Process Biochemistry 48 (2013) 272–282

Contents lists available at SciVerse ScienceDirect

Process Biochemistry

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

Review

Advances in ethanol production from hardwood spent sulphite liquors

Susana R. Pereira, Diogo J. Portugal-Nunes, Dmitry V. Evtuguin, Luísa S. Serafim, Ana M.R.B. Xavier*

CICECO, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, P-3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 27 July 2012
Received in revised form 5 December 2012
Accepted 9 December 2012
Available online 20 December 2012

Keywords:
Hardwood spent sulphite liquors
Yeast bioprocessing
Pentose fermentation
Bioethanol
Sulphite pulping
Detoxification

ABSTRACT

Hardwood spent sulphite liquors (HSSLs) are by-products from the pulping industry rich in pentoses, which are not yet fully exploited for bioprocessing, namely for the production of bioethanol. The sustainable fermentation of pentoses into bioethanol is a challenge to overcome. Besides sugars, HSSLs contains inhibitors that decrease the possibility of bioprocessing of these by-products. Nevertheless, recent studies have brought new insights in using HSSLs for bioethanol production. This paper reviews the results of relevant studies carried out with HSSLs towards bioprocessing to bioethanol. The composition of SSLs was compared and related with the wood origin stressing specificity of microbial inhibitors from HSSL and their anti-microbial effect. The different fermentative processes, the microorganisms used, and the strategies to improve yield and productivity used so far were also reviewed. This review allowed concluding that research is still needed in several areas, including optimization of detoxification processes, fermentation strategies and selection of suitable microbial strains in order to achieve the integration of the different steps needed for HSSLs bioconversion into ethanol thus contributing for sustainability of pulping mills within biorefinary concept.

Contents

1. Introduction

The world is facing a decline of fossil fuels resources, petroleum, natural gas, and charcoal, while energy requirements are progressively growing up. Moreover, the finding of new fossil sources is decelerating and the costs of extraction are increasing. Accordingly, the search for sustainable alternatives to produce fuels and chemicals from non-fossil feedstocks, especially biomass, is attracting a considerable interest worldwide [1,2].

Among all biofuels, ethanol is currently being produced on a large scale, and can be easily mixed with gasoline and used in internal combustion engine vehicles [3,4]. Alternatively bioethanol may be converted to ethylene, ethylene glycol or butadiene to produce bio-based poly(ethylene), poly(ethylene terephthalate) and butadiene rubber/styrene, respectively [5].Currently, bioethanol is produced mainly from sugar-containing biomass such as sugarcane and corn [4]. However, the growth of bioethanol industry and the consequent increase in the usage of cereals food crops for ethanol production raised questions regarding the sustainability of the so-called "first generation" biofuels. The use of raw materials belonging to the human and animal food chains for biofuels production resulted in the rise of prices of food all over the world and,

* Corresponding author. Tel.: +351 234370716; fax: +351 234370084.
E-mail address: abx@ua.pt (A.M.R.B. Xavier).

1359-5113/$ – see front matter
http://dx.doi.org/10.1016/j.procbio.2012.12.004

Table 1
Chemical composition and dimensions of wood fibres.

Fibre type	Cell dimensions		Chemical composition		
	Average length (mm)	Average diameter (μm)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Softwood	3.3	33	40–44	23–28	25–31
Hardwood	1.0	20	45–50	25–35	18–24

Adapted from [12,13].

consequently, in social disturbance [1,4,6]. For these reasons, the research efforts are focused on the use of forestry, agricultural and industrial wastes, rich in biomass to generate the so-called "second generation" biofuels [4,7].

The recalcitrance of lignocellulosic biomass (LCB) hinders its conversion to monomeric sugars and consequently to ethanol [1,8]. Hence the use of industrial wastes, which contain fermentable sugars, is an attractive prospect. In this context, spent sulphite liquors (SSLs), by-products from the acidic sulphite pulping process of wood in pulp and paper industry, can be considered as promising raw materials for the production of bioethanol [6,9,10] since, 90 billion litres of SSLs are produced annually [11]. The main objective of the wood pulping process is the removal of lignin from wood, maintaining the cellulose and hemicelluloses integrity, thus providing the cellulosic fibres with desired composition (percentage of cellulose and hemicelluloses) and appropriate yield (depending on the degree of the delignification) [12,13]. Various wood species like softwoods, hardwoods or mixture of both, can be used by the pulp and paper industry [12,14]. The extreme conditions, that include high temperature (125–145 °C) and the medium acidity (pH 1–2), applied during acidic sulphite pulping cause the partial hydrolysis of hemicelluloses releasing monomeric sugars and oligosaccharides, which could be easily fermented into ethanol [12,13]. This fact is an advantage of SSLs over LCB raw materials and their complex hydrolytic processes needed for the production of 2nd generation bioethanol and other bio-based products [6,15].

Not all the liquors generated by pulping processes are suitable as substrates for fermentative processes. The spent liquors that result from alkaline kraft pulping, responsible for more than 90% of cellulosic pulp production worldwide, have a chemical composition unsuitable for ethanol production [16]. Namely, most of sugars/oligosaccharides released from wood in kraft spent liquor are degraded to C_2–C_6 hydroxy- and dicarboxylic acids [13,17].

The composition of acidic SSLs depends strongly on the type of wood used in the pulping process [12,13], and will be discussed in Section 2. Thus, SSLs obtained from pulping of softwoods (coniferous) contain a high proportion of hexoses (>70%), while those obtained from pulping of hardwoods (deciduous) contain mainly pentoses (>70%) [12]. This difference in composition will be pointed out in Section 3. The fermentative conversion of hexoses to ethanol by robust yeast *Saccharomyces cerevisiae* is a well-known industrially implemented process [18–20]. However, *S. cerevisiae* cannot naturally ferment pentoses [20–22]. Moreover, pentose-utilizing yeasts showed difficulties in fermenting pentoses from HSSL due to a lack of appropriate resistance to toxic contaminants [6,10,23]. Pentose rich hemicelluloses are predominant in vegetable biomass but still a non-used raw material [4,20]. Research and development of sustainable fermentation processes for bioethanol production from raw materials rich in pentoses is an important challenge for the future.

In this work, the problems associated with bioethanol production from hardwood spent sulphite liquors will be discussed after a brief introduction. The chemical composition of hardwoods and softwoods is compared in Section 2. The generation of hardwood spent sulphite liquors (HSSLs) is presented in Section 3 followed

Table 2
Chemical composition (%, w/w) of hardwoods.

Wood species		Cellulose [12,14,17,41]	Hemicelluloses		Lignin [9,13,14,41]	Extractives [13,14,41]	Ash [9,13,14,41]
Common name	Scientific name		Glucuronoxylan [9,14,41,57]	Glucomannan [9,14,57]			
Red maple	*Acer rubrum*	40.7–45.0	22.1–25.0	3.1–4.0	22.8–25.4	2.5–5.3	0.3–5.2
Yellow birch	*Betula alleg haniensis*	45.0–47.0	15.0–30.0	2.0–5.0	21.2	2.6	1.7–2.9
White birch	*Betula papyrifera*	39.4–45.0	29.7–35.0	1.4	18.9–21.4	2.6	–
Mockernut hickory	*Carya tomentosa*	43.5–48.0	15.0–30.0	1.5	23.6	5.0	0.4
Blue gum[a]	*Eucalyptus globulus*	50.0–53.0	18.0–24.0	2.0–4.0	19.0–22.0	1.0–2.7	0.3–0.5
Beech	*Fagus sylvatica*	39.4–43.0	26.0–29.0	1.5–3.0	23.0–24.8	1.5–2.5	0.4
American beech	*Fagus gradifolia*	36.0–49.0	25.0–28.0	2.7–3.0	22.0–30.9	3.0–4.0	0.4
White ash	*Fraxinus americana*	39.5–41.0	20.0–26.0	3.8	24.8	6.3	0.3
Sweet gum	*Liquidambar styraciflua*	40.8–46.0	17.0–24.0	3.2	22.4	5.9	0.2
Yellow poplar	*Liriodendron tulipifera*	39.1–45.0	15.0–20.0	4.9	25.3–30.3	2.4–3.6	0.3–2.8
Sweet bay	*Magnolia virginiana*	44.2	15.0–25.0	4.3	24.1	3.9	0.2
Water tupelo	*Nyssa aquatica*	45.0–45.9	15.0–25.0	3.5	25.1	4.7	0.4
Black tupelo	*Nyssa sylvatica*	42.6–45.0	15.0–21.0	3.6	26.6	2.9	0.6
Eastern cottonwood	*Populus deletoids*	46.5–47.0	16.0–20.0	4.4	25.9	2.4	0.6
Quaking aspen	*Populus tremoides*	48.0–50.0	18.0–21.0	2.0–5.0	18.2	2.4	4.0
Aspen	*Populus tremulus*	47.0–50.0	16.0–20.0	2.0–5.0	21.0–23.0	1.0–2.0	0.3–0.4
White oak	*Quercus alba*	41.7–47.0	15.0–25.0	3.1	24.6	5.3	0.2
Scarlet oak	*Quercus coccinea*	43.2–46.0	16.0–25.0	2.3	20.9	6.6	0.1
Southern red oak	*Quercus falcata*	40.5–42.0	17.0–25.0	1.7	23.6	9.6	0.5
Blackjack oak	*Quercus marylandica*	33.8–44.0	15.0–23.0	2.0	30.1	6.6	1.3
Chestnut oak	*Quercus prinus*	40.8–46.0	17.0–26.0	2.9	22.3	6.6	0.4
Northern red oak	*Quercus rubra*	42.2–46.0	17.0–22.0	3.3	20.2	4.4	0.2
Black oak	*Quercus velutina*	39.6–48.0	15.0–25.0	1.9	25.3	6.3	0.5
American elm	*Ulmus americana*	42.6–51.0	18.0–22.0	4.0–4.6	24.0–27.8	1.9–2.0	0.8

[a] Plantation wood.