

## Process design and sustainability in the production of bioethanol from lignocellulosic materials

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### Abstract

**Background:** Bioethanol is produced mainly from sugar cane and corn. In the last years it has been subject of debate due to the effects in food prices and land use change. The use of lignocellulosic materials for bioethanol production, such as agroindustry, forestry and municipal residues, wood or dendroenergetic species, has been proposed as a sustainable way for producing this biofuel. The design of a sustainable process for producing bioethanol requires a methodological approach whereby economical, environmental and social criteria are systematically integrated from the early stages of process design.

**Results:** Until now a methodology for guiding the design of a sustainable process for bioethanol production is not available, and there are just a few studies on this subject. Moreover, with the recent global concerns on climate change, developed technologies have been confronted with additional requirements to validate their sustainability. In this sense, the inclusion of sustainability criteria on process design becomes necessary for defining a systematic methodology to select the most appropriate operations in the process stages to achieve a sustainable bioethanol production.

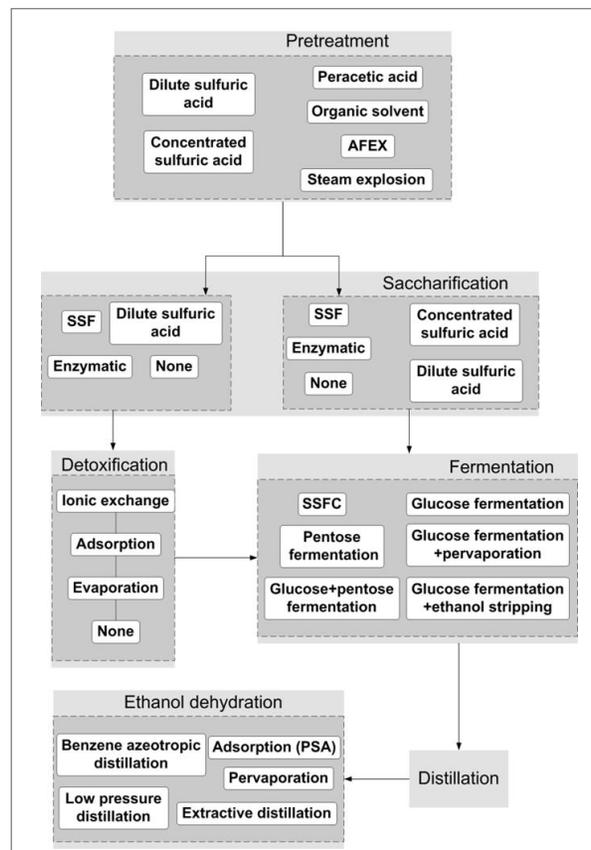
**Conclusions:** A description of the stages for the production of bioethanol from lignocellulosic materials is provided in this review and the main findings in relation to the more important sustainability indicators are presented.

**Keywords:** bioethanol, life cycle analysis, lignocelluloses, sustainability.

### INTRODUCTION

Bioethanol has been used as a biofuel in large scale since the implementation of the Brazilian alcohol program (Goldemberg et al. 2004). However, its production from sugar cane in Brazil and corn grains in the United States has been subject of debate regarding its effects on food prices and land use change (LUC). Production of bioethanol from lignocellulosic materials (LC), also called second-generation bioethanol (bioethanol 2G), is proposed as an alternative without such adverse effects. Bioethanol 2G has been an active field of research in the last decades and nowadays there are several companies scaling up their process in what seems to be the beginning of a learning process for having commercial scale production processes no later than 2020.

Compared to the accessibility of sucrose in sugar cane and starch in grains, cellulose and hemicellulose in LC are hardly available for saccharification and fermentation due to the presence of lignin, and a stage of “pre-treatment” is required to facilitate its conversion to fermentable sugars. A number of methods have been described, proposed and tested as a pre-treatment stage where the biomass structure is significantly altered to improve the accessibility of cellulolytic enzymes to the cellulose matrix. These enzymes convert cellulose into a mixture of cellobiose and glucose that fermenting microorganisms (yeasts and bacteria) will transform into bioethanol. Distillation is used for bioethanol recovery from the fermented, which is concentrated up to the azeotropic point (ca. 95% w/w bioethanol) and then dehydrated. An overview of the process structure and the many alternatives developed can be seen in Figure 1. The number of feasible process alternatives makes the decision of the most appropriate sequence of operations a difficult problem, since the stages are interconnected, and changes in process conditions change the behaviour of the entire process and the economic and environmental indicators as well.



**Fig 1. Diagram of the process alternatives for producing second generation bioethanol from lignocellulosic materials.**

Many authors have emphasized the importance of Life Cycle Assessment (LCA) as a tool for measuring sustainability indicators in the production of bioethanol 2G, comparing its environmental impacts with those of corn-based and sugar based-bioethanol, also called first generation bioethanol, and also with gasoline (Kemppainen and Shonnard, 2005; Luo et al. 2009; Maclean and Spataro, 2009). The LCA is a process of compilation and evaluation of the inputs, such as feedstock and energy, the outputs, like sub-products and pollutant emissions, and the potential environmental impacts of a production system throughout its life cycle (Zah et al. 2007). The results obtained allow the comparison of processes, products and services currently available or under development. LCA can identify potential environmental impacts at an early stage of a process design, and provides the opportunity for making decisions to improve its sustainability before process implementation (Quintero et al. 2008). The environmental performance of proposed processes for the production of

lignocellulosic bioethanol are still under discussion due to the state of development of the technology and the differences in focus and assumptions of the LCA practitioners (Singh et al. 2009).

Several reviews have been published in the last decade related to bioethanol 2G production (Balat, 2011; Walker, 2011), pre-treatment processes (Mosier et al. 2005; Zhao et al. 2009; Galbe and Zacchi, 2012), saccharification and fermentation (Sun and Cheng, 2002; Lin and Tanaka, 2006; Hahn-Hägerdal et al. 2007; Taherzadeh and Karimi, 2007a; Taherzadeh and Karimi, 2007b; Olofsson et al. 2008; Brethauer and Wyman, 2010), industrial implementation (Tomás-Pejó et al. 2008), economics (Gnansounou and Dauriat, 2010), process integration and intensification opportunities (Cardona and Sánchez, 2007). However, the coupling of sustainability analysis and process design for bioethanol 2G production has not been addressed. In this review, recent studies concerning process design for producing bioethanol 2G, including both traditional methodological approaches and sustainability criteria, are reviewed and analyzed.

## PROCESS DESIGN

Process synthesis and design are engineering activities oriented to the identification of novel process configurations or flow sheets able to produce the target product. These activities are part of a much broader field known as Process System Engineering, characterized for analyzing the productive systems as a whole, studying how the components and their interactions contribute to the overall 'behavior' of the system (Stephanopoulos and Reklaitis, 2011). Quoting Grossmann and Westerberg (2000): "Process Systems Engineering is concerned with the improvement of decision-making processes for the creation and operation of the chemical supply chain. It deals with the discovery, design, manufacture, and distribution of chemical products in the context of many conflicting goals". From the above definition, it is clear that process design deals not only with the selection of equipment and operations, but also with social, economic and environmental issues that the production process can affect. Conceptual process synthesis and design emerged from the concept of unit operation process, allowing decomposition of a complex interconnected network of equipment and activities into well-defined blocks with specific objectives and common features. This concept was introduced by A.D. Little in 1915 (Little, 1933). He stated that any chemical process can be represented as a series of "unit operations" such as solid separation, reaction or heat exchange. This set the cornerstone for the heuristic process system synthesis approach, which builds upon the knowledge and expertise of the designer to achieve suboptimal designs, limiting time and resources consumed when the synthesis problem is too big or too complex. A heuristic method proposed by Rudd (1968) is based on decomposition, whereby a design problem for which no previous technology existed is broken down into a sequence of sub-design problems until the level of available technology is reached. As it will be shown along this section, this represents the widely used method for process design in bioethanol production.

The optimization based approach for process synthesis relies on the formulation of a superstructure of process flow sheets among which the optimal process is selected via mathematical programming. This approach often leads to a class of problem known as *Mixed Integer Non-Linear Programming problem* (MINLP) composed of integer variables (binary variables in most cases), representing the selection of one of the candidate processes in the superstructure, and continuous variables to account for compositions, temperatures and other decision variables (Grossmann, 1996; Grossmann and Ruiz, 2012). Since many of the unit operations commonly used in chemical engineering are described by non-convex equations, the synthesis problem involves the solution of a non-convex MINLP hampering the detection of the global optimum. Despite difficulties in MINLP methods, this and other optimization-based process design methodologies are expected to contribute to the development of biorefineries and bioethanol production processes (Villegas and Gnansounou, 2008; Grossmann and Guillén-Gosálbez, 2010; Stephanopoulos and Reklaitis, 2011).

Knowledge based and optimization based process synthesis have been applied for the design of bioethanol production processes. Since, formulation of well posed optimization problems leading to the synthesis of bioethanol processes requires mathematical models that adequately represent the behaviour of the unit operations under analysis, this method has not been extensively used compared to the knowledge-based process design; however, its application has been largely dominated by heuristic methods, with the exception of a recently published work in knowledge-based hierarchical decomposition (Sánchez and Cardona, 2012).

To help a more structured revision of the relevant advances in this area, a generic bioethanol production process will be divided into stages and the process alternatives within it will be analyzed. Each stage is composed of several unit operations, and material and energy exchange occur between stages not only in an acyclic fashion, but also with possible recycling and energy integration between them. The process stages are defined by their objectives: (i) pre-treatment, aimed to improve enzymatic accessibility to cellulose while recovering monosaccharides from hemicelluloses; (ii) saccharification, aimed to convert cellulose and hemicellulose to glucose and other monosaccharides; (iii) fermentation, for bioethanol production from the released monosaccharides; (iv) bioethanol recovery, aimed to get a biofuel able to be mixed or readily used, and (v) waste water treatment, aimed to comply with regulations and to recover as much energy as possible. Due to excellent reviews in enzymatic hydrolysis and fermentation (Sun and Cheng, 2002; Olofsson et al. 2008; Brethauer and Wyman, 2010; Balat, 2011), only new and integrated strategies for these stages will be reviewed in this work.

Waste water treatment is a surprisingly overlooked subject in the literature., despite being a key issue in bioethanol production since it contributes with nearly 20% of the total installed equipments cost and represents up to 15% of the minimum bioethanol selling price (MESP), this is the product selling price required to pay for the operational and capital expenditures having no further income (Humbird et al. 2011). Regarding experimental studies, the performance of anaerobic treatment on stillage produced by conventional and second generation bioethanol production processes were compared and no relevant differences were found on biogas yield nor in COD removal, but lower biogas productivity was found for waste water treatment of second generation stillage (Wilkie et al. 2000). Concerning process design and evaluation, several possible configurations of biological waste water treatment suitable to replace the energy consuming evaporation of stillage in a simulated second generation bioethanol facility were compared in a techno-economical study (Barta et al. 2010). Finally, Harris Group and NREL designed a waste water treatment process based in anaerobic digestion, activated sludge systems and reverse osmosis that forms the basis of the NREL cellulosic bioethanol model (Steinwinder et al. 2011).

### Knowledge-based process design

**Pre-treatment.** Pre-treatment processes have been in the core of bioethanol production research for the last decades (Mosier et al. 2005; Hendriks and Zeeman 2009; Galbe and Zacchi, 2012). As an effective pre-treatment for hemicellulose removal, dilute sulfuric acid hydrolysis has been extensively used (Lloyd and Wyman, 2005; Taherzadeh and Karimi, 2007a). The most common acid catalyst is sulphuric acid; a comparison between phosphoric and sulphuric acid concluded that hemicellulose removal and subsequent enzymatic hydrolysis after dilute sulphuric acid pre-treatment outperforms phosphoric acid (Um et al. 2003). A key variable in this pre-treatment is acid consumption, since after pre-treatment the remaining acid has to be neutralized in order to proceed with saccharification and fermentation. Neutralization is often made with lime, producing insoluble sulphate salts that precipitate and have to be separated and disposed. Efforts to reduce sulphuric acid load lead to identify two key process variables in pre-treatment: acid concentration in reaction liquor and acid dosage per unit mass of LC (corn stover) (Chen et al. 2012). The authors found that, when acid is dosed on reaction liquor basis, glucose yield after enzymatic hydrolysis is highly dependent on the solid loading. However, when using constant acid dosage based on the mass of corn stover (g acid/ g dry LC), saccharification yield is relatively constant between 15 and 30% w/w solids. Hence, it was found that acid loading based on total solids (g acid/g dry biomass) rather than the acid concentration (g acid/g pre-treatment liquid) governs the pre-treatment efficiency. Additionally, using highly active commercial enzyme preparations (CellicCTEC2) allows maintaining high conversions even when acid dosage was reduced by 50% and much milder pre-treatment conditions were used: 170°C for 15-20 min compared with 190°C for 1-5 min. Auto-hydrolysis pre-treatment, also known as hot liquid water or hydrothermal pre-treatment, has several conceptual advantages over dilute acid hydrolysis since no corrosive resistant alloys are needed and solid waste (gypsum) generation is minimized. The process involves heating an aqueous suspension of LC, typically at temperatures ranging from 200 to 230°C. Operated under suitable conditions, hemicellulose is converted into soluble saccharides (Garrote et al. 1999), whereas the treated solids show an increased susceptibility to cellulolytic enzymes (Garrote et al. 2008; Ostergaard-Petersen et al. 2009; Ares-Peón et al. 2011). Recognizing the tradeoffs between pre-treatment and saccharification and fermentation processes, Romaní et al. (2012) use a response surface methodology (RSM) with the following independent variables: pre-treatment severity, solid fraction in simultaneous saccharification and fermentation (SSF, Figure 2b) and the enzyme to substrate ratio. As a result of the RSM optimization, 91% cellulose to bioethanol yield was achieved

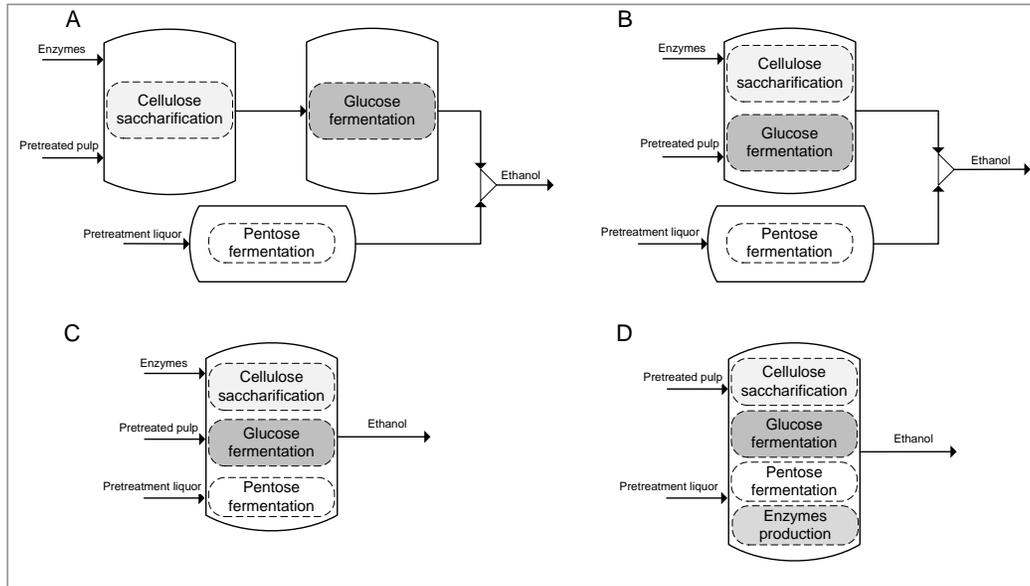
with 20% w/w solid loading and 16 filter paper units (FPU)/g glucan. A study on rice straw auto-hydrolysis used a semi-continuous fixed bed reactor achieving near complete saccharification (Ingram et al. 2009). The authors claimed several advantages compared to other reactor configurations: high solid-to-water-ratios (1:10), prevention of degradation product formation and energy savings since no biomass comminuting is necessary.

Among the pre-treatments aimed to remove lignin as a way to enhance enzyme accessibility to recalcitrant substrates, organic solvent based processes have been extensively studied. The process involves contacting the lignocellulosic material with a mixture of water, mineral acids at low concentration –not always used- and an organic solvent at high temperatures. The use of solvent based pretreatments for improving enzymatic hydrolysis of LC has been recently reviewed (Zhao et al. 2009). As a strategy for improving hemicellulose recovery, Romání et al. 2011 developed a pretreatment process based on sequential stages of auto-hydrolysis (to promote the solubilization of hemicellulose) and Organosolv pulping (to dissolve lignin, leaving solids enriched in cellulose). Other pre-treatments aimed to reduce the lignin content of the lignocellulosic material are Ammonia Fiber Expansion and lime treatment (AFEX). This process relies in the use of liquefied ammonia at elevated pressures instead of water. It is an alkaline method with delignification capability, where the material is treated for 10 to 60 min at a temperature close to 100°C (Alizadeh et al. 2005; Teymouri et al. 2005; Balan et al. 2009; Bals et al. 2010). The process is more effective in low lignin content LC such as switchgrass or corn stover, being less efficient in softwoods and hardwoods, where harsher conditions are required (Balan et al. 2009). The main drawback of this method is that has to be recovered and compressed for a new pre-treatment cycle. Lime pretreatment is typically performed at 100°C, for approximately 1 hr using calcium hydroxide. However, if lignin content is above 18% w/w oxidative conditions or longer times (up to 8 weeks at 55-65°C) are necessary (Sierra et al. 2009).

**Process integration in the saccharification and fermentation stages.** Saccharification and fermentation stages, as reacting systems, represent the core of any bioethanol production process. Process design in these areas has been hindered by the many tradeoffs between pre-treatment, saccharification and fermentation stages. Regarding pre-treatment, a high severity one enhances cellulose saccharification yield but often destroys part of the hemicellulose fraction and produce inhibitory compounds that impair the fermentation stage (Delgenes et al. 1996; Cantarella et al. 2004). Concerning the tradeoffs between saccharification and fermentation, cellulolytic enzymes have an optimal operation temperature close to 50°C, while most fermenting microorganisms have an optimal growing temperature between 30 and 35°C. Additionally, glucose and xylose produced during saccharification act as inhibitory compounds for cellulase and  $\beta$ -glucosidase, thus reducing the saccharification rate (Mosier et al. 1999; Hodge et al. 2008). As a way to overcome this inhibition, saccharification and fermentation could be performed in a single reactor (Figure 2b), thus coupling the reactions of sugars release and consumption, so reducing sugars concentration and thus relieving end-product inhibition when compared to SHF (Figure 2a). However, a compromise temperature must be used, decreasing the enzymatic saccharification rate and affecting the glucose to ethanol yield of the fermenting microorganism. In SHF and SSF, glucose is the main sugar reacted into ethanol; however pentoses like xylose and arabinose represent a relevant carbohydrate fraction that needs to be used to improve the LC to ethanol yield. Simultaneous saccharification and co-fermentation (SSCF, Figure 2c) uses naturally fermenting -or engineered- microorganisms to ferment five carbon sugars (Olofsson et al. 2008; Tomás-Pejó et al. 2008).

The concept SSF was early suggested in a patent issued to Gauss et al. (1976), where they claim that a higher bioethanol yield and a lower end-product inhibition were observed compared with sequential hydrolysis and fermentation (SHF, Figure 2a). A complete review on SSF can be found in Olofsson et al. (2008); a somewhat more general but remarkably clear presentation on the subject can be found in Sun and Cheng (2002), while in the work reported by Cardona and Sánchez (2007) the process was treated from a reaction-reaction process intensification viewpoint. In this review, new modifications to SSF and SHF processes are discussed. Also, relevant efforts to integrate enzyme production, saccharification and fermentation in the so called consolidated bioprocess (CBP, SSF, Figure 2d) are reviewed. The reaction mixture in SHF and SSF at high solid loadings shows a transition from a solid-like viscous material to a liquid suspension as reaction progresses (Stickel et al. 2009; Knutsen and Liberatore, 2010). To promote its rapid liquefaction, a pre-hydrolysis step prior to SSF using optimal saccharification temperature has been proposed. However, lower yields using pre-hydrolysis followed by SSF has been found compared to pure SSF (Öhgren et al. 2007). A further modification involves an intermittent feeding of solids during the pre-hydrolysis stage to achieve up to 20% of solids in the reactor (Gupta et al. 2012).

Kang et al (2012) studied a temperature shift SSF process (TS-SSF) as a way to tackle the temperature difference trade-off between the saccharification and fermentation processes. The process consists in a high temperature phase at 45°C, where AFEX pre-treated wheat straw (16% w/v solid loading) was contacted with cellulase,  $\beta$ -glucosidase and *K. marxianus* (CHY1612), a thermo-tolerant yeast. After a time ranging from 6 to 24 hrs, the fermenter was left to cool down to 35°C and the time course of SSF was monitored during 72 hrs.



**Fig 2. Reaction-reaction integrated schemes for LC ethanol production. (a) SHF; (b) SSF; (c) SSCF; and (d) CBP.**

Another approach to deal with the difference in the optimal temperatures of saccharification and fermentation is the so-called non-isothermal saccharification and fermentation (NSSF). In this configuration, saccharification and fermentation are performed simultaneously at their optimal temperatures, but in separate reactors. In a fixed bed saccharification reactor, pre-treated lignocellulose is retained and the withdrawn liquor is pumped to a heat exchanger, cooled to fermentation temperature and sent to a fermenter coupled with a cell retention system (Wu and Lee, 1998). Using this configuration, a reduction of the overall enzyme requirement by 30-40% was obtained.

A batch cascade of simultaneous saccharification for xylose and glucose fermentation has been proposed as a way to improve the overall process yield by using the hemicellulose fraction (Li and Kim, 2012). The system is composed of two sequential SSF phases operating on pentose and hexose. In the first phase, pentose conversion to ethanol is achieved using xylanase, endo-glucanase, and recombinant *E. coli* (KO11) with minimal glucose consumption. In the second phase, hexose conversion is performed using cellulase,  $\beta$ -glucosidase, and *S. cerevisiae* (D5A). Using four reactors and an equivalent solid loading of 6% w/v distributed in two second phase reactors; an ethanol yield of 60% was achieved at 27 g/L of ethanol. A previous work by the same authors used a straightforward method consisting in only two stages (Li et al. 2010). A final bioethanol titer of 22.3 g/L was achieved, equivalent to 84% of the theoretical yield. Unfortunately, results from both studies are not comparable since only one load of solids was used to achieve an initial solid concentration of 6% w/v in Li et al. (2010). CBP is believed to be an advanced solution to reduce process complexity and production cost. *Clostridium phytofermentans* was tested on AFEX-treated corn stover. At optimal conditions with 0.5% (w/w) glucan, *C. phytofermentans* hydrolyzed 76% of glucan and 88.6% of xylan in 10 days without any external enzyme dosage. Decomposition products from AFEX pre-treatment helped to increase bioethanol yield somewhat during CBP, although the explanation for this behaviour is still unknown (Jin et al. 2011).

An even more integrated one-step conversion method was published using the white-rot fungus *Phlebia* sp. MG-60 (Kamei et al. 2012a). The fungus was able to delignify untreated oak wood chips in aerobic solid-state fermentation. After 56 days of aerobic incubation, 40.7% of the initial lignin was degraded with minimal glucan degradation. After this biological pre-treatment step, culture conditions were shifted to semi-aerobic triggering the saccharification ability of *Phlebia* sp. MG-60. After 20 days of simultaneous saccharification and fermentation, 43.9% of the theoretical yield based on pre-treated wood chips was achieved, without any external enzyme addition. It is worth mentioning that since no meaningful glucan or hemicellulose degradation occurred, this yield also corresponds to the yield based on the initial carbohydrate content of wood chips. It remains unclear if cellulase and  $\beta$ -glucosidase supplementation would be able to improve the reported yields. No improvement would suggest that the accessibility of enzymes or the fermentation capabilities are the process bottleneck. Regarding the fermentation capability of *Phlebia* sp. MG-60, bioethanol yields of 0.44 g/g glucose, 0.41 g/g mannose, 0.40 g/g galactose, 0.41 g/g fructose and 0.33 g/g xylose were found, but the fungus was unable to ferment arabinose (Kamei et al. 2012b). Time needed for fermentation of the above mentioned sugars, with initial concentrations ranging between 20 and 23 g/L, was 120 hrs, suggesting that fermentation capability is not the process limiting step.

**Pilot and demonstration plants.** Advances in bioethanol production have allowed the construction and operation of pilot and demonstration plants, mainly in Europe and in the United States (Table 1). The Lignol process, developed in Canada, uses the Organosolv process as pre-treatment of the LC to produce bioethanol, high quality and pure lignin and, potentially, furfural, acetic acid and xylose (Arato et al. 2005). Iogen Corporation, also based in Canada, uses an acid catalyzed steam explosion pre-treatment, followed by SHF without prior solid separation or washing. Enzymes are produced by Iogen's proprietary technology. After SHF, lignin and unreacted cellulose is separated for energy production (Tolan, 2002). Steam explosion is also used by Abengoa Bioenergy, followed by SHF in their facilities in Babilafuente, Spain. FibreEtOH, developed in Finland by a consortium integrated by pulp and paper, enzyme production and process design industries, an ethanol distributor and VTT Technical Research Centre of Finland, aims to process a mixture of solid recovered fibers (SRF) and Kraft pulp fibers. SRF are treated by acid catalyzed steam explosion and then mixed with pulp fibers. The mixture is fed to a continuous liquefaction system (cL), with a residence time of 6 hrs, and the outlet product is sent to a batch SSF reactor (Kemppainen et al. 2012). Several projects are based in dilute acid processes. POET, a US based ethanol producer in partnership with Royal DSM, uses a single stage dilute acid pre-treatment followed by saccharification and fermentation, solids are not separated prior to fermentation and to promote aggregation of the solid particles, before entering to a distillation column, a thermal treatment is used (McDonald et al. 2012). Earlier, Inbicon (a subsidiary company of DONG Energy, the mayor energy producer in Denmark) worked with a two-step pre-treatment based in dilute acid; now it uses a one-step auto-hydrolysis (AH), followed by two stage SSF. In the first step LC is liquefied in a horizontal reactor designed for handling high concentrations of solids, and then transferred to a conventional fermenter. The product broth is stripped under vacuum and the removed ethanol distilled and rectified. The solids in the column bottoms are separated, and part of the liquid is recycled to the pre-hydrolysis reactor. The rest is combined with pre-treatment liquors, concentrated in evaporators and commercialized as molasses rich in 5-carbon sugars (Larsen et al. 2012). The most relevant feature of the process is that it is entirely continuous.

Finally, Mascoma (US based company linked to Dartmouth College's Thayer School of Engineering) has claimed to produce bioethanol via CBP, using proprietary engineered microorganisms, e.g. modified thermophilic bacteria as *Thermoanaerobacterium saccharolyticum* (Shaw et al. 2008).

### Optimization-based process design

Integration of first and second generation bioethanol production process is considered to be an intermediate step towards full scale lignocellulosic bioethanol production. Recognizing that in sugarcane based industries bagasse is already used in electricity generation, a simulation and optimization approach was used to optimize plant operation (Furlan et al. 2012). Only two decision variables were considered: the fraction of feedstock entering the boiler, and the fraction of the bagasse surplus (not burned) used for second generation bioethanol production, being the rest sold. The process was simulated using the software EMSO, and the optimization variables were handled by a particle swarm optimization algorithm. The authors showed that the production of 2G bioethanol increases thermal demands in at least 25%, which narrows the decision feasible range on how much bagasse, can be diverted to production of second generation fuel. Furthermore, electric power surplus is diminished in at least 31%.

On the other hand, a flow sheet for the production of bioethanol from switch grass via biochemical route was proposed by optimizing a superstructure embedding a number of alternatives (Martín and Grossmann, 2012). Two technologies were considered in the pre-treatment stage: dilute acid and ammonia fiber explosion. Cellulose to bioethanol conversion was achieved by using SHF and a number of distillation and dehydration alternatives were considered: rectification, adsorption in corn grits, molecular sieves, and pervaporation. The problem was formulated as a mixed-integer nonlinear programming (MINLP). Since, only two pre-treatments were included, the superstructure is optimized by decomposing the MINLP for each of the pre-treatments. After this decomposition, each problem is a nonlinear programming problem, and hence can be solved more easily. The optimal flow sheet consists of dilute acid hydrolysis and molecular sieves. With this configuration, a production cost of 21 cUSD/L was calculated.

**Table 1. Selected pilot and demonstration plants process design and capacities.**

Company	Material	Process	Capacity ( $\text{m}^3\text{y}^{-1}$ )
Lignol Energy Corp.	Wood chips	Org-SSF/SHF	100
Iogen Corporation	Wheat, barley	STE-SHF	2000
Inbicon	Wheat straw	AH-SSF	5000
Abengoa Bioenergy	Cereal straw	STE-SHF	4000
FibreEtOH	SRF+kraft pulp	STE-cL-SSF	-
Mascoma Corporation	Wood, switchgrass	CBP	600
POET	Corn residues	DA-SHF	75

Capacity in  $\text{m}^3\text{y}^{-1}$  of bioethanol. Plant capacities and materials from Bacovsky et al. 2010.

Bioethanol is one of the many products within the concept of biorefinery. Selection of the optimal products and processes for producing them is an immense combinatorial problem. Recently, a shortcut method for the synthesis and screening of integrated biorefineries was presented (Bao et al. 2011). The method is based on a structural representation based on chemical species and conversion operators that relate them. An optimization approach is developed to screen and determine optimum network configurations for various technology pathways using simple data. Although the method was used for synthetic gasoline process selection, it can be readily adapted for bioethanol production and, more importantly, for a mix of products including bioethanol. A similar process synthesis approach was presented in the same year involving a two-step algorithm. In the first step, a set of possible intermediates was identified given a LC composition and flow rate. In the second step, given a desired product (ethanol among others), necessary species and pathways leading to it are identified and a matching is done of intermediates identified on both steps (Pham and El-Halwagi, 2011).

### Sustainability of the production of bioethanol

The sustainability assessment of the production of 2G bioethanol must integrate the economic, social and environmental criteria, providing relevant information in the decisions of process design and, at the same time, increasing the inherent complexity of the process synthesis. This is mainly due to the high number of interacting parameters or indicators, in which a wide range of stakeholders: investors and insurers, employees and contractors, suppliers, customers and local communities are involved.

The sustainability indicator system has been developed focused on the impact of process operations, mainly environmental impacts and to a lesser extent social impacts. In the last decade the awareness about sustainability has increased and the concept of "life cycle thinking" has been implemented. It includes the determination of environmental, social and economic impacts of a product over its entire life cycle (Curran, 2007) and in the latest years has been progressively more relevant and has driven companies to adopt cleaner technologies and better management techniques.

There are several reports on LCA of the production of bioethanol 2G (Zhi-Fu et al. 2003; Spatari et al. 2005; Luo et al. 2009; Singh et al. 2009; Spatari et al. 2010; Borrion et al. 2012; González-García et al. 2012a; Kumar and Murthy 2012; Wang et al. 2012). Due to the wide variety of raw materials, geography and climate conditions, and process alternatives, the results of these analyses show a wide dispersion for the different impact categories evaluated (Zhi-Fu et al. 2003; Sheehan et al. 2003;

Spatari et al. 2010). Table 2 shows the variation in impact categories for bioethanol production from different raw materials.

Azapagic et al. (2006) developed a methodology called Process Design for Sustainability (PDfS), establishing indicators for each criteria in each stage of the process under development, and the most relevant sustainability indicators were identified to obtain a preliminary assessment for each stage that allowed making decisions on the design of the stage. Microeconomic indicators, such as net present value, cash flow analysis, return rate on capital invested and others were taken into account to assess the economical sustainability. The environmental sustainability was determined using LCA, while in the social criteria, indicators like occupational health, safety or public acceptability were used. Nevertheless, Azapagic et al. (2006) excluded an integrated sustainability assessment, but they related the theoretical principles of sustainability to the design practice.

**Table 2. Impact categories for lignocellulosic bioethanol in comparison with fossil fuels.**

	Tan and Culaba (2002)	Zhi-Fu et al. (2003)	Sheehan et al. (2003)	Zah et al. (2007)	González-García et al. (2010)	Cherubini and Jungmeier (2010)	Cherubini and Ulgiati (2010)	González-García et al. (2012c)		González-García et al. (2012a)		
Feed stock	corn stover	wood chips	corn stover	wood	poplar	switchgrass	corn stover	wheat straw	wood chips	eucalyptus	black locust	poplar
GWP	↓	↓↑	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
AD	↓	nd	nd	nd	↓	↓	↓	↓	↓	nd	nd	nd
AC	↑	↑	↑	↑	↑	↑	↓	↓	↓	↓	↓	↑
EP	↑	↑	nd	↑	↑	↑	↑	↑	↑	↑	↓	↑
OLD	nd	↓	↓	nd	↓	↓	↓	↓	↓	nd	nd	nd
PS	↓	nd	↑	↓	↑	↑	↓	↓	↓	↑	↑	↑
HT	↑	↑	nd	nd	↑	↑	↓	↓	nd	nd	nd	nd
TE	nd	nd	nd	nd	↑	↑	↓	↓	nd	nd	nd	nd
ME	nd	nd	nd	nd	↑	↑	↓	↓	nd	nd	nd	nd
FE	nd	nd	nd	nd	↑	↑	↓	↓	nd	nd	nd	nd

GWP: Global Warming Potential. AD: Abiotic Depletion. AC: Acidification. EP: Eutrophication. OLD: Ozone Layer Depletion. PS: Photochemical Smog. HT: Human Ecotoxicity. TE: Terrestrial Ecotoxicity. ME: Marine Aquatic Ecotoxicity. FE: Fresh Water Aquatic ecotoxicity. ↑: Increase. ↓: Decrease. nd: non-determined.

### Economic criteria in bioethanol production

Economic criteria for process design of bioethanol production are the commonly used in traditional design approaches, which can be grouped in Micro-economic (Capital costs, Operating costs, Profitability and Investments) and Macro-economic (Value added, Taxes paid and Other Investments) aspect. However, due to the inclusion of environmental criteria in the design stage, the economic performance can be improved by obtaining “green” incentives, *i.e.*: carbon credits.

### Social criteria in bioethanol production

The transformation of conventional farms into farms dedicated to the production of raw materials for bioethanol production has changed the income, employment, and quality of life of farming communities in rural areas, particularly in developing countries (Inoue et al. 2010). In order to determine the

influence of bioethanol production on the social issues, the main indicators suggested are: provision of employment, health and safety (of employees/contractors, customers and citizens), nuisance (by odour, noise and visual impact) and public acceptability of process and product (Azapagic et al. 2006). In addition, bioethanol production is indirect competition with agriculture for land use (land use change), affecting food security. In the case of bioethanol, these indicators allow designing frameworks of social criteria for bioethanol feedstock production for the international acceptance (Andrews et al. 2009).

### **Environmental criteria in bioethanol production**

LCA has allowed quantifying environmental sustainability criteria for process assessment in bioethanol production. Current studies on LCA are focused on comparing a technology scheme for bioethanol production to fossil fuels or other alternative processes for bioethanol production (Borrion et al. 2012; González-García et al. 2012b).

Some of the most relevant sustainability criteria for environmental assessment are directly related to the source of raw material, energy consumption, emissions (into air, water and land) and environmental impacts (global warming, ozone depletion, acidification, human toxicity, eco-toxicity, summer smog and, eutrophication). LCA studies have shown environmental and social benefits associated with lignocellulosic bioethanol and its use in light-duty vehicles compared to gasoline and corn bioethanol (Sheehan et al. 2003; Spatari et al. 2005). To date, most of the studies have focused on modeling the upstream agricultural processes in specific geographic locations as well as the end uses, and have considered only a limited set of feedstocks in addition to a single pre-treatment technology.

The production and use of biofuels has the potential to reduce greenhouse gas (GHG) emissions, particularly with the development of bioethanol from agricultural wastes or lignocellulosic crops such as switch grass (Benoit and Mazijn, 2009). Alizadeh et al. (2005) proposed that in order to validate the lignocellulosic bioethanol production a reduction of 20% in GHG emissions must be achieved.

### **Technologies and sustainability**

Different technologies for converting lignocellulosic feedstocks to bioethanol are under development at laboratory, pilot, and demonstration scales as was described above. As these developing technologies may differ in their feedstock requirements as well as in process energy and chemical inputs, they exhibit a range of life cycle energy and environmental performance, aspects that have not been well acknowledged in the literature. Optimum process conditions for maximizing bioethanol production with minimum environmental impacts depend on the type of feedstock and conversion technology. There are several technologies proposed for lignocellulosic bioethanol production, and the different routes and system boundaries considered are the main reasons for the different results obtained in the LCA reports (Kumar and Murthy, 2012).

Most of the LCA studies on bioethanol production have been focused on assessing the farming systems with general assumptions on the process. Very few have addressed the environmental issues related to the process, probably due to the process uncertainties and the lack of a commercial scale plant. The industrial scale up of this process appears to be delayed by technological issues or by the lack of information from demonstration facilities (Kemppainen and Shonnard, 2005). This lack of industrial scale information contributes to the data uncertainty within the life cycle inventories required in these studies.

**Enzyme production.** According to Zhi-Fu et al. (2003) the cultivation of raw material and the production of the enzyme are the main contributors to eutrophication. In enzyme production main impacts come from feed production, since grains are usually needed for the fermentation broth, and the process have air and water emissions that have to be considered. In the impact category of acidification, the contribution comes from: the emissions involved in the generation of the energy required by the process, the agricultural activities for feedstock production, and the fermentation. The contribution from feedstock cultivation is mainly due to the emissions from the nutrients use in farming, field operations and phosphate manufacturing. MacLean and Spatari (2009) reported a range emissions from 1000 to 10,000 g CO<sub>2</sub> eq./kg enzyme depending upon the implemented technology. On the other hand, Kumar and Murthy (2012) determined the emissions from enzyme production in the range from 278.3 to 340 kg CO<sub>2</sub> eq./10,000 MJ of produced bioethanol.

Kadam (2000) analyzed the effect of enzymatic hydrolysis on the environmental impact of bioethanol production. He also compared the alternative of using acid hydrolysis for cellulose saccharification, showing that it was better than enzyme saccharification with respect to GHG reduction, natural resource depletion, acidification potential and eutrophication potential. Due to the higher proportion of biomass sent to the boiler for electricity production, it leads to lower SO<sub>x</sub>, NO<sub>x</sub>, and fossil CO<sub>2</sub> emissions. MacLean and Spatari (2009) showed that the environmental impact of chemical and enzyme inputs contributed only in 3% of the fossil energy use and in 3% of the GHG emissions for corn bioethanol, but in the case of lignocellulosic bioethanol the enzyme is responsible for 30 to 40% of the fossil energy use and 30 to 35% of GHG emissions of the total life cycle.

**Pre-treatment.** Kumar and Murthy (2012) compared four different pre-treatment methods for bioethanol production (dilute acid, dilute alkali, hot water, and steam explosion). Authors found that technologies used for ethanol production had major impact on total fossil energy use and GHG emissions, having the steam explosion pre-treatment the lowest contribution in these impact categories. In addition, they showed that it was possible to reduce the fossil energy demand between 57% and 112% to produce 10,000 MJ of ethanol compared to gasoline; however, about 0.35 ha of land is required to produce this energy. For all evaluated pre-treatments, co-product energy from the cogeneration system using lignin residues and biogas produced from waste water treatment produced enough steam to exceed the process requirements; however, excess electricity was obtained only in the case of steam explosion. Therefore, fossil energy use during ethanol production in that case was a negative value. Fossil energy reductions higher than 100% are due to the low process energy used (thermal and electricity) and high co-product energy produced during the ethanol production process. The authors assumed that this steam and electricity will replace the energy and emissions associated with the required steam and electricity production from fossil energy sources. In this sense, a negative value of fossil energy demand was due to the energy replaced by excess electricity, which was otherwise produced from fossil fuels. On the other hand, Wang et al. (2012) evaluated different bioethanol production scenarios using waste paper from different sources without pre-treatments and two cases considering acid and lime pre-treatment from office paper and newspaper, respectively. They found that an oxidative lime pre-treatment reduced GHG emissions and the overall environmental impact when compared to bioethanol production with non pre-treated newspaper, whereas a dilute acid pre-treatment increased GHG emissions when compared to the non pre-treated office paper.

**Energy cogeneration and energy ratio.** Zhi-fu et al. (2003) determined that E-10 fuel will produce less GHG than traditional gasoline, but if fossil-based electricity is used in bioethanol production it has a negative effect on the impact category of GHG. González-García et al. (2012c) have shown that most of the emissions from the bioethanol conversion process are due to emissions from the energy cogeneration system. In this sense, cogeneration takes relevance in the environmental impact of the process.

Kumar and Murthy (2012) compared the effect of including cogeneration in different pre-treatments technologies and found that fossil energy used was maximum when using dilute alkali pre-treatment because of the decrease in the available lignin for cogeneration, while net fossil energy use was found negative for bioethanol production in LCA using steam explosion as pre-treatment. They showed that the energy supply by cogeneration exceeded the needs of energy for the process.

## CONCLUDING REMARKS

Bioethanol production from LC has been widely studied during the last decades. However, despite the advances in pre-treatment technologies and cellulose saccharification, a satisfactory design for its production has not been yet scaled-up to commercial level and few works at pilot scale have been successfully implemented. Moreover, with the recent global concerns on climate change, developed technologies have been confronted with additional requirements to validate their sustainability. In this sense, the inclusion of sustainability criteria on process design becomes necessary for defining a systematic methodology to select the most appropriate operations in the process stages to achieve a sustainable bioethanol production. Until now, the reports in this issue indicates that enzyme production and energy consumption (due to the energy source) are the stages with the higher levels of environmental impacts; however, the important increase in the specific activities of the enzymes complexes reached by the main companies involved in this field, for sure will alleviate these impacts. Regarding energy consumption, co-generation using lignin must be considered to decrease these impacts.

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## REFERENCES

- ALIZADEH, H.; TEYMOURI, F.; GILBERT, T.I. and DALE, B.E. (2005). Pretreatment of switchgrass by ammonia fiber explosion (AFEX). *Applied Biochemistry and Biotechnology*, vol. 124, no. 1-3, p. 1133-1142. [\[CrossRef\]](#)
- ANDREWS, E.; BARTHEL, L.; BENOÎT, C.; CUCUZZELLA, C.; HÉBERT, J.; LESAGE, P.; MANHART, A.; MAZEAU, P.; MAZIJJ, B.; METHOT, A.L.; PARENT, J.; PRAKASH, S.; REVERET, J.P.; UGAYA, C. and WEIDEMA, B. (2009). Guidelines for Social Life Cycle Assessment of Products. *UNEP/SETAC Life Cycle Initiative at UNEP, CIRAIG, FAQDD and the Belgium Federal Public Planning Service Sustainable Development*. 103 p. ISBN 978-92-807-3021-0.
- ARATO, C.; PYE, E.K. and GJENNESTAD, G. (2005). The lignol approach to biorefining of woody biomass to produce ethanol and chemicals. In: DAVISON, B.; EVANS, B.; FINKELSTEIN, M. and MCMILLAN, J. eds. *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*. Humana Press, p. 871-882.
- ARES-PEÓN, I.A.; VILA, C.; GARROTE, G. and PARAJÓ, J.C. (2011). Enzymatic hydrolysis of autohydrolyzed barley husks. *Journal of Chemical Technology and Biotechnology*, vol. 86, no. 2, p. 251-260. [\[CrossRef\]](#)
- AZAPAGIC, A.; MILLINGTON, A. and COLLETT, A. (2006). A methodology for integrating sustainability considerations into process design. *Chemical Engineering Research and Design*, vol. 84, no. 6, p. 439-452. [\[CrossRef\]](#)
- BACOVSKY, D.; DALLOS, M. and WOERGETTER, M. (2010). Status of 2nd generation biofuels demonstration facilities in June 2010. *IEA Bioenergy Task 39: Commercializing 1st and 2nd generation liquid biofuels from biomass*; July Report T39-P1b.
- BALAN, V.; DA COSTA SOUSA, L.; CHUNDAWAT, S.P.S.; MARSHALL, D.; SHARMA, L.N.; CHAMBLISS, C.K. and DALE, B.E. (2009). Enzymatic digestibility and pretreatment degradation products of AFEX-treated hardwoods (*Populus nigra*). *Biotechnology Progress*, vol. 25, no. 2, p. 365-375. [\[CrossRef\]](#)
- BALAT, M. (2011). Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. *Energy Conversion and Management*, vol. 52, no. 2, p. 858-875. [\[CrossRef\]](#)
- BALS, B.; ROGERS, C.; JIN, M.; BALAN, V. and DALE, B. (2010). Evaluation of ammonia fibre expansion (AFEX) pretreatment for enzymatic hydrolysis of switchgrass harvested in different seasons and locations. *Biotechnology for Biofuels*, vol. 3, no. 1, p. 1. [\[CrossRef\]](#)
- BAO, B.; NG, D.K.S.; TAY, D.H.S.; JIMÉNEZ-GUTIÉRREZ, A. and EL-HALWAGI, M.M. (2011). A shortcut method for the preliminary synthesis of process-technology pathways: An optimization approach and application for the conceptual design of integrated biorefineries. *Computers & Chemical Engineering*, vol. 35, no. 8, p. 1374-1383. [\[CrossRef\]](#)
- BARTA, Z.; RECZEY, K. and ZACCHI, G. (2010). Techno-economic evaluation of stillage treatment with anaerobic digestion in a softwood-to-ethanol process. *Biotechnology for Biofuels*, vol. 3, no. 1, p. 21. [\[CrossRef\]](#)
- BORRION, A.L.; MCMANUS, M.C.; and HAMMOND, G.P. (2012). Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. *Renewable and Sustainable Energy Reviews*, vol. 16, no. 7, p. 4638-4650. [\[CrossRef\]](#)
- BENOIT, C. and MAZIJJ, B. (2009). Guidelines for Social Life Cycle Assessment of Products, UNEP/SETAC Life Cycle Initiative at UNEP, CIRAIG, FAQDD and the Belgium Federal Public Planning Service Sustainable Development. Belgium. 104 p. ISBN 978-92-807-3021-0.
- BRETHAUER, S. and WYMAN, C.E. (2010). Review: Continuous hydrolysis and fermentation for cellulosic ethanol production. *Bioresource Technology*, vol. 101, no. 13, p. 4862-4874. [\[CrossRef\]](#)
- CANTARELLA, M.; CANTARELLA, L.; GALLIFUOCO, A.; SPERA, A. and ALFANI, F. (2004). Comparison of different detoxification methods for steam-exploded poplar wood as a substrate for the bioproduction of ethanol in SHF and SSF. *Process Biochemistry*, vol. 39, no. 11, p. 1533-1542. [\[CrossRef\]](#)
- CARDONA, C.A. and SÁNCHEZ, Ó.J. (2007). Fuel ethanol production: Process design trends and integration opportunities. *Bioresource Technology*, vol. 98, no. 12, p. 2415-2457. [\[CrossRef\]](#)
- CHEN, Y.; STEVENS, M.A.; ZHU, Y.M.; HOLMES, J.; MOXLEY, G. and XU, H. (2012). Reducing acid in dilute acid pretreatment and the impact on enzymatic saccharification. *Journal of Industrial Microbiology & Biotechnology*, vol. 39, no. 5, p. 691-700. [\[CrossRef\]](#)
- CHERUBINI, F. and JUNGMEIER, G. (2010). LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. *The International Journal of Life Cycle Assessment*, vol. 15, no. 1, p. 53-66. [\[CrossRef\]](#)
- CHERUBINI, F. and ULGIATI, S. (2010). Crop residues as raw materials for biorefinery systems – A LCA case study. *Applied Energy*, vol. 87, no. 1, p. 47-57. [\[CrossRef\]](#)
- CURRAN, M.A. (2007). Studying the effect on system preference by varying coproduct allocation in creating life-cycle inventory. *Environmental Science & Technology*, vol. 41, no. 20, p. 7145-7151. [\[CrossRef\]](#)
- DELGENES, J.P.; MOLETTA, R. and NAVARRO, J.M. (1996). Effects of lignocellulose degradation products on ethanol fermentations of glucose and xylose by *Saccharomyces cerevisiae*, *Zymomonas mobilis*, *Pichia stipitis*, and *Candida shehatae*. *Enzyme and Microbial Technology*, vol. 19, no. 3, p. 220-225. [\[CrossRef\]](#)
- FURLAN, F.F.; COSTA, C.B.B.; FONSECA, G.D.C.; SOARES, R.D.P.; SECCHI, A.R.; CRUZ, A.J.G. and GIORDANO, R.D.C. (2012). Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling. *Computers & Chemical Engineering*, vol. 43, no. 10, p. 1-9. [\[CrossRef\]](#)

- GALBE, M. and ZACCHI, G. (2012). Pretreatment: The key to efficient utilization of lignocellulosic materials. *Biomass and Bioenergy*, vol. 46, p. 7-78. [\[CrossRef\]](#)
- GARROTE, G.; DOMÍNGUEZ, H. and PARAJÓ, J.C. (1999). Mild autohydrolysis: An environmentally friendly technology for xylooligosaccharide production from wood. *Journal of Chemical Technology & Biotechnology*, vol. 74, no. 11, p. 1101-1109. [\[CrossRef\]](#)
- GARROTE, G.; YÁNEZ, R.; ALONSO, J.L. and PARAJÓ, J.C. (2008). Coproduction of oligosaccharides and glucose from corncobs by hydrothermal processing and enzymatic hydrolysis. *Industrial & Engineering Chemistry Research*, vol. 47, no. 4, p. 1336-1345. [\[CrossRef\]](#)
- GAUSS, W.; SUZUKI, S. and TAKAGI, M. (1976). US Patent no. 3,990,944. Washington, DC, U.S.
- GNANSOUNOU, E. and DAURIAT, A. (2010). Techno-economic analysis of lignocellulosic ethanol: A review. *Bioresource Technology*, vol. 101, no. 13, p. 4980-4991. [\[CrossRef\]](#)
- GOLDEMBERG, J.; COELHO, S.T.; NASTARI, P.M. and LUCON, O. (2004). Ethanol learning curve—the Brazilian experience. *Biomass and Bioenergy*, vol. 26, no. 3, p. 301-304. [\[CrossRef\]](#)
- GONZÁLEZ-GARCÍA, S.; GASOL, C.M.; GABARREL, X.; RIERADEVALL, J.; MOREIRA, M.T. and FEIJOO, G. (2010). Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe. *Renewable Energy*, vol. 35, no. 5, p. 1014-1023. [\[CrossRef\]](#)
- GONZÁLEZ-GARCÍA, S.; MOREIRA, M.T.; FEIJOO, G. and MURPHY, R.J. (2012a). Comparative life cycle assessment of ethanol production from fast-growing woods crops (black locust, eucalyptus and poplar). *Biomass and Bioenergy*, vol. 39, p. 378-388. [\[CrossRef\]](#)
- GONZÁLEZ-GARCÍA, S.; MOREIRA, M.T. and FEIJOO, G. (2012b). Environmental aspects of eucalyptus based ethanol production and use. *Science of the Total Environment*, vol. 438, p. 1-8. [\[CrossRef\]](#)
- GONZÁLEZ-GARCÍA, S.; IRIBARREN, D.; SUSMOZAS, A.; DUFOUR, J. and MURPHY, R.I. (2012c). Life cycle assessment of two alternative bioenergy systems involving *Salix* spp. biomass: Bioethanol production and power generation. *Applied Energy*, vol. 95, p. 111-112. [\[CrossRef\]](#)
- GROSSMANN, I.E. (1996). Mixed-integer optimization techniques for algorithmic process synthesis. *Advances in Chemical Engineering*, vol. 23, p. 171-246. [\[CrossRef\]](#)
- GROSSMANN, I.E. and WESTERBERG, A.W. (2000). Research challenges in process systems engineering. *AIChE Journal*, vol. 46, no. 9, p. 1700-1703. [\[CrossRef\]](#)
- GROSSMANN, I.E. and GUILLÉN-GOSÁLBEZ, G. (2010). Scope for the application of mathematical programming techniques in the synthesis and planning of sustainable processes. *Computers & Chemical Engineering*, vol. 34, no. 9, p. 1365-1376. [\[CrossRef\]](#)
- GROSSMANN, I. and RUIZ, J. (2012). Generalized Disjunctive Programming: A framework for formulation and alternative algorithms for MINLP optimization. In: LEE, J. and LEYFFER, S. eds. *Mixed Integer Nonlinear Programming*. Springer New York, vol. 154, p. 93-115.
- GUPTA, R.; KUMAR, S.; GOMES, J. and KUHAD, R.C. (2012). Kinetic study of batch and fed-batch enzymatic saccharification of pretreated substrate and subsequent fermentation to ethanol. *Biotechnology for Biofuels*, vol. 5, no. 11, p. 16. [\[CrossRef\]](#)
- HAHN-HÄGERDAL, B.; KARHUMAA, K.; FONSECA, C.; SPENCER-MARTINS, I. and GORWA-GRAUSLUND, M.F. (2007). Towards industrial pentose-fermenting yeast strains. *Applied Microbiology and Biotechnology*, vol. 74, no. 5, p. 937-953. [\[CrossRef\]](#)
- HENDRIKS, A.T.W.M. and ZEEMAN, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology*, vol. 100, no. 1, p. 10-18. [\[CrossRef\]](#)
- HODGE, D.B.; KARIM, M.N.; SCHELL, D.J. and MCMILLAN, J.D. (2008). Soluble and insoluble solids contributions to high-solids enzymatic hydrolysis of lignocellulose. *Bioresource Technology*, vol. 99, no. 18, p. 8940-8948. [\[CrossRef\]](#)
- HUMBIRD, D.; DAVIS, R.; TAO, L.; KINCHIN, C.; HSU, D. and ADEN, A. (2011). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. *National Renewable Energy Laboratory*. Technical Report, NREL/TP-5100-47764, Golden, Colorado.
- INGRAM, T.; ROGALINSKI, T.; BOCKEMÜHL, V.; ANTRANIKIAN, G. and BRUNNER, G. (2009). Semi-continuous liquid hot water pretreatment of rye straw. *The Journal of Supercritical Fluids*, vol. 48, no. 3, p. 238-246. [\[CrossRef\]](#)
- INOUE, Y.S.; NAKAJIMA, M.; NAKASHIMA, S. and YASUHIRO, N. (2010). Behavior modeling of socially sustainable activities: A case study of bioethanol feedstock production in Khon Kaen, Thailand. *The 16<sup>th</sup> Annual International Sustainable Development Research Conference 2010*, Hong Kong, p. 1-12.
- JIN, M.; BALAN, V.; GUNAWAN, C. and DALE, B.E. (2011). Consolidated bioprocessing (CBP) performance of *Clostridium phytofermentans* on AFEX-treated corn stover for ethanol production. *Biotechnology and Bioengineering*, vol. 108, no. 6, p. 1290-1297. [\[CrossRef\]](#)
- KADAM, K.L. (2000). Environmental life cycle implications of using bagasse-derived ethanol as a gasoline oxygenate in mumbai (Bombay). *National Renewable Energy Laboratory*. Technical report NREL/ DE-AC36-99-GO10337, Golden, Colorado. 92 p. ISBN 978-1249205241.
- KAMEI, I.; HIROTA, Y. and MEGURO, S. (2012a). Integrated delignification and simultaneous saccharification and fermentation of hard wood by a white-rot fungus, *Phlebia* sp. MG-60. *Bioresource Technology*, vol. 126, p. 137-141. [\[CrossRef\]](#)
- KAMEI, I.; HIROTA, Y.; MORI, T.; HIRAI, H.; MEGURO, S. and KONDO, R. (2012b). Direct ethanol production from cellulosic materials by the hypersaline-tolerant white-rot fungus *Phlebia* sp. MG-60. *Bioresource Technology*, vol. 112, p. 137-142. [\[CrossRef\]](#)
- KANG, H.W.; KIM, Y.; KIM, S.W. and CHOI, G.W. (2012). Cellulosic ethanol production on temperature-shift simultaneous saccharification and fermentation using the thermostable yeast *Kluyveromyces marxianus* CHY1612. *Bioprocess and Biosystems Engineering*, vol. 35, no. 1-2, p. 115-122. [\[CrossRef\]](#)

- KEMPPAINEN, A.J. and SHONNARD, D.R. (2005). Comparative life-cycle assessments for biomass-to-ethanol production from different regional feedstocks. *Biotechnology Progress*, vol. 21, no. 4, p. 1075-1084. [\[CrossRef\]](#)
- KEMPPAINEN, K.; RANTA, L.; SIPILÄ, E.; ÖSTMAN, A.; VEHEMAANPERÄ, J.; PURANEN, T.; LANGFELDER, K.; HANNULA, J.; KALLIOINEN, A.; SIIKA-AHO, M.; SIPILÄ, K. and VON WEYMARN, N. (2012). Ethanol and biogas production from waste fibre and fibre sludge - The FibreEtOH concept. *Biomass and Bioenergy*, vol. 46, p. 60-69. [\[CrossRef\]](#)
- KNUTSEN, J.S. and LIBERATORE, M.W. (2010). Rheology modification and enzyme kinetics of high solids cellulosic slurries. *Energy & Fuels*, vol. 24, no. 5, p. 3267-3274. [\[CrossRef\]](#)
- KUMAR, D. and MURTHY, G.S. (2012). Life cycle assessment of energy and GHG emissions during ethanol production from grass straws using various pretreatment process. *The International Journal Life Cycle Assessment*, vol. 17, no. 4, p. 388-401. [\[CrossRef\]](#)
- LARSEN, J.; HAVEN, M.O. and THIRUP, L. (2012). Inbicon makes lignocellulosic ethanol a commercial reality. *Biomass and Bioenergy*, vol. 46, p. 36-45. [\[CrossRef\]](#)
- LI, X.; KIM, T.H. and NGHIEM, N.P. (2010). Bioethanol production from corn stover using aqueous ammonia pretreatment and two-phase simultaneous saccharification and fermentation (TPSSF). *Bioresource Technology*, vol. 101, no. 15, p. 5910-5916. [\[CrossRef\]](#)
- LI, X. and KIM, T.H. (2012). Bioconversion of corn stover derived pentose and hexose to ethanol using cascade simultaneous saccharification and fermentation (CSSF). *Bioprocess and Biosystems Engineering*, vol. 35, no. 1-2, p. 99-104. [\[CrossRef\]](#)
- LIN, Y. and TANAKA, S. (2006). Ethanol fermentation from biomass resources: Current state and prospects. *Applied Microbiology and Biotechnology*, vol. 69, no. 6, p. 627-42. [\[CrossRef\]](#)
- LITTLE, A.D. (1933). Chemical Engineering Research. In: KIRKPATRICK, S.D. ed. *Twenty-five Years of Chemical Engineering Progress*, American Institute of Chemical Engineers, New York, p. 1-14.
- LLOYD, T.A. and WYMAN, C.E. (2005). Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresource Technology*, vol. 96, no. 18, p. 1967-1977. [\[CrossRef\]](#)
- LUO, L.; VAN DER VOET, E.; HUPPES, G. and UDO DE HAES, H.A. (2009). Allocation issues in LCA methodology: A case study of corn stover-based fuel bioethanol. *The International Journal of Life Cycle Assessment*, vol. 14, no. 6, p. 529-539. [\[CrossRef\]](#)
- MACLEAN, H.L. and SPATARI, S. (2009). The contribution of enzymes and process chemicals to the life cycle of ethanol. *Environmental Research Letters*, vol. 4, no. 1, p. 1-10. [\[CrossRef\]](#)
- MARTÍN, M. and GROSSMANN, I.E. (2012). Energy optimization of bioethanol production via hydrolysis of switchgrass. *AIChE Journal*, vol. 58, no. 5, p. 1538-1549. [\[CrossRef\]](#)
- MCDONALD, W.; STUTZMAN, N. and CARLSON, D. (2012). U.S. Patent no. 0129234 A1. Washington, DC, U.S.
- MOSIER, N.S.; HALL, P.; LADISCH, C.M. and LADISCH, M.R. (1999). Reaction kinetics, molecular action, and mechanisms of cellulolytic proteins. In: TSAO, G.T.; BRAINARD, A.P.; BUNGAY, H.R.; CAO, N.J.; CEN, P.; CHEN, Z.; DU, J.; FROODY, B.; GONG, C.S.; HALL, P.; HO, N.W.Y.; IRWIN, D.C.; IYER, P.; JEFFRIES, T.W.; LADISCH, C.M.; LADISCH, M.R.; LEE, Y.Y.; MOSIER, N.S.; MÜHLEMANN, H.M.; SEDLAK, M.; SHI, N.Q.; TSAO, G.T.; TOLAN, J.S.; TORGET, R.W.; WILSON, D.B. and XIA, L. eds. *Recent Progress in Bioconversion of Lignocellulosics*. Springer, Berlin, Heidelberg, vol. 65, p. 23-40.
- MOSIER, N.; WYMAN, C.; DALE, B.; ELANDER, R.; LEE, Y.Y.; HOLTZAPPLE, M. and LADISCH, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, vol. 96, no. 6, p. 673-686. [\[CrossRef\]](#)
- ÖHGREN, K.; VEHEMAANPERÄ, J.; SIIKA-AHO, M.; GALBE, M. VIIKARI, L. and ZACCHI, G. (2007). High temperature enzymatic prehydrolysis prior to simultaneous saccharification and fermentation of steam pretreated corn stover for ethanol production. *Enzyme and Microbial Technology*, vol. 40, no. 4, p. 607-613. [\[CrossRef\]](#)
- OLOFSSON, K.; BERTILSSON, M. and LIDÉN, G. (2008). A short review on SSF - an interesting process option for ethanol production from lignocellulosic feedstocks. *Biotechnology for Biofuels*, vol. 1, no. 1, p. 7. [\[CrossRef\]](#)
- OSTERGAARD-PETERSEN, M.; LARSEN, J. and HEDEGAARD-THOMSEN, M. (2009). Optimization of hydrothermal pretreatment of wheat straw for production of bioethanol at low water consumption without addition of chemicals. *Biomass and Bioenergy*, vol. 33, no. 5, p. 834-840. [\[CrossRef\]](#)
- PHAM, V. and EL-HALWAGI, M. (2011). Process synthesis and optimization of biorefinery configurations. *AIChE Journal*, vol. 58, no. 4, p. 1212-1221. [\[CrossRef\]](#)
- QUINTERO, J.A.; MONTOYA, M.I.; SÁNCHEZ, O.J.; GIRALDO, O.H. and CARDONA, C.A. (2008). Fuel ethanol production from sugarcane and corn: Comparative analysis for a Colombian case. *Energy*, vol. 33, no. 3, p. 385-399. [\[CrossRef\]](#)
- ROMANÍ, A.; GARROTE, G.; LÓPEZ, F. and PARAJÓ, J.C. (2011). *Eucalyptus globulus* wood fractionation by autohydrolysis and organosolv delignification. *Bioresource Technology*, vol. 102, no. 10, p. 5896-5904. [\[CrossRef\]](#)
- ROMANÍ, A.; GARROTE, G. and PARAJÓ, J.C. (2012). Bioethanol production from autohydrolyzed *Eucalyptus globulus* by Simultaneous Saccharification and Fermentation operating at high solids loading. *Fuel*, vol. 94, p. 305-312. [\[CrossRef\]](#)
- RUDD, D.F. (1968). The synthesis of system designs: I. Elementary decomposition theory. *AIChE Journal*, vol. 14, no. 2, p. 343-349. [\[CrossRef\]](#)
- SÁNCHEZ, Ó.J. and CARDONA, C.A. (2012). Conceptual design of cost-effective and environmentally-friendly configurations for fuel ethanol production from sugarcane by knowledge-based process synthesis. *Bioresource Technology*, vol. 104, p. 305-314. [\[CrossRef\]](#)

- SHAW, A.J.; PODKAMINER, K.K.; DESAI, S.G.; BARDSLEY, J.S.; ROGERS, S.R.; THORNE, P.G.; HOGSETT, D.A. and LYND, L.R. (2008). Metabolic engineering of a thermophilic bacterium to produce ethanol at high yield. *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, no. 37, p. 13769-13774. [\[CrossRef\]](#)
- SHEEHAN, J.; ADEN, A.; PAUSTIAN, K.; KILLIAN, K.; BRENNER, J.; WALSH, M. and NELSON, R. (2003). Energy and environmental aspects of using corn stoves for fuel ethanol. *Journal of Industrial Ecology*, vol. 7, no. 3-4, p. 117-146. [\[CrossRef\]](#)
- SIERRA, R.; GRANDA, C.B. and HOLTZAPPLE, M.T. (2009). Lime pretreatment. In: MIELENZ, J.R. ed. *Biofuels, Methods and Protocols*. Humana Press, p. 115-124.
- SINGH, A.; PANT, D.; KORRES, N.E.; NIZAMI, A.S.; PRASAD, S. and MURPHY, J.D. (2009). Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: Challenges and perspectives. *Bioresource Technology*, vol. 101, no. 13, p. 5003-5012. [\[CrossRef\]](#)
- SPATARI, S.; ZHANG, Y. and MACLEAN, H.L. (2005). Life cycle assessment of switchgrass- and corn stover-derived ethanol-fueled automobiles. *Environmental Science & Technology*, vol. 39, no. 24, p. 9750-9758. [\[CrossRef\]](#)
- SPATARI, S.; BAGLEY, D.M. and MACLEAN, H.L. (2010). Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies. *Bioresource Technology*, vol. 101, no. 2, p. 654-667. [\[CrossRef\]](#)
- STEINWINDER, T.; GILL, E.; GERHARDT, M. and BEACH W.P. (2011). Process design of wastewater treatment for the NREL cellulosic ethanol model. *National Renewable Energy Laboratory*. Technical report NREL/SR-5100-51838, Golden, Colorado.
- STEPHANOPOULOS, G. and REKLAITIS, G.V. (2011). Process systems engineering: From Solvay to modern bio- and nanotechnology: A history of development, successes and prospects for the future. *Chemical Engineering Science*, vol. 66, no. 19, p. 4272-4306. [\[CrossRef\]](#)
- STICKEL, J.J.; KNUITSEN, J.S.; LIBERATORE, M.W.; LUU, W.; BOUSFIELD, D.W.; KLINGENBERG, D.J.; SCOTT, C.T.; ROOT, T.W.; EHRHARDT, M.R. and MONZ, T.O. (2009). Rheology measurements of a biomass slurry: An inter-laboratory study. *Rheologica Acta*, vol. 48, no. 9, p. 1005-1015. [\[CrossRef\]](#)
- SUN, Y. and CHENG, J.Y. (2002). Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology*, vol. 83, no. 1, p. 1-11. [\[CrossRef\]](#)
- TAHERZADEH, M. and KARIMI, K. (2007a). Acid-based hydrolysis processes for ethanol from lignocellulosic materials: A review. *BioResources*, vol. 2, no. 3, p. 472-499.
- TAHERZADEH, M.J. and KARIMI, K. (2007b). Enzymatic-based hydrolysis processes for ethanol from lignocellulosic materials: A review. *BioResources*, vol. 2, no. 4, p. 707-738.
- TAN, R.R. and CULABA, A.B. (2002). Life-Cycle Assessment of conventional and alternative fuels for road vehicles. De La Salle University, Department, C.E.D.a.M.E. Philippine.
- TEYMOURI, F.; LAUREANO-PÉREZ, L.; ALIZADEH, H. and DALE, B.E. (2005). Optimization of the ammonia fiber explosion (AFEX) treatment parameters for enzymatic hydrolysis of corn stover. *Bioresource Technology*, vol. 96, no. 18, p. 2014-2018. [\[CrossRef\]](#)
- TOLAN, J.S. (2002). Logen's process for producing ethanol from cellulosic biomass. *Clean Technologies and Environmental Policy*, vol. 3, no. 4, p. 339-345. [\[CrossRef\]](#)
- TOMÁS-PEJÓ, E.; OLIVA, J.M. and BALLESTEROS M. (2008). Realistic approach for full-scale bioethanol production from lignocellulose: A review. *Journal of Scientific & Industrial Research*, vol. 67, no. 11, p. 874-884.
- UM, B.H.; KARIM, M.N. and HENK, L.L. (2003). Effect of sulfuric and phosphoric acid pretreatments on enzymatic hydrolysis of corn stover. *Applied Biochemistry and Biotechnology*, vol. 105, no. 1-3, p. 115-125. [\[CrossRef\]](#)
- VILLEGAS, J.D. and GNANSOUNOU, E. (2008). Techno-economic and environmental evaluation of lignocellulosic biochemical refineries: Need for a modular platform for integrated assessment (MPIA). *Journal of Scientific & Industrial Research*, vol. 67, no. 11, p. 927-940.
- WALKER, G.M. (2011). 125<sup>th</sup> Anniversary Review: Fuel alcohol: Current production and future challenges. *Journal of the Institute of Brewing*, vol. 117, no. 1, p. 3-22. [\[CrossRef\]](#)
- WANG, L.; TEMPLER, R. and MURPHY, R.J. (2012). A Life Cycle Assessment (LCA) comparison of three management options for waste papers: Bioethanol production, recycling and incineration with energy recovery. *Bioresource Technology*, vol. 120, p. 89-98. [\[CrossRef\]](#)
- WILKIE, A.C.; RIEDESEL, K.J. and OWENS, J.M. (2000). Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. *Biomass and Bioenergy*, vol. 19, no. 2, p. 63-102. [\[CrossRef\]](#)
- WU, Z. and LEE, Y.Y. (1998). Nonisothermal simultaneous saccharification and fermentation for direct conversion of lignocellulosic biomass to ethanol. *Applied Biochemistry and Biotechnology*, vol. 70-72, no. 1, p. 479-492. [\[CrossRef\]](#)
- ZAH, R.; BÖNI, H.; GAUCH, M.; HISCHIER, R.; LEHMANN, M. and WÄGER, P. (2007). Life Cycle Assessment of Energy Products: Environmental Impacts Assessments of Biofuels. Executive Summary Report, EmpaTechnology and Society Lab, Switzerland, p. 20.
- ZHAO, X.; CHENG, K. and LIU, D. (2009). Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Applied Microbiology and Biotechnology*, vol. 82, no. 5, 815-827. [\[CrossRef\]](#)
- ZHI-FU, G.; CHAN, A.W. and MINNS, D.E. (2003) Life cycle assessment of bio-ethanol derived from cellulose. *The International Journal Life Cycle Assessment*, vol. 8, no. 3, p. 137-141. [\[CrossRef\]](#)

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