



Evaluation of strategies for second generation bioethanol production from fast growing biomass *Paulownia* within a biorefinery scheme



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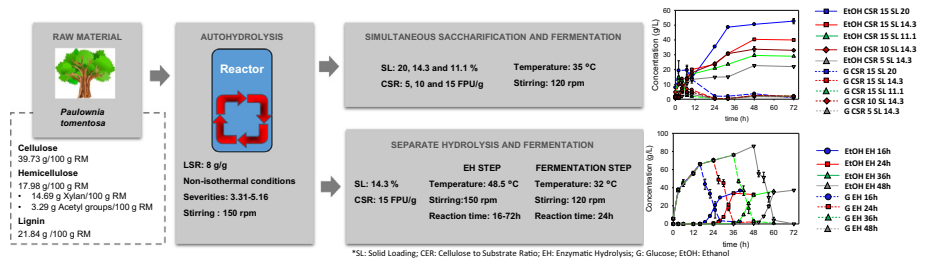
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HIGHLIGHTS

- Autohydrolysis of *Paulownia* biomass was studied as first step of a biorefinery.
- At $S_0 = 4.19$, 78.9% of xylan was recovered as xylose and xylooligosaccharides.
- At $S_0 = 4.19$, 47% higher ethanol concentration was achieved by SHF than SSF.
- At $S_0 = 4.72$, 52.7 g/L of ethanol (80% of conversion) was obtained by SSF.
- An energy production of 648,074 MJ/ha-year could be produced from this process.

GRAPHICAL ABSTRACT



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ABSTRACT

Fast-growing and short-rotation biomass is identified as glucan-rich feedstock to be used for bioenergy purposes. For the first time to our knowledge, fast growing biomass (*Paulownia tomentosa*) was evaluated for bioethanol production in a biorefinery scheme. For that, *Paulownia* wood was subjected to autohydrolysis pretreatment under severity (S_0) conditions in the range of 3.31–5.16. The effect of this treatment on its fractionation was evaluated by means of hemicelluloses solubilization as hemicellulose-derived compounds in liquid phase and enzymatic hydrolysis of glucan (remained in the solid phase) into glucose. A xylose and xylooligosaccharides concentration of 17.5 g/L was obtained at $S_0 = 3.99$ which corresponds to complete xylan solubilization. On the other hand, glucose yield of enzymatic hydrolysis increased up to reach 99% at $S_0 = 4.82$. In addition, separate and simultaneous saccharification and fermentation assays (SHF and SSF) of autohydrolyzed *Paulownia* were compared for ethanol production. An increase of 47% in ethanol concentration was obtained by SHF in comparison with results achieved by SSF for *Paulownia* treated at $S_0 = 4.19$. In SSF, *Paulownia* was successfully converted into ethanol (52.7 g/L which corresponded to 80% of ethanol yield) operating at 20% solid loadings and $S_0 = 4.72$. Energy analysis of results obtained in this work showed that 83% of energy respect to raw material can be recovered considering the ethanol and the combustion of residual lignin. This work provides a feasible process for bioethanol production using fast growing specie which could enrich the feedstock needs for biofuels sector.

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Nomenclature

Abbreviations

EH	enzymatic hydrolysis
F	furfural
FPU	Filter Paper Units
HMF	hydroxymethylfurfural
IU	International Unit
SHF	separate hydrolysis and fermentation
SSF	simultaneous saccharification and fermentation

Parameters and constants

ρ	density (g/L)
ω	empirical constant (14.75 °C)
[Biomass]	dry biomass concentration at the beginning of the fermentation (g/L)
[Cellobiose]	cellobiose concentration (g/L)
[EtOH] _f	ethanol concentration at the end of the fermentation (g/L)
[EtOH] ₀	ethanol concentration at the beginning of the fermentation (g/L)
[Glucose]	glucose concentration (g/L)
C _{ETMAX}	maximal ethanol concentration (g/L)
CSR	cellulase to Substrate Ratio (FPU/g)
E _{EG}	energy produced from ethanol from glucan (MJ)
E _{ELP}	energy produced from ethanol from liquid phase (MJ)
E _{LIGNIN}	energy produced from lignin (MJ)
f	cellulose fraction of dry biomass (g/g)
Gn	glucan content (g glucan/100 g spent solid, oven dry basis)

HHV	Higher Heating Value (MJ/kg)
KL	Klason Lignin content (g Klason lignin/100 g spent solid, oven dry basis)
LSR	liquid to solid ratio (g/g)
NVC	non-volatile compounds (g NVC in liquid phase per 100 g raw material, oven dry basis)
O + M	oligosaccharides + monomers (kg)
Q _{PETMAX}	productivity calculated at maximal concentration of ethanol (g/L/h)
R ²	coefficient of determination (dimensionless)
R ₀	severity factor (min)
S ₀	severity (dimensionless)
SY	solid yield (g solid recovered/100 g raw material, oven dry basis)
t	time (h)
T(t)	temperature profile in the heating stage (°C)
T'(t)	temperature profile in the cooling stage (°C)
t _{1/2}	reaction time needed to reach 50% of Y _{GMAX} (h)
t _F	time needed for the whole heating–cooling period (min)
t _{MAX}	time needed to achieve the target temperature (min)
T _{MAX}	target temperature (°C)
T _{REF}	reference temperature (100 °C)
Y _{Et}	ethanol yield (%)
Y _G	glucose yield (%)
Y _{GMAX}	maximum glucose yield achievable at infinite reaction time (%)
Y _{Gt}	glucose yield at time t (%)

1. Introduction

Currently, the search for alternative raw materials to be used as renewable sources for energy production is one of the most important challenges to achieve a sustainable growth based on a bioeconomy strategy [1]. In this context, lignocellulosic biomass is one of the most promising raw material for biofuel production considering its great availability and limited price [2]. Lignocellulosic materials (LCM) such as wood provide abundant and renewable feedstock that doesn't compete with food crops [3].

LCM structural composition includes a complex structure composed of cellulose (a linear polymer made from glucose structural units), hemicellulose (branched polymer made up of sugars and substituents) and lignin (polymer made up of oxygenated phenylpropane structural units) [4]. In order to produce bioethanol, the sugars forming polysaccharides can be hydrolyzed by cellulolytic enzymes and subsequently fermented by microorganisms such as *Saccharomyces cerevisiae* [5,6]. Nevertheless, the three-dimensional and recalcitrant structure of LCM hinders the enzymatic hydrolysis of cellulose and subsequent fermentation of glucose to ethanol [7].

Bioethanol from lignocellulosic feedstock remains on the verge of commercialization due to higher capital and operating costs [8]. Second generation bioethanol could be made cost-competitive by the development of biorefinery-based processes for the integral use of lignocellulosic biomass [9]. An effective pretreatment plays a key role in the success of the process since it critically influences the subsequent stages of biofuel production [10].

Pretreatment using water at high temperature (also known as autohydrolysis or liquid hot water) consists in an attractive hydrolyzing medium that enable a wide variety of reactions without catalyst [11,12]. The autohydrolysis reaction may be

considered either as a fractionation process or as a pretreatment to enhance biomass susceptibility to enzymatic hydrolysis. Hemicellulose is solubilized selectively by autohydrolysis, yielding spent solids mainly composed of acid insoluble lignin and cellulose, more susceptible to enzyme action [13].

The production of bioethanol from pretreated lignocellulosic biomass can be carried out by consecutive stages of enzymatic hydrolysis and fermentation (method known as separate hydrolysis and fermentation, SHF) or by a single stage of saccharification and fermentation (known as simultaneous saccharification and fermentation, SSF) [4,14]. The main advantage of the SHF process is that both steps (saccharification and fermentation) can be carried out at their individual optimal process conditions. While in the SSF process, a compromise should be accomplished on the reaction conditions. The main advantage of the SSF process is that the glucose produced is simultaneously consumed by yeast. This consumption decreases the product inhibition of enzyme catalysis. In addition, the SSF process can be carried out in one process step [15], resulting in overall cost reduction from the use of only one reactor [16].

Paulownia tomentosa is a fast growing, short-rotation woody crop plant with high biomass production, 50 t/(ha year) [17], significantly higher than the production of other species (such as poplar, switchgrass, miscanthus or willow), with values of 6–17 t/(ha year) [18]. In addition, *P. tomentosa* presents an elevate degree of tolerance to different abiotic stress conditions (such as resistance to rooting, drought and poor soils) [19,20]. These features are of utmost importance to select *P. tomentosa* as feedstock to produce bioethanol [21].

In previous research, *Paulownia* biomass was evaluated for pulping paper manufacture and lignin applications using combined processes of autohydrolysis and delignification [22,23]. Moreover,

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