THE EVOLUTION OF BIOFUELS

Introduction

For several decades, experts have regarded fuels extracted from biomass as the solution to the world's energy crisis. Utilizing energy stored inside biomass is not a new concept. After all, humans learned how to utilize biomass to create fire in the early stone age. The challenge here is to convert the biomass into liquid so that it is compatible with existing energy infrastructure. Several generations of advancements have been made to convert biomass into biofuels. Figure 1 demonstrates the four generations of biofuels advancement thus far. Functionality of the biofuels does not vary from generation to generation; instead, the source from which the fuel is extracted varies. The first generation of biofuels are extracted by processing starch, sugars, fats, and oils from a variety of food crops. The second generation of biofuels mainly addresses the Food vs. Fuel controversy generated by the first-generation biofuels, as the fuel here is derived from non-edible biomass. The first two generations of biofuels require valuable resources like water, land, and intense labor. Addressing this issue, the third generation of biofuels, extracted from algae, requires minimal resources and has faster yield. Technological advancements over the years have contributed to the emergence of the fourth generation of biofuels, mainly solar fuels, which may turn out to be revolutionary for the biofuel industry. The succession of biofuels, from first-generation biofuels to, most recently, fourth-generation biofuels, is a tale of overturning obstacles, safeguarding energy security, and making strides towards a renewable world.

First Generation Biofuels:

The first-generation of biofuels—mainly bioethanol and biodiesel—are synthesized from food crops such as corn, sugarcane, sugar beet, maize, and rice. These food crops are fermented, resulting in the production of biofuels. Bioethanol, for example, is produced from the fermentation of sugars with the aid of yeast variants like Saccharomyces cerevisiae [1]. Sugarcane and corn are two main sources of first-generation bioethanol. The extraction of bioethanol from sugarcane is rather simple—sugarcane passes through an extractor where it is crushed in water, which is then purified with the aid of fermentation yeast to extract bioethanol [2]. Corn is carbohydrates heavy; therefore, it must undergo preliminary hydrolysis of starch, which requires expensive enzymes such as a-amylase, to extract sugars which result in the production of biofuels after fermentation [3].

Biodiesel, apart from bioethanol, is the only other first-generation biofuel that is produced at industrial scale. Biodiesel production involves three key ingredients—oil and fats derived from oily plants and seeds; alcohol, which is usually methanol in used oil or ethanol in crude oil; and a catalyst which is generally potassium hydroxide (KOH) or sodium hydroxide (NaOH) [4]. The oils and fats are mainly composed of triglycerides, which are molecules

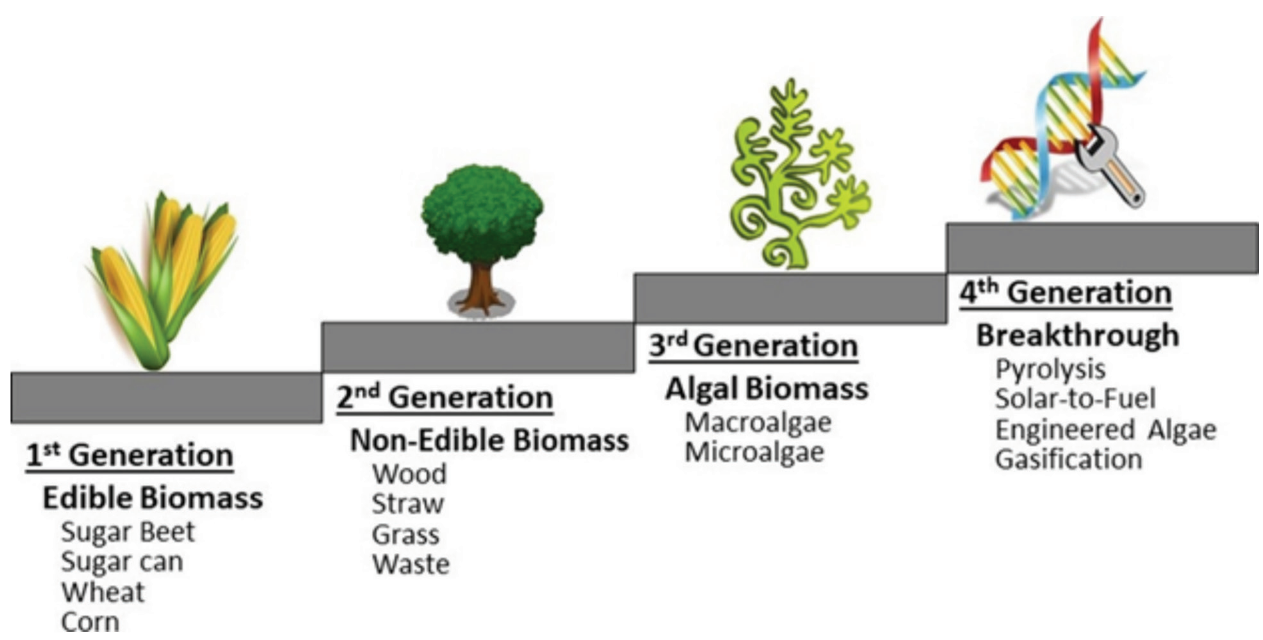

Figure 1: Generations of Biofuels [1]

consisting of glycerol esterified with three fatty acids. Triglycerides are reacted with an alcohol, usually methanol, by a chemical process called transesterification or esterification reaction, in which sodium hydroxide (NaOH) is the catalyst [5]. This reaction leads to glycerin and three molecules of fatty acid esters. Esters have lower density than glycerol, so they float and separate from glycerol. The molecules of fatty acid esters make up biodiesel [6].

The first-generation of biofuels seemed viable to solve the global energy crisis—not only are they carbon neutral, but they are also functionally equivalent to fossil fuels and are compatible with existing energy infrastructure—until researchers realized that the production of these fuels on an industrial scale is time, energy, and resource intensive. The production of food crops in itself requires valuable resources such as land, water, labor, and fertilizers (which cause pollution). Not to mention, the adverse effect that these biofuels have on the agriculture sector all over the world as higher demands drive up food crop prices [7].

Second-Generation Biofuels:

Learning from first-generation shortcomings, the second-generation biofuels used non-edible biomass, specifically food residues made up of lignocellulose compounds such as coconut husks, cotton wastes, switchgrass, sugar bagasse, forestry wood residues, and waste papers. The extraction process for second generation biofuels is classified by two distinguished processes: biochemical and thermochemical [8].

The biochemical conversion process uses enzymes and microorganisms to convert biomass into sugars and those sugars into biofuels. Firstly, biomass undergoes a pretreatment process so that it can be decomposed easily in the subsequent steps [9]. Steam explosion, classical pulping, and organosolv pulping methods are typically used to break down and separate biomass into cellulose, hemicellulose, and lignin compounds [10]. After pretreatment, biomass undergoes an expensive process called saccharification, where enzymes such as pullulanase break the cellulose chains into glucose and hemicellulose chains into xylose, mainly because it is easy to ferment these simple sugars into ethanol or other biofuels [11]. Thereafter, biofuel is produced at the fermentation stage, where bacteria or microbes, such as yeast, can break sugars into secreted compounds that are used [9].

The thermochemical conversion process uses heat to break down biomass into intermediates, such as gas or bio-oil, that can be upgraded to biofuels [9]. The first step in the thermochemical process is called purification or gasification, this method uses heat and pressure to turn biomass, often wood material such as forest residue, into a hydrogen and carbon monoxide rich gas called synthesis gas (syngas) [12]. Gasification takes place in a carefully controlled environment that typically contains oxygen or steam. The syngas is then conditioned to produce the desired ratio of carbon monoxide and hydrogen to achieve the maximum yield from chemical reactions in subsequent steps [12]. Pressurized hot syngas is then passed through a catalyst contained in a reactor to transform the gas into liquid. At this stage, the carbon monoxide and hydrogen molecules are combined to form larger hydrocarbon molecules. The molecules are subsequently cooled, condensed, and refined into biofuels [13].

While second-generation biofuels are clearly an upgrade, mainly because cheap food residues are used instead of food crops, the extraction process is still time-consuming and money intensive. Additionally, the gasification process, where the biomass is heated at high temperatures and high pressures, leads to air pollution, which in turn can cause respiratory diseases [15].

Third-Generation Biofuels:

Third-generation biofuels are mainly extracted from algal biomass. Algal biomass is an ideal source because, depending on its species, about fifty to eighty percent of its dry weight is made up of oil [16]. Algae species with high lipid content, such as Chlorella, are typically cultivated and harvested for biofuels as more comparative fuel can be extracted from these species [16]. There are mainly two ways algae is cultivated: raceway ponds and bioreactors. A raceway pond is essentially a long, shallow pool where the fertilizer-rich water mixture is kept moving with paddle wheels. Algae forms on the surface of the raceway ponds by converting water, nutrients, carbon dioxide, and sunlight into lipids [17]. Only about one percent of the algae can be cultivated per surface area in a raceway pond (about 1 g algae per 10 kg of water). A bioreactor, on the other hand, is expensive to build but has a higher level of productivity provided the same amount of space as the raceway pond. After cultivation, algae are harvested or dewatered with the aid of techniques such as flotation and reverse osmosis. The flotation technique skims off the algae from the surface of water after it is cluttered together and, in reverse osmosis, the algae are extracted by desalination of the water [18]. After cultivation and harvesting, multiple methods may be used to extract the oil from algae cells [19]. Traditional methods such as mechanical extraction, where the algae cells are broken by mechanical stress, and chemical extraction, where the cells are broken by pH levels that algae cannot tolerate, are typically used [19]. More recently, ultrasound waves have also been used as an alternative way to squeeze the oil out of the algae cells. When ultrasound waves, with an incredibly high frequency of about twenty thousand hertz, pass through the algae mixture, a high-pressure environment is created that collapses the algae cells [20]. The extracted oil is then converted into biofuel through transesterification.

Third-generation biofuels sources are faster to harvest compared to the first and second generation biofuels sources, as algae can double its biomass in less than a day. Additionally, there is no need for valuable resources such as clean water, as algae can be grown in wastewater or non-potable water [16]. While the production of third generation biofuels is more efficient compared to first and second generation biofuels, it is still unable to compete with cheap fossil fuel prices. Algae harvesting consumes a lot of energy, making the process of extracting third generation biofuels expensive. Field experts and manufactures have made efforts to lower the prices but, as of now, they have not been successful [16].

Fourth Generation Biofuels:

The emergence of solar fuels, the fourth generation of biofuel, may hold the keys to a future with endless clean energy. The sun is perhaps the biggest source of energy; it provides more energy in an hour than humans can consume in a year [21]. Although there have been significant advances made in efficiently harvesting sun's energy, little has been accomplished regarding reliably storing that energy [21]. Since the sun does not always provide energy, there is a greater need to store its energy when it does, so that we can use it regardless of cloudy weather and time of day. Nature stores the sun's energy by converting it into chemical energy, this conversion process is known as photosynthesis. Like nature's photosynthesis, scientists have recently developed artificial photosynthesis, where the energy from the sun is captured in chemical bonds using inorganic semiconductor materials [21]. More specifically, a photoactive semiconductor electrode is used to split a water molecule into hydrogen and oxygen using the sun's energy in a process called electrolysis [22]. The photoactive photoelectrochemical cells absorb sunlight to generate an electron and an electron hole. The electron hole goes to a solution through the semiconductor material where it oxidizes water to create oxygen gas [23]. The electron goes through an external circuit into a metal cathode and then to the solution where it reduces the proton to form hydrogen gas. Hydrogen gas is then combined with carbon dioxide in a water gas shift reaction to obtain carbon monoxide and hydrogen [24]. This synthesis gas mixture can then be refined in a Fisher-Tropsch reaction to finally obtain methane. Hydrogen is converted into methane mainly because methane is easy to store and is less hazardous. When the energy needs to be released, methane can be burned in a combustion reaction which needs oxygen and provides water and carbon dioxide as byproducts [25].

Currently, it has been challenging to engineer photoelectrochemical cells that are inexpensive, efficient, and stable. Thus far, photoelectrochemical cells were operated at room temperatures, but now scientists are testing how the photoelectrochemical cells operate at higher temperatures [26]. The hypothesis is that this change will make the reaction faster and efficient as kinetically, reactions get faster at high temperatures and thermodynamically, electrolysis takes less energy. Although there is potential, solar fuels require further research and development before they can be produced on industrial scale [26].

Conclusion

Scientists have been trying to discover a biofuel extraction process that is inexpensive, not time consuming, and sustainable for almost four decades. It has been a long journey thus far and the road ahead may contain many obstacles, but each step on this journey is a step towards a stable, secure, and renewable world. With increasing energy demands, the demand for biofuels is growing every year, while the availability of fossil fuels is projected to decline steadily. Slow, steady progress towards a renewable world is noticeable. Scientists are constantly coming up with new and ingenious ways to solve the world's energy problems. While time is of the essence, these breakthroughs and innovations may lead to a world powered by clean and sustainable energy.

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