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Second-generation bioethanol production: A review of strategies for waste valorisation

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Abstract. This paper reviews second–generation biofuel production chain and focuses on its energetic, economic and environmental impacts. The biggest challenge in the production of bioethanol from lignocellulosic material refers to the biomass waste that is left over after the separation of bioethanol in the distillation process. This waste still has high energetic value and could be further utilised to add value to the production chain. Furthermore, the environmental impact of untreated waste from bioethanol production is very high, which also requires attention. Anaerobic digestion of bioethanol production waste has been proposed as a possible solution to utilise the energetic potential of this waste and lower its environmental impact.

Key words: lignocellulosic biomass, biofuel, anaerobic digestion, zero–waste, ERoEI.

ABBREVIATIONS:

AD	Anaerobic digestion
BOD	Biochemical oxygen demand
E_{ret}	Returned/gained energy in the form of the biofuel
E_{req}	Energy input required to produce E_{ret}
ERoEI	Energy return on energy invested
GHG	Greenhouse gas
Mtoe	Million tonnes of oil equivalent
SHF	Separate hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation
TFC	Total final consumption

INTRODUCTION

In 2014, the energy production of the world was 13,805.44 million tonnes of oil equivalent (Mtoe), more than 100% increase compared to 1973 consumption of 6 213.69 Mtoe. Coal made up 28.8% of it, crude oil 31.2%, natural gas 21.2%, nuclear power 4.8%, hydroenergy 2.4%, biofuels and waste 10.2% and other sources (includes geothermal, solar, wind, heat and electricity trade) 1.3% (OECD/IEA, 2016).

Due to the increase of the energy production (mainly from non–renewable energy sources), petroleum prices, and environmental impacts caused by fossil fuels, there is a need for alternative sources of energy. Among the renewable sources of energy, second–

generation biofuel production, using lignocellulosic biomass as a feedstock, is emerging as an important biofuel for the transportation sector. Biofuels are a replacement for petroleum fuels, a way of limiting the greenhouse gas emissions, improving air quality, and utilising new energetic resources (Jaecker-Voirol et al., 2008; Nigam & Singh, 2011).

Lignocellulosic biomass is a promising feedstock for biofuel production, due to its low cost, vast abundance and sustainability (Agbor et al., 2011). The two most common and viable liquid biofuels in the transportation sector are bioethanol and biodiesel. However, the production of liquid biofuels has obstacles regarding the costs and efficiency of the process. Bioethanol production is still very costly, due to the energy input required (De Paoli et al., 2011), and inefficient use of biomass due to the quantity of waste–products that are left unused at the end of the process (Kaparaju et al., 2009). In order to make bioethanol production feasible, the costs must be optimised and biomass must be used to its fullest potential. Waste–products generated during bioethanol production must be valorised for example, through further anaerobic digestion (AD).

This paper reviews second–generation biofuel production chain with the emphasis on the maximisation of its energetic and commercial value, and minimising its environmental impact.

SECOND-GENERATION BIOETHANOL PRODUCTION

Classification of biofuels

Biofuels can be divided into primary and secondary biofuels based on the processing they undergo prior to their utilisation. Primary biofuels use organic compounds in its unprocessed form such as wood chips, pellets, firewood, and forest residues. These materials are used mainly for heating, cooking and electricity production, especially in developing countries (Voloshin et al., 2016). Secondary biofuels can be solid, liquid or gaseous, and use processed materials. They are further divided into first–generation, second–generation and third–generation biofuels, according to the feedstock and the technology used for its production (Nigam & Singh, 2011).

First–generation biofuels are the most widely used of the three. They are produced from mainly starch, oil and sugar-based feedstock (Demirbas, 2011). However, first–generation biofuels have some limitations due to the competition with food production changes in the land use, and high water requirements (Podkuiko et al., 2014). Thus, great attention has been paid to second–generation biofuels that are produced from lignocellulosic feedstock (Sims et al., 2010; Kikas et al., 2016; Raud et al., 2017).

Second–generation biofuels use lignocellulosic biomass from forest, agriculture, fishery, and municipal wastes. It includes non–food crops, straw, grass, sawdust and wood chips (Sun & Cheng, 2002; Nigam & Singh, 2011). The chemical composition of each one of these organic compounds will influence the potential for bioethanol production.

Composition of lignocellulosic biomass

Lignocellulosic material is composed of three main polymers: cellulose (40–60%), hemicellulose (20–40%) and lignin (10–25%) (McKendry, 2002). These polymers are connected with each other and their relative content in lignocellulosic material varies with the substrate (Table 1).

Table 1. Contents of cellulose, hemicellulose, and lignin for different feedstocks (adapted from (Reddy & Yang, 2005; Saini et al., 2015))

Feedstock	Cellulose	Hemicellulose	Lignin
Cotton, flax	80–95	5–20	–
Grasses	25–40	25–50	10–30
Hardwoods	45 ± 2	30 ± 5	20 ± 4
Hardwood barks	22–40	20–38	30–55
Softwoods	42 ± 2	27 ± 2	28 ± 3
Softwood barks	18–38	15–33	30–60
Corn stalk	39–47	26–31	3–5
Corn stover	38–40	28	7–21
Sorghum stalks	27	25	11
Sorghum straw	32	24	13
Rice straw	28–36	23–28	12–14
Wheat straw	33–38	26–32	17–19
Barley straw	31–45	27–38	14–9
Bagasse	32–48	19–24	23–32

Cellulose and lignin content also depends on the harvesting time of the crops (Tutt et al., 2013). Thus, both culture and the harvesting time should be considered when suitable biomass is selected.

Cellulose, generic formula $(C_6H_{10}O_5)_n$, is the main structural constituent of plant cell walls. It is crystalline, very fibrous, and rigid due to the hydrogen links between cellulose molecules. Cellulose is chemically stable and mechanically robust, making it water insoluble and more resistant to de–polymerization. Usually, it is covered by hemicellulose forming a cellulose-hemicellulose complex that inhibits the access of enzymes, influencing the hydrolysis rates, and therefore, the production of fermentable sugars and the digestibility of lignocellulosic biomass (Harmsen et al., 2010; Zabed et al., 2016). High cellulose content in lignocellulosic material is a promising condition for biofuel production (Raud et al., 2014).

Hemicellulose, generic formula $(C_5H_8O_4)_n$ is the second most abundant polymer of plant cell walls and is mainly composed of xylan and mannan. Comparing to cellulose, hemicellulose has a lower degree of polymerization, it is chemically heterogeneous, and it has a random and amorphous structure (Agbor et al., 2011; Yu et al., 2017). As hemicellulose is wrapped around the cellulose fibrils, it needs to be removed in order to increase the cellulose digestibility. Thus, increase in hemicellulose removal increases the accessibility of the cellulose and its hydrolysis rate (Zabed et al., 2016).

Lignin is a three–dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol and 4-propenyl-2.5-dimethoxyl phenol, and it is the third most abundant constituent of lignocellulosic biomass. Lignin provides structural support to the plants, and contributes to the impermeability and resistance against microbial attack (Hendriks & Zeeman, 2009). This compound ties all the constituents of lignocellulosic biomass making it insoluble in water, and more difficult to degrade. Due to its properties, lignin is the main obstacle to enzymatic hydrolysis (Agbor et al., 2011). In addition, it influences the digestibility of the biomass. High lignin content results in low digestibility of the biomass therefore, increasing the lignin removal increases the biomass digestibility (Chang & Holtzapple, 2000).

Bioethanol production process

Due to the complex composition of the lignocellulosic biomass, its conversion into ethanol requires three sequential steps: (1) pretreatment – to separate hemicellulose and lignin from cellulose, (2) hydrolysis of cellulose – to obtain fermentable sugars, and (3) fermentation – to convert sugars into ethanol – followed by distillation – to separate and purify the ethanol (Demirbas, 2011).

Pretreatment

The pretreatment is essential step prior to the conversion of the lignocellulosic material to ethanol since the three main structural units of lignocellulosic biomass – cellulose, hemicellulose and lignin, are organized into a complex structure, which is recalcitrant to decomposition (Phitsuwan et al., 2013). Therefore, the plant cell walls are very difficult to hydrolyse and pretreatment is a necessary step in order to expose cellulose and hemicellulose for subsequent enzymatic hydrolysis.

Pretreatment methods are divided into: physical, chemical, physio–chemical and biological pretreatments (Mohd Azhar et al., 2017). Physical pretreatments include chipping, grinding, and milling particles. Chemical pretreatments include treatments with dilute acids, concentrated acids, alkali, ozone, ionic liquids, and Organosolv. Physio–chemical pretreatments include uncatalysed steam, acid catalysed steam, liquid hot water/hydrothermal, ammonia fibre explosion, ammonia recycling percolation, soaking aqueous ammonia, wet oxidation, CO_2 explosion. Biological pretreatments include pretreatments with microorganisms (Zabed et al., 2016). It is also possible to combine different pretreatment methods and further improve the efficiency of pretreatment (Mupondwa et al., 2017).

Even though the most common pretreatment methods are dilute acid pretreatment, hydrothermal pretreatment and alkaline pretreatment (Adekunle et al., 2016), other pretreatments have been reported in the literature as efficient for the pretreatment of lignocellulosic biomass. Nitrogen explosion, compressed air and steam explosions have also been shown as effective methods of pretreatment that increase glucose and ethanol yields (Tutt et al., 2014; Raud et al., 2016a; Raud et al., 2016b; Tutt et al., 2016)

From the economic and environmental point of view, some pretreatment methods are more expensive and harmful to the environment than others. As the pretreatment represents 33% of the total costs of the process (Tomás-Pejó et al., 2008), chemical free pretreatments like N_2 explosive decompression and steam explosion are cheaper and environmentally attractive solutions (Raud et al., 2016a).

A range of pretreatment methods have been studied over the years however, none have been singled out as efficient, simple and cost–effective. Pretreatments using moderate conditions are cheaper and simpler, but result in low sugar and ethanol yields. Pretreatments using extreme conditions have higher sugar and ethanol yields, but require expensive chemicals and equipment, making the process unfeasible (Tutt et al., 2012).

Hydrolysis

Pretreatment is followed by hydrolysis, also called saccharification. In this step, cellulose is converted into glucose, using acids or enzymes (Cardona et al., 2010; Raud et al., 2017). Table 2. presents the main characteristics of acid and enzymatic hydrolysis.

Acid hydrolysis is the most common method at the moment, and it utilizes dilute or concentrated acids, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), trifluoracetic acid (TFA) or phosphoric acid (H_3PO_4) (Gírio et al., 2010).

In the enzymatic hydrolysis, the fungi *Trichodermareesei* is commonly used (Menind et al., 2012) or commercially available enzyme mixtures. Overall, enzymatic hydrolysis is more promising than hydrolysis using concentrated or dilute acids since the product yields are higher (Cardona et al., 2010), and the utility costs are lower (Sun & Cheng, 2002). Hydrolysis represents 20% of the total costs of cellulosic ethanol production (Mupondwa et al., 2017) and it is affected by several parameters, such as pretreatment conditions, quantity of lignin present in the feedstock, substrates concentration, and cellulase activity (Sun & Cheng, 2002; Raud et al., 2015; Raud et al., 2016c).

Table 2. Main characteristics of the different hydrolysis processes (adapted from (Kamzon et al., 2016))

Hydrolysis processes	Concentrated acid hydrolysis	Dilute acid hydrolysis	Enzymatic hydrolysis
Materials	30–70% H_2SO_4	< 1% H_2SO_4	Cellulases with 5–35 FPU g^{-1} of substrate
Temperature (°C)	40	215	70
Time	2–6 h	3 min	1.5 days
Glucose yield	90%	50–70%	80%–95%
Industrial application	Getting out of date	Industrially adopted Cost-effective	Industrially adopted Process of the future
Environmental impact	Yes	Yes	No

Fermentation

Fermentation is used to convert glucose into ethanol (Raud et al., 2016c). Simultaneous saccharification and fermentation (SSF) and separated hydrolysis and fermentation (SHF) are the two most common processes used in the fermentation of lignocellulosic hydrolysate (Gupta & Verma, 2015).

In SSF, enzymes hydrolyze cellulose into sugars and ferment the hexoses into ethanol, at the same time (Kamzon et al., 2016).This process has several known advantages. It has low capital costs, low enzyme requirements, high hydrolysis efficiency and ethanol yields, reduced process time, low risk of inhibition and contamination, and it does not require reactors with large volumes. However, it has some limitations regarding the compatibility of the temperature of the hydrolysis and fermentation, and inhibition of enzymes (Sun & Cheng, 2002; Chen & Fu, 2016).

In case of SHF on the other hand, hydrolysis and fermentation can proceed at their optimum conditions, but in separate vessels. Although, it has some problems due to the inhibition and the possibility of contamination since it is a long process (Kamzon et al., 2016; Chen & Fu, 2016).

Several microorganisms have been pointed out for fermentation of sugars but, the ideal microorganism (capable of fermenting efficiently both pentoses and hexoses) has not been found (Talebnia et al., 2010). The yeast *Saccharomyces* and the bacteria *Escherichia coli* are the most common microorganisms used to convert the sugars into ethanol (Tong et al., 2012). The yeast *Saccharomyces* can produce ethanol from glucose with almost 90% of theoretical yield (Gupta & Verma, 2015). Nonetheless, it cannot ferment the C5 sugars, so these are converted into furfural, which is toxic to the yeast itself and affects the ethanol yields (Saxena et al., 2009; Farias et al., 2017).

Distillation

The recovery of ethanol from fermentation broth is done by distillation. Different separation methods can be used, and include ordinary distillation, azeotropic distillation, extractive distillation, liquid extraction fermentation hybrid, absorption and membrane separation (Adekunle et al., 2016).

The ordinary distillation can give an ethanol recovery of 95% however, to achieve 99.9% of ethanol recovery (anhydrous ethanol), further dehydration is needed (Zabed et al., 2016). Nevertheless, this purification technique has high-energy requirements, limited capacity for the separation of volatile compounds (since they tend to lodge more in ethanol), and high costs. The costs of the distillation depend on the efficiency of the enzymatic hydrolysis and on the fermentation, and increase with low ethanol concentrations (Onuki et al., 2008; Saini et al., 2015; Farias et al., 2017).

In this step a large quantity of waste–products is generated and left unused. Valorisation through AD has been reported as an efficient handling option for this highly valuable residue (Kaparaju et al., 2009).

ANAEROBIC DIGESTION

AD uses microorganisms in the absence of oxygen to degrade organic material and to convert it into biogas. The four main steps of AD are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Ariunbaatar et al., 2014).

The hydrolysis uses exoenzymes to convert complex compounds as cellulose, proteins, polysaccharides, and lipids into monomers, such as amino acids, fatty acids, sugars and alcohols (Chandra et al., 2012; Zhen et al., 2017). In this step, the degradation of lignocellulose is a slow process (Deublein & Steinhauser, 2008).

In the acidogenesis, the hydrolysed material is converted into organic acids, alcohols, hydrogen, and carbon dioxide, by anaerobic bacterias as *Peptoccus*, *Clostridium*, *Lactobacillus*, *Geobacter*, *Bacteroides, Eubacterium*, *Phodopseudomonas*, *Desulfovibrio, Desulfobacter*, and *Sarcina* (Zhen et al., 2017).

Acetogenesis uses acetogenic bacteria as *Syntrophobacter*, *Syntrophus*, *Pelotomaculum, Syntrophomonas*, *Syntrophothermus, Moorella,* and *Desulfovibrio* to reduce the products of the acidogenic phase into acetic acid (Chandra et al., 2012; Zhen et al., 2017).

Lastly, in the methanogenesis, acetate is metabolised to produce methane. In this step, organisms, such as *Methanosarcina*, *Methanosaeta*, *Methanobacterium* and *Methanoculleus*, are commonly used (Zhen et al., 2017).

In the AD, the bacterial activity is influenced mainly by pH, biochemical oxygen demand (BOD), and concentration of volatile fatty acids. Efficiency of the AD depends on the temperature, particles size, substrate C/N ratio, substrate mixing, inoculum, organic loading rate, hydraulic retention time, and solid concentration of the mix (Croce et al., 2016).

AD plays an important role in the final energy production, as an alternative source of energy for the transportation sector (Taherzadeh & Karimi, 2008). The biogas is produced mainly from energy crops and waste, such as manure, wastewater sludge or municipal solid waste (Teghammar et al., 2010). Lignocellulosic wastes such as agricultural wastes, energy crops and forestry wastes can also be used for AD (Loow et al., 2015). This process is particularly attractive due to its low environmental impact, and high potential for energy recovery. Table 3 presents the methane yield for different crops.

Table 3. Methane yields for different crops [adapted from (Murphy et al., 2011)]

Crop	Methane yield (m^3 ton^{-1} VS added)
Flax	212
Grass	298–467
Hemp	355–409
Jerusalem artichoke	300–370
Maize (whole crop)	205–450
Barley	353–658
Straw	242–324
Leaves	417–456
Sorghum	295–372
Sugar beet	236–381
Oats (grain)	250–295
Rye (grain)	283–492
Wheat (grain)	384–426

Anaerobic digestion of biomass

Although it is possible to use untreated material for AD, due to the complex structure of the lignocellulosic material, the methane production of untreated material is inferior to the methane production from treated material (Jimenez et al., 1990; Bauer et al., 2009; Zheng et al., 2009; Teghammar et al., 2010; De Paoli et al., 2011; Song et al., 2013; Taherdanak et al., 2016). Usually, the first step for AD production is the pretreatment, to increase the digestibility and improve methane yields (Xiao & Clarkson, 1997).When pretreated with different methods, biomass has higher methane yields, than raw material (Bauer et al., 2009; Kaparaju et al., 2010; Teghammar et al., 2010; Ziemiński et al., 2012).

In addition, pretreated material reaches the maximum methane production sooner than untreated material, the initial hydrolysis rate and the degradation rate increase in pretreated samples (Rouches et al., 2016). Untreated material has higher digestion time, and lower amounts of dry matter of substrate reduction (total solids and volatile solids) when compared with pretreated material (Zheng et al., 2009).

Anaerobic digestion of waste–products

In the bioethanol production process, a large quantity of biomass waste is generated (Moraes et al., 2015). Several solutions have been proposed as handling options for this biomass waste. These include: discharge, marine outfall, return to agricultural fields, sewage treatment, lagoon treatment, anaerobic digestion, incineration, and drying to an animal feed (Willington & Marten, 1982).

The optimum handling option should take into consideration the characteristics of the waste–products such as the energy return on energy invested, the economic feasibility and their environmental impacts. Table 4 outlines the main characteristics of alcohol stillage handling options.

Table 4. Characteristics of alcohol stillage handling options (adapted from (Willington & Marten, 1982))

	Discharge	Marine Outfall	Agricultural Fields	Sewage treatment	Lagoon treatment	AD	Incineration	Drying
Energy								
Net energy	0	–	–	–	0	+	+[b]	–
Economy								
Capital cost	L	L–M	L–M	H[a]	M	H	H	H
Operating cost	L	L	M–H	H	L	M	M	M
Further treatment	N	N	N	N	Y	Y	N	N
Useful product	N	N	Y	N	N	Y	Y	Y
Environment								
Land use effect	0	0	H	L	M	L	0	0
Water quality	H	M–H	L–M	L	L	0–L	0	0
Air quality impact	0	0	L–M	0	0	L	L	L
Odour potential	M–H	L–M	L–M	L	L–M	L–M	0	L
Flora/Fauna	M–H	L–M	L–M	L	L	L	0	0

0 Zero
– Negative
+ Positive

L Low
M Moderate
H High

N No
Y Yes

[a] Capital cost to the distillery is lower if using municipal sewage facilities;
[b] Depends on the feedstock.

From several handling options for stillage presented in Table 4, AD presents a low land use impact, low water quality impact, low air quality impact, low–moderate odour potential, and a low flora/fauna impact, compared to discharge, marine outfall and return to agricultural fields.

Environment

Waste-products from bioethanol production are a source of environmental pollution due to the large quantity of products generated, and their high pollutant potential. Up to 20 litres of stillage can be generated for each litre of ethanol produced, and the BOD of the liquid phase of stillage can vary between 10 and 100 g $O_2 \cdot L^{-1}$ (Dererie et al., 2011; Kaparaju et al., 2010). Moreover, the environmental risk can be even greater, as the BOD measurements often underestimate the BOD_7 (Raud et al., 2012).

AD of stillage can be presented as an environmental solution for these waste–products, making use of their high BOD for biogas production. AD has high BOD removal efficiency, and it can convert more than 50% of BOD into biogas (Wilkie et al., 2000; Kaparaju et al., 2010). AD of waste-products has several environmental advantages. Firstly, it reduces the organic matter content and therefore, the pollution potential, and secondly, it reduces CO_2 and other greenhouse gas (GHG) emissions by using the waste-products for energy production, reducing the utilisation of fossil fuels.

Costs

From the economic point of view, despite the high–quality fuel produced during bioethanol production, the costs of energy input are still high, making it difficult to compete with petrol and diesel from fossil sources. A solution to offset the costs of bioethanol production and add value to the production chain is the AD of the waste–products.

Several studies reported the value added of AD of waste–products. It can reach up to 30% of the value of the principal product, improving the production costs (Mojović et al., 2012). The use of these high–energy wastes can bring direct and indirect economic revenues. The direct revenues are associated with the energy produced in the form of methane, and the indirect revenues come from the costs avoided with fertilisers, odour reduction and protection of the environment (Pabón Pereira et al., 2013).

Research shows that AD is an economically viable option and a feasible process for the utilisation of biomass wastes (Wilkie et al., 2000), especially when bioethanol waste is used as a raw material. Its AD does not require further pretreatment due to the pretreatment that has already taken place in the bioethanol production, reducing the investment costs (Dererie et al., 2011). It implies that the revenue is enough to cover the upgrade process of waste–products recovery, which includes operational and capital costs and costs of collection and transport (of ethanol waste–products to other facilities for further AD).

Transport and collection include the transport of the feedstock from the field to the biorefineries, and the transport of the waste-products to other facilities for further AD. Long transport distances have several negative disadvantages to the bioethanol production chain. It increases the GHG and CO_2 emissions and influences the viability of the project. If the transportation costs are too high, due to long distances, the project can turn out economically unfeasible. Table 5 illustrates the ethanol transportation costs by water, truck, and rail, in U.S. and Brazil.

Table 5. Ethanol transportation costs by water, truck, and rail, in the U.S. and Brazil (Worldwatch, 2012)

Transportation mode	Cost (€ m^{-3})	
	U.S.	Brazil
Water (including ocean and river barge)	€8–€25	€10
Short distance trucking (less than 300 km)	€8–€17	
Long distance trucking (more than 300 km)	€17–€83	€26
Rail (more than 500 km)	€17–€40	€17

Energy

The full use of biomass resources can be achieved by the utilisation of the waste–products for the production of energy in the form of methane. The energy of these waste–products represents 51–71% of the total energy content of the crops, and it can give higher net energy outputs (Pabón Pereira et al., 2013). In addition, the use of waste–products improve the speed and the rate of the process. As the pretreatment has already taken place, the process starts more rapidly than when using biomass that has not been through bioethanol production (Dererie et al., 2011).

Energy return on energy invested (ERoEI)

ERoEI is the ratio of energy gained from unit of fuel and the energy input required to carry out its production and can be given by Eq. 1. (adapted from (Hammerschlag, 2006; Seghetta et al., 2014)):

$$\mathrm{ERoEI} = \frac{\mathrm{E_{ret}}}{\mathrm{E_{req}}} \qquad (1)$$

where E_{ret} is the returned/gained energy in the form of the fuel and E_{req} is the energy required to produce that amount of fuel. For biofuels, E_{req} includes the energy spent in plantation, production, harvesting, transporting and purification of the feedstock and of the biofuel. Table 6 presents the ERoEI for different types of fossil fuels, and for several alternative sources of energy.

Table 6. ERoEI for different energy sources (adapted from (Hall et al., 2014))

Resource	Year	Country	ERoEI
Fossil fuels (oil and gas)			
Oil and gas production	2006	Global	18
Oil and gas production	2010	Canada	15
Oil and gas production	2008	Norway	40
Oil and gas production	2009	Mexico	45
Oil and gas production	2010	China	10
Fossil fuels (others)			
Natural gas	2005	US	67
Natural gas	2009	Canada	20
Coal (mine–mouth)	2007	US	60
Coal (mine–mouth)	2010	China	27
Other non–renewables			
Nuclear	n/a	US	5 to 15
Nuclear	2010	New Zealand*	9 to 14
Renewables			
Hydropower	n/a	n/a	> 100
Hydropower	2010	New Zealand*	94
Wind turbine	n/a	n/a	18
Wind turbine	2010	New Zealand*	22
Geothermal (electricity)	2010	New Zealand*	9
Wave energy	2010	New Zealand*	18
Tidal energy	2010	New Zealand*	40
Ocean thermal energy conversion	2010	New Zealand*	4
Solar collectors			
Flat plate	n/a	n/a	1.9
Concentrating collector	n/a	n/a	1.6
Photovoltaic	n/a	n/a	6 to 12
Photovoltaic	2010	New Zealand*	9
Passive solar	2010	New Zealand*	6
Biomass			
Solid biomass	2010	New Zealand*	20
Bioethanol	2010	New Zealand*	5
Corn	n/a	US	0.8 to 1.6
Sugarcane	n/a	n/a	0.8 to 10
Biodiesel	n/a	US	1.3
Biodiesel	2010	New Zealand*	2
Electricity	2010	New Zealand*	13

*Source: (Dale, 2010).

From Table 6 it is possible to analyse the different ERoEI for fossil fuels (oil, gas and coal) and for alternative sources of energy. This ratio (ERoEI) is a measure of the efficiency of any kind of production. The lower the ERoEI of a production chain, the higher its energy requirements (making it energetically but also economically and environmentally, disadvantageous), and higher the risk of being considered as an energy sink (Worldwatch, 2012). The fuels most commonly used have higher ERoEI than for example, ethanol produced from cellulosic material (Fig. 1).

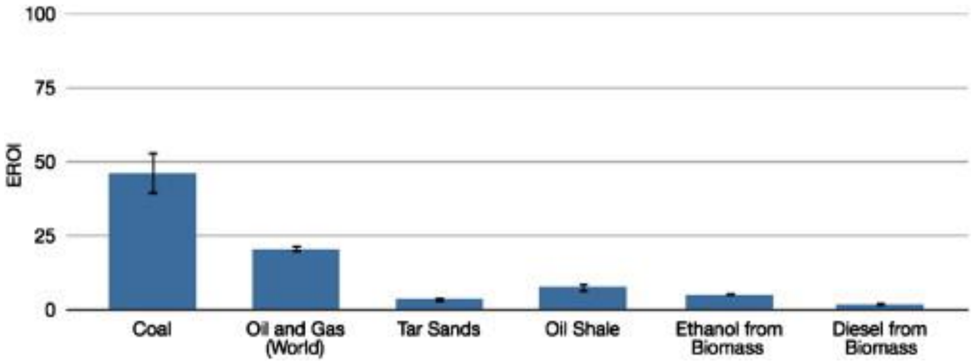

Figure 1. ERoEI for coal, oil and gas (world), tar sands, oil shale, ethanol from biomass and diesel from biomass (Hall, 2017).

AD of bioethanol waste–products can increase the ERoEI of the bioethanol production chain since the waste–products are used to generate energy for the process or/and sell it to the grid. This solution can make the bio-refineries self-sufficient and can offset its energetic needs from external sources of energy to process the waste–products (Worldwatch, 2012).

RESEARCH GAPS AND CHALLENGES

Despite the fact that bioethanol has been used as a biofuel since the 1900s, and the quality of the fuel produced is high, its production still has environmental, economic, and energetic limitations.

Environment

Biofuels production has some environmental constraints regarding, land and soil loss. It can have a high ecological footprint and a high GHG effect. Apart from that, the other environmental restriction is regarding the high pollutant potential of the waste-products generated after the distillation process. The handling options include discharge; marine outfall; agricultural fields; sewage treatment; lagoon treatment; AD; incineration; and drying. However, the best handling option is still not clear, due to the different environmental impacts. Further studies taking into consideration the environmental impacts of bioethanol waste–products, should be carried out.

Costs

From the economic point of view, the main hurdle is associated with the high costs of bioethanol production, and with the high dependence of its economic feasibility on the crude oil prices.

Pretreatment and enzymatic hydrolysis are the two most costly parts of the production process. Pretreatment of raw material represents 1/3 of the total costs of bioethanol production, and it influences the cost of enzymatic hydrolysis and fermentation. Despite the fact that some methods of pretreatment are promising solutions for bioethanol production, it is important to find the optimum pretreatment for each type of lignocellulosic biomass, decrease the overall production costs and the costs of enzymes, and increase the glucose and ethanol yields.

AD of waste–products is a prospective solution to lower the overall production costs, due to its low financial input. Even though its utilisation contributes to the reduction of bioethanol production costs (Yadav et al., 2016), the economic quantification of the benefit of AD of waste-products to the bioethanol production chain still not clear.

The different costs of collection and transport are influenced by the distance between the ethanol production and the distribution grid. This factor shows the importance of adequate planning when building the power plants that should include an economic analysis containing the transport and distribution costs.

Energy

Due to the high-energy content, waste-products can be used for processing energy, through AD to add value to the production chain and improve the energy balance. Although waste-products give a positive energy credit to the ERoEI, some studies do not consider this in their analysis (Giampietro & Mayumi, 2009). Currently, ERoEI is not a consensual subject due to the big range of different results obtained for each feedstock. Different authors consider different energy inputs for the calculations, making the results inconsistent. Some of the energy inputs that are usually taken into consideration include the energy inputs of the seeders / planters, fertilisers, pesticides, and transportation of water to the fields. Other energy inputs are required for harvesting, transporting (from the fields to the facilities), processing (hydrolysis and fermentation), and purifying (distillation). ERoEI is also influenced by the geographical / climatic conditions. Tropical plants have better ERoEI ratios, due the growth conditions (Worldwatch, 2012).

Waste-products

Bioethanol production results in valuable waste-products, after the fermentation process. These waste–products have a high energetic value and large pollution potential. Further utilisation of this biomass waste can improve the overall efficiency of bioethanol production, and the bioethanol economics, by adding value to the production chain. In addition, the maximisation of its utilisation can also be seen as an environmental handling solution, due to its high pollution potential.

The best economic, energetic and environmental handling option for this waste–products still under discussion, but some studies refer to AD as a solution (Willington & Marten, 1982; Dererie et al., 2011; Rabelo et al., 2011).

OUTLOOK AND POSSIBILITIES

As the conversion of lignocellulosic material into ethanol still has economic, technical and environmental obstacles (Sánchez & Cardona, 2008), different feedstocks and methods are being studied to make it more feasible. Bioethanol production method has to be efficient (high energy yields), cost effective (energy return on investment) and environmentally beneficial, in order to be feasible.

From the economic point of view, the costs of bioethanol production are still high, due to large energy inputs. Waste–products of bioethanol production process cannot be used as a transportation fuel, so their AD can help balance the costs of bioethanol production, adding economic value to the production chain, without further energy input.

Technically, these waste–products present high–energy potential. Research has shown that their AD does not need any further pretreatment, due to the initial pretreatment (Dererie et al., 2011), influencing speed and efficiency of the process. The process will start more rapidly than with untreated biomass that has not been through bioethanol production, leading to time and cost efficiency. This process occurs without any additional energy input, increasing the ERoEI and contributing, at the same time, to the economic valorisation of the production chain. Combining ethanol waste–products with biogas production can also help increase the share of renewable energy in the transportation sector.

From the environmental perspective, waste from the bioethanol production is highly polluting (Salomon & Silva Lora, 2009; Kaparaju et al., 2010), so its reutilisation can be seen as an environmental solution to the large quantity of waste–products with high BOD generated during the bioethanol production.

Thus, in Fig. 2, AD of bioethanol waste–products (a) has been proposed as a technical solution for the valorisation of the production chain and for recycling the waste from bioethanol production. Its feasibility should be compared with AD of pretreated biomass (b) and direct AD of untreated biomass (c).

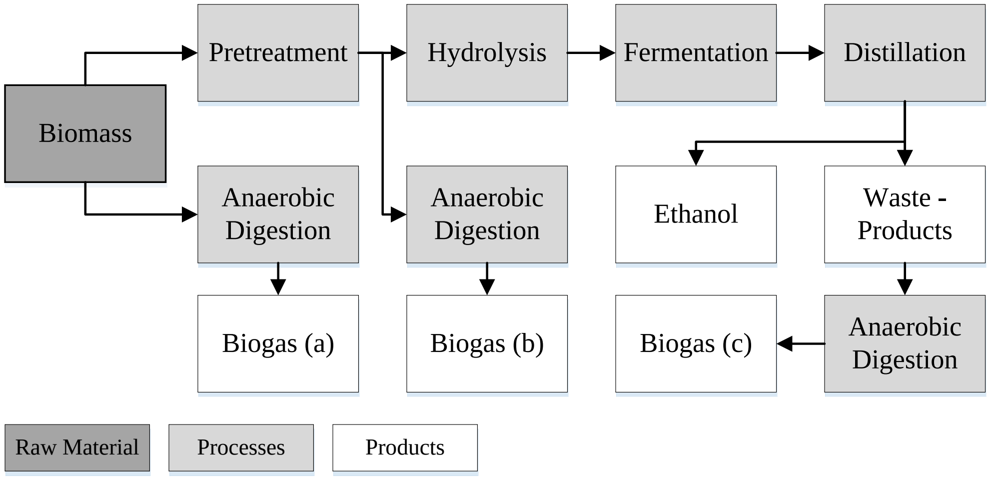

Figure 2. Bioethanol production chain and different possibilities for utilisation of AD process in it (AD of untreated material, pretreated material and waste–products).

A cost–benefit analysis focusing on time vs efficiency of the process should be carried out (and include positive externalities, such as the environmental gains), to assure that the additional energy value from AD of production waste will be enough to give a return on investment into AD technology.

CONCLUSIONS

Bioethanol presents energetic, economic and environmental challenges, in all the steps of its production (pretreatment, hydrolysis, fermentation and distillation). These challenges include lack of cost–efficient technology, low yields, costly pretreatments, cellulose enzymes, and lack of microorganisms capable of ferment both C5 and C6 sugars. Further research needs to be done in all the stages of the process to increase the efficiency of the production, and decrease the costs.

In the distillation process, the biggest challenge refers to the large fraction of biomass waste that is produced and left unused at the end of the process. The best solution for utilisation of these waste–products is still under investigation.

Utilisation of waste–products through further AD has been proposed as a possible path to reduce costs of bioethanol production by adding economic value to the production chain, increasing the efficiency of the process, and as an environmental solution to a large quantity of process residue with high BOD that is generated during bioethanol production.

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