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Review

Biofuels journey in Europe: Currently the way to low carbon economy sustainability is still a challenge

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ABSTRACT

The growing need for any type of energy is leading the transport biofuels sector to develop technologies for an energy-efficient future, by using synergistically different forms of energy. Several biofuels are successful in addressing environmental concerns, but some create skepticism on their global sustainability. This study is built around key topics related to four generation biofuels development, aiming to highlight advantages, drawbacks, negative externalities, and constraints, for their effective commercialization. It offers a short state-of-the-art review of terrestrial and marine biomass conversion into automotive and jet biofuels, and focuses on the biochemical and thermochemical conversion pathways and the role of processing conditions to maximize the production of renewable fuels. It concludes that there is still no clear answer on which generation biofuels meets the global sustainability criteria better. In all cases, it is important to take into account the scale of economy, bioresources availability and planetary boundaries for biomass supply, to design viable technologies and consider the Food-Energy-Water and Carbon-Nitrogen Nexus challenges. Although the European Commission is looking at cost-efficient ways to make the European economy more climate-friendly and less energy-consuming by addressing the importance of biomass availability, proper legislation must deal with the multifaceted confrontation of the global sustainability which should also be driven by the socio-economic criteria.

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Abbreviations

AFEX	Ammonia Fiber Expansion
ASTM	American Society for Testing and Material
BTL	Biomass-to-Liquids
DME	Dimethyl Ether
EC	European Commission
EU	European Union
EUR	Euros
FAO	Food and Agriculture Organization of the United Nations
FCC	Fluid Catalytic Cracking
FT	Fischer – Tropsch
GBEP	Global Bioenergy Partnership
GHG	Green House Gas
GL	Giga Litre
GWh	Gigawatt hour of energy
HDO	Hydrodeoxygenation
IATA	International Air Transport Association
ISO	International Standards Organization
kVA	Kilovolt Ampere
LCA	Life Cycle Assessment
MCPFE	Ministerial Conference on the Protection of Forests in Europe
MTBE	Methyl Tert-Butyl Ether
MWh	Megawatt hour of energy
NADPH	Nicotinamide Adenine Dinucleotide Phosphate
PBRs	Photobioreactors
PM	Particulate Matter
PPP	Public-Private Partnership
R&D	Research and Development
R&I	Research and Innovation
RED	Renewable Energy Directive
SCWG	Supercritical Water Gasification
SFs	Solar Fuels
SPK	Synthetic Paraffinic Kerosene
TOE	Tonne of Oil Equivalent
USD	United States Dollar
USDA	United States Department of Agriculture
VGO	Vacuum Gas Oil
xG	x Generation biofuel

1. Introduction

Rapid population growth has been accompanied by an increase in energy and transport fuels consumption, which has resulted in an irreversible degradation of the environment and climate change. It is expected that the planet population will surpass the 9 billion (10^9) by 2050 and the energy demands will increase by 84%, thereby making possible for biofuels to provide at least the one-third of the additional fuel (Dutta et al., 2014).

Transportation is fundamental in the current globalized economy as it allows the exchange of goods and citizens. It is in parallel one of the sectors to use fossil fuels, releasing large quantities of gaseous pollutants. In the EU, transport is responsible for an estimated 21% of all greenhouse gas emissions that are contributing to global warming. In order to meet sustainability goals, in particular, the reduction of greenhouse gas emissions agreed under the Kyoto Protocol, it is essential to find ways of reducing emissions from transport (García-Olivares et al., 2018).

Biofuels are energy-enriched chemicals produced from biomass which is in abundance in nature, resulting from photosynthesis that converts the atmospheric carbon dioxide into sugars, by using solar energy and water (Shuba and Kifle, 2018). In 2007 biofuels production in EU reached an amount of 8500 ktoe, while in 1996 the amount was less than 500 ktoe. Globally in 2010, 15.5% of power generation and 1.3% of energy consumption was attributed to renewable energy, while today 86,000 kt per year of biofuels are estimated to be produced, with USA and Brazil being the primal producers (Rastogi and Shrivastava, 2017).

Usage of biofuels became more significant due to visions of resource higher efficiencies, decarbonizing societies and exploitation of local renewable energy sources, by which the economy of each country can seek its independence from imported oil (Radionova et al., 2017; Alaswad et al., 2015). In Europe, the dominant countries in producing biofuels are Germany and France, with an annual production rate of 3198 and 2226 kTOE respectively in 2016. Other European countries that managed to produce more than 1000 ktoe in 2016, are the Netherlands and Spain (Statista, 2018).

The transition to a low carbon transport sector requires suitable technologies and availability of energy resources (Dominković et al., 2018). Environmentally, economically, and socially sustainable technologies are needed for the sustainable production of liquid fuels. The chance of biofuels to replace conventional fuels is highly dependent on biomass production and availability of proper agro-energy districts.

Biofuel production can provide positive ecological, social and economic opportunities for many agricultural regions, however, the investment in infrastructure is crucial. The Public-Private

Partnership (PPP) contracts in the agro-energy regions can lead to the establishment of appropriate bioenergy infrastructure (Fantozzi et al., 2014). However, for a PPP contract to be successfully implemented in an agro-energy district, it needs to be profitable for the private sector and socially acceptable for the public sector, and to satisfy the needs of the consumers (Manos et al., 2014). Studies reported by Italian and Greek researchers (Fantozzi et al., 2014) were found in the literature on the implementation of PPP contracts, where the economic viability of handling biomass production and agriculture implications were discussed.

The scale of economy is also important for the biofuels production. Large crops-based biofuels production has been associated with risks and concerns, referred to biodiversity, deforestation, increased demand for agricultural land and water scarcity, impending its deployment (Zabaniotou, 2018). Therefore, the biofuels' journey is long; various generations of biofuels were developed to face the above issues and conflicts, with the algal and waste feedstocks to be on the table (Doshi et al., 2016).

The objective of the study is to discuss the journey of 4 generations biofuels in Europe and shed light on their sustainability. In this study, the classification of the 4 generations biofuels is based on the type of the raw materials used for their production, the technological feasibility and viability and the fulfillment of the sustainability goals (Alaswad et al., 2015). The focus is on the biochemical and thermochemical conversion pathways from terrestrial and marine resources, and on the role of processing conditions to maximize the production of renewable fuels. Current advances, environmental and economic issues are summarized, hypothesizing that the requirements of the sustainability concept are not yet thoroughly fulfilled, due to emerging carbon-nitrogen, food-energy-water nexus, and socio-economic challenges. The confirmation or refutation of the initial hypothesis is important for the scientific community, the transport sector and the industry, in order to orient properly the R&I efforts towards meeting sustainability and standards and/or investigate new energy resources with higher energy density.

2. Methodology

The methodology followed in this review, was based on reviewing published papers on the 4 generation biofuels (1G, 2G, 3G, 4G) and their sustainability. The ISI Web-of-Science, Google Scholar, Google were used. In addition, EU legislation EU, FAO reports were also consulted. A retrospective comparison of studies comparing systematic reviews by searching scoping reviews published between 2007 and 2018. The bibliographies of the most recently selected studies (2017–2018) were examined to find other relevant studies. The very recent studies (2016–2018) take in account sustainability constraints, beyond GHG emissions, with an emphasis of 2018-studies on solar fuels and solar economy.

The comparison of biofuels with the fossil fuels, as it was resulted from reviewing the international literature is depicted in Table 1**.**

3. Material and methods

Four different generations (1G, 2G, 3G, 4G) of biofuels have been developed during the last 2 decades (Dutta et al., 2014). The 4 generations are differentiated by the feedstock and processing technology cost and sustainability level (Alaswad et al., 2015).

3.1. 1G biofuels (vegetable oils and animal fats)

First generation (1G) biofuels (bio-diesel and bio-ethanol) are produced from food carbohydrates, vegetable oils and animal fats (Radionova et al., 2017). High purity bio-ethanol is generated after the separation of carbon dioxide and water. However, many conflicts of 1G biofuels with food have raised. The use of only 2% of the planet's arable land to produce the 1G biofuels had a significant impact on food and animal feed prices (Shuba and Kifle, 2018), although the precise influence of biofuels in the increment of food prices remains unknown (Dutta et al., 2014).

Fig. 1 depicts the processes used to produce the 1G biofuels (biodiesel and bio-ethanol).

3.2. 2G biofuels (lignocellulosic non-edible biomass-based biofuels)

Lignocellulosic biomass can be converted to 2G biofuels through two different conversion routes, the biochemical and thermochemical, (Fig. 2**).** Agricultural residues, known as lignocellulosic resources, can produce more sustainable biofuels by achieving a higher reduction of GHG emissions (Radionova et al., 2017). The main components of lignocellulosic biomass are cellulose, hemicellulose and lignin**.** Hemicellulose units are connected to phenolic compounds, known as lignin, through covalent bonds (Rastogi and Shrivastava, 2017).

The production of synthetic fuels from biomass via Fischer–Tropsch (FT), known as the biomass-to-liquids (BTL) process, constitutes a promising route for future fuels. Fischer–Tropsch (FT) synthesis follows gasification with intermediate gas cleaning and conditioning, to produce synthetic transport fuels. The environmental and economic considerations of the BTL process should also be considered based on techno-economic and lifecycle analysis studies (Lappas and Heracleous, 2016).

Table 1
Differences between biofuels and fossil fuels.

Biofuels	Fossil fuels
Carbon emissions	
• CO_2 neutral	• Non- CO_2 neutral
• Closed carbon cycle by photosynthesis the plants	• Greenhouse gases emissions responsible for global warming
Renewable sources	
• Biofuels are derived from biomass available in nature, requiring a shorter time to be generated compared to conventional fossil fuels.	• Fossil fuels require millions of years to generate from the degradation of organic matter.
Safety	
• Energy corps, residues, and wastes are considered a safe way to produce biofuels	• The extraction of fossil fuels is a hazardous process and accidents like oil spill can cause disastrous consequences in the environment.
Economic and social impact	
• Biofuels boost an independent economy and provide new job opportunities.	• Economies relying on oil can be easily affected by economic and social upheavals.
Energy content – Heating value	
• Due to the presence of high concentrations of oxygen, the energy content of biofuels is much lower compared to conventional fossil fuels.	• Fossil fuels have high energy content and have been the building blocks of energy supply.

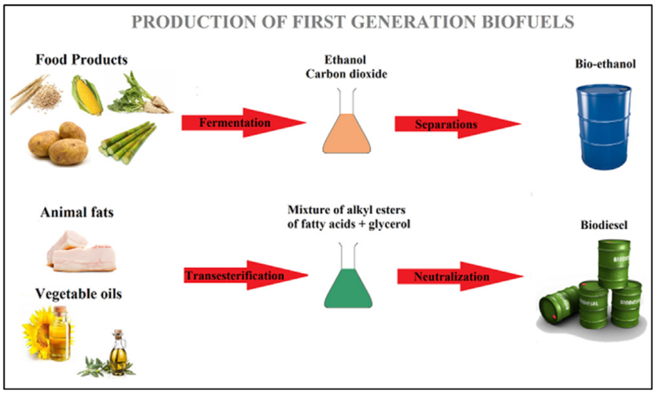

Fig. 1. 1G biofuels production processes.

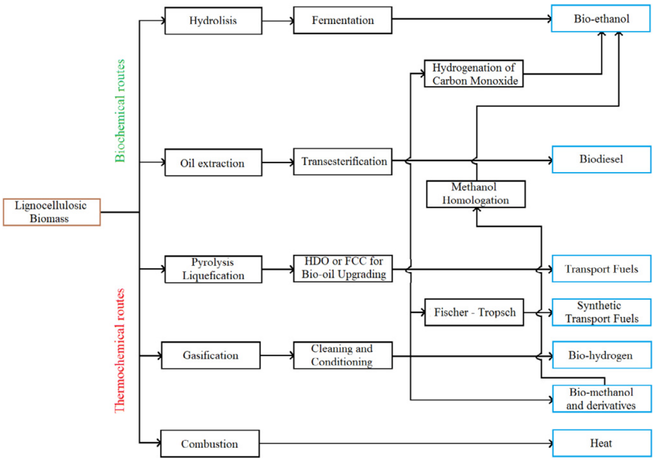

Fig. 2. 2G biofuels production processes.

Bio-ethanol can also be produced thermochemically from syngas either directly through hydrogenation of the carbon monoxide contained inside syngas or by using the bio-methanol derived from syngas, through a process known as methanol homologation (Sikarwar et al., 2017). Pyrolysis derived liquid product commonly known as bio-oil, can be upgraded to transport biofuel. The upgrading can be achieved with the oxygen reduction, through hydrotreatment (HDO) or catalytic pyrolysis (FCC) with zeolites (Thegarid et al., 2014).

3.2.1. *Biochemical pathways*

The biochemical pathways are the fermentation and transesterification processes of biomass, for the production of bioethanol and biodiesel respectively, which however are more expensive and complicated than the thermochemical route (Sikarwar et al., 2017). One of the methods to extract oil from the non-edible seeds is the usage of pressure shockwaves. Maroušek et al. (2014b) studied the utilization of an underwater high-voltage discharge system, which can create pressure shockwaves through a water plasma expansion capable of breaching the lignocellulosic tissues of different types of seeds and of expanding their external surface area and micropore volume. The method was tested on *Jatropha Curcas* L. seeds and achieved an oil extraction yield of 94%.

Bio-ethanol produced from residues and wood process waste is considered as a 2G biofuel (Dutta et al., 2014). It can be produced with hydrolysis of lignocellulosic biomass and fermentation, in a two stage-process (Rastogi and Shrivastava, 2017). The biggest problem with 2G bio-ethanol production is the hydrolysis of the cellulose and hemicellulose. While the step of hydrolysis is relatively fast and simple in the 1G biofuel production, this is more difficult in the 2G bio-ethanol production. A pretreatment step used to aid the hydrolysis is Steam Explosion, which avoids the use of costly and dangerous catalysts (Maroušek et al., 2014a). Ozonolysis and Ammonia Fiber Expansion (AFEX) can also be used to improve the reactivity of cellulose and enrich the production of fermentable sugars by enhancing the carbohydrate yields produced with hydrolysis. Other advantages include the obstruction of the synthesis of pentoses, generated from hemicellulose, the separation of lignin, which can be used for the formation of valuable co-products and the minimization of energy inputs required for the bio-ethanol production (Rastogi and Shrivastava, 2017).

Special enzymes are used for the hydrolysis, which boost the degradation of lignocellulosic biomass into glucose and xylene. However, a drawback of the process is that the sugars produced through hydrolysis can be inhibitors in the activity of the enzymes, thereby reducing the bio-ethanol yield. Efforts have been made for the hydrolysis and fermentation stages to occur simultaneously in one single reactor, but without managing to find the optimum operating parameters for the process (Rastogi and Shrivastava, 2017).

The hydrolysis step can be facilitated with genetic modification of the lignocellulosic raw materials. This method enables the expression of appropriate genes that increase the resistance to drought, herbicides, and pesticides, while they also moderate the need of fertilizers and water. The implementation of metabolic engineering in bioethanol production improves the efficiency of the hydrolysis of lignocellulosic biomass without modifying its composition. It can also boost the production yields of alternative alcohols, such as iso-propanol and butanol, which have recently gained the interest in biofuel production, due to their higher calorific value and lower tend to corrode equipment in contrast to ethanol (Dutta et al., 2014).

Transesterification is still viewed as one of the best techniques to biochemically produce biodiesel at industrial scale, because of its high conversion efficiencies and low costs. The blending of renewable biodiesel with conventional diesel can highly increase the power generation with less carbon and sulfur emissions (Bhuiya et al., 2014). It was reported that the blend of biodiesel produced from *Jatropha* or *Karanja* oils with fossil fuel, managed to power a diesel engine with 7.5 kVA electrical supply (Dutta et al., 2014). It was also estimated that a mixture of biodiesel and conventional diesel, with a ratio of 20:80, would not provoke any damages in the engine (Bhuiya et al., 2014).

3.2.2. *Thermochemical pathways*

The thermochemical route consists of three different pathways; the combustion for heat generation, the gasification, and pyrolysis.

Gasification converts solid and liquid lignocellulosic biomass into syngas at 800–900 °C (Sikarwar et al., 2017). The energy required for the endothermicity of the gasification reactions is provided by the combustion of the residual char. Syngas can be utilized to produce: a) transport biofuels through an FT synthesis, b) bio-hydrogen and c) bio-methanol, which can be converted to fuel additives, such as bio-dimethyl ether (DME) and Methyl tertiary butyl ether (MTBE). The combination of biomass gasification with FT synthesis in the presence of metal cobalt or iron catalysts, is considered as a very promising option for the production of synthetic transport fuels (Sikarwar et al., 2017). During the FT synthesis, which occurs in temperature and pressure ranges equal to 200–300 °C and 10–60 bar respectively, CO is absorbed in the surface of the catalyst. H_2 is driven in the surface of the catalyst through a dissociative absorption.

Hydrogen is widely known as the most environmentally friendly energy carrier for power generation. It is a zero-carbon energy carrier and when combusted it releases zero carbon emissions. Hydrogen has the highest energy content from all fossil fuels and it can replace them as primary fuel, both in the automotive industry and aviation (Dimitriou and Tsujimura, 2017). Hydrogen from biomass can be produced via various gasification technologies. Gasification can be carried out by using supercritical water as a gasifying agent (SCWG) to produce high hydrogen yields Although this method provides high H_2 production efficiency, it has the disadvantages of high cost and high energy penalty (Sikarwar et al., 2017). Steam gasification or wet-biomass gasification could be more effective than air gasification because it enhances the production of hydrogen. Bartocci et al. (2018) used charcoal pellets to generate 0.03 kg of H_2 per 1 kg of raw material by coupling steam gasification with a pyrolysis plant to reform gasification volatile products and sustaining the energy demands of the pyrolysis and gasification processes.

It seems that hydrogen economy can provide zero-carbon fuels, however, the transition is not expected to occur in the following years, due to associated high production costs. The production cost of hydrogen from steam methane reforming, which is one of the most widely used methods for hydrogen generation, is equal to 3.8 EUR/kg (4.7 USD/kg). For hydrogen to be easily used in the automotive industry, a target of 1.6–3.25 EUR/kg (2–4 USD/kg) of the production cost must be achieved, including the compression, storage and dispensing costs (Ramsden et al., 2013).

Syngas can produce crude bio-methanol with an efficiency of 99%, if inserted in a methanol reactor where H_2O vaporization takes place. Bio-ethanol can also be produced directly from syngas through the selective hydrogenation of carbon monoxide in the presence of a rhodium-based catalyst (Sikarwar et al., 2017). Bio-methanol can further produce bio-ethanol via a reductive carbonylation, in the presence of a cobalt-copper based catalyst. Bio-methanol can produce DME and MTBE, for fuel upgrading (Sikarwar et al., 2017).

Pyrolysis is the process of the thermal decomposition of biomass in an inert atmosphere. It produces char, condensable and non-condensable gaseous products. Bio-oil can be derived in large quantities from fast pyrolysis and flash pyrolysis followed by rapid cooling of the generated vapors. It has been reported that the bio-oil produced through fast pyrolysis contains up to 70% of the energy initially contained in the biomass feedstock (French and Czernik, 2010).

Bio-oil derived from the lignocellulosic biomass pyrolysis, is a complex dark-brown liquid, with a strong odor. It consists of nearly 400 types of different organic compounds, whose molecular weight varies from 18 to 5000 g/mol, many of which are oxygenated (Stefanidis et al., 2016).

Bio-oil is not without its drawbacks: It has a low heating value of 16–19 MJ/kg, contains high oxygen and water mass ratios of 40–50% and 15–30% respectively (Bridgwater, 2012); It has incomplete volatility, high viscosity, high acidity, thermal and chemical instability, poor ignition and combustion properties and ineligibility with conventional fuels that do not allow its application as a transport fuel (French and Czernik, 2010). It is chemically unstable due to the rapid condensation of depolymerization products derived from the cellulose, the hemicellulose, and the lignin contained in biomass (French and Czernik, 2010). These drawbacks along with the associated high cost, render the HDO a very difficult fuel (Thegarid et al., 2014).

Bio-oil needs further upgrading to reduce the oxygen content. Hydrodeoxygenation (HDO) and Fluid Catalytic Cracking (FCC) are considered to be the main processes used for the oxygen removal (Thegarid et al., 2014). Sulfated catalysts NiMo and CoMo and some metals, such as platinum and ruthenium, can be used in hydrogenation due to their high catalytic activity. Water produced from the deoxygenation can cause the deactivation of the catalysts (Bridgwater, 2012).

Research showed that hydrodeoxygenated pyrolysis oils could successfully be co-processed with vacuum gas oil (VGO) in a lab-scale FCC unit, to bio-fuels with the hydrodeoxygenation step taking place at ~300 °C under 200–300 bar of hydrogen. However, hydrodeoxygenation step is energy demanding, thus eliminating or replacing it by a less energy demanding upgrading step, would largely benefit the FCC co-processing of pyrolysis oils to bio-fuels (Thegarid et al., 2014).

FCC is operated under atmospheric pressure, avoids the use of hydrogen and manages the separation of oxygen in the form of water or carbon oxides, with the usage of special catalysts known as zeolites. Catalytic cracking can be defined as a combination of dehydration, decarboxylation and decarbonylation reactions, which take place simultaneously to achieve deoxygenation (French and Czernik, 2010).

One of the differences between HDO and FCC is that the latter produces more aromatic compounds. FCC takes place in temperatures that are similar to the temperature, in which the bio-oil is produced from fast pyrolysis, thereby allowing the integration of the two processes in one single reactor. Specifically, there have been attempts for the condensable vapors to be upgraded *in situ* before their condensation (Stefanidis et al., 2016). The process of *in situ* fast pyrolysis, can take place in either one or two steps. If the process takes place in two stages, vapors are produced by pyrolysis in the first stage and then in contact with a catalytic bed, can be upgraded. In the case of a one-step process, the production and upgrading of the vapors occur simultaneously, by biomass contact with hot catalyst, which act as means of heat transport (Bridgwater, 2012).

One of the most studied catalysts for the pyrolysis of biomass is the zeolite ZSM-5. It is known for the reduction of oxygenates via deoxygenation reactions and the simultaneous increase of aromatic compounds (Bridgwater, 2012). French and Czernik (2010) tested forty different types of catalysts in biomass catalytic cracking. These included modified zeolite catalysts and commercial ZSM-5 catalysts. They concluded that ZSM-5 and catalysts impregnated with nickel, cobalt, iron, and gallium are more efficient in achieving high hydrocarbons yields. The *in situ* catalytic upgrading of lignocellulosic biomass pyrolysis vapors was tested with ZSM-5 catalysts, impregnated with the nickel and cobalt metals and magnesium oxide catalysts, prepared from natural Greek magnesite rocks. Carbonaceous solids, commonly known as coke, can be produced in addition to bio-oils, due to the dehydration of oxygenated organic compounds, having a high oxygen ratio. Coke can cause the deactivation of the catalysts by reducing their specific surface area and thus reducing their catalytic activity.

It is necessary to assess the efficiency of the catalysts used in pyrolysis to produce high yields of hydrocarbons and small amounts of coke, for any type of feedstock. Continued and systematic efforts need to be made on catalyst design to obtain optimum and effective hydrotreating and hydrocracking. Hydro processing of oils and fats has been a subject of extended research works and discussions especially in the aviation industry (Vásquez et al., 2017). Modeling of the upgrading of three biomass-derived liquids (bio-oil, vegetable oil and algal oil) through a hydrotreating process to produce advanced biofuels was performed by Atsonios et al. (2018). It was considered that magnesium oxide catalysts could help in the economic sustainability of the process (Stefanidis et al., 2016).

Zetterholm et al. (2018) estimated the production costs of biofuels from forest biomass and found to be in the range of 36–60

EUR/MWh for crude pyrolysis liquids, and 61–90 EUR/MWh upgraded to diesel and petrol, while the CO_2 mitigation potential for the pyrolysis liquids was in the range of 187–282 t-CO2/GWh biomass. However, their commercialization requires favorable policy support, continued technology development, and/or increased fossil fuel prices, while integration with existing industrial infrastructure can contribute to cost reductions (Zetterholm et al., 2018).

3.3. 3G biofuels (macro and micro algae-based biofuels)

Although lignocellulosic 2G biofuels are considered sustainable, there is a drawback of lignocellulosic feedstocks limitation (Shuba and Kifle, 2018). Additional drawbacks are the costs of pretreatment and advanced technologies needed for its conversion to biofuels (Dutta et al., 2014).

To confront with these drawbacks, the 3G biofuels produced from macro algae and micro-algae, are emerged (Alaswad et al., 2015). The advantage of algae is that their cultivation can take place all over the year, except if it is inhibited by sun irradiation (Dutta et al., 2014). Since they do not need arable lands for cultivation, they avoid pesticides, herbicides, and fertilizers (Gaurav et al., 2017). The dry weight per cell of algae can attain oil yields that are far greater than those of the terrestrial crops (Alaswad et al., 2015).

The cultivation and the growing of algae can take place either in open seas, shallow lagoons or special shallow artificial ponds, known as raceway ponds. Closed ponds, such as photobioreactors (PBR_s) along with environments rich in carbon dioxide can also be used for the cultivation of algae (Doshi et al., 2016). The water used for their cultivation can be derived from wastewater and sewage, which can have different contents of salt and thus there is no demand for the consumption of freshwater.

3.3.1. Classification of algae

There are two different types of algae: macro-algae and micro-algae. Macro-algae or “seaweeds” are macroscopic, multicellular organisms (Alaswad et al., 2015).

3.3.1.1. Macro-algae. The 90% of marine biomass consists of different species of macro-algae (Gaurav et al., 2017). Examples of different families of macro-algae are the brown *Sargassum*, the red *Porphyra* and the green *Ulva* (Alaswad et al., 2015). There is a large diversity of macro-algae in the marine environment. Approximately 250 different species have been studied for their potential contribution in biofuel production, medicine and pharmaceutical uses (Gaurav et al., 2017).

The advantages all macro-algae are: a) They can be processed in less hazardous acidic conditions compared to lignocellulosic biomass; b) They require lower temperatures, and shorter reaction times (Alaswad et al., 2015); c) Seaweeds' lignin and cellulose levels are quite low and high respectively, compared to other sources of biomass and thus they can be used to produce biofuels (Gaurav et al., 2017).

3.3.1.2. Micro-algae. A drawback of macro-algae is that they are not capable of producing high amounts of lipids. On the other hand, micro-algae or microphytes consist of lipids, proteins, and carbohydrates, 5–23%, the 6–52% and the 7–23% of weight respectively (Juárez et al., 2016). Their content is highly affected by the cultivation and types of nutrients used. A lot of different species of micro-algae have already been studied for their properties (Shuba and Kifle, 2018). Table 2 lists some representative species of micro-algae.

Since micro-algae can technically reach up to a lipid content of 60–80%, they are considered as the best source of oil extraction (Alaswad et al., 2015).

3.3.2. Harvesting and cultivation of algae

Cultivation of algae need sunlight. Photosynthesis is an important biochemical process in which algae convert the energy of sunlight to chemical energy. Harvesting algae after its growing cycle is the first step in processing it into biofuel in a commercial process. Harvesting techniques depend on the type of algae used.

3.3.2.1. Macro-algae. There is a wide availability of seaweed in nature. Harvesting of algae is of low cost. One of the ways to obtain macro-algae is by harvesting them from the sea and lagoons, using a variety of different mechanical options. Although there is a wide availability of seaweed in nature, skepticism was raised, since production of biofuels requires large quantities of seaweed biomass, which cannot be obtained in adequate time through harvesting and without the use of any technology. In addition, there is a great risk of environmental damage. Thus, it stands preferably to collect seaweed by hands without the use of advanced technologies.

For marine biomass to play a major role in the production of biofuels, it is necessary to cultivate algae instead of harvesting

Table 2
Lipid content of macro-algae families and some representative micro-algae species (Alaswad et al., 2015; Shuba and Kifle, 2018).

Macro-algae			Micro-algae	
Name	Lipid content wt.%		Name	Lipid content wt.%
***Chlorophyceae* class**			***Chlorophyceae* class**	
Ulva	2.1		*Chlolorella sorokiniasa*	22
Enteromorpha	0.3		*Chlolorella emersonii*	29
Monostroma	1.2		*Dunaliella primolecta*	23
***Rhodophyceae* class**			*Dunaliella bioculata*	8
Porphyra		4.5	*Ettlia oleoabundans*	35–54
Rhodymenia		1.7	*Tetraselmis suecica*	15–23
Gracilaria		1.8		
***Rhodophyceae* class**			***Bacillariophyceae* class**	
Porphyra	4.5			
Rhodymenia	1.7		Skeletonema costatum	21
Gracilaria	1.8		Navicula saprophila	51
Phaeophyceae class			***Dinophyceae* class**	
Laminaria	2.4		Crypthecodinium cohnii	20
Alaria	3.6			
Sargassum	2.9			
Padina	1.7			

them. There are many ways in which macro-algae cultivation can take place, such as inshore cultivation, inshore cultivation attached with other aquaculture activities, offshore cultivation and enhanced offshore cultivation with wind turbine towers (Roberts and Upharm, 2012). Inshore cultivation is usually performed in natural aquatic environments, such as bays and coastlines.

Inshore cultivation can aid in the removal of heavy metal ions from water, such as zinc, nickel and other contaminants that could be toxic for nearby fish farms. This bioremediation advantage of macro-algae can lead to the cleaning and exploitation of contaminated coasts, which can be used for aquaculture (Zeraatkar et al., 2016).

Inshore cultivation can draw a lot of controversies, because of the visual impact caused by the occupation of coastlines (Alaswad et al., 2015). Offshore cultivation can avoid that kind of controversy, but it has a negative impact on the economy, because it occurs in special tanks sometimes lighted up with artificial means instead of natural light and it also requires the use of nutrients and phytohormones. A solution to this is the provision of renewable energy. Wind turbine towers can be used to provide the necessary energy for the function of the offshore cultivation, and thus reduce the cost of the process (Roberts and Upharm, 2012).

3.3.2.2. Micro-algae. The cultivation of micro-algae can take place either in open ponds, known as raceway ponds or in closed systems, such as the PBRs (Slade and Bauen, 2013). For their normal cultivation, micro-algae need the addition of phosphorus and potassium nutrients. However, the existence of too many nutrients can ultimately cause the death of lots of animals, if these nutrients end up in lakes or other aquatic systems. This phenomenon is widely known as eutrophication and the reason behind its negative impact is that nutrients will cause the dense growth of plants, which consume big quantities of oxygen (Slade and Bauen, 2013). There is also a small need for water resources, in order to deal with the possible evaporation of the water inside the ponds. Although it has been referred that the cultivation of algae can occur by using wastewaters and sewage, it is preferable to avoid the recirculation of already used water, because there is a chance to provoke the infection of the algae from different types of bacteria, fungi, viruses, organic and inorganic compounds. In order to avoid the cost of pumping, the ponds can be built near natural tidal flows, which can be used as a water source (Slade and Bauen, 2013). Raceway ponds have been proved to be good, because of their easy construction and operation compared to other cultivation systems. However, a lot of caution is needed to find extensive construction areas with adequate sunlight, to avoid evaporation losses, and to try not to harm the wild animals and the ecosystem in general (Alaswad et al., 2015).

PRBs are artificial and controlled arrays of tubes or flat-plates, which can achieve greater production rates of micro-algae, but with higher costs and energy demands (Slade and Bauen, 2013). One of the greatest benefits of PBRs is the protection of micro-algae from contaminations and pathogens. Further advantages include the creation of an environment with controlled temperature, which is unaffected by climate changes and handles the carbon dioxide in a better way than raceway ponds (Alaswad et al., 2015). It has been reported that PBRs can achieve carbon dioxide fixation efficiencies of around 75%, while open raceway ponds can manage efficiencies less than 10%. Utilities used for the operation of PBRs include water for the cooling of the tubes or plates and nutrients for the growth of algae (Slade and Bauen, 2013). It should be mentioned that another possible shape of PBRs is the pyramidal one, which is the most controlled and automated system compared to the others (Shuba and Kifle, 2018).

The harvesting techniques of micro-algae are flocculation, centrifugation, filtration, and flotation (Shuba and Kifle, 2018). Although the harvesting of macro-algae is not a challenging process, micro-algae cannot be easily harvested, due to their small size (Alaswad et al., 2015).

The capital cost of the harvesting of micro-algae is very high, which makes their cultivation process quite alluring (Shuba and Kifle, 2018). For this method to be economically affordable, macro-algae must be cultivated in areas, where natural solar energy can easily be exploited and there is no high tidal activity.

3.3.3. *Processing of algae for the production of biofuels*

The algal biomass can be processed either biochemically or thermochemically. Biochemical ways include: a) the transesterification of the oils extracted from algae to produce biodiesel, b) the anaerobic digestion of algal biomass to generate biogas and c) the fermentation, from which bio-ethanol can be derived. Biogas, whose main components are methane and carbon dioxide, can be further processed to generate electricity or thermal energy (Slade and Bauen, 2013). The thermochemical routes can be used, in order to convert algal biomass to syngas and bio-oil (Francavilla et al., 2015). The different pathways of 3G biofuel production from algae are summarized in Fig. 3**.** The technologies mentioned do not exhibit many differences with the previous generations and thus only some of them are analyzed further below.

3.3.3.1. Products. The products biodiesel and bio-oil are highly dependent on the lipid content of algae. Macro-algae are not used to produce the aforementioned products, due to their low lipid contents and thus they are used mainly for the production of biogas through anaerobic digestion (Alaswad et al., 2015). Further products derived from algal biomass include the bio-hydrogen, which is obtained during the photosynthesis process either directly or indirectly with photofermentation (Radionova et al., 2017).

3.3.3.2. Processes. Micro-algae can be processed in a variety of ways, to produce biofuels. Micro-algae compared to lignocellulosic biomass present the advantage less expensive processing due to the absence of lignin (Juárez et al., 2016). However, most micro-algae are also associated with the drawbacks of the low content of carbohydrates and low yields of bio-ethanol.

- Anaerobic Digestion

Anaerobic digestion produces methane and carbon dioxide, through the mechanism of methanogenesis (Alaswad et al., 2015). Due to its capability of recovering the valuable nutrients used during the cultivation, anaerobic digestion can play a major role in the sustainability of algae-based biofuels.

Although all components of algae (carbohydrates, proteins, and lipids) can be used in biogas production, its yield and composition

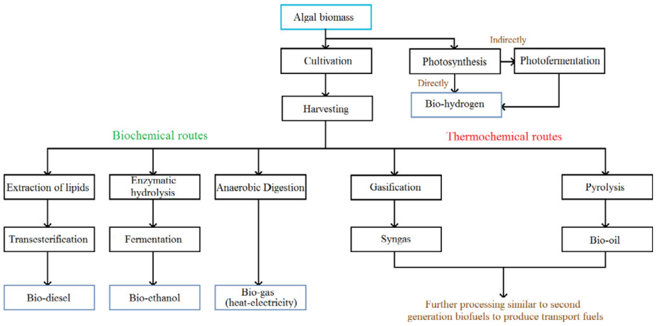

Fig. 3. 3G biofuels production processes.

depend on some parameters such as carbon to hydrogen (C/H), and carbon to oxygen (C/O) ratios of the biomass. The concentration of lipids, proteins, and carbohydrates highly influence these ratios of the algae (Alaswad et al., 2015). To first separate the oil and then use it to produce biofuels while convert the residual algal biomass into biogas by anaerobic digestion, could be an effective cascade pathway. The process of anaerobic digestion constitutes of hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Alaswad et al., 2015). The methanogenesis is carried out by special bacteria, which require the carbon to nitrogen ratio of algal biomass to be higher than 20, in order to achieve the production of methane. If the ratio is lower than 20, the formation of ammonia will take place, which will impede the methanogenic bacteria.

- Enzymatic Hydrolysis

Carbohydrates can be found inside the micro-algae cell walls in the forms of cellulose and hemicelluloses or inside the cell in the form of starch (Juárez et al., 2016). Enzymatic hydrolysis or saccharification can be used to break down carbohydrates for bio-ethanol production. Juárez et al. (2016) proposed an alkaline-peroxide pretreatment step of micro-algae, obtained from different types of wastewater, to increase sugar solubilisation. However, a lot of caution is needed, because alkaline-peroxide pretreatment can also lead to the production of organic acids and bio-methanol, through the sugar oxidation, and to the reduction of the final sugar contents of the micro-algae hydrolysis products, which can be proved critical if these products are destined for fermentation.

- Fermentation

Pretreatment methods, such as the addition of nutrients during their cultivation or the adjustment of the acid concentration used during the hydrolysis of carbohydrates can decrease the drawbacks of the low content of carbohydrates and low yields of bio-ethanol (Shuba and Kifle, 2018). Miranda et al. (2012) cultivated the micro-algae *Scenedesmus obliquus* in a nitrogen environment and achieved a maximum sugar content of 29% $_{w/w}$ of biomass, with a final bio-ethanol productivity level of 11.66 g/L via fermentation with *k. marxianus* as yeast. Thu et al. (2009) used the *Chlamydomonas reinhardtii*, which was hydrothermally pretreated with sulphuric acid and they managed to upgrade the sugar content of algal biomass to a maximum of 58% $_{w/w}$. The final bio-ethanol yield obtained from sugars, via fermentation with *Saccharomyces cerevisiae* as yeast, was 29.2%.

- Anaerobic Dark Fermentation

Bio-ethanol can also be produced directly from micro-algae without hydrolysis or pretreatment through the anaerobic dark fermentation of the intracellular starch, which is called dark because it doesn't require light energy. However, this process grants small yields of bio-ethanol and thus there is no interest in using it in industrial scale (Miranda et al., 2012).

- Enzymatic hydrogenesis and Photofermentation

One of the biggest advantages of algae is that they have the potential to produce bio-hydrogen (Shuba and Kifle, 2018). However, oxygen produced can hinder the hydrogenase production, because it deactivates the enzymes that are used for the catalysis of the reaction (Radionova et al., 2017).

Another possible pathway to produce bio-hydrogen through photosynthesis involves the further processing of the produced hydrocarbons with photofermentation. This is a more indirect method to produce bio-hydrogen compared to the anaerobic hydrogenase reaction and manages to generate hydrogen, without the intervention of oxygen (Radionova et al., 2017).

3.4. 4G biofuels (genetically modified algae and wastes)

The genetically modified algae are defined as a new type of biomass used to produce 4G biofuels (Stephen and Periyasamy, 2018). Except for genetically modified algae, the concept of producing biofuels from wastes is being studied by many scientists (FAO, 2018). The EU is adopting policy measures to promote the use of advanced biofuels for transport made from sustainable sources including wastes and residues.

3.4.1. Genetic modification of biomass

Many scientists argue that the genetic processing of algae should be included in 4G biofuels instead of 3G (Dutta et al., 2014), while others classify the genetically processed algae as a feedstock used in the 3G of biofuels (Radionova et al., 2017).

Genetic modification of algae, based on the concept of metabolic engineering, can increase algae lipid contents (Shuba and Kifle, 2018) introducing the 4G biofuels by obtaining desired properties with different types of feedstock (Stephen and Periyasamy, 2018). Micro-algae by genetic modifications can increase their temperature tolerance levels (Dutta et al., 2014). Additional features that can be added through genetic modification include the protection of algae cells from photooxidation and the limitation of photoinhibition, which decreases the growth of the algae during high, midday light intensity (Shuba and Kifle, 2018). All these changes can lead to the production of higher quantities of biomass (Slade and Bauen, 2013).

3.4.2. Waste-to-biofuels

Different types of wastes, such as municipal or city garbage, sewage, plastic and organic wastes can be used for the production of large quantities of biofuels including food processing wastes (Fig. 4). Nowadays, landfill sites are mainly filled with solid food wastes (FAO, 2018). Except for the environmental issues, food wastes are comprised of complex carbohydrates, lipids, vitamins and other components, which can be properly processed. Bio-oil can be directly produced from food wastes through pyrolysis (Karmee, 2016). Mixed food wastes and waste cooking oil can also

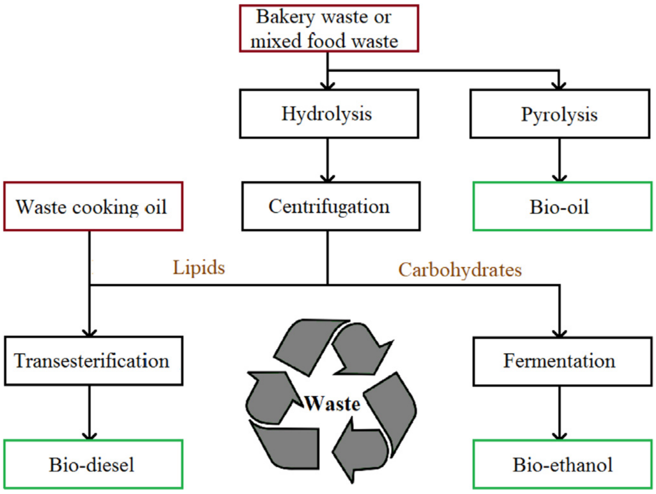

Fig. 4. 4G biofuels production processes.

be converted to biodiesel through transesterification (Stephen and Periyasamy, 2018). In the transition to Circular Bioeconomy, the approach to sustainable use of food wastes for the transition from a mono-process pathway to a cascade biorefinery can satisfy the recovery of added value components and biofuels in an integrated way (Zabaniotou et al., 2018).

3.5. *Aviation biofuels*

Aviation consumes about 200 Mt of kerosene worldwide, which is responsible for the 2% of carbon dioxide emissions due to human activity (Gutiérrez-Antonio et al., 2017). The International Air Transport Association (IATA) suggested the use of a renewable aviation fuel, known as synthetic paraffinic kerosene (SPK) (European Commission, 2018). Other bio-jet fuels include the synthesized paraffinic kerosene plus aromatics and the synthesized iso-paraffins (Neuling and Kaltschmitt, 2018). The composition of the bio-jet fuel to aromatics is lower than conventional jet fuel and thus bio-jet fuels are considered cleaner fuels. However, a significant number of aromatics still exist in bio-jet fuels (Gutiérrez-Antonio et al., 2017). Table 3 compares properties of the conventional Jet-A1 fuel with a renewable jet fuel that derives from *jatropha*. Jet-A1 is generated from crude oil and is basically used by civil aviation.

Four main production routes, which comprise the hydroprocessing of triglyceride feedstock, thermochemical gasification and FT synthesis of lignocellulosic biomass, reforming and FT synthesis of biogas, and usage of alcohols for bio-jet fuel production are presented here. The cost of each technology is affected by the raw material used. The supplying of triglycerides is high, but the cost of their processing is low, while the opposite occurs with the lignocellulosic biomass because of its complex composition (Neuling and Kaltschmitt, 2018). Fig. 5 presents jet-biofuels main technologies.

Hydro processing of triglyceride feedstocks can occur in two different reactors to produce bio-kerosene, under high pressure and temperature and in the presence of a catalyst and hydrogen. Hydro processing is used to a high extent, due to the expertise of the traditional refineries (Gutiérrez-Antonio et al., 2017).

Table 3
Properties between a type of jet fuel and a type of bio-jet fuel (Gutiérrez-Antonio et al., 2017).

Property	Jet fuel (Jet-A1)	Bio-jet fuel (from jatropha)
Boiling range (ºC)	170–300	172–243
Freezing point (ºC)	−47	−57
Flash point (min 38 °C)	38	46.5
Density at 15ºC (kg/m^3)	775–840	751–840
Viscosity at −20ºC (mm^2/s)	8.0	3.66
Energy content (MJ/kg)	43.28	44.3

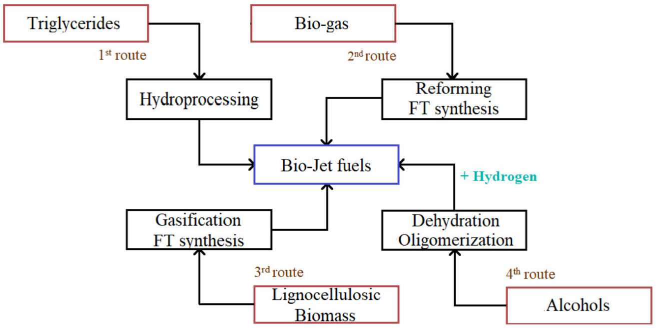

Fig. 5. Jet-biofuels production processes.

Bio-kerosene is produced by the process known as biomass-to-liquids and its main disadvantage is the high energy costs of the syngas technology that do not balance adequately with the low cost of feedstock (Gutiérrez-Antonio et al., 2017).

Except for using triglycerides and lignocellulosic biomass as a feedstock, the methane contained inside bio-gas can also be converted to liquid bio-jet fuels, through a series of processes. (Neuling and Kaltschmitt, 2018).

Sugars and starch can be obtained from different types of feedstock (food, lignocellulosic, algae, wastes) and be converted mainly to bio-ethanol and other alcohols via fermentation. The alcohols can be further processed in order to produce bio-jet fuel through a series of reactions, which are dehydration, oligomerization and hydrogenation. This route that combines the aforementioned reactions is called alcohol-to-jet (Gutiérrez-Antonio et al., 2017). During the dehydration step, sulphuric and phosphoric acids are added in the alcohols to achieve the water separation and the formation of alkenes, with a chain similar to the initial alcohols. After the completion of the reactions a separation step takes place, in order to retrieve the bio-jet fuel (Neuling and Kaltschmitt, 2018).

4. Discussion

Biofuels represent a technological innovation which holds the substantial potential to reduce the carbon significance of automotive and aviation (Filimonau et al., 2018). A 100% renewable economy with a green transport system, would give a lasting solution to the challenges raised by climate change, energy security, sustainability, and pollution. However, the conversion of the present transport system appears to be one of the most difficult aspects of such renewable transition (García-Olivares et al., 2018). A transition of this sector especially for heavy-weight, long-range vehicles and airplanes towards a sustainable one requires suitable technologies and availability of energy resources (Dominković et al., 2018).

Assessing the potential of alternative fuels to become viable options requires technological, environmental, economic, and social insights and analysis while the key environmental challenge is the longer-term reductions in GHG emissions (Gilbert et al., 2018). Utilization of bio-resources needs to take into consideration their spatial context and their role in eco-systems (Narodoslawsky, 2017).

Due to the recent international enormous R&D effort, many technologies that can produce biofuels, capable of satisfying a large portion of the energy demand, have been generated. However, there is still a need for further technological improvement, especially in increasing the efficiency and sustainability of biofuels production to ensure a real improvement.

Novel integrated processes that have the potential to produce more liquid fuel from a given quantity of biomass, need synergistic processes, which use sustainable carbon-free energy sources, such as solar fuels. This synergy can increase the process of carbon efficiency, reach higher energy efficiency and significantly decrease land area requirement.

Prior to implementing policy changes, there is a necessity to estimate the resources needed to meet an advanced biofuel target. To assess the availability of agricultural and forestry residues, and biogenic wastes that could potentially be used for advanced biofuel production in the EU Member States, an analysis is needed to incorporate specific information on agricultural, forestry, waste production, management practices, and environmental risks in each Member State (Zabaniotou, 2018).

Many states can meet the target by using local resources, but other may need to import either feedstock or advanced biofuel from neighboring countries to meet the target (Searle and Malins, 2016). It is expected that solid biomass imports of Northwest

Europe will be between 22 and 30 Mt in 2020, while in 2030 they will approach the range of 19–21 Mt. The amount of imported biofuel is estimated to be 6 and 4.6 Mt in 2020 and 2030 respectively. The above mitigation on biomass and biofuel imports is related mainly to the low fossil fuels prices and to a boost to the vehicle efficiencies (Dafnomilis et al., 2017). However, the import of biomass has difficulty in finding a reasonable trading price and it is affected by the weather conditions and high distances, which may not allow continuous supply. Moreover, lack of coordination and communication between stakeholders and importing countries can also pose a risk in biomass trade (Raychaudhuri and Ghosh, 2016).

To ensure the economic and environmental viability of waste feedstocks, it is critical to gain an understanding of the spatial and temporal variability of waste production, waste characteristics, available conversion technologies, overall energy conversion efficiency, logistics, and transport. Up to 22.3 GL/y (5.9 Bgal/y) of a biocrude oil intermediate that can be upgraded and refined into a variety of liquid fuels, in particular renewable diesel and aviation kerosene, can be produced by those wastes, as estimated by American researchers (Skaggs et al., 2018).

4.1. European legislation as driver for transportation biofuels deployment

The Renewable Energy Directive (RED) 2009/28/EC promotes the use of renewable energy and minimization of GHG emissions. The Directive sets as a primary goal the replacement of 20% of total energy and of 10% of transport sector fuels by renewable sources. In 2015, Renewable Energy Sources (RES) provided the 17% of the total energy demand (European Commission, 2018).

The final proposal of RED was issued on the 17th of October 2012 and its primal targets were the limitation of the consumption of conventional biofuels to achieve the agreed percentages and the mitigation greenhouse gas emissions to 60% until 2012 instead of 2018. It also aimed at a higher penetration of advanced biofuels in the market and it requested the Member States and the fuel suppliers to report the emissions derived from biofuels.

The protection of the biodiversity, landscapes, and specific natural elements are ensured by measures set by the Council Decision 89/367/EEC34 (European Commission, 2018). Advanced biofuels are produced from forest biomass, which is extracted from specific areas. These areas are determined by national laws and enacted by the Ministerial Conference on the Protection of Forests in Europe, known as Forest Europe MCPFE.

According to Article 25 of the document of the European Commission (2018), which refers to the mainstreaming renewable energy in the transport section, the producers of biofuels are forced to include and declare a percentage of biofuel to be mixed with conventional fuel in transport. This percentage is set at least 1.5% by January 2021, while is expected to reach 6.8% until 2030. In this way, it is estimated that the GHG emissions will be reduced at least to 70% in January 2021 (European Commission, 2018).

For the legislation in aviation, the Biofuel Flightpath Initiative was enacted on the 24th of June 2011, at the 49th International Paris Air Show Le Bourget, by the contribution of the EC, Airbus and high-level representatives of the Aviation, and Biofuel producers industries. This action targets the production of 2 Mt of sustainable biofuels, to be used as a mixture with conventional kerosene in the EU civil aviation sector until 2020.

Furthermore, IATA expressed its concerns about the growing carbon dioxide emissions and in 2009 it declared that fuel efficiency must increase by 1.5% annually for the next decade. It was also suggested that all industries should become carbon-neutral until 2020 and that carbon dioxide emissions should be reduced by 50% until 2050. The latter was also supported by the White Paper, *The Transport 2050 roadmap to a Single European Transport Area*, adopted on the 28th of March 2011 by the EC and listed as a goal the reduction of carbon emissions by 60% until 2050 (USDA, 2017).

4.2. Biofuels' specifications defined by standards

For a biofuel to be appropriate for use, it must fulfill some requirements concerning its properties, which are determined by the European Commission (2018). Biodiesel is one of the most widely known biofuels, whose main production methods, which were presented above, target to satisfy those requirements. Table 4 presents the standard properties as the Directive 2009/28/EC defines, of biodiesel along with the test methods used to check if it fulfills the necessary requirements.

Aviation fuels must also follow strict quality specifications, which are defined by ASTM D 7566 standard. Many properties of conventional fuels are similar to the ones of biofuels, as shown in Table 4, however the energy content differs as Table 5 illustrates. Biofuels have generally lower energy content than fossil fuels.

Table 4
Standard properties of diesel and biodiesel (European Committee of Standardization, 2018).

Property	Unit	Limits		Test method	Limits		Test method
		Min.	Max.		Min.	Max.	
		Diesel			Biodiesel		
Cetane number	–	51	–	EN ISO 5165 EN 15195	51	–	EN ISO 5165
Density at 15 °C	kg/m^3	820	845	EN ISO 3675 EN ISO 12185	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C	mm^2/s	2.0	4.5	EN ISO 3104	3.5	5	EN ISO 310
Sulfur content	ppm	–	10	EN ISO 20846 EN ISO 20847 EN ISO 20884	–	10	prEN ISO 20846 prEN ISO 20884
Flash point	°C	55	–	EN ISO 20846 EN ISO 20884	101	–	ISO/ CD 3679
Carbon residue	% (*m*/*m*)	–	0.3	EN ISO 10370	–	0.3	EN ISO 10370
Ash content	% (*m*/*m*)	–	0.01	EN ISO 6245	–	0.02	ISO 3987
Water content	ppm	–	200	EN ISO 12937	–	500	EN ISO 12937
Contamination	ppm	–	24	EN 12662	–	24	EN 12662
Copper strip corrosion (3 h at 50 °C)	rating	Class 1		EN ISO 2160	Class 1		EN ISO 2160
Oxidation stability	hr	20	–	EN 15751	6	–	EN 14112

Table 5
Energy content of different types of biofuels and fossil fuels as defined by Directive 2009/28/EC (European Commission, 2018).

Fuel	Energy content by weight (lower calorific value, MJ/kg)	Energy content by volume (lower calorific value, MJ/L)
Fuels from Renewable Energy Sources		
Biodiesel	37	33
Hydrotreated bio-oil for the replacement of diesel or kerosene	44	34
Hydrotreated bio-oil for the replacement of gasoline	45	30
Bio-methanol	20	16
Bio-ethanol	27	21
Synthetic transport fuels from Fischer-Tropsch synthesis	44	33–34
DME	28	19
Bio-hydrogen	120	–
Fossil fuels		
Gasoline	43	32
Diesel	43	36

4.3. 1G biofuels

For the liquid biofuels deployment critical factors significantly differ at different times. In the long term (2030–2050), the development of liquid biofuels is highly dependent on the availability of biomass resources while in the medium term (2020–2030), biomass availability and feedstock price are critical. For the previous decade (2005–2015), in addition to conflicts with food and feed production, concerns about sustainability for both the environment and biodiversity were raised, related to the cultivation of plants destined for biofuel production requiring large amounts of soil, water, and chemical fertilizers. These resulted in a decline of 1G biofuel production and the research shifted to alternative solutions.

4.4. 2G biofuels

The 2G biofuels came up as a more valuable solution that ought to take into close consideration all the controversy and lessons obtained from the 1G biofuels. They have higher yields of products and usually they have a more profitable production compared to 1G biofuels. However, project investments and cost estimates have more risk and uncertainty for 2G biofuels that is related to the high capital costs and longer timeframe required for the feedstock cultivation (Eijick et al., 2014).

Furthermore, 2G biofuels should address the three pillars of the sustainability as they are interconnected to each other (Mohr and Raman, 2013). The contribution of 2G biofuels in the environment is also being questioned. Ahmed and Sarkar (2018) developed a model to see how the different stages of the transformation of the residual biomass to biofuels contribute to the environmental problems and production costs. They found that the crucial factor that is related to the 88.5% of the total carbon emissions is the transportation of biomass and biofuels to biorefineries and markets respectively. They estimated that the total carbon emissions correspond to the 0.18% of the production costs which is still significant for the environment (Ahmed and Sarkar, 2018). Even if the carbon emissions are considered acceptable since there are much lower than those emitted by fossil fuels, 2G biofuels fail to be produced sustainably on a large scale due to the occupation of a remarkable amount of land (Acheampong et al., 2017).

The utilization of synthetic biology to modify lignocellulosic biomass and partially solve the aforementioned issues still has restrictions because of its uncertain environmental and socio-economic impacts (Mohr and Raman, 2013).

4.5. 3G biofuels

It became evident that microalgae are a promising aquatic culture for supplying biofuels and other bio-products in the near- to medium-term (Colling Klein et al., 2018), due to the lower direct or indirect utilization of land, water, and no usage of pesticides compared to previous generations of biofuels (Correa et al., 2017).

At cultivation level neither the raceway ponds nor the PBRs are considered as promising methods since they both require proper optimization (Carneiro et al., 2017). Open ponds are not so energy demanding as PBRs and they can be optimized with the mitigation of the carbon dioxide emissions of industrial areas and the recycling of water and nutrients (Correa et al., 2017).

Nutrients can be reused if they are recycled from the non-fuel fraction of the produced microalgal biomass through anaerobic digestion or various hydrothermal treatments. It must be mentioned though that these closed-loop recycling methods have been applied only in laboratory scale and still require scaling up (Barbera et al., 2018).

Attention should also be paid to sustainable cultivation methods, which include wastewater treatment and bioremediation to capture carbon dioxide and fix nitrogen and phosphorus requirements, by using industrial, agricultural, and municipal wastes (Raheem et al., 2018). However, the combination of the production of algae with wastewater treatment is associated with high capital costs and high demands of energy which make difficult the transition to industrial scale and they decrease the earnings (Hoang Nhat et al., 2018).

Life Cycle Assessment (LCA) studies have proven that the production of biofuels from alga-biomass can either be environmentally friendly or energy demanding with high carbon emissions like fossil fuels depending on the technologies used for their production. The economic viability of a biorefinery producing biofuels from algal biomass is also insecure since the co-processing of further bio-products still requires a lot of research (Baudry et al., 2018).

4.6. 4G biofuels

Genetic modification of algae, which is based on the concept of metabolic engineering, introduces the 4G biofuels. R&I primary target is to implement desired properties with different types of feedstock, such as plants, oil seeds or algae, and redesign them accordingly to enhance their characteristics (Stephen and Periyasamy, 2018). The genetic engineering cultivation of algae was proven beneficial due to its higher economic feasibility compared to the 3G algae but it can provoke the production of hazardous algae which can damage the environment.

The price of produced fuels is highly affected by the cost of the raw material and thus the usage of food wastes as feedstock would normally result in sustainable fuels with lower price (Karmee, 2016).

Food wastes also contribute to the 4G biofuels. However, Stephen and Periyasamy (2018) stated that biofuels generated from organic wastes have limitations despite their low-cost feedstock, due to expensive and energy demanding production, and unsystematic waste accumulation methods. This problem requires more research efforts for 4G algae to meet sustainability (Adeniyi et al., 2018).

4.7. Bio-jets fuels

Bio-jet fuels have recently gained attention in the scientific and technological community. The processes of bio-jet fuel production are the key to satisfy both technical and economic goals (Neuling and Kaltschmitt, 2018).

Wider bio-jet adoption is constrained by high costs compared to fossil-based jet fuels. Higher costs, investor uncertainty, and poor policy awareness at Member State level have contributed to the nascent state of biojet fuel in Europe.

New policy approaches are needed to set international standards and ensure bio-jet development (Deane and Pyea, 2018). Generally, jet fuels must satisfy some strict specifications, such as high energy density and good combustion quality, in order to be capable to carry out long flights with efficient use of fuel. Furthermore, they must have easy transportation, storage, and pumping and at the same time they must be available in high quantities and fulfill all the safety rules (Neuling and Kaltschmitt, 2018).

Research efforts attempt to produce bio-jet fuels that both satisfy the necessities and contribute to the protection of the environment.

To reduce aviation's lifecycle GHG emissions by 50% by 2050, policies will have to significantly incentivize and prioritize the production of aviation jet-fuels over other potential uses of these resources (Staples et al., 2018).

Market-based instruments, i.e. carbon pricing policy and excise tax preferences, can stimulate the medium- and long-term development of biofuels. However, in the near-term, subsidies are highly necessary.

4.8. The food-energy-water nexus challenge

While the Earth's population is growing, the supply per person of land and resources to produce food, energy, and water is decreasing. Concerns over sustainable development with securing food, energy, water and bioresources to an increasing world population have stressed the importance of critical interactions between those factors, the so-called *Food-Energy-Water* nexus which connects food, energy, water and climate to the global economy in terms of complex systems (Schmid and Matthews, 2018). 1G biofuels from food crops have impacted nexus resources, land, and food, but also water and fossil energy resources that are required during cultivation and processing. Big amounts of soil and energy are also required for the production of 2G biofuels. The main issue with 1G and 2G biofuels is the difficulty of achieving proper landscape management. Many options should be considered, such as the utilization of recycling water from small wastewater treatment plants or rain water or the exploitation of polluted soil in order to decrease the competition with food and feed production (Lucia et al., 2018).

Solutions to the nexus challenges require synergistic interactions such as interactions between biomass supply and the nexus sectors in value chain optimization to improve productivity and reduce losses and environmental impacts (Martinez-Hernandez and Samsatli, 2017). Alignments of the nexus with sustainability programs, and the Sustainable Development Goals, must be reconsidered (Schmid and Matthews, 2018). Spatial scales should receive more attention (Bijl et al., 2018). From a market and industry perspective, successful Food-Energy-Water nexus projects need a transdisciplinary approach, ecological technology practices, and sustainable supply chains. Due to many interrelationships of the nexus, R&I opportunities may include methodological developments, social concerns, performance indicator-based systems, and meta-social evolutions in technology and policy (Bergendahl et al., 2018).

4.9. The carbon-nitrogen nexus challenge

Although biofuels journey from 1G to 4G along with related technological innovations made their sustainability more evident, there is still a need for further technological improvement especially in increasing the efficiency and the sustainability to ensure a real improvement over fossil fuels.

One important issue is the carbon-nitrogen nexus for which there is a trade-off between a low C footprint and low reactive nitrogen (Nr) emissions footprint. Biofuels usually have lower C footprint and higher Nr emissions due to intensive farming processes, while fossil fuels have a high C footprint and lower Nr emissions (Liu et al., 2018).

In the case of algae, big amounts of fertilizers will eventually end up in the ecosystem via wastewater. Some pretreatment methods, such as hydrothermal hydrolysis, can be used to decrease the total Nr emissions but they are also associated with additional GHG emissions and fossil fuels usage and thus higher C footprint (Mu et al., 2017).

However, some cases such as low farming inputs switchgrass (2G) and low intensity high diversity grassland-based biofuels (2G), or waste feedstock (4G), (for example municipal solid waste-based biofuels), have low C and Nr footprints, making them better options for transportation fuels.

Due to ecosystems limited capacity to supply bio feedstocks, biofuels are facing sustainability issues, especially in huge populations countries, where huge amounts of biomass are required for their production to cover all population needs (Liu et al., 2018).

4.10. Potentialities of hydrogen and solar economy

For a successful large-scale deployment of biomass-to-liquid fuel for any kind of transportation, it is imperative to maximize the production of liquid fuel from biomass, with solar energy expected to play a central role. The exploitation of biofuels in industry scale meets constraints due to limited availability of bioresources on the planet and ecosystems boundaries. Synergistic processes using energy from sustainable carbon-free energy sources are needed, such as the so called Solar Fuels (SFs) (Bergendahl et al., 2018).

Current development on various options and routes with respect both to redox oxide materials chemistry as well as to solar reactor concepts for hydrogen and/or syngas production via redox-pair-based, water/carbon dioxide splitting thermochemical cycles are reported by researchers (Agrafiotis et al., 2018).

New challenges, materials, engineering, and economics must all be interconnected and optimized towards achieving a system-level solution and accelerate the transition to hydrogen or solar economy.

It seems that hydrogen economy can provide zero-carbon fuels, however, this transition is not expected to occur in the following years, due to associated hydrogen high production costs. The production cost of hydrogen from steam methane reforming, which is one of the most widely used methods for hydrogen generation is equal to 3.8 EUR/kg (4.7 USD/kg) higher than the viable target of 1.6–3.25 EUR/kg (2–4 USD/kg) for the automotive industry.

Further beyond the low-carbon fuels and economy, solar fuels (SFs) seem to be an energy opportunity. Although SFs have been studied by researchers for the last 40 years, advances are now being made. SFs are chemical fuels produced using sunlight, carbon dioxide, and water, without contributing to climate change and they rely on the principle of artificial photosynthesis, in order to convert solar energy into carbohydrate and bio-inspired versions (Cogdell et al., 2018).

Solar power has a great potential as a clean, cheap, renewable and sustainable source of energy but it must be captured and transformed into useful forms of energy. This can be done by storing the solar energy in the form of chemical bonds of SFs, such as hydrogen or hydrogen peroxide, while at the time producing oxygen from water, as natural photosynthesis does (El-Khouly et al., 2018).

5. Conclusions

Biofuels' journey in Europe is long. Various generations of biofuels were developed to face the raised sustainability issues.

The review of the recently published papers confirmed that: all 4 generations of biofuels are facing various levels of sustainability limitations. There is still no clear answer on which generation biofuels meets the sustainability criteria better.

1G and 2G biofuels are currently still the major building blocks of the biofuels contributing to the transportation sector. However, 1G biofuels failed to fulfill the requirements of sustainability, due to conflict with food and feed.

2G biofuels are the most abundant. Although some have low carbon and nitrogen footprints, they do not satisfy the food-energy-water nexus.

3G algae-based biofuels could be the future in automotive and aviation sectors but they are still linked to some serious drawbacks. Microalgae are a promising aquatic culture for supplying biofuels in the near- to medium-term, delivering a complementary biofuel platform, however, their cultivation is considered as energy demanding and it also highly affects the nitrogen cycle.

4G biofuels, mainly industrial, agricultural and municipal wastes-based are promising in also accelerating the circular economy. In addition, they exhibit low carbon and nitrogen footprints. However, they are associated with expensive and energy demanding processing methods.

Large-scale biofuels production requires huge amounts of bio resources, which should be carefully considered considering the ecosystems limited capacity to supply bio feedstocks.

Biofuels production still requires a lot of R&I efforts and appropriate policy supporting to meet the sustainability criteria. Subsidies are highly necessary for the near-term, while for medium- and long-term market-based instruments, such as carbon pricing policy and tax preferences, can stimulate the development of biofuels.

At R&I level, it is important to redesign tailored properties of biofuels in accordance to their feedstock characteristics (plants, oil seeds, algae, various wastes), to meet environmental criteria.

The European Commission is looking at cost-efficient ways to make the European economy more climate-friendly and less energy-consuming, by addressing the importance of biomass availability in the context of Circular Bioeconomy, that actually is being developed in Europe, with cascade waste-based biorefineries in the forefront of R&I. EU is also funding R&I projects on biofuel production, especially for the aviation sector.

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