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Technical suitability mapping of feedstocks for biological hydrogen production

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ABSTRACT

The objective of this work was to map and compare the technical suitability of different raw materials for biological hydrogen production. Our model was based on hydrogen yield potential, sugar mobilization efficiency, fermentability and coproduct yield and value. The suitability of the studied raw materials was ranked in the order: sugar beet juice > sweet sorghum juice > potato steam peels > barley straw > miscanthus > sweet sorghum bagasse > carrot press cake > wheat grains > wheat straw > wheat bran. The results indicated that raw materials with similar chemical composition may have different technical suitability for hydrogen production. Therefore, further research on the specific technical characteristics, including pretreatment requirements, of each raw material is recommended.

1. Introduction

Significant research work has been carried out recently on the exploration of new renewable energy sources and sustainable conversion processes for the production of renewable fuels, chemicals and energy. Biomass as a sink of solar energy is an attractive energy source and includes agricultural, forestry, agro-industrial residues and energy crops. Several conversion technologies have been studied, including combustion and gasification (Khan et al., 2009), pyrolysis (Bridgwater, 2012), ethanol fermentation (Hamelinck et al., 2005) and biological hydrogen fermentation (Das and Veziroglu, 2008; Claassen et al., 2010).

Hydrogen is a clean fuel with zero CO_2 emission when burnt and it is the prime energy carrier to be used in fuel cells for electricity generation. It has been predicted that hydrogen will be the main energy carrier by 2100 (Dunn, 2002). Conventional hydrogen production technologies are regarded as high energy demanding. For example, water electrolysis may be the cleanest technology for hydrogen production, but it is competitive for industrial use only in areas with established cheap electricity availability.

Biological hydrogen production is a viable alternative to chemical methods for hydrogen production. Biological conversion has key advantages compared to the other technologies because it is relatively efficient, it has relatively low energy demands and it can use a variety of organic wastes, including organic material with high moisture content, as substrate (de Vrije and Claassen, 2003; Levin et al., 2004). These characteristics of biological hydrogen production bring it in line with sustainable development and waste minimization energy strategies. Although the biological hydrogen production process involves the production of carbon dioxide, this process is considered as carbon dioxide neutral because carbon dioxide is released from biomass but also sequestered again in this biomass.

Biological methods of hydrogen production include the use of algae and cyanobacteria, photosynthetic bacteria and fermentative bacteria. Extreme thermophilic anaerobic bacteria have attracted high interest because of their high yield with respect to hydrogen production. High hydrogen yields of circa 3 mol/mol hexose have been reported by de Vrije et al. (2009) and reviewed by Jones (2008) and Kengen et al. (2009). These yields correspond to approximately 75% of the maximal theoretical value of 4 mol hydrogen/mol glucose. Moreover, application of thermophilic bacteria in hydrogen production is advantageous compared to for

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example industrial yeasts employed for ethanol production, since the fermentative action of these bacteria can lead to employment of hexose and pentose sugars as well as oligomeric carbohydrates for hydrogen production.

Dark hydrogen fermentation is the type of fermentation in which the organic compounds, that break down toward hydrogen production, constitute the sole carbon and energy source providing metabolic energy. Dark hydrogen fermentation is an incomplete oxidation, therefore the organic matter is not completely oxidized to carbon dioxide but to intermediate compounds such as acetic acid. These physiological drawbacks of dark hydrogen fermentation can be eradicated by coupling the process to a subsequent fermentation. This can be photoheterotrophic fermentation, which can convert dark fermentation derived organic acids to hydrogen and carbon dioxide. Higher amounts of hydrogen are produced because in photoheterotrophic fermentation additional hydrogen is produced from the organic acids (Claassen et al., 2010). In particular, with use of glucose as the sole substrate in dark anaerobic fermentation, where acetic acid is the predominant metabolite product, a total of 12 mol hydrogen is expected in the combined process from one mol of glucose.

The utilization of several raw materials towards biological hydrogen production has been recently studied. Raw materials such as energy crops (Claassen et al., 2004; Hussy et al., 2005; de Vrije et al., 2009), agricultural residues (Datar et al., 2007; Kongjan et al., 2010; Özgür and Peksel, 2013) and agroindustrial residues (Mars et al., 2010; Özgür et al., 2010; Panagiotopoulos et al., 2013) have attracted significant attention. However, important issues concerning the overall technical suitability of different raw materials on a comparative basis have not always been sufficiently emphasized. Moreover, different methodological approaches followed by research groups worldwide have often led to results not easily comparable to each other.

The goal of this study was to develop a tool for the comparison of the utilization of different raw materials for biological hydrogen production and for the identification of possible raw material-related disadvantages. It was our intention to maintain a pretreatment severity level similar to all raw materials. The comparison of suitability reported in similar studies which have employed different assumptions in their evaluation should be undertaken with great care. Due to the complexity of the mapping, some interactions between the considered parameters could not have been fully avoided. However, it was our intention to keep the interaction between the selected parameters to a limited extent. Our model consisted of a MS Excel worksheet, which was divided into four parameters: yield potential, sugar mobilization efficiency, fermentability and coproduct yield and value. Rhombic graphs were constructed to give the graphical representation of the technical suitability map (TSM).

2. Materials and methods

The description of the TSM and the calculation of its parameters are presented below.

2.1. Description of the model

The objective of the TSM was to determine the technical suitability of different raw materials for biological conversion to hydrogen. The conceptual design of the technical suitability was constructed with recently obtained results from experimental work which was carried out either specifically for the purposes of the present paper or generally for the purposes of the HYVOLUTION Project (Claassen et al., 2010). According to this design, the proposed TSM consisted of four independent parameters which are presented in Table 1. For each parameter, scores were assigned to each raw material, based on compositional data as well as experimental data from pretreatment, fermentation and coproduct valorization.

2.1.1. Calculation of hydrogen yield potential

The hydrogen yield potential was calculated in kg of hydrogen per ton of dry raw material on the basis of the combination of dark fermentation and photofermentation in 2 stages, and then it was normalized on a 0–100 scale. The theoretical ratios of 8, 4, 3.3 mol hydrogen per mol of sucrose, glucose, xylose, respectively were considered for thermophilic fermentation (de Vrije et al., 2007). The theoretical ratio of 4 mol hydrogen per mol of acetic acid was considered for photofermentation (Claassen and de Vrije, 2006). The chemical composition of the raw materials (Table 2) was used to determine their carbohydrate composition and eventually calculate the potential hydrogen yield. The conversion efficiency of fermentable substrates to hydrogen was 80%, taking into account 20% utilization of biomass for bacterial growth (Panagiotopoulos et al., 2010b).

2.1.2. Calculation of sugar mobilization efficiency

The sugar mobilization efficiency was calculated on the basis of the carbohydrates present in the raw material that can be converted to fermentable sugars. Obviously, soluble monomeric and dimeric sugars form the ideal medium for biological hydrogen production. Starch, which is a polymer of glucose, is considered to be an easily degradable compound and can also be converted to hydrogen. Typically starch requires enzymatic hydrolysis to be converted to soluble glucose. Cellulose and hemicellulose are the main carbohydrate polymers present in lignocellulosic biomass. Cellulose, like starch, is a polymer of glucose but, unlike starch, has a crystalline structure making it water insoluble and resistant to depolymerisation. Hemicellulose of agricultural origin is a branched polymer of glucose and/or xylose, substituted with arabinose, galactose, fucose, mannose or glucuronic acid, depending on the species. Both hemicellulose and cellulose typically require pretreatment and enzymatic hydrolysis to be converted to fermentable sugars and thus have relatively low mobilization efficiency, depending on the efficiency of the pretreatment and the yield of enzymatic hydrolysis. It should be noted that in this work we intended to maintain a pretreatment severity level similar to all raw materials.

Table 1
Brief description of the parameters of the technical suitability map (TSM).

Parameter	Definition
Yield potential	Maximum hydrogen yield based on two-step stoichiometric hydrogen fermentation, assuming 80% conversion to hydrogen and 20% to microbial biomass production and other byproducts
Mobilization efficiency	Percentage of all carbohydrates in the raw material that can be converted to fermentable sugars
Fermentability	Tendency of pretreated raw material to improve or inhibit fermentation
Coproduct yield and value	Characterization of both the volume and the value of the coproduct from pretreatment/hydrolysis