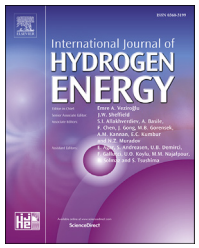
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Impact of furfural on biological hydrogen production kinetics from synthetic lignocellulosic hydrolysate using mesophilic and thermophilic mixed cultures

Chinaza Akobi [a], *Hisham Hafez* [b,c], *George Nakhla* [a,b,*]

[a] *Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada*

[b] *Department of Civil and Environmental Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada*

[c] *GreenField Specialty Alcohols Inc., Chatham, Ontario, N7M 5J4, Canada*

ARTICLE INFO

Article history:
Received 10 January 2017
Received in revised form
23 March 2017
Accepted 24 March 2017
Available online 19 April 2017

Keywords:
Kinetics
Furfural
Biohydrogen
Mesophilic
Thermophilic
Hydrolysate

ABSTRACT

The impact of furfural on hydrogen production and microbial growth kinetics was assessed using mixed anaerobic cultures at mesophilic and thermophilic conditions. Mesophilic experiments showed a hydrogen yield of 1.6 mol H_2/mol initial sugars at 1 g/L furfural which is a 45% enhancement from the control (0 g/L furfural) at a substrate-to-biomass ratio (S°/X°) of 4 gCOD/gVSS. On the other hand, thermophilic experiments showed no enhancement at 1 g/L furfural but rather a 53% decrease in hydrogen yield from its control. Furfural inhibition threshold limit was observed to be greater than 1 g/L for mesophilic experiments and less than 1 g/L for thermophilic experiments. In both cases, 4 g/L was the most recalcitrant furfural concentration, with propionate and lactate the most predominant soluble metabolites in the mesophilic and thermophilic experiments respectively. It was also noted that in the presence of furfural, hydrogen-producers in both mesophilic and thermophilic mixed cultures were inactivated as no hydrogen was produced until furfural was completely degraded irrespective of sugars degradation. This study also presents the kinetics of microbial growth and substrate degradation obtained using the Monod model on MATLAB®, ignoring an inhibition term. IC_{50} of the mesophilic and thermophilic experiments were 1.03 g/L and 0.5 g/L respectively indicating that the thermophilic hydrogen producers were more strongly affected by furfural than the mesophilic cultures.

Introduction

As the world strives towards a low-carbon future, the need to zero down on a fuel that is emissions-free, cheap and reliable cannot be over-emphasized. Hydrogen has been described as an important energy carrier for the future as it burns clean (zero CO_2 emissions) [39,43], has a high heating value (142 MJ/kg) [52], and can be produced from waste biomass [38].

* *Corresponding author*. Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada.
E-mail address: gnakhla@uwo.ca (G. Nakhla).

http://dx.doi.org/10.1016/j.ijhydene.2017.03.173
0360-3199/

Hydrogen can be generated through several means, most of which are fossil-fuel reliant, energy intensive and expensive but biological hydrogen production is fast gaining widespread attention as a viable and sustainable substitute to the current traditional methods of hydrogen production [44]. The most favorable method of biological hydrogen production is dark fermentation which is a process where microorganisms convert sugars to hydrogen, carbon dioxide and organic acids [48]. It is a light-independent process and is considered the most beneficial method of hydrogen production since it can be carried out in simple reactors, can be used on a wide range of substrates at non-sterile conditions and produces hydrogen at high rates and costs [21,48,53,55].

Lignocellulosic wastes have been identified as ideal substrates for hydrogen production as they are carbohydrate–rich, abundant in nature, cheap, do not compete for land with food and their use could help alleviate land pollution [41,42]. Examples of lignocellulosic wastes include agricultural and food processing wastes such as corn stover, sugarcane bagasse, rice straw etc., municipal solid wastes and forestry wastes such as poplar wood [1,48]. These wastes, however, are made up of complex carbohydrates (mainly cellulose and hemicellulose) which need to be broken down into simpler sugars for easy conversion to hydrogen. This breakdown is done using pre-treatment processes which produce several by-products in addition to simple sugars. One of these by-products is furfural, a furan derivative, which is formed when pentoses present mainly in the hemicellulosic component of lignocellulosic biomasses are broken down during under severe pretreatment conditions such as in the presence of acid or alkali [2,8]. Furfural is thought to adversely affect the membrane growth, integrity and permeability of hydrogen-producing bacteria by reducing biological and enzymatic functions, destroying DNA and inhibiting protein synthesis, which leads to decreased hydrogen production rates and yields [31]. For these reasons, furfural is often described as an inhibitor and limiting factor in the fermentation biohydrogen production process.

The impact of furfural on the kinetic parameters of hydrogen production in a mixed culture environment is not available in the literature. To the best of the authors' knowledge, no kinetic model has been used to describe the impact of furfural on biohydrogen production from lignocellulosic wastes using mixed cultures. Monlau et al. [34] indicated properties such as increase in surface area, solubilisation of the cellulose, hemicellulose and lignin components of the lignocellulosic biomass amongst others as factors that impact biofuel/bioenergy production, and further reported that furfural had little or no impact on methane production but the impact of furfural on hydrogen production was not clear. A batch fermentative hydrogen production study by Siqueira and Reginatto [49] using mixed cultures grown on 40 g/L glucose in the presence of furfural concentrations in the range 0 g/L to 2 g/L discussed furfural inhibition in terms of the Gompertz model. The aforementioned authors revealed a decrease in the hydrogen yields, maximum hydrogen production potential, and maximum hydrogen production rate with increasing furfural concentration. Also, the lag phase duration increased with increasing furfural concentration.

Mesophilic mixed cultures are mostly used for biogas production but mixed cultures at thermophilic conditions are gaining wide-spread interest as they have been reported to produce very high hydrogen yields [56]. While progress has been made in optimizing pretreatment methods of lignocellulosic biomass to achieve higher sugar yields, potential inhibition by furfural as well as other industrially important fermentation products needs to be thoroughly studied in order to reduce their inhibitory effects and enable the cost-effective and practical conversion of this biomass. Understanding furan derivatives is important in the production of biofuels from lignocellulosic biomass as they have diverse effects on hydrogen fermentation and microbial communities [32,54]. The aim of this study, therefore, was to investigate the impact of furfural on hydrogen production and microbial kinetics, from lignocellulosic biomass using mixed cultures (both mesophilic and thermophilic anaerobic digester sludge). The knowledge of these biokinetic parameters through modeling will enhance biohydrogen process design and optimization and facilitate effective scale-up and design of bioreactors.

Materials and methods

Microbial seed and substrate

Mesophilic anaerobic digester sludge (ADS) was obtained from the Guelph Wastewater Treatment Plant, Guelph, Canada while thermophilic ADS was collected from the Ravensview Wastewater Treatment Facility, Kingston, Canada. Both mesophilic and thermophilic ADS used for biohydrogen production were preheated at 70 °C for 30 min prior to use to suppress the activity of hydrogen-consuming bacteria [19]. The substrate utilized was synthetic lignocellulosic hydrolysate as real hydrolysate may contain other inhibitory compounds such as acetic acid, phenol, hydroxyl methyl furfural (HMF), syringaldehyde etc which can produce synergistic effects and make the extrapolation of results rather complex. It was prepared in the laboratory utilizing analytical reagent grade chemicals obtained commercially to simulate the composition of a typical pretreated lignocellulosic hydrolysate. Half the concentration of each component of the synthetic hydrolysate utilized in Akobi et al. [3] was used in this study. The substrate comprised, on a gCOD (gram Chemical Oxygen Demand) basis, 97% sugars of which 83% are pentoses (C5 sugars). The characteristics of the ADS and substrate used for this study are presented in Tables 1a and b respectively.

Experimental setup

Akobi et al. [3] studied the impact of varying furfural concentrations (0, 1, 2 and 4 g/L) and substrate-to-biomass ratios (S°/X° 0.5, 1, 2 and 4 gCOD/gVSS) on biohydrogen production using synthetic lignocellulosic hydrolysate with mesophilic ADS and observed that hydrogen yields were enhanced at 1 g/L furfural while 4 g/L furfural was the most recalcitrant of all concentrations tested. This study therefore tested furfural concentrations of 0 g/L (control), 1 g/L and 4 g/L in parallel at both mesophilic and thermophilic conditions to confirm these