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GLOBAL POTENTIAL OF BIOETHANOL PRODUCTION FROM BIOWASTE

Memòria i Annexos

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ABSTRACT

Circular economy and waste-to-resource technologies play a key role in the search for sustainable development and in the fight against global warming.

The main objective of this thesis was to study the global potential for the production of a green biofuel, specifically bioethanol from biowaste. For this purpose, the different available routes for bioethanol production were analysed along with the current production capacity and uses. The different sources of biowaste that could be used for the production of second-generation bioethanol were allocated, and an estimation of the availability of these wastes was performed in order to assess the potential production capacity.

Moreover, Life Cycle Assessment of first- (1G) and second-generation (2G) bioethanol and oil-derived fuels was performed, allowing us the quantification of the benefits of 2G generation bioethanol in terms of environmental impact in comparison to the alternatives mentioned. A brief economic analysis was also included to check the viability of this technology.

It was estimated that about 325,847,039-763,688,076 tonnes of 2G bioethanol could be produced per year using biowaste as feedstock. It would allow to satisfy the current global ethanol demand and to meet the future goals in terms of green fuels usage. Furthermore, it was observed that using 2G bioethanol instead of oil-based fuels would allow to reduce greenhouse gases (GHGs) emissions up to 40%.

Key words: Bioethanol Production; Biowaste; Lignocellulosic Biomass; Non-Edible Organic Matter; Life Cycle Assessment; Waste Generation; Waste-to-Resource Technologies; Circular Economy.

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NOMENCLATURE

1G	First generation
2G	Second generation
3G	Third generation
4G	Fourth generation
ABE	Acetone, butanol and ethanol
AFEX	Ammonia fibre explosion
AP	Acidification Potential
ARP	Ammonia recycled percolation
BSM	Blackstrap molasses
CBP	Consolidated bioprocessing
DCB	Dichlorobenzene
DMC	Direct microbial conversion
DSSF	Dry simultaneous saccharification and fermentation
EP	Eutrophication Potential
FAETP	Freshwater Aquatic Ecotoxicity Potential
FPU	Filter Paper Units
GHGs	Greenhouse gases
GWP	Global Warming Potential
HCAs	Hydroxycinnamic acids
HS	Humic substances

LCA	Life Cycle Assessment
LHV	Lower Heating Value
LSSCF	Liquefaction plus simultaneous saccharification and co-fermentation
MESP	Minimal ethanol selling price
MSW	Municipal Solid Waste
MSWM	Municipal Solid Waste Management
NPV	Net Present Value
NS-OFMSW	Non-Sorted Collection
OFMSW	Organic Fraction of Municipal Solid Waste
PPS	Pulp and paper sludge
rMBRs	Reverse membrane bioreactors
ROI	Return on Investment
SCCF	Simultaneous saccharification and co-fermentation
SHF	Separated hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation
SS-OFMSW	Source Sorted Collection
TEEA	Technical, Economic, Environmental Assessment
XOS	Xylooligosaccharides

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1- Introduction

1.1-Bioethanol

Ethanol is an alcohol with numerous applications commonly obtained in the petrochemical industry from the hydrolysis of ethylene. When this alcohol is produced from biological organic sources through the fermentation of starches, sugars or cellulose, it can be referred as bioethanol. Ethanol and bioethanol are therefore chemically identical (C_2H_5OH), with the only appreciable difference in the isotopic composition of the carbon atoms, due to their different origin (Kim, et al., 2009).

Depending on the type of feedstock used for bioethanol production, distinction among first- (1G), second- (2G) or even third- (3G) or fourth-generation (4G) bioethanol can be made. First-generation bioethanol is obtained using edible biomass, mainly from sugar and corn crops. The main disadvantage of this kind of bioethanol is that the biomass used as feedstock could be used as food or feed. Taking into account the hunger crisis many people suffer all around the world and the zero hunger goal set by the United Unions in the 2030 Agenda for Sustainable Development (UN, 2015), it's a must to find a solution to avoid this food versus fuel competition. An answer to this conflict would be second generation bioethanol. Second-generation bioethanol uses non-edible biomass as feedstock, mostly lignocellulosic biomass, such as forestry residues or agriculture, crop wastes. This kind of biomass is made of cellulose, hemicellulose and lignin, and it can be considered as renewable since it doesn't compete with food or feed (Vohra, et al., 2014). Although at present most of 2G bioethanol is produced from lignocellulosic agricultural biomass, other non-edible biowaste such as the organic fraction of Municipal Solid Waste or some agro-food and forest waste could be used for 2G bioethanol production.

United States is currently the world leader in bioethanol production (54 % of global bioethanol production in 2019) followed by Brazil (30 %) and the European Union (5 %) (RFA, 2019), as shown in Figure 1.

At present, most part of bioethanol production corresponds to first-generation bioethanol. In Europe, in 2019, just 4.3 % of the total bioethanol produced came from non-edible lignocellulosic biomass (ePURE, 2019), as it is shown in figure 2.

The production process for the different types of bioethanol will be further analyzed within chapter 2.

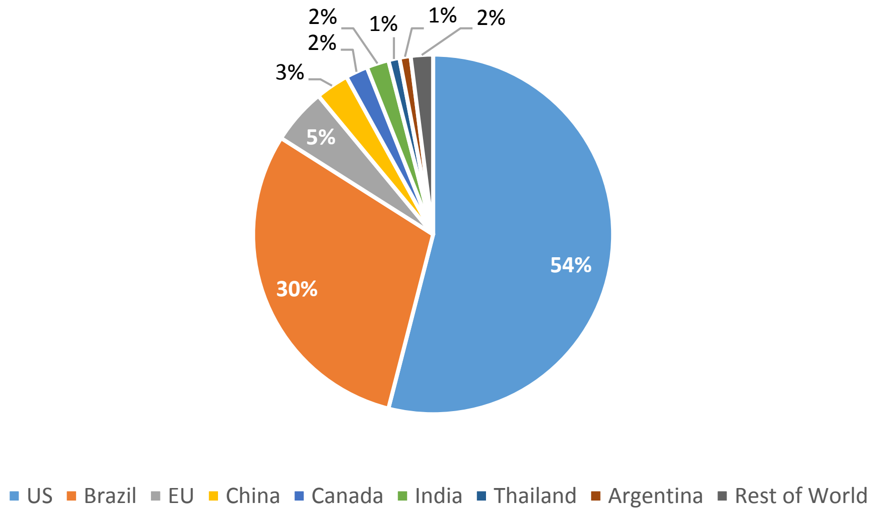


Figure 1: Share of World Fuel Ethanol Production from each country in 2019. Source: Data collected by RFA from public and private data sources.

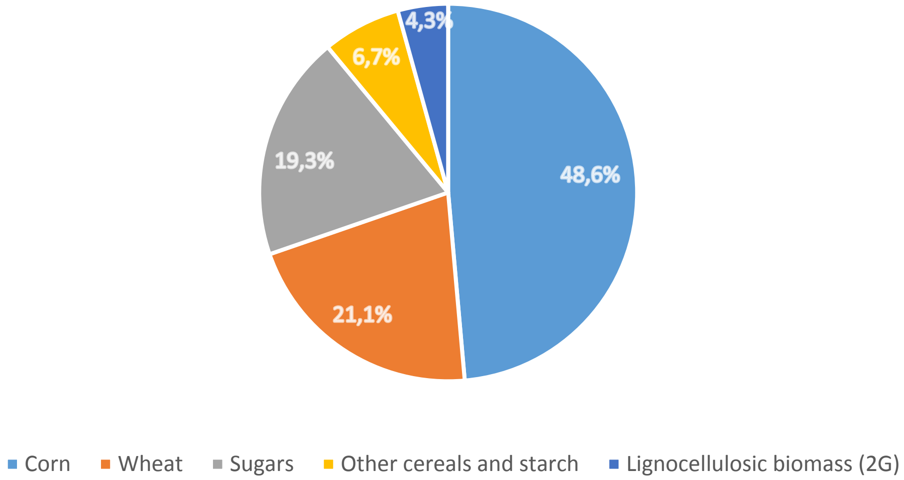


Figure 2: Share of European Bioethanol Production from each feedstock type in 2019. Source: Data collected from ePURE (European Renewable Ethanol).

1.2- Applications of bioethanol

Ethanol applications are very extensive. It can be used as fuel in transportation, in pharmaceutical and food industry, and in many other chemical industrial processes like cosmetics. As already mentioned, unlike synthetic ethanol, bioethanol is a non-oil-derived compound, which is why it is mainly used as a biofuel for heavy or light transportation vehicles, industrial engines or heating systems. More than three quarters of global bioethanol production are used as fuel by automotive and transportation industry (Mordor Intelligence, 2020), as it is shown in Figure 3.

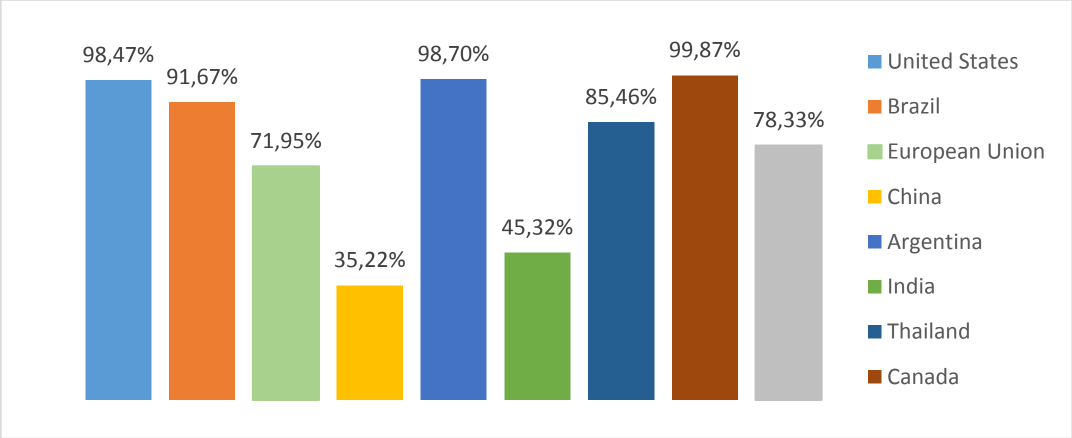


Figure 3: Percentage of bioethanol used as fuel from total bioethanol domestic use in main producer and consumer countries between 2017 and 2019.

Source: Percentages calculated using data from Statistical annex (Table C.40.1 - Ethanol projections: Production and use) of OECD-FAO Agricultural Outlook 2020-2029 (OECD and FAO of the United Nations, 2020)

1.2.1- Bioethanol as fuel

Global warming is one the biggest challenges for 21st century. The goal is to try to avoid an increase in the global average temperature of 2ºC before 2100, taking into account the estimation of a safety threshold between 1.5-2ºC (Schleussner, et al., 2016). To reach this objective, it is essential to reduce greenhouse gases (GHGs) emissions. These gases are mainly carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and water vapor, with the CO_2 as the main contributor to global warming (Al-Ghussain, 2019), not because of its global warming potential, which is lower than methane or nitrous oxide (Grossi, et al., 2019), but because of its high concentration in the atmosphere and its capacity to accumulate in it (Reisinger & Clark, 2018).

When oil-based fuels are burned, large amounts of CO_2 are released, along with small quantities of methane and nitrous oxide. This is why vehicles using oil-derived fuels are one of the main contributors to GHGs emissions (Santos, 2017). In 2019, in Europe 29 % of GHGs emissions came from transport (22 % if considering just road transport, excluding aviation and navigation) (EEA, 2020), with similar trends expected for 2020 and increasing in the following years. It should be noted that this estimation was made right before COVID-19 crisis, so its impact on GHGs emissions, which are expected to be notable due to the global mobility reduction, were not considered (EEA, 2020). In 2018, in the US, where around 90 % of vehicles uses oil-derived fuels, 28.2% of GHGs emissions came from transport (EPA, 2018).

For all these reasons, it is necessary to find an alternative to oil-based fuels. Biofuels like bioethanol are an available effective alternative to reduce GHGs emissions, although they are barely used at the moment. It has been calculated that in 2018, 62.8 million tonnes of CO_2 equivalent emission was avoided by the use of bioethanol as fuel in transport, and 493 million tonnes from 2008 to 2018 (Sydney, et al., 2019). In order to calculate net CO_2 emissions from bioethanol use as fuel, only emissions from production process should be taken into account, since CO_2 released when burning the biofuel in vehicle's engines is considered as biogenic CO_2 (EU, 2021), which means it is consumed by the biomass used as raw material. It should be noted that when producing 1G bioethanol, cultivating processes and land treatments are needed, which means that higher CO_2 emissions should be expected than when producing 2G bioethanol (Sydney, et al., 2019). This statement shall be proved within following chapter. In view of the latter, it could be concluded that the reduction in the GHGs emissions would be considerably larger if 2G bioethanol were used instead of 1G bioethanol.

One of the most important parameters when testing a fuel is its octane number, which represents the resistance of the fuel to knock or to ignite prematurely (Stauffer, et al., 2008). Octane number of bioethanol is higher than octane number of gasoline. When a fuel has a high octane number, it can run at a high compression ratio since it won't knock or ignite, which means that the combustion efficiency will be higher than that reached by a fuel with a lower octane number (Wibowo, et al., 2018). On the other hand, heating value of gasoline is higher than heating value of ethanol, which means larger quantity of bioethanol than gasoline is needed to generate the same amount of energy (Hsieh, et al., 2002). For these reasons, bioethanol is currently used as a fuel blended with gasoline. This kind of biofuel is labelled with an E followed by a number, which represents the percentage in volume of bioethanol in the mix (E100 means 100% of bioethanol, 0% of gasoline). Bioethanol increases the octane number of gasoline, and hence, the combustion efficiency is increased. It means that a better combustion is performed, which is why when increasing the fraction of bioethanol in the fuel mix, it is observed that both CO and UHC (Unburned Hydro-Carbons) emissions are reduced (Elfasakhany, 2014). It should be noted that CO_2 emissions are increased, but as mentioned before, this CO_2 is considered biogenic, so it shouldn't be considered in the net emissions balance.

Current use of bioethanol as fuel all around the world is still very low compared with oil-based fuels, and it doesn't meet the targets of use set by different countries to reduce GHGs emissions. In 2019, in Europe, only 8.4% of total fuel used in transport came from renewable sources (EEA, 2020). The target set by the Directive 2009/28/EC of the European Parliament and of the Council in 2009 (European Parliament and Council of the EU, 2009) was to reach a 10% of total fuel transport consumption coming from renewable sources by 2020. This directive was updated in 2018, with a new target of 14% renewable source derived-fuel by 2030 (European Parliament and Council of the EU, 2018). In 2019, in US, 7.3% of total fuel consumption in transport corresponded to biofuels (eia, 2020). In February 2020, a new target of 15% of total fuel transport covered by biofuels by 2030, and 30% by 2050 was set (USDA, 2020).

Considering the evidence regarding the significant room for improvement and the need to increase bioethanol usage, and taking into account the already mentioned fact that most of bioethanol currently used is 1G bioethanol, the global potential for 2G bioethanol production needs to be further analysed.

1.3- Sustainability, circular economy and bioethanol

A key concept to achieve economic growth and development along with sustainability is the circular economy. The main purpose of circular economy is to recover resources instead of import resources, typically non-renewable and from outside the system, in order to create a closed cycle (Barros, et al., 2020). These resources are both material and energetic, so applying a circular economy system would mean savings in both emissions and costs, from production, raw materials or waste treatment. The current global economy is based on linear economy, which relies basically on production-consumption-disposal, while circular economy would rely on a closed loop of production-consumption-recovery-production (Korhonen, et al., 2018). It is estimated that just 9.1% of current global economy is circular (Wit, et al., 2018), although there is a 91% possibility for improvement (Barros, et al., 2020).

In 1959 an eco-industrial park was started in Kalundborg (Denmark). Over the years, it has been developed and new partners have been incorporated, based on a symbiosis production system, which would be a perfect example for circular economy. The purpose of this model is to connect all the streams in Kaldunborg, including energy, water and materials, by providing, sharing and reusing resources to create a shared value (Figure 4). It means that the by-product of one company can be used as raw material for another. In 2015, a life cycle assessment of all the flows taking part in the system was performed, which allowed to conclude that both economic and environmental benefits are achieved. Also, an annual reduction of CO_2 emissions of 635,000 tonnes was estimated. (Kalundborg Symbiosis, 2021)

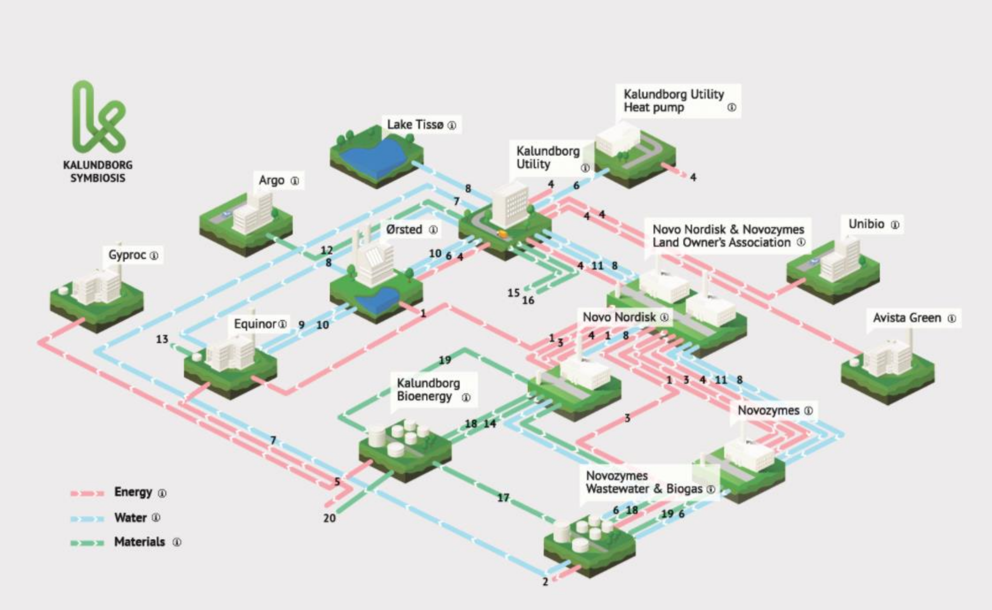


Figure 4: Scheme of all stream connections at Kalundborg Symbiosis Eco-Industrial Park. Source: Image taken from the Kalundborg Symbiosis official website (Kalundborg Symbiosis, 2021).

Producing second-generation bioethanol instead of first-generation bioethanol is an opportunity of turning a linear economy system into a circular economy system. As it is shown in figure 5, in 1G bioethanol production, it is necessary to import feedstock (crops) and residues are not recovered or reinserted within the system. On the other hand, the feedstock used for 2G bioethanol is the result of the treatment of different wastes generated by human activity. This waste-to-resource model is very beneficial for waste reduction as well as for raw materials savings, leading to cost savings and emissions reduction.

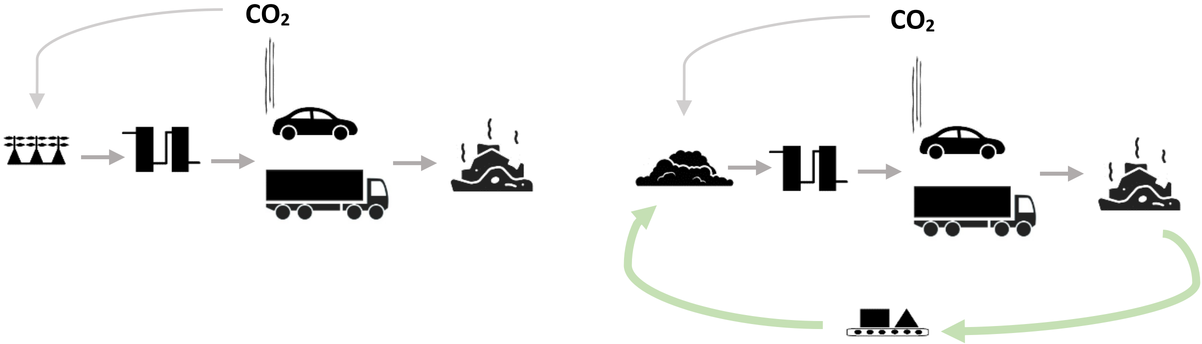


Figure 5: Linear Economy (1G bioethanol) vs Circular Economy (2G bioethanol) scheme

Although 2G bioethanol is clearly a sustainable option, it still has some drawbacks that should be minimized, which are mainly the feedstock limitations, the use of land and the cost of pretreatments (Darda, et al., 2019). For these reasons, third- and fourth-generation bioethanol are under study.

3G bioethanol is produced using micro or macro-algae as raw material. The main advantages of producing 3G bioethanol instead of 2G bioethanol is that no land is needed, the cultivation of the algae can take place during all year and using water coming from waste water treatment plants is possible. Nevertheless, there is still room for improvement for this technology since it also has some drawbacks, such as eutrophication as consequence of the nutrients involved in the process, or the low yields of bioethanol. (Darda, et al., 2019)

The next generation of bioethanol (4G) would be the one based on genetic engineering applied on any source producing fuel from CO_2, such as micro or macro-algae, consisting on modifications at cellular levels, and related with the concept of metabolic engineering (Stephen & Periyasamy, 2018). Genetic modification could lead to lower production costs and higher productivity by adding the desired properties to the feedstock (Darda, et al., 2019).

2- Bioethanol production

The production process of bioethanol is directly related with the kind of feedstock used, but despite this, there are some general basic steps that are common for any type of feedstock used.

The overall process is always based on three elementary steps: pretreatment, fermentation and separation (Vohra, et al., 2014). The aim of pretreatment is to obtain a solution where fermentable sugars are present. For this purpose, carbohydrates must be extracted or become more accessible, and fibres must be converted into sugars through hydrolysis for further fermentation. Fermentation consists basically on the transformation of simple sugars into ethanol and CO_2, by means of microorganisms such as yeasts or bacteria. Since the fermented product has a concentration of ethanol between 8-14% in volume, it’s necessary to include the separation step to concentrate it. Different kinds of distillation, such as adsorption distillation, azeotropic distillation, diffusion distillation, extractive distillation or membrane distillation, can be used for the separation process (Aditiya, et al., 2016). Dehydration can be applied after distillation to obtain a bioethanol with a purity of 99.6% (Vohra, et al., 2014).

As it is obvius in figure 6, there is a difference in the number of steps needed for the bioethanol production depending on the nature of the feedstock used. If simple sugars such as molasses or juice are used as raw material, then no pretreatment is needed since they can be directly fermented. When starchy feedstock is used, a mechanical pretreatment and hydrolysis are necessary before the fermentation process. In the case of lignocellulosic based feedstock, a more complex pretreatment must be performed prior to fermentation (Vohra, et al., 2014).

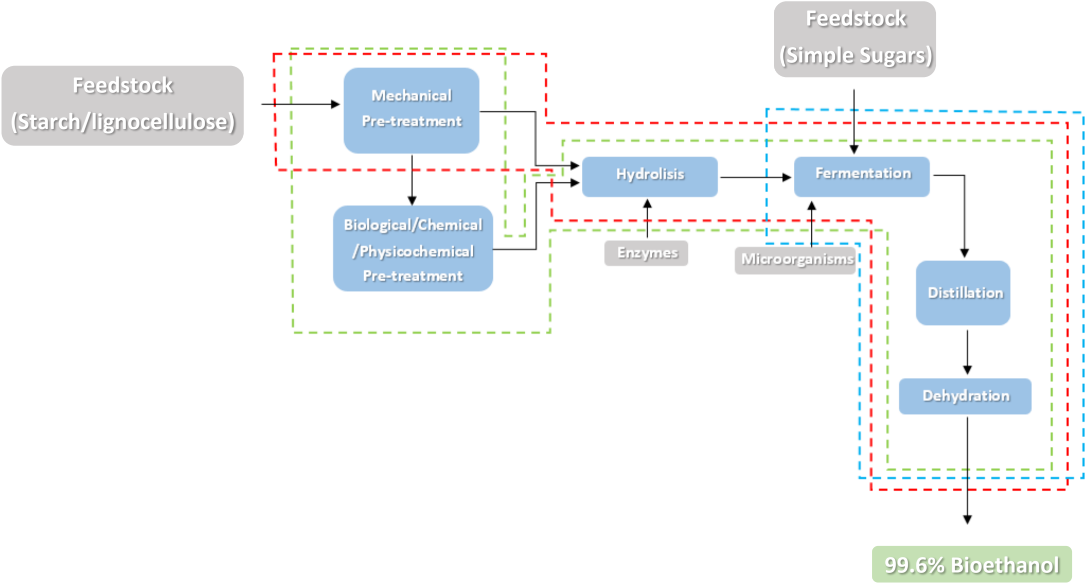


Figure 6: Overall process scheme for bioethanol production. Routes for starchy (red), lignocellulosic (green) and sugar based (blue) feedstock are boxed with discontinues lines in different colors.

Sucrose based feedstock, such as sugar cane or sweet sorghum, consists of simple sugars, which means it can be directly fermented with no need of hydrolysis or a complex pretreatment. The process for bioethanol production from sugarcane is presented in Figure 7. It starts with the extraction of the juice rich in sugars by means of mechanical rollers. Then lime is added in order to make fiber and sludge precipitate (bagasse). After filtration, crystals of sugars obtained by evaporation are removed, obtaining the BSM syrup ("blackstrap molasses") that will be fermented into ethanol. Apart from bioethanol, sugar, electricity and steam are obtained as co-products. This production process ensures high yield and low cost, but it has the already mentioned drawbacks of 1G bioethanol in addition to seasonal availability (Vohra, et al., 2014).

Corn is widely used as raw material for bioethanol production. Unlike sugar cane, it mainly consists of starch (60-70% content) (Vohra, et al., 2014). Starch is basically long chains of glucose units. In order to get the sugar syrup that will be fermented into ethanol, it is necessary to break these chains. Hydrolysis is the process that allows to convert the polymers of glucose into simple sugars by breaking the long chains of the starch. This process is based on hydrolytic catalytic reactions, using enzymes as catalysts (Vohra, et al., 2014).

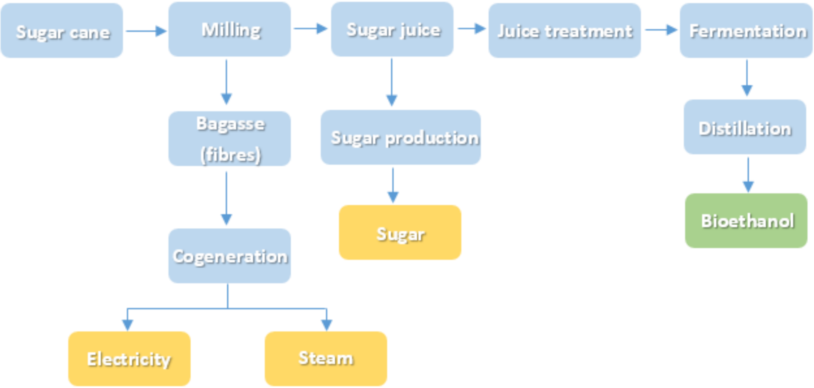


Figure 7: Overall process scheme for bioethanol production from sugar cane.

The production of bioethanol from starchy feedstock can be carried out by mean of two different methods: dry milling process (Figure 8) or wet milling process (Figure 9).

The dry-milling process starts with the milling of the corn grains to enable the entrance of water and enzymes, in addition to size reduction. Then, by addition of some enzymes along with hot water to increase the temperature, the liquefaction of starch takes place. After cooling to room temperature, saccharification takes place by means of hydrolysis, degrading the starch into maltose and glucose. Amylolytic enzymes (amylases) are used for this purpose (Aditiya, et al., 2016). Finally, glucose is fermented by yeast giving place to ethanol and carbon dioxide. The bioethanol is then purified in distillation columns.

The hydrolysis and fermentation processes can be performed at the same time by means of a process called SSF (simultaneous saccharification and fermentation), leading to production costs reduction, higher ethanol conversion and shorter times required (Sewsynker-Sukai & Kana, 2018).

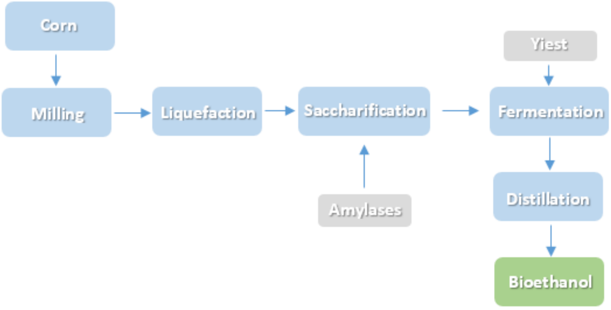


Figure 8: Dry-milling process scheme for bioethanol production from corn.

The wet-milling process differs from the dry one in the pretreatment of the corn grains prior to the saccharification and fermentation. In this process, by means of an aqueous medium, the corn kernel is separated into its three composing parts: the hull, the germ and the endosperm. (Vohra, et al., 2014)

Shelled corn enters the wet mill and undesired material is removed. In order to soften the kernel, the cleaned corns are then put in steep tanks, soaked in sulfuric acid. The bonding protein that holds starch components together gets broken and so all soluble components can be removed. In degerminating mills, the germ, which can be used to produce corn oil, is separated from starch, gluten and fibrous material. This fibrous material is then separated from starch and gluten, and the starch is finally separated from gluten by centrifugation, obtaining a purified starch slurry. From this point, the process is very similar to the dry-milling process. After a pH adjustment by the addition of lime, the liquefaction takes place, followed by the saccharification and fermentation. Again, bioethanol is purified in distillation columns. (Vohra, et al., 2014)

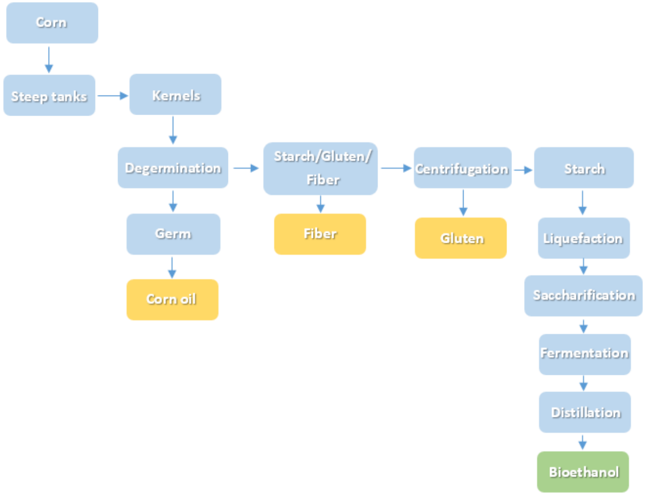


Figure 9: Wet-milling process scheme for bioethanol production from corn.

2.1- Bioethanol production from lignocellulosic feedstock.

Lignocellulosic matter consists of three different components: lignin, cellulose and hemicellulose. Lignin acts as a binder holding the different components together, cellulose is a polysaccharide with β-D-glucopyranose as repeating unit, and hemicellulose is a simpler polysaccharide containing different types of sugars. The content of lignin, cellulose and hemicellulose will be different depending on the nature of the lignocellulosic material (Vohra, et al., 2014).

There are many routes and technologies available for bioethanol production from lignocellulosic biomass, but all of them are based on one of these two methods: biochemical conversion (sugar-based) or thermochemical conversion (syngas-based). The biochemical conversion method is similar to the process used for bioethanol production from starch. It is based on the conversion of the biomass to simple sugars that are then fermented into bioethanol. In the thermochemical method, the biomass is gasified, giving place to syngas, which is converted into bioethanol by means of chemical catalysts or by biological reaction. (Vohra, et al., 2014; Sharma, et al., 2020)

2.1.1- Biochemical conversion

The overall process for bioethanol production from lignocellulosic feedstock by means of biochemical conversion consists of four main steps: pretreatment, hydrolysis, fermentation and distillation. The scheme of the overall process can be observed in Figure 11.

Pretreatment:

The kind of pretreatment used depends on the nature of the feedstock used; that is the chemical composition and the physical structure (Sharma, et al., 2020). The choice of the pretreatment is a critical point in the production process design because it has a huge impact on the overall production cost (Vohra, et al., 2014), since it is the most expensive step. It may have also impact on the final yield, but it seems to be more influenced by the composition and nature of the feedstock where it is applied rather than the kind of pretreatment itself (Sharma, et al., 2020; Sadhukhan, et al., 2019).

The aim of this step is to reduce the size of biomass and to expose both cellulose and hemicellulose in order to make them more accessible for enzymes (Vohra, et al., 2014; Sharma, et al., 2020). This is done by reducing the crystallinity degree of the cellulose matrix. A lower crystallinity degree ensures a better hydrolysis performance (Aditiya, et al., 2016). Also, the lignin is separated from cellulose and hemicellulose, and can be used for energy production (Sharma, et al., 2020). Lignin residues from bioethanol production have been tested also as raw materials for added-value products like nanoparticles or nanocomposite films (Rivière, et al., 2021).

The different types of pretreatments can be clustered in biological, physical, chemical or physicochemical (Vohra, et al., 2014). Biological pretreatment is based on the use of microorganisms. This kind of technology is environmentally friendly (Aditiya, et al., 2016) but it has the main drawback of low conversion rate (Sharma, et al., 2020). Physical pretreatments, such as milling, grinding or extrusion, are necessary for size reduction but they are high energy demanding (Sharma, et al., 2020). At least a third of total energy consumption in the overall production process corresponds to physical pretreatment (Aditiya, et al., 2016). Chemical pretreatments can be based on dilute acids, alkalis or ionic liquid (Vohra, et al., 2014). They are the most used type of pretreatment at industrial scale (Aditiya, et al., 2016), although they have some drawbacks like the formation of inhibitors or the need of pH adjustments when acids are applied (Sharma, et al., 2020). The most popular physicochemical pretreatment is steam explosion. This technology is based on hydrothermal (chemical) and pressure changes (physical) that give place to an explosion of the fibres present in biomass (Aditiya, et al., 2016). Steam explosion is suitable for feedstock rich in hemicellulose, because they contain acetyl groups that get auto-hydrolysed to acetic acid when temperature is increased (Aditiya, et al., 2016). This kind of technology implies low capital investment, low environmental impact, less hazardous conditions and high energy efficiency (Vohra, et al., 2014; Aditiya, et al., 2016), but it still has important drawbacks to be overcome like the production of inhibitors (Sharma, et al., 2020).

Other examples of physicochemical pretreatments are ammonia fibre explosion (AFEX) and ammonia recycled percolation (ARP) (Aditiya, et al., 2016).

Hydrolysis:

Hydrolysis is a very important step because the quality of the fermentation depends on the efficiency of this process (Aditiya, et al., 2016). The purpose of this operation is to break down the polysaccharides giving place to simple sugars that can be fermented (Vohra, et al., 2014). There are mostly 3 methods for hydrolysis: dilute acid hydrolysis, concentrated acid hydrolysis and enzymatic hydrolysis. Acid hydrolysis methods are barely used at industrial scale, and enzymatic hydrolysis is the most widely applied method at the moment. This technology can be carried out at mild conditions, and it ensures better yield, less inhibitors and waste water treatment costs than when using acids (Vohra, et al., 2014; Sharma, et al., 2020).

By means of enzymatic hydrolysis, cellulose is converted into glucose, and hemicellulose is converted into pentoses, including xylose, arabinose and rhamnose, and hexoses, specifically glucose, galactose and mannose (Vohra, et al., 2014). Due to its amorphous property, hemicellulose is easier to hydrolyse than cellulose (Aditiya, et al., 2016).

The enzymes used for the cellulose conversion into glucose are very specific. Different cellulases are involved in the process, mainly endoglucanase, exoglucanase and β-glucosidase. Endoglucanase is responsible for creating free chain-ends by attacking regions of the fibre with low crystallinity, the exoglucanase degrades the molecule and removes cellobiose units from free-chain ends and the β-glucosidase hydrolyzes the cellobiose giving place to glucose (Vohra, et al., 2014; Aditiya, et al., 2016). This process is represented in Figure 10.

The pretreatment must ensure the removal of lignin since, because of its resistance to cellulase activity, it may affect the quality of the hydrolysis (Aditiya, et al., 2016).

One of the main drawbacks of enzymatic hydrolysis and an important challenge to be overcome in bioethanol production industry from lignocellulosic feedstock is the need of large amount of cellulases and the associated costs (Sharma, et al., 2020). A possible solution to this could be the integration of different processes such as hydrolysis and fermentation. Different possibilities of integration will be analysed further on. Also, it has been reported that by adding soluble soy protein, a more efficient enzymatic hydrolysis takes place, which would mean higher sugars generation and hence higher ethanol production, in addition to lower enzymes requirements (Demiray, et al., 2021).

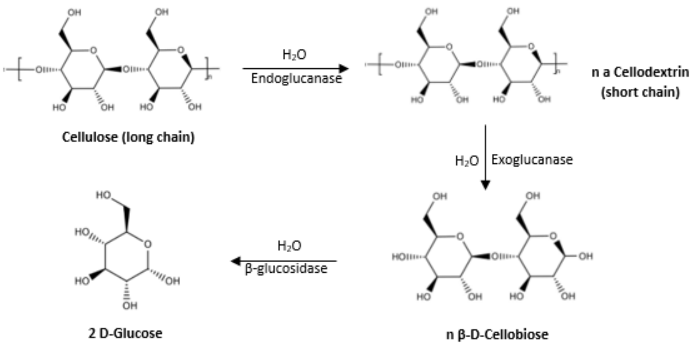


Figure 10: Enzymatic hydrolysis of cellulose.

Source: Section 2.2.1. Enzymatic hydrolysis of lignocellulosic biomass from 'Second generation bioethanol production: A critical review' (Aditiya, et al., 2016)

Fermentation:

Fermentation consists of the transformation of sugars into ethanol and carbon dioxide by means of yeasts or bacteria (Sharma, et al., 2020). After the hydrolysis, sugars to be fermented are mainly glucose, which is easily fermentable, and hemicellulose-derived pentose sugars such as xylose or arabinose. No microorganism has been found in the nature capable of fermenting both glucose and xylose at the same time and at high yields. For this reason, microorganisms have been genetically modified to achieve this capacity (Vohra, et al., 2014).

Modified *Saccharomyces cerevisiae* is the most widely used genetically modified microorganism at industrial scale for lignocellulose-derived hydrolysates fermentation. By means of metabolic engineering modifications, it is capable to ferment not only glucose but also xylose into ethanol at high yields and with no side products generation (Vohra, et al., 2014). Theoretically, 1k g of glucose and xylose is expected to produce 0.49 kg of CO_2 and 0.51 kg of ethanol respectively (Hamelinck, et al., 2005). One of the main issues when fermenting lignocellulose-derived hydrolysates by means of *S. cerevisiae* is the presence of inhibitors, which are called LDMIC (lignocellulose-derived microbial inhibitory compounds). In order to reduce their concentration and to ensure a high efficiency fermentation, hydrolysates are diluted, which means sugars concentration is also reduced and hence bioethanol production decreases. Addition of allopurinol has been proved to increase the tolerance of LDMICs to *S. cerevisiae*, leading to a more efficient fermentation (Agu, et al., 2018). Another effective solution to mitigate inhibitors influence on fermentation is the use of reverse membrane bioreactors (rMBRs). This technology can efficiently increase inhibiters tolerance and enhance detoxification while fermenting both glucose and xylose, everything at the same time (Mahboubi, et al., 2020). Nevertheless, it still has some challenges to overcome such as the preparation of hydrolysates prior to the fermentation in order to be applicable at industrial scale (Mahboubi, et al., 2020).

Although lignocellulose-derived hydrolysate contains mainly glucose and xylose, it also contains arabinose. Modified *S. cerevisiae* is not able to ferment both xylose and arabinose at high efficiency apart from glucose (Vohra, et al., 2014). *Pseudomonas putida* has been successfully engineered to make it capable of co-fermenting simultaneously glucose, xylose and arabinose as well as acetic acid and p-coumarate, which is a lignin related compound (R. Elmore, et al., 2020). This technology is very promising for bioethanol production from lignocellulose-based feedstock but is still under research.

Distillation:

Distillation is the last step in the route for bioethanol production from lignocellulosic biomass by means of biochemical conversion. It is necessary to remove the water content, giving place to the final anhydrous bioethanol, with a water content smaller than 0.5 % (Aditiya, et al., 2016). The main types of distillation processes that can be applied for water removal are adsorption processes, vacuum distillation, azeotropic distillation, diffusion distillation, membrane processes, chemical dehydratation and extractive distillation (Kumar, et al., 2010).

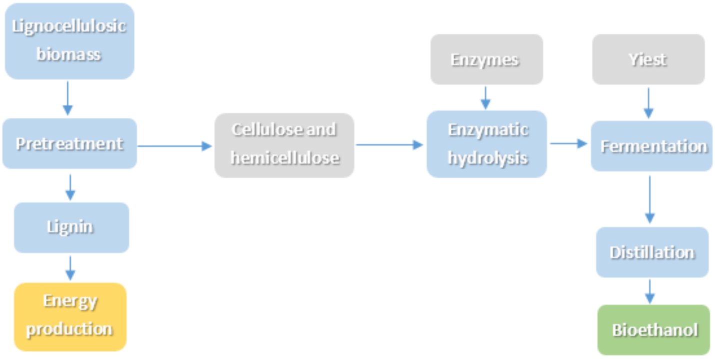


Figure 11: Scheme of bioethanol production process from lignocellulosic biomass by means of biochemical conversion.

Process integration:

In order to reduce costs of the overall production process as well as enzymes requirements, some integrated processes have been developed (Figure 12).

One of the most common process integration is the simultaneous saccharification and fermentation (SSF). Unlike separated hydrolysis and fermentation (SHF), in this process the saccharification and fermentation take place at the same time and at the same unit. It means that sugars are fermented into ethanol as soon as they appear from hydrolysis (Vohra, et al., 2014). As already mentioned, hydrolysates contain inhibitors that affect the fermentation. If hydrolysates are fermented right after their formation, the presence of inhibitors is reduced and hence higher yields and rates are achieved (Vohra, et al., 2014; Sharma, et al., 2020). Since a single unit is used for two processes, lower investment cost as well as faster production and lower amount of enzymes are needed when applying this process integration (Sharma, et al., 2020; Aditiya, et al., 2016). The main hurdle of this technology is to find the optimal conditions for both enzymes responsible for hydrolysis and microorganisms used for fermentation (Rastogi & Shrivastava, 2017).

Another option of process integration is simultaneous saccharification and co-fermentation (SCCF). This technology is very similar to the SSF, but in SSF glucose and xylose are fermented separately, while in SCCF both hexoses and pentoses are fermented at the same time by genetically modified microorganisms like *S. Cerevisiae* (Sharma, et al., 2020). Like SSF, low cost and lower inhibitory effects are the main advantages of this technology, in addition to lower contamination risk and shorter operation time (Rastogi & Shrivastava, 2017).

Another process integration possibility is the consolidated bioprocessing (CBP), also called direct microbial conversion (DMC). This technology consists on a single reactor where all enzymes and bioethanol are produced simultaneously (Vohra, et al., 2014). It means that not only the hydrolysis of both pentoses and hexoses and the fermentation take place at the same unit, but also the production of cellulases. This is done by using microorganisms capable to run all these tasks (Aditiya, et al., 2016). This process integration would lead to significant reduction in investment cost, energy use and enzymes related costs (Sharma, et al., 2020; Aditiya, et al., 2016), although it still has some issues to overcome in order to be applicable at industrial scale, such as the low rate of ethanol conversion and the low ethanol yield (Aditiya, et al., 2016). Genetic engineering on microorganisms may be a promising solution to these problems (Aditiya, et al., 2016).

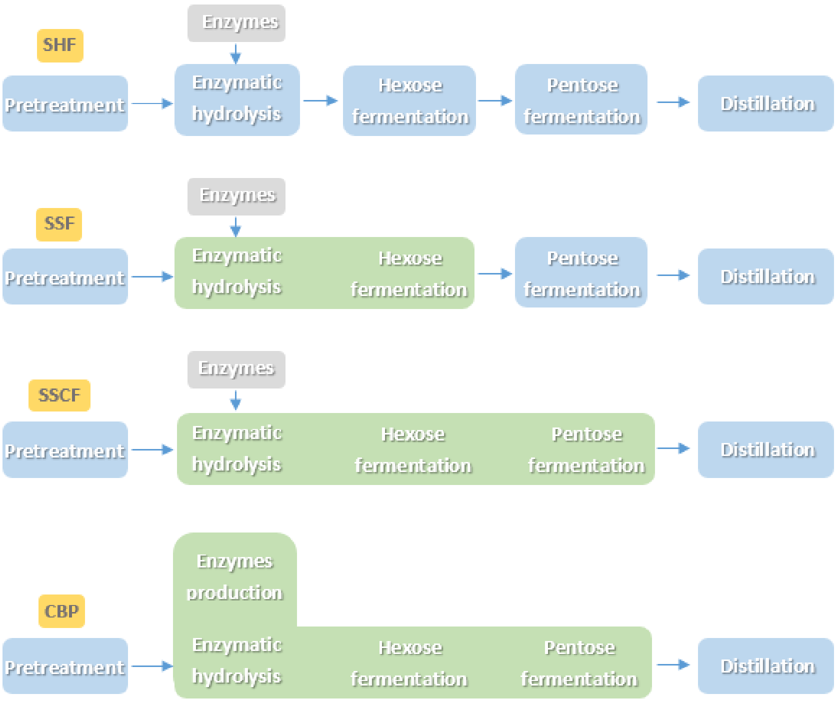


Figure 12: Possibilities of process integration.
Source: Section 2.3. Fermentation from 'Second generation bioethanol production: A critical review' (Aditiya, et al., 2016)

2.1.2- Thermochemical conversion

This method is based on the gasification of the lignocellulosic biomass to produce syngas and the fermentation of this syngas into ethanol by means of two possible routes: metal-catalytic conversion (Figure 13) or bio-catalytic methods (Figure 14) (Vohra, et al., 2014).

Catalytic conversion starts with the gasification of the lignocellulosic biomass at 700-800º C. The gasification gives place to a mixture of different gases called syngas, including mainly CO, H_2, CH_4, N_2, CO_2 and other hydrocarbons. After filtration to remove undesired pollutants, the Fischer-Tropsch process takes place, which consists of a catalytic conversion of syngas into ethanol, methanol and higher alcohols. Main catalysts used for this process are rhodium, cobalt or molybdenum. Alcohol is added to the gas mixture prior to the catalysis in order to increase the reaction yield. Approximately 60 % of CO is converted into ethanol. After Fischer-Tropsch process, non-reacted syngas is separated by means of condensation and the different alcohols are separated by distillation. (Vohra, et al., 2014)

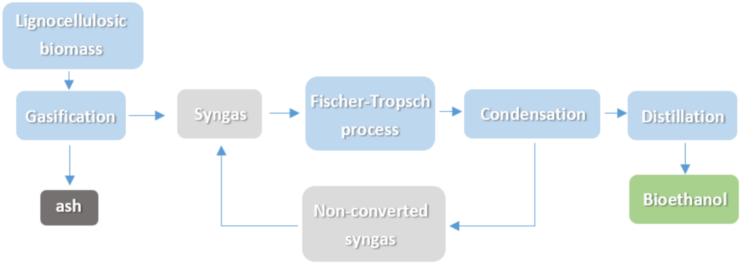


Figure 13: Scheme of thermochemical conversion of lignocellulosic biomass into ethanol by means of catalytic conversion.

The bio-catalytic route is a thermo-chemical-biological process very similar to the previously mentioned catalytic conversion, where instead of converting the syngas into ethanol by means of the Fischer-Tropsch process, the syngas is fermented by microbial catalysts, producing ethanol and acetic acid. Gas mixture must be cleaned and cooled to room temperature prior to fermentation. There are different bacteria capable of fermenting the syngas to produce ethanol. *Clostridium ljungdahlii*, *Butirybacterium methylotrophicum* and *Clostridium autoethanogenum* are some examples of bacteria with this ability. This method has the advantage of lower temperature and pressure requirements, but it also has the significant drawback of the low productivity of the bioreactor (Vohra, et al., 2014).

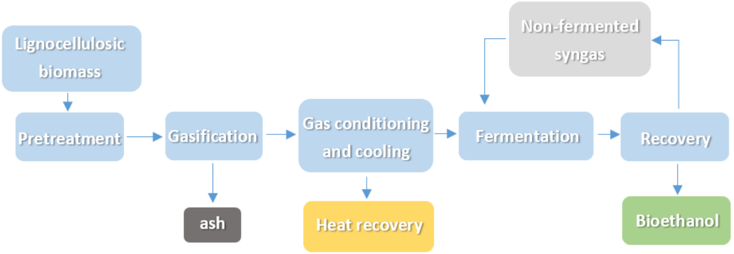


Figure 14: Scheme of thermochemical conversion of lignocellulosic biomass into ethanol by means of bio-catalytic method.

3- Waste as raw material

The biowaste with potential to be used as feedstock for 2G bioethanol production can be divided in two main groups: Agricultural waste and Municipal Solid Waste (MSW).

Agricultural biowaste consists mostly of lignocellulosic biomass, although some sugar-based and starchy non-edible agro-food waste should be also considered for 2G bioethanol production, such as fruits waste (sugar-based) or potato and other discarded food waste (starchy). Organic fraction from MSW, composed mainly by food waste, has been successfully assessed as feedstock for bioethanol production. Paper fraction might also be considered as a potential raw material.

Apart from these main sources, other non-edible biowaste such as woody biomass from forest waste should be also analyzed as potential feedstock for 2G bioethanol production.

3.1- Agricultural and industrial waste

SUGARCANE TRASH (STRAW)

Sugarcane is one of the most cultivated crops around the world. It generates mostly 2 kinds of wastes: bagasse and trash. They both are lignocellulosic biomass that can be used for bioethanol production. Approximatively 2/3 of sugarcane is lignocellulosic biomass (Singh, et al., 2008). This trash, also known as straw, is generated during harvesting of sugarcane stem (Khaire, et al., 2021) and it consists of dry leaves and tops. Sugarcane straw represents approximately 1/3 of sugarcane crops (Aguiar, et al., 2021).

It is estimated that 1 ha of sugarcane crop generates 6-12 tonnes of dry leaves (Singh, et al., 2008; Khaire, et al., 2021), and 10-18 tonnes of dry sugarcane trash (Leal, et al., 2013), including tops and dry leaves, which are mostly burned. Burning the trash has several negative consequences for environment. It provokes soil pollution by reducing germination capacity of the soil, loss of nutrients and organic matter (Khaire, et al., 2021) and contaminant emissions to the atmosphere (Aguiar, et al., 2021). For these reasons, new restrictions have appeared and straw burning shall be forbidden by the end of 2021 in some countries such as Brazil (Aguiar, et al., 2021). Also, high amounts of straw in the soil provoke excess N_2O emissions (Aguiar, et al., 2021), so it would be beneficial to exploit part of the trash for bioethanol production. It is estimated that up to 50% of trash can be removed without affecting the quality of the soil (Khaire, et al., 2021). The main drawback of this feedstock is that it needs to be harvested and transported (Aguiar, et al., 2021).

According to literature, chemical composition of sugarcane trash is approximatively 40-45% of cellulose, 25-30% of hemicellulose and 15-20% of lignin (Singh, et al., 2008; Khaire, et al., 2021; Aguiar, et al., 2021).

As it has already been mentioned for lignocellulosic feedstock, due to the high crystallinity index and high order molecular packing of this kind of biomass, pretreatment is needed (Singh, et al., 2008). Different pretreatments have been assessed for sugarcane trash.

Biological pretreatment can be applied, with *A. Terreus* as best microorgsnism for this purpose: high delignification, proper reduction of C/N ratio, good solubilisation of cellulose and high cellulase production were observed by Singh et al. (Singh, et al., 2008) when applying biological treatment on sugarcane trash.

Screening of transition metals, such as ferric chloride and sodium hydroxide, for crude glycerol assisted pretreatment has been also proved to reduce properly hemicellulose and lignin content and to ensure low formation of inhibitors, leading to a reducing sugar yield of 0.78 g/g dry biomass, a fermentation efficiency of 78.89% and a final ethanol concentration of 31.928 g/L (Raghavi, et al., 2016), which is the highest ethanol yield reached compared with other types of pretreatments (Khaire, et al., 2021). Considering the reducing sugar yield, the fermentation efficiency and the theoretical conversion of glucose and xylose to ethanol (0.51 kg ethanol/kg sugar fermented (Hamelinck, et al., 2005)), 0.31 g of bioethanol per g of dried sugarcane trash biomass could be produced.

<u>*SUGARCANE BAGASSE*</u>

As mentioned before, the two main waste generated by sugarcane crops are sugarcane trash and bagasse. Bagasse, which is the hard fibrous layer of sugarcane, is obtained as by-product during sugar juice extraction and it is usually burned for energy generation (Bernier-Oviedo, et al., 2018; Niju & Swathika, 2019).

Approximately, 1 tonne of sugarcane would generate 0.3 tonnes of bagasse. Considering the average 80 tonnes of sugarcane per cultivated hectare, 25 tonnes of bagasse could be produced per hectare of sugarcane crop, which is a very high per unit area yield compared with others crop residues (Huang, et al., 2020).

Bagasse is a suitable feedstock for bioethanol production due to its high lignocellulosic content. Dried bagasse contains 45-50 % of cellulose, 25-30 % of hemicellulose and 25 % of lignin. In addition, it presents a low ash content (2.4-9 %) (Niju & Swathika, 2019). Based on cellulosic contents, it is estimated that 300 L of bioethanol could be produced from 1 tonne of bagasse (Santosh, et al., 2017), which means a theoretical yield of 0.24 g of bioethanol per g of dried biomass.

Apart from its promising yield, there are some other factors that indicate that bagasse could be considered as a potential 2G bioethanol feedstock. Bagasse is a by-product of sugarcane processing, so it doesn't need extra harvesting or transportation, as it happens with other wastes such as straw. Also, during the squeezing of sugarcane, the bagasse is size-reduced, which is beneficial for further pretreatments and leads to energy and economic saves, since physical treatments requirements are reduced (Huang, et al., 2020).

Different pretreatments have been tested for bagasse to efficiently produce bioethanol. By using dilute nitric-acid pretreatment, cellulose to glucose conversion resulted in 66.47-82.54 % and in 75-96.42 % for hemicellulose to pentose conversion, in addition to a 77 % of efficiency for the fermentation process (Santosh, et al., 2017). Pretreatment based on alkaline hydrogen peroxide has been proved to be good for delignification (lignin reduction up to 85%) and to ensure high sugar reduction during hydrolysis (85-97 % of cellulose conversion into glucose) (Niju & Swathika, 2019). Also, it can be run at room temperature and no formation of inhibitory products is observed (Niju & Swathika, 2019). Steam explosion and acid hydrolysis have also been proved to efficiently reduce lignin and hemicellulose contents and to achieve very high reducing sugars yields (Bernier-Oviedo, et al., 2018). Auto-hydrolysis is a hydrothermal pretreatment used for co-production of bioethanol and xylooligosaccharides (XOS), with an 82.28 % efficiency during fermentation into ethanol (Zhang, et al., 2020). During this process, hemicellulose is directly converted into XOS and a solid residue rich in cellulose is generated, which is used for the bioethanol production (Zhang, et al., 2020). Regarding the inhibitors generated during pretreatments and hydrolysis, atmospheric cold-plasma has been successfully tested on sugarcane bagasse biomass reducing both inhibitors and toxic compounds and to enhancing the fermentation process (Lin, et al., 2020).

Green solvents such as imidazole are a very promising and environmentally friendly alternative to alkali and acid pretreatments for sugarcane bagasse biomass. Pretreatment with imidazole reduces efficiently lignin and hemicellulose contents, and a 100 % of conversion for both glucose and xylose can be achieved under specific time and temperature conditions. At 160ºC and after 1h of pretreatment, which are the optimal conditions observed for imidazole-based pretreatment, an 83% efficiency during fermentation was achieved. With this efficiency, 218 L of bioethanol could be produced per tonne of bagasse; that is 72.67 % of the theoretical yield, which means a final ethanol yield of 0.172 g of ethanol per g of sugarcane bagasse. (Valladares-Diestra, et al., 2020)

According to the results reported for the different pretreatments, assuming an 80% conversion for cellulose and hemicellulose and a fermentation efficiency of 75%, and taking into account the theoretical ethanol yield of bagasse (0.24 g/g), a real yield of approximately 0.14 g of bioethanol per g of dried biomass may be expected for sugarcane bagasse.

CORN STOVER

Corn stover is one the most generated biomass waste in many countries all around the world (Díaz & Willis, 2019). The corn stover is the non-grain part of corn plant, which is left in the land when harvesting corn, and that includes stalks, cobs, leaves and husks. This biowaste has a high carbohydrates content, with an average composition of 40.67 % cellulose, 31.1% hemicellulose and 11.7% lignin (Mensah, et al., 2021). It is estimated that a certain amount of corn produced generates approximately the same amount of corn stover, which means a corn/corn stover ratio of 1 (Mensah, et al., 2021).

The high glucan content in addition to the wide availability of this biowaste makes it suitable for 2G bioethanol production. Many possible routes for 2G bioethanol production from corn stover have been reported with promising results. By means of sequential steam explosion and alkaline pretreatment prior to simultaneous saccharification and fermentation (SSF), an increase of 76% in glucan content and an efficient crystallinity reduction were observed, leading to a final ethanol yield of 199 g of bioethanol per kg of corn stover, which is 35% higher than that obtained with just sodium carbonate pretreatment (Molaverdi, et al., 2021).

As with other lignocellulosic biomass, one of the main drawbacks for 2G bioethanol production is the high cost of the overall process. For this reason, different approaches including co-generation of valuable products apart from the bioethanol have been reported in order to reduce costs. One option of integrated process to reduce costs is the valorization of lignin by recovering hydroxycinnamic acids (HCAs). By means of mild alkaline treatment, HCAs can be directly extracted, which also provokes a partial delignification, leading to a sugars reduction yield of 85% and a 45% decrease in the minimal ethanol selling price (MESP) (Johnston, et al., 2020). Another possibility for cost reduction is the co-production of bioethanol and biodiesel. Alavijeh et al. (Alavijeh, et al., 2020) described a possible route for this co-generation. In this process, corn stover is pretreated by dilute acid hydrolysis to separate hemicellulose and cellulose fractions. The cellulose fraction is hydrolyzed and fermented into ethanol by using *M. indicus*, capable of fermenting both pentoses and hexoses. *M. indicus* residue biomass from previous process is cultivated with the hemicellulose derived fraction, containing glucose and xylose, along with nutrients, giving place to bioethanol and large amounts of lipids that are converted into biodiesel. Yields reported are 214 g of bioethanol and 22 g of biodiesel per kg of corn stover. Another promising option is the co-generation of furfural and bioethanol. Li et al. (Li, et al., 2020) described a process for furfural and bioethanol co-production based on two-steps pretreatment. By means of sulphuric acid pretreatment, the hemicellulose fraction gave place to 40 g furfural per kg of corn stover by dehydration of the xylose, and the cellulose fraction gave place to 96 g ethanol per kg of corn stover after an alkaline pretreatment for lignin removal prior to SSF.

Harvest timing has been proved to have an influence on the ethanol yield. If corn stover was harvested during dent stage instead of the end of physiological stage, which is the conventional, then ethanol yield might increase since sugar-based juice present in the corn stover could be used along with the dried bagasse biomass. However, it should be noted that an early harvesting may have a negative impact on the quality of the corn grain as food. (Zhang, et al., 2020; Zhang, et al., 20)

RICE STRAW

Rice crops are one of the most common crops all around the world, especially in Asian countries (Kumar, et al., 2019). Large amounts of rice straw are generated. Approximately 50% of rice crops consist on non-edible biomass that remains as straw, including stem, leaf blades and leaf sheaths (Bhattacharyya, et al., 2020). Most of straw generated is burned, which contributes to air pollution. During November and December of 2017, in New Delhi, capital of India, 70% of air pollution was due to straw burning (Bhattacharyya, et al., 2020). Also, dust and fine particles affecting air quality are released.

Rice straw has an average composition of 35-40% cellulose, 20-25% hemicellulose and 15-20% lignin (Sheetal, et al., 2019). Taking into account the lignocellulose content of rice straw, generation of 2G bioethanol might be considered as an alternative to burning.

Many studies have assessed the potential of rice straw as feedstock for bioethanol production. By means of sodium carbonate pretreatment and dry simultaneous saccharification and fermentation (DSSF) an ethanol yield 153 g of ethanol per kg of rice straw was achieved by Molaverdi et al. (Molaverdi, et al., 2019). Microwave assisted $FeCl_3$-H_3PO_4 pretreatment has also been proved to efficiently break the recalcitrance of this lignocellulosic biomass (Kumar, et al., 2019).

In order to reduce overall costs of the process, different possibilities have been reported. Mohammadi et al. (Mohammadi, et al., 2019) proved the efficiency of morpholinium ionic liquid (1-H-3-methylmorpholinium) for pretreatment. This cheap ionic liquid ensures low inhibitory compounds production with no high temperature or pressure requirements. By means of separated hydrolysis and fermentation (SHF) a glucose yield of 70.1% and fermentation efficiency of 64% were reported for this kind of pretreatment. Ma et al. (Ma, et al., 2019) proposed a cost reduction scenario based on the co-generation of humic substances (HS) and bioethanol. HS can be used as plant growth promoter. Using residues from HS production for bioethanol production might enhance ethanol yields since inhibitory effects on fermentation would be reduce by the removal of polyphenols. Another possibility for costs reduction might be the production of value added product using the residues generated during bioethanol production. Phenolic acids can be converted into 4-vinylgluaiacol and 4-vinylphenol, which can be used as food additives (Hou, et al., 2020).

RICE HULLS

Rice hulls are another biowaste generated from rice production that can be considered for 2G bioethanol production. They are generated during the rice milling process (Sim, et al., 2020). Part of it can be used at farming industries, but it is generally disposed as waste due to its low digestibility and high ash content (Saha & Cotta, 2007). Rice hulls present the following mean composition: 36% cellulose, 12% hemicellulose, 16% linin and 20% ash (Dagnino, et al., 2013; Saha & Cotta, 2007).

Different ethanol yields have been reported for rice hulls with different pretreatments applied. By means of dilute acid pretreatment prior to enzymatic hydrolysis and fermentation with *S.*

cerevisiae, a final ethanol yield of 110 g/kg of rice hull was achieved by Dagnino et al. (Dagnino, et al., 2013). Using an alkaline peroxide pretreatment, a sugars reduction efficiency during enzymatic hydrolysis of 97% was achieved by Saha & Cotta (Saha & Cotta, 2007), leading to ethanol yields of 210 g and 200 g per kg of rice hulls for SHF and SSF respectively, using recombinant *E. coli* in both cases. A novel chemical-free green pretreatment based on extrusion followed by ultrasound was successfully used to enhance enzymatic hydrolysis by Zhang et al. (Zhang, et al., 2020), achieving 381.59 g of fermentable sugars per kg of rice hulls, which means a 77.5% of glucose yield. Assuming an efficiency of 70-80% for fermentation, an considering the theoretical yield (0.51 g ethanol per kg of fermentable sugars (Hamelinck, et al., 2005)), around 136.23-155.69 g ethanol per kg of rice hulls could be produced.

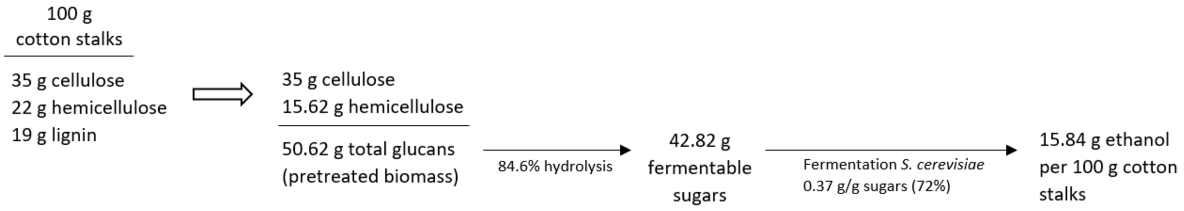
Extraction of phytic acid in addition to the bioethanol production is a possibility for process integration and reduction of the overall cost (Sim, et al., 2020).

COTTON STALKS

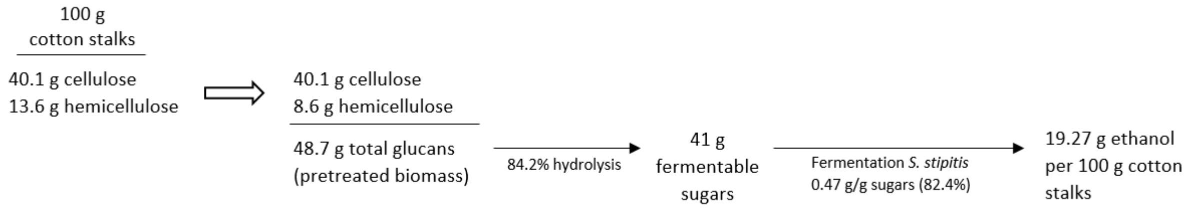
Cotton represents 40% of global fiber production (Keshav, et al., 2016). It is the most abundant crop in tropical and subtropical countries (Singh, et al., 2017). After harvesting the cotton, tonnes of stalks are left in the field. This affects the cultivation and might cause cotton disease (Malik, et al., 2020), which is why most of the stalks are burned (Singh, et al., 2017). The average composition of stalks is 45-70% of cellulose and hemicelluloses, 19-28% of lignin and 5.5% of ash (Singh, et al., 2017). Approximately 2 tonnes of dry matter are generated per hectare of cotton crop (Keshav, et al., 2016). Given the composition and the viability of this biowaste, its potential to be converted into bioethanol has been assessed.

Different kinds of pretreatments and routes have been successfully proved to enhance sugars reduction and fermentation yield (Malik, et al., 2020).

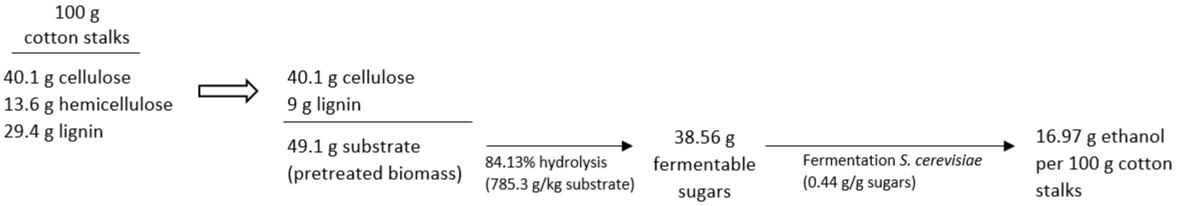
By means of physicochemical pretreatment based on microwave assisted $FeCl_3$ (Singh, et al., 2017), hemicellulose and lignin contents were efficiently reduced, leading to a yield of 84.6% during hydrolysis and 72% in fermentation. Taking into account the composition of the raw material before and after the pretreatment, the ethanol yield on native feedstock basis can be estimated:



By means of sequential steam explosion and dilute acid pretreatment (Keshav, et al., 2018), yields of 84.2% and 82.4% were achieved for hydrolysis and fermentation respectively. As in the previous case, the ethanol yield in terms of input feedstock can be estimated considering the composition of raw material reported:



In the case of sequential steam explosion and alkali extraction (Keshav, et al., 2016), 85.07% removal of lignin and 100% removal of hemicellulose were achieved, leading to a yield of 82.13% during hydrolysis. Again, the ethanol yield on native feedstock basis can be estimated as follows:



Non-chemicals-based pretreatment consisting on hot water treatment has also been assessed for bioethanol production from cotton stalks (Jiang, et al., 2015). When applied separately on the different part of the stalks (branch, stem and ball shell), it resulted on a final ethanol yield of approximately 160 g of ethanol per kg of cotton stalks.

WHEAT STRAW

Wheat is the most abundant crop in the world. Large amounts of wheat straw are generated every year. Approximately 1.3 tonnes of wheat straw are generated per tonne of wheat. Most of the waste is burned or left in the field, which has negative environmental consequences. Part of the wheat straw must be left in the soil. Also, some is used as feed for animals. That means that up to 60% of the wheat straw generated is available for valorization. Given the lignocellulosic composition of this biomass (33-40% cellulose, 20-25% hemicellulose and 15-20% lignin), one of the possibilities of valorization for this biowaste is the production of 2G bioethanol. (Talebnia, et al., 2010)

Different studies have reported suitable conditions and routes for bioethanol production from wheat straw with acceptable ethanol yields. By means of phosphoric acid plus hydrogen peroxide pretreatment a 70.8% of delignification and 100% of hemicellulose removal were achieved, leading to a final ethanol yield of 155 g/kg wheat straw by SSF (Qiu, et al., 2018).

In order to reduce the overall cost of the process, different approaches have been suggested towards the production of value-added products apart from the bioethanol.

Given the high content of ash in this waste (6-16%), the silica present in the ash (approximately 75% of the ash) can be pre-extracted not just to enhance hydrolysis performance but also to be recovered as a value-added product with numerous applications (Yuan, et al., 2018). Alkaline pre-extraction of silica followed by alkaline-hydrogen peroxide pretreatment, which allows efficient isolation and recovery of lignin, resulted in final yields of 0.311 g of ethanol/g of wheat straw, 0.104 g/g for lignin and 0.047 g/g for silica (Yuan, et al., 2018).

Tomás-Pejó et al. (Tomás-Pejó, et al., 2017) studied the possibility of co-generation of bioethanol and bio-oil from wheat straw. Steam-explosion pretreatment was used for this process, and the lignin residue from the bioethanol production was converted into bio-oil by means of fast pyrolysis. This cogeneration increased mass and energy yields 1.9 and 1.7-folds respectively compared to the simple generation of bioethanol. Also, by-products from fast pyrolysis were successfully integrated within the process by heat generation.

Lopez-Hidalgo et al. (Lopez-Hidalgo, et al., 2017) also assessed the possibility of co-production of bio-hydrogen and bioethanol from wheat straw by fermenting the pentoses fraction of the hydrolysate with *Escherichia coli* WDHL strain, obtaining promising results that might be applied in bio-refineries for multi-fuels production.

OAT STRAW

Oat is one of the five most cultivated crop in the world (Romaní, et al., 2016; Lago, et al., 2020). As with most cereal crops, some residues are generated during harvesting and others during processing of the oat grains. Unlike rice hulls, hulls from oat are suitable for animal feeding (Lago, et al., 2020) but dry mass generated during harvesting, known as straw, is mostly left in the fields or burned. Oat straw has a high content of celluloses and hemicellulose, which makes it suitable for bioethanol production (Lago, et al., 2020; Espinosa, et al., 2017).

Valorization of oat straw hasn't been as studied as other straws such as rice or wheat straw (Dererie, et al., 2011), but still, some promising results have been reported, confirming the potential of this biowaste for 2G bioethanol production.

Dererie et al. (Dererie, et al., 2011) compared three different pretreatments for bioethanol production from oat straw. The highest ethanol yield was obtained by means of steam explosion pretreatment prior to fermentation with *S. cerevisiae* J672, producing 150 g of bioethanol per kg of dried oat straw. 115 g/kg and 85 g/kg were produced for sequential steam explosion-dilute sulfuric acid impregnation pretreatment and lime pretreatment respectively. In this study, methane was produced additionally to bioethanol by biogas digestion of unfermented residues from the process, increasing the amount of energy generated per kg of dried oat straw compared to the energy produced by direct biogas digestion with no ethanol production.

Romaní et al. (Romaní, et al., 2016) assessed two possible routes for bioethanol production from oat straw: sequential auto-hydrolysis and lime pretreatment plus SSF and lime pretreatment plus SSCF. First route led to a final ethanol yield of 159 g of ethanol/kg of oat straw, whereas lime pretreatment plus SSCF gave place to a higher ethanol yield of 223.2 g/kg of oat straw.

BARLEY STRAW

Barley is another relevant crop with a large generation of straw. 1 tonne of barley grains generates approximately 0.76 tonne of straw (Han, et al., 2013). Barley straw has an average composition of 35-40% cellulose, 20-30% hemicellulose and 8-15% lignin. The high carbohydrates content and the abundant availability are the reasons why this biowaste has been assessed for the production of 2G bioethanol.

Different routes with different ethanol yields have been reported in literature. Saha & Cotta (Saha & Cotta, 2010) compared the release of sugars and the final ethanol yields achieved for different pretreatment methods. Alkaline peroxide pretreatment led to the highest hydrolysis efficiency (604 mg of fermentable sugars/g of barley straw) and the highest ethanol yield (0.27 g ethanol/g of barley straw). Dilute acid pretreatment and lime pretreatment resulted in lower sugars released (566 mg/g and 582 mg/g respectively) but similar ethanol yield (0.26 g/g of barley straw for both of them).

Han et al. (Han, et al., 2013) reported a final ethanol yield of 0.144 g/g of barley straw and 76.56% glucose recovery when applying a sodium hydroxide continuous pretreatment in a twin-screw extruder. By means of a twin-screw extruder, but combining alkali and enzyme-extrusion pretreatment, Duque et al. (Duque, et al., 2020) reported a final ethanol yield of 0.158 g/g of barley straw after liquefaction plus simultaneous saccharification and co-fermentation (LSSCF) with modified *S. cerevisiae* strain.

Valorization of lignin by the preparation of adsorbing lignin-based bio-composite using ultrasound-assisted pretreatment for lignin extraction from barley straw has been successfully assessed as a possibility to reduce overall cost of bioethanol production process (Mohammadabadi & Javanbakht, 2020).

RYE STRAW

Rye is another crop widely cultivated around the world, especially in European countries. During harvesting of rye large amounts of straw are generated (Smuga-Kogut, et al., 2017). 1 tonne of rye generates around 0.5-2 tonnes of straw (Domanski, et al., 2016). Rye straw has an average composition of 37% cellulose, 40% hemicellulose and 22% lignin (Smuga-Kogut, et al., 2017), which is why it might be considered as a potential feedstock for 2G bioethanol production.

There are many studies about possibilities of pretreatment for rye straw to enhance sugars reduction during saccharification or to efficiently isolate and recover some fractions from this biomass such as the lignin fraction (Ingrama, et al., 2009; Ingram, et al., 2011; Mikulski & Kłosowski, 2020; Perez-Cantu, et al., 2013; Wörmeyer, et al., 2011). However, there are just a few publications where final ethanol yields on native rye straw basis are reported.

Franceschin et al. (Franceschin, et al., 2011) used a simulation program to assess co-production of bioethanol and xylitol from hot water pretreated rye straw by fermentation of glucose fraction to bioethanol and the xylose fraction to xylitol, which is a valuable product with applications as sweetener, oral health and caries prevention. Assuming average composition of rye straw and considering reported yields for pretreatments, hydrolysis and fermentation, a final ethanol yield of 177.86 g of ethanol per kg of rye straw was achieved in this simulation. It should be noted that only hexoses were fermented to bioethanol, which means that higher ethanol yields might be obtained if both pentoses and hexoses were used.

COFFEE RESIDUES

Coffee is the second most consumed drink in the world, just after water, and one of the most marketed products. During wet-processing of the coffee, some residues are generated including silver skin, parchment, mucilage, pulp and pericarp. These residues represent more than 50% of coffee fruit (Orrego, et al., 2018). Mucilage and pulp are the most abundant waste generated, representing 11.8% and 43.2% of the waste fraction from wet-processing (Orrego, et al., 2018).

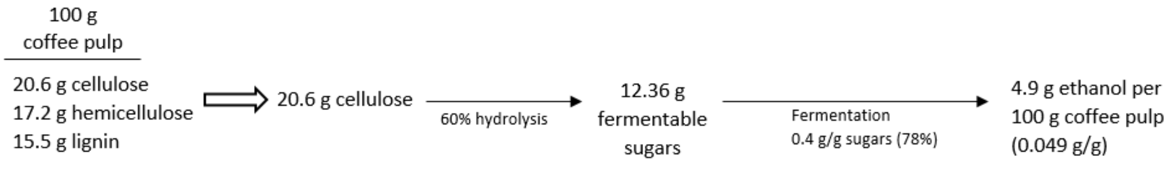
Mucilage represents approximately 22% of the grain wet weight (Orrego, et al., 2018), and it is made of 85-91% of water and 6.2-7.4% of sugars, of which 63% are simple sugars directly fermentable into ethanol (Orrego, et al., 2018).

Pulp is the main residue generated during coffee wet-processing. It represents between 40-42% of the overall weight of coffee fruit (Phuong, et al., 2019; Gurram, et al., 2016). Pulp can be used as fertilizer or as fuel by direct combustion, but given the large amount of pulp generated, there is a need to find alternative valorization pathways for this waste (Menezes, et al., 2013; Woldesenbet, et al., 2016; Gurram, et al., 2016). Furthermore, pulp use as feed is limited by its caffeine and tannins content (Gurram, et al., 2016). Average composition of coffee pulp is 25.88% cellulose, 3.6% hemicellulose and 20.07% lignin (Phuong, et al., 2019), which is why it has been considered as a potential raw material for 2G bioethanol production.

Many studies have assessed the suitability of these residues for bioethanol production. Some of them have used mucilage or pulp coffee separately as feedstock, whereas some others have considered the possibility of using all the coffee residues together as raw material.

Main advantage of mucilage is that it doesn’t need pretreatment or hydrolysis since it can be directly converted into ethanol. By means of sequential batch fermentation, an ethanol yield of 0.33 g per g of mucilage substrate was reported by Orrego et al. (Orrego, et al., 2018).

Menezes et al. (Menezes, et al., 2014) assessed the conversion of the pulp into ethanol by means of alkaline pretreatment prior to enzymatic hydrolysis and fermentation. 60% of cellulose to glucose conversion and 0.4 g of ethanol/g of glucose were achieved. Taking into account the composition of the feedstock used (20.6% cellulose, 17.2% hemicellulose and 15.5% lignin), the final ethanol yield on native feedstock basis can be estimated:



Gurram et al. (Gurram, et al., 2016) carried out a simulation of a process consisting on dilute acid pretreatment, enzymatic hydrolysis and fermentation with S. cerevisiae of coffee pulp using AspenPlus. Considering the composition of the feedstock, a final ethanol yield of 0.105 kg per kg of coffee pulp was obtained.

The possibility of using all the coffee residue waste together as feedstock for bioethanol production was studied by Choi et al. (Choi, et al., 2012). Popping pretreatment was used for delignification and hemicellulose removal. Hydrolysis efficiency of 85.6% and fermentation efficiency of 87.2% were achieved by SSF, leading to an ethanol yield of 0.153 g/g of dried biomass. It should be noted that the coffee residue had 74% moisture content.

Using all the coffee residues together for the production of 2G bioethanol has been successfully proved by means of Lice Cycle Assessment to be a sustainable approach in terms of economy, environment and social impact (Anon., 2021).

OLIVE POMACE

During olive oil production process, two fractions are generated apart from the olive oil itself: aqueous phase known as olive mill wastewater, and olive mill solid waste, commonly known as pomace (Miranda, et al., 2019). 1 tonne of olive oil production generates about 0.6 tonne of olive mill solid waste (Tayeh, et al., 2020). This solid waste includes pulp, peel and crushed olive stones (Padilla-Rascón, et al., 2020). It has 50% of moisture content and 3% of oil content, with 35.3-49% polysaccharides and 30-41.6% lignin (Miranda, et al., 2019). Main component of the pomace is olive stones. Olive stones represent approximately 10% of olive weight (Padilla-Rascón, et al., 2020), and they have a composition of 20.1-40.4% cellulose, 18.5-32.5% hemicellulose and 25.3-48.8% lignin. Olive pomace can be used for composting, feeding or methane production (Tayeh, et al., 2020), whereas olive stones are mostly used as fuel given their high heating value (Padilla-Rascón, et al., 2020), but taking into account the content of carbohydrates, they are also considered as a potential feedstock for 2G bioethanol production.

Olive stones are usually separated from pulp for the extraction of pomace oil, but both stones and solid biomass from pomace waste can be used together for bioethanol production (Miranda, et al., 2019). Some studies have assessed the possibility of bioethanol production from olive pomace with and without olive stones and also from olive stones separated from the rest of the solid wastes.

Tayeh et al. (Tayeh, et al., 2020) used olive mill solid waste without olive stones particles, which were previously removed, for bioethanol production. Applying microwave pretreatment prior to enzymatic saccharification and fermentation a final yield of 91 g of ethanol per kg of olive mill solid waste was achieved.

Conversion of olive stones into ethanol was evaluated by Cuevas et al. (Cuevas, et al., 2015). By means of liquid hot water pretreatment plus dilute sulfuric acid and organoslov delignification prior to SSF, resulted in a maximum ethanol yield of 130 g per kg of olive stones.

Miranda et al. (Miranda, et al., 2019) studied the valorization of both olive pomace and olive stones together. Mild hydrothermal treatment and enzymatic hydrolysis led to a glucose yield of 67 g per kg of dry feedstock. This value is lower than sugars yield reported for separated olive stones. By means of sequential acid hydrolysis and seam explosion, 83% of sugars contained in olive stones biomass were recovered during enzymatic hydrolysis by Padilla-Rascón et al. (Padilla-Rascón, et al., 2020). This highlights the need to investigate on valorization of olive pomace and olive stone biomass together as feedstock.

OLIVE TREE PRUNING BIOMASS

Olive tree biomass is an agricultural waste generated when unproductive branches are removed to enhance olive tree cultivation (Martínez-Patiño, et al., 2017). This waste is mostly burned or landfilled. Up to 3 tonnes per hectare of olive trees cultivated can be generated when the pruning takes place, which is every two years (Negro, et al., 2014; Martínez-Patiño, et al., 2015). As other agricultural waste, this is a lignocellulosic biomass that can be used as feedstock for bioethanol production.

Different ethanol yields have been reported by means of different routes. In all cases, water extraction is necessary before pretreatment. Sequential dilute acid plus alkaline pretreatment followed by SSF with *S. cerevisiae* gave place to 150 g ethanol per kg of raw olive tree biomass (Martínez-Patiño, et al., 2017). Steam explosion pretreatment, using phosphoric acid catalyst, in addition to SSF *S. cerevisiae* for glucose rich fraction and fermentation with *S. stipites* for xylose rich fraction resulted in a final ethanol yield of 160 g per kg of water extracted olive tree biomass (Negro, et al., 2014). It should be noted that extracted olive tree biomass represents approximately 80% of the raw olive tree biomass (Oliva, et al., 2020). This means that the ethanol yield on native feedstock basis would be 128 g/kg. By means of dilute acid pretreatment and fermentation with *E. coli* an ethanol yield of 132 g per kg of raw material was achieved (Martínez-Patiño, et al., 2015). Acid-catalyzed steam explosion plus detoxification to overcome inhibitory effects prior to fed-batch fermentation with recombinant *S. cerevisiae* F12 led to a final ethanol yield of 180 g per kg of water extracted olive tree biomass (Oliva, et al., 2020). Again, assuming that extracted olive tree biomass represents approximately 80% of raw waste, ethanol yield on raw biomass basis would be 144 g/kg.

SWEET SORGHUM BAGASSE

Sweet sorghum bagasse is the solid residue that remains after juice extraction from the sweet sorghum (Thanapimmetha, et al., 2019). Bagasse represents approximately 50-60% of sweet sorghum (Tinôco, et al., 2021). Between 20-28 tonnes of bagasse are generated per hectare of sweet sorghum cultivated (Tinôco, et al., 2021). This biowaste is widely available since sweet sorghum can grow twice a year instead of just once as the cases of other similar crops such as sugarcane (Tinôco, et al., 2021). Also, sweet sorghum is able to grow in nutrient-poor soils (Marx, et al., 2014; Cao, et al., 2012). Lignocellulose content of this waste makes it suitable as feedstock for 2G bioethanol production.

Cao et al. (Cao, et al., 2012) compared different possibilities of pretreatment for sweet sorghum bagasse, including dilute NaOH solution autoclaving pretreatment, high concentration NaOH solution immersing pretreatment, dilute NaOH solution autoclaving plus H_2O_2 immersing pretreatment, alkaline peroxide pretreatment and autoclaving pretreatment. Dilute NaOH solution autoclaving plus H_2O_2 immersing pretreatment proved to be the most suitable pretreatment for sweet sorghum bagasse, achieving the highest hydrolysis yield (74.29 % and 90.94 g total sugars/100 g dry matter).

Thanapimmetha et al. (Thanapimmetha, et al., 2019) compared three different routes for bioethanol production from hydrogen peroxide-NaOH pretreated sweet sorghum bagasse. The three routes analyzed were SHF, SSF and delayed SSF, where pretreated bagasse was first enzymatically hydrolyzed and then the yeast was added for the fermentation. *S. cerevisiae* TISTR 5606 was used in all cases. Delayed SSF proved to be the most efficient method, presenting a 26% higher productivity than SSF and SHF.

By means of acid-base pretreatment and fermentation with *K. marxianus* CCT7735, Tinôco et al. (Tinôco, et al., 2021) reported a final ethanol yield of 90.358 g per kg of bagasse. In this study, just the glucose fraction was used for the bioethanol production. Marx et al. (Marx, et al., 2014) reported a yield of 198.8 g of ethanol per kg of bagasse (0.252 m^3/tonne of bagasse) by means of simultaneous pretreatment and hydrolysis with microwave irradiation prior to fermentation with *Z. mobilis* and *S. cerevisiae* for the conversion of both pentoses and hexoses. Barcelos et al. (Barcelos, et al., 2016) achieved a yield of 194.88 g ethanol per kg of bagasse (247 L/tonne of bagasse) by applying sequential acid and alkali pretreatment prior to SSF with *S. cerevisiae*, again fermenting both pentoses and hexoses.

In order to reduce the cost of the overall process, co-production of ethanol, butanol and acetone from sweet sorghum bagasse was studied by Su et al. (Su, et al., 2020). The route proposed consists on alkali pretreatment prior to fed-batch enzymatic hydrolysis and batch ethanol fermentation with S. cerevisiae. Then the unfermented xylose fraction is separated from the ethanol produced by means of vacuum distillation and fermented by *Clostridium acetobutylicum*, giving place to acetone, butanol and ethanol (ABE fermentation). Final yields obtained were 144.8 g of ethanol per kg of bagasse, 17.3 g of butanol/kg of bagasse and 4.8 g of acetone/kg of bagasse.

<u>*AGRO-FOOD WASTE*</u>

Large amounts of food are discarded during harvesting or industrial processing due to different reasons related with minimum quality requirements, such as inappropriate size, damaging during harvesting or injuries provoked by pests and insects. For instance, in the case of potato, which is one of the largest food crop in the world, up to 30% of potatoes are discarded because of these reasons. Apart from discarded food, peels and other waste are also generated during industrial processing, accounting for an important fraction of the total food biomass. Up to 40% of potato mass is lost during peels removal. (Torres, et al., 2020)

The case of potato is especially interesting because of its high content in carbohydrates and its abundant availability. Some approaches have assessed the potential ethanol yield for potato biomass, potato peels and sweet potato, which has a similar composition to potato.

Wang et al. (Wang, et al., 2020) predicted the ethanol yield of sweet potato based on dry matter content of 29 different varieties of sweet potato, for a route that consisted on pretreatment plus liquefaction prior to SSF. Ethanol yields ranged from 81.6 to 147.6 g ethanol per kg of dry sweet potato.

Potato peels were used as feedstock for bioethanol production by Chohan et al. (Chohan, et al., 2020). By means of soaking assisted thermal pretreatment in addition to liquefaction process and SSF with *S. cerevisiae* BY4743 a yield of 320 g ethanol per kg of substrate was achieved.

However, it is not clearly specified if this yield was calculated on native feedstock basis or per kg of fermentable sugars.

Potato starch as feedstock for bioethanol production was studied by Liu & Lien (Liu & Lien, 2016). By means of SSF with *Z. mobilis* in a vertical mass-flow type reactor, an ethanol yield of 370 g/kg of raw starch was obtained. Considering that average starch content in potato ranges between 15-18% (w/w %) (Choi, et al., 2020), the ethanol yield on potato feedstock basis would be between 55.5-66.6 g/kg.

Fruits are another kind of discarded food with potential to be used as feedstock for bioethanol production. Most of fruits are sugar-based or starchy biomass. Due to the reasons already mentioned above, large amounts of fruits are also discarded during harvesting and industrial processing. Potential ethanol yields have been reported by different authors for some fruit waste.

Dates are sugar-based fruits suitable for bioethanol production. Around 10-50% of produced dates are wasted, and their sugar content ranges between 72-88% in dry basis, including glucose, fructose, sucrose and other fibers (Taghizadeh-Alisaraei, et al., 2019). Assuming 63% of extractable sugars and a fermentation yield of 40-48%, Taghizadeh-Alisaraei et al. (Taghizadeh-Alisaraei, et al., 2019) estimated an ethanol yield of approximately 300 g/kg of dates waste.

Grapes are another sugar-based fruit with potential for bioethanol production. Grapes are one of the major fruit crop in the world, and most of it is used for wine or juice production. During wine or juice production process, grape pomace is generated as waste, representing 25% of the weight of the grapes (Sirohi, et al., 2020). This waste contains between 15-33% of fermentable sugars and between 19-38% of fibers (Sirohi, et al., 2020). Fermentation of this waste might produce up to 213 g of ethanol per kg of grape pomace according to Sirohi et al (Sirohi, et al., 2020).

The fact that this kind of organic waste is not mixed with any other organic or inorganic matter, as it happens with municipal food waste, makes it possible to ensure an efficient characterization of the waste and hence an easier valorisation, with many different routes available, which might be the reason why its potential as possible feedstock for 2G bioethanol production hasn’t been as studied as for other kind of biowaste with no possibility of valorisation apart from bioethanol production.

It seems evident that the potential of agricultural waste to be converted into bioethanol has been widely studied. Many different approaches have been purposed and very promising results in terms of ethanol yield have been achieved for all kind of agricultural waste by means of different pretreatments and conversion techniques.

3.2- Municipal solid waste

ORGANIC FRACTION OF MSW

Municipal solid waste (MSW) generation has grown widely over the years due to the increase of global population. The design of a sustainable municipal solid waste management (MSWM) scheme is one of the main challenges in present-day cities all around the world (Heidari, et al., 2019). Currently, most of MSW is landfilled or incinerated, contributing negatively to global warming (Cremiato, et al., 2018).

The organic fraction of MSW (OFMSW) contains mostly food waste along with garden waste. The exact composition of OFMSW is influenced by different factors such as the collecting methods, the geographical location, the weather conditions or the culture and economic development of the society (Mahmoodi, et al., 2018; Barampouti, et al., 2019). The heterogeneous nature of this biowaste is what makes it challenging to be used as feedstock for bioethanol production at large scale (Moreno, et al., 2021).

Approximately 46 % of total municipal waste is organic matter, containing mostly carbohydrates with potential to be converted into ethanol (Yaashikaa, et al., 2020). Using municipal solid waste as feedstock for 2G bioethanol production is an opportunity to give a circular economy solution to MSWM. One of the main drawbacks for this route is the high costs of this technology. However, different approaches have been suggested for cost reduction, like the co-generation of methane, biogas and biodiesel by simultaneously valorising the lipids content present in the organic matter along with non-fermentable carbohydrates (Barampouti, et al., 2019) (Figure 15).

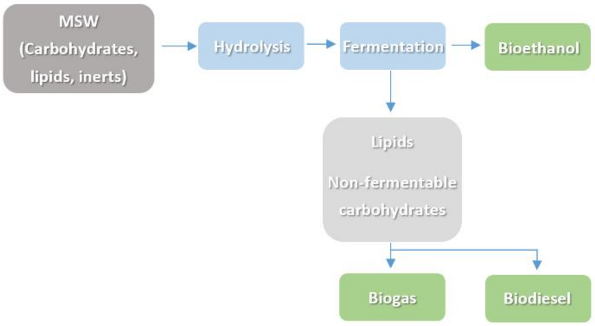


Figure 15: Scheme of possible route for bioethanol, biodiesel and biogas production from MSW

One of the main factors affecting the OFMSW composition is the collecting method used. Collecting methods can be separated into 2 main groups: source sorted collection (SS-OFMSW) and non-sorted collection (NS-OFMSW) (Moreno, et al., 2021; Barampouti, et al., 2019). In the sorted collection, organic fraction includes food waste and garden waste. Food waste generation is typically higher than garden waste generation (Moreno, et al., 2021). Non-sorted collection is separated after collection by means of mechanical sorting.

Regardless of the collection method or the origin of the OFMSW, it can be observed that glucans (starch, celluloses and other glucose polymers) are the main component of this biowaste, which make it suitable for 2G bioethanol production. Barampouti et al. (Barampouti, et al., 2019) compiled different reported composition analysis from different places all around the world, including 28 cities and 13 countries, and by means of different collecting methods. Reported results show that approximately 50% of OFMSW are carbohydrates (32.2-68.2%). Proteins (6.8-25.8%) and fats and oils (5.6-24.7%) were also present in the organic matter. Starch seems to be the main compound of OFMSW (20.2 ± 13.9 %), followed by cellulose (15.2 ± 14.6 %), free sugars (10.6 ± 6 %), lignin (9.1 ± 6.6 %) and hemicellulose (7.4 ± 4.6 %).

The influence of collecting method can be observed on the experiment carried out by Moreno et al. (Moreno, et al., 2021), where 8 source sorted collected samples and 8 non-sorted collected samples were analyzed. In other to avoid the influence of the other factors already mentioned, the samples were taken from different cities from both north and south of Europe (UK and Spain) and during the 4 seasons of the year. A content of total glucans between 33.9-61.3% was reported for SS-OFMSW and between 26.4-33.6 % for NS-OFMSW. Starch content was between 25.5-43.1% for SS-OFMSW and between 5.8-16.7 % for NS-OFMSW. For both collecting methods, glucans where the main component, but it can be observed that higher amount of glucans is present on SS-OFMSW, and that the starch/other glucans ratio (other glucans includes cellulose and other glucose polymers) is also higher for SS-OFMSW. It might be due to the more efficient separation in SS-OFMSW than in NS-OFMSW, which would lead to a higher presence of food waste (mostly starch-based biomass) within the sorted collected waste and to the presence of more inert materials, such as metal, glass or plastics, within the non-sorted collected waste. The analyzed samples were used for bioethanol production by means of non-isothermal simultaneous saccharification and fermentation. *S. cerevisiae* was used for fermentation. A glucose yield between 45-82% and a fermentation yield up to 80% were obtained for SS-OFMSW. For NS-OFMSW, a glucose yield between 43-56 % and a fermentation yield up to 59% were achieved. The higher glucose yield on SS-OFMSW is due to the higher presence of starch, which is easier to hydrolyze than cellulose (Moreno, et al., 2021). Taking into account the total glucans content, the glucose yield, the fermentation efficiency and the theoretical glucose-to-ethanol conversion (51% (Hamelinck, et al., 2005)), the overall ethanol yield (g ethanol/g dried OFMSW) can be calculated as:

SS-OFMSW: (33.9-61.3) % x (45-82) % x 80 % x 51 % = 6-20.5 % = **0.06-0.205 g/g**

NS-OFMSW: (26.4-33.6) % x (43-56) % x 59 % x 51 % = 3.4-5.66 % = **0.034-0.0566 g/g**

It should be noted that no pretreatments were used apart from mechanical sorting and size reduction. It has been proved that the global efficiency of the process can be improved if the OFMSW is pretreated with thermal and chemical methods (Mahmoodi, et al., 2018). Mahmoodi et al. (Mahmoodi, et al., 2018) studied 2G bioethanol production by means of hydrothermal pretreatment from OFMSW collected in Isfahan (Iran). It is not specified if the waste was source sorted or non-sorted, but taking into account the lack of recycling and sorting in general municipal waste management in Iran (Rupani, et al., 2019), it can be assumed as NS-OFMSW. The OFMSW was mechanically sorted prior to hydrothermal pretreatment. The sorted and dried

OFMSW contained 56.51% starch and 20.5% lignocellulose. By means of hydrothermal pretreatment, lignin content was reduced and a solid fraction, rich in cellulose and hemicellulose, and a liquid fraction rich in starch were obtained. It should be noted that depending on the starch/cellulose ratio of the waste, different kinds of enzymes, focused on starch hydrolysis or cellulose hydrolysis, should be used. In this case, hydrolysis of starch and cellulose were performed separately, with a high overall glucose yield of 520 g glucose per kg of dry OFMSW. *Mucor indicus* was used for fermentation of the starchy and cellulose hydrolysates, with a final ethanol yield of 191.10 g ethanol per kg of dry biowaste. A similar experiment was performed using dilute acid pretreatment instead of hydrothermal (Mahmoodi, et al., 2018). A similar final yield of 194 g ethanol per kg of dry biomass was obtained.

In all the mentioned studies, residues from fermentation, consisting mainly on lipids, proteins and non-fermented carbohydrates, were converted into biogas, showing high methane yields (Mahmoodi, et al., 2018; Moreno, et al., 2021).

When food waste coming directly from restaurants, households or kitchens is used instead of OFMSW, higher ethanol yields are achieved (Karmee, 2016). That means that a more efficient sorting when collecting OFMSW would lead to higher content of food waste and hence higher ethanol yields.

PAPER FRACTION

Another municipal waste with potential to be used as feedstock for 2G bioethanol production is paper waste.

There are 2 possible sources for paper waste as feedstock: paper waste sludge coming from recycling plants and virgin paper production plants, and paper waste from paper fraction of MSW such as newspapers or office paper waste (Figure 16).

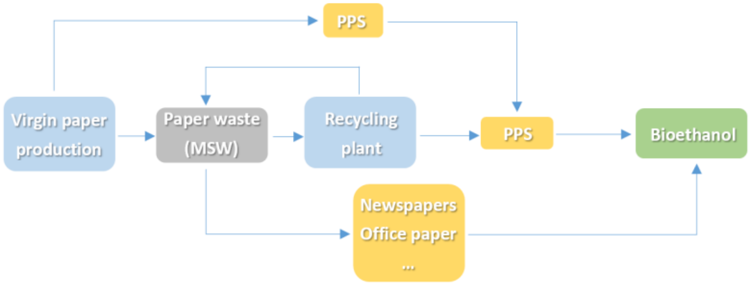


Figure 16: Possibilities for 2G bioethanol production from paper waste

Pulp and paper sludge (PPS) is a rich cellulosic material, with a 40% of carbohydrates content (Dey, et al., 2021). It is estimated that 1 tonne of paper production generates 300 kg of industrial paper waste and 50 kg of primary sludge. These wastes are mostly landfilled or incinerated, contributing to ground water contamination, soil degradation and methane emissions. Approximately 2.69 tonnes of equivalent CO_2 are released per tonne of paper sludge landfilled (Alkasrawi, et al., 2021).

By means of sequential pretreatment of steam explosion and sodium hydroxide treatment prior to semi-simultaneous saccharification and fermentation, a maximum overall ethanol yield of 240 g ethanol per kg of paper sludge was achieved by Dey et al. (Dey, et al., 2021). The PPS was collected from a recycling plant in India, with a composition of 41.2% cellulose, 27.6% hemicellulose and 18.5% lignin.

Fiber separation from contaminants, mostly fillers and additives, is a key process to achieve high ethanol yields. One of the issues of fiber separation is the large amount of waste water generated. In-situ fiber recovery instead of mechanical or chemical recovery has been reported to achieve higher ethanol yields and to reduce substantially the waste-water generation. A yield of 0.53 g ethanol per g of glucose was obtained by using in-situ recovery whereas 0.16 g/g and 0.23 g/g were obtained for mechanical and chemical recovery respectively. (Alkasrawi, et al., 2021)

The other source of paper waste available for bioethanol production is the paper fraction from urban waste. Around 35-40% of MSW consists on paper waste (Byadgi & Kalburgi, 2016). Bioethanol production might be a suitable complementary alternative for recycling since not all paper waste can be recycled. Large amounts of paper are discarded because of paper quality specifications (Wang, et al., 2013). Also, if paper has been mixed with organic matter, it is quite difficult to recycle it, so mechanically sorted paper from NS-MSW would be a good feedstock (Wang, et al., 2013).

Already recycled paper has special interest for bioethanol production. Recycled paper waste is usually too degraded for further recycling. Furthermore, it doesn't require severe pretreatment, since delignification takes place during pulping process. (Wu, et al., 2014)

Diverse paper waste typically present in MSW, such as newspapers, magazines, office paper or cardboards, has been tested for bioethanol production. Saini et al. (Saini, et al., 2020) reported a yield of 125 g ethanol per kg of paper waste for newspapers, 155 g/kg for examination papers and 168 g/kg for laser printed papers, by using different deinking treatments, including cellulose, laccase, ozone and chemical treatment. Wu et al. (Wu, et al., 2014) achieved a yield of 286 g ethanol per kg of newspaper waste (with 9% of moisture) by means of alkali pretreatment and sequential acid and enzymatic hydrolysis in situ for saccharification. Wang et al. (Wang, et al., 2013) reported a yield of 228.8 g ethanol per kg of newspaper lime pretreated waste, 330.6 g/kg of office paper dilute acid pretreated waste, 107.3 g/kg of magazine waste and 195 g/kg of cardboard waste, all of them in dry basis.

3.3- Other waste

WOODY BIOMASS:

Wood waste biomass is generated from forest harvesting and from construction and demolitions. Woody biomass is typically divided in two types of wood: softwood and hardwood. Gymnosperms or evergreen trees such as pines or spruces are considered as softwood, whereas angiosperms or deciduous trees such as poplars or birches are considered as hardwood (Bay, et al., 2020).

Most of wood waste is burned for energy production. In Europe, in 2018, 47 million tonnes were generated (European Commission, 2021), of which 21.37 million tonnes were combusted for energy production (45.5%), 19.82 million tonnes were recycled (42%) and 0.36 million tonnes were incinerated or landfilled (0.77%) (European Commission, 2021). Combustion is a suitable option for valorization although it also has some drawbacks such as soil, air and water contamination by wood ash (Pettersson, et al., 2020). Given the lignocellulosic nature of this biomass in addition to its wide availability and low cost, it might be also considered as a potential feedstock for 2G bioethanol production.

Buzala et al. (Buzała, et al., 2017) studied the suitability of 7 different species of wood as feedstock for bioethanol production, including both softwoods and hardwoods. The production route consisted on cellulosic pulps preparation, enzymatic hydrolysis and fermentation with S. cerevisiae. The 5 hardwood species analyzed resulted in similar final ethanol yields, ranging from 0.11 to 0.14 g ethanol/g of dry wood. Softwoods analyzed were bleached and unbleached pine. Bleached pine gave place to an ethanol yield of 0.2 g/g of dry wood, whereas by using unbleached pine as feedstock, a low yield of 0.02 g ethanol/ g of dry wood was obtained.

NaOH and Na_2CO_3 alkaline pretreatments were compared for the conversion of softwood (pine) and hardwood (poplar) biomass into ethanol by means of enzymatic hydrolysis and SSF by Bay et al. (Bay, et al., 2020). NaOH pretreatment was observed to enhance ethanol yield by 297.5% and 249.5% for softwood and hardwood respectively compared to the non-pretreated biomass. The maximum ethanol yields achieved were 109.83 and 101.44 g/kg of initial wood, applying NaOH alkaline pretreatment in both cases.

Boboescu et al. (Boboescu, et al., 2018) assessed the possibility of using softwood along with construction and demolition woody biomass for 2G bioethanol production. The woody feedstock (80% of softwood and 20% of construction and demolition waste) was pretreated by steam explosion and fermented with S. cerevisiae, resulting in a maximum ethanol yield of 81.24%. The potential of this kind of feedstock for bioethanol production was successfully proved, although no ethanol yields on native feedstock basis were reported.

3.4- Summary of yields reported

Table 1: Compilation of ethanol yields reported in literature for different biowaste presented in this work.

Waste	Process	Yield (g bioethanol/g feedstock)	Reference
SUGARCANE TRASH (STRAW)	Screening of transition metals for crude glycerol assisted pretreatment	0.31 g/g * (dried feedstock)	(Raghavi, et al., 2016)
SUGARCANE BAGASSE	Imidazole-based pretreatment	0.172 g/g	(Valladares-Diestra, et al., 2020)
	Dilute nitric-acid pretreatment	0.14 g/g *	(Santosh, et al., 2017)
	Alkaline hydrogen peroxide pretreatment		(Niju & Swathika, 2019)
	Steam explosion and acid hydrolysis pretreatment		(Bernier-Oviedo, et al., 2018)
	Auto-hydrolysis hydrothermal pretreatment		(Zhang, et al., 2020)
CORN STOVER	Sequential steam explosion and alkaline pretreatment + SSF	0.199 g/g	(Molaverdi, et al., 2021)
	Dilute acid hydrolysis pretreatment + fermentation with *M. indicus* + conversion of lipids	0.214 g/g (0.022 g biodiesel/g)	(Alavijeh, et al., 2020)
	Sulphuric acid pretreatment + alkali pretreatment	0.096 g/g (0.04 g furfural/g)	(Li, et al., 2020)
RICE STRAW	Sodium carbonate pretreatment + DSSF	0.153 g/g	(Molaverdi, et al., 2019)
RICE HULLS	Dilute acid pretreatment	0.11 g/g	(Dagnino, et al., 2013)
	Alkaline peroxide pretreatment + SHF with *E.coli*	0.21 g/g	(Saha & Cotta, 2007)
	Alkaline peroxide pretreatment + SSF with *E.coli*	0.20 g/g	
	Extrusion + ultrasound pretreatment	0.136-0.155 g/g *	(Zhang, et al., 2020)
COTTON STALKS	Physicochemical pretreatment based on microwave assisted $FeCl_3$	0.158 g/g *	(Singh, et al., 2017)
	Sequential steam explosion and dilute acid pretreatment	0.193 g/g *	(Keshav, et al., 2018)
	Sequential steam explosion and alkali extraction	0.17 g/g *	(Keshav, et al., 2016)
	Hot water pretreatment	0.16 g/g	(Jiang, et al., 2015)

Waste	Process	Yield (g bioethanol/g feedstock)	Reference
WHEAT STRAW	Phosphoric acid plus hydrogen peroxide pretreatment + SSF	0.155 g/g	(Qiu, et al., 2018)
	Alkaline pre-extraction of silica followed by alkaline-hydrogen peroxide pretreatment	0.311 g/g (0.104 g lignin/g) (0.047 g silica/g)	(Yuan, et al., 2018)
OAT STRAW	Steam explosion pretreatment + fermentation with *S. cerevisiae* J672	0.15 g/g (dried feedstock)	(Dererie, et al., 2011)
	Sequential steam explosion-dilute sulfuric acid impregnation pretreatment + fermentation with *S. cerevisiae* J672	0.115 g/g (dried feedstock)	
	Lime pretreatment + fermentation with *S. cerevisiae* J672	0. 085 g/g (dried feedstock)	
	Sequential auto-hydrolysis and lime pretreatment + SSF	0.159 g/g	(Romaní, et al., 2016)
	Lime pretreatment + SSCF	0.223 g/g	
BARLEY STRAW	Alkaline peroxide pretreatment	0.27 g/g	(Saha & Cotta, 2010)
	Dilute acid pretreatment	0.26 g/g	
	Lime pretreatment	0.26 g/g	
	Sodium hydroxide continuous pretreatment in a twin-screw extruder	0.144 g/g	(Han, et al., 2013)
	Alkali and enzyme-extrusion pretreatment in a twin-screw extruder + LSSCF	0.158 g/g	(Duque, et al., 2020)
RYE STRAW	Hot water pretreatment	0.178 g/g	(Franceschin, et al., 2011)
COFFEE RESIDUES	Sequential batch fermentation	0.33 g/g (mucilage)	(Orrego, et al., 2018)
	Alkaline pretreatment	0.049 g/g * (pulp)	(Menezes, et al., 2014)
	Dilute acid pretreatment	0.105 g/g (pulp)	(Gurram, et al., 2016)
	Popping pretreatment	0.153 g/g	(Choi, et al., 2012)
OLIVE POMACE	Microwave pretreatment	0.091 g/g (without stones)	(Tayeh, et al., 2020)
	Liquid hot water pretreatment + dilute sulfuric acid and Organoslov delignification + SSF	0.130 g/g (olive stones)	(Cuevas, et al., 2015)
OLIVE TREE PRUNING BIOMASS	Sequential dilute acid + alkaline pretreatment + SSF	0.15 g/g	(Martínez-Patiño, et al., 2017)
	Steam explosion pretreatment using phosphoric acid catalyst + SSF with *S. cerevisiae* and *S. stipites*	0.128 g/g (0.16 g/g (water extracted))	(Negro, et al., 2014)

Waste	Process	Yield (g bioethanol/g feedstock)	Reference
	Dilute acid pretreatment + fermentation with *E. coli*	0.132 g/g	(Martínez-Patiño, et al., 2015)
	Acid-catalyzed steam explosion + fed-batch fermentation with recombinant *S. cerevisia*e F12	0.144 g/g (0.18 g/g (water extracted))	(Oliva, et al., 2020)
SWEET SORGHUM BAGASSE	Acid-base pretreatment + fermentation with *K. marxianus* CCT7735	0.09 g/g	(Tinôco, et al., 2021)
	Simultaneous pretreatment and hydrolysis with microwave irradiation + fermentation with *Z. mobilis* and *S. cerevisiae*	0.199 g/g	(Marx, et al., 2014)
	Sequential acid and alkali pretreatment + SSF	0.195 g/g	(Barcelos, et al., 2016)
	Alkali pretreatment + fed-batch enzymatic hydrolysis + batch ethanol fermentation + fermentation with *Clostridium acetobutylicum*	0.145 g/g (0.017 g butanol/g) (0.005 g acetone/g)	(Su, et al., 2020)
AGRO-FOOD WASTE	Pretreatment + liquefaction + SSF	0.082-0.148 g/g (sweet potato)	(Wang, et al., 2020)
	Soaking assisted thermal pretreatment + liquefaction + SSF with *S. cerevisiae* BY4743	0.32 g/g (potato peels)	(Chohan, et al., 2020)
	SSF with *Z. mobilis* in a vertical mass-flow type reactor	0.055-0.066 g/g * (potato)	(Liu & Lien, 2016)
	-	0.30 g/g (dates)	(Taghizadeh-Alisaraei, et al., 2019)
	-	0.213 g/g (grape pomace)	(Sirohi, et al., 2020)
ORGANIC FRACTION OF MSW	Non-isothermal SSF	0.06-0.205 g/g * (source-sorted)	(Moreno, et al., 2021)
		0.034-0.0566 g/g * (non-sorted)	
	Dilute acid pretreatment + fermentation with *Mucor indicus*	0.191 g/g (dried waste)	(Mahmoodi, et al., 2018)
	Hydrothermal pretreatment + fermentation with *Mucor indicus*	0.194 g/g (dried waste)	(Mahmoodi, et al., 2018)
PAPER FRACTION	Steam explosion and sodium hydroxide sequential pretreatment + semi-SSF	0.24 g/g (paper sludge)	(Dey, et al., 2021)
	Deinking pretreatments	0.125 g/g (newspapers)	(Saini, et al., 2020)
		0.165 g/g (examination papers)	
		0.158 g/g (laser printed papers)	

Waste	Process	Yield (g bioethanol/g feedstock)	Reference
	Alkali pretreatment + sequential acid and enzymatic hydrolysis in situ	0.286 g/g (newspapers)	(Wu, et al., 2014)
	Lime pretreatment	0.229 g/g (dry newspapers)	(Wang, et al., 2013)
	Dilute acid pretreatment	0.331 g/g (dry office paper)	
	-	0.107 g/g (magazine waste)	
	-	0.195 g/g (cardboard waste)	
WOODY BIOMASS	Cellulosic pulps preparation + enzymatic hydrolysis + fermentation	0.11-0.14 g/g (dry hardwood)	(Buzała, et al., 2017)
		0.2 g/g (dry bleached softwood)	
		0.02 g/g (dry unbleached softwood)	
	NaOH alkaline pretreatment + SSF	0.11 g/g (softwood)	(Bay, et al., 2020)
		0.101 g/g (hardwood)	

** These ethanol yields have been calculated using yields and results appearing on respective reports, so they don't appear on the reference mentioned.*

Looking at the table above, it can be observed that straw shows the best results in terms of ethanol conversion, concretely wheat and sugarcane straw (0.31 g/g). Agro-food waste and coffee mucilage also present good results (up to 0.3 g/g). These results might be due to the fact that straw as feedstock for 2G bioethanol has been studied in more detail than other biowaste such as OFMSW. A larger number of pretreatments and routes have been tested for agricultural residues than for OFMSW.

Regarding the pretreatments, it can be concluded that the efficiency of the pretreatment will depend on the kind of feedstock, since the same pretreatment reports different results for different raw materials. Dilute acid pretreatment, alkaline pretreatment and hot water pretreatment show promising results for most of the cases in terms of ethanol yield. Furthermore, it can be observed that when sequential pretreatments are applied, such as steam explosion + dilute acid pretreatment, hot water + dilute acid pretreatment or dilute acid + alkaline pretreatment, the final ethanol yield of the process is enhanced in many of the cases reported.

4- Global potential of bioethanol production

4.1- Waste generation

SUGARCANE TRASH (STRAW)

It is estimated that 1 ha of sugarcane crop generates around 10-18 tonnes of dry sugarcane trash (Leal, et al., 2013) and up to 50% of this trash can be removed without affecting the quality of the soil (Khaire, et al., 2021).

In 2019, about 26,777,041 ha were cultivated with sugarcane all around the world, with Brazil as main producer (10,081,170 ha) followed by India (5,061,090 ha) (KNOEMA, 2020). This means that around 267,770,410-481,986,738 tonnes of dry sugarcane trash is expected to be generated annually, of which 133,885,205-240,993,369 tonnes would be available for 2G bioethanol production.

SUGARCANE BAGASSE

1 tonne of sugarcane generates approximately 0.3 tonne of bagasse (Huang, et al., 2020). Taking into account that on average approximately 80 tonnes of sugarcane are produced per cultivated hectare, then about 25 tonnes of bagasse could be produced per hectare (Huang, et al., 2020).

Considering the total area cultivated with sugarcane in 2019 (26,777,041 ha), 669,426,025 tonnes of sugarcane bagasse can be produced every year.

This waste is usually burned for energy generation, so we can assume 50% of availability, that would mean 334,713,012 tonnes of sugarcane bagasse available for bioethanol production.

Moisture content of sugarcane bagasse is approximately 50% of its weight (Rabelo, et al., 2015).

CORN STOVER

Production of corn generates same amount of corn as corn stover, that is a corn/stover ratio of 1 (Mensah, et al., 2021).

World production of corn during 2019/2020 crop year was 1,116,520,000 tonnes (Foreign Agricultural Service/USDA, 2021) so the same amount of corn stover should be expected to be produced. US is the major corn producer in the world, with 345,960,000 tonnes produced during 2019/2020, followed by China and Brazil, with 260,780,000 and 102,000,000 tonnes of corn produced respectively (Foreign Agricultural Service/USDA, 2021).

Considering that part of the waste must remain in the field to keep soil quality, a 50% of availability for bioethanol production can be assumed, that is 558,260,000 tonnes of corn stover.

RICE STRAW

Non-edible biomass, including stem, leaf blades and leaf sheaths, represents approximately 50% of rice crops (Bhattacharyya, et al., 2020).

Ratio of straw to paddy ranges from 0.7-1.4 according to the International Rice Research Institute (IRRI, 2018). 497,000,000 tonnes of rice were produced worldwide during 2018/2019 and 2019/2020 seasons, with China and India as main producers (148,000,000 and 119,000,000 tonnes respectively) (Foreign Agricultural Service/USDA, 2021).

Considering the ratio range of 0.7-1.4 kg/kg and the annual rice production it can be estimated that around 347,900,000-695,800,000 tonnes of rice straw can be produced every year, which is similar to the estimation reported by Hung et al. (Hung, et al., 2019), who estimated a global rice straw production of 370–520 million tonnes per year based on rice/straw biomass ratios observed for a common rice variety.

Assuming about 50% of availability for bioethanol production considering that part of the waste must remain in the field, 173,950,000-347,900,000 tonnes of rice straw could be valorised. The moisture content of rice straw is about 15-18% (w/w %).

RICE HULLS

Rice hulls represent approximately 20% of rice crops in dry weight (Dagnino, et al., 2013).

According to the International Rice Research Institute 1 kg of milled rice generates approximately 0.28 kg of rice husk (IRRI, 2016). Global milled rice production was 497.7 million tonnes in the 2019/2020 season (Shahbandeh, 2021), so approximately 139,356,000 tonnes of rice hulls are produced per year.

Rice hulls can be burned, landfilled or used at farming industries (Saha & Cotta, 2010), although they have low digestibility, so 50% of availability can be assumed, which would result in 69,678,000 tonnes of rice hulls available for bioethanol production.

COTTON STALKS

2 tonnes of dry matter are produced per hectare of cotton cultivated (Keshav, et al., 2016). According to the USDA, 35,030,000 hectares were cultivated during 2019/2020 crop year, with India as the major cotton producer, with 13,500,000 hectares cultivated (Foreign Agricultural Service/USDA, 2021).

With this estimation, it is expected that 70,060,000 tonnes of cotton stalks per year are produced. Assuming an availability of 50% due to the need to leave some waste in the field to ensure good soil quality, 35,030,000 tonnes of cotton stalks could be used for bioethanol production every year.

WHEAT STRAW

As already mentioned, approximately 1.3 tonnes of wheat straw are generated per tonne of wheat produced (Talebnia, et al., 2010)

763,860,000 tonnes of wheat were produced worldwide in 2019/2020 crop year (Foreign Agricultural Service/USDA, 2021). EU, China and India are the main producers of wheat in the world, with 154,340,000, 133,590,000 and 103,600,000 tonnes respectively (Foreign Agricultural Service/USDA, 2021). Therefore 993,018,000 tonnes of wheat straw can be produced per year.

Part of the straw is burned, used for feed or left in the field, so up to 60% of the wheat straw generated is available for bioethanol production (Talebnia, et al., 2010), which means 595,810,800 tonnes/year.

Wheat straw has a 10% of moisture content (McCartney, et al., 2006).

OAT STRAW

Analysing 18 different varieties of oat, Kafilzadeh, et al. (Kafilzadeh, et al., 2012) calculated that the amount of straw generated per hectare cultivated ranges from 4.42 to 7.48 tonnes/ha, with a mean of 5.85 tonnes/ha.

In the 2019/2020 season, 9,580,000 hectares were cultivated with oat worldwide, with EU and Russia as main producers (2,550,000 ha and 2,430,000 ha respectively) (Foreign Agricultural Service/USDA, 2021). This means that approximately 56,043,000 tonnes of oat straw are generated per crop year.

Dry mass generated during harvesting, is mostly left in the fields or burned. Taking into account that part of it must be left in the field to keep a proper soil quality, an availability of 50% can be assumed, which would mean 28,021,500 tonnes of oat straw available for bioethanol production.

Moisture content of oat straw is approximately 10% (w/w %) (McCartney, et al., 2006).

BARLEY STRAW

Approximately 0.76 tonne of straw are generated per tonne of barley grain produced (Han, et al., 2013). 156,700,000 tonnes of barley were produced in 2019/2020 crop year (Foreign Agricultural Service/USDA, 2021). EU, Russia and Canada are the main barley producers in the world, with 63,320,000, 19,940,000 and 10,380,000 tonnes of barley produced during 2019/2020 respectively (Foreign Agricultural Service/USDA, 2021).

Taking into account this data, it can be expected that about 119,092,000 tonnes of barley straw will be generated per crop year.

Again, 50% of availability can be assumed; that is 59,546,000 tonnes of barley straw available for bioethanol production.

Barley straw has 10% (w/w %) of moisture content (McCartney, et al., 2006).

RYE STRAW

1 tonne of rye generates around 0.5-2 tonnes of straw (Domanski, et al., 2016). During 2019/2020 crop year 12,260,000 tonnes in of rye were globally produced, with EU as main producer with 8,430,000 tonnes (Foreign Agricultural Service/USDA, 2021).

Taking into account the rye/straw ratio, around 6,130,000-24,520,000 tonnes of rye straw might be produced per year.

A 50% of availability can be assumed, which would mean between 3,065,000-12,260,000 tonnes of rye straw per year.

Moisture content of rye straw is about 8.4% (w/w) (McCartney, et al., 2006).

COFFEE RESIDUES

Residues or non-edible parts of coffee represent more than 50% of the coffee fruit (Orrego, et al., 2018). Mucilage represents approximately 22% of the grain wet weight (Orrego, et al., 2018) and 11.8% of waste the fraction from wet-processing (Orrego, et al., 2018). Pulp represents 40-42% of the overall weight of coffee fruit (Phuong, et al., 2019) and about 43.2% of the waste fraction from wet-processing (Orrego, et al., 2018).

It is estimated that more than 10 million tonnes of solid residues are generated yearly from coffee agro-industry worldwide, including spent coffee grounds, pulp and mucilage. (Echeverria & Nuti, 2017)

An availability of 25%can be assumed, considering that part of the waste will be discarded because of the difficulty to be recovered or used for other purposes, which would mean approximately 2,500,000 tonnes of coffee residues available for bioethanol production.

Moisture content of coffee residue is about 75% (w/w %) (Choi, et al., 2012).

OLIVE POMACE

About 0.6 tonne of olive mill solid waste or pomace are generated per tonne of olive oil produced (Tayeh, et al., 2020). Olive pomace has a 50% (w/w %) of moisture and a 3% (w/w %) of oil (Miranda, et al., 2019).

Olive oil production during 2019/2020 season reached 3,207,000 tonnes, with Spain as the major producer in the world with 1,125,300 tonnes (IOC, 2021).

That annual production would generate around 1,924,200 tonnes of olive pomace. If we consider an availability of 50% due to other possible valorisation routes such as burning or composting, then 962,100 tonnes of olive pomace could be used for bioethanol production.

OLIVE TREE PRUNING BIOMASS

1.5 and 3 tonnes per hectare of olive tree cultivated can be generated every two years when the pruning takes place (Negro, et al., 2014; Martínez-Patiño, et al., 2015).

Approximately 10,614,846 ha of olive are cultivated in the world annually, (Atlas Big, 2019) which means that between 15,922,269- 31,844,538 tonnes of olive tree biomass can be generated every two years.

Taking into account that part of the waste should stay in the field to enhance soil quality and assuming an availability of 50%, around 7,961,134-15,922,269 tonnes of olive tree biomass would be available for bioethanol production.

It must be mentioned that water extracted olive tree biomass represents approximately 80% of the raw olive tree biomass (Oliva, et al., 2020).

SWEET SORGHUM BAGASSE

20-28 tonnes of bagasse are generated per hectare of sweet sorghum cultivated (Tinôco, et al., 2021)

According to the Food and Agriculture Organization of the United Nations, 40,826,460 ha of sorghum were cultivated in 2019 (FAO, 2020). 816,529,200-1,143,140,880 tonnes of bagasse would hence be generated.

However, bagasse waste is only generated by the sugar extraction of sweet sorghum, which is just one of the numerous varieties of sorghum that are cultivated. In view of the latter, an availability of 10% was assumed. 81,652,920-114,314,088 tonnes of bagasse are then available for bioethanol production.

AGRO-FOOD WASTE

Potato production is over 350,000,000 tonnes worldwide annually, with China and India as major producers (Statista, 2021). Approximately 0.16 tonnes of solid waste are generated per tonne of potato processed (Pathaka, et al., 2017). Potato waste includes peels, pulp and rejects. It is estimated that between 70,000-140,000 tonnes of peels are generated worldwide annually (Javed, et al., 2019).

Peels has a high moisture content of approximately 85.06% (w/w) (Pathaka, et al., 2017).

Part of potato peels and waste are used for animal feeding, so a 20% of availability for bioethanol production may be assumed; that is between 14,000-28,000 tonnes.

Regarding dates, 10-50% of produced dates are wasted (Taghizadeh-Alisaraei, et al., 2019). Global production of dates in 2019 was 9,070,000 tonnes, with Egypt as main producer (Statista, 2021), it means that 907,000-4,535,000 tonnes of wasted dates would be generated.

The amount of dates wasted during processing and harvesting and what amount could be considered as municipal food waste is not specified in literature, so a 10% of availability will be assumed, which would mean around 90,700-453,500 tonnes of wasted dates that could be used for bioethanol production.

As for grapes, grape pomaces, which is the waste generated during wine production, represent about 25% of the weight of the grapes (Sirohi, et al., 2020). Approximately 9 million of grape pomaces are generated annually (Sirohi, et al., 2020).

They have a moisture content of 3.3-7.6% (w/w) (Sirohi, et al., 2020). Assuming an availability of 50%, 4,500,000 tonnes of grape pomaces would be available for bioethanol production.

ORGANIC FRACTION OF MSW

Approximately 2 billion tonnes of MSW are generated per year all around the world (Karak, et al., 2012). Organic fraction represents 32-57% of MSW (Babu, et al., 2021), which means that 640,000,000-1,140,000,000 tonnes of organic municipal solid waste are generated per year.

There are different routes available for OFMSW management, such as anaerobic digestion, composting, pyrolysis or landfilling (Babu, et al., 2021), so an availability for bioethanol production of 20% will be assumed. This would lead to an availability of 128,000,000-228,000,000 tonnes of organic municipal solid waste per year. Moisture content of OFMSW is around 70% (w/w %) (Barampouti, et al., 2019).

PAPER FRACTION

Approximately 35% of MSW comes from paper and pulp industry (Saini, et al., 2020), which means a generation of 700,000,000 tonnes of paper fraction from MSW per year.

In US, approximately 67 % of paper waste is recycled (EPA, 2020), and about 72% in Europe (EPRC, 2019), a 30% of availability for 2G bioethanol production can be assumed. About 210,000,000 tonnes of paper waste would hence be available for this purpose.

WOODY BIOMASS

The huge availability of this waste makes it difficult to estimate the total amount of forest residues and municipal wood waste generated worldwide. Just in the US, about 370 million tonnes of forest residue are generated annually (Bay, et al., 2020).

Most of it can be burned for energy recovery or recycled, so a very small fraction would be available for 2G bioethanol production.

4.2- Potential bioethanol production

Based on the ethanol yields reported by different authors, the rough production of waste estimated worldwide and the availability assumed for each waste, the potential production of 2G bioethanol from the different sources considered has been calculated (Table 2).

Ethanol yields have been set as ranges when the difference between the highest and the lowest yield reported was significant, and it has been considered as the mean value when the differences between the different yields reported was not notable.

It should be noted that moisture content has been taken into account only in the cases where ethanol yields were specifically indicated to be calculated on dry basis, that is sugarcane trash (rough generation was already on dry basis), OFMSW and oat straw. In the rest of the cases, moisture content has been ignored, which can affect the real ethanol production that should be expected if ethanol yields were actually calculated on dry basis but not indicated on reports. Furthermore, the amount of waste production for some cases might have been estimated on dry basis even though this was not specified on the respective paper, which would also modify the real ethanol production to be expected if the yield reported was calculated on raw feedstock basis.

Also, the amount of olive pruning biomass should be considered every 2 years instead of every year, since it takes place every two years.

Table 2: Potential bioethanol production from different biowaste sources

Raw material	Rough Annual Generation (tonnes/year)	Availability	Moisture content (w/w %)	Ethanol yield (g ethanol/g feedstock)	Bioethanol production (tonnes/year)
SUGARCANE TRASH (STRAW)	267,770,410-481,986,738	50%	-	0.31	41,504,414-74,707,944
SUGARCANE BAGASSE (STALKS)	669,426,025	50%	50%	0.156	52,215,230
CORN STOVER	1,116,520,000	50%	-	0.096-0.214	53,592,960-119,467,640
RICE STRAW	347,900,000-695,800,000	50%	15%	0,153	26,614,350-53,228,700
RICE HULLS	139,356,000	50%	-	0.11-0.21	7,664,580-14,632,380
COTTON STALKS	70,060,000	50%	-	0.17	5,955,100
WHEAT STRAW	993,018,000	60%	10%	0.155-0.311	92,350,674-185,297,159
OAT STRAW	56,043,000	50%	10%	0.085-0.223	2,143,645-5,623,915
BARLEY STRAW	119,092,000	50%	10%	0.144-0.27	8,574,624-16,077,420
RYE STRAW	6,130,000-24,520,000	50%	8%	0.178	545,570-2,182,280
COFFEE RESIDUES	10,000,000	25%	75%	0.153	382,500
OLIVE POMACE	1,924,200	50%	-	0.091-0.130	87,551-125,073,000
OLIVE TREE PRUNING BIOMASS	15,922,269-31,844,538	50%	-	0.139	1,106,598-2,213,195
SWEET SORGHUM BAGASSE	816,529,200-1,143,140,880	10%	-	0.09-0.199	7,348,763-22,748,504
AGRO-FOOD WASTE (potato peel)	70,000-140,000	20%	85%	0.055-0.32	770-8,960
AGRO-FOOD WASTE (dates waste)	907,000-4,535,000	10%	-	0.3	27,210-136,050
AGRO-FOOD WASTE (grape pomace)	9,000,000	50%	5%	0.213	958,500
ORGANIC FRACTION OF MSW	640,000,000-1,140,000,000	20%	70%	0.06-0.194	7,680,000-44,232,000
PAPER FRACTION	700,000,000	30%	-	0.107-0.331	22,470,000-69,510,000
TOTAL	-	-	-	-	325,847,039-763,688,076

In the graphic below (Figure 17) annual global production of bioethanol in the last years from any sort of source is compared to the potential annual bioethanol production from biowaste. It can be observed that annual global bioethanol production during the last year was around 80 million tonnes. As it was explained in the introduction section, most of bioethanol produced is 1G bioethanol, obtained from corn or sugarcane. It seems evident that even in the most conservative scenario, where around 326 million tonnes of 2G could be produced from biowaste, all the current bioethanol demand could be covered by this 2G bioethanol.

In the case of the lowest potential production, the current production could be increased more than 4-folds using just biowaste as raw material, whereas in the most optimistic scenario, where 763.69 million tonnes of bioethanol could be produced, the current production could increase almost 10-folds.

As already mentioned at the beginning of this work, the target set by the Directive 2009/28/EC of the European Parliament and of the Council in 2009 (European Parliament and Council of the EU, 2009) was to reach a 10% of total fuel transport consumption coming from renewable sources by 2020 and 14% by 2030 (European Parliament and Council of the EU, 2018). In the US, these targets are 15% and 30% by 2030 and 2050 respectively (USDA, 2020).

The results obtained suggest that the huge amount of biowaste available for bioethanol production and the technologies already proved to efficiently convert this biowaste into bioethanol will allow to meet all the goals set up by different countries in terms renewable fuels usage with no need for 1G bioethanol.

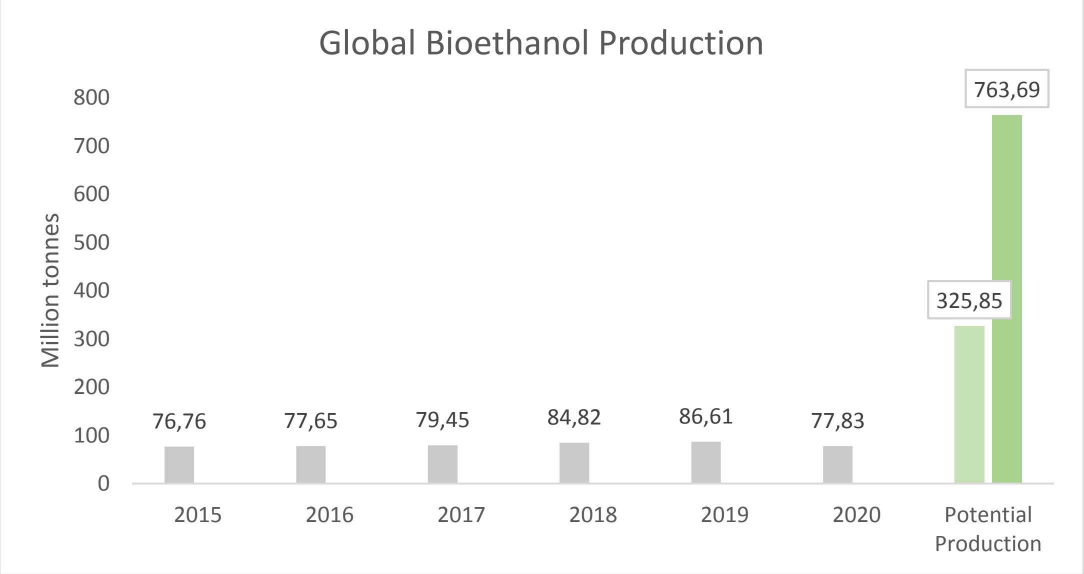


Figure 17: Comparison between reported production of bioethanol in the last 6 years and the potential global production according to the biowaste availability and reported yields.

Source: Data obtained from the Renewable Fuels Association (RFA, 2021)

5- Life Cycle Assessment

5.1- Goal and scope

The goal of this assessment is to compare the environmental impact of gasoline and different kind of biofuels, covering all the stages from the production of the raw materials to the final use as fuel for vehicles, mostly in terms of Global Warming Potential (GWP).

4 different scenarios will be analyzed:

1. Gasoline as fuel
2. E85 fuel (1G bioethanol from sugarcane)
3. E85 fuel (2G bioethanol from OFMSW)
4. E85 fuel (2G bioethanol from a typical agriculture residue (straw))

The functional unit for the assessment will be 100 km drive in a specific car and under certain conditions that will be further described, which means that all the calculations and inputs will be referred to the amount of fuel necessary for each case.

For all the cases, the general stages that will be included in the life cycle of each product are Sourcing of raw material, Transportation, Production, Distribution and Use, as shown in Figure 18.

Figure 18: Stages of the life cycle assessment for all the scenarios.

For the cases of bioethanol as fuel it will be considered as E85, which means that 85% (v/v %) of the fuel is bioethanol and the rest is gasoline.

5.2- Scenarios description and inventory

5.2.1- Gasoline as fuel

The overall process of gasoline use as fuel starts with the crude oil extraction, followed by the production process, distribution and final use. The refinery process for the production of the gasoline is the most complex stage and the one which will make the biggest difference in respect to the other scenarios.

In the refinery process, the crude oil is first desalted and fed into a distillation column where an atmospheric distillation takes place, fractionating the crude oil by density and boiling points. Different fractions leave the distillation column. Gases are released through the top of the column and are separated by a liquid gas system, giving place to methane, ethane, propane and butane. Straight-run naphtha is released through the upper trays of the column in two fractions, the light naphtha fraction and the heavy naphtha fraction. The light fraction is subjected to a chemical sweetening process. Part of the fraction leaving the chemical sweetening process is directly blended to gasoline and the main fraction is sent to the isomerization units, where iso-paraffins are obtained. The heavy naphtha fraction is led to a reformer unit, giving place to iso-paraffins and aromatics, and then sent to the gasoline blending system along with the fraction from the isomerization unit, giving place to the final gasoline product. (Schuller, 2019)

For the simulation in GaBi, the process can be simplified by considering just the atmospheric distillation, where the gasoline is produced, as shown in figure 19. The inputs of the process would be crude oil, steam, fresh water, fuel (methanol or ethanol) and electricity whereas the output would be the gases, gasoline, middle distillates and atmospheric residues. However, it should be noticed that the overall process is more complex, with many by-products and different parallel operations. (Schuller, 2019; Serge-Bertrand & Radisovich, 2020)

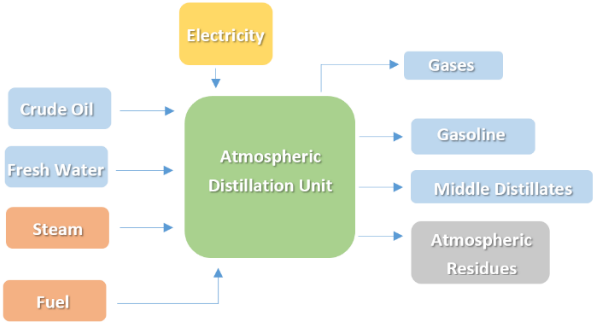


Figure 19: Simple scheme for gasoline production process, including input and output streams.

According to The GaBi Refinery Model (Schuller, 2019), 1 kg of crude oil would produce 0.036 kg of gases, 0.184 kg of gasoline, 0.337 kg of middle distillates and 0.443 kg of atmospheric residues whereas 0.54 MJ of fuel, 0.028 kg of steam and 0.005 kWh of electricity are required for the process. Similar results were reported by Serge-Bertrand & Radisovich (Serge-Bertrand & Radisovich, 2020), who also noted the requirement of fresh water, approximately 10 % of the amount of crude oil entering the process.

As mentioned before, 100 km drive will be used as functional unit. Under certain conditions and for a specific type of car engine (Table 3), approximately 0.0916 L of gasoline are needed to drive 1 km (Jhang, et al., 2020); that is 9.16 L/100 km or 6,8 kg/100 km (density 0.7457 kg/L) (Jhang, et al., 2020), which means that 37 kg of crude oil must be processed. The inventory will be hence calculated for 37 kg of crude oil entering the process (Table 4). Same drive conditions and engine type will be considered for all the other scenarios, as well.

Table 3: Speciation of vehicle used to test fuel consumption (Jhang, et al., 2020)

Engine Type	EW 10 J4 (RFR)
Bore × Stroke	85 mm × 88 mm
Displacement	1997 cc
Type of Drive	Front wheel drive
Compression Ratio	10.8
Max Power (hp/rpm)	137 hp/6000 rpm
Max Torque (kg-m/rpm)	19.8 kg-m/4100 rpm

It is considered that the production will take place in Europe, concretely in Greece, so it will be assumed that the oil crude must be transported from Middle East by truck and boat for 600 km and 1100 km respectively. For the distribution stage, the same distance for all the scenarios (100 km) and in the same type of transport (diesel truck) will be assumed.

Table 4: Inventory of scenario 1

Stage	Description	Value	Unit
Raw Material	Crude Oil Extraction	37	kg
	Truck	600	km
	Boat	1,100	km
Production	Fresh water	3.7	kg
	Steam	3.16	MJ
	Fuel	19.98	MJ
	Electricity	0.185	kWh
	Gases	1.332	kg
	Gasoline	6.808	kg
	Middle Distillates	12.469	kg
	Atmospheric Residues	16.391	kg
Distribution	Truck	100	km
Use	Gasoline Vehicle	100	km

5.2.2- 1G bioethanol from sugarcane

The main stages for 1G bioethanol production from sugarcane would be the raw material sourcing, including agricultural production, harvesting and transportation, the production process, that would include sugar extraction, filtration, fermentation and distillation, transportation and use. In parallel to these stages, the gasoline production, including the oil extraction, the refinery process and the transport, in addition to the blending process of both fuels should also be considered (Figure 20).

Within the agricultural production stage, the production of fertilizers, herbicides, fungicides and insecticides must be taken into account. Energy, irrigation water and land use are other important requirements. The output of this stage will include nitrate, phosphorous, soil emissions, methane, ammonia and nitrous oxide, apart from sugarcane and straw. During sugar extraction stage, bagasse will be generated as waste and will be recovered as energy. Also, it is assumed that 100% of the sugar will be used for bioethanol production. CO_2 is generated as co-product during fermentation whereas vinasse and fuel oil is generated during distillation. The production of yeast needed for fermentation must also be taken into account.

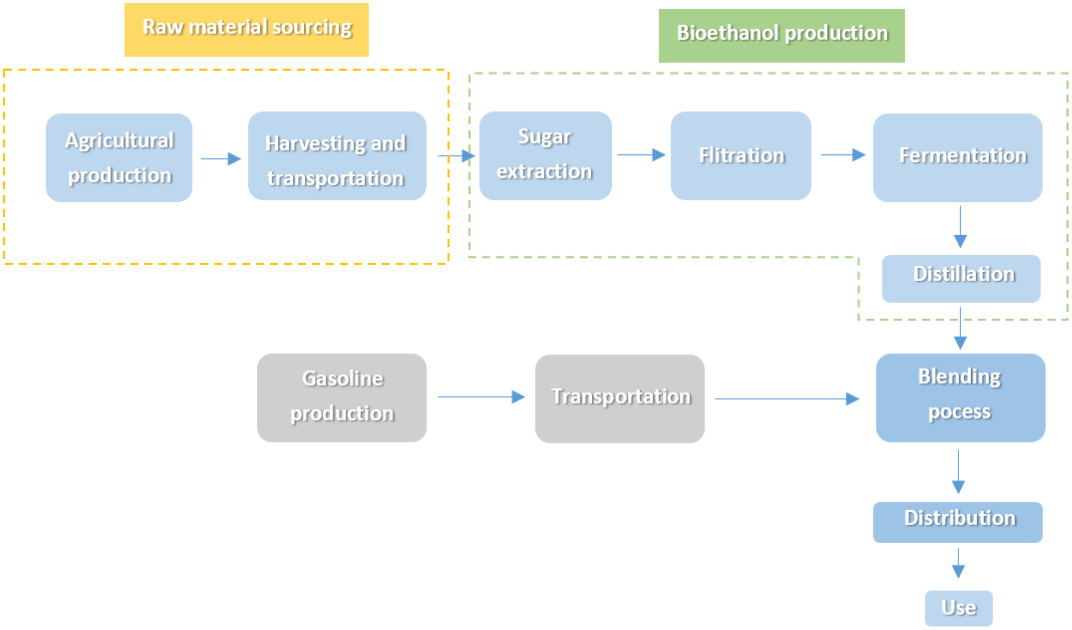


Figure 20: Block diagram for E85 fuel production from sugarcane

As mentioned in the previous scenario, under specific conditions and for the specified type of car engine, a 100 km drive requires approximately 9.16 L or 6.8 kg of gasoline. Taking into account the lower heating value (LHV) of gasoline (44,650 kJ/kg) (Engineering ToolBox, 2007), about 303,620 kJ are necessary for the 100 km drive. Considering the LHV of E85 (30,000 kJ/kg) (Engineering ToolBox, 2007), it can be estimated that approximately 10.12 kg or 12.99 L of E85 fuel are necessary for 100 km drive. 11.04 L of ethanol and 1.95 L of gasoline are hence needed, which means that about 8.71 kg of ethanol and 1.45 kg of gasoline must be produced. Benjamin et al. (Benjamin, et al., 2014) studied ethanol yields for juice from different species of sugarcane. Results ranged between 5,248-10,196 L of ethanol per cultivated hectare of sugarcane, with a mean of approximately 8,400 L/ha, which is about 6,628 kg/ha. Taking into account that about 80 tonnes of sugarcane are produced per hectare cultivated (Huang, et al., 2020), then an ethanol yield of 83 g ethanol/kg sugarcane can be assumed. Since 8.71 kg ethanol must be produced, approximately 105 kg of sugarcane must be processed and 0.0013 ha must be cultivated.

Most of parameters from agriculture production and bioethanol production have been taken from Hiloidhari et al. (Hiloidhari, et al., 2021), who collected data for sugarcane harvesting and processing from official sources. Some parameters like bagasse, straw, land occupation or CO_2 from fermentation have been estimated by information already described in this work. Energy requirements for the whole bioethanol production process, assuming conventional distillation, has been estimated from the results reported by Dias et al. (Dias, et al., 2011). The emissions from fertilizers will not appear in our inventory since they will be included within the production process of fertilizers from GaBi database. The emissions from pesticides were calculated as CO_2 equivalent using 5.1, 6.3 and 3.9 as emission factors (kg CO_2/kg) for insecticide, herbicide and fungicide respectively (Hiloidhari, et al., 2021). It is assumed that the harvesting takes place 50 km away from the bioethanol plant. Also, gasoline is assumed to be produced 50 km away from the plant, and the blending process takes place at the same plant where bioethanol is produced. As for all the scenarios, 100 km for final distribution by truck are assumed. Furthermore, it will be assumed that half of straw will be burned for energy recovery and the other half will be landfilled. For the blending process of the gasoline and ethanol, an energy consumption of 10 MJ by the mixer is assumed (CFG mixers, 2020).

For the yeast production, GaBi suggests a process consisting on fermentation and distillation with molasses as growth medium (GaBi, 2021), which means that sugarcane would be the main raw material. Approximately 8 tonnes of molasses are necessary for the production of 1 tonne of yeast (Dar Al Khalaf, 2020), whereas approximately 0.04 tonne of molasses are generated per tonne of sugarcane (Nikodinovic-Runic, et al., 2013). Since 0.028 kg of yeast are necessary, then 5.6 kg of sugarcane are required. This would mean 110.6 kg sugarcane and 0.0014 ha cultivated if the requirements for the bioethanol production are added. The energy requirements of the overall process are about 40 MJ per kg of yeast produced (Dunn, et al., 2012).

Table 5: Inventory of scenario 2

Stage	Description		Value	Unit
Agriculture	Electricity for irrigation	Coal	1,42	kWh
		Natural gas	0,106	kWh
		Nuclear	0,135	kWh
		Hydro	0,076	kWh
	Diesel	For irrigation	0,160	L
		for farm operation	0,110	L
	Irrigation water		33.41	m^3
	Land occupation		0,0014	ha
	Lubricant		0,002	L
	Fertilizers	Urea	0,429	kg
		Single superphosphate	0,182	kg
		Muriate of Potash	0,182	kg
		$FeSO_4$	0,026	kg
		$ZnSO_4$	0,02	kg
		$MnSO_4$	0,012	kg
		Borax	0,005	kg
	Pesticides	Insecticide (Phorate)	0,02	kg
		Herbicide (Atrazine)	0,002	kg
		Fungicide (Mancozeb)	0,002	kg

Stage	Description		Value	Unit
	Outputs	Sugarcane	110,6	kg
		Straw	24,6	kg
		CO_2	0,130	kg
Transport	Truck		50	km
Yeast production	Energy		1.12	MJ
	Sugarcane		5.6	kg
	Outputs	Yeast	0.028	kg
Bioethanol production	Sugarcane		105	kg
	water		97.75	L
	Milling (juice extraction)	Lime	0.151	kg
		Sulphur	0.061	kg
		Caustic soda	0.189	kg
		Phosphoric acid	0.196	kg
		Lubricant	0.011	L
	Fermentation	Yeast	0.028	kg
		Antifoam	0.010	kg
		Urea	0.006	kg
	Energy	Steam requirement	48.78	kg
		Production from bagasse (steam)	0.081	kg
	Outputs	Ethanol	8.71	kg
		Fuel oil	0.022	L
		Vinasse	0.044	L
		Bagasse	0.032	kg
		CO_2	8.37	kg
Gasoline production	Gasoline from ref. plant (data scenario 1)		1.45	kg
	Transport	Truck	50	km
Blending process	Gasoline		1.45	kg
	Bioethanol		8.71	kg
	Mixer		10	MJ
	Outputs	E85	10.12	kg
Distribution	Truck		100	km
Use	Gasoline vehicle		100	km

5.2.3- 2G bioethanol from OFMSW

The life cycle for this scenario would consist on the transportation of the collected waste, followed by the bioethanol production, including pretreatment, hydrolysis, fermentation and distillation, distribution and use. Again, as in the previous case, gasoline production and blending process must be considered.

Taking into account the different routes reported for bioethanol production from OFMSW, the overall production process would consist basically on mechanical sorting, pretreatment, hydrolysis, fermentation and distillation. Hydrothermal pretreatment prior to hydrolysis and fermentation is considered. The cellulose, hemicellulose and starch will be hydrolysed by using different kinds of enzymes such as α-amylase glucoamylase, cellulase and hemicellulase which means that enzymes production must be taken into account. Apart from the yeast, different chemicals would be necessary for this process, including NH_4PO_4, $(NH_4)_2SO_4$, $MgSO_4{\cdot}7H_2O$ and KH_2PO_4. Energy requirements for distillation should be also taken into consideration. Also, as in the previous scenario, the production of yeast must be included.

Like in the previous scenario, 8.71 kg bioethanol (11.04 L) and 1.45 kg gasoline (1.95 L) must be produced for the 100 km drive. Assuming the maximum ethanol yield reported in section 3 for OFMSW by means of hydrothermal pretreatment (0.194 g/g), then 44.9 kg of OFMSW must be processed.

As shown in Figure 21, for the simulation in GaBi the hydrolysis, fermentation and distillation as a single stage shall be considered, in which yeast production, enzymes production, energy requirements and emissions are included. The inventory for the emissions at this stage will take as reference the model proposed by Kalogo et al. (Kalogo, et al., 2007) for bioethanol production from MSW, who also estimated the energy consumption of the hydrolysis-fermentation-distillation process at 166 MJ per metric tonne of wet MSW.

It will be assumed that the moisture content of the MSW is 80% (López-Gómez, et al., 2019; Barampouti, et al., 2019). The drying process prior to the pretreatment stage will be ignored since it usually consists on natural drying by sun exposure (Mahmoodi, et al., 2018) without any energy requirement. The OFMSW entering the process will be hence considered to be dried. Also, as it is indicated in the corresponding paper, it will be assumed that the ethanol yield was calculated on dry basis.

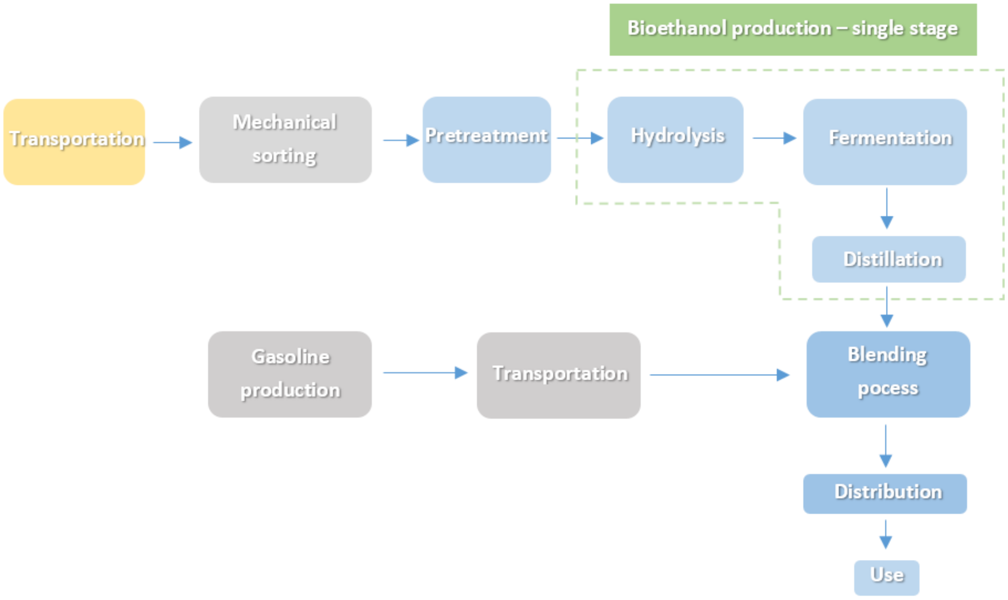


Figure 21: Block diagram for E85 fuel production from OF-MSW

It is assumed that source-sorted waste will be used and hence the mechanical sorting stage can be ignored.

For the hydrothermal pretreatment, Sharma et al. (Sharma, et al., 2020) estimated that about 30,450 MJ are required per tonne of dry matter treated with hot water. It will be assumed that both energy demands required for pretreatment and production process will be obtained from incineration of biomass, which could be the MSW discarded for the bioethanol production.

All the transportation stages will be assumed to be the same than in the previous scenarios.

The energy requirements for enzymes production was calculated by using the data reported by Dunn et al. (Dunn, et al., 2012) and this can be observed in Table 6.

Table 6: Energy requirements for enzymes production

Enzyme	Total Energy Consumption (MJ/kg enzyme)	Steam (MJ/kg enzyme)	Electricity (MJ/kg enzyme)
α-amylase	23	7,96	15,04
Glucoamylase	100	23,97	76,03
Cellulase	45	14,12	30,88
Total	168	46,06	121,94

According to Mahmoodi et al. (Mahmoodi, et al., 2018) 1.13 g of α-amylase, 1.13 g of glucoamylase and 250 g of cellulases per kg of dry OFMSW are needed, considering 90 filter paper units (FPU) per mL and a density of 1.12 g/cm^3 for the cellulase enzymes (CTec2-1.15 g/cm^3 and HTec2-1.09 g/cm^3) (Megyeri, et al., 2015).

For the yeast production, sugarcane production must be included as it was described in the previous scenario. According to Mahmoodi et al. (Mahmoodi, et al., 2018), 0.04 g of yeast are necessary per kg of OFMSW, which means that 0.36 kg of sugarcane must be produced (Dar Al Khalaf, 2020; Nikodinovic-Runic, et al., 2013). The quantities required for the rest of chemicals used during fermentation will be also assumed to be like the ones reported by Mahmoodi et al. in the study about bioethanol production from OFMSW by means of hydrothermal pretreatment.

Table 7: Inventory of scenario 3

Stage	Description		Value	Unit
Transportation	Truck		50	km
Hydrothermal Pretreatment	MSW		44,9	kg
	Energy		1367,21	MJ
Bioethanol production	Pretreated MSW		44,9	kg
	Yeast		0,001796	kg
	Enzymes		11,326474	kg
	Energy		37,27	MJ
	NH_4PO_4		0,001796	kg
	$(NH_4)_2SO_4$		0,001796	kg
	$MgSO_4 \cdot 7H_2O$		0,000225	kg
	KH_2PO_4		0,003592	kg
	Outputs	VOC	0,0209	kg
		CO	0,008980	kg
		NOx	0,0218	kg
		PM10	0,001796	kg
		SOx	0,009205	kg
		CH_4	0,0272	kg
		N_2O	0,000225	kg
		CO_2	12,37	kg
		Bioethanol	8,71	kg
Enzymes production	α-amylase		0,0507	kg
	Glucoamylase		0,0507	kg
	Cellulase		11,23	kg
	Energy	Steam	160,13	MJ
		Electricity	351,23	MJ
Yeast production	Sugarcane (process scenario 2)		0,359	kg
	Energy		0,0718	MJ

Stage	Description		Value	Unit
	Outputs	Yeast	0,001796	kg
Gasoline Production	Gasoline from ref. plant (process scenario 1)		1,45	kg
	Truck		50	km
Blending process	Gasoline		1,45	kg
	Bioethanol		8,71	kg
	Mixer		10	MJ
	Outputs	E85	10,12	kg
Distribution	Truck		100	km
Use	Gasoline vehicle		100	km

5.2.4- 2G bioethanol from agriculture residue (straw)

Scenario 4 will focus on the production of bioethanol from sugarcane straw and its use as fuel blended with gasoline. The overall process includes the straw production, transportation to the bioethanol plant where pretreatment, hydrolysis, fermentation and distillation take place, in addition to the production of gasoline, the blending process, distribution and final use (Figure 22).

The agricultural process for the production of the straw is the same than the one already described for sugarcane production in scenario 2. Taking into account the ethanol yield estimated for sugarcane straw in section 3 (0.31 g ethanol per g of feedstock) approximately 28.1 kg straw are necessary to produce 8.71 kg bioethanol. Assuming that 50% of the straw can be removed without affecting the quality of the soil, then 56.2 kg straw must be produced. If we consider that 18 tonnes of straw are generated per hectare of sugarcane, then 0.00312 ha must be cultivated and about 250 kg of sugarcane will be produced. Since straw is a waste generated during sugarcane production and the ratio straw/sugarcane is considerably low, all energy, chemicals and water requirements will be allocated by mass as well as all emissions.

The bioethanol production process will be considered to start with dilute acid pretreatment followed by simultaneous saccharification and co-fermentation (SSCF) and distillation. These three processes will be included as a single stage in GaBi. All the inputs and outputs for this stage were collected from data reported by Spatari et al. (Spatari, et al., 2010), who compiled the inventory for different kind of lignocellulosic agricultural residues.

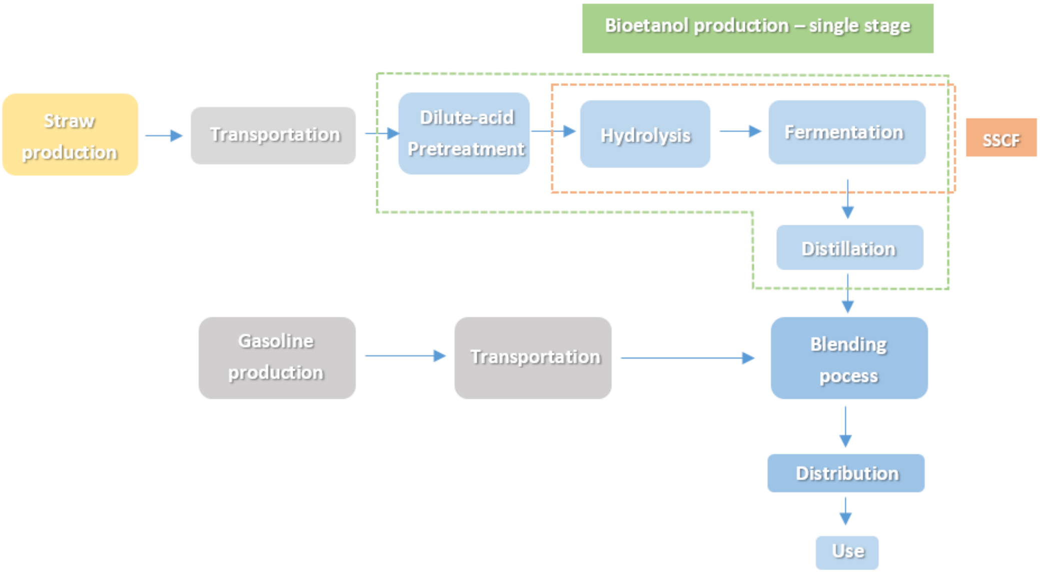


Figure 22: Block diagram for E85 fuel production from sugarcane straw

Since hydrolysis and fermentation take place in a single step, only one type of microorganism is required, capable to carry out both processes. According to Spatari et al. (Spatari, et al., 2010), 9.2 kg of cellulase are required per tonne of straw processed. NH_3, $(NH_4)_2$, SO_4, CaO, Liquefied Petroleum Gas (LPG), sulphuric acid and electricity are necessary for the cellulase production.

The energy required for the bioethanol production (pretreatment, SSCF and distillation) will be considered to be the same than in the previous scenario. This energy can be assumed to be totally covered by the co-generation from the burning of the lignin along with other solid waste non-fermented during the process and the biogas from digestion produced during waste water treatment process (Silalertruksa & H.Gheewala, 2013).

Again, all the transportation stages will be assumed to be the same than in the previous scenarios.

Table 8: Inventory of scenario 4

Stage	Description		Value		Unit
				Allocation	
Agriculture (Straw production)	Electricity for irrigation	Coal	3.211	0.590	kWh
		Natural gas	0.240	0.044	kWh
		Nuclear	0.304	0.056	kWh
		Hydro	0.171	0.031	kWh
	Diesel	For irrigation	0.362	0.066	L
		for farm operation	0.247	0.045	L
	Irrigation water		75,46	13.86	m^3
	Land occupation		0,00312	0.00057	ha
	Lubricant		0,00476	0.00087	L

Stage	Description		Value		Unit
	Fertilizers	Urea	0.968	0.178	kg
		Single superphosphate	0.412	0.076	kg
		Muriate of Potash	0.412	0.076	kg
		$FeSO_4$	0.059	0.0109	kg
		$ZnSO_4$	0.048	0.0087	kg
		$MnSO_4$	0.026	0.0048	kg
		Borax	0.012	0.0022	kg
	Pesticides	Insecticide (Phorate)	0.048	0.0087	kg
		Herbicide (Atrazine)	0.00476	0.00087	kg
		Fungicide (Mancozeb)	0.00476	0.00087	kg
	Outputs	Sugarcane	249.78	81.63%	kg
		Straw	56.20	18.37%	kg
		CO_2	0.293	0.054	kg
Transport	Truck		50		km
Bioethanol Production	H_2SO_4		0.731		kg
	$Ca(OH)_2$		0.815		kg
	LPG		0.0056		kg
	Cellulase		0.258		kg
	Diammonium phosphate		0.053		kg
	Straw		28.10		kg
	Energy		4.66		MJ
	Outputs	Carbon monoxide	0.031		kg
		Nitrogen oxides	0.033		kg
		Sulphur oxides	0.044		kg
		PM_{10}	0.00055		kg
		Furfural	0.017		kg
		Ethanol to air	0.0055		kg
		HMF	0.0022		kg
		Acetic acid	0.012		kg
		Solid waste	3.75		kg
		Bioethanol	8.71		kg
Cellulase production	NH3		1.35		kg
	$(NH_4)_2$		0.450		kg
	CaO		1.63		kg
	LPG		0.0056		kg
	H_2SO_4		2.19		kg
	Electricity		0.242		kg

Stage	Description		Value	Unit
	Outputs	Cellulase	0.258	kg
Gasoline Production	Gasoline from ref. plant (process scenario 1)		1.45	kg
	Truck		50	km
Blending process	Gasoline		1.45	kg
	Bioethanol		8.71	kg
	Mixer		10	MJ
	Outputs	E85	10.12	kg
Distribution	Truck		100	km
Use	Gasoline vehicle		100	km

5.3- GaBi Simulation

Within this section, the flowsheets built in GaBi for each scenario are presented, including all stages and processes necessary, as well as the results obtained by the simulation.

5.3.1- Flowsheets

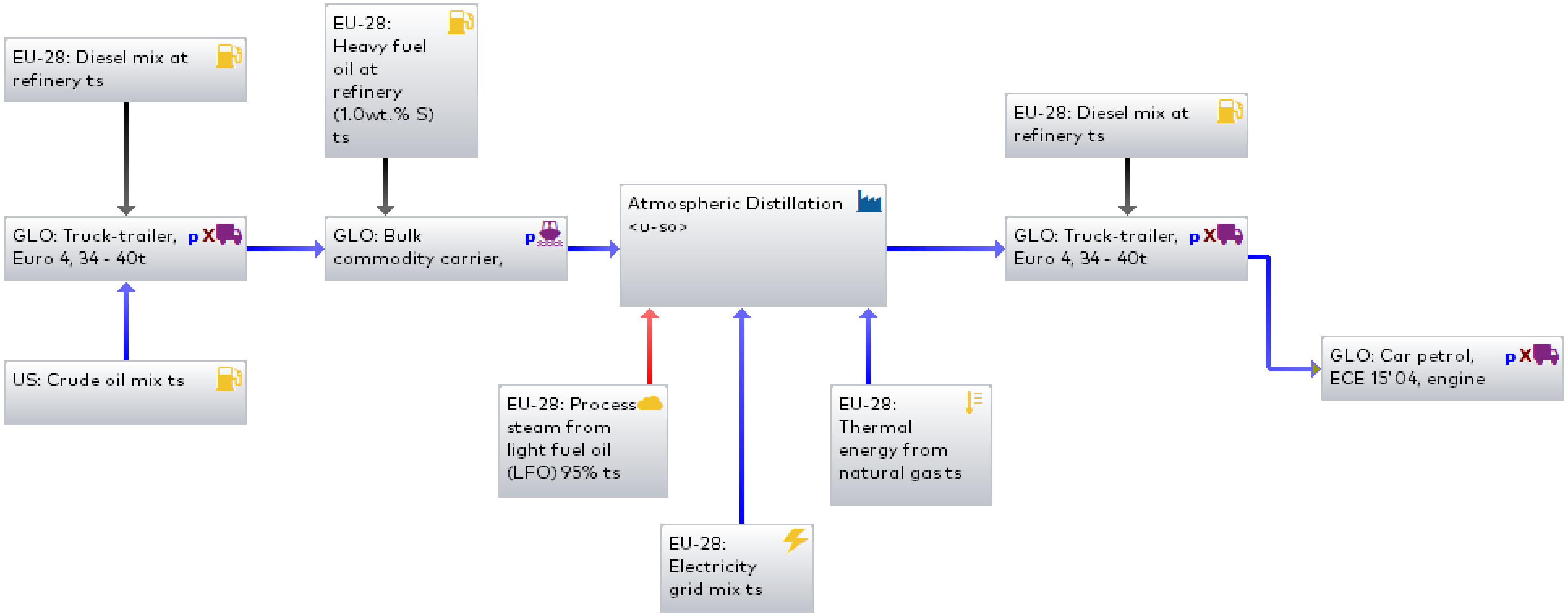


Figure 23: Flowsheet of scenario 1 (Gasoline) in the software GaBi.

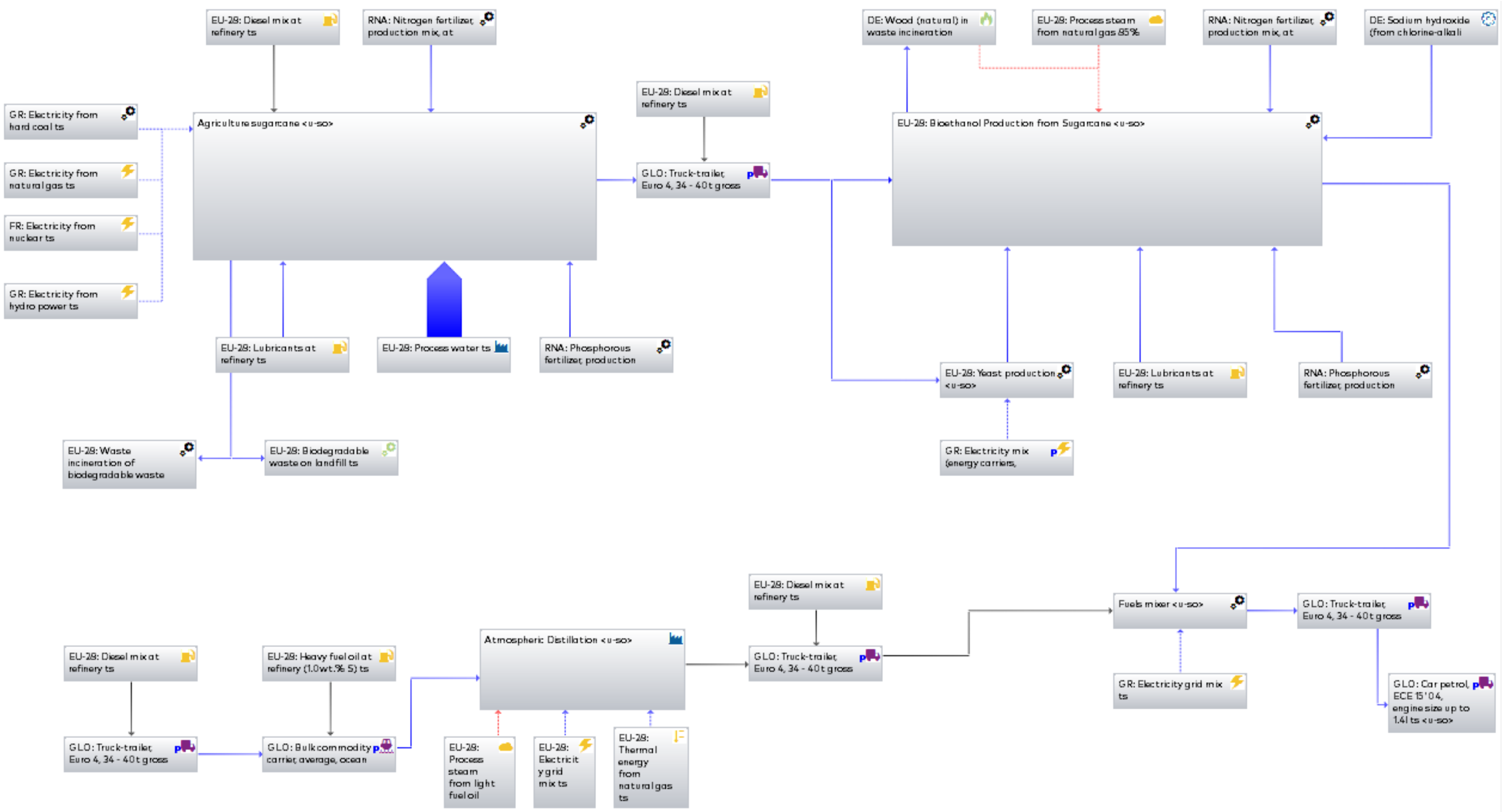


Figure 24: Flowsheet of scenario 2 (1G bioethanol from sugarcane) in the software GaBi.

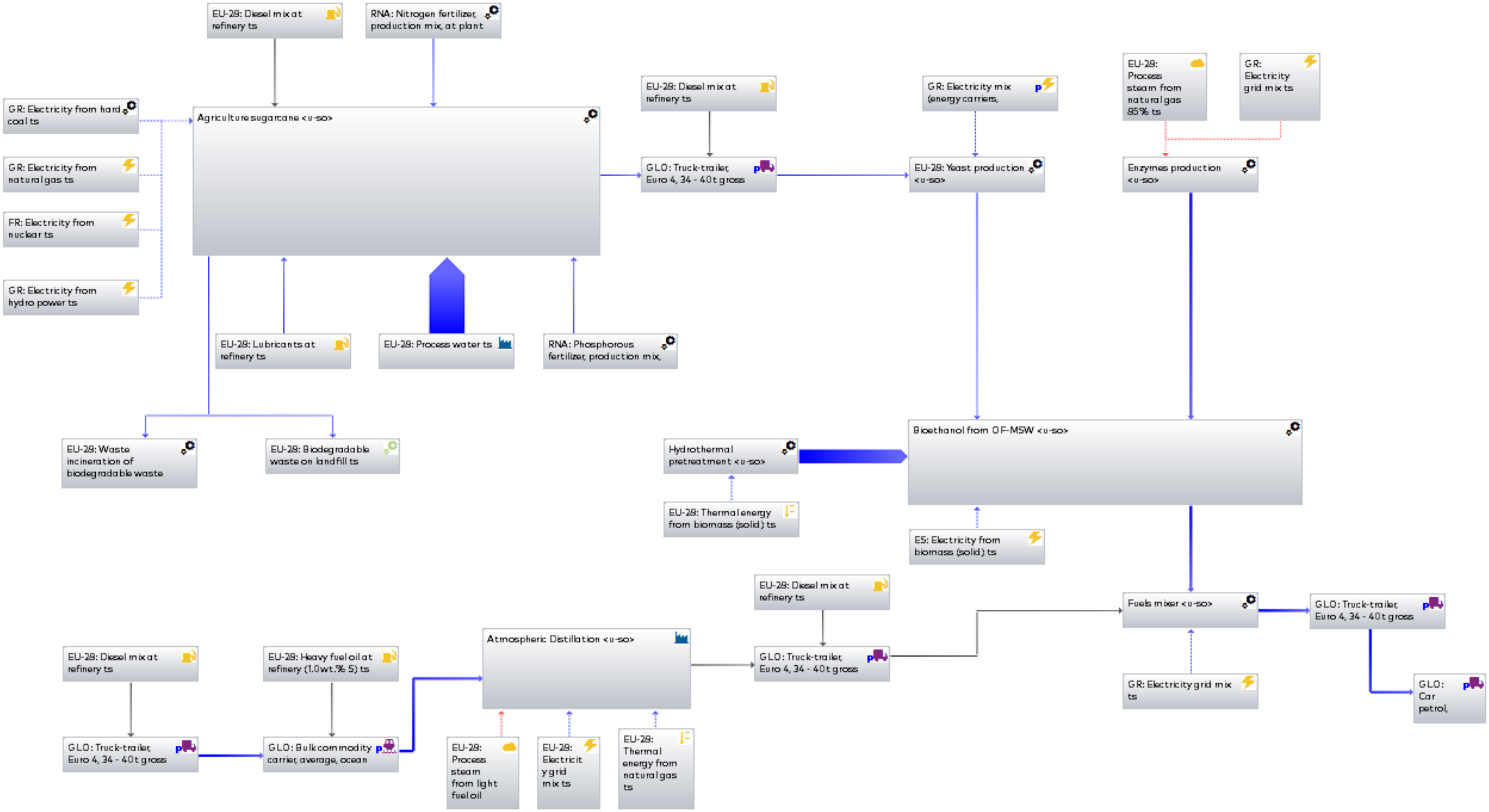


Figure 25: Flowsheet of scenario 3 (2G bioethanol from OFMSW) in the software GaBi.

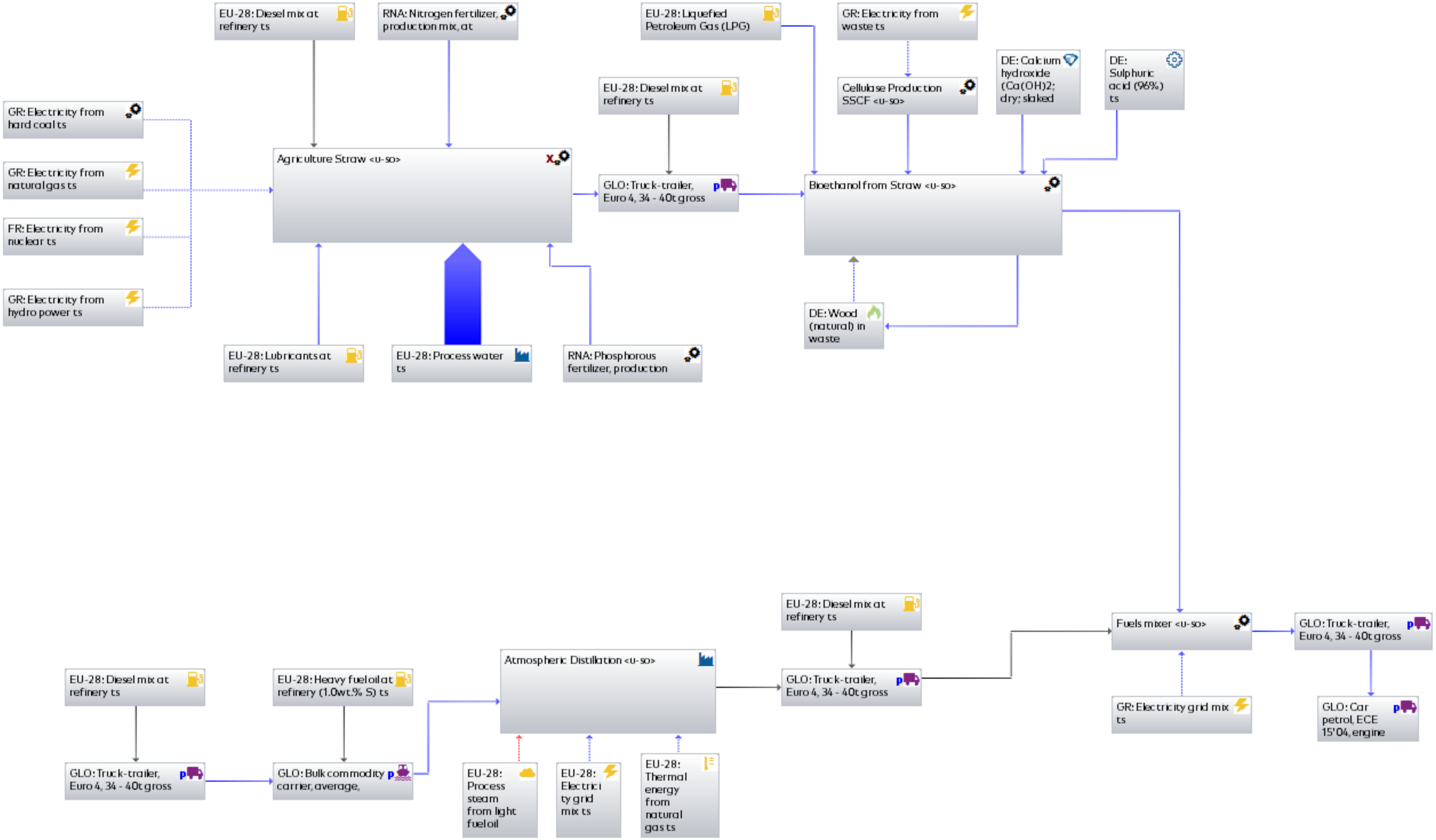


Figure 26: Flowsheet of scenario 4 (2G bioethanol from sugarcane straw) in the software GaBi.

5.3.2- Results and discussion

Global Warming Potential (GWP) is one of the most significant parameters when assessing the environmental impact of a process. All the greenhouse emissions in terms of kg of CO_2 equivalent are taken into account. In the graphic below (Figure 27), the GWP of the 4 scenarios analysed is presented. It must be mentioned that the CO_2 released by the car using the fuel hasn't been included since it is considered as biogenic CO_2, a concept already explained in the introduction section of this work.

When performing a Life Cycle Assessment (LCA) of any process, it is required that the process is described in detail, with in-depth information at every single stage, in order to provide accurate results. In this work, general routes are assessed which are applicable in many different ways. That is why it should be noted that the aim of this simulation is not to estimate the precise GWP value for the overall process, which can suffer variations if it was performed under different conditions, but to compare it in respect to the different alternatives purposed in general terms.

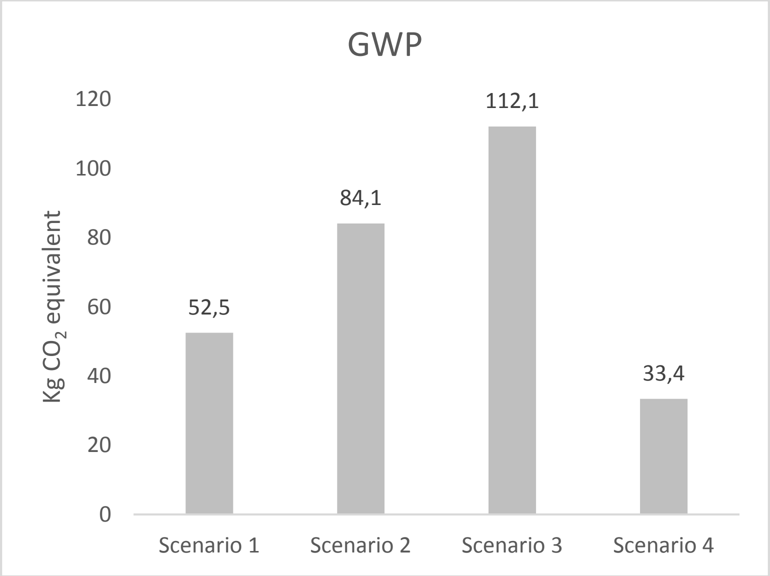


Figure 27: Global Warming Potential in terms of kg CO_2 equivalent emissions for the different scenarios analyzed.

According to the results obtained in GaBi, scenario 4 presents the lowest GWP whereas scenario 3 presents the highest value, followed by scenario 2 and 1. It might be expected that fossil fuel would report a higher carbon footprint than any of the bioethanol production scenarios, however 1G bioethanol from sugarcane and 2G bioethanol from OFMSW resulted in a higher carbon footprint. If we pay attention just to the use of the products as fuel, it can be observed that gasoline shows the most negative environmental impact compared to the different bioethanol alternatives. But when we look into the overall process, gasoline reports better results than scenarios 2 and 3. The case of scenario 2, based on 1G bioethanol production from sugarcane, might be explained by the huge amount of process water needed for the irrigation during sugarcane production. Approximately 39.2 kg CO_2 equivalent are released by this process; that is about 47% of total emissions, which means that a carbon footprint of 44.9 kg CO_2 equivalent would be expected if this process is excluded. The results obtained for scenario 3, consisting on the 2G bioethanol production from OFMSW, can be explained by the high enzyme load required for the process and its corresponding electricity demand. Electricity mix consumption contributes about 65% to the net GWP, with the enzymes production process accounting for the 97% of the total electricity demand. This contribution is consistent with the results reported by Janssen et al. (Janssen, et al., 2016), who stated that enzymes production is the most influencing process in terms of environmental impact for the overall bioethanol production process, accounting for the 67-77% of the total GWP. A carbon footprint of 39.2 kg CO_2 equivalent should be expected if electricity demand was excluded in scenario 3. These results are presented in figure 28.

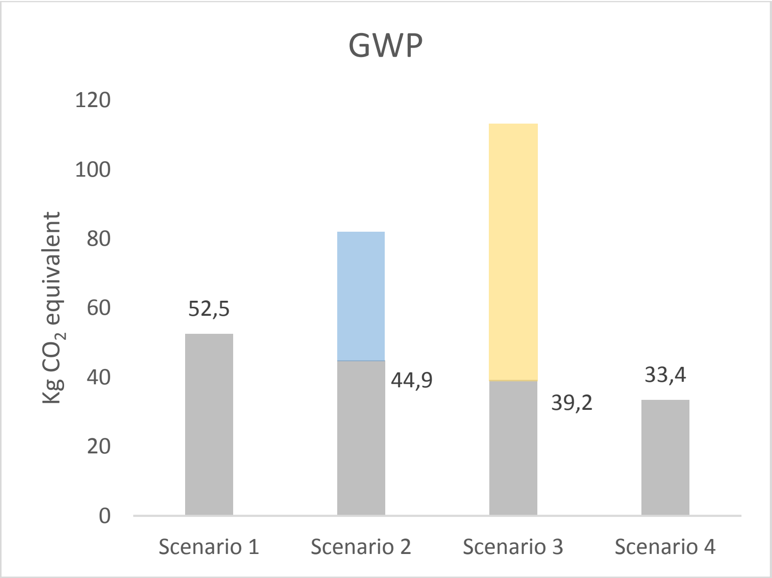


Figure 28: Global Warming Potential in terms of kg CO_2 equivalent emissions for the different scenarios analyzed excluding process water and electricity requirements in scenario 2 and 3 respectively.

Looking at these results, the potential of OFMSW as feedstock is apparent in terms of environmental behavior. It must be noted that the route selected for this scenario was based on laboratory scale experiments, which are expected to be efficiently applicable at industrial scale. Hence, it is to be expected that some parameters such as enzymes load or energy requirements will be decreased. Moreover, process integration, including energy recovery from a fraction of the waste or co-generation of different by-products along with bioethanol, would lead to a reduced carbon footprint of the overall process (Ingrao, et al., 2021).

Scenario 4, where sugarcane straw is used as raw material for the bioethanol production, still presents the best results, mostly due to the possibility of covering all the energy requirements by burning the waste generated during the bioethanol production in addition to the very low requirements for the production of the straw. The selection of SSCF instead of SHF might also have a positive impact on the final results (Ingrao, et al., 2021). According to these results, almost 40% of emissions would be avoided if E85 from straw is used instead of 100% of oil-based fuel. The assumption of the percentage of straw removed from the soil has a significant impact on the final GWP (Cherubini & Ulgiati, 2010). If we had assumed that 100% of the straw generated could be used for bioethanol production, then the GWP obtained would be 24.5 kg CO_2 equivalent, which means a reduction over 50% in respect to the oil fuel scenario.

Similar results have been provided by different authors. Wang et al. (Wang, et al., 2013) reported 45% reduction of greenhouse gases emissions when comparing the life cycle of bioethanol as fuel versus gasoline, whereas Jeswani et al. (Jeswani, et al., 2015) pointed out that around 83-96% reduction can be achieved. Variations in the results are common and might be due to assumptions, different production processes or different data sources.

Some other parameters giving information about the environmental impact of the different scenarios are presented in the figure below (Figure 29). These parameters are the Acidification Potential (AP), the Eutrophication Potential (EP) and the Freshwater Aquatic Ecotoxicity Potential (FAETP), which are measured in kg of equivalent SO_2, phosphate and DCB (dichlorobenzene) respectively. The high impact of gasoline production and use (scenario 1) on freshwater aquatic ecotoxicity as well as the high acidification potential of E85 production and use from OFMSW (scenario 3) should be noted. These results are in line with the conclusions reported by different authors. Even though GWP is observed to decrease when bioethanol is blended with gasoline instead of pure gasoline, some other environmental impact indicators such as the AP or the EP are increased (Borrion, et al., 2012).

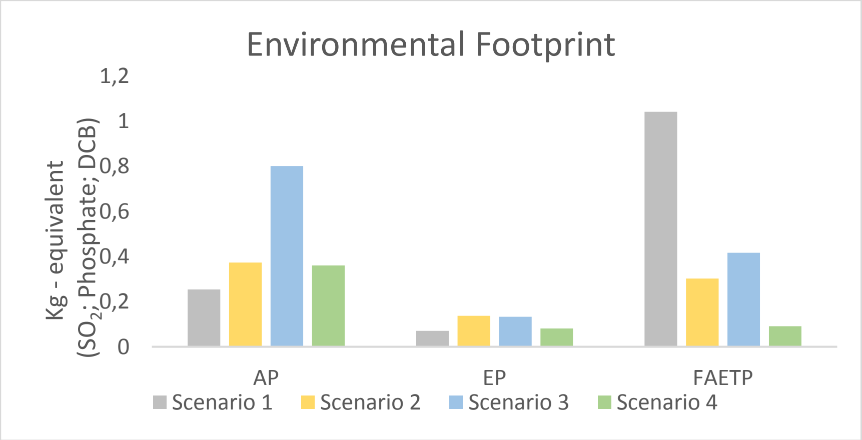


Figure 29: Environmental Footprint in terms of Acidification Potential (AP) (kg SO_2 equiv.), Eutrophication Potential (EP) (kg phosphate equiv.) and Freshwater Aquatic Ecotoxicity Potential (FAETP) (kg DCB equiv.) for the different scenarios analysed.

6.- Economic considerations

Bioethanol production from biowaste can be considered as a novel technology still under development. However, different economic assessments and forecasts reported in bibliography suggest that this approach is feasible in general terms, even though efficiency of the processes taking part in the overall production processes must still be optimized.

In 2020, the sale price for gasoline and E85 was 0.68 and 0.6 USD/L respectively (Demichelis, et al., 2020). Different authors performed economic analysis in order to estimate the production costs for different lignocellulosic feedstock. Quintero et al. (Quintero, et al., 2013) reported a production cost between 0.58-0.77 USD/L whereas Tye et al. (Tye, et al., 2011) estimated production cost as 5.6 USD/GJ, not far from oil-based fuel production, approximately 5.1 USD/GJ. Production costs can be reduced not just by optimizing the operations of the process but by taking into considerations other factors, such as the co-production of different products or the scale of the production plant. Duarte et al. (Duarte, et al., 2021), who assessed production cost from coffee waste, concluded that the production costs are smaller for large facilities rather than small facilities. 0.504 and 0.515 USD/L were reported for large and small facilities respectively. Quintero et al. (Quintero, et al., 2013) proved that when a co-production approach was applied, production costs were reduced from 0.58-0.77 to 0.49-0.68 USD/L.

Investment is another important parameter that must be taken into account. Demichelis et al. (Demichelis, et al., 2020) performed a Technical, Economic, Environmental Assessment (TEEA) for bioethanol production from 5 different kind of biomass, including sugar-based, starch-based and lignocellulosic-based biomass. Economical profitability was achieved for all the cases, according to the NPV (Net Present Value) and ROI (Return on Investment) values reported for each type of biomass (table 9).

Table 9: NPV and ROI values for different biomass used as feedstock.

Source: Data estimated by Demichelis et al. (Demichelis, et al., 2020)

	Sugarcane	Potatoes	Rice Straw	Cattle Manure	OFMSW
ROI	15.7%	15.6%	7.8%	7.5%	10.1%
NPV	0.85	0.11	0.09	0.11	0.39

Viability for 2G bioethanol depends mostly on the development of the current technologies, which would lead to increase ethanol yields and to reduce energy and microorganism requirements. Process integration, including waste valorisation and co-production of different products, is also the key to reduce costs of the overall process. According to the International Energy Agency (IEA), cost reductions between 10-40% in the medium-term, and even higher in the long term can be expected (IEA Bioenergy, 2020). Some factors affecting the agricultural stage, such as the productivity and the harvesting, should be also optimized in case of agriculture residues. Policies implemented by authorities also play a key role on the viability of 2G bioethanol. Measures to guarantee minimal renewable fuel use or tax benefits for producers and consumers would stimulate the production and use of 2G bioethanol (Aditiya, et al., 2016).

It should also be noted that implementing 2G bioethanol production would have positive consequences in economic terms, not only by the reduction of environmental costs or by enhancing gross domestic product, but also by the creation of new employment opportunities (Haputtaa, et al., 2020).

7.- Conclusions

Three main factors make it essential to assess the potential of bioethanol production from biowaste. These factors are the need to increase global bioethanol production in order to meet the goals set by different countries regarding the use of renewable fuels, the need to substitute the current 1G bioethanol with 2G bioethanol to avoid the *fuel versus food* dilemma, and the huge availability of biowaste with potential to be converted into bioethanol.

It seems obvious the need to reduce the production and use of oil-based fuels in order to reduce GHGs emissions. Oil fuels will be eventually substituted by green technologies, including electric cars or nuclear fusion technology, but this transition will take place in the long-term. It is thus necessary to find a solution to GHGs emissions in the short and medium-term, which must include existing vehicles with gasoline engines. 2G bioethanol is argued the most suitable solution as it can be used blended with gasoline with no need to modify the car engine and its production at an industrial scale is already possible.

All kinds of waste-sources have been analysed in this work, including lignocellulosic, starch-based, and sugar-based biowaste. Both waste availability and current technologies for the conversion into bioethanol have been exposed, leading to the conclusion that not only current bioethanol demand could be satisfied by using just 2G bioethanol, but also future demand will be possible to be fully covered by 2G bioethanol from biowaste, with a potential global production of 325,847,039-763,688,076 tonnes of 2G bioethanol per year.

As other authors previously verified by means of a life cycle assessment, it has also been proved that 2G bioethanol can help in the fight against global warming, due to its lower GWP in comparison to oil-based fuels. According to the results obtained in this work, GHGs emissions can be reduced up to 40 %. However, it should be noted that for some waste such as the organic fraction of MSW, the production process must be developed in order to reduce overall energy requirements.

Finally, regarding the economic viability of this approach, many authors suggest that even with the current technologies used for 2G bioethanol production, the production and use of 2G bioethanol as fuel is profitable and might be competitive with oil fuels. This suggests that the development of the current conversion technologies, in addition to the increase of the current bioethanol demand, will lead 2G bioethanol to become an attractive business opportunity. It is also key that national governments promote the production and use of 2G bioethanol, by providing beneficial conditions to both investors and consumers.

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