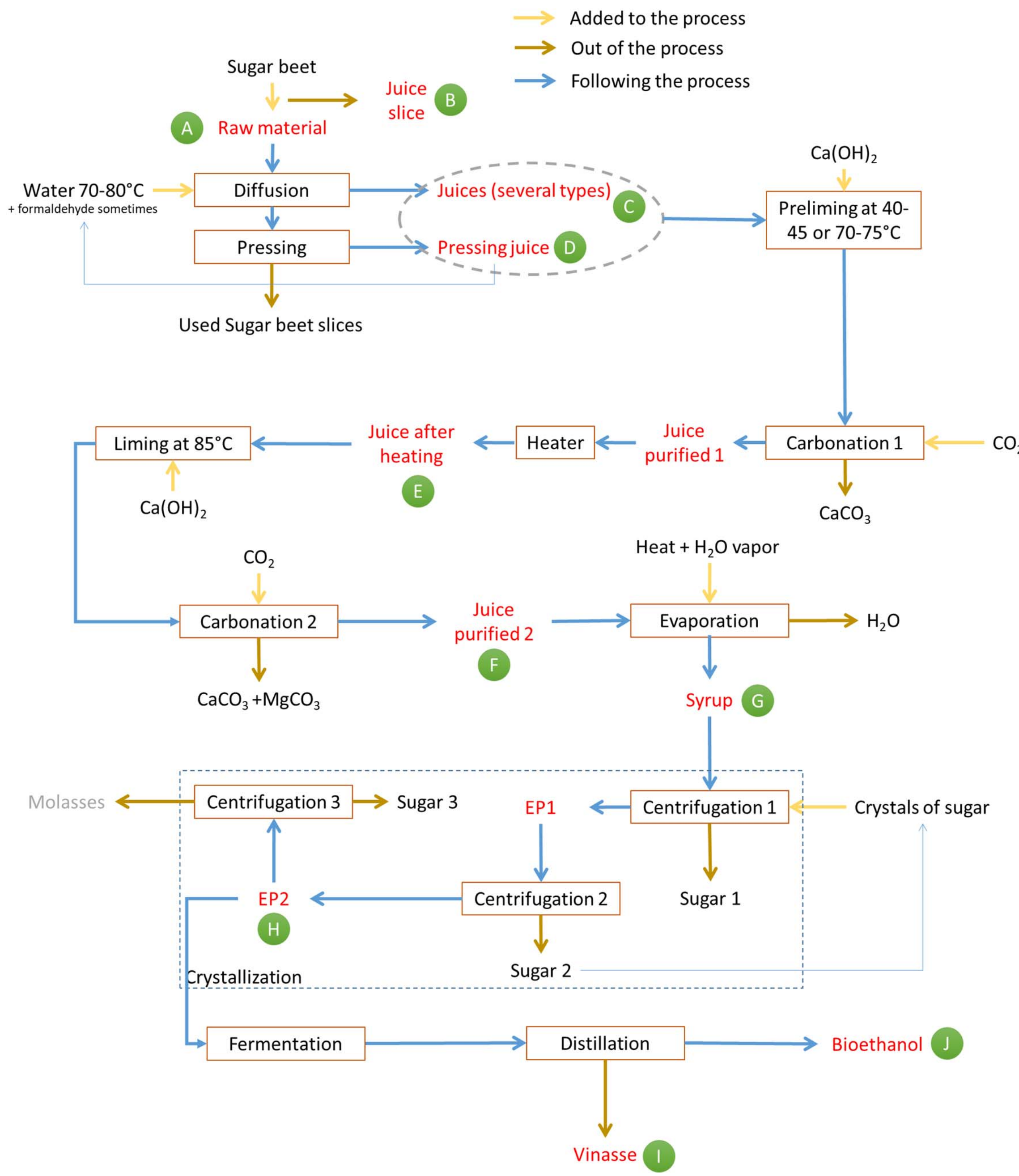

Fig. 1. Scheme of bioethanol production process studied in the present work.

agricultural lignocellulosic biomass corresponding to non-edible food crop production or whole plants biomass. The main advantages of the second generation are the absence of fuel-food competition and the low cost of the raw material, because it is a byproduct of other processes [2,7,8,10]. However, production of second generation bioethanol requires sophisticated equipment and the transformation yield reached is lower than the obtained for the first-generation processes [7]. Finally, a third generation of biofuels is being developed [11–13] and they are being implemented quickly in the case of biodiesel [13], although this emerging technology is still not widely used for bioethanol production.

At the end of the production process, bioethanol may contain organic as well as inorganic pollutants, among them trace metals [14–17]. The appearance of these metallic species affects notably the quality of the product. Some of them, (*e.g.*, Pb, Tl, Hg, Cd or As) can cause health [4,18,19] and environmental [20–23] problems even at low concentrations. Finally, other metals, such as Fe or Cu, lead to a degradation in the vehicle engines and a modification of the ethanol stability [4,24].

Elucidating the origin of metals in bioethanol is a challenging task. Some authors reported that they may appear during fuel transportation and storage [4,18,19,24,25] or may be added to the final bioethanol as additive [4,21]. However, other reports have suggested that the main source of metals and metalloids in bioethanol is the raw material [4,24,26–29]. In such case, the metal content depends on the atmospheric pollution and the soil where the raw material has grown [18,28]. Additional findings have reported that bioethanol can also be contaminated during its production process [20,24,26].

Several works have been focused on the development of analytical methodologies to carry out the determination of metals in both bioethanol [4,15,16] and the raw materials employed to obtain this biofuel [27–29]. The main conclusion of these works is that a large number of elements were found at rather low concentrations, being Na, Fe, Ni, Co,