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Fermentable sugars from *Eucalyptus globulus*: Process optimization

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ABSTRACT

In the last years, bioethanol production from lignocellulosic materials is receiving more attention from researchers since it is an abundant raw material in certain regions, it is cheaper, does not compete with foods like sugarcane or corn, and can reduce up to 86% of carbon dioxide emissions when compared with gasoline. However, the process economy is linked to the pretreatment needed to make the cellulose accessible for further steps of enzymatic hydrolysis and fermentation. Then, the motivation of this work is to propose a MILP model to perform an optimal synthesis of the pretreatment for obtaining fermentable sugars from the *Eucalyptus globulus* specie. For this purpose, a General Disjunctive Program (GDP) is formulated. The obtained results suggest that there is a small difference between a two-step pretreatment process (pretreatment with posthydrolysis) and one-step pretreatment of diluted acid process.

1. Introduction

Research in biofuels production has increased in the last decade due to the growth in the energy demand, the uncertainty in the amount of fossil reserves and the environmental issues that arise in relation to the use of fossil fuels. Among different biofuels, ethanol is an important one because it is produced in several countries using different raw materials: sugarcane in Brazil and corn in the United States of America. They are both massive producers, totalizing 90% of the world production that was 65.3 millions of cubic meters in 2008 (Machado, 2010), and 75.1 million in 2011 (Amarasekara, 2014). Biofuels from sugarcane and corn are widely criticized because they compete with food production. This is the reason for seeking alternative raw materials, in particular lignocellulosic ones. In the work by Yue et al. (2014), the authors mention that lignocellulosic and algae-based biofuels have advantages over first-generation biofuels as regards the implications in food prices and land competition. Čuček et al. (2014) developed a generic mathematical model that can be used for analyzing the optimal utilization of raw materials, production processes, and products, in any biomass supply chain network, incorporating recycling and heat integration. Similarly, Miret et al. (2015) presented a Mixed Integer Linear Program (MILP) in which economic, environmental, and social dimensions are included. As a result of this multi-objective model, they observed that wood-based fuels have advantages over corn-based as regards the economic and environmental dimensions. In the work by Drigo et al. (2009), the amount of sawmill wastes in Argentina is reported to be about 1700 annual tons without including the waste produced from forest harvesting, which could also represent an important amount. Considering residuals from sugarcane and other agricultural exploitations together with those previously mentioned, the amount of lignocellulosic materials would be around 3.2 million of annual tons. Even with a conservative conversion, that amount would yield about 600 thousand tons of ethanol per year, an important quantity that cannot be ignored. By the Energy Independence and Security Act of 2007, USA sets annual targets for biofuels production from lignocellulosic materials from 2010–2022 to reach 47.8 million tons by 2022. Some studies indicate that the use of ethanol produced from lignocellulosic materials is associated with a balance of carbon dioxide that is 86% lower than gasoline and 82% lower than the use of ethanol obtained from corn (Wang et al., 2007).

The obtention of fermentable sugars from corn and sugarcane is relatively easy but it is not the case when talking about lignocellulosic materials because a pretreatment process is needed to decompose the polysaccharides that form celluloses and hemicelluloses, which form the cell wall. Although there have been several experiments to decompose lignocellulosic material without previous treatments, the results show a very low yield in the production of fermentable monosaccharides. This is due to the existence of a wall of hemicellulose and lignin which protect the cellulose

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Nomenclature

Index

c	compounds
j	connections
nd	nodes
t	processing times
t	temperatures
a	acid concentrations
i	integration steps

Continuous variables

$fobj1$, $fobj2$	objective functions (streams of cellulose and xylose) (kg/h)
$f_{j,c}$	stream of compound ***c*** in connection ***j*** (kg/h)
F_j^{Sld}	stream of solids in connection ***j*** (kg/h)
F_j^{Slt}	stream of solutes in connection ***j*** (kg/h)
F_j^{Slv}	stream of solvent in connection ***j*** (kg/h)
F_j^{Total}	total stream in connection ***j*** (kg/h)
$StLoss$	loss of steam per kg of dry wood ($kg_{steam}/kg_{dry\ wood}$)

Binary variables

Y_{prc}	decision variable that takes the unit value when the process *prc* is installed
$U_{prc,p}$	decision variable that takes the unit value when the piece of equipment *i* and size *t* is installed
$W_{prc,p,t,a}$	decision variable that takes the unit value when the piece of equipment *i*, size *t* is installed in number *n*

Sets

$Inhib_c$	fermentation inhibitors
Sld_c	solid compounds
Slt_c	soluble compounds
Slv_c	solvent compounds (water)
$NodIN_{j,nd}$	input connections *j* to node *nd*
$NodOUT_{j,nd}$	output connections *j* to node *nd*
$WaPrcIN_{prc,j}$	input of process water *j* to process *prc*
$ProdPrcIN_{prc,j}$	input stream of product *j* to process *prc*
$WaWashIN_{prc,j}$	input of washing water *j* to process *prc*
$ProdPrcOUT_{prc,j}$	product stream output *j of* a process *prc*
$HydrPrcOUT_{prc,j}$	hydrolyzate stream output *j of* a process *prc*
Prt_{prc}	pretreatment process
$PIN_{prc,j}$	$WaPrcIN_{prc,j} \cup ProdPrcIN_{prc,j} \cup WaWashIN_{prc,j}$
$POUT_{prc,j}$	$ProdPrcOUT_{prc,j} \cup HydrPrcOUT_{prc,j}$

Parameters

ε	epsilon parameter for epsilon-constraint
$MaxCon_c$	maximum concentration of inhibitors
$Productivity$	amount of raw material per hour (kg/h)
$RMComp_c$	raw material composition
$WSRPrt_{prc}$	water to solid ratio for pretreatment *prc*
$WSRWash_{prc}$	water to solid ratio for washing *prc*
$HOutWash_{prc}$	humidity of product output
$SteamExp$	steam per kg of dry wood for SE process
pt_p	processing time (min)
T_t	processing temperature (°C)
A_a	acid concentration in acid diluted process (%wt)
$K_{prc,c,c',t,a}$	formation rate of the compound *c* from *c′* at temperature *t* and concentration *a* of catalyst (see Annex) (1/min)
$m_{i,c}$	amount of compound *c* in the *i* step of integration (kg)
m_c^{t0}	amount of compound *c* at initial time (kg)
m_c^{tf}	amount of compound *c* at final time (kg)
Δt_p	time step for integration when a pt_p processing time has been chosen (min)

microfibers. To overcome this obstacle, at least a partial decomposition of those materials is required (Bhaskar et al., 2011). Several pretreatment processes exist but the most studied one is the thermochemical one. The acid process has a high level of maturity. It was studied during the Second World War (Wang and Sun, 2010). There are several variants of this process but the dilute acid is the most promising one. In recent years, the autohydrolysis (hot liquid water) and steam explosion processes have become more relevant.

A work by Zaldivar describes the proposed current process for the production of ethanol from lignocellulosic materials rich in pentose (Zaldivar et al., 2001). This process starts by acid hydrolysis, followed by liquid-solid separation and washing. The liquid phase is subsequently detoxified and pentose fermentation is performed while the solid phase is enzymatically hydrolyzed and the produced hexoses are then fermented. The lignin remaining (solid) is separated and used to generate the required energy. They also mention the efforts to integrate and simplify the process. In the article by Cardona et al. (2010), a review of the various processes that have been studied for the production of ethanol from sugarcane is presented. They also present a general outline of each studied technology within the corresponding processing steps. In both descriptions, it is considered that the fermentation of the liquid stream may be performed after detoxification, while in cases of autohydrolysis and steam explosion it is also recommended to carry out a second hydrolysis process to the liquid phase for obtaining a greater amount of monosaccharides. This also enables the use of less severe pretreatment conditions, decreasing the formation of furfural and 5-hydroximethyl-2-furfural (HMF) (Duarte et al., 2009; Guo, 2012; Wyman, 2013).

Ethanol production processes present differences according to the cellulosic raw material depending on the hardness or softness of wood, the difference being based on the hemicellulose composition. In the case of hardwoods and other xylose-rich species, the fermentation step involves a greater challenge than that for softwoods. Hardwoods imply the fermentation of pentoses, which is a more complex process than fermentation of hexoses, although there have been many advances in recent decades (Antunes et al., 2014; Kuhad et al., 2011; Mishra and Singh, 1993; Zaldivar et al., 2001). In recent years, great emphasis has been placed on the development of simultaneous fermentation of hexoses and pentoses (or co-fermentation). This technology involves major challenges (Stambuk et al., 2008), but several advances have occurred through genetic modification of microorganisms, such as the *Zymomonas mobilis* bacteria (Mohagheghi et al., 2002), *Saccharomyses cerevisiae* yeast (Erdei et al., 2013; Ishola et al., 2015; Ohgren et al., 2006) and *Escherichia coli* bacteria (Takahashi et al., 2000). In this sense, some advances were made by co-culture of microorganisms (Fu et al., 2009; Mishra and Singh, 1993). The work by Dutta et al. (2010) compares different configurations for fermented saccharides that are presented in corn stover (an xylose-rich material). The microorganisms used are *S. cerevisiae* and genetically modified *Z. mobilis*. The most economical arrangement is separate fermentation of cellulose-rich solid and the hydrolyzate streams.

Two simplified flowsheet alternatives for the process of ethanol obtention from lignocellulosic materials are shown in Fig. 1. The schema of Fig. 1a is adequate for xylose-rich materials, such as hardwoods, due to the complexity of performing a co-fermentation stage. The liquid stream after pretreatment is mainly composed