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Cellulosic ethanol and its co-products from different substrates, pretreatments, microorganisms and bioprocesses: A review

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ABSTRACT

Cellulosic ethanol involves the following production steps: physical and/or chemical pretreatment, biological treatment, fermentation and distillation. First three steps are also the bottlenecks for the production of cellulosic ethanol and its co-products. Their production still pose some difficulties in terms of pretreatment, the high cost of enzymes for substrate hydrolysis, the formation of inhibitory compounds in the hydrolyzate, the lack of efficient and viable microorganisms for industrial fermentation of hexose and pentose among others. The solution or minimization of these difficulties may lead to numerous socio-environmental, political, and economic advantages for cellulosic ethanol production. This paper highlights the potential of different substrates, pretreatments, microorganisms and bioprocesses for cellulosic ethanol production.

Keywords: Cellulosic Ethanol; Pretreatments; Fermentation

1. INTRODUCTION

The difference between the production of cellulosic ethanol and sugarcane-based ethanol lies basically in the conversion of polymeric compounds that are presented in cellulosic biomass into fermentable sugars and in the fermentation of hexoses and pentoses. Cellulosic ethanol involves the following production steps: physical and/or chemical pretreatment, biological treatment, fermentation and distillation [1-3].

One of the processes to obtain ethanol from cellulose and hemicellulose is the enzymatic hydrolysis or the chemical hydrolysis of polysaccharides into disaccharides and monosaccharides for further fermentation. However, the recalcitrance of this lignocellulosic material requires pretreatment to facilitate enzymatic action [4,5]. Several methods of plant biomass pretreatment have been studied, e.g., milling [6], acid [7-9], irradiation [10], hydrothermal [11,12], hydrothermal alkaline [13], pyrolysis [14], steam explosion [15,16], catalyzed steam explosion [17, 18], carbon dioxide [19], chlorine dioxide, nitrogen and sulfuric acid [20], organosolvation [21,22], microwave and alkaline treatments [23] and biological treatments [24-27].

The production of ethanol from lignocellulosic compounds, which originated basically in Germany and Russia more than 80 years ago, involves saccharification by acid hydrolysis [28]. Today, the production of ethanol from low added value carbohydrates is a reality in some countries. However, higher medium-term expectations for the viability of cellulosic ethanol focus on the possible use of microbial metabolism in the degradation and saccharification of the plant cell wall to minimize the presence of inhibitors during fermentation [3] and maximize the fermentation of hexoses and pentoses [29]. **Table 1** lists different substrates, microorganisms, pretreatments and fermentation processes for cellulosic ethanol production discussed by various researchers.

2. PERSPECTIVES AND CELLULOSIC ETHANOL CO-PRODUCTS

The industrial-scale production of cellulosic ethanol from plant biomass is expected benefit society and the environment in numerous ways. These benefits of eco-

Table 1. Production of cellulosic ethanol from different pretreatments, microorganisms and bioprocesses.

Substrate	Physical/chemical pretreatment	Microorganism	Bioprocess	Ethanol (g/g)	Reference
Cotton stalks	None	*Saccharomyces cerevisiae*	Batch/SSB/SHF	0.004	[30]
Cotton stalks	None	*Saccharomyces cerevisiae*	Batch/SHF	0.027	[30]
Cotton husks and straw	Alkaline digestion	*Saccharomyces cerevisiae*	Batch/SSF	0.48	[31]
Canola straw	Acid digestion, hydrothermal	*Saccharomyces cerevisiae*	Batch/SHF	0.21	[32]
Wheat straw	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Batch/SSF	0.13	[33]
Wheat straw	Acid digestion, steam	*Saccharomyces cerevisiae*	Batch/SSCF	0.35	[34]
Wheat straw	Steam explosion	*Kluyveromyces marxianus*	Batch/SSF	0.32	[35]
Wheat straw	Steam explosion	*Kluyveromyces marxianus*	Batch/SSF	0.27	[36]
Wheat straw	Acid digestion, overliming	*Escherichia coli*	Batch/SHF	0.21	[37]
Wheat straw	Acid digestion	*Escherichia coli*	Batch/SHF	0.24	[37]
Wheat straw	Acid digestion, overliming	*Escherichia coli*	Batch/SSF	0.21	[37]
Wheat straw	Acid digestion	*Escherichia coli*	Batch/SSF	0.17	[37]
Rice husks	Alkaline digestion	*Escherichia coli*	Batch/SHF	0.21	[38]
Rice husks	Alkaline digestion	*Escherichia coli*	Batch/SSF	0.20	[38]
Wild sugarcane bagasse	Acid digestion, steam	*Pichia stipitis*	Batch/SSF	0.35	[39]
Sugarcane bagasse	Acid digestion, steam explosion	*Pichia stipitis*	Batch/SSF	0.39	[40]
Sugarcane bagasse	Milled	*Pichia stipitis*	Batch/SSF	0.29	[41]
Sugarcane bagasse	Milled	*Pichia stipitis*	Batch/SHF	0.27	[41]
Sugarcane bagasse	Acid digestion, steam, electrodialysis	*Pachysolen tannophilus*	Batch	0.53	[9]
Sugarcane bagasse	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Batch/SSF	0.44	[40]
Sugarcane bagasse	Acid digestion, steam explosion, delignification	*Saccharomyces cerevisiae*	Batch/SSF	0.32	[42]
Sugarcane bagasse	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Batch/SSF	0.29	[42]
Sugarcane bagasse	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Batch/SHF	0.30	[43]
Sugarcane bagasse	Acid digestion, steam explosion, delignification	*Saccharomyces cerevisiae*	Batch/SHF	0.35	[43]
Corn cobs	Acid digestion, steam	*Saccharomyces cerevisiae*	Batch/SSCF	0.39	[44]
Corn cobs	Acid digestion, steam	*Pichia stipitis*	Batch/ SHF	0.44	[45]
Algarroba	Acid digestion, steam, delignification	*Pichia stipitis*	Batch/SHF	0.39	[46]
Algarroba	Acid digestion, steam, delignification	*Saccharomyces cerevisiae*	Batch/SHF	0.49	[46]
Rice straw	Acid digestion, steam	*Mucor indicus*	Batch/SHF	0.43	[47]
Rice straw	Acid digestion, steam	*Rhizopus oryzae*	Batch/SHF	0.41	[47]
Rice straw	Acid digestion, steam	*Saccharomyces cerevisiae*	Batch/SHF	0.45	[47]
Rice straw	Acid digestion, steam	*Saccharomyces cerevisiae*	Batch/SSF	0.09	[48]
Spruce	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Batch/SSF	0.44	[49]
Spruce	Acid digestion, steam explosion	*Saccharomyces cerevisiae*	Feed batch/SSF	0.43	[49]
Waved old paper	Acid digestion	*Saccharomyces cerevisiae*	Batch/SSF	0.32	[50]
Waved old paper	Acid digestion	*Kluyveromyces marxianus*	Batch/SSF	0.31	[50]

Continued

Thin paper	Acid digestion	*Kluyveromyces marxianus*	Batch/SSF	0.33	[50]
Thin paper	Acid digestion	*Saccharomyces cerevisiae*	Batch/SSF	0.33	[50]
Cellulose floccules	Acid digestion	*Saccharomyces cerevisiae*	Batch/SSF	0.31	[50]
Cellulose floccules	Acid digestion	*Kluyveromyces marxianus*	Batch/SSF	0.34	[50]
Sweet sorghum bagasse	Steam explosion	*Kluyveromyces marxianus*	Batch/SSF	0.31	[35]
Mustard residue	Steam explosion	*Kluyveromyces marxianus*	Batch/SSF	0.35	[35]
Maize ear	Acid digestion, steam	*Saccharomyces cerevisiae*	Batch/SSF	0.53	[51]
Maize cob	Acid digestion	*Pichia stipitis*	Batch	0.44	[52]
Maize cob	Acid digestion, overliming	*Zymomonas mobilis*	Batch	0.42	[53]
Banana cellulosic residue	Drying	*Clostridium thermocellum* and *C. thermosaccharolyticum*	Batch	0.36	[54]
Banana cellulosic residue	Acid digestion	*Clostridium thermocellum* and *C. thermosaccharolyticum*	Batch	0.40	[54]
Banana cellulosic residue	Alkaline digestion	*Clostridium thermocellum* and *C. thermosaccharolyticum*	Batch	0.42	[54]
Banana cellulosic residue	Drying	*Clostridium thermocellum* and *C. ethanolicus*	Batch	0.33	[54]
Banana cellulosic residue	Acid digestion	*Clostridium thermocellum* and *C. ethanolicus*	Batch	0.36	[54]
Banana cellulosic residue	Alkaline digestion	*Clostridium thermocellum* and *C. ethanolicus*	Batch	0.39	[54]

SHF: Separate hydrolysis and fermentation; SSF: Simultaneous saccharification and fermentation; SSCF: Simultaneous saccharification and co-fermentation; SSB: Solid state bioprocess.

efficiency include the use of organic waste of plant origin, which will allow for augmented biofuel production, optimization of production units (ethanol production from sugarcane residues in the harvesting off-season), extension of landfill service life and reduction of organic pollution. However, so far there is no consolidated biotechnological process for cellulosic ethanol production, especially in terms of pretreatment, and chemical and biochemical hydrolysis, or in pentose fermentation [2,3,55,56].

Moreover, one of the difficulties of the process is the action of lignin, which is able to adsorb cellulolytic and hemicellulolytic enzymes, impairing enzymatic hydrolysis [5]. In the pretreatment process, delignification of the substrate by an alkaline substance is desirable to reduce the amount of lignin [57]. One way to produce biodegradable plants is by modifying them genetically to reduce their lignin content, which affects pretreatment and enzymatic hydrolysis [58].

The physicochemical pretreatment of plant biomass releases inhibitory compounds that affect the fermentation process, e.g., furfural, hydroxymethylfurfural, phenolic compounds and acetic acid [59,60]. Moreover, some of these processes produce vinasse and excessive amounts of wastewater.

Higher expectations concerning the viability of cellulosic ethanol focus on the possible use of microbial metabolism to degrade plant biomass into disaccharides and monosaccharides, thereby enabling fermentation [5]. The efficient use of xylose together with hexose allows for significantly lower cellulosic ethanol production costs [61]. The use of microorganisms that produce cellulases, hemicellulases and ligninases, allied to the use of low cost substrates, may help reduce the price of commercial enzymes [5].

Industrially viable microorganisms should be obtained by genetic engineering [62,63] or prospection [64,65]. Such microorganisms should increase the efficiency of fermentation of hydrolyzed substances containing hexoses and pentoses, and augment the resistance to high sugar concentrations, as well as the presence of inhibitory compounds generated during hydrolysis and fermentation, as in ethanol production.

After plant biomass has been pretreated, the lignin-rich fraction that is separated from the hemicellulose can be burned to supply energy to biorefineries or it can be converted into synthesis gas (syngas) [66]. Moreover, lignin can be degraded into smaller fractions and used in the production of polyurethane foam, phenolic resin and epoxy, as a source of phenol and ethylene [67], or be converted into carbon fibers [68]. Lignin can also be employed to produce phenol, acetic acid, vanillin and phenol-formaldehyde resins [69]. The kinetics of lignin pyrolysis may differ according to the procedures utilized in pretreatment and delignification [14], affecting its use. Furfural can be hydrolyzed into maleic acid or form resins with the addition of phenol or urea [70]. The hydro-

xymethylfurfural produced can be cleaved into formic and levulinic acids, and the latter can be used as feedstock for the production of polyesters [71]. Acetic acid can be used as a chemical reagent or in the form of vinegar. Vinasse, in turn, can be used as a soil fertilizer.

The use of plant biomass in ethanol production augments the generation of many co-products, e.g., ethanol steam for hydrogen production to obtain fuel cells [72, 73], the production of ethylene, ethylene glycol, acetaldehyde, acetate, ethyl acetate, glycols, acrylates, ethyl chloride, butane, propylene and butadiene [71], and the production of ethane resulting from ethanol dehydration, which is precursor of a wide range of products such as polyethylene, polypropylene and vinyl polychloride. In Brazil, these ethanol co-products are expanding due the increasing production of ethanol [74]. Moreover, the increasing use of ethanol to replace methanol in biodiesel production [75], as well the conversion of ethanol into ethylene for the production of bioplastics, contributes to boost the demand for ethanol. Lastly, the carbon dioxide generated during ethanol production can be used as carbon source for microbial cultivations and converted into microbial protein biomass [66,76].

3. FINAL REMARKS

The production of cellulosic ethanol still poses some difficulties in terms of pretreatment, the high cost of enzymes for substrate hydrolysis, the formation of inhibitory compounds in the hydrolyzate, the lack of efficient and viable microorganisms for industrial fermentation of hexose and pentose, the gasification of carbon dioxide generated during fermentation, the removal of lignin, furfural and hydroxymethylfurfural from enzymatic and fermentation processes and its proper utilization, as well as adequate reuse of water during the process. The solution or minimization of these difficulties may lead to numerous socioenvironmental, political, and economic advantages for cellulosic ethanol production.

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