Biofuels - A Sustainable Energy Solution

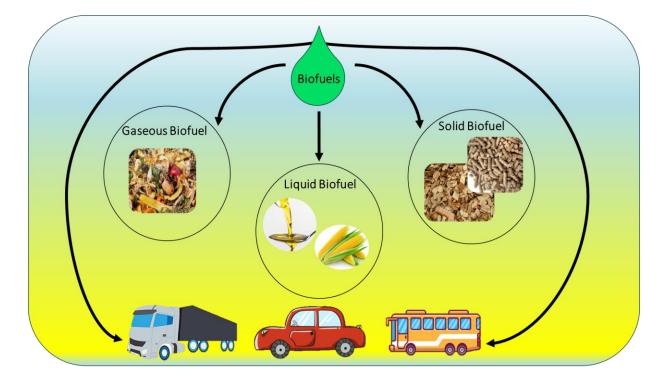
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ABSTRACT

Biofuels, a significant subset of renewable energy sources, have gained prominence in the quest for sustainable alternatives to fossil fuels. Their development has evolved over the years, and today, various types of biofuels exist, each with its own unique properties and applications. These renewable fuels, derived from organic materials such as crops, algae, and waste, come in various forms—solid, liquid, and gaseous—and offer a sustainable alternative to conventional energy sources. We examine several kinds of biofuels in this chapter. It delves into the advantages of biofuels, such as reduced greenhouse gas emissions, lower air pollutants, and decreased reliance on finite fossil fuel reserves. The positive impacts of biofuel production on rural economies, as it creates opportunities for agricultural diversification and job growth. The global community seeks cleaner and more sustainable energy solutions, and biofuels stand at the forefront, contributing to a greener and more resilient energy future.

Keywords- Biofuels, Sustainable, Solid Biofuels, Liquid Biofuels, Gaseous Biofuels

I. INTRODUCTION

Plant biomass and its processed derivatives, which may be burned to provide heat and light energy, are included in the category of biofuels. These biofuels, like fossil fuels, come in solid, liquid, and gaseous states (1). Biofuels, often referred to as agrofuels when derived from agricultural and forestry sources, are versatile energy sources with numerous benefits. These fuels are created from organic matter, commonly known as biomass, and offer various advantages. They are recognized for their sustainability, as they can be produced from renewable resources, which also contributes to lower greenhouse gas emissions. Additionally, biofuels support regional development by promoting agricultural activities and have positive impacts on social structures. They enhance energy security by diversifying sources of supply and can be categorized into primary types such as biodiesel and bioalcohols, including bioethanol and biobutanol, which are sometimes referred to as biogasoline (2). Lignocellulosic biomethanol stands out for its minimal emissions. The carbon content in this alcohol primarily originates from carbon captured during the growth of the bio-feedstock, resulting in its release into the atmosphere being essentially a release of previously sequestered carbon (3).

In the last century, global energy consumption has experienced a significant surge, resulting in substantial emissions of CO_2 , SO_2 , and NO_x because of the use of fossil fuels, which contributes to air pollution. Biomass has emerged as an essential renewable energy source on a global scale, serving as a viable alternative to mitigate the depletion of fossil fuel reserves.

There are three primary reasons why biomass is viewed as an appealing feedstock.

- 1. It is a renewable resource that can be developed sustainably over the long term.
- 2. It boasts highly favorable environmental attributes, leading to no net release of carbon dioxide (CO₂) and possessing low sulfur content.
- 3. It holds substantial economic potential, particularly if fossil fuel prices were to rise in the future.

II. HISTORY

The history of biofuels illustrates humanity's persistent quest for alternative energy sources. Biofuels, harnessed from renewable biological resources like plants, algae, and microorganisms, have served various purposes for thousands of years. Initially, they were primarily used for heating and cooking, employing materials such as wood and straw. However, the modern era of biofuels is marked by significant milestones.

Early manufacturing of ethanol was documented among American settlers. It is created by the fermentation of carbohydrates from crops like corn and sugarcane. The late 19th century led to the dominance of petroleum-based fuels due to their higher energy density and convenience, leading to a temporary decline in biofuel usage. Yet, during World War II, when petroleum supplies were constrained, biofuels, particularly alcohol fuels like ethanol and

methanol, experienced a resurgence, sourced from various agricultural crops and wood. The oil crises of the 1970's sparked renewed interest in alternative fuels, prompting governments and researchers to explore biofuels as a means to reduce reliance on imported oil. This period saw significant advancements in biofuel research and development. Brazil played a pivotal role by championing sugarcane ethanol production as a viable gasoline alternative, establishing itself as a global leader in biofuels. Firewood was the most used fuel for cooking and heating before to the 19th century. Up to the early 20th century, wood-burning cook stoves, fireplaces, and heaters were common household appliances in the United States. Even today, over 40% (2.6 billion people), mostly in rural parts of poor countries in Asia and sub-Saharan Africa, rely on firewood for their energy requirements, burning about 1730 million m3 yearly. India, China, the United States, and Japan, respectively, used 308, 185, 40, and 0.8 million m3 of firewood in 2012 (4", 5"). Global firewood usage has increased by 3% during the previous 13 years, but its proportion to overall energy consumption has decreased (4).

In essence, the history of biofuels traces a cyclical pattern of adoption and adaptation, with biofuels evolving to meet changing energy needs, from ancient civilizations to the modern world's pursuit of sustainable and environmentally friendly energy sources.

III. TYPES OF BIOFUELS

The term "biofuel" refers to fuels made from organic materials, usually from renewable sources like plant and animal waste. Based on their physical states, they may be divided into three primary categories: solid, liquid, and gaseous biofuels (1).

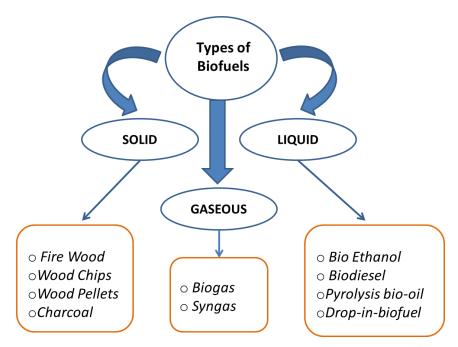


Fig. 1: Types of Biofuels: The figure represents the types of biofuels and the sources used to prepare these biofuels.

A) Solid Biofuels

1) FIREWOOD

Since the beginning of time, people have utilized wood and other plant resources for cooking and warmth. Firewood served as the main domestic fuel source prior to the discovery of fossil fuels. When plant materials, like wood, are heated to temperatures of 220–300°C or higher, they ignite, producing heat and light as a result of the stored bioenergy being released. This combustion process begins with the pyrolysis of wood, which generates solid char and gaseous fumes around 260°C. Then, the char transforms into ash, and the fumes turn into flames. In its simplest form, fire, also known as the combustion of organic matter, is the fast oxidation of bio-carbon molecules by oxygen at high temperatures and it may be summed up as follows:

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O + heat + light$$
(1)

Usually, firewood is exchanged and packed according to volume. The unit of measurement for firewood in the US is "cords," with one cord equaling 128 cubic feet (40 x 80 x 40 inches), or around 3.6 cubic metres. Depending on the type of wood and moisture level, a cord of firewood might weigh between 1350 and 2600 kilogrammes. Green, unseasoned firewood typically has 40% to 100% moisture, although it can contain up to 150% on a dry mass basis. Seasoned, air-dried firewood normally has a moisture content of 10 to 25%. Because part of the heat produced during burning is utilised to transform water into steam, "wetter" firewood has a lower energy content. Therefore, green firewood has to be dried out for at least six months in a well-ventilated space before usage in order to have the moisture level below 20%. About 15 megajoules per kilogramme, or between one-third and half that of fossil fuels, may be found in well-seasoned firewood (6).

Unfortunately, incomplete combustion frequently occurs when wood and other raw plant materials are burnt in ordinary furnaces. The substantial amount of smoke produced by this incomplete combustion includes water vapour, volatile organic compounds, carbon black particles, and creosote (smoke condensate), all of which can be hazardous to equipment, the environment, and human health (13). Burning firewood also produces trace amounts of carbon monoxide, methane, nitrogen oxides, and sulphur oxides. Low temperatures, poor mixing, and inadequate oxygen are common causes of inefficient firewood combustion (8).

The most effective way to use bioenergy is to directly burn firewood as opposed to using refined or processed biofuels. The heavy nature of firewood, however, makes it unsuitable for use in automated, small-scale heating systems (9). On the other hand, it is anticipated that future worldwide firewood consumption would continue to be largely steady. On a more localised level, as industrialisation progresses and stove efficiency increases, firewood use may decline. The creation of new technologies aimed at enhancing the combustion and energy efficiency of firewood furnaces will be the key trend.

2) WOOD CHIPS-

Cutting tree trunks and branches using a wood chipper yields wood chips, which are tiny fragments of wood with lengths ranging from 1.3 to 7.6 centimetres. Historically, they have been used for playground surface, wood pulp manufacture, and landscape mulching. However, the usage of wood chips for producing electricity (biopower) and heating (bioheat) has increased since the beginning of the twenty-first century (9).

It's important to note that, due to the limited supply and high cost of wood chippers among inhabitants, wood chips are not frequently utilised in rural parts of developing nations. Contrarily, in the US, wood chips are frequently more affordable and accessible than firewood because automated wood chippers can effectively transform all tree pieces into wood chips, making them easy to handle, store, and transport. Many American institutions have switched to mechanically fed wood chip boilers for their heating, hot water, and power requirements in an effort to minimise carbon emissions. For instance, Colgate University in Hamilton, New York, employs a wood chip boiler that uses 20,000 tonnes of locally obtained wood chips yearly to heat the campus to a level of over 75%.

Another method is known as co-firing, in which several coal-fired power stations mix wood chips with pulverised coal (usually in mixes of 15 to 30 percent) in order to produce energy using steam turbines. In co-firing, the efficiency of converting biomass to power generally falls between 33% and 37% (9). Additionally, 222 power plants

in the U.S. use wood chips as their primary fuel, producing 7.5 billion kWh of energy annually (11). 57.6 billion kWh of power were produced from wood chips in the U.S. in 2012, making up 1.42% of all electricity produced [3]. The capacity for the production of biopower on a worldwide scale was 70 GW in 2010 and is anticipated to reach 145 GW by 2020 (12).

Wood chips burn with considerably lower levels of sulphur oxides (SOx) and nitrogen oxides (NOx) than coal (14). It's crucial to keep in mind that during storage, wood chips may lose some of their dry matter weight and energy content (15). This may be avoided by storing pre-dried wood chips under cover, which has been shown to be cost-effective for recovering bioenergy (16). Torrefaction, which comprises heating wood in the absence of air at temperatures between 240 and 300°C for partial pyrolysis, is another method to reduce wood chip deterioration during storage. This process lowers the dry mass of wood chips by roughly 20% and, as a result, lowers their heating value by 10% while producing a product that is dry, hydrophobic, sterile, and stabilised. It is required to screen wood chips to eliminate smaller bits before utilising them in boilers that are automatically fed. Because wood ash has a stronger propensity to fuse than coal ash at temperatures below 750°C, boiler slagging and fouling can become an issue when wood chips are utilised in co-firing at rates greater than 30%. In order to improve the performance and energy efficiency of wood chip-based biopower and bioheat systems, research is now being done (17). Future production and consumption of biopower and bioheat produced from wood chips are anticipated to continuously rise due to existing climate change policies, renewable portfolio standards, and environmental laws (14).

3) WOOD PELLETS

A more specialised type of biofuel is represented by wood pellets. These pellets are made utilising a multi-step process that includes employing a hammer mill to ground wood pieces into sawdust, which is then compressed through tiny holes (typically 6-8 mm in diameter) in a pelletizer's die. The natural lignin in the wood particles becomes plasticized as a result of the high pressure used in this process, effectively serving as a binding agent when the pellet cools. Wood pellets typically measure 2-3 centimetres in length. If the wood feedstock is torrefied prior to the pelletization process, the energy content of wood pellets can be greatly boosted, from 9 to 18 megajoules per cubic metre (MJ m3) (18). Other materials can also be converted into pellets, including grasses, agriculture byproducts, and nutshells.

High-quality wood pellets usually have low moisture contents (between 5 and 10 percent) and a high packing density of around 650 kg/m3. They have a light brown colour, are mechanically robust with less than 0.7% mineral ash and less than 1% fine powders after each handling, and fewer than 2.5% of them break into finer particles (19). They are suited for automated feeding with perfect calibration because of their smooth, cylinder-shaped form and tiny size. Wood pellets' grain-like shape, high density, and low moisture content also enable cost-effective long-distance shipping, efficient bunker transfer, and compact storage. It's crucial to keep in mind that wood pellets are often more expensive than wood chips, which restricts their main application to domestic heating in wealthy nations. However, wood pellets are also utilised to generate biopower in nations including China, Japan, Germany, the United Kingdom, and the Netherlands.

4) CHARCOAL

Wood fuels like firewood, wood chips, and wood pellets often have lower energy contents than fossil fuels but higher combustion emissions. Furthermore, wood fires often burn at temperatures that are inadequate to melt many metals (20) are below 850°C. Ancient civilizations used pyrolysis procedures to turn wood into charcoal, a carbon-rich, porous, grayish-black solid, in order to overcome these restrictions. The wood components are heated in a kiln or retort at a temperature of around 400°C without the presence of air until no visible volatiles are released. Equation (21) may be used to depict the pyrolysis process' chemical reaction:

 $C_{6}H_{10}O_{5} - 3.75CH_{0.60}O_{0.13} \text{ (charcoal)} + 2.88H_{2}O + 0.5CO_{2} + 0.25CO + C_{1.5}H_{1.25}O_{0.38}(tar)$ (2)

A third of the initial dry wood mass is yielded as charcoal, or around 35%. High-quality charcoal has an energy level that is greater than coal, ranging from 28 to 33 megajoules per kilogramme (MJ kg1). It reaches temperatures as high as 2700°C (21) without flame or smoke. Consequently, briquettes for barbecues are usually made using wood charcoal. Small amounts of anthracite coal, mineral charcoal, starch, sodium nitrate, limestone, borax, and sawdust are frequently added to sawdust-derived charcoal to produce barbeque charcoal briquettes. These chemicals serve as binders, improve ignition, guarantee consistent burning, and speed up production (22). Since the "Bronze Age" approximately 3000 B.C., when it was used to process ores for copper and iron, charcoal has been used in metallurgy. Charcoal was chosen as the official fuel for cooking and heating in China's Tang Dynasty approximately

700 A.D. Wood gas, a combination of carbon monoxide and hydrogen produced by partially burning charcoal in a gasifier, was used to power numerous cars between 1931 and 1960 in China and during World War II in Europe when petrol was in short supply (23). Today, charcoal is still a vital substance used for heating, cooking, cleaning the air and water, creating art, and even making steel.

Worldwide output of wood charcoal increased by 5% from 2008 to 51 million tonnes in 2012. In African nations, over 31 million tonnes were produced. Brazil produced 7.6, 2.9, 1.7, 0.85, 0.85, and 0.053 million tonnes of charcoal in the same year as China, India, the United States, and Russia, respectively (4). It is anticipated that the yearly production and consumption of wood charcoal would stay reasonably consistent at 50 million tonnes worldwide based on historical trends over the last five years.

B) Liquid Biofuels

1) Bioethanol

Petroleum (crude oil) is cracked to produce petrol, a flammable liquid made up mostly of hydrocarbons in the C4–C12 range. It is currently the main fuel used to power internal combustion engines in cars. Notably, around 19 gallons of petrol may be processed from a single barrel of crude oil (equal to 42 gallons) (24). To guarantee a consistent supply of petrol, the worldwide passenger transportation industry significantly relies on crude oil. However, this excessive reliance on crude oil has had negative effects on the environment and the economy. Therefore, it is vital to research renewable alternatives to petrol that can easily fit into the current systems for supplying liquid fuel.

Biomass is now the only renewable feedstock available for making liquid fuels. One known commercial method includes the generation of ethanol, an alcohol-based fuel, by the fermentation of simple sugars produced from plant biomass, such as glucose, fructose, and other monosaccharides. For internal combustion engines in particular, ethanol is a practical replacement for petrol. In reality, ethanol was used as an engine fuel long before the 1913 start of commercial petrol manufacturing. American inventor Samuel Morey created an internal combustion engine in 1826 that could propel a boat at 7 to 8 mph using a fuel mixture of ethanol and turpentine. Another internal combustion engine that ran on a mixture of ethanol and other fuels was created in 1860 by the German engineer Nicolaus August Otto (25). These historical cases emphasise the ethanol fuel source's long-standing potential and adaptability, and there are several other examples throughout history that demonstrate its use in a variety of contexts.

Biochemical processes are used to manufacture bioethanol, which is ethanol produced from vegetative biomass through fermentation. The conversion of starch, cellulose, and sugar into glucose and fructose is one of these processes. Hemicellulose is also converted into xylose, mannose, and arabinose. These sugars are then transformed into ethanol and carbon dioxide.

 $(C_6H_{10}O_5)n$ (starch, cellulose, sugar) + nH_2O - $nC_6H_{12}O_6$ (glucose, fructose) (3)

 $(C_5H_8O_4)n$ (hemicellulose) + $nH_2O-nC_5H_{10}O_5$ (xylose, mannose, arabinose, etc.) (4)

 $C_6H_{12}O_6 - 2CH_3CH_2OH \text{ (ethanol)} + 2CO_2$ (5)

$$C_5H_{10}O_5 - 5CH_3CH_2OH \text{ (ethanol)} + 5CO_2 \tag{6}$$

Because cellulose, hemicellulose, and lignin are the basic building blocks that make up plant cell walls, theoretically any plant resources might be used as sources for producing bioethanol. But it's a difficult process to disassemble these intricate structures and depolymerize cellulose and hemicellulose into simple sugars. The development of efficient "pretreatment" techniques for extracting these simple sugars from lignocellulosic materials has thus been the subject of much research.

Milling, liquefaction, saccharification, fermentation, distillation, drying, and denaturing are a few of the common procedures in the production of bioethanol from food crops. If maize is used as the feedstock, for instance, the maize kernels are crushed into a 3–4 mm flour, combined with water to make a slurry, and then heated during the cooking process. During the liquefaction and saccharification processes, enzymes such glucoamylase and -amylase are introduced, respectively. Following yeast fermentation at a high

temperature on the resultant saccharified maize mash, ethanol is produced in the slurry. Distillation is used to separate the ethanol, molecular sieves are used to dehydrate it, and a little amount of petrol is added to denature it. Typically, 1 bushel (25.4 lb.) of maize grains may provide 2.5 to 2.9 liters of bioethanol.

Often referred to as "first-generation" biofuel, bioethanol produced from food crops competes with natural resources used to create human and animal sustenance. Researchers have been investigating the synthesis of "second-generation" bioethanol using non-food lignocellulosic plant materials to address these issues. These substances, including tree trimmings, agricultural waste, yard garbage, food processing waste, and municipal organic waste, can be used as bioethanol feedstock. Additionally, certain biomass crops may be produced on marginal land for this purpose, including switchgrass, miscanthus, giant reed, energy cane, napier grass, grain sorghum, and hybrid poplar (26). Feedstock costs, sugar preparation costs, and ethanol production costs are the three primary cost categories associated with the manufacture of lignocellulosic bioethanol. The main scientific and financial difficulty is the conversion of cellulosic components into fermentable sugars, and research has been concentrated on creating efficient ways to extract these sugars from lignocellulosic biomass. Acid hydrolysis and enzymatic hydrolysis are two potential feedstock treatment strategies (27).

Acid Hydrolysis: An acid solution, usually sulfuric acid, is used to treat finely powdered plant material in acid hydrolysis. When using a diluted acid, such as 1-10% H2SO4, high temperatures (about 237°C) and high pressures (around 13 atm) are needed. Compared to cellulose-based calculations, this procedure delivers only approximately 50% of the sugars, while being quick (less than 15 seconds) and continuous. The faster conversion of the sugars generated under these challenging conditions into compounds like furfural and others is the cause of the reduced sugar recovery.

A two-stage acid hydrolysis procedure can be used to address this problem, particularly with regard to the pentoses, which are 5-carbon sugars, degrading more quickly than hexoses, which are 6-carbon sugars. The plant biomass in this process is first subjected to gentler conditions (such as 135°C) to recover pentoses, and subsequently to harsher conditions to release hexoses (45). For every dry tonne of wood used in this process, 55 litres of ethanol are produced (27).

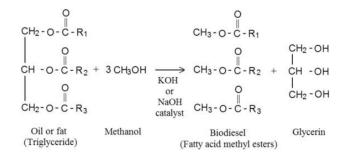
Alternately, the procedure comprises a preliminary treatment with a dilute acid at mild circumstances (for example, 100° C) for 2–6 hours to recover pentoses if a concentrated solution, such as 30–40% H2SO4, is utilised. Following a rinse, press-drain, and 2-4 hours of soaking in the concentrated acid solution at $100-150^{\circ}$ C, the solid residue is removed. The reactor's contents are filtered to eliminate lignin, and then they can be recycled to make more acid in the dilute acid hydrolysis reactor. Up to 80% of the original sugar can be recovered with this technique. It takes longer, though, and it might be difficult to distinguish the acid from the sugar solution. If acid recovery is not possible, lime must be added to neutralise the sugar solution prior to fermentation, which incurs additional expenditures and produces calcium sulphate waste. Per dry tonne of maize stover, this process may generate 60–70 gallons of ethanol (27).

Enzymatic Hydrolysis: Enzymatic hydrolysis is the process of dissolving lignocellulosic materials into simple sugars by adding active enzymes. However, cellulose found in plant materials is very resistant to enzymatic assault because it has a well-organized crystalline structure and is shielded by layers of hemicellulose and lignin. In order to first breakdown hemicellulose and solubilize lignin, pretreatment procedures including freezing, radiation, steam explosion, or auto hydrolytic hydrothermal deconstruction are required (46).

Using enzymes like glycoside hydrolases and carbohydrate esterases, pre-treated lignocellulosic substrates may be efficiently converted into fermentable sugars. The fungus Trichoderma reesei is known for its capacity to generate cellobiohydrolases (exo-1,4-glucanases) and Cx-cellulases (endo-1,4-glucanases), which effectively depolymerize cellulose. Research has concentrated on the commercial production of these cellulases. This fungus is equipped with 200 glycoside hydrolase genes that generate at least 10 distinct enzymes required for the thorough hydrolysis of lignocelluloses.

2) **BIODIESEL**

A yellowish liquid known as biodiesel is created from a variety of materials, including vegetable oil, animal fats, algal lipids, and waste grease. It is produced by a procedure known as "transesterification," which uses alcohol and an alkaline catalyst (as stated in Eq.).



(7)

In this equation, the aliphatic hydrocarbon groups R1, R2, and R3 might either be the same or different from one another.

Biodiesel is made up chemically of mono-alkyl fatty acid esters. Depending on the lipids used as a source, the particular characteristics of biodiesel can vary, but in general, it has the following characteristics: a specific gravity of 0.873 to 0.884, a kinematic viscosity of 3.8 to 4.8 mm s-2, a cetane number between 50 and 62, a cloud point of 4 to 14°C, and a flash point in the vicinity of 110 to 190°C. Its energy density, often known as its high heating value, ranges from 38 to 45 MJ kg-1, which is around 90% of petroleum-based diesel's (28) energy density.

Vegetable oils, algal lipids, animal fats (such as cattle tallow, hog lard, and chicken fat), and old vegetable oil known as yellow grease can all be utilised as feedstocks for the generation of biodiesel. Camelina, canola, castor bean, coconut, jatropha, palm, peanut, rapeseed, soybean, sunflower, and tung are typical oilseed plants utilised as sources for biodiesel. Researchers have recently looked at certain algae species as possible fuel for biodiesel. Due to their high oil content (about 40%) and substantial biomass potential (over 40 dry tonnes per hectare per year), several of these algae strains have showed promise.

Chaetoceros calcitrans, Skeletonema costatum, Phaeodactylum tricornutum, Chlamydomonas reinhardtii, Calluna vulgaris, Dunaliella salina, Dunaliella teriolecta, Scenedesmus obliquus, and Neochloris oleabundans are a few of the promising algae species mentioned above.

In the schematic (Fig. 2), the typical process for creating biodiesel is shown. Vegetable oil that is free of moisture is first heated to a temperature between 50 and 60 °C. Methanol (20% of the volume of the oil) and sodium hydroxide (5 g per litre of oil) are combined to create "methoxide," which is then added to a sealed reactor to start the transesterification process (as shown in the equation). To get rid of water and debris, yellow grease that is utilised as the feedstock must first go through preprocessing. Before beginning the base-catalyzed transesterification, this process first includes a "acid-catalyzed esterification" phase using methanol to get rid of free fatty acids.

The mixture is allowed to settle at room temperature for a duration ranging from 2 to 12 hours after transesterification takes place for around 2 hours at 50 to 60°C with mechanical stirring. During this time, a funnel draining procedure separates the top layer carrying crude biodiesel from the lower layer holding crude glycerin. Methanol, soap, and mono, di, and triglycerides may be present in trace amounts in the crude biodiesel. These contaminants must be eliminated in order to make the material appropriate for use as fuel. Purification is often accomplished using techniques like water washing and drying thereafter or by using membrane refining (29). The volume of biodiesel produced by the transesterification process often equals the volume of the initial feedstock oil, which is important to note (29).

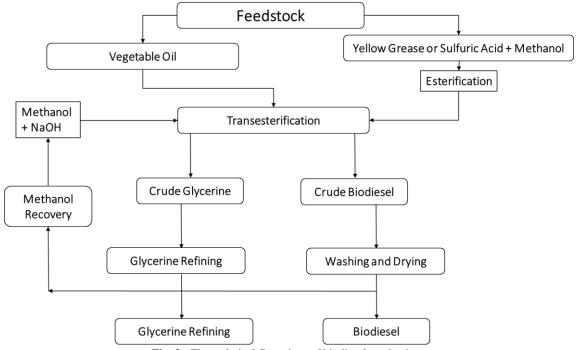


Fig. 2: The technical flow chart of biodiesel production

The cost-effective growing of algae, the energy-efficient harvesting of algal biomass, and the efficient extraction of algal oil all still present formidable obstacles. To make algae biodiesel a practical and sustainable source of biofuel, several issues must be resolved.

3) Pyrolysis bio-oil

In the process of pyrolysis, plant biomass is heated to temperatures between 300 and 900 $^{\circ}$ C without the presence of oxygen or air. It's interesting to note that this method has a long history, having been used for three to five thousand years by indigenous Amazonian groups to produce biochar and in China to produce charcoal. Three main products are produced when plant materials are pyrolyzed:

<u>Biochar</u>: The solid waste product known as biochar is distinguished by its dark colour and consistent carbon content.

<u>Bio-oil:</u> The vapour condensate that occurs during pyrolysis and has a brownish colour and contains a variety of organic chemicals is known as bio-oil.

<u>Syngas</u>: Syngas is the vapour phase of pyrolysis that does not condense into a liquid. Syngas is an acronym for synthesis gas. Carbon monoxide (CO), hydrogen (H2), carbon dioxide (CO2), and other gases are frequently present in it (Fig. 3).

There are two primary categories of pyrolysis methods that are often used:

<u>Slow pyrolysis:</u> In this process, organic wastes are heated in batch reactors between 300 and 600 °C without the presence of air. The long-lasting slow pyrolysis process often lasts for several hours or days. Based on the dry feedstock biomass utilised, slow pyrolysis typically produces 35% biochar, 30% bio-oil, and 35% syngas as typical yields (31).

<u>Fast Pyrolysis</u>: Fast pyrolysis, in contrast, runs at greater heating rates and temperatures, often between 400 and 600 °C. Compared to slow pyrolysis, this approach yields a larger percentage of bio-oil and takes less time overall to process. Fast pyrolysis can produce as much as 75% bio-oil while producing just minor amounts of charcoal and syngas.

Due to their capacity to transform biomass into useful products like biochar for soil development, bio-oil for energy or chemical uses, and syngas for different industrial and energy operations, these pyrolysis techniques have attracted a lot of interest. Furthermore, the decision between slow and rapid pyrolysis relies on particular goals and feedstock qualities, demonstrating the adaptability of this technique in the use of sustainable biomass.

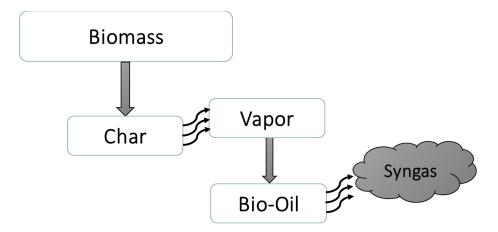


Fig. 3: Pyrolysis of plant biomass to generate char, bio-oil, and syngas.

4) Drop-in biofuels

Drop-in biofuels are liquid hydrocarbons made from biomass that adhere to the same standards as petroleum distillate fuels. They don't require major adjustments because they are made to connect easily with the existing infrastructure and fuel supply. Drop-in biofuels, which are still at the research and development stage, have the benefit of posing less infrastructural and engine compatibility problems. Butanol, liquefied biomass, sugar-based hydrocarbons, syngas complexes, and others are examples of drop-in biofuels (32). They are created as biofuels.

through several processes, such as lignocellulosic sugar fermentation, catalytic lignocellulosic sugar conversion, hydropyrolysis of biomass, hydrothermal biomass liquefaction, bioethanol transformation, and syngas upgrading. For instance, butanol may be produced utilising the solventogenic clostridia bacterium strains Clostridium

acetobutylicum EA2018 and Clostridium beijerinckii BA101, which transform biomass-derived sugars into butanolbutanol-ethanol (ABE) (33). This technology is now being commercialised and will make it simple to convert bioethanol plants to produce biobutanol. The conversion of lignocellulosic sugars into hydrocarbon fuels resembling petrol can be accomplished with the use of catalyst-assisted hydrogenolysis, dehydrogenation, hydrogenolysis, and cyclization processes (34). Algal biomass pyrolyzes at temperatures between 300 and 400 °C in the presence of hydrogen gas, mostly producing hydropyrolysis oil (around 85%), which may then be further processed to produce high-quality biofuels (35). Similar to this, an organic liquid appropriate for upgrading into drop-in biofuels may be created by hydrothermally processing a water-based slurry containing 20% oil-rich algal biomass at 300–350°C under 150–200 atm pressure (36). Using certain catalysts, such as ruthenium diphosphine (37), it is possible to efficiently convert ethanol to n-butanol. Syngas to Gasoline Plus (STG+) is a new biofuel technology that uses a series of catalysed reactions to transform biomass-derived syngas into gasoline. These reactions include CO + 2H2 -> CH3OH (methanol); 2CH3OH -> CH3OCH3 (dimethyl ether) + H2O; and nCH3OCH3 -> C6-C10 hydrocarbons (gasoline). So, a potential future path for the development of renewable fuels is represented by the production and use of drop-in biofuels. But to make these technologies more economically viable and cost-effective, much research is needed.

C) Gaseous Biofuels

1) **BIOGAS**

Natural gas, which is a gaseous fossil fuel formed from the remains of buried plants and animals subjected to extreme heat and pressure over thousands of years, is primarily composed of 95% methane (CH4), along with 5% each of ethane (C2H6), propane (C3H8), butane (C4H10), nitrogen (N2), and carbon dioxide (CO2). 38.2 megajoules per cubic metre (MJ m3) or 53.5 megajoules per kilogramme (MJ kg1) are the energy contents of natural gas. At normal pressure and temperature (1 atm) it has a density of 0.717 kilogrammes per cubic metre (kg m3). In Fredonia, New York, natural gas was first used commercially in 1821, mostly for lighting needs (38). Natural gas is used often nowadays for industrial manufacture, transportation, energy generation, cooking, and heating. The world produced 4096 billion standard cubic metres (N m3) of natural gas in 2011, with the United States being the top producer with about 20% of the total production (39). Contrarily, biogas is a sustainable gaseous fuel substitute for natural gas that is produced by the anaerobic digestion of organic waste. Raw biogas contains tiny amounts of water vapour, hydrogen (H2), and hydrogen sulphide (H2S), as well as 60–65% methane (CH4), 30–35% carbon dioxide (CO2), and other elements (40). The enhanced biogas, now known as biomethane, can be used as a replacement for natural gas after being purified to get rid of CO2, H2S, and other pollutants.

In the natural environment, microbes gradually break down organic waste products into simpler compounds, such as plant wastes. When there is a sufficient amount of oxygen present, chemical breakdown normally produces carbon dioxide (CO2) and water (H2O). However, anaerobic conditions prevail in settings with little oxygen, including landfills and manure lagoons, causing certain microbes to break down organic leftovers into methane (CH4) and carbon dioxide (CO2). Anaerobic digestion refers to this microbial breakdown of biomass materials without the presence of oxygen. Four basic biological stages are involved in anaerobic digestion:

<u>Hydrolysis</u>: Anaerobic bacteria, such as Bacteriocides, Clostridia, Bifidobacteria, Streptococci, and Enterobacteriaceae, make it easier for complex organic molecules to be broken down into more basic ones, such as sugars for carbohydrates, amino acids for proteins, and fatty acids for lipids.

<u>Acidogenesis</u>: These straightforward organic compounds are further transformed by acidogenic bacteria into carbon dioxide, hydrogen, ammonia, and organic acids.

<u>Acetogenesis</u>: Acetogenesis is the process through which acetogenic bacteria convert organic acids into acetic acid, as well as extra hydrogen, ammonia, and carbon dioxide.

<u>Methanogenesis</u>: Bacteria that produce methane and carbon dioxide from the breakdown of acetic acid. The entire response of anaerobic digestion may be summed up as follows:

 $C_6H_{12}O_6 - 3CO_2 + 3CH_4$ (8)

Anaerobic digestion is a commonly utilised technique for waste management and energy production in a variety of industries, including zoos, sewage treatment facilities, and private residences. In order to produce biogas, it involves decomposing organic resources including sewage, sludge, kitchen scraps, yard trash, and manure from livestock. The high lignin concentration of woody debris makes it unsuitable for anaerobic digestion since most anaerobic microbes can't break it down effectively (40). The procedure normally entails putting organic waste in a "anaerobic digester," which is a sealed container. Within 7 to 14 days, biogas production starts, and depending on the temperature and type of waste, anaerobic digestion typically takes 30 to 60 days to complete, after which biogas output sharply declines (41). The digester's remaining material, which consists of solids and a dark, smelly liquid, has to be taken out and replenished with new organic waste.

On a dry weight basis, one tonne of biowaste may generate 120 cubic metres of biomethane, which can be used to generate about 200 kWh of power. On a worldwide level, the use of biogas is still only somewhat restricted, but it has a lot of promise. A significant part of organic waste may be anaerobically digested to create biogas, which would be able to replace a quarter of the natural gas now consumed and provide 6% of the world's main energy needs. If agricultural byproducts like manure and crop residues are processed widely through anaerobic digestion, along with domestic waste like municipal organic solid refuse, food processing waste, and sewage sludge, this could result in the annual production of more than 1000 billion cubic metres of biomethane (43).

2) Syngas

Another gaseous biofuel created by gasifying or pyrolyzing plant components is called syngas. Chemically, syngas generally contains between 30 and 60 percent carbon monoxide (CO), 25 to 30 percent hydrogen (H2), 5 to 15 percent carbon dioxide (CO2), and 0 to 5 percent methane (CH4), along with trace quantities of water vapour, hydrogen sulphide (H2S), carbonyl sulphide (COS), ammonia (NH3), and other substances. Depending on the kind of feedstock utilised and the manufacturing circumstances, the composition may change (43).

Gasification is the recognised process for creating syngas in the commercial world. This procedure involves rapidly raising carbon-rich materials—such as coal, oil, natural gas, and dry plant biomass—to temperatures above 700 °C in a gasifier, a high-temperature combustion chamber. Syngas is produced as a result of the partial combustion of these components in the presence of regulated airflow. Typically, gasification of wood biomass occurs via three stages of thermal transformation:

<u>Dehydration</u>: Air-dried biomass rapidly loses moisture during this first phase before temperatures of 200°C are reached.

Pyrolysis: Pyrolysis: As the temperature rises, biomass is subjected to pyrolysis, which produces char and vapour.

<u>Partial Oxidation</u>: In the presence of oxygen (O2), char partly oxidises to create carbon monoxide (CO) and carbon dioxide (CO2), whereas vapour burns to produce CO2 and water (H2O). More reactions take place when various elements, such as hot char particles, CO, CO2, and H2O, climb into the combustion chamber. Char can be oxidised by either CO2 or H2O to create both CO and H2. Additionally, CO and H2O combine to form CO2 and H2. Syngas is produced from the resultant combination of CO, H2, and CO2. The following list of crucial reactions can be distilled down to:

Wood - char + vapor Char + $O_2 - CO + CO_2$ Vapor + $O_2 - CO_2 + H_2O$ Char + $CO_2 - CO$ Char + $H_2O - CO + H_2$ CO + $H_2O - CO_2 + H_2$

The average carbon conversion rate (from wood to CO, CO2, CH4), hydrogen conversion rate (from wood to H2, CH4), and energy conversion rate (from wood bioenergy to syngas energy) during the gasification of wood to create syngas are 92%, 71%, and 62%, respectively. Approximately 1.2 normal cubic metres of syngas are produced for every kilogramme of wood (or 2.3 normal cubic metres if the nitrogen level is 48%) (44) (44). As herbaceous biomass tends to have greater ash contents, notably in terms of silica and potassium, which might cause gasifier slagging problems, woody biomass with low nitrogen and ash content is often favoured for the manufacture of syngas.

IV. Advantages and disadvantages of Biofuels

The advantages and disadvantages of different types of biofuels are beautifully given in (Guo, et. al.) (1).

V. Conclusion

Since ancient times, humans have relied heavily on biofuels, which are made from organic materials like plants, algae, and microbes. Originally, these fuels were used primarily for heating and cooking. Modern biofuels, such as ethanol and biodiesel, have grown to be an essential answer to the problems caused by fossil fuels throughout time. The benefits of using biofuels are numerous and persuasive. They boost regional development, strengthen social structures and agriculture, encourage sustainability by utilising renewable resources, lower greenhouse gas emissions, and improve energy security by utilising a variety of supply sources. Biofuels provide a possible route towards a more sustainable and environmentally friendly future in the face of increasing global energy demands and environmental concerns.

Biofuels do have certain difficulties and drawbacks, though. They may compete for resources with food production, raising food costs and aggravating hunger problems. Concerns of deforestation and altered land uses are also related to the production of biofuels. Furthermore, as compared to fossil fuels, some biofuel manufacturing techniques might be energy-intensive and may not necessarily result in a considerable reduction in greenhouse gas emissions. As we make our way through the confusing world of biofuels, it becomes clear that they are an important component of the renewable energy system. The environmental, financial, and social ramifications of the production and use of biofuels must be addressed in order for these fuels to reach their full potential. We can use the potential of biofuels to move towards a more sustainable and clean energy future by carefully analysing the pros and cons and making educated decisions.

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