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Comprehensive assessment of 2G bioethanol production

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Abstract

The advancements in second-generation bioethanol produced from lignocellulosic biomass, such as crops residues, woody crops or energy grasses are gaining momentum. Though, they are still representing less than 3% of total bioethanol production, the GHG reduction potential is higher than for 1G-bioethanol. The environmental impacts of bioethanol production are totally dependent on feedstock availability and conversion technology. The biochemical conversion route must overcome several technological and economical challenges such as pre-treatment, fermentation, hydrolysis process and separation. A completely mature technology is still to be developed and must adapted to the nature of the feedstock. Nevertheless, using process simulation software, Life Cycle Assessment and integrating the different steps of bioresource harvesting and treatment processes, including the energy balances and the water requirements, it is shown that 2G bioethanol production will reduce environmental impacts provided the evaluation addresses a long-time perspective, including all conversion steps and the regeneration of the bioresource.

Keywords: 2G (second generation) bioethanol, lignocellulosic biomass, fermentation, process simulation, environmental impact

Highlights

- 1 – Production of 2G bioethanol remains technologically challenging
- 2 – 2G bioethanol production is increasing but still less than 3% of total bioethanol
- 3 - The biochemical route must tackle with both pentose and hexose conversion
- 4 –The evaluation of a treatment pathway includes process simulation
- 5 – Agro-resource renewal and soil impacts are added for a complete LCA

Introduction

Due to the increasing consumption pattern of fossil fuels, the demand for alternate energy is continuously growing. Almost 100 GWy are issued from biomass. This represents almost one third of wind-power energy and 10 % of hydropower (Bertrand et al. 2016). The transportation sector with about 15 % of the emission of greenhouse gases mainly depends on liquid biofuels, due to their high caloric volumetric value: 35.7 MJ/L for petrol, 23.4 MJ/L for ethanol. Consequently there is a lifelong interest for improving ethanol production pathways. The world production market of bioethanol was 110 BL (billion litres) in 2018 and is expected to reach 140 BL in 2022. This increasing market reflects an intensified demand for the development of techno-economically feasible and sustainable processes based on the recycling of a fraction of carbon biomass. Considering the different raw materials and technology used for their production, both liquid biofuels (ethanol, butanol, biodiesel...etc.) and gas biofuels (methane, hydrogen and syngas) are classified into four generations (Demirel, 2018) depending on the way they are produced and the nature of the feedstock.

When biofuels are produced using specific cultivation areas from seeds, grains and starch-based feedstock such as sugarcane, corn, potato, cassava, they are referred to as first-generation biofuels. Using food-grade crops for energy production requires cultivable land and generates conflicts with food/feed use of feedstock (Min et al., 2013). Therefore, even if they represent more than 96% of total worldwide production of biofuels in 2020, they cannot successfully become a long-term viable fuel source. The advancements in second-generation biofuels produced from lignocellulosic biomass, such as crops residues, woody crops or energy grasses are gaining momentum. Lignocellulosic biomass (rice straw, corn cob, wheat straw, sugarcane bagasse, cotton stalk) are the best alternatives as they are abundant, renewable and relatively cheap (Cardona and Sánchez, 2007; Hahn-Hägerdal et al., 2006; Zaldivar et al., 2001). Algal biomass (macroalgae and microalgae) is considered as a third-

generation biofuel. Microalgae are known as emerging feedstock for the biodiesel production as they contain high lipid concentration up to 50% of dry biomass (Chen et al., 2018). This permits economically feasible scale-up and development of large scale cultures plants (Gouveia et al., 2017). It has several advantages: eco-friendly, non-toxic, less water consumption, high photosynthetic growth rate in autotrophy and therefore a high capacity for CO₂ capture (Simas-Rodrigues et al., 2015). Some algal strains (*Chlamydomonas reinhardtii*, *Porphyra*, *Chlorella vulgaris*) are rich in carbohydrates (starch, glycogen, and cellulose) that are be directly used in the production of ethanol (Khan et al., 2018). However, the commercial production of third generation biofuels by microalgae cultivation has still several technical bottlenecks that need to be solved, including important investment costs, energy input for harvesting, risks of contamination in open pond systems, extensive downstream processing (Griffiths et al., 2011). Fourth-generation biofuels is basically an extension of third-generation biofuels in which algae are modified by the use of genetic engineering to improve the yield and lipid content of the cells. Genetically modified algae (GM algae) increase the ability of CO₂ capture and rate of production of specific compounds, e.g. triacylglycerol. With genetic modifications, they are upgraded in terms of properties and cellular metabolism (Abdullah et al., 2019). Despite these advantages, high investment cost is necessary for using GM algae at industrial scale in order to limit and control the risk of contamination for the environment and the ecosystems. These high-tech requirements are the principal limitation for the developments of fourth-generation biofuels. It is still in its infant stage or in under research on a lab scale.

The market of bioethanol fuel has shown a dramatic increase and growing at a compound annual growth rate (CAGR) of 7.6% from 2016 to 2022. Several countries, like the U.S.A., Brazil, European Union, China, India has made an effort in order to diversify the use of fossil fuels by adding ethanol in different proportions to gasoline. The bioethanol fuel market is

distributed on the basis of feedstock, blend (E5, E10, and E85) type of vehicle and geographical area. Global bioethanol production has been increased from the last few years and the U.S.A. is one of the global powerhouses in the ethanol industry followed by Brazil, the European Union, China, and Canada (“Annual Ethanol Production,” 2019). Two countries answer for 84 % of the bioethanol produced worldwide: the USA with 56 % a production capacity of 62.5 BL plus 1.3 BL in construction, Brazil with 28 % (30 BL) followed by the European union with 5%, (5.5 BL), China 4% and Canada 2% (Figure 1).

Figure 1. World Ethanol production in 2018 (Cooper et al., 2019; Mohanty and Swain, 2019)

More than 94% of US bioethanol is obtained from corn starch, the remaining part coming cellulosic biomass. A major part of bioethanol produced in Brazil is issued from sugar-rich feedstock sugarcane and to a less extend from starchy crops (corn and wheat) (Mohanty and Swain, 2019). According to the EU regulatory framework 2009, a 10% contribution to the use of renewable energy in road transport fuels was targeted by 2020 (Al-Riffai et al., 2010; European Union, 2009). The total European production and consumption of bioethanol have reached 5.5 BL in 2018. Only a small fraction (less than 1%) was 2G bioethanol (IEA Bioenergy Task 39, 2020). This globally meets the global objective of 20 % for renewable energy but does not meet the 10 % renewable energy target for the transport sector (EU-28, 2018). Around 81% of the renewable ethanol produced in Europe is used for fuel. European Union is the fourth largest ethanol market in the world. The production capacity of bioethanol is expected to increase as increasing in the commercialization of cellulosic ethanol (second generation ethanol) (Phillips et al., 2018). The consumption of bioethanol is increasing with more blending as according to taxation policy, reduction in tax on E-10 fuel while increase for pure gasoline.

The fast growth of the bioethanol production market in the transport sector has also generated some challenges in regards to sustainability and impact on biodiversity, direct and indirect land-use change and feedstock and water availability. There are also some challenges to the feedstock supply system. The main hurdle is the transportation of a massive volume of feedstock in an energy-saving manner to the biorefineries. The sustainability of a biorefinery will depend on the type of feedstock and its growing conditions and its transportation. The total ethanol production cost depends on various factors, such as feedstock production including the use of fertilizers, labour for farming, harvesting, collecting, transporting the biomass and the conversion process (Hess et al., 2007).

Among all of these, lignocellulosic biomass valorisation is a potential resource for production of second-generation ethanol, which can significantly reduce greenhouse gas emissions and offer positive environmental impacts. In general, second generation liquid biofuels (ethanol, biodiesel and liquid alkanes) are considered as important renewable fuels able to at least partly replace petroleum-based ones. The production of ethanol has gained industrial maturity and is considered as a future alternative to gasoline for transport, as it has the appropriate characteristics such as high octane number, the high heat of vaporization and low cetane number. It is also less toxic to the environment considering the reduction in GHG emissions and other pollutant emissions (Nigam and Singh, 2011; Ojeda et al., 2011).

There are different criteria to measure the sustainability of biofuels (Baudry et al., 2017). Life cycle assessment (LCA) is one of the assessment methods to analyse the efficiency of the production process in terms of environmental sustainability. It is mandatory to determine which conversion process and feedstock can qualify in terms of environmental sustainability. This review examines 2G-ethanol production from the biochemical conversion process and its environmental impacts by recent LCA studies with the help of process simulation.

Feedstock for second-generation ethanol production

Second-generation ethanol production is derived from non-food crops or crop residues with the main component that is lignocellulosic biomass. Lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin including also water in small amount and some trace amounts of protein, minerals, and other components that are also present in the raw material. The general structure of lignocellulosic material shows that the cellulose microfibrils (at least 1000 – 5000 glucose units connected by β -1,4-glycosidic linkages) are bonded by van der Waals forces and hydrogen bonds. Hemicellulose is an amorphous heterogeneously branched polymer of pentoses and hexoses (at least 500–3000 sugar monomers) located at the primary cell wall. Lignin differs from cellulose and hemicellulose as it contains aromatic rings rather than long molecular chains with diverse chemical structures and monomer composition. The location of lignin is between the cellulose and the hemicellulose to bind them together (Bamdad et al., 2018).

Lignocellulosic biomass includes wood and woody biomass (poplar, sawdust, willow, wood residue, etc.), energy crops such as perennial grass (miscanthus grass, switchgrass, etc.), agricultural biomass (corn straw, rice straw, wheat straw, etc.) and municipal solid biomass. Each group of biomass has persuasive characteristics that show potential, promising and abundant feedstock for the bio-refineries (Zabed et al., 2017). Some chemical compositions of different biomass feedstock are reported in Table 1.

Cellulose is a major component (makes up about 45% dry weight of wood) and polymers of d-glucopyranose (C₆ sugars) linked with the β 1-4 glycosidic bond between the glucose monomer forming cellobiose molecules (Chen, 2014; Kumar et al., 2009). These chain polymers linked together by hydrogen bond and van der Waals force, in which the glucose unit is compactly tie-up with each other and form elemental fibrils. These united or grouped microfibrils are called cellulose fibrils which are coated with hemicellulose (Chundawat et al.,

2011; Lee et al., 2014; Pereira Ramos, 2003). The crystallinity of cellulose depends on this organized structure of cellulose fibrils (*Cellulose Chemistry and Properties: Fibers, Nanocelluloses and Advanced Materials*, 2016; Saini et al., 2015). Due to the strong interaction of hydrogen bonding between the cellulose fibrils, it is insoluble in the water but soluble in dilute acid solution at high temperature (Chen and Chen, 2014).

Hemicellulose is a heteropolymer composed of different pentose, hexose sugars and uronic acids. The common sugars found in the hemicellulose are xylose, arabinose, mannose, galactose with 50-200 units (Saha, 2003). The structure and composition of hemicellulose are different in different raw materials/biomass and their producing areas (Chen and Chen, 2014). 1,4 β -D-xylopyranose linked with each other to form a linear chain of xylan (Chen and Chen, 2014). It also contains the branch chain of glucuronic acid that are easily degraded in acid and alkaline solutions (Bajpai, 2016a; Saha, 2003). Mannose sugar residues are linked together by a β 1-4 glycosidic bond to form a backbone chain of mannan. The linear chain of mannan is linked to galactose with α 1-6 glycosidic bond to form galactomannan and if it is linked with glucose by β 1-4 bond then the linear chain of glucomannan is formed (Bajpai, 2016b; Chen and Chen, 2014). The main content of agricultural biomass and hardwood hemicellulose is xylan whereas glucomannan is the main content in softwood (Bajpai, 2016b). Due to the presence of pentose sugars, hemicellulose has an affinity to water and at high concentration aqueous solutions become viscous (Chen and Chen, 2014).

Lignin is a heteropolymer of phenyl propionic alcohol units i.e. coumaryl alcohol, sinapyl alcohol and coniferyl alcohol, which are linked with each other by carbon-carbon (C-C) and ether (C-O) linkages. This type of linkage makes the stability of plant cell walls and resistance to pathogen infections (Mooney et al., 1998). It acts as a physical barrier for enzymatic hydrolysis and microbial degradation as it is tightly bound to the cellulose fibrils (Avgerinos and Wang, 1983; Bajpai, 2016b). Enzymatic or microbial delignification is difficult as the

derivatives from lignin act as toxic compounds for microorganisms and reduces the activity of hydrolytic enzymes (Bajpai, 2016b).

The physical structure of feedstock and its carbohydrate composition directly impact the selection of an efficient and sustainable pre-treatment process. There are several pre-treatment methods used for the removal of lignin from the other components and make cellulose and hemicellulose accessible for enzymes of degradation. The final efficiencies of the different treatment processes, including pre-treatment pathways are very similar in terms of final ethanol yields for a given feedstock. It almost depends on the composition of raw materials. For woody biomass, containing 25 – 30 % lignin the yield is at average 300 - 350 L / ton, provided both cellulose and hemicellulose fractions are converted into ethanol. On the contrary, the greenhouse gases (GHG) reduction potential versus gasoline depends on the feedstock, the cultivation methods and harvesting and treatment pathway. Table 1 summarizes the key values for different feedstock including GHG reduction potential obtained with current processes. Clearly, the robustness of the physical structure of the vegetal biomass has consequences on the efficiency of the treatment and finally on the GHG reduction potential. The total production capacity of 2G bioethanol, including pilot plant facilities under development has reached 3 BL in 2018 with a rapid increase. These data are calling for a deeper investigation of what are the bottlenecks to overcome for reaching a good technical degree of maturity and the key descriptors that must be considered in overall conversion a given feedstock into bioethanol.

Table 1: Chemical composition of different feedstock and estimated GHG reduction potential versus gasoline for 2G-ethanol production (Bertrand et al, 2016)

Conversion technologies for 2G bioethanol production

There are mainly two conversion technologies for the production of bioethanol: biochemical and thermochemical. The biochemical conversion comprises pre-treatment, hydrolysis, and fermentation (Soccol et al., 2011) while in the thermochemical conversion gasification of the lignocellulosic biomass leads to syngas and then ethanol is produced from FT (Fischer-Tropsch) conversion (Damartzis and Zabaniotou, 2011).

The biochemical conversion process is a common and effective technique for producing bioethanol (Achinas and Euverink, 2016; Robak and Balcerek, 2018). The general steps in bioethanol production via the biochemical route starts with pre-treatment in which lignocellulosic biomass is processed (separation of lignin, cellulose, and hemicellulose) and makes cellulose more accessible for the next step, i.e. hydrolysis. There are various pre-treatment methods such as physical, chemical, physicochemical and biological. The purpose of pre-treatment is to decrease the crystallinity of cellulose and make it more susceptible to the hydrolysis in which sugar monomers are produced either by the use of acids or enzymes. The next step after hydrolysis is fermentation; it involves the conversion of sugars into ethanol during microbial fermentation mainly performed by bacteria and/or yeast (Soccol et al., 2011).

a. Pre-treatment

Pre-treatment is the first step and very crucial, complicated and costly step in order to make bioethanol production from the lignocellulosic biomass. The goal of any pre-treatment technology is delignification to alter the structure of cellulose to make it more accessible to hydrolysis and increase the yield of sugars from cellulose and hemicellulose which can be fermented into ethanol (Zabed et al., 2017). The main goal is to separate into independent fractions cellulose, hemicellulose and lignin fibres in order to make accessible for further conversion cellulose and hemicellulose, lignin remaining to be separated from the soluble media and valorised independently, at least for its calorific value.

There are different pre-treatment processes that have been developed to fractionate, solubilize and separate cellulose, hemicellulose and lignin components by using physical, chemical, physicochemical and biological treatment methods. As shown in Figure 2 each method has some pros and cons (Tomás-Pejó et al., 2011).

Figure 2: General scheme of pre-treatment processes

Physical methods such as grinding, milling, sonication are used to reduce the size of the raw material and crystallinity of biomass but they are considered as an energy-demanding process. Chemical pre-treatment includes ionic liquids/green solvents, acid treatment (strong and dilute) and Organosolv treatment, the latter using an aqueous organic solvent (acetone, methanol, ethanol, etc.) at temperatures ranging from 140 to 220 °C. The main drawback of chemical pre-treatment is the inhibitors formation for downstream processes and pH adjustment before hydrolysis when acid treatment is used.

Biological pre-treatment uses microbial degradation of feedstock. It is considered environmentally safe because of various reasons, such as no chemicals required for this process, low energy demand; in turns, it doesn't produce toxic products. However, the low conversion rates and required long residence times make this process inefficient and laborious.

Physicochemical pre-treatment involves steam-explosion, Ammonia fibre explosion (AFEX), Co-solvent Enhanced Lignocellulosic Fractionation (CELF). Steam explosion treatment is a hydrothermal method involves both mechanical and chemical effects under high temperature and high pressure in the presence of steam where chipped biomass is treated to high pressure, high-temperature steam (160 - 270 °C, 20 - 50 bar) for few minutes. Then the pressure is released and due to explosive decompression, fibres get separated with minimal loss of other components. In this pre-treatment method, hemicellulose and lignin hydrolysis improves the accessibility of biomass to enzymes (Alvira et al., 2016).

There are some parameters that affect the efficiency of this method such as residence time, particle size and temperature. It requires a strong catalyst like H₂SO₄ to increase the high sugar yield but it also leads to the formation of inhibitory compounds. Thus, it requires washing with water after pre-treatment for the removal of inhibitors (Pielhop et al., 2016; Sassner et al., 2008). It has also many disadvantages like the production of inhibitory components such as furfural, HMF, which acts as inhibitors for the fermentation downstream process and the requirement of costly equipment increases the cost of the overall process.

b. Hydrolysis

The next step is hydrolysis, in which polymeric carbohydrates are converted into sugar monomers. Acid-catalyzed and enzyme-catalyzed are the two ways to perform saccharification (Jahnavi et al., 2017). Acid-catalyzed hydrolysis mostly occurs in the high temperature (100 - 240 °C) and a high probability of inhibitor formation because of the high temperature and acidic condition. In fact, it is a combination of pre-treatment and hydrolysis processes. Enzymatic hydrolysis has several advantages over acid-catalyzed hydrolysis as it can operate at mild conditions (the temperature at 50 - 60 °C with pH 4.8 - 5.0) and high sugar recovery with no inhibitor formation (Balat, 2011). There are various factors such as temperature, pH, enzyme loading, time that affects the productivity of enzymatic saccharification. Cellulases are the group of enzymes that are used to degrade the cellulose by cleaving the β 1-4 glycosidic bond (Kuhad et al., 2011a). The demand for cellulases is continuously increasing as it has broad applications in several industries like pulp and paper industry, textile industry, food processing industry, etc. The cost of enzyme is the biggest hurdle in bioethanol refineries because of its huge consumption in the saccharification (Wang, 2013). Nowadays, microbial enzymes are widely used in various industries to make the process economically feasible. There are a number of microorganisms that are naturally secreting cellulolytic enzymes. *Clostridium*, *Thermomonospora*, *Trichoderma*, *Aspergillus* are

the common bacterial and fungal strains for the production of cellulases (Kuhad et al., 2011a). Among all, *Trichoderma* species are the most desirable and potential candidate for cellulase production (Imran et al., 2016). There are three main types of cellulase that are involved in the enzymatic saccharification, i.e. exoglucanases (EC 3.2.1.74 and 3.2.1.91), endoglucanases (EC 3.2.1.4), and β -glucosidases (EC 3.2.1.21).

Exoglucanase (E.C. 3.2.1.91) acts on the reducing and non-reducing ends of cellulose and releases cellobiose units; endoglucanase (E.C. 3.2.1.4) cleaves randomly β 1-4 glycosidic bonds resulting in the production of new ends, i.e. cellobiose and cellotriose units; β -glucosidase (E.C. 3.2.1.21) attacks the cellobiose units to form simple sugar (glucose) units (Kuhad et al., 2011b; Wang, 2013). 1,4- β -D endoxylanases (E.C. 3.2.1.8) and β -xylosidases (E.C. 3.2.1.37) are the most common enzyme used for the degradation of the xylan present in the hemicellulose (Walia et al., 2017).

Enzyme stability, substrate/product inhibition and catalytic efficiency are the main challenges in the production of microbial enzymes. Several recent advances in genetic modifications, recombinant DNA techniques and adopting different strategies for strain improvement lead to increase the production and make the enzyme more robust and economically feasible (Adrio and Demain, 2014).

c. Fermentation

Fermentation is the biological process in which microorganisms, mainly yeast and bacteria, convert monomeric sugars into acids, gases, and ethanol. *Saccharomyces cerevisiae* (baker's yeast) is the commonly used organism in the alcohol production process because of its high productivity and ethanol yield from different feedstock (Mohd Azhar et al., 2017). Other than

Saccharomyces cerevisiae, *Pichia stipites*, *Kluyveromyces fragilis*, and *Candida shehatae* were also reported yeast strains for the production of ethanol from different sugars (Gonçalves et al., 2016; Mohd Azhar et al., 2017; Tian et al., 2009). The master stoichiometric equations characterizing the fermentation of hexose ($C_6H_{12}O_6$ equivalent) and pentose ($C_5H_{10}O_5$ equivalent) to ethanol lead to the same mass yields (51.1 %) the complementary part being CO_2 .

This yield is a maximum conversion yield, knowing that associated biomass and by-products production decrease the actual yields at least by a factor of 10 to 20% (Barnett, 2003; Fugelsang and Fugelsang, 1997). In terms of kinetics of production, there are several factors that inhibit the efficiency of *Saccharomyces cerevisiae* yeast to produce ethanol like high ethanol concentration, high temperature, osmotic stress, bacterial contamination and of course presence of inhibitors.

There are some fermentation technologies, i.e. separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF) and consolidated bioprocessing (CBP) used in biorefineries (Jahnavi et al., 2017).

In Separate Hydrolysis and Fermentation (SHF), hydrolysis and fermentation are carried out separately in different units. After pre-treatment, biomass slurry is subjected to the hydrolysis reactor where it is degraded into simple sugars and thereafter a fermentation process occurs in the fermentation unit to convert sugars into ethanol (Taherzadeh and Karimi, 2007). End-product inhibition is the main drawback of this process. By example, cellobiose produced in hydrolysis acts as an inhibitor for cellulase itself (Axelsson, 2011). It is also a time-consuming process considering the residence time is long in hydrolysis and expensive due to high enzyme loading and material cost for two separate units.

In Simultaneous Saccharification and Fermentation (SSF), hydrolysis and fermentation are carried out in the same unit (Kádár et al., 2004). It is considered as a better option for industries as compared to SHF as it has many advantages with high ethanol yield (Wingren et al., 2003). The main advantage of SSF is low investment cost and no end product inhibition by glucose as it is consumed immediately by ethanol-producing microorganism resulting in an increase of the rate of hydrolysis and ethanol yield. Ethanol inhibition for enzymes, microorganisms and temperature in the reactor are the only drawback of this process. The optimal temperature for yeast is 35 °C and hydrolysis occurs at 50 °C (Axelsson, 2011).

In Simultaneous Saccharification and Co-Fermentation (SSCF), hydrolysis and fermentation are carried out in the same unit with co-fermentation of pentose sugars (Bondesson and Galbe, 2016). Knowing that *Saccharomyces cerevisiae* cannot ferment the pentose sugars, genetically modified *Saccharomyces cerevisiae* strains that are xylose-fermenting are used for the co-fermentation process. An ethanol yield of 0.32g / g of sugars was observed for a genetically modified *Saccharomyces cerevisiae* strain (Bondesson and Galbe, 2016). It is a suitable process for xylose-rich lignocellulosic although the ethanol yield is 35% lower than the maximum yield. It is a suitable process for feedstock like hardwood and agricultural residues (Olofsson et al., 2010).

Consolidated BioProcessing (CBP) is a single-step process in which all the processes including enzyme production, hydrolysis and fermentation occur in the same unit. *Clostridium thermocellum* is the mainly used microorganism in this process with a natural synthesis of cellulases to degrade the biomass into fermentable sugars and produce ethanol (Hasunuma and Kondo, 2012). Though it is at an infant stage, this process has several advantages like low investment and enzyme cost, less chance of contamination.

d. Distillation

The main challenge of bioethanol biorefinery is the separation of ethanol from the fermentation broth to produce pure bioethanol. Due to the presence of an azeotrope, the separation of ethanol from the ethanol-water mixture requires special attention. Three conventional methods exist: azeotropic distillation, Liquid-Liquid extraction, and extractive distillation (Nitsche and Gbadamosi, 2017). There are other techniques that are raising in the future like pervaporation and salt distillation (Nagy et al., 2015; Soares et al., 2015) considering they are less energy consuming. The most commonly used technique is extractive distillation, which is used for large scale operations (Ravagnani et al., 2010). A separating solvent is used. It has specific properties: non-volatile (high boiling point) and miscible to the mixture. The separating agent is added to the azeotropic mixture to alter the relative volatility of the key component without additional azeotrope formation. When these solvents are added to the mixture, it causes the change in the volatilities of the components (Pfenning, 2004). In the extractive distillation technique, a dissolved salt can be used as a separating agent for the ethanol-water mixture, e.g. Calcium Chloride salt. Extractive distillation works on two variables, the solubility of the solvent and the difference in the boiling point of the components whereas in Liquid-Liquid distillation the process is based on the solubilities of ethanol in an organic phase, permitting to significantly increase the ethanol concentration resulting to decrease the energy consumption.

Process Simulation

Process simulation is basically a representation of chemical, physical, biological, other technical processes and unit operations in a simulation software (Luyben, 1989). The simulation models also allow the interpolation and extrapolation within certain limits. The process simulation software delineates the whole process in a flowsheet where all unit operations are connected with the streams in order to find the optimal parameters or

conditions. The basic knowledge of chemical kinetics, chemical reactions, and the thermodynamic properties are required for calculation of process parameters of any unit operation. The main purpose of the process simulation is to generate mass and energy balances. It also gives details about the performances of the various elements of the process, i.e. reactors, distillation columns and analyses them in terms of balances in the context of interconnected unit operations leading to economical evaluation and sustainability.

Numerous chemical simulators are available, which are used industrially or on the academic scale. Aspen plus, Chemcad, Prosimplus, Hysys are some examples of chemical engineering simulators that are widely used in the industries. Aspen plus is widely used process simulation software in the field of biorefinery. In the case of bioethanol production from biomass feedstock, there are several unit operations and complex process streams. Pre-treatment, hydrolysis, fermentation and distillation are interconnected with each other. The pre-treatment is the most crucial and complex step to incorporate in simulation software when addressing ethanol production from lignocellulosic biomass. The main reason is that pre-treatment is related to a Solid Liquid Gas unit operation and requires a consistent knowledge of physicochemical properties of the compounds, including specific heats, heat of dissolution and thermophysical properties of complex materials at relatively high temperature (100 – 250°C). Moreover, the different pre-treatment techniques that are mainly classified into four categories physical, chemical, physiochemical and biological involve acid base pre-treatment requiring being able to simulate complex concentrated acid base solutions and highly concentrated aqueous salt solutions.

In order to give a baseline value, the global ethanol yield obtained with Aspen plus for a liquid hot water pre-treatment process is in the order of 350 L bioethanol / ton dry matter and with an energy consumption at least reaching 87 MJ / L bioethanol (Quintero and Cardona, 2011) that is consistent with values obtained at pilot and industrial plant level. These values

give departure orders of magnitude for final results that can be obtained with different feedstock.

Life cycle assessment

a. General framework

The concept of life cycle assessment (LCA) has been introduced in the 1970s and several efforts have been done to develop the methodology of LCA. Many international and national organizations promoted, supported and developed the concept of LCA (SETAC- Society of Environmental Toxicology and Chemistry, USEPA- the United States Environmental Protection Agency, ISO- International Organisation of Standardization, ILCAJ- Institute of Life Cycle Assessment, Japan). As a result, a Concord has been established on the LCA framework and inventory methodology (The International Standards Organisation, 2006). The Global Energy Partnership Task Force (GBEP) has also been developed the LCA methodology for the bioenergy system and compare it from the lifecycle of the fossil- fuel energy system (Hayashi et al., 2014). The LCA methodology comprises mainly 4 stages: Definition of goal and scope, Life Cycle Inventory Analysis (LCIA), Impact assessment, and Interpretation of the results.

The goal and scope stage examines the inputs and outputs of materials, including technical details like the functional unit, system boundaries, and allocation methods. The functional unit is based on volume (L), mass (kg) of the product and the land area (ha), energy (MJ) and distance (km) are also used. It gives the reference unit to which the inputs and outputs can be related. The Life Cycle Inventory Analysis stage (LCIA) involves the compilation and quantification of inputs and outputs for a given product system. It gives a description of flow model of input (water, raw material) and output (products and emissions such as CO₂, SO₂, NO_x, CO, etc.) for a given product system. The impact Assessment stage converts the

inventory results into related environmental impacts including global warming potential, acidification, eutrophication, human eco-toxicity, etc. In the characterization steps, the impact potential of each emission is estimated by using scientific factors using LCIA methodologies (The International Standards Organisation, 2006). There are various LCIA methodologies depending on the different impact categories and selection of indicators such as CML 2002, Eco-indicator 99, ReCiPe, LIME, Lucas, TRACI, etc. (Owsianiak et al., 2014; Rosenbaum et al., 2017). The interpretation of the results provides a conclusion for decision-making. It is a technique to identify and quantify the results of the inventory analysis and life cycle impact assessment.

b. LCA studies on bioethanol produced from biochemical conversion pathway

The life cycle of lignocellulosic ethanol has been evaluated by the methodology of LCA to measure the economic and environmental impact of the production system (Kim and Dale, 2005a).

. In several studies, it has been observed that lignocellulosic bioethanol leads to a remarkable reduction in GHG emission (Table 1) (IEA Bioenergy Task39, 2019; Fleming et al., 2006; González-García et al., 2012; Mabee et al., 2006; Spatari et al., 2005; van Vliet et al., 2009; Wyman, 1994). However, crop residues are the leftover in the field after harvest. It contributes to improve the structure of soil and also provide protection from the direct impacts of rain, sunlight, and wind. Excessive use of crop residues leads to soil erosion and decreases the quality and fertility of the soil. Although N-based fertilizer during cultivation can be used, it leads to eutrophication and acidification because nitrogen and phosphorus are released from the soil. The overall result must be evaluated considering that synthetic fertilizers may also contribute to global warming (Kim and Dale, 2005a).

(i) LCA studies on ethanol produced from agro-residues

Wheat straw is widely used as a feedstock in the production of lignocellulosic ethanol. In Borrion *et al.* (2012), study, there is an evaluation and comparison of two ethanol blend fuel i.e. E15 and E85 from wheat straw. The highest the blending the better are the results, i.e. E85 reduces by 73% GHG while E15 reduces only by 13% for GHG emission compared to conventional gasoline. However, in acidification, eutrophication and water depletion environmental issues, the ethanol blend fuel doesn't show any benefit compared with conventional fuel. The assessment of global environmental performances included global warming, ozone depletion, acidification, eco-toxicity, etc. It was characterized by the ReCiPe methodology and SIMAPRO was used to build the inventory and impact assessment analysis (Borrion *et al.*, 2012). In the case of rice straw, high energy is consumed, i.e. 72% of the total for the preparation of rice straw from paddy production. CML 2001 method is used to assess the acidification, climate change, eutrophication, and, in turns, the impact on environment. Borrion *et al.* (2012) concluded that baling, straw transportation, methane, and N₂O in flue gas and high-pressure construction are the main sources of GHG emission that has been confirmed by Shafie *et al.* (2014). Perennial grasses can increase carbon sequestration in soils. Process residues and co-products should be considered for energy production in order to save fossil energy (Cherubini *et al.*, 2009).

E-85 blend lignocellulosic ethanol from corn stover is capable of reducing GHG emission by 86 - 113% as compared to conventional fuels (Davis *et al.*, 2009; Sheehan *et al.*, 2003a). Corn stover ethanol lowers the GHG emission as compared to corn-grain ethanol (Kim and Dale, 2005b; Williams *et al.*, 2009). Ozone layer depletion and abiotic resources are decreased if corn stover ethanol is used as compared to gasoline, which is independent of any allocation method. However, GWP (Global Warming Potential) increases in economic allocation while it decreases when mass/energy allocation method is applied (Luo *et al.*, 2009). Some

researchers reported that the fuel from straw doesn't show a positive effect on the environment because of water eutrophication and land use (Uihlein and Schebek, 2009). Excessive removal of straw (wheat straw) from the field shows the effect on environmental emissions (Gabrielle and Gagnaire, 2008). It is also observed that some definite portion of crop residues can be removed without affecting the quality of soil, conditional to the soil types, season and location (Nelson, 2002; Reijnders, 2008). Some researchers suggest that 60% of corn stover should be harvested and collected for the biorefineries (Sheehan et al., 2003b), while some stated that only 25% would be harvested, higher proportions affecting the soil fertility (Blanco-Canqui and Lal, 2009). In a recent agricultural implementation, the study shows that only 28% of corn stover might be considered to be harvested and collected without degrading the soil quality (Graham et al., 2007). The carbon proportion of ethanol from corn stover would have to be in the range 10 - 44% of gasoline (Kaufman et al., 2010), knowing that when higher proportions are used the GHGs emission during the storage of resource plays an important role,, except if performing equipment available on the commercial scale is used (Sheehan et al., 2003b).

Nevertheless, the lignocellulosic biomass is considered as most favourable feedstock regarding its present high availability and low cost. In any case the production cost of feedstock will have to be incorporated in the global analysis when intensifying and concentrating the production in specific areas, the economic viability being to consider with this perspective. Technological issues need to be solved for the large-scale commercial production of lignocellulosic bioethanol (Hatti-Kaul et al., 2007; Tan et al., 2008). For instance, the use of various chemicals such as sulphuric acid, lime in the biochemical conversion cannot be neglected as it contributes to GHG emission and water consumption (Mu et al., 2010).

(ii) LCA studies on bioethanol produced from forest residues and woody biomass

Presently, the contribution of bioethanol produced from forest residues and woody biomass is not really significant compared to energy crops in terms volume of produced bioethanol but it may become active and will be developed in the future (Sims et al., 2006) considering the resource is mostly composed of forest industry waste and residues. This entails reduced production costs and availability but on the contrary high transportation costs for concentrating the production to large-scale industrial plants. The majority of LCA studies on energy crops report that reduction in GHG emission and fossil energy consumption must be evaluated globally (Cherubini and Ulgiati, 2010; Schmer et al., 2008; Sims et al., 2006; von Blottnitz and Curran, 2007). It is mandatory to consider all environmental factors both related to conversion process of feedstock and to the production of feedstock itself, such as acidification and eutrophication increase (Cherubini and Ulgiati, 2010).

By example, the lignocellulosic ethanol pathway from switch-grass avoids 65% of GHG emissions if E85 is used. E85 reduces GHG emission but is less effective for other impacts such as photochemical oxidation and eutrophication (Bai et al., 2010). Bioethanol produced from switch-grass leads to a reduction in GHG emission of 94% compared to gasoline but it will be necessary to further intensify the biofuel yield and energy sustainability of switch-grass by genetic and agronomical improvement (Schmer et al., 2008). It is reported that switch-grass is effective at storing soil organic carbon (SOC) not only at soil surface but at depth beneath 30 cm where carbon is less vulnerable to mineralization and loss (Liebig et al., 2005; Schmer et al., 2008). Studies show that the soil organic carbon (SOC) and water-extractable organic carbon (WEOC) are higher in the perennial grass systems than the annual corn system and switch-grass had lower SOC and WEOC in among all perennial grass systems (Hahn-Hägerdal et al., 2006).

Guo *et al.* (2014) have compared two pre-treatment methods on poplar and with different blends, i.e. E-10, E-85, and E-100. Pre-treatments of poplar are done by dilute acid or by liquid hot water and followed by SHCF by *Zymomanas mobilis* to produce bioethanol. LCA modeling is done by SIMAPRO7.3.3 and simulation by ASPEN PLUS. Dilute acid showed an environmental advantage over liquid hot water considering higher enzyme load is required for liquid hot water pre-treatment. The enzyme used in the hydrolysis process also contributes to 20-40% of environmental burdens in toxicity and eutrophication. E85 shows a similar environmental profile to E100 (Guo *et al.*, 2014). In another study, the net process energy efficiency is estimated for the production of bioethanol from poplar (35% to 37%) with the ethanol yield approximately ranging between 303 to 316 L / t dry biomass. Modeling was done by the process simulation tool Aspen Plus to understand the production process from poplar and help in the design and optimization of the production process (Porzio *et al.*, 2012). Black locust is also used as a potential woody biomass for the production of bioethanol and also has a lower impact on environment because of low levels of agricultural inputs used during cultivation whereas poplar has higher impact in acidification and eutrophication due to emission of N₂O in environment from the N-based fertilizers required in the poplar farming. Eucalyptus also shows higher impact on environment due to use of heavy machinery requirements during harvesting (González-García *et al.*, 2012). In their study González-García *et al.*, (2012) also compare bioethanol production from poplar, black locust and eucalyptus with E-85 blend with gasoline. Black locust is the best candidate in terms of minimal contributions from the field activities with an estimated reduction by 97% in GWP₁₀₀ (Global Warming Potential over 100 years). In a similar way, sugar beet, genetically modified for herbicide-free crop shows less toxic impact to the environment and human health in comparison to conventional growing crops in terms of lower emissions from herbicide, transportation and field operations (Bennett *et al.*, 2004).

Conclusion

This overview shows that environmental impacts of 2G bioethanol production depend on the availability and the regeneration of feedstock and reactants and on the distribution of the products. Bioethanol produced from lignocellulosic biomass via biochemical route must overcome several difficulties like fermentation of both pentose and hexose carbohydrates, configuration of hydrolysis process in such a way that inhibitors are eliminated, and recycling of byproducts and waste treatment. The evaluation of economical viability and environmental sustainability must include: i) simulation for designing optimal process design; ii) analysis of soil quality and agriculture techniques to prevent productivity loss and soil exhaustion.

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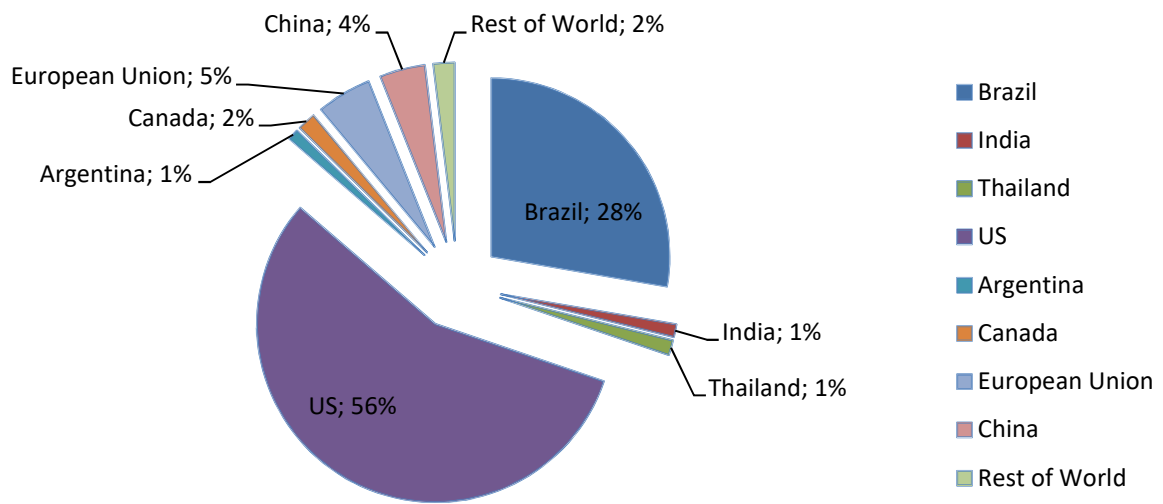


Figure1. World Ethanol production in 2018 (Cooper et al., 2019; Mohanty and Swain, 2019)

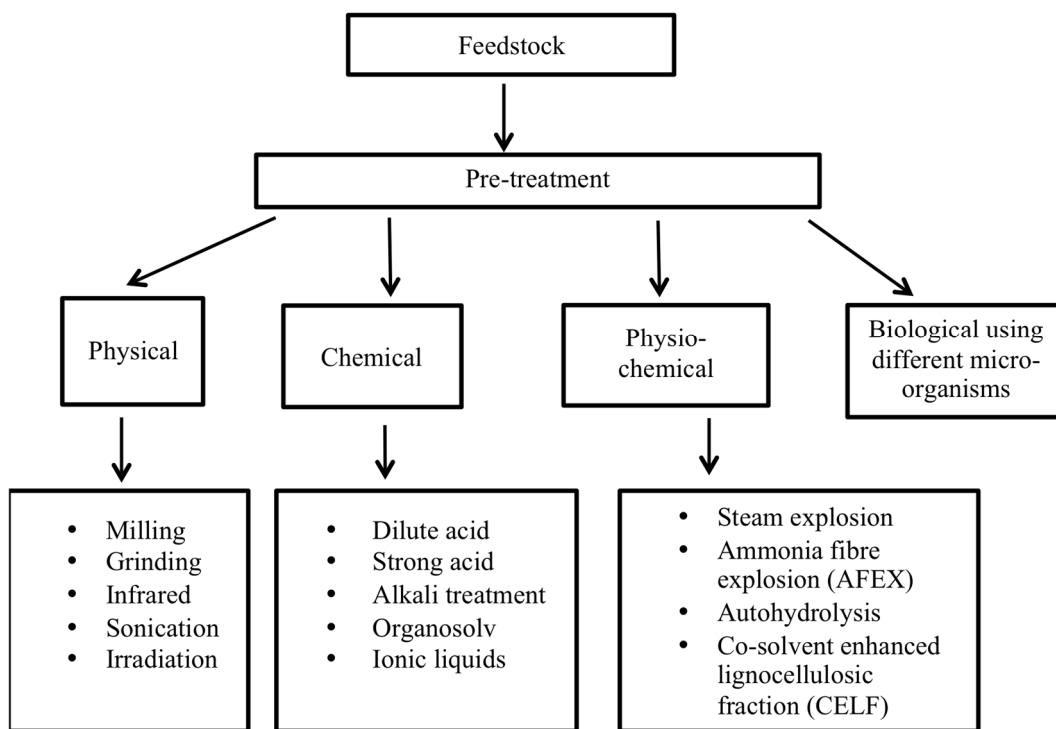


Figure 2: General scheme of pre-treatment processes

Biomass	Lignin	Cellulose	Hemicellulose	GHG reduction potential (%)	Reference
Poplar	21 - 29	42 - 49	16 - 23	30 - 70	(Sannigrahi et al., 2010)
Willow	19 - 20	36 - 39	21 - 22	10 - 90	(Sassner et al., 2008; Szczukowski et al., 2002)
Pine Sawdust	26 - 28	34 - 40	28 - 34.6		(Fayoud et al., 2016)
Miscanthus	20 - 23.8	41 - 53	20 - 25.3	90 - 130	(Gismatulina and Budaeva, 2017)
Switchgrass	17.8	39.5	20.3	80 - 100	(Kim, 2018)
Wheat straw	20	34 - 40	20 - 25	30	(Kapoor et al., 2016)
Rice straw	21 - 22	39 - 40	16		(Singh et al., 2014)
Corn cob	12.5	43.7	23.7	100	(Sun Yong et al., 2012)

Table 1: Chemical composition of different feedstock (weight % fresh matter) and estimated GHG reduction potential versus gasoline for 2G-ethanol production (Bertrand et al, 2016)

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