

# The Importance of Renewable Fuels and Their Different Processes

Pedro Malpartida

*Intern, Advanced Biofuels USA*

*Mechanical Engineering Major, Volgenau School of Engineering, George Mason University*

*Renewable Energy Minor, College of Science, George Mason University*

## Abstract

This paper presents information about the topic of biofuels and renewable fuels and the different processes. There are still huge developments being studied and researched globally, but some types of biofuels have already been established. Biofuel production has become a universal idea and can be implemented anywhere around the world. Transportation plays a huge part in the consumption of fossil based fuel and biofuels seem to be a promising alternative to combat dependence on it.

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## 1. Introduction

Typically, when the topic of renewable energy comes up, people tend to think mainly of solar or wind, or they are the first two categories to be mentioned. This makes sense since these two types of renewable energy are the most common and are established sources of energy.

### *1.1. Solar and wind energy sources environmental drawbacks*

Although solar and wind energy sources have proven to replace non-renewable sources of power, they may not be as green as they seem to be. These energy sources have crucial environmental drawbacks. The production of photovoltaic panels used for solar energy is a major problem. These panels are made of polysilicon and silicon, which, while being produced, can release environmentally dangerous by-products. More specifically, when inadequate waste treatment occurs, silicon tetrachloride and hydrofluoric acid are released into the environment [\[1\]](#).

As for wind energy, the dismantling of a wind turbine during its end of life isn't so environmentally friendly. One option is to incinerate it, but by doing so, inorganic loads in the material become a pollutant. Another option is to recycle the materials, but an efficient recycling method has not been established quite yet [\[2\]](#).

Although renewable electricity is needed to replace fossil carbon for transportation powered by electricity, there is a need for a better replacement of oil and gas used in transportation. A very promising renewable transportation fuel is said to be biofuel [\[3\]](#).

### *1.2. Biofuels in gas pumps*

The most common biofuel for transportation produced is ethanol, which makes up 10-15% of the fuel in today's gasoline-powered cars in the US. Not only has ethanol been incorporated into gasoline to reduce greenhouse gas emissions, but it also helps with engine deterioration. There are three other commonly used biofuels for transportation: biodiesel and renewable diesel, which differ from regular petroleum diesel; and renewable natural gas (RNG). Similarly to ethanol with gasoline, biodiesel and renewable diesel can be mixed in with regular diesel to improve certain combustion characteristics. RNG can replace or be mixed with natural gas or methane in compressed natural gas vehicles.

Fossil fuels still make up almost 80% of the energy consumption worldwide [\[4\]](#). It may be decreasing, but it is not decreasing fast enough. As global warming becomes a bigger threat, the need for an environment-friendly source of energy becomes more crucial [\[5\]](#). This being the

case, extensive research and testing is being done to make biofuels a more viable option to reduce CO<sub>2</sub> emissions.

## 2. Biofuels

A biofuel can be classified as a fuel in the form of a solid, liquid, or gas derived from organic materials. There are two categories of biofuels: primary and secondary. Primary biofuels are mainly used for heating and electricity, while secondary biofuels are used as transportation fuels [6]. Within the secondary biofuels, there exist four generations that need to be considered. The differences between these generations depend on their feedstock and conversion technologies. Though the first two generations of secondary biofuels have been established for quite some time, there are two other generations (third and fourth) that are in their early stages.

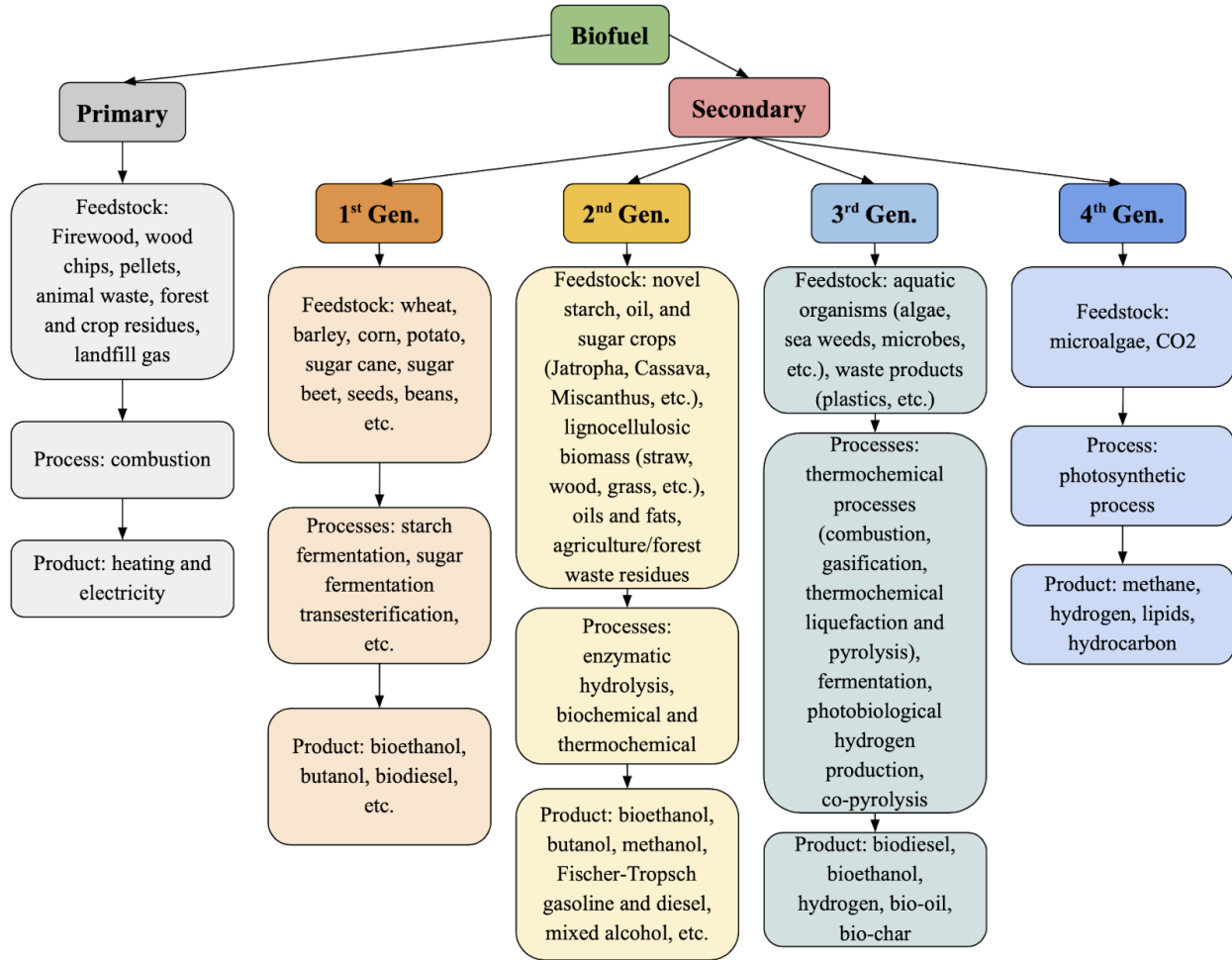
### 2.1. Primary biofuels

Primary biofuels are produced through the direct combustion of natural biomass that have not been processed. The feedstocks that can be used consist of unmodified organic material such as firewood, wood chips, pellets, etc.. The applications of primary biofuels can be utilized in small and large-scales ranging from supplying cooking fuel to heating and electricity [5]. These applications are useful, but they are not enough to reduce CO<sub>2</sub> emissions by a significant amount.

### 2.2. The four generations of secondary biofuels

The first generation is primarily produced from food crops (e.g. soybeans, corn, oil seeds, etc.). Ethanol made from corn is a primary example of a first generation biofuel. The second generation consists of fuels generated from non-food biomass (e.g. agricultural residues, straw, sugar cane bagasse) [7] and non-bio waste products (e.g. plastics), which may have originated mainly from petroleum products [8]. Cellulosic ethanol stemming from corn stover is considered a top second generation biofuel that can be highly promising in a short period of time [9]. Biodiesel, renewable diesel and sustainable aviation fuel (SAF) are also prime examples of second generation biofuels when made from non-food feedstock [10]. The third generation is any biofuel derived from aquatic organisms. Biodiesel and bioethanol derived from algae and/or seaweed are great examples of third generation biofuels [6]. Similar to third generation biofuels, the fourth generation utilizes algae (microalgae) and other microorganisms, but by using less destructive methods (e.g. photosynthetic process) [11]. In essence, the fourth generation process(es) don't necessarily destroy the biomass; rather the biological process creates transportation fuel range hydrocarbons directly.

The outcome (product) of the processes shown in Fig 1 can be identified as liquid biofuels or non-liquid biofuels. These different biofuels are derived from fermentation, hydrolysis, transesterification, biological, thermochemical, etc. [5].



**Fig. 1.** Biofuels breakdown with examples of feedstocks, processes, and products (adopted and modified from [5]) [8,11].

### **3. The first generation**

As industrialization grows rapidly, the need for a more sustainable solution rises as well. The first generation of biofuels is what paved the way for its more efficient and advanced successors. The use and development of first generation biofuels have been around for a decent amount of time (over a hundred years).

#### *3.1. First generation feedstock*

First generation biofuels use biomass that is also considered as food. Generally, they are made from sugars and starches, which are extracted from the feedstock that is used [\[5\]](#). Feedstocks containing high levels of sugar are favorable, but there are many different types of feedstocks that are utilized. The following is a list of possible feedstocks: wheat, barley, corn, potato, sugar cane, sugar beet, seeds, beans, vegetable oil, etc. Different feedstocks undergo different processes and result in several kinds of biofuels. Certain feedstocks are more favorable in different scenarios.

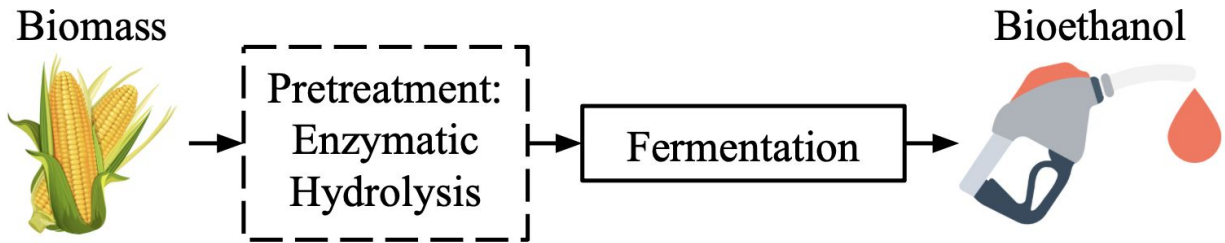
#### *3.2. Biofuels and process(es)*

Different feedstocks undergo different processes and result in several kinds of biofuels. The two main fuels which first generation biofuels are associated with and have been quite established are ethanol and biodiesel [\[12\]](#).

##### *3.2.1. Ethanol from first generation*

Ethanol, also known as bioethanol, is what gets mixed into gasoline to reduce emissions, provide octane, and improve engine life. In the U.S., only a small percentage (10-15%) of cars' fuel systems are made for high blends of ethanol (E85 or 85% ethanol). In some cars (flex-fuel vehicles), ethanol can make up more than half of the total gas in a tank. Ethanol can be first produced through a pretreatment called enzymatic hydrolysis of crops that are starch rich (e.g. corn, wheat). This can be considered as a chemical digestion process used to break down the biomass and release the necessary glucose [\[13\]](#). Once the glucose is obtained, it can undergo a process called fermentation, which is defined as a metabolic process where microorganisms secrete enzymes and cause chemical changes in an organic substrate. This then results in the production of Ethanol. Fig. 2 highlights this process starting from the biomass to the resulting biofuel (bioethanol).





**Fig. 2.** Simplified bioethanol process.

The most recognizable and utilized type of ethanol in the United States is corn ethanol. Ethanol can also be used as a feedstock to produce ethyl tertiary butyl ether (ETBE), which serves as an oxygenate for gasoline [\[12\]](#) and is more compatible with pipelines. ETBE is produced through a catalytic reaction using ethanol and isobutylene [\[14\]](#).

#### *3.2.1.1. Advantages of ethanol*

As mentioned previously, ethanol can lower emissions of vehicles and improve engine life. When using ethanol, a car produces less life cycle CO<sub>2</sub> into the environment. However, the primary reason for having gasoline across the U.S. be made up of ~10% ethanol is because having ethanol in gasoline also increases the octane rating in place of the very carcinogenic methyl tert-butyl ether (MTBE), which is an additive for unleaded gasoline. Octane is the measurement of ignition quality of the fuel. The lower the octane rating, the more susceptible the fuel is to causing engine knocking [\[15\]](#). The addition of ethanol in gasoline mitigates engine knocking.

#### *3.2.2. Biodiesel from first generation*

Biodiesel, also known as bio-esters and chemically known as fatty acid methyl esters (FAME), is similar to ethanol in the way that it can be used as an additive to its environmentally-unfriendly counterpart (diesel). There are also ways of making biodiesel be more than just a small part of petroleum diesel through engine modifications. This biofuel can be made from vegetable oils and animal fats through a process called transesterification, which makes the feedstock react with an alcohol using a catalyst [\[5,12\]](#).

##### *3.2.2.1. Advantages of biodiesel*

Researchers have concluded that having biodiesel make up 20% of the diesel in an engine has the most success. This is a pretty big fraction of the total fuel in a vehicle, which lets it be more environmentally friendly considering that biodiesel is said to be “carbon-neutral” [\[5\]](#).

### *3.3. Disadvantages of first generation*

The idea of using first generation biofuels seemed to be like the holy grail of renewable energy at first, but further examination proved otherwise. There's a caveat about using the same crops used for food as fuel. These commodities are extensively used for food and the demand for it keeps increasing. If food crops being converted to biofuel creates competition between food and fuel, this could raise the cost for the consumer. This conflict with food supply raises questions and concerns about the long-term sustainability of first-generation biofuels production. This being the case, a new biofuel generation stemming from non-edible biomass was born [\[5\]](#).

## 4. The second generation

The scrutiny on producing biofuels from biomass that is in direct competition with food production led to the birth of second generation biofuels. When compared with first generation biofuels, the second generation has better land use efficiency [5]. In the beginning, second generation feedstock had lower cost, but now, the cost has increased enough to prevent successful development of second generation biofuels.

### 4.1. Second generation feedstock

The feedstock used for this generation is not used for food. These types of feedstock include crops that are grown as bioenergy crops in areas that are suitable and non suitable for food production and the part of food crops and trees that aren't edible. The following are examples of these kinds of feedstocks: starch, oil, sugar crops (corn stover, Jatropha, cassava, Miscanthus, etc.) and lignocellulosic biomass (straw, wood, grass, etc.) [16].

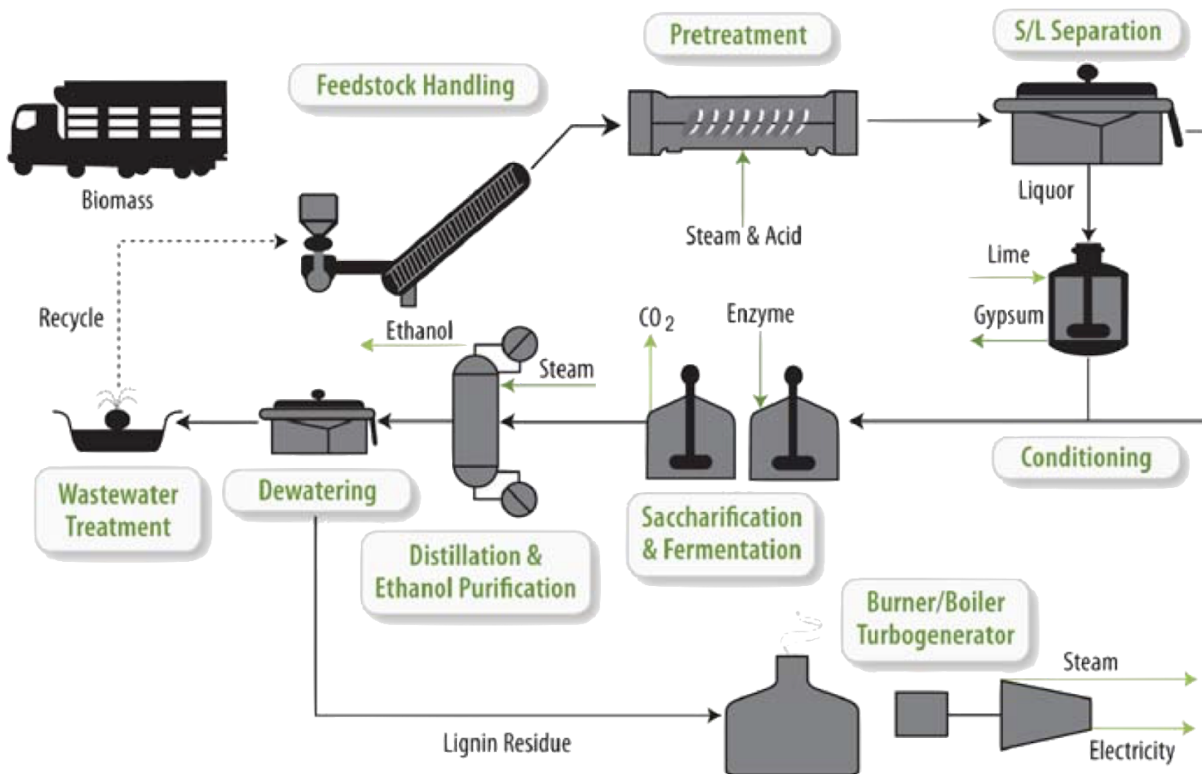
### 4.2. Second generation biofuels and process(es)

The two main ways to produce second generation biofuels are biological and thermochemical processes from the non-edible biomass [5]. Second generation renewable fuels require more sophisticated processes than first generation ones. Ethanol and butanol are produced biochemically, while methanol, refined Fischer-Tropsch liquids, dimethyl ether, and unrefined fuels are produced thermochemically. Biochemical processes rely on biocatalysts (e.g. enzymes and microbial cells) with heat and chemicals as a pretreatment. Then it can be converted to a liquid biofuel through fermentation or similar process. Thermochemical processes rely on heat and/or physical catalyst to turn the non-edible biomass to a gas or liquid, which is then converted to a biofuel through a conversion step. There are two categories within the thermochemical process: gasification and pyrolysis. Gasification depolymerizes the biomass through the limitation of oxygen at high heat (greater than 850 °C). Pyrolysis mildly depolymerizes biomass, which produces liquid intermediates, known as pyrolysis oil or “bio-oil”, through the absence of oxygen at lower temperatures than gasification (400-650 °C) [17]. In essence, biochemical processes tend to be more of a gentle approach to producing biofuel, while thermochemical processes force the conversion of the biomass.

#### 4.2.1. Ethanol from second generation

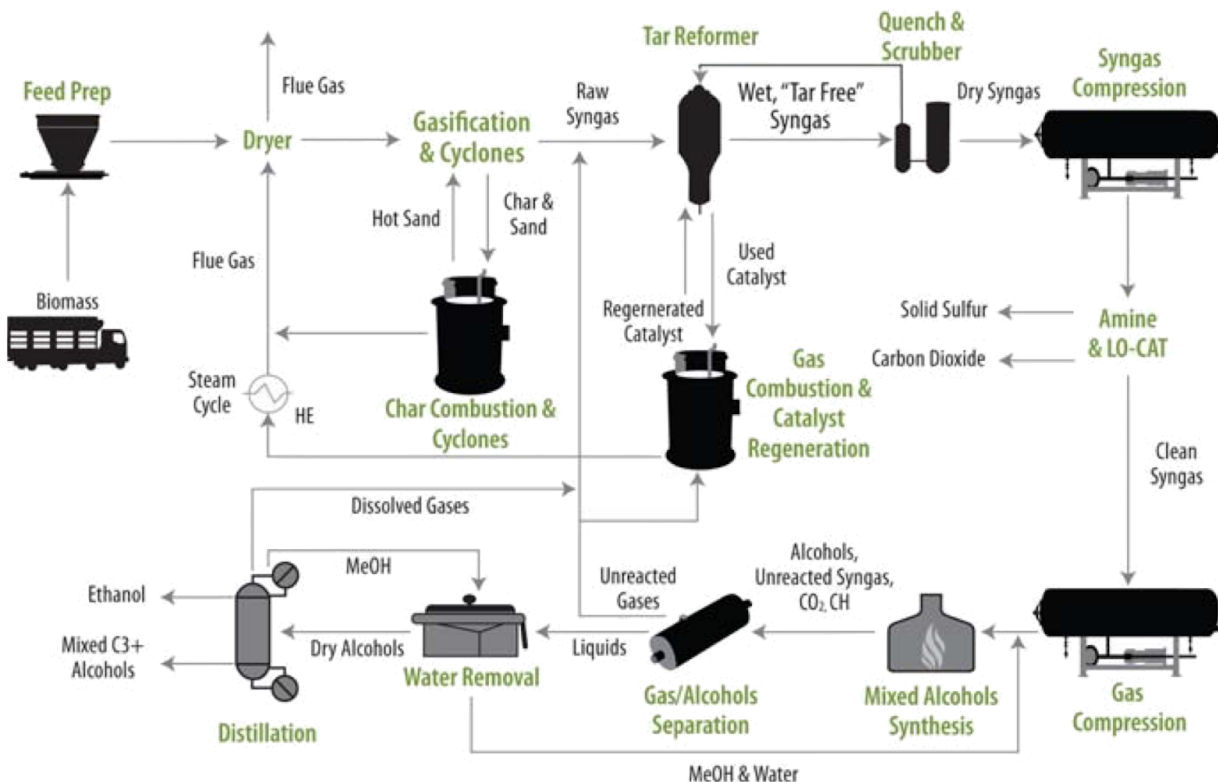
Ethanol can also be produced as a second generation biofuel without using the food crops used in first generation biofuels. An example feedstock used in this case is corn stover, rather

than the actual corn used for food. More specifically, ethanol can be produced from a biochemical process using corn stover. The process begins with the corn stover being washed/milled and prepped for pretreatment. The pretreatment process is used to attack the matrix of the corn stovers' polymeric compounds so that another process can take place to create ethanol. Fig. 3 illustrates a detailed biochemical conversion process of ethanol, in which a hybrid hydrolysis (saccharification) and fermentation (HHF) process is used after pretreatment [\[17\]](#).



**Fig. 3.** Example of biochemical conversion process using HHF process [\[17\]](#).

Second generation ethanol can also be produced through a thermochemical process using a lignocellulosic biomass like wood chips. Fig. 4 depicts this example of a thermochemical process. Similar to corn stover in the biochemical process, wood chips are first brought in to be screened, milled, and dried. This example utilizes the gasification method as a pretreatment. The resulting product is then processed through a mixed alcohol synthesis to be finally converted into ethanol.



**Fig. 4.** Example of thermochemical gasification conversion process using mixed alcohol synthesis [17].

#### 4.2.2. Renewable diesel from second generation

Renewable diesel, also classified as green diesel, is a suitable transportation fuel used in diesel engines. Although renewable diesel and biodiesel might sound the same, they are actually very distinct. A major difference is the way they are produced. Biodiesel uses transesterification as a process of acquisition, whereas renewable diesel is produced through numerous types of processes including hydrotreating (isomerization), gasification, pyrolysis, etc. Another difference is the feedstock used for acquiring renewable diesel, which include, in addition to all the feedstocks for biodiesel, crop residues, woody biomass, etc.) [18]. Table 1 shows a general comparison of properties commonly referred to describe fuels between fossil-base diesel (FB Diesel), biodiesel and renewable diesel. Some of the values may vary widely depending on the feedstock and process used to make that biofuel. Nevertheless, it is evident that renewable diesel has more similar characteristics to the fossil-based diesel than biodiesel [19].

**Table 1**

Comparison of properties between petroleum diesel, biodiesel, and renewable diesel (Adopted from [19]) [20,21,22,23,24].

Properties	FB Diesel	Biodiesel (B100)	Renewable Diesel
Cetane #	40-55	50-65	75-90
Energy Density, MJ/kg	43	38	44
Density, g/ml	0.83-0.85	0.88	0.78
Energy Content, BTU/gal	129 K	118 K	123 K
Sulfur	<10 ppm	<5 ppm	<10 ppm
NOx Emission	Baseline	+10	-10 to 0
Cloud Point, C	-5	20 <sup>a</sup>	-9 <sup>b</sup>
Oxidative Stability	Baseline	Poor <sup>c</sup>	Excellent
Cold Flow Properties	Baseline	Poor	Excellent <sup>d</sup>
Lubricity	Baseline	Excellent	Poor <sup>e</sup>

<sup>a</sup> Depends on feedstock. The cloud point of B100 starts around -1°C to 0°C (30°F to 32°F) and can go as high as 20°C (68°F) or higher for biodiesel from highly saturated feedstocks [22].

<sup>b</sup> Cloud point can vary widely. Depends on ratio of n- to iso-paraffins in fuel. In the US, range is -35°C (-31°F) to -9°C (16°F) [23].

<sup>c</sup> Antioxidants, whether natural or incorporated as additives, can significantly increase the storage life or stability of B100 [22].

<sup>d</sup> Only with sufficient isomerization [24].

<sup>e</sup> Requires additives to meet specifications [24].

#### 4.2.2.1 Advantages of renewable diesel

When compared to regular petroleum diesel, renewable diesel is a lot more similar than biodiesel. This allows for renewable diesel to be a better replacement of petroleum diesel.

#### 4.3. Disadvantages of second generation

Though second generation biofuels have a better appeal than the first generation, there are still some drawbacks that hinders its production. Before its potential can be realized, a number of technical barriers need to be tackled, which makes this generation non cost-effective [12]. There needs to be an improvement to refinery technologies for getting non-food feedstock converted into biofuel for there to be an increase in second generation production [16].

## 5. The third generation

The third generation is primarily sourced from aquatic organisms such as algae and cyanobacteria. Jet fuel, renewable diesel and sophisticated biodiesels when made from these feedstocks can be classified as a type of third generation biofuel.

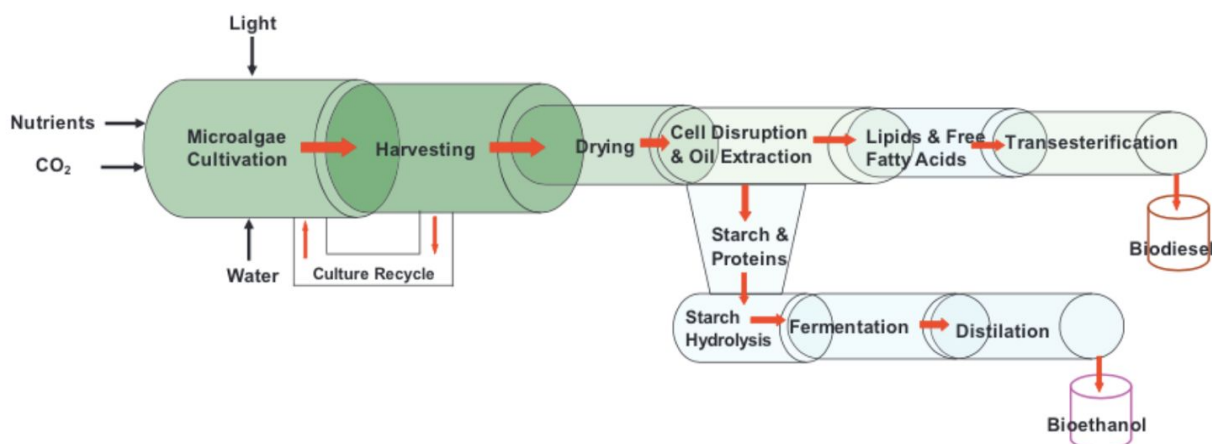
### *5.1. Third generation feedstock*

The biomass used for third generation production are aquatic organisms, and the non-biomass are waste products originally produced with the consumption of fossil fuels. The following are examples of these feedstocks: algae, seaweeds, microbes, etc.). Algae is becoming a popular feedstock for this generation due to its high lipid (fat) content and rapid growth rate [25]. Another feedstock for third generation that has been getting some attention are oleaginous microorganisms [26].

#### *5.1.1. Biofuels and processes*

There are several biofuels resulting from microalgal conversion production (hydrogen, bioethanol, methane, bio-oil, etc.). A big issue is finding efficient ways of harvesting algae. They can be chemically, mechanically, biologically, or electrically harvested. A pretreatment known as flocculation is utilized to increase the cell size of the algae. Similar to the second generation, there are many ways of converting microalgae to biofuel, which include biochemical, thermochemical, reaction, etc.).

Fig. 5 shows a simplified schematic of how microalgal biomass can be converted into biodiesel and bioethanol using transesterification and fermentation, respectively. Only 30% of the biomass can be converted to make bioethanol and biodiesel. The remaining 70% is considered as an algae by-product, which can be used as nutrients for feedstock, pharmaceutical ingredients, cosmetics, etc. [25]. For example, the proteins on the bioethanol pathway can't be converted to fuel, but they can be used as animal feed or for human dietary supplements.



**Fig. 5.** Biodiesel and bioethanol production process from algae biomass [25].

Microbial technology has also been gaining some traction lately. Species of yeasts and fungi are currently being examined as they have immense availability. They can also be consistent lipid accumulators making them a good source for biofuel production. Also, they are known to use carbon sources for lipid production. Lipids are an essential part of renewable fuel as they can be used to convert into biofuels using methods like transesterification [27].

### 5.1.2. Advantages of third generation biofuels

Compared to lignocellulosic feedstock, algae is known to be able to produce biomass faster while using less land surface. As for microbial technology, their abundance can play a huge role in advancing the way third generation biofuels are processed.

### 5.1.3. Disadvantages of third generation biofuels

A major disadvantage with third generation biofuels is the challenges it faces for producing biofuel. Algae production into biofuel requires extensive amounts of water to serve at an industrial scale. The extraction of lipids can also be a hassle due to the high water content [27].



## 6. The fourth generation

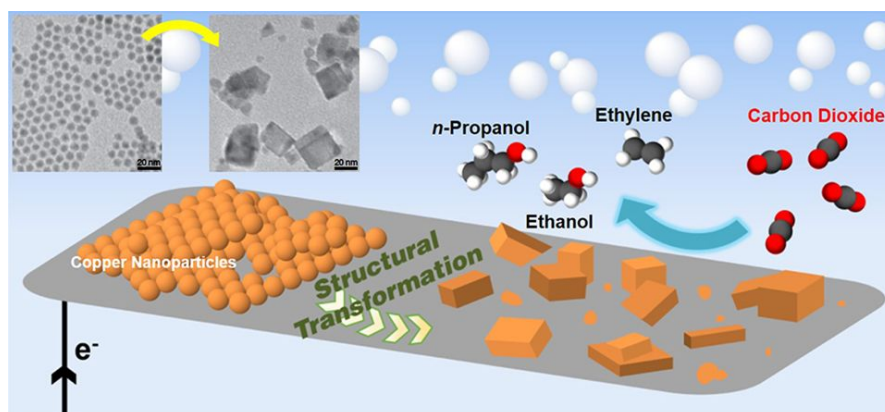
The fourth generation of biofuels is still a young generation of renewable fuel but has been said to be the most environmentally friendly. They don't require the destruction of biomass to produce its biofuel. This generation refers to photobiological solar fuels and electro fuels. Its technology has become very interesting that could revolutionize the way we produce fuel [28]. They can also be described as biofuels produced with the use of petroleum-like hydroprocessing, advanced bio-chemistry, or revolutionary processes like Joule's "solar-to-fuel" method [29].

### 6.2. Fourth generation feedstock

Fourth generation biofuels use raw materials that are inexhaustible, cheap, and widely available [28]. Over the past several years, there has been research done in figuring out ways to reduce carbon dioxide ( $\text{CO}_2$ ) or use it to produce fuel.

### 6.3. Biofuel, process(es), and advantages

Scientists at the Department of Energy's Lawrence Berkeley National Laboratory (Berkeley Lab) have come up with a way to convert  $\text{CO}_2$  into multi-carbon fuels and alcohols using a new electrocatalyst while inputting low amounts of energy [30]. Peidong Yang, a Berkeley Lab scientist, led a team that discovered an electrocatalyst made from copper nanoparticles. This electrocatalyst had the sufficient qualities to break down  $\text{CO}_2$  and form ethylene, ethanol, and propanol. Fig. 6 depicts a simplified version of this  $\text{CO}_2$  conversion process [30].



**Fig. 6.** Simplified schematic of Berkeley labs copper nanoparticles catalyst converting  $\text{CO}_2$  to multi-carbon products [30].

At Linköping University in Sweden, researchers are trying to convert CO<sub>2</sub> into fuel with the use of sunlight. These researchers are attempting to recreate the photosynthetic process that plants use to capture CO<sub>2</sub> and turn it into fuel. They have proven that they are able to methane and carbon monoxide through their process. Their method consists of using graphene grown on silicon carbide, which creates a graphene-based photoelectrode. This photoelectrode can then be combined with cathodes to produce fuels [\[31\]](#).

#### *6.4. Disadvantages of fourth generation*

Although the fourth generation seems to be a promising fossil-based fuel alternative, it still has a long way to go. Research and testing are still at their early stages. There needs to be further development to get this type of technology to industrial scale. Also, these processes can be very costly.

## 7.0. Other Renewable Fuels

### 7.1. Fuel from municipal solid waste (MSW)

There are waste-to-energy plants that burn MSW to produce steam that can generate electricity or heat buildings. This helps in minimizing the amount of material that gets left behind in landfills. A result of burning some MSW is methane gas, which can also be used for electricity generation [32]. Other forms of MSW include anaerobic digestion and gasification.

### 7.2. Fuel from flue gas

Flue gas can be considered a mixture of products of combustion. The primary components of flue gas include particulates, organic carbon compounds, acid gases, heavy metals, and dioxins. Particulates are the non-combustible fraction of the waste used combined with carbon or other products of incomplete combustion. Polycyclic aromatic hydrocarbons (PAHs) are an example of organic carbon compounds and are also a product of incomplete combustion. PAHs are non-biodegradable and can increase the risk of cancer. Acid gases can be simple to remove from flue gas and include gases like hydrogen chloride (HCl), hydrogen fluoride (HF), sulphur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) [33].

LanzaTech, a New Zealand company founded in 2005, developed a technology that can convert greenhouse gas emissions from industrial facilities into ethanol using a biological process. Their process enables polluting companies to convert their emissions into jet fuel or building blocks for plastics. This technology battles our planet's gas emitting problem and society's demand for oil [34]. Their process consists of a chemical recycling platform of gasification coupled with gas fermentation [35].

## **8. Conclusion**

As industrialization and human population increases, a need for a more sustainable way of life becomes more necessary. Biofuels have been around for quite some time now, but certain drawbacks call for better generations and solutions. The “food vs. fuel” debate plays a big role in the hindering of first generation biofuels. But even the successors of this first generation have their limitations. Although the third and fourth generations are fairly new, they propose the closest solutions to mitigate greenhouse gas emissions. Sure enough there will be a fifth generation to arise, which will hopefully provide the answers we need. There is also an increase in the research of recycling of waste products to convert into renewable fuels, which have resulted in promising results.

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