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Review

Biomass residues as raw material for dark hydrogen fermentation – A review

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ABSTRACT

It is now widely recognized that considerable amounts of hydrogen can be produced from renewable resources without using energy from fossil fuels. Biological processes and mainly bacterial hydrogen fermentation are considered as the most environmentally friendly alternatives for satisfying future hydrogen demand.

In particular, biohydrogen production from agricultural and agro-industrial solid waste and wastewater is considered as highly advantageous as materials of this kind are abundant, cheap and biodegradable. Apart from economic considerations, the conversion of such materials into hydrogen is in many cases stimulated by the need to solve environmental problems. However, the suitability of various kinds of biomass-derived feedstock for industrial-scale hydrogen production is widely differentiated.

In this paper, on the basis of numerous research contributions published mainly in the period 2008–2013, recent findings on the use of biomass residues and waste for biohydrogen production by bacterial fermentation are reviewed. The focus is on second generation (lignocellulosic) biomass substrates that are most widely available but can be fermented only after appropriate pretreatment which is rather costly at present and therefore requires further development. Research results pertaining to the use of selected sugar-containing and starchy residues are also mentioned as the conversion of these materials into biohydrogen is not in competition with food production, and their pretreatment is cheaper than that of lignocellulosic biomass.

In addition to an extensive literature review, the state of the art in the area of pretreatment of biomass residues for hydrogen fermentation is evaluated, and the authors' view of challenges for future research is presented.

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Introduction

Growing interest in hydrogen as an energy carrier of the future is in contrast to the fact that at present, most of hydrogen produced worldwide comes from thermo-chemical conversion of fossil fuels [1,2] and the involved production processes contribute to carbon dioxide emissions. It is now widely recognized that a real benefit for CO_2 abatement can only be obtained if H_2 is produced from renewable resources without using energy from fossil fuels, as the associated release of CO_2 can then be considered as a part of the natural oxygen–carbon dioxide cycle In this context, biological processes and mainly conversion of carbohydrate-containing biomass by bacterial hydrogen fermentation are considered among the most environmentally friendly alternatives for satisfying future H_2 demand.

Bacterial hydrogen fermentation is a family of processes that can be roughly divided into three groups: dark fermentation, photofermentation for which the availability of light is necessary, and two-stage processes combining dark fermentation either with photofermentation or with bio-electrogenesis in microbial fuel cells [3–5]. Each group includes processes that differ in the microorganisms used and process conditions. As for the dark fermentation, depending on the type microorganism, the temperature level is in the mesophilic, thermophilic or extreme thermophilic range.

Dark fermentation consists in converting simple sugars or disaccharides to hydrogen, carbon dioxide and organic acids. Suitable heterotrophic bacteria include strict anaerobes (such as *Clostridia* and thermophiles), facultative anaerobes (like *Enterobacter*) and aerobes (for example *Alcaligenes* and *Bacillus*). Anaerobic bacteria produce hydrogen from hexoses in acetic acid, butyric acid and acetone-butanol-ethanol fermentations. The maximal theoretical value of 4 mol H_2/mol glucose can be reached in acetic acid fermentations. When other organic acids and alcohols are produced by facultative anaerobic bacteria, the yield of hydrogen is decreased to about 2 mol H_2/mol hexose. The hydrogen yields and production rates of thermophilic and extreme thermophilic bacteria (e.g., *Thermoanaerobacterium thermosaccharolyticum, Caldicellulosiruptor saccharolyticus* and *Thermotoga neapolitana*) growing at temperatures above 60 °C, are often higher than those of mesophilic bacteria growing at ambient temperature because thermophilic bacteria produce acetic acid as the main fermentation byproduct.

According to Demirbaş, biomass resources can be defined as wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing and aquatic plants and (macro)algae [6]. This definition should perhaps be extended by adding vegetal waste from public green spaces, waste from non-food industrial uses of biomass including biofuel production, organic loaded effluents from biomass processing industries, and microalgal biomass.

A number of review articles on the use of biomass waste and biomass-derived wastewater for biohydrogen production are available in the literature, however most of them focussing on the issues of process technology. Some of them take a broad perspective [7–9] while others are focused on more narrow areas like the application of mixed microbial cultures [10], processing of lignocellulosic waste [11] or agricultural waste [12], and wastewater processing [13]. A different approach is adopted in the present paper as it is intended to illustrate the diversity of biomass residues and waste used as raw material for bacterial hydrogen fermentation. In reviewing numerous research contributions published mainly in the period 2008–2013, the focus is on second generation (lignocellulosic) biomass substrates that are most widely available. The uses of some sugar-containing and starchy residues are mentioned only if justified by research results that can be of importance to the lignocellulosic materials.

A systematic approach is adopted by reviewing research on wastes generated along the paths of biomass schematically shown in Fig. 1, from the farming sector (agricultural waste), through biomass-processing industries (agro-industrial residues and effluents), to the retail sector and consumers (food waste comprising kitchen waste and discarded food from the retail sector). It has variously been estimated that all these wastes can account for over 30% of worldwide agricultural productivity [14].

Vegetal agricultural waste

According to UN definition [15], agricultural waste is waste produced as a result of various agricultural operations. It includes manure and other wastes from farms, poultry houses and slaughterhouses; harvest residues; fertilizer run-off from fields; crop protection products that enter into water, air or soils, etc. In this review, harvest residues and mainly wheat straw, corn stover, barley straw etc. deserve special attention as these materials are widely available in vast quantities and have for many years been investigated as potential input to large-scale industrial processes that employ various bioenergy technologies including the production of biofuels other than biohydrogen.

Although fully convincing results of the research on bioenergy (incl. biohydrogen) production potential from the different harvest residues are rather scarce, some of the studies done in the European Union or Germany (the largest EU member) deserve recognition for their systematic approach including the evaluation of uncertainty of results. Scarlata et al. [16] provided a resource-based assessment of

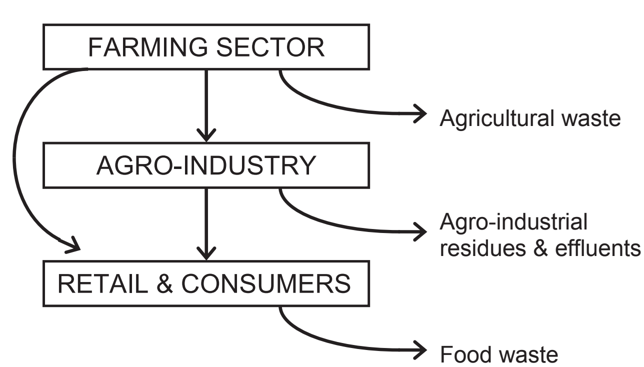

Fig. 1 – Scheme of material flows related to biomass use and generation of biomass waste.