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Scaling Up Sustainable Biofuels for a Low-Carbon Future

Tahira Shafique and Javeria Shafique

Abstract

Fossil fuels oil, coal, and gas are valuable resources that are depleting day by day around the world and also imparting a negative impact on the environment. Biofuel because of its dynamic properties; its market values; and being sustainable, renewable, biodegradable, economic, non-pollutant, and abundant is an alternate source of energy. Each country can produce it independently, and because of these valuable properties biofuels have become superior over fossil fuels. This chapter gives a concise preface to biofuels and its impact on the environment. It includes definitions; classifications; impact on environment; implications; types of production techniques like chemical, biochemical, physical, and thermochemical techniques; types of resources like lignocellulosic-biomass, feedstock energy crops, algae, micro-algae, all kinds of solid wastes; and biofuels of prime importance like solid biofuels (biochar, solid biomass), gaseous biofuels (biogas, bio-syngas, and bio-hydrogen), and the most important liquid biofuels (bioethanol, biodiesel, and bio-oil). Due to increasing global warming and climate-changing conditions, in the near future biofuel being an environment-friendly resource of energy will be a substantial part of the world's energy demand, with no or zero polluting agents.

Keywords: biofuels, biodiesel, renewable energy resources, global warming solutions, alternate of fossil fuels, energy investment, future fuels, biodiesel, ethanol, oils, TAGs, biogas, green-diesel, algae, macroalgae, plants, wood

1. Introduction

Biofuels: a term that has broad implications in regard to the world's needs, biofuels have been a part of human life for a long time ever since the first person burned wood to get heat. Over time, he found the value of heat and started cooking by burning wood. So, the biofuels have an extended history than humanity's record and civilizations because these were present in the form of grass and wood before when we human beings found and used the fire.

With the progression of human civilizations, biofuels took an important place in the human's life. For example, CH_4 gas also known as domestic gas or biogas was used to warm water to take a bath in the 10th BC [1]; $\text{CH}_3\text{CH}_2\text{OH}$ or bioethanol was used in a combustion engine in 1826 [2]; Sadi's Carnot engines used biodiesel also known as Rudolph's diesel [3]; and for the very first time, peanut oil was used in the busses and trucks in 1896 [4]. Many other such applications developed and changed people's lives around the world [5].

In contrast with fossil fuels natural gas, coal, and oil, biofuels have some advantages:

- These are renewable [6]
- Resources of biofuels are abundant [6]
- Biofuels do not play any role in ozone layer depletion as these are neutral to greenhouse gases [7]
- Sulphur oxide emissions are zero or negligible [8]
- They result in fewer nitrous oxide emissions [9]
- Biofuels are friendly to the environment [10]
- These are easy to produce [11]
- All biofuels are biodegradable [12]
- All kinds of biofuels are sustainable [13]
- Biofuels production procedures are safe [14]

Biofuels also have some economic benefits:

- These fuels will lead to rural and agricultural development [15]
- These fuels enhance supply range [16]
- They lead to reduced dependence of energy on imports [14, 17]
- These fuels increase opportunity of jobs [14, 18]
- They improve rural economy [16].

To increase and promote the biofuel industry, several countries have planned many rules and objectives. Here, documents issued in the European Union, USA, Brazil, Thailand, India, and China are mentioned in **Table 1**.

| Country | Target or mandate | References |
|---------------|--|------------|
| EU | Mandate: minimum of 10% of transport fuel from renewable fuels by 2020 | [19] |
| United States | Mandate: 36 billion gallons of biofuel by 2022 | [19] |
| Brazil | Mandate: biodiesel use set at 10% by 2020 | [19] |
| India | Indicative: 20% blending for both ethanol and biodiesel by 2017 | [19] |
| China | Target: solid biofuels (10,000 t/year), biogas (billion m ³ /year), nonfood bioethanol (10,000 t/year), biodiesel (10,000 t/year) by 2020 | [19] |
| China | Target: 12.7 Bnl ethanol and 2.3 Bnl biodiesel consumption in 2020 15% of fuel consumption to be non-fossil fuel by 2020 | [19] |
| Thailand | Ethanol: E20 mandatory since 2008 Biodiesel: B2 mandatory since 2008 and B5 since 2012 | [19] |

Table 1.
Set of policies ordered by global biofuel producers.

2. Biofuel

2.1 Definitions

The term fossil fuels was used for fuels like natural gas, coal, and oil gotten from the decomposition of different plants and a variety of animals that remain buried underneath the earth's deepest layer for many years [14]. Over time, the word "biofuel" started being used. Till now, there are many distinctive definitions for the word "biofuel." Some of these statements are

- Bio-fuels are obtained from or with the help of microorganisms [14].
- Biofuels are those fuels that are obtained from biomass, petroleum, natural gas, and firewood [20].
- We derive these from different biological and plant materials [21].
- Bio-fuels are the products obtainable from natural resources, which include timber, peat or bagasse, or transformed chemically from biomass to synthesize ethanol, charcoal, bio-oil, and biogas [4, 22].
- These fuels are extractable from biomass feedstock or waste materials [15].
- Bio-fuels include liquid, solid, and gaseous fuels obtained from organic material like plants and animals [19].
- These are also known as the renewable fuels like biodiesel, bio-hydrogen, charcoal, bioethanol, and biogas obtained from biomass gotten from the organic waste materials and are reliable for transportation [10, 19, 23].
- Liquid biofuels: these include biodiesel extracted from fats and oils, bioethanol extracted from lignocellulosic material, sugar and starch, etc. [18].

According to the above definitions, "biofuel" can be defined as any kind of fuel that is produced by or from any renewable living organisms.

2.2 Significance

"Biofuels" or "bio-fuels" are significant in many ways such as:

- Biofuel is employed to supply heat, energy, light, and power.
- Biofuel is also claimed as a living fuel, that is produced from different living micro/macro-organisms: (the "bio" springs from the Greek word "bios," means "life"); these are the ways in which these fuels differ from all other fuels like fossil fuels having hydrogen and carbon.
- Biofuels are renewable, therefore the living organism can reproduce it in a relatively short time. While fossil fuels took many years and are non-renewable (this property of biofuels made it significant over fossil fuel).
- Biofuels might be obtained from plant structure, water algae, micro-algae, manure, animal waste, sludge, etc.

- Biofuel could be a solid, gas, or liquid.
- One type of biofuel is interconvert able to another type of fuel.

2.3 Classification

As we know there are many definitions of “biofuels”; similarly there are many classifications of biofuels according to different eras and research groups. According to the very first classification based on commercialization position of the biofuel production and resources, these are usually classified into two groups: one is conventional biofuels and the other is advanced biofuels (**Figure 1**). Commercialization can be ranked accordingly: research < demonstration < early commercial < commercial. The conventional or traditional bio-fuels contain such biofuels that are based on biodiesel gotten from the trans-esterification process; bioethanol obtained from starch and bio-methane or biogas from animal waste obtained via anaerobic digestion process. With regard to advanced bio-fuels, an early commercial-stage biofuel is a hydrologically treated oil. The demonstration level and research level stages contain lignocellulosic or cellulosic bioethanol, BtL (biomass-to-liquid) biodiesel, bio-hydrogen, and biodiesel obtained from micro-algae. We know that advanced biodiesel is not dominant at commercial level but because of its environmental and economic demand, it will be dominate in the market and will be fully commercialized in more advanced form in near future. Based on feedstock resource availability and synthetic techniques, many researchers classify this biofuels into two groups like 1st-generation and 2nd-generation biofuels [24, 25]. This classification is shown in **Figure 2**. Biofuels of 1st generation contain biodiesel, biogas, and bioethanol [24, 26]. The unsaturated and saturated edible plant-oils obtained from the corn, soybean, sunflower, canola-seeds, and some oils containing fruits like palm, olives, and coconut are categorized under liquid bio-fuels [25, 26]. It also has been stated in different researches that the solid biofuels like agricultural waste material, dried manure, and fire-wood are also part of the 1st-generation biofuels. The lipid-derived bio-fuels obtained from the waste of vegetable-oils, insects, animal fats, and oil-producing microbes are categorized under biofuels of 2nd generation [25]. At present biofuels of 1st generation are fully commercialized, while 2nd-generation biofuels are still under developmental stages [24].

Biofuel’s generations according to many other studies are classified in 1st, 2nd, and 3rd-generation biofuels [10, 27] mentioned in **Figure 3**. Biodiesel, biogas, bio-alcohols, bio-syngas, and vegetable oil, which are commonly known as biofuels

| | Conventional biofuels | Advanced biofuels | | |
|-------------|-----------------------|-------------------|---------------|------------|
| | Commercial | Early commercial | Demonstration | Research |
| Bioethanol | Sugar and starch | Cellulosic | | |
| Biodiesel | Transesterification | HVO | BtL | Microalgae |
| Biomethane | Biogas | | Biosyngas | |
| Biohydrogen | | | Biohydrogen | |

Figure 1.
Classification of biofuels and commercial status.

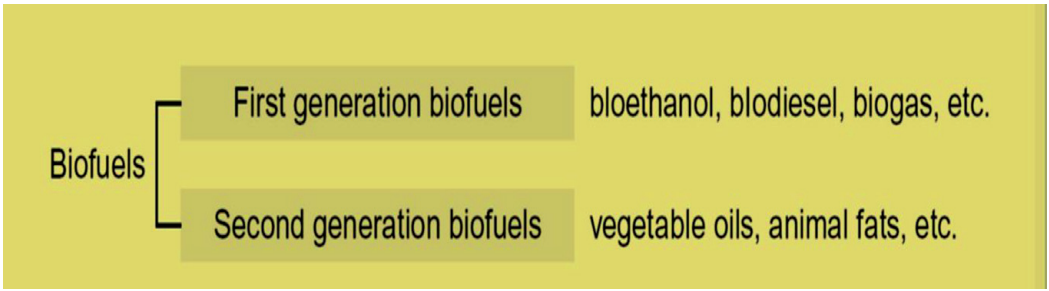


Figure 2.
Two generations of biofuels.

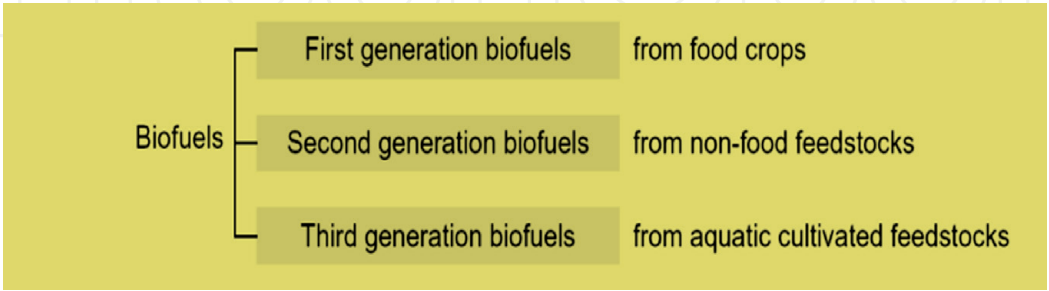


Figure 3.
Three generations of biofuel.

of 1st generation and obtained from edible crops: wheat, soybeans, vegetable oil, starch, corn, sugar, and grains, [28], are also contained within ryegrass, straw, wood, domestic refuse, switchgrass, grass cake, charcoal, grass cuttings, and dried manure [29]. The biofuels of 2nd generation includes biodiesel-FT(Fischer Tropsch), dimethyl ether, bioethanol, bio-syngas, biodiesel BTL(biomass-liquid) are synthesized from feedstock (lignocellulosic-biomass), nonfood material like cereal straw, wood grass, forest residues, sugar-cane, bagasse, energy crops (vegetative plants and short lifecycle forests) and domestics waste material [10, 30, 31].

The biofuels derived from feedstocks that are aquatically cultivated like cyanobacteria, algae, and micro-algae are 3rd-generation biofuels; these include biodiesel, bio-methane, bio-butanol, aviation fuels, bioethanol, jet fuels, gasoline, and vegetable oil [10, 32].

In another classification, biofuels are categorized into two groups: (i) primary biofuels included many solid biofuels without modifications like wood, grass, and wood slices that are burned for heating purposes and to cook different foods directly and (ii) secondary type biofuels have three generations of biofuels shown in **Figure 4** [33, 34].

According to some studies, biofuels are categorized into four groups: (i) natural bio-fuels are derived from simple organic materials like firewood, plants, vegetables, landfill gas, and animal waste and are used for heating, cooking, brick kiln, and production of electricity; (ii) the biofuels of 1st generation are obtained from eating able feedstocks, mostly palm, wheat, corn, soybean, maize, rapeseed, sugarcane, sugar beet, and oil crops [34]; (iii) the lignolytic feedstocks contain jatropha, miscanthus, sterculia, ceiba foetida, switchgrass, pentandra, and poplar are included in the 2nd-generation biofuels; (iv) algae feedstocks are the main source of 2nd generation biofuels **Figure 5** shows its classification [34].

With the advancement of research, oil-containing (jatropha) crops and nonfood (cassava) crops were known as one and a half- or 1.5-generation bio-fuels. Then biofuels took a new place in the classification tree and were re-classified into four groups: (1G) 1st-generation, (1.5G) 1.5-generation, (2G) 2nd-generation, and (3G) 3rd-generation of biofuels as shown in **Figure 6**. Some researchers grouped these

bio-fuels as 1st, 2nd, 3rd, and 4th generations of biofuels [3, 35–40]. **Figure 7** shows all the four groups and the uses of biofuels and types of feedstocks that were used to produce these four generations of bio-fuels are represented in **Table 2**. Some important merits versus demerits are also briefly described in **Table 3**. With the advancement of biofuels production and kind, we can classify these into the five different groups: 0th, 1st, 2nd, 3rd, and 4th generations of biofuels, as shown in **Figure 8**.

The 1st to 4th types of biofuels are like the above-described generations. The biofuels of the 0th-generation biofuels are naturally existing bio-fuels like raw feedstocks and can be used directly with no processing, special treatment, or modifications.

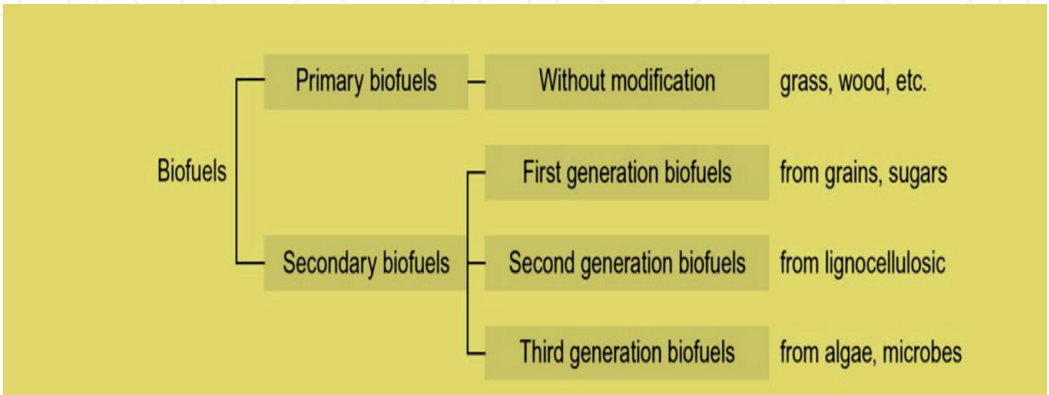


Figure 4.
Primary and secondary bio-fuels.

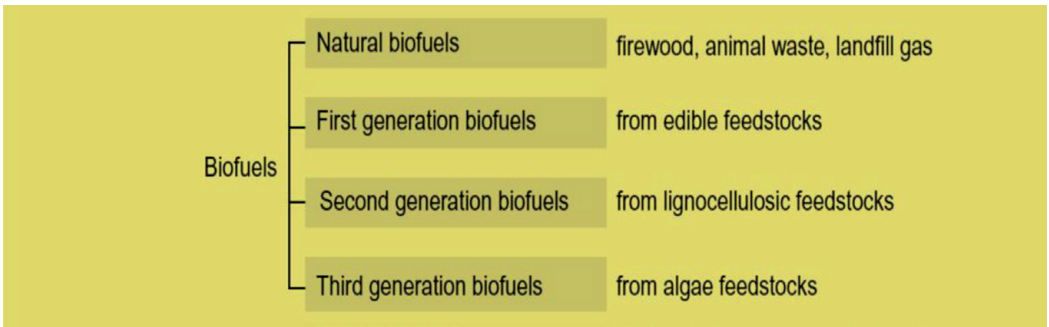


Figure 5.
Four groups of bio-fuels.

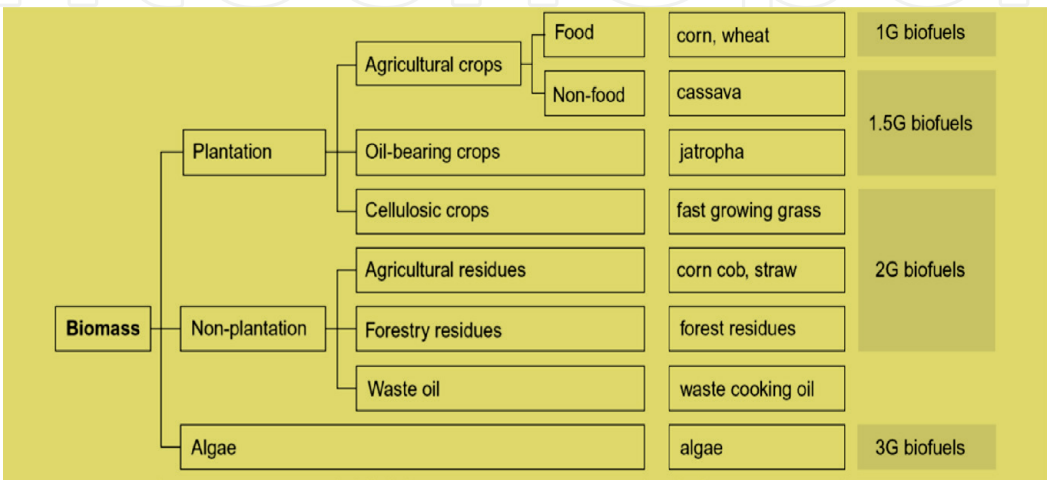


Figure 6.
Biofuels categorization into five generations.

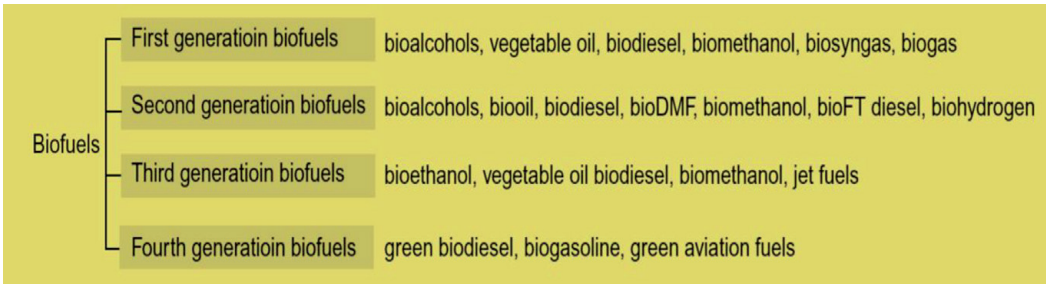


Figure 7.
Four groups classification of bio-fuels.

| Biofuels | Examples | Feedstocks |
|---|--|---|
| 1st generation | Bio-alcohols, vegetable oil, biodiesel, bio-methanol, bio-syngas, biogas | Sugar, starch, animal fats, soybean, soya, rapeseed, mustard, sunflower, maize, sugarcane, sugar beet, sorghum, potato, palm oil, coconut, canola, plant, cassava, castor, jatropha, sewage waste |
| 2nd bio-alcohols, bio-oil, biodiesel, bio-DMF, generation | Bio-methanol, bio-Fischer-Tropsch diesel, bio-hydrogen | Nonfood crops, wheat straw, corn, wood, switchgrass, cereal straw, sugarcane bagasse, reed canary grass, forest residues, energy crops, municipal solid wastes, alfalfa, agave, jatropha |
| 3rd generation | Bioethanol, vegetable oil, biodiesel, bio-methanol, jet fuels | Microbial species, algae, yeast, fungi, cyanobacteria |
| 4th generation | Green diesel, bio-gasoline, green aviation fuel | Vegetable oil, biodiesel |

Table 2.
Four generations of biofuels, feedstocks.

| Biofuel | Merits | Demerits |
|----------------|---|---|
| 1st generation | 1. Biodegradable | 1. Competition of land use |
| | 2. Energy security | 2. Blending with conventional fuel |
| | 3. Feedstock can be easily produced by already existing infrastructure and technology | 3. Highest carbon footprint compared with other generations of biofuel |
| | 4. Environmental and social benefits | 4. Requires large amount of inputs in terms of fertilizer, water and land area thereby reducing net energy ratio |
| | 5. Feedstocks available at large quantities | 5. Contributes to higher food prices owing to competition with food |
| 2nd generation | | 6. Might potentially have negative impacts on biodiversity |
| | 1. No competition with food | 1. Even though requires less compared to 1st-generation biofuels, the land required for production of 2nd-generation feedstock is substantial |
| | 2. Use of whole plant instead of only seeds or grains, and use of residues means more energy produced per hectare of land | 2. The use of agriculture and forest residue degrades soil quality and also induces soil erosion |
| | 3. Marginal lands can be used for planting of advanced feedstock such as <i>Jatropha</i> sp. | 3. Complex processes are required |
| | 4. Higher yield and lower land requirement | 4. Low conversion as compared with petroleum fuel |

| Biofuel | Merits | Demerits |
|----------------|--|--|
| | 5. Available feedstocks in large quantities | 5. Conversion technologies are under development |
| | 6. Feedstock can be easily produced by already existing infrastructure and technology | 6. Lack of technological and research breakthrough |
| | 7. Low cost for feedstock | 7. Lack of efficient technologies for commercial applications |
| | 8. Energy security | |
| | 9. Production of high-value added products | |
| 3rd generation | 10. Close to meeting the claimed environmental benefits | |
| | 1. No food or land competition | 1. Difficult to harvest and process |
| | 2. Produces more energy per acre than conventional crops | 2. High processing cost |
| | 3. Algae can be grown using land and water unsuitable for food production | 3. Lack of technological and research breakthrough |
| | 4. High oil yield | 4. Not yet commercially feasible |
| | 5. No toxic content | 5. Production technology is under development |
| | 6. Energy security | 6. Requires new technologies from the production of feedstock to processing into final biofuel product |
| | 7. Bioengineered algae are renewable | |
| | 8. Low and sometimes no cost for feedstock | |
| | 9. Improves performance of 1st- and 2nd-generation biofuels when employed in integrated biofuels | |
| 4th generation | 1. 4th-generation biofuel is argued to be carbon negative rather than simply carbon neutral, as it “locks” away more carbon than it produces | 1. Lack of study on its practical performance in terms of technical and economic aspects |
| | 2. Synthetic raw materials to produce biofuels is a possibility | 2. High cost |
| | 3. Energy security | 3. Still in research and development stage |
| | | 4. Requires new technologies from the production of feedstock to processing into final biofuel product |

Table 3.
Merits versus demerits of the all four generations of biofuels.

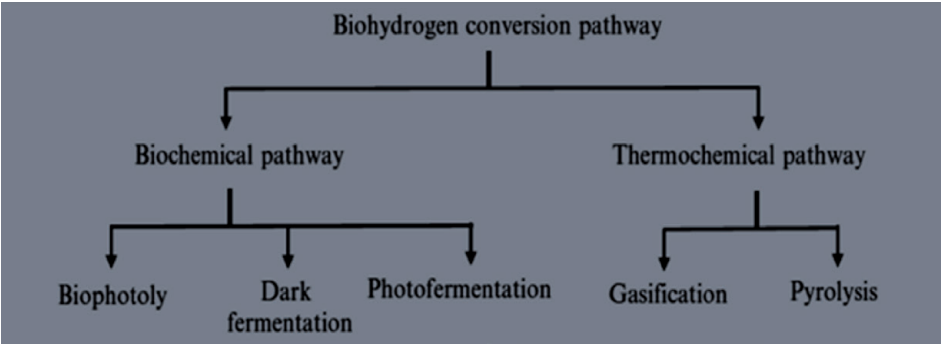


Figure 8.
Bio-hydrogen gas production pathways.

3. Gaseous bio-fuel synthesis techniques

Global warming and adverse climatic condition are propelling the researchers to bring a revolution with sustainable and renewable energy resources to reduce reliance on fossil fuels, which are depleting constantly. In this scenario, gaseous biofuels are environment friendly, will make vital contribution and will be a substantial part of the world's energy demand. The most valuable gaseous biofuels are bio-gas and bio-hydrogen.

3.1 Biogas (bio-methane)

A renewable, most sustainable and versatile energy source is biogas [41]. Shortly, biogas will make a remarkable impact to meet the energy demand. Biogas or bio-methane production resources are easily available at low cost and some even at no-cost like animal waste, domestic waste, animal feedstock waste, and municipal-organic, industrial effluent, for example, fat-separator wastes, glycerin, and food processing effluents waste material and residues of cereal crops [42, 43]. Biogas is the best replacement for fossil fuels [44]. It is safe to use in vehicles, generators, and combustion engines just like natural gas or fossil fuel gas.

The percentage of methane content in biogas defines its flammability and energy capacity. Production of biogas is mainly accomplished from the digestion of anaerobic biomass. It has 50–75% CH₄ (methane), 25–50% CO₂ (carbon dioxide), sulfur traces, water, hydrogen sulfide, oxygen, hydrogen, and ammonia. Production of biogas in methane treatment-plant that upgrades methane has similar properties just like natural gas and contains about 95% methane. To generate heat and electricity in co-generation units, de-sulfurized and dried bio-gas is safe to use [44]. With recent research, algae, water algae, and micro-algae are of prime importance for the production of bio-gas with outstanding results [42].

Anaerobic production of biogas is mainly divided into four steps: (a) hydrolysis, (b) acidification (also called acido-genesis), (c) de-hydrogenation/aceto-genesis, and (d) methanation [41]. As different anaerobic bacteria are used for biogas production, anaerobic conditions, pH, nutrient, and temperature are provided according to the demand for biogas production.

3.2 Bio-hydrogen

Bio-hydrogen is just simple hydrogen produced from the biochemical or thermochemical conversion of biomass like feedstock, residues of crops, cereal crops, agricultural grasses residues, livestock waste, forest biomass, waste-oil, algae, and micro-algae biomass, and industrial effluents [45, 46].

Hydrogen is a low-molecular mass gas having a higher heating value (HHV) of combustion products. The important thing that makes it perfect for the environment is that during chemical combustion after releasing energy, only water (H₂O) is the product. It has no harmful effect on the environment and global warming condition. Greenhouse gases are not produced during bio-hydrogen combustion. Bio-hydrogen production technologies are still under development [47, 48]. There are two techniques for bio-hydrogen production: (a) thermochemical (b) biochemical as shown in **Figure 8** [49].

3.2.1 Thermochemical method

Thermochemical process of bio-hydrogen production is further subdivided into two different methods like (a) gasification and (b) pyrolysis. Mainly,

gasification is a common method to produce bio-hydrogen gas. In this method, carbon-rich material is converted into bio-hydrogen thermochemically with/without catalyst at high temperature [50]. Energy is not released directly in the form of heat of combustion; rather it is converted in the form of bond energy as a lightweight fuel.

3.2.2 Bio-chemical method

The biochemical process of bio-hydrogen production is further subdivided into three different methods like (a) bio-photolysis, (b) dark fermentation, and (c) photo-fermentation. Nitrogenase, Fe-hydrogenase, and Ni-Fe-hydrogenase have commonly been used enzymes in the bio-chemical production method to convert biomass to bio-hydrogen [51, 52]. The bio-photolysis process is catalyzed by Fe-hydrogenase. This could be an indirect or direct process.

In the photo-fermentation process, a nitrogenase enzyme is used. By using water and nitrogen-deficient organic acids in the presence of light and nitrogenase enzyme, photosynthetic bacteria produce bio-hydrogen gas [53]. Dark fermentation is carried out by anaerobic bacteria by using carbohydrate-containing sources during the catabolism process of which carbohydrate-containing substrate bio-hydrogen gas is liberated [51].

4. Liquid bio-fuels

Liquid biofuel mainly includes biodiesel, which is of prime importance. Many techniques are in practice to produce the biodiesel.

4.1 Biodiesel

FAME (fatty_acid_methyl_ester) is a chemical name for biodiesel. It is a renewable bio-fuel and derived from the recycled greases, animal fats, and vegetable oils [54]. This fuel is just like petroleum-based diesel fuel and with very little to no reforms, it is safe to use in diesel engines also known as the compression ignition engine. Because of some important factors, biodiesel is superior over conventional diesel; for example, it does not contain sulfur residues, has lower life-cycle GHG emissions, and has lower particulate matter. Because of the high viscosity of vegetable oils, these can create problems; so we cannot use them directly. Vegetable oil has low volatility and its viscosity is 11–17× greater than the conventional diesel fuel; hence it forms deposits inside the fuel-injector of diesel engines because it does not burn completely [55]. The viscosity of vegetable oil can be reduced by following different methods. The most common production techniques are four in number (i) micro-emulsion, (ii) thermal-cracking also known as pyrolysis, (iii) dilution, and (iv) transesterification [56]. Transesterification is the preferable technique and it produces good-quality fuel. It is a chemical reaction between fat and oil by using alcohol mediums in the presence of a catalyst, which results in the formation of glycerol and esters [36].

4.2 Biodiesel: intensification techniques

As the use of fossil-fuel has influenced both human lives and the environment. Therefore, Biodiesel has revealed an optimistic effect to resolve environmental issues and helping to achieve energy requirements as a renewable energy resource [57].

Nonedible plants such as *Ceiba pentandra* (kapok), *Jatropha*, *Hevea brasiliensis* (rubber seed) should be preferred for the better quality of biodiesel production for social and economic values [58]. To find the easiest and economic way for biofuel production is the basic objective of the researchers. To enhance the ester product, the transesterification process should be fast and simple. Hydrodynamic cavitation, co-solvent, microwave heating, ultrasonic irradiation, the use of supercritical methanol, and in situ transesterification processes are novel applications to improve the biodiesel production [59]. According to literature, there are many studies about transesterification by microwave-assisted techniques using the nonedible plant-based oil.

4.2.1 Microwave-based method

A microwave-assisted technique reduces the processing time and also saves energy because the electromagnetic field is the main source of energy in this technique [60]. As to enhance the biofuel production and reaction rate in a very short period via a harmless and suitable method at optimum temperature, this microwave technique is of prime importance and is widely accepted as a chemical reaction tool [45]. In the transesterification method, catalysts like alkali convert the crude oil into fatty-acid-alkyl-esters (biodiesel) by using the monohydric-alcohol substrate. For biodiesel commercialization, the major issue is the operating cost.

To resolve this issue, a microwave-assisted technique as shown in **Figure 9** is the finest method to increase biodiesel yield and reduce reaction time; the transesterification method is an energy-saving and fast method for biodiesel production than the conventional method. This microwave method can make the separation process easier and also speed up the rate of reaction by providing specific heat during transesterification reaction [46]. An increase of dipolar rotation phenomenon can reduce the activation energy when microwave electromagnetics interact with reaction components (triglycerides, alcohol) [61].

4.2.1.1 Factors influencing the reaction rate

The transesterification process is ruled by the amount and by type of alcohol. Methanol is one of the most preferable reactants that are used in both techniques of transesterification like microwave-based and conventional methods. Methanol

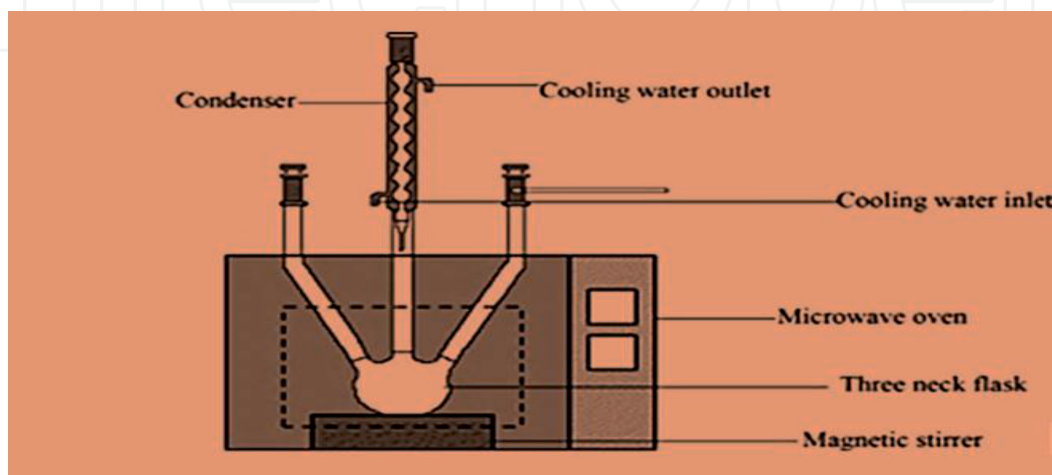


Figure 9.
Microwave setup for biodiesel synthesis.

is mostly used to achieve maximum production of biodiesel by using non-edible oils as those shown in **Table 4**. Methanol allows easier methyl ester formation and separation of glycerol simultaneously compared to other alcohols like ethanol [62]. So, this is because, in the catabolism of methane anion ethoxide ($C_2H_5O^-$) have low reactivity compared to methoxide (methanolysis) [63]. The sensitivity of ethanol causes the formation of soap in the non-edible oil.

Vitally, methanol has more ability to absorb the microwave spectrum than ethanol under microwave irradiation. The electromagnetic energy storage in material measures the capacity of substances to insulate charges from each other in dielectric constant. The material becomes polarized easily in the electric field at high dielectric constant due to decrease in the dielectric constant through the growing straight chain in the R-OH. Methanol is more favorable for biodiesel production via microwave technique due to its smallest path between the hydroxyl and hydrocarbons group and a remarkable nucleophilic property.

Ethanol produced from renewable biomass is an appropriate product for the production of biodiesel; there are five types of alcohol in the transesterification process [64]. The obtained values show the ascending conversion order such as isopropyl-alcohol < 2-butyl-alcohol < iso-propenyl-alcohol < iso-butyl-alcohol < methanol. So, we concluded that methanol is one of the efficient absorbers compared to the iso-butyl and iso-propenyl alcohol in a microwave field. Though microwave technique is very efficient for a transesterification reaction, there is a barrier with the immiscibility of oils with alcohols, which direct the minor triglycerides to biodiesel conversion.

Hence, to achieve a better yield, increasing the reaction rate and catalysts solubility of alcohol is of prime importance [65]. These catalysts can catalyze the reaction both heterogeneously as well as homogeneously. Under microwave operating reaction requirement of a catalyst excluded about tenfold as compared to the conventional heating method in transesterification [62, 66]. Different catalysts such as alkaline (NaOH, KOH, CH_3ONa , CH_3OK) and acidic (H_2SO_4 , HCl, H_3PO_4) are used in biodiesel production because of their highest performance [67].

Therefore, at the molecular scale of the microwave method, there is the inability for the suspended heterogeneous constituent part; so in this case, homogeneous catalysts are more preferable. The catalysts ions help to increase the molecular interaction of solvents because of their strong electric field. So it is concluded that the rate of reaction of acidic catalysis is slower 4000 times than the basic catalysis reactions, therefore, acidic catalysis reactions are less common because of their acidic nature rather than the basic nature [68, 69]. Catalysts like sodium-methoxides and potassium are better and preferable for a large-scale production process [70].

In another case, water causes the saponification and the formation of fatty acids in the strong basic medium [71]. In methoxide solutions, these catalysts do not liberate H_2O during the transesterification process and behave like weak Lewis-bases. Negligible ester dissolution in glycerol and fewer yield losses are observable under methoxide catalysis transesterification reactions. In another way, sodium and potassium hydroxides are inexpensive catalysts.

Homogeneous catalyst's drawbacks of homogeneous catalysts are controlled by using heterogeneous catalysts. Heterogeneous catalysts are reusable and recyclable due to inexpensive production costs with very good performance rate to avoid undesired saponification reactions [72]. It is reported that heterogeneous acid base-catalyzed reaction can act as an intermediate in both transesterification and esterification processes and they provide easier separation and cleaner products at the same time. SRO, $Al_2O_3/50\% KOH$, CaO, BaO, $SiO_2/50\% H_2SO_4$ etc. are the best solid catalysts for the production of biodiesel [73–75].

| Microwave-assisted base-catalyzed transesterification reaction | | | | | | | |
|--|-------------------|-----------------------------------|--------------|------------|-----------|----------------|------------|
| Feedstock | Alcohol:Oil ratio | Catalyst (wt%) | Temp. (°C) | Time (min) | Power (W) | Conversion (%) | References |
| Waste cooking oil | Methanol 6:1 | CH ₃ ONa 0.75% | – | 3 | 750 | 97.9 | [42] |
| | Methanol 6:1 | NaOH 0.75% | – | 3 | 750 | 96.2 | [42] |
| | Methanol 6:1 | NaOH 1% | 64 | 5 | 600 | 93.36 | [44] |
| | Methanol 6:1 | KOH 2% | 78 | 5 | 300 | 95 | [57] |
| | Methanol 6:1 | SrO 1.85% | Around 80°C | 3 | 1000 | 93 | [42] |
| Jatropha oil | Methanol 30:1 | NaOH 4% | 55 | 7 | 1200 | 86.3 | [43] |
| | Methanol 7.5:1 | KOH 1.5% | 65 | 2 | 1200 | 97.4 | [58] |
| Cottonseed oil | Methanol 6:1 | KOH 1.5% | 60 | 7 | 21% | 92.4 | [76] |
| Karanja oil | Methanol 33.4 wt% | KOH 1.33% | – | 2.5 | 180 | 89.9 | 0.3 [59] |
| Palm oil | Ethanol 4:1 | KOH 1.5% | – | 5 | 70 | 97.4 | [60] |
| | Methanol 20:1 | K ₂ CO ₃ 3% | ≈alcohol B.P | 180 | 1000 | 85.63 | [38] |
| | 2-propanol 20:1 | K ₂ CO ₃ 3% | | 180 | 1000 | 49.51 | [38] |
| | Methanol 18:1 | CaO 15% | – | 4 | 900 | 96.7 | [45] |
| Macauba oil | Ethanol 9:1 | Novozyme 435 2.5% | 30 | 15 | – | 45.2 | [46] |
| | Ethanol 9:1 | Lipozyme IM 5% | 40 | 5 | – | 35.8 | [46] |

Table 4.
Catalysis of trans esterification reaction under microwave assisted technique.

In the conventional method, at the higher temperature crude oil viscosity decreases with an increase of reaction rate exhibiting positive influence and reaction time reduction in both microwave and conventional methods [77]. In microwave reaction system, rapid heat transfer is achievable by molecular interactions of ionic and dipolar compounds via electromagnetic field that dramatically accelerates the reaction rate and also produces heat energy by volumetric distribution compared to conventional method where heat is transferred via radiation. However, reaction yield increases with increasing irradiation power [78].

4.2.2 Ultrasonic sound waves-based method

While using solid and liquid mediums for the process of intensification ultrasonic method is preferable [79]. Mechanical energy is required for continuous mixing and initiation of reaction in transesterification process. Ultrasonic sound wave energy of higher frequencies can be used [80]. It speeds up the reaction and also enhances the biodiesel yield. Cavitation is a phenomenon that creates chemical and physical effects on the reaction [81]. Ultrasonic cycles generate and also increase the size of cavitation bubbles from ten to a hundred times bigger [82]. High temperature (5000°C) and pressure (500 atm) occur due to collision of bubbles in less than a microsecond and lead to the vigorous mixing and rapid heating in the system between the two immiscible reactants shown in **Figure 10**. There are cycles of expansion and compression because of introducing ultrasonic waves to liquid. A positive pressure push liquid molecules closer in the compression cycle and negative pressure pull apart in expansion cycles [83]. Collision between the molecules generate radicals (H^+ and OH^-) promoting reaction rate between the reactants [84]. Hielscher Ultrasonic GmbH ultrasonic reactor (frequency: 18–20 kHz) for biodiesel production was introduced in 2000 [81, 85] and used low frequencies (28–40 kHz) for transesterification of vegetable oils. However, at 28 kHz there was a high yield production and reaction time was shortened considerably at 40 kHz [86].

Production of biodiesel from the oil of the Schleicher Triguga plant is influenced by ultrasonic irradiation [87]. The esterification reaction using H_2SO_4 catalyst reduced the acid value from 21.65 to 0.84 mg/g in the first step (reaction time: 20 min at 40°C). While a during a second step of transesterification reaction, a catalyst $Ba(OH)_2$ is used (80 min at 50°C) with the 96.8% conversion of

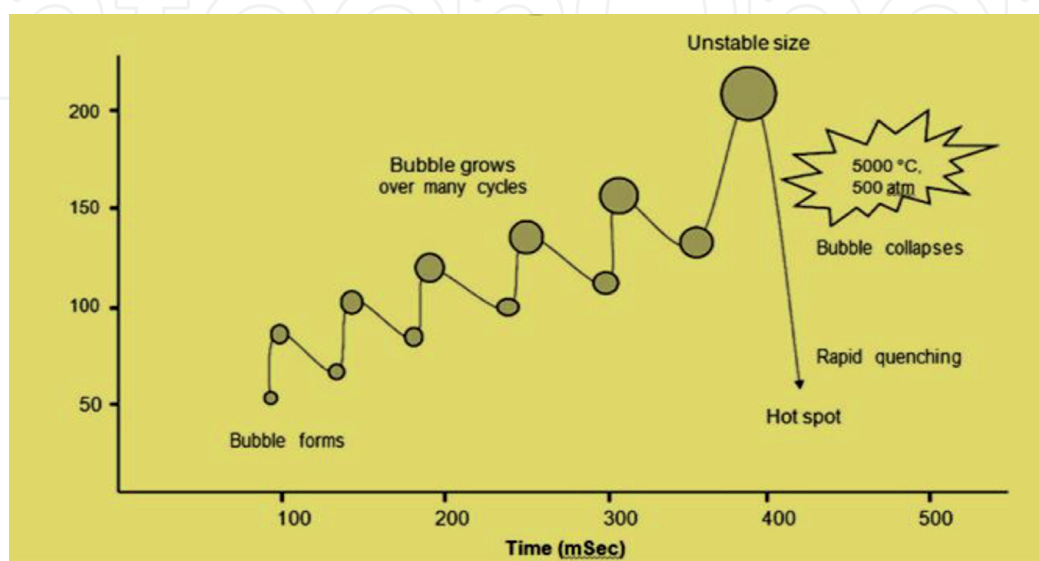


Figure 10.
Collapse and formation of bubbles inside the cavity.

| Methods | Feedstock | Catalyst | Optimum reaction condition | Yield/conversion (Wt %) | References |
|---------|------------------------------|--------------------------------|---|-------------------------|------------|
| MS | Waste cooking oil | KOH | Cat. 1 wt%, MeOH/oil 6:1, T 70°C, t 1 h | Y 98.2 | [46] |
| MS | Used frying | NaOH | Cat. 1.1 wt%, MeOH/oil 7:1, T 70°C, t 0.33 h | Y 88.8 | [47] |
| MS | Waste cooking oil | H ₂ SO ₄ | Cat. 4 wt%, MeOH/oil 20:1, T 95°C, t 20 h | C>90 | [48] |
| MS | Rubber seed oil (42.5% FFA) | H ₂ SO ₄ | Cat. 10.74 wt%, MeOH/oil 10:1, T 65°C, t 60 min | FFA conversion 98.6% | [41] |
| MS | Rubber seed oil (40.14% FFA) | H ₂ SO ₄ | Cat. 7.5 wt%, MeOH/oil 23:1, T 50°C, t 30 min | FFA conversion 75% | [56] |
| UM | Rubber seed oil (40.14% FFA) | H ₂ SO ₄ | Cat. 7.5 wt%, MeOH/oil 23:1, T 50°C, t 30 min | FFA conversion 98% | [56] |
| UM | Soybean oil | KOH | Cat. 1.5–2.2 wt%, MeOH/oil 6:1, T 40°C, t 0.25 h | Y 99.4 | [47] |
| UM | Waste cooking oil | KOH | Cat. 1 wt%, MeOH/oil 4:1, T 27–32°C, t 0.016 h | Y 99 | [48] |
| UM | Oleic acid | H ₂ SO ₄ | Cat. 5 wt%, Ethanol/acid 3:1, T 60°C, t 2 h | C>90 | [49] |

Table 5.
Comparison between conventional stirring and ultrasonic irradiations.

triglyceride. So, in conventional methods, ultrasonic waves accelerate the transfer of mass in heterogeneous nature catalyzed reactions [88]. **Tables 5** and **6** show the comparison of the ultrasonic-assisted method as well as a method of conventional stirring for the transesterification reactions. In several studies, RSO (rubber seed oil) and non-edible oil is reported as acid pre-treated by using the ultrasonic method [89]. To harvest 98% of FFA conversion this reaction took only 30 min, while some researchers reports 60, and 90 min [90–93]. In mechanical stirring, observed FFA conversion was only 75%.

4.2.3 Bio-gasoline and green diesel: thermochemical upgraded processes

4.2.3.1 Hydro-deoxygenation catalytic process

For cracking of long-chain gas oils into small-chain petroleum product distillates, olefin hydrocarbons saturation, and removal of heteroatoms, catalytic hydro-processing is the most preferable petrochemical method. Hydro-deoxygenation of vegetable oil occurs at a temperature of 300–450°C, with lowest space velocity and hydrogen pressure above 3 MPa. Vegetable oils are converted into saturated long-chain hydrocarbons with boiling points (180–360°C) [94]. HDO technology has been established by many commercial companies like HP-Innovations, UOP-Honeywell, Nest Oil-Corporation, Valero Energy-Corporation, and ConocoPhillips

| Method | Feedstock | Catalyst | Optimum reaction condition | Yield/conversion (Wt %) | References |
|--------|-------------------|-------------------------------------|---|-------------------------|------------|
| MS | Palm oil | KF/Ca-Al hydrotalcite | Cat. 4 wt%, MeOH/oil 12:1, T 65°C, t 5 h | Y 97.98 | [51] |
| MS | Palm kernel | CaO | Cat. 6 wt%, Alcohol/oil 30:1, T 60°C, t 3 h | Y 98 | [52] |
| MS | Palm oil | CaO/Al ₂ O ₃ | Cat. 6 wt%, MeOH/Oil 12:1, T 65°C, t 5 h | Y 98.64 | [53] |
| MS | Soybean oil | 15-KOH/CaO | Cat. 4 wt%, MeOH/oil 16:1, T 65°C, t 1 h | Y 97.1 | [50] |
| MS | Soybean oil | Calcined sodium silicate | Cat. 3 wt%, MeOH/oil 7.5:1, T 60°C, t 1 h | Y>95 | [57] |
| MS | Soybean oil | K ₂ CO ₃ /MgO | Cat. 1 wt%, MeOH/oil 6:1, T 70°C, t 2 h | Y 99 | [58] |
| MS | Jatropha oil | Mg-Al hydrotalcite | Cat. 1 wt%, MeOH/oil 4:1, T 45°C, t 1.5 h | Y 95.2 | [47] |
| MS | Waste cooking oil | K ₃ PO ₄ | Cat. 4 wt%, MeOH/oil 6:1, T 60°C, t 2 h | Y 97.30 | [60] |
| MS | Waste cooking oil | MgO/TiO ₂ | Cat. 10 wt%, MeOH/oil 50:1, T 170°C, t 6 h | Y 91.6 | [45] |

Table 6.
Synthesis of biodiesel with heterogeneous base catalyst by mechanical stirring.

in green-diesel synthesis process. They successfully introduced the substantial potential of catalytic hydro-processing.

4.2.3.2 Factors affecting green-diesel production

Hydrogen consumption, properties, and rate of an exergonic reaction in liquid biofuels are greatly influenced by the feedstock [95]. It is stated that higher unsaturated and long carbon chain lipid containing feedstock cause undesirable aromatization, oligomerization, cyclization, and dimerization of unsaturated long-chain carbon compounds intermediates inhibits the catalytic activities [96]. In the hydro-processing technique, temperature range depends on the product of interest. Temperature is the most important factor to harvest the hydrocarbons in diesel range; so for this purpose, many researchers have done many experiments to optimize the temperature range for the production of hydrocarbon chains within the diesel range. For long-chain hydrocarbons, for thermal cracking process to yield lower carbon chains, best temperature is above 400°C.

5. Conclusion

With the increasing demand for energy, continually depleting fossil fuels and energy resources, and a substantial environmental risk because of the consumption

of fossil fuels, there is a demand for alternative resource. These factors are not ignorable; keeping in mind this situation, many researchers have introduced biofuels as an alternative, sustainable, and renewable source of energy. These are producible at a very low cost by using organic raw material, feedstock, domestic waste, animal waste, plant waste, energy crops, seed oils, biological organisms, micro-algae, water algae, macro-algae, etc.; biofuels can be produced through different chemical and biochemical techniques and many advancements are being introduced day by day with new researches. Biofuels are the future of this universe due to their environment-friendly nature.

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