



## Research review paper

## Do furanic and phenolic compounds of lignocellulosic and algae biomass hydrolyzate inhibit anaerobic mixed cultures? A comprehensive review

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## ABSTRACT

Nowadays there is a growing interest on the use of both lignocellulosic and algae biomass to produce biofuels (i.e. biohydrogen, ethanol and methane), as future alternatives to fossil fuels. In this purpose, thermal and thermo-chemical pretreatments have been widely investigated to overcome the natural physico-chemical barriers of such biomass and to enhance biofuel production from lignocellulosic residues and, more recently, marine biomass (i.e. macro and microalgae). However, the pretreatment technologies lead not only to the conversion of carbohydrate polymers (i.e. cellulose, hemicelluloses, starch, agar) to soluble monomeric sugar (i.e. glucose, xylose, arabinose, galactose), but also the generation of various by-products (i.e. furfural and 5-HMF). In the case of lignocellulosic residues, part of the lignin can also be degraded in lignin derived by-products, mainly composed of phenolic compounds. Although the negative impact of such by-products on ethanol production has been widely described in literature, studies on their impact on biohydrogen and methane production operated with mixed cultures are still very limited.

This review aims to summarise and discuss literature data on the impact of pre-treatment by-products on H<sub>2</sub>-producing dark fermentation and anaerobic digestion processes when using mixed cultures as inoculum. As a summary, furanic (5-HMF, furfural) and phenolic compounds were found to be stronger inhibitors of the microbial dark fermentation than the full anaerobic digestion process. Such observations can be explained by differences in process parameters: anaerobic digestion is performed with more complex mixed cultures, lower substrate/inoculum and by-products/inoculum ratios and longer batch incubation times than dark fermentation. Finally, it has been reported that, during dark fermentation process, the presence of by-products could lead to a metabolic shift from H<sub>2</sub>-producing pathways (i.e. acetate and butyrate) to non-H<sub>2</sub>-producing pathways (i.e. lactate, ethanol and propionate) and whatever the metabolic route, metabolites can be all further converted into methane, but at different rates.

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## Introduction

Fossil fuels coming from coal, natural gas and petroleum represent about 80% of the primary energy resources consumed in the world, leading not only to their rapid depletion but also to many environmental damages, including global warming (Nigam and Singh, 2010; Saidur et al., 2011). Recently, the development of renewable energy sources has become a worldwide issue. Particularly, the production of second generation biofuels (i.e. bioethanol, biohydrogen and methane) through conversion of lignocellulosic substrates (i.e. agricultural residues, energy crops cultivated in no-arable lands and softwoods) has taken high consideration due to their composition rich in carbohydrates, their abundance, their renewability and they do not enter in competition with food feedstock (Hendriks and Zeeman, 2009; Mata-Alvarez et al., 2000; Monlau et al., 2013a; Mosier et al., 2005). Even though, most of the research has focused so far on terrestrial biomass, the utilisation of marine biomass such as micro and macro algae to produce so called “third” generation biofuels has gained a tremendous attention worldwide (Chen et al., 2013; John et al., 2011; Jung et al., 2013; Prajapati et al., 2013; Rojan et al., 2011; Ruiz et al., 2013; Sialve et al., 2009).

Among renewable biofuels, biohydrogen and methane produced respectively by dark fermentation and anaerobic digestion (AD) when operated with mixed cultures, represent promising routes for the valorisation of lignocellulosic and algal biomass (Fig. 1). Anaerobic digestion is a process consisting in four physiological steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. During AD, the biomass is transformed into biogas, a mixture of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ). The process can also be stopped at the acidogenic phase, so-called dark fermentation, where VFAs (Volatile Fatty Acids) and a biogas composed of a mixture of  $\text{H}_2$  and  $\text{CO}_2$  are produced concomitantly. To avoid the methanogenic step, the operational parameters in the reactor are fixed to inhibit methanogens, such as low pH, short hydraulic retention time and heat-shock pre-treatment of the inoculum (Guo et al., 2010; Hawkes et al., 2007; Nath and Das, 2004).

One major challenge in using lignocellulosic biomass is their native recalcitrant structure due to their natural physicochemical barriers, which inherently provide tensile strength and protection against pests and pathogens, but also confers a resistance to hydrolysis for further conversion by anaerobic fermentative bacteria (Monlau et al., 2012a; Vancov et al., 2012). Carbohydrate compounds (i.e. cellulose and

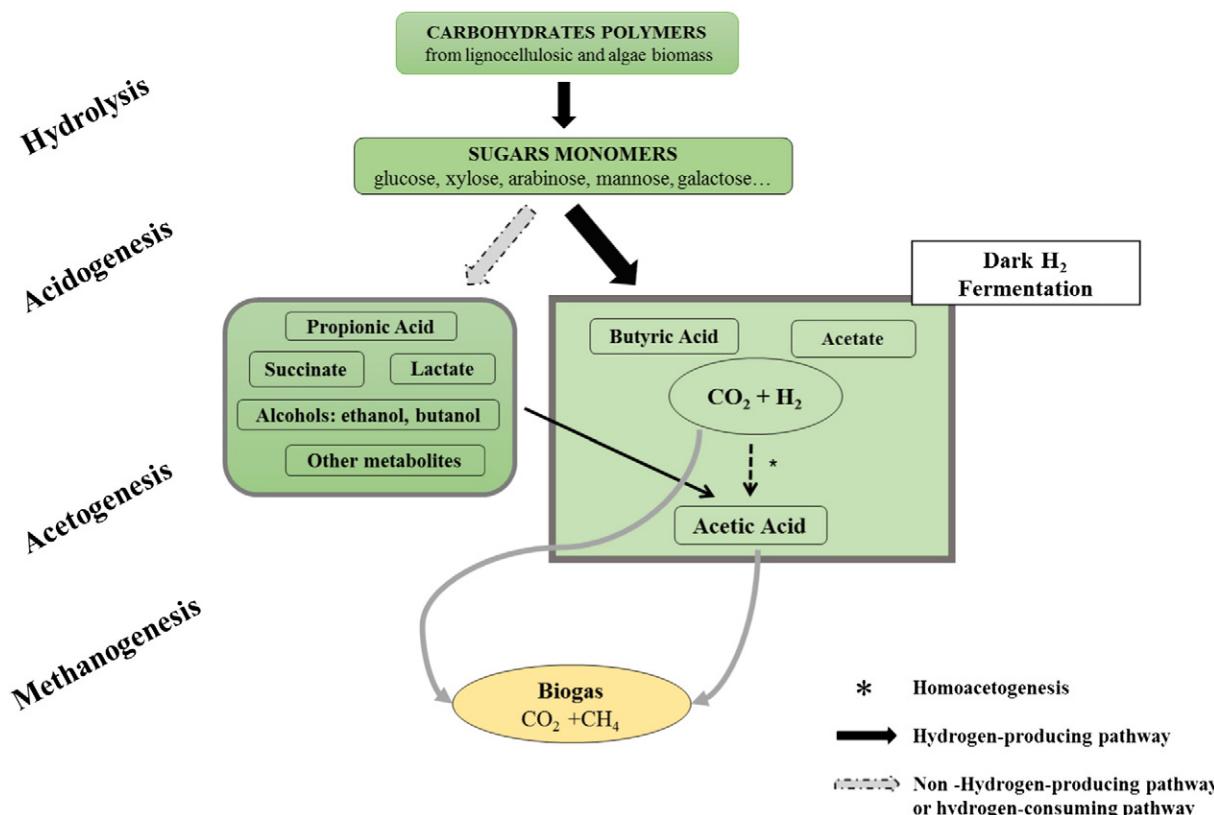


Fig. 1. Scheme of carbohydrate polymers degradation through dark fermentation and anaerobic digestion bioprocesses operated with mixed cultures (adapted from Monlau et al., 2013a).

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