COMBUSTION OF BIO-FLUIDS AS AN ALTERNATIVE ENERGY SOURCE: PROSPECTS AND CHALLENGES

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Abstract: **This paper is a further contribution on alternative energy sources with emphasis on the prospects and challenges of combustion of biofluids in internal combustion engines. The paper thus reviewed the performances of the different types of biofluids in three types of internal combustion engines – the Compression Ignition (CI), Spark Ignition (SI) and the Homogeneous Charge Compression Ignition (HCCI), and noted that each type of engine exploits the physical and chemical properties of the fuel it burns. Technically, biofuels technology has grown from the initial first-generation food crop-based source to third and fourth generation biofuels that rely on algae and better extraction processes. In terms of performance, all types of biofuels demonstrated reduced emissions of CO, CO_2, unburned hydrocarbons (HC), nitrogen oxides (NOx) and solid particulates. Specifically, biodiesels, and green diesels also demonstrated improved combustion efficiencies by decreasing both the maximum cylinder pressure and the rate of pressure increase, mainly due to its higher cetane number which shortens the ignition delay period and the premixed combustion phase. Also, the lower viscosity of green diesel allows a better mixing of the liquid fuel droplets with air and reduces the ignition delay. These benefits, notwithstanding, the paper also noted some drawbacks in the combustion of biofuels as they produce complicated mixture of additional chemicals that are potentially harmful to humans and the environment, like acetaldehyde, formaldehyde, peroxyacetyl nitrate (PAN) increase relative to straight gasoline. Also, biodiesels are also more prone to atmospheric oxidation than diesel, thereby, making the biofuels acidic and forming insoluble gums and sediments that plug the fuel filters and impact of the engine performances. As part of improving the combustion efficiencies, vehicle manufacturers are working hard to decrease the exhaust emissions produced by internal combustion engines down within legal limits by using systems such as high-pressure fuel injection, multi-stage injection, three way catalytic converter, exhaust gas recycling, particle filters and injection start control through diesel engine management. While these are ongoing efforts, the paper recommends for vehicle manufacturers to also consider developing engines that will run solely on biofluids. Finally, the paper further recommended for a more collaborative global efforts towards more consistent policies to manage the entire life cycle of biofuel production to combustion, while also legislating for standards for biofuel compatible engines, for mass production if this energy transition to renewables by 2040 will be of any consequence.**

Keywords: **Biofluids, International Combustion Engines, Emissions, Pollutants, Renewables, Non-Renewables.**

1. INTRODUCTION

Combustion has been erroneously used synonymously with "burning," because of its association with fire, though both are technically different. While to burn something is to set it on fire, combustion involves the process of rapid oxidation that leads to the consumption of both the material (or fuel) and the oxidizer (usually the oxygen in air) with the release of heat and light. So, while all fires and burning involve combustion, but not all combustion technically involves fire in the form of visible, hot flames, as there are combustions with invisible flames that also release heat, and there are flames that though they emit light but evolve very little heat, and such flames are called "cool flames." (Encyclopedia.Com, 2020).

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The science of combustion was pioneered by Johannes (or Jan) Baptista van Helmont, a Flemish physician and alchemist who lived from 1580 to 1644, who experimented the relationship among a burning material, smoke and flame. This led to the classical theory of combustion called phlogiston in the 1600s, developed by the German alchemist Johann Becher and his student Georg Ernst Stahl at the end of the seventeenth century, which postulates that combustible materials contain a substance, the phlogiston, that is emitted by the material as it burns. A non-combustible material, such as ashes, will not burn, according to this theory, because all phlogiston contained in the original material, such as wood had been driven out. (Science.jrank, 2020). The phlogiston theory gave way to a more scientific definition of combustion by a French chemist Antoine Laurent Lavoisier (1743-1794), using his knowledge of some recent critical discoveries in chemistry, as the process by which some material combines with oxygen, generates heat during oxidation. This also led to the principle of thermochemistry by another French scientist, Pierre Simon Laplace (1749-1827), which stated that the amount of heat needed to decompose a compound is the same as the amount of heat liberated during its formation from its elements. (Science.jrank, 2020). Technically, combustion is a chemical process in which a substance, called fuel, reacts rapidly with oxygen, as the oxidizer to form a new substance called the exhaust and with the generation of heat. Both the fuel and the oxidizer can all exist as solid, liquid, or gas. (NASA, 2015). This presupposes that combustion process requires three key elements, which are, the fuel to be burned, a source of oxygen or oxidizer, and a source of heat, such that, if need be, the entire process of combustion can be controlled or re-engineered by changing or controlling the type and amount of fuel, the amount of oxygen available, or by changing the source of heat generation. (NASA, 2015). Combustion thus started with biomass as the first set of fuel by the burning of wood for cooking and heating, however, this soon changed with the discovery of much cheaper and relatively more abundant fossil fuel, especially during World war II. Also, the early automotive industry designed their vehicles with biofuels as the main fuel. Rudolf Diesel, the German inventor of the diesel engine, designed the diesel engine to run on peanut oil while Henry Ford later designed the Model T car which was produced from 1903 to 1926 to run on hemp derived biofuel. As fossil fuel became popular, car manufacturers, especially during World War II, initiated a blend of biofuels with fossil fuel, and subsequently redesigned the combustion technologies to accommodate the cheaper fossil fuel, especially from the gulf countries. With time, fossil fuel also began to suffer some setbacks from series of fuel crises mostly from geopolitical conflicts and other natural disasters, coupled with the impact of greenhouse gas, thus making way again for energy shift to biofuels. (Biofuel, 2010). The second coming of biofuel has triggered aggressive innovations and technologies technology to improve its combustion efficiency from first generation, which was based on food crops, to second generation, to third and fourth generation biofuels. The biofuel evolution was to solve the problems of land use, and competition with edible crops, and price hikes in the food industry that were associated with the first-generation fuel. The use of biofuels in internal combustion engines shows that performance and exhaust emission results varied depending on the type of biofuels and engines used. However, on a general note, biofuels have been reported to offset about 80% of the life cycle greenhouse gas emissions in the internal combustion engines. (Hossain et al 2017). This is as combustion of fossil fuel produces besides soot, SOx, NOx, unburned hydrocarbons (UHC), and carbon monoxide (CO), greenhouse gases that cause global warming and climatic challenges. Such greenhouse gases include Carbon dioxide (CO_2), which contributes about 52% of all global warming. (Acciona, 2019). In spite of these greenhouse gas challenges, fossil fuel continues to dominate in the energy mix even up to 2040 with nearly 80% by 2040, as shown in figure 1. Figure 2 shows various policy scenario of how to combat the greenhouse gas effect, pending the full transition to renewable energy source, with the sustainable development option as the best policy direction to drive down the impact of the green house gas effect.
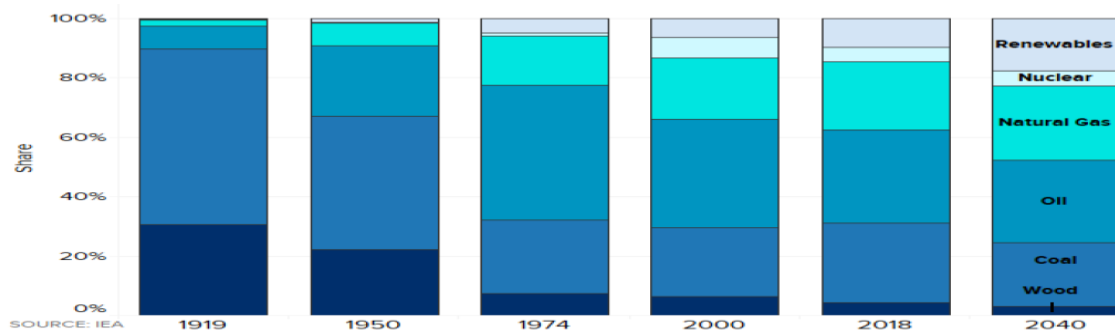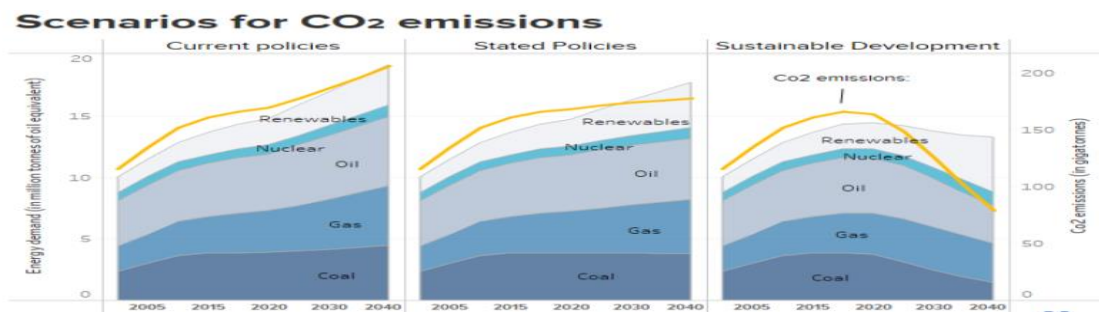

Figure 1: Global Energy Demand: Source Stevens, 2019, excerpts from IEA World Energy Outlook 2019 report

Figure 2: Policy Scenarios for Co2 emissions: Source Stevens, 2019, excerpts from IEA World Energy Outlook 2019 report

Besides the devastating effect of the greenhouse gas from fossil fuel, the energy transition is also to guarantee energy security due to the constant depletion of the non-renewable fossil fuel sources, with steadily increasing finding and production costs. (Westbrook, 2013). Changing the fuel system will also require re-engineering of the entire combustion system, since Green power represents those renewable energy resources and technologies that provide the highest environmental benefit. Figure 3 shows a representation of different power systems, with the green power as the most beneficial of all.
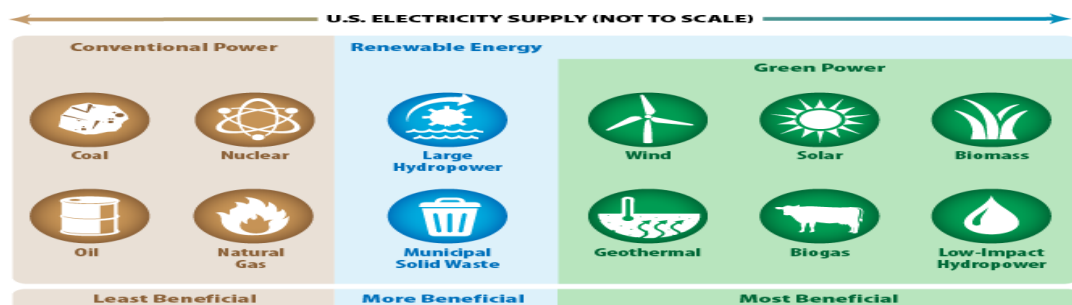
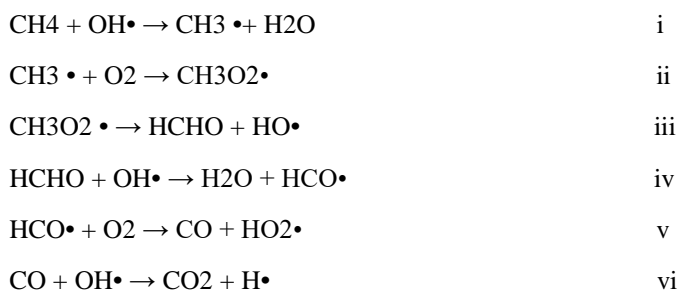**Figure 3: Pictorial representation of different power systems. Source: EPA, 2019**

The whole essence of green power system is to set the emissions standards at sufficiently low levels to keep the ambient air clean enough to protect human health and the natural environment, and technically, low emissions are achieved by a combination of fuel selection and preparation, combustion system design, and treatment of the products of combustion. All of these will require some engineering tradeoffs between low emissions, high efficiency, and low cost. (Ragland and Bryden, 2011). The United States Environmental Protection Agency in their report on Green Engineering in 2019, (EPA, 2019), recommended innovative green engineering processes, right from the design and development phases of the process and fuel system, in order to ensure pollution reduction, promotes sustainability, and minimizes risk to human health and the environment without sacrificing economic viability and efficiency. This transition seeks to remodel exiting engine systems to optimize the compression ratio, injector geometry, cylinder and piston materials, and dual fuelling techniques as solutions for adapting waste derived pyrolysis oils in the engines. Besides reengineering of the engines, biofuels are also modified for enhanced engine performance, such as in oxygenated biofuels that produces lower soot emissions than fossil-based hydrocarbon fuels, and those that produce less Carbon dioxide, (CO_2) and unburnt Hydrocarbon (HC) emissions than fossil diesel. Biofuels also maintain about the same level of ignition delay but decreases the maximum in-cylinder pressure when compared with fossil diesel. When blended with alcohols, they also reduce pollution, while alcohol (ethanol) blended with diesel have also reported low NOx and CO_2 emissions. Finally, using emulsification techniques with biodiesel has been found to reduce the high emission of Nitrogen oxides (NOx) and Particulate emissions (PM). (Hossain et al 2017).

2. DESCRIPTION

This section presents further details on combustion, and the different fuel types.

2.1 Classification of Combustion: As was pointed out earlier, altering the fuel, oxygen or heat availability can control the process and final product of any combustion, since there are many kinds of fuels: wood, natural gas, gasoline, diesel,

ethanol and biofuels, among others. Combustion is very essential to man, as about 90% of the energy used for transportation, power production and heating comes from combustion of liquid, solid and gaseous fuels. Therefore the study of combustion becomes critical to ensure conservation of the energy sources while also guaranteeing minimal pollution in a world. (Ragland and Bryden, 2011). Combustion, in a more technical language is a complex sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat or both heat and light in the form of either a glow or flames. The combustion process converts the energy stored in the chemical bonds of the fuel into heat and produces light which propagates in the cylinder of the engine in the form of a flame. Depending on the type of the fuel, the heat that produces the flame will be generated from a spark in gasoline/petrol engines or heated (compressed) air in diesel engine. Again, as a special oxidation chemical reaction, the combustion process is self-sustaining through the heat it produces, as the process continues until the entire fuel is burnt out. This is explained during the combustion of a hydrocarbon fuel, where the heat breaks the hydrocarbon bonds to release the hydrogen and carbon atoms to combine with oxygen to form to form carbon dioxide, CO_2, and water vapor, H_2O. The process continues as the energy released by the formation of these new bonds heats the remaining hydrocarbons and breaks more bonds in order to sustain the combustion process. As an exothermic reaction, the amount of heat and hence energy released is dependent on the type of fuel, and the amount of heat needed to break the bonds. (Markgraf, 2018). The process of combustion produces both heat and mass transfer and unless the fuel and oxidant are both simple molecules (e.g. hydrogen and oxygen, leading to water), the products of combustion can be, and often are, as complex and varied as the combustion processes, forming as many compounds as originally present, if not more. Even a molecule as simple as methane burning in air can lead to larger molecules and soot, and therefore the heterogeneity of real-world combustion creates a complex process that results in the formation of a wide range of compounds. (Russel, 2013). During the combustion process, Russel, 2013, added that the reaction process is controlled by such local conditions as temperature, abundance of oxygen, and time, and that oxidation will immediately take place in the presence of oxygen that will break down the fuel into smaller organic molecules until ultimately forming carbon monoxide (CO) and CO2, as shown in the combustion reaction sequence of :

CH4 + OH• → CH3 •+ H2O   i

CH3 • + O2 → CH3O2•   ii

CH3O2 • → HCHO + HO•   iii

HCHO + OH• → H2O + HCO•   iv

HCO• + O2 → CO + HO2•   v

CO + OH• → CO2 + H•   vi

where the • indicates a very reactive radical intermediate.

The different classifications are presented below:

2.1.1 Premixed versus NonPremixed Combustion: The process of premixed and non-premixed is explained with the Bunsen flame in Figure 4. A premixed flame occurs when the fuel and the air mix and travel together within the burner tube while the non-premixed flame occurs when the fuel and the oxygen, that were initially separated are transported to a common region for mixing and reactions to occur. Here, the outwardly directed fuel react almost completely with the inwardly directed oxygen. Generally, premix flames are not common in nature because they would have already reacted even if they are only slightly reactive. For proper mixing, during premixed process, one of the reactants should be in either the gaseous or the liquid phase for its molecules to "spread around" the other reactant. Nonpremixed systems, such as condensed fuels in oxidizing atmospheres, requires the mixing of the reactants as part of the flow process through diffusion, the reasons why non-premixed combustion is also known as "diffusion combustion". The reactants are transported by diffusion to effect mixing at the molecular level. Under premixed combustion, diffusion is required, but this time only to transport the premixture to, and the thermal energy and the combustion products away from the reaction region where the reactants are consumed.. (Chung, 2006).
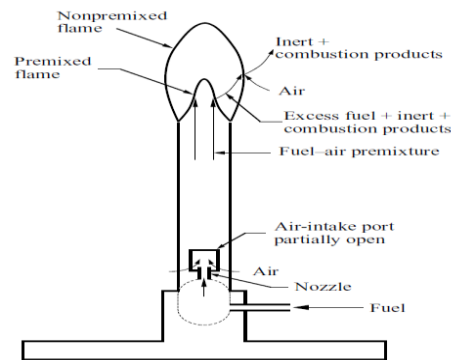
Figure 4: Schematic of the Bunsen flame. Source: Chung, 2006.

2.1.2 Laminar versus Turbulent Combustion: The flow of fuel within the combustion chamber can either be laminar or turbulent depending on the flow velocity. It is laminar when the velocity of incoming gaseous flow of fuel and air is low, while at high gas flows, both the flow and the flame may be in turbulent. Flames can also be laminar premixed, laminar diffusion, turbulent premixed or turbulent diffusion as indicated in table 1. figure 5 shows the transition from laminar to turbulent flame takes place as the flow velocity increases. In addition, they can also be categorized into stationary flames or propagating (travelling) flames, the former being the most widely used in domestic or industrial burners, the latter being involved in explosions. (Williams, 2011).

Table 1: Different ways of mixing fuel and oxidant

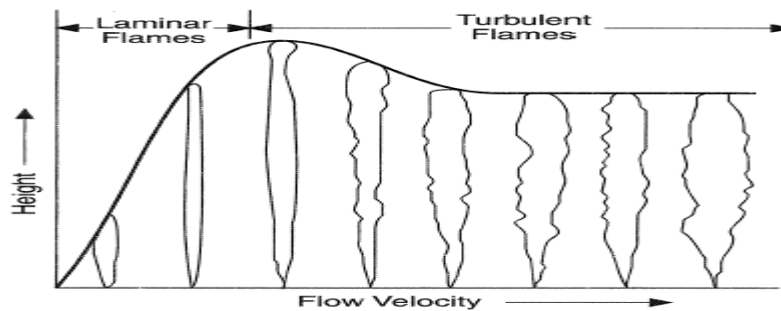| Mixing arrangement	Flow	
	Low gas velocity	High gas velocity
Premixed	Premixed laminar flame	Turbulent premixed flame
Diffusive	Laminar diffusion flame	Turbulent diffusion flame

Figure 5: Change in flame type with increase in gas velocity: Source: Williams, 2011

Combustion under laminar flow exhibits distinct streamlines for the bulk, convective motion, whereas in a turbulent flow lacks such streamlines, which allows the flow quantities to fluctuate randomly at any point in space in time. Turbulent combustion is the most used for industrial application (such as gas turbines, diesel engines, etc.) because the turbulence helps the mixing process between the fuel and oxidizer. Generally, the existence of turbulence facilitates the coarse mixing process, and therefore has a particularly strong influence on nonpremixed systems in which reactant mixing is essential. (Williams, 2011)

2.1.3 Subsonic versus Supersonic Combustion. Combustion can also be subsonic or supersonic based on the flow velocity. In a subsonic flow, the molecular collision processes of diffusion are predominant while reactions also have more time to complete. These are the flames that are encountered most frequently on day to day, such as the candle flame and the pilot flame. In supersonic combustion the high flow velocity usually renders convective transport to dominate diffusive transport. Reactions also have less time to proceed. Wave motions involving shocks and rarefactions are likely to be present. Supersonic combustion is usually associated with explosions and supersonic flights. (Chung, 2006)

2.1.4 Homogeneous versus Heterogeneous Combustion. A combustion phenomenon is called homogeneous if both reactants initially exist in the same fluid phase, either gas or liquid such as the Bunsen flame, and are heterogeneous combustion when the two reactants initially exist in different phases, whether gas–liquid, liquid–solid, or solid–gas, such as in coal particle burning in air. Homogeneous-versus-heterogeneous combustion is sometimes also used to designate the uniformity of the mixture. Thus a process is called homogeneous when there is no temperature or concentration gradient in the mixture, such as in the explosion of a uniform mixture of fuel and air, in the HCCI engine. However, if combustion occurs in a gaseous mixture containing fuel vapor pockets produced through, say, vaporization of fuel droplets, then the process is sometimes called heterogeneous. (Chung, 2006).

2.1.5 Complete Combustion. Complete combustion according to Leite, 2012, involves the combustion of fuel with oxygen without any fuel left over that will require additional time, turbulence and temperature high enough to ignite all the combustible elements. In practice, combustion is never complete, resulting in combustion by-products like carbon monoxide. Combustion efficiency defines the mole percentage of combustion emissions that are completely oxidized to CO_2:

% Combustion Eff.=100×CO2/(CO2+CO+THC+soot), where

CO_2 is carbon dioxide percent by volume

CO is of carbon monoxide percent by volume

THC is Total (unburned) hydrocarbons percent by volume

According to Speight, 2011, in complete combustion, the reactants burn in oxygen, producing a limited number of products. When a hydrocarbon burns in oxygen, the reaction will only yield carbon dioxide and water. In most industrial applications and in fires, air is the source of oxygen (O_2). Nitrogen does not take part in combustion, but at high temperatures, some nitrogen will be converted to nitrogen oxides (NO_x):

CH4+2O2+N2→CO2+2H2O+N2+CO+NOx+heat
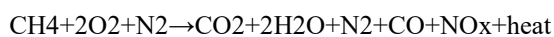
2.1.6 Incomplete Combustion: Incomplete combustion occurs when there is not enough oxygen to allow the fuel to react completely with the oxygen to produce carbon dioxide and water, and also when the combustion is quenched by a heat sink such as a solid surface or flame trap. Complete or incomplete combustion (an indicator of the combustion efficiency) is a calculation of how well the equipment is burning a specific fuel, shown in percent. Complete combustion efficiency would extract all the energy available in the fuel, however, 100% combustion efficiency is not realistically achievable, as typical combustion processes produce efficiencies from 10 to 95%. Combustion efficiency calculations assume complete fuel combustion and are based on three factors: (1) the chemistry of the fuel; (2) the net temperature of the stack gases; and (3) the percentage of oxygen or CO_2 by volume after combustion. Combustion efficiency increases with increasing temperature of the reactants, increasing time that the reactants are in contact, increasing vapor pressures, increasing surface areas, and increasing stored chemical energy. One way of increasing the temperature of the reactants and their vapor pressures is to preheat them by circulating them around the combustion chamber and throat before being injected into the combustion chamber. (Speight, 2011).

2.1.7 Low Temperature Combustion.Low-temperature combustion (LTC) is a lower temperature flameless combustion, in which a diluted fuel-air mixture is compressed until it auto ignites. Diluting the fuel mix means less fuel is needed, making this form of combustion more efficient than diesel combustion. Another benefit to LTC is the control of autoignition timing and the heat-release rate. Having a lower temperature also means the engine will not lose as much energy to its surroundings. The engine can work longer and will not knock as in spark ignition. This can reduce engine noise and damage. (Dotson, 2018).

2.2 CLASSIFICATION OF FUELS

As was earlier mentioned in this work, three key components are critical for combustion to occur, and these are the fuel, the oxidizer, and the heat generating source, which is the engine structures. From a combustion device perspective, the critical aspects of a fuel are how it is transported within the combustion device and how it is combusted. Based on this, fuel is classified primarily as gaseous, liquid, or solid. Besides these engineering classifications, fuels are also classified according to their source and their impact on the environment, which differentiates them into fossil fuels and biofuels, renewable fuels and non-renewable fuels, or carbon neutral and non-carbon neutral fuels.

This section presents the different types of fuel and their characteristics.

2.2.1 Fossil Fuel and Nonrenewables

Fossil fuels are non-renewable and deplete much faster than new reserves can be discovered. This fuel source, according to the estimates provided by the US Energy Information Administration (EIA), accounts for 86% of the total energy produced in the world, with petroleum oil as the dominant fuel with 33% share as at 2009, but has been forecasted to drop to 27% by 2035 because of economic constraints. (Gautam, 2019). Fossil fuels consist of coal, petroleum, natural gas, oil shales, bitumen, tar sands, and heavy oils, and are formed through the process of geochemical transformations of prehistoric biomass that accumulated at the bottom of water bodies under the weight of the overburden and heat over long periods. The biomass were mixed with varying amounts of inorganic materials (sediment) before burial over geological time. The process of conversion which occurred in three general stages, often termed diagenesis, catagenesis, and metagenesis, happened much faster than ambient microbes could remineralize and recycle it. Most coal were formed from the residues of terrestrial plants and trees that accumulated in marshes and swamps while most petroleum formed from algae residues that accumulated in marine or lacustrine areas. The petroleum and coal that were formed by the biogeochemical processes over geological time at moderate temperatures (<400 deg C), contain thousands of organic compounds and macromolecules derived from ancient biomass. The collective processes of petrogenesis imbue the fossil fuels with physical and chemical features that help forensic investigators differentiate fossil fuels and refined products from different geological formations. (Emsbo-Mattingly et al 2016). Petroleum fossil fuels became the primary source of fuel after World War II, while coal has been in use to power industrial technology and transportation since the 18th-century industrial revolution. However, because of its non renewable nature with continuous depletion, it is generally agreed that petroleum may likely run out within 50 years, natural gas within 65 years, and coal in about 200 years at the current rate of consumption. This plus its adverse greenhouse gas effects are they key drivers towards bioenergy alternative sources. (Balachandar and Das, 2013). Another challenge with fossil fuel is that their reserves are concentrated in a few regions of the world, which is also posing threats to secured supply of fossil fuel. (Revankar, 2019). Though fossil fuels are non-renewables with depleting reserves, Kopp,2020, showed that advances in technology such as hydraulic fracturing (fracking), rotary drilling, and directional drilling—have made it possible to extract smaller and difficult-to-obtain deposits of fossil fuels at a reasonable cost, thereby increasing the amount of recoverable material. Also, as reserves of the conventional (light-to-medium) oil became depleted, some companies shifted to extracting heavy oil, as well as liquid petroleum pulled from tar sands and oil shales. One of the main by-products of fossil fuel combustion is carbon dioxide (CO_2), as stated in earlier sections of this work, the ever-increasing use of fossil fuels in industry, transportation, and construction has added significant amounts of CO_2 to Earth's atmosphere, which is the main causes of the greenhouse gas and the associated global warming. Besides CO2, there is also Methane (CH_4), another potent greenhouse gas, a chief constituent of natural gas, with CH_4 concentrations in Earth's atmosphere rising from 722 parts per billion (ppb) before 1750 to 1,859 ppb by 2018. The current efforts at transiting to green energy is therefore to mitigate against this greenhouse gas effects on the global atmosphere. (Kopp, 2020).

2.2.2 Renewables and Green Fuels

Renewable energy is derived from sources that are regenerative in nature and can easily be replenished, and therefore include solar, geothermal, wind, biomass, and hydropower energy. (IEA, 2019). Other definitions of renewable energy as reported by Felix, 2020, are given below:

- The US Environmental Protection Agency defines renewable energy as "Energy resources that are naturally replenishing such as biomass, hydro, geothermal, solar, wind, ocean thermal, wave action, and tidal action."

- The EPA's Green Power Partnership defines the term as "renewable energy includes resources that rely on fuel sources that restore themselves over short periods of time and do not diminish."

- The Intergovernmental Panel on Climate Change defines renewables as "energy sources that are, within a short timeframe relative to the earth's natural cycles, sustainable, and include non-carbon technologies such as solar energy, hydropower, and wind, as well as carbon neutral technologies such as biomass

2.2.2.1 Biomass

Biomass according to Ragland and Bryden (2011), refers to a range of organic materials recently produced from plants and waste from animals that feed on plants, and therefore includes crop residues, forest and wood processing residues, dedicated energy crops including grasses and trees, livestock and poultry wastes, municipal solid waste (excluding

plastics and non-organic components), and food processing waste. As a cellulosic material, biomass can be broadly classified as either woody or herbaceous (non-woody), and as either residues or dedicated energy crops. Dedicated woody energy crops are grown on tree farms and harvested in two to seven years depending on the tree type and location, while Herbaceous energy crops are harvested annually such corn, sugar beets, switchgrass, and miscanthus. Biomass has an as-received moisture content that varies widely from approximately 5% for well-dried material to greater than 50% for green wood. On the other hand, dry biomass consists of cellulose, hemicellulose, lignin, resins (extractives), and ash forming minerals. Cellulose (C6H10O5) is a condensed polymer of glucose (C6H12O6), while Hemicellulose consists of various sugars other than glucose that encase the cellulose fibers and represent 20%–35% of the dry weight for wood. Lignin (C40H44O6) is a non-sugar polymer that gives strength to the fiber, accounting for 15%–30% of the dry weight. Extractives from lignin include oils, resins, gums, fats, and waxes, while inorganic constituents that make up the ash are mainly calcium, potassium, magnesium, manganese, and sodium oxides and lesser amounts of other oxides such as silica, iron, and aluminum. In terms of elemental content of wood, the major elements in wood are carbon, hydrogen, oxygen, nitrogen, and sulfur. The carbon content of wood is about 50%, slightly higher in softwoods and slightly lower in hardwoods, due to differences in lignin and extractive content. Hydrogen content is about 6% in all species. Oxygen content is 40%–44%, nitrogen content is 0.1%–0.2%, and sulfur content is less than 0.1%. The HHV of wood species varies less than 15%, with softwoods at 20–22 MJ/kg and hardwoods at 19–21 MJ/kg.

Besides wood, Ragland and Bryden (2011), also captured the elemental analysis of switchgrass as being similar to that of wood: carbon content is 46%–48%, hydrogen content is about 6%, and oxygen content is 40%–42% by weight. Ash content of switchgrass is generally in the range of 6%. Nitrogen content is a function of the fertilization schedule but is in the range of 0.6%.

2.2,2.2 BIOFUELS: Biofuels are derived from biological material, mainly from plants, microorganisms, animals and wastes, and are products of "present-day" photosynthetic conversion of solar energy to chemical energy, which sets them apart from fossil fuels that are based on ancient photosynthetic processes. (Aro, 2016). From practical consideration, any fuel that is produced from organic matter (living or once living material) in a short period of time (days, weeks, or even months) is considered a biofuel. However, based on the production technologies, biofuels are classified as first, second and third generation biofuels, while the fourth-generation biofuels make use of novel synthetic biology tools and are just emerging at the basic research level: (a).First-generation or conventional biofuels, are derived from edible feedstock such as vegetable oils extraction (soybean, sunflower), with or without esterification for biodiesel, and alcohols (most commonly ethanol and butanol) from fermentation of simple sugars from starch crops (corn, wheat) or sugar crops (sugarcane) (Costa and Piazzullo, 2018); (b).Second-generation or advanced biofuels according to Aro, 2016, are produced from feedstock of lignocellulosic, non-food materials that include straw, bagasse, forest residues and purpose grown energy crops on marginal lands. Second generation biofuels include (i) plants that are either specifically grown for bioenergy production (bioenergy crops) on marginal lands, i.e. areas not suitable for food production and on (ii) inedible parts of ordinary crops and forest trees that should be efficiently processed for bioenergy by improving the current technologies. However, Costa and Piazzullo, 2018 reported that the second generation biofuels are manufactured from different biomasses through different processing technologies as: Thermochemical conversion, as gasification, where carbon-based materials are converted into a synthesis fuel gas or syngas, this last being increasingly considered as a source for micro-cogeneration (combined heat and power, CHP) systems; Biochemical conversion through enzymatic-hydrolysis of lignocellulosic material. The sugars derived from this process are fermented into alcohol and then distilled into ethanol.(c) Third-generation biofuels are derived from algae, as these produce oil that can be easily refined into diesel or certain components of gasoline or can be genetically manipulated to produce both alcohols or even gasoline and diesel fuel directly. (Costa and Piazzullo, 2018), (d) Fourth generation biofuels- as captured by Aro, 2016, take advantage of synthetic biology of algae and cyanobacteria. They are Photobiological solar fuels and electrofuels that are expected to bring fundamental breakthroughs in the field of biofuels. Technology for production of such solar biofuels is an emerging field and based on direct conversion of solar energy into fuel using raw materials that are inexhaustible, cheap and widely available. This is expected to occur via revolutionary development of synthetic biology as an enabling technology for such a change. The biofuel conversion technology employed, as shown in table 2, along with the chemical and physical characteristics of the original feedstock, determine the structural features of the resulting properties of the biofuel, thus affecting the combustion efficiency and resulting noxious emissions when used in Internal Combustion Engines (ICEs). The high variability of these different biofuels has motivated several researches on how to improve the operation of ICEs fuelled with these renewable sources

Table 2: State of development of main biofuel production technologies.

Source: (Costa and Piazzullo, 2018).

Biofuels generally are classified chemically as Ethanol, Biodiesel, Methanol, or Biobutanol. Ethanol, when compared to petrol, has about half the energy per mass of gasoline. Though Ethanol burns cleaner than gasoline, and produces less carbon monoxide, it however, produces more ozone depleting effect than gasoline and contributes substantially to smog. Biodiesel, when compared to petrodiesel has only slightly less energy than regular diesel and is also more corrosive to engine parts than standard diesel, which means engines must be designed to take biodiesel. However, it burns cleaner than petrodiesel, producing less particulate and fewer sulfur compounds. Methanol when compared to Methane, is a liquid, while methane is a gas, and has about one third to one half as much energy as methane. Finally, Biobutanol has slightly less energy than gasoline, but can run in any car that uses gasoline without the need for modification to engine components. (Biofuel, 2010).

2.2.2.2.1 Alcohols: They are characterized by a hydroxyl group (–OH) at one of the molecule carbons atoms. The most common alcohol, bioethanol, accounts for more than 85% of the total biofuel use, mainly derived from fermentation of sugars or from chemical reactions of ethylene with steam. The steps for wide-scale ethanol production are: sugars fermentation, dehydration, distillation. Before fermentation, some crops undergo saccharification or carbohydrates hydrolysis (as starch and cellulose) into sugars. The microbial fermentation of these lead to ethanol. The two main plants components, cellulose and starch, are both composed of sugars, and can be in principle converted to sugars through fermentation. Water must be removed if ethanol is used as a fuel, generally through distillation, where the purity is limited to 94–95% due to the formation of a low-boiling water-ethanol azeotrope (a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation). (Costa and piazzullo, 2018).

2.2.3 Biodiesel and Green diesel: Diesel fuel is a petroleum distillate rich in paraffinic hydrocarbons, and is produced from fractional distillation of crude oil between 200C (392F) and 350C (662F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule as shown in figure 6. The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom. The heavy bottom fractions are often cracked into lighter, more useful products. All the fractions are processed further in other refining units. Petrodiesel falls under the specifications outlined by ASTM D975 in the United States and EN 590 in Europe.
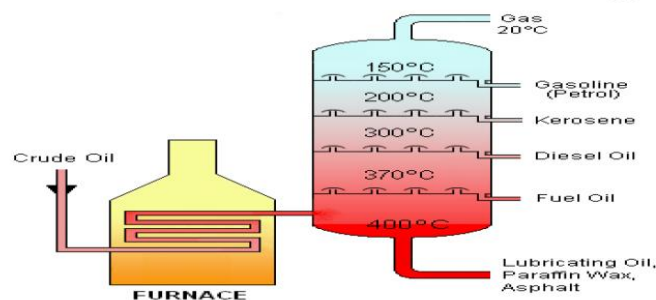
Figure 6. Schematics of Crude Oil fractional distillation. Source: Yoon, 2011

2.2.3.1 Biodiesel: Biodiesel is relatively clean burning alternative fuel, produced from domestic and renewable resources, and contains no petroleum components, but can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free from sulphur and aromatics. It can be used in compression-ignition (diesel) engines with little or no modifications. It is produced by the transesterification of triglycerides contained in biomass matter such as vegetable oils (e.g. rapeseed, soybean, cottonseed, palm, corn, sunflower, coconut, peanut, camelina, carinata and jatropha oils), animal fats, micro-algal oils and used cooking oils. Transesterification is the chemical process of the biomass lipids usually with methanol, in which triglycerides are transformed into Fatty Acid Methyl Esters (FAME or biodiesel) and glycerol in presence of a homogeneous alkaline catalyst such as KOH or NaOH, at a temperature of about 60 °C and atmospheric pressure. (Douvartzides, 2019). Biodiesel is defined under the standard of ASTM D6751 as "a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Biodiesel is chemically different from petrodiesel and renewable diesel because it contains oxygen atoms. This leads to different physical properties for biodiesel. Biodiesel can be used in its pure form, or blended with petrodiesel as an additive. Biodiesel in its pure form is designated B100 where the "100" refers to 100% biodiesel. Biodiesels blended with petrodiesel follow a similar nomenclature. For instance, a blended fuel comprised of 20% biodiesel and 80% petrodiesel is called B20. (Yoon, 2011). Biodiesel as a product of biological origin has significantly lower net CO2 accumulation in atmosphere since biomass is produced with an equal adsorption of atmospheric CO2 during the process of photosynthesis. At the same time, biodiesel is an oxygenated fuel which does not contain any sulfur and its combustion is cleaner leading to reduced emissions of CO, unburned hydrocarbons (HCs) and smoke. It also has enhanced lubricity which protects the engine components of the fuel delivery system, such as fuel pumps and injectors. (Douvartzides, 2019). On the other hand, high oxygen content means that biodiesel has some important disadvantages, such as low oxidative stability, high viscosity and poor cold weather performance (due to high cloud point and high pour point). In addition, biodiesel shows lower stability during storage and it also attacks certain metals such as copper, zinc, tin and lead, causing corrosion or swells various elastomers used for the sealing of the engines. In 2006 about two thousand fuel stations in Europe were providing "pure" biodiesel (B100), but concerns over the compatibility of B100 with the equipment of modern compression ignition engines (common rail fuel injection systems, particulate filters etc.) have limited the maximum allowable concentration of biodiesel for use in EU vehicles to 7% by volume (B7). Finally, biodiesel increases the emission of nitrogen oxides (NOx) and has a lower energy content than petroleum diesel. As a result, the utilization of B100 or biodiesel blends with high biodiesel content results in a noticeable drop of the engine thermal efficiency and brake power output. ((Douvartzides, 2019).

2.2.3.2 Renewable (Green) Diesel: Renewable Diesel, often called "green diesel" or "second generation diesel," refers to petrodiesel-like fuels derived from biological sources that are chemically not esters and thus distinct from biodiesel. Renewable diesel is chemically the same as petrodiesel, but it is made of recently living biomass, and thus green diesel or Hydrogenated Vegetable Oil (HVO) can be produced from biomass sources such as animal or fish fats. Although vegetable oils are preferred as the main lipid source for biodiesel and green diesel production, animal and fish fats have also great potential for the production of biofuels. Rich triglyceride sources are also waste cooking oils (WCO) such as waste palm oil, waste rapeseed oil and waste sunflower oil. Green diesel production seeks to enhance biodiesel production, by reducing the concentration of unsaturated fatty acid, which is susceptible to oxidative instability or may react with the alkaline catalysts to give soaps. The process thus involves the saturation of the triglycerides with H2 and results in a blend of saturated hydrocarbons regardless the initial feedstock. This eliminates the oxygen in green diesel and thus makes it more stable, noncorrosive and has a heating value similar to petroleum diesel. Green diesel also has superior cold weather behavior than biodiesel, it does not increase NOx emissions and has a higher cetane number (CN) which translates to easier ignition in CI engines. Finally, green diesel produced by the hydro-processing of triglycerides has propane as by-product which is a gaseous fuel of high market value. This fact makes green diesel production more attractive in economical terms when compared to the production of biodiesel. (Yoon, 2011). Four technologies converts biomass to green diesel: a) hydro-processing, b) catalytic upgrading of sugars, starches and alcohols, c) thermal conversion (pyrolysis) and upgrading of bio-oil and c) biomass to liquid (BTL) thermochemical processes. Hydro-processing aims to convert the triglycerides of the biomass oils and fats into saturated hydrocarbons through catalytic processing with hydrogen. The catalytic upgrading of sugars and alcohols involves liquid phase technologies such as aqueous phase reforming (APR). Thermal conversion involves the pyrolysis of biomass and the production of bio-oil which is then refined into green diesel, while BTL processes involve the high temperature gasification of the biomass for the production of syngas which is rich in H2 and CO and the subsequent chemical synthesis of liquid green diesel through the well known Fischer-Tropsch (FT) process. The green diesel produced by the Fischer-Tropsch method is sometimes referred as FT green diesel. (Yoon, 2011). Renewable diesel can be made from the same feed stocks as biodiesel since

both require the tricylglycerol containing material from biomass. Renewable diesel blends also follow the same nomenclature as biodiesel, such that renewable diesel in its pure form is designated R100 while a blend comprised of 20% renewable diesel and 80% petrodiesel is called R20. Because renewable diesel is chemically the same as petrodiesel, it can be mixed with petrodiesel in any proportion but users may need to add an additive to address lubricity issue associated with compounds with no oxygen.(Yoon, 2011).

2.2.4Third Generation Biofuel: Third generation biofuel refers to biofuel derived from algae, in order to separate it from second generation biofuels, since algae are capable of much higher yields with lower resource inputs than other feedstock.(Behera et al, 2015). One major advantage is that, algae biomass does not compete with agricultural food and feed production, as their production is just through the simple photosynthesis that require mainly light, carbon dioxide, and some nutrients (nitrogen, phosphorus, and potassium). They produce large amount of lipids and carbohydrates, which can be further processed into different biofuels and other valuable coproducts. Also, because of their low content in hemicelluloses and about zero content of lignin, there is an increased hydrolysis and/or fermentation efficiency. Besides biofuels, algae have applications in human nutrition, animal feed, pollution control, biofertilizer, and wastewater treatment. According to Behera et al, 2015, algae are generally a diverse group of prokaryotic and eukaryotic organisms ranging from unicellular genera such as Chlorella and diatoms to multicellular forms such as the giant kelp, a large brown alga that may grow up to 50 m in length. Algae can therefore be either autotrophic or heterotrophic: autotrophic algae require only inorganic compounds such as CO2, salts, and a light energy source for their growth, while the heterotrophs are non-photosynthetic, which require an external source of organic compounds as well as nutrients as energy sources. Microalgae are very small in sizes usually measured in micrometers, which normally grow in water bodies or ponds, but contain more lipids than macroalgae and have the faster growth in nature. There are about more than 50,000 microalgal species out of which only about 30,000 species have been taken for the research study. The short harvesting cycle of algae is the key advantage for its importance, which is better than other conventional crops having harvesting cycle of once or twice in a year. Asides from their short harvesting cycle, Behera et al, 2015 reported other advantages for biofuels production: (a) ability to grow throughout the year, therefore, algal oil productivity is higher in comparison to the conventional oil seed crops; (b) higher tolerance to high carbon dioxide content; (c) the consumption rate of water is very less in algae cultivation; (d) no requirement of herbicides or pesticides in algal cultivation; (e) the growth potential of algal species is very high in comparison to others; (f) different sources of wastewater containing nutrients like nitrogen and phosphorus can be utilized for algal cultivation apart from providing any additional nutrient; and (g) the ability to grow under harsh conditions like saline, brackish water, coastal seawater, which does not affect any conventional agriculture. Inspite of these numerous advantages, there are few disadvantages of algal biomass as feedstock such as the higher cultivation cost as compared to conventional crops. Similarly, harvesting of algae require high energy input, which is approximately about 20–30% of the total cost of production. Several techniques such as centrifugation, flocculation, floatation, sedimentation, and filtration are usually used for harvesting and concentrating the algal biomass. The algae can be converted into various types of renewable biofuels including bioethanol, biodiesel, biogas, photobiologically produced biohydrogen, and further processing for bio-oil and syngas production through liquefaction and gasification, respectively. These technologies are categorized into three different path ways, i.e., biochemical, chemical, and thermochemical conversion and make an algal biorefinery, which has been depicted in Figure 7. The biofuel products derived from algal biomass using these conversion routes have been explored in detail in the subsequent sections.
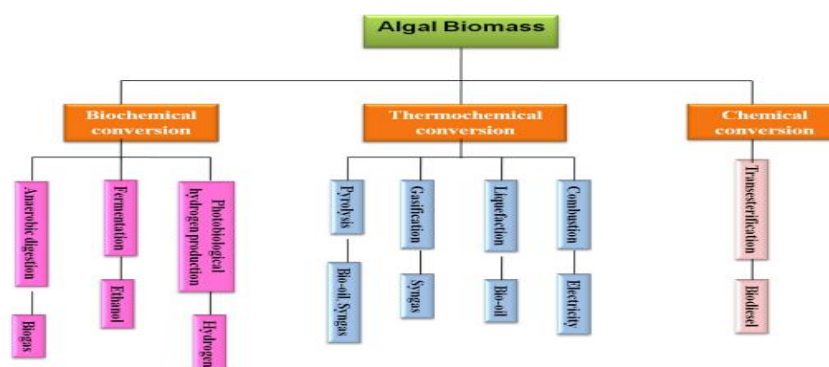

Figure 7. Algal biomass conversion process for biofuel production. Source: Behera et al, 2015.

2.2.5 Fourth Generation Biofuels: Fourth generation biofuels take advantage of synthetic biology of algae and cyanobacteria. They are Photobiological solar fuels and electrofuels that are expected to bring fundamental breakthroughs in the field of biofuels. Technology for production of such solar biofuels is an emerging field and based on direct conversion of solar energy into fuel using raw materials that are inexhaustible, cheap and widely available. This is expected to occur via revolutionary development of synthetic biology as an enabling technology for such a change. These generation of biofuels according to Aro, 2016, are produced (i) by designer photosynthetic microorganisms to produce photobiological solar fuels, (ii) by combining photovoltaics and microbial fuel production (electrobiofuels) or (iii) by synthetic cell factories or synthetic organelles specifically tailored for production of desired high-value chemicals (production currently based on fossil fuels) and biofuels. Fourth Generation Biofuel can also be produced through engineered carbon capture and storage technology as reported by ISAAA (International Service for the Acquisition of Agri-biotech Applications), 2007. According to ISAAA, fourth generation biofuels, are simply a step further from the third generation biofuels. The feedstock is tailored not only to improve the processing efficiency, but also designed to capture more carbon dioxide, as the crop grows in cultivation. The processing methods (mainly thermochemical) are also coupled to "carbon capture and storage" technologies which funnels off the carbon dioxide generated into geological formations (geological storage, for example, in exhausted oil fields) or through mineral storage (as carbonates). Zhang, 2015 showed a schematic representation of the carbon capture and storage process in figure 8. Here, the specially engineered plants or biomass with higher energy yields or lower barriers to cellulosic breakdown are grown on non-agricultural land or bodies of water. The engineered plants become efficient 'carbon capturing' machines that take CO_2 out of the atmosphere and store it in their branches, trunks and leaves. Then, the carbon-rich biomass is converted into fuel and gases by means of second-generation techniques. Crucially, before, during or after the bioconversion process, the carbon dioxide is captured by utilizing so-called pre-combustion, oxyfuel or post-combustion processes. The greenhouse gas is then geosequestered - stored in depleted oil and gas fields, in unmineable coal seams or in saline aquifers, where it stays locked up for hundreds, possibly thousands of years.
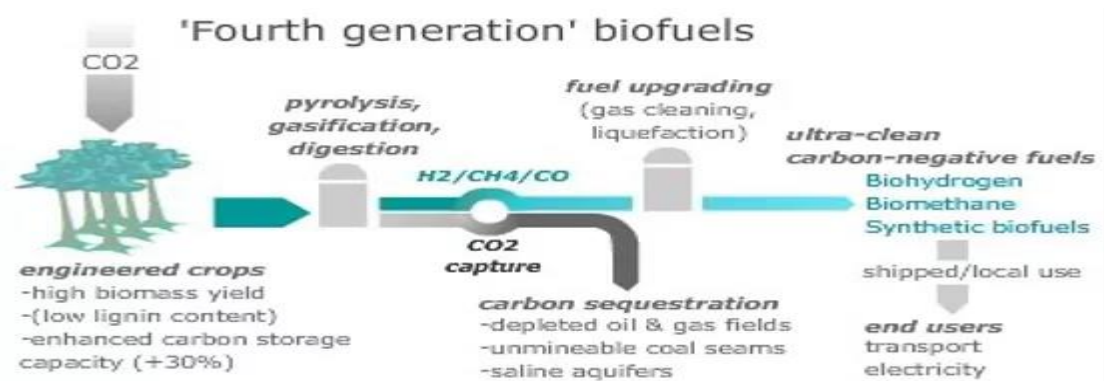
Figure 8: Schematics on Production of Fourth Generation Biofuels. Source: Zhang, 2015.

The resulting fuels and gases are not only renewable, they are also effectively carbon-negative. Only the utilization of biomass allows for the conception of carbon-negative energy; all other renewables (wind, solar, etc) are all carbon-neutral at best, carbon-positive in practice. Fourth generation biofuels instead take historic CO_2 emissions out of the atmosphere. The system not only captures and stores carbon dioxide from the atmosphere, it also reduces carbon dioxide emission by replacing fossil fuels.'

2.2.6 Syngas: Syngas is the short name for a gasification product, mostly from waste biomasses, known as "synthesis gas," consisting of a mixture of H_2, CO, and CO_2 that could be used as a potential intermediate in the conversion of biomass into fuel. (Capodaglio and Bolognesi, 2019). Syngas production is a two-step process. In the first step, the pyrolysis of sewage sludge at around 600°C in an oxygen-deficient atmosphere takes place, which leads to the production of carbon-rich char. In the second step, the char is gasified in the presence of oxygen or air and produces syngas. (Tyagi, 2016). The primary use of syngas is in the production of other fuels, namely methanol and diesel fuel. In some industrial settings (steel milling, petroleum refining, etc.), large amounts of waste gas with these characteristics are produced. The production of diesel fuel from syngas relies on the Fischer-Tropsch process, a series of chemical reactions converting CO and H_2 into liquid hydrocarbon. Methane from landfills could serve as feedstock for producing diesel fuel, technically considered biodiesel because it is not derived from fossil fuels. A novel use of syngas is to directly power

hydrogen fuel cells; hydrogen is simply captured from the gas, and refined for use in fuel cells. (Costa and piazzullo, 2018). There are, however, several challenges such as low yield of syngas fermenting microorganisms, mass transfer limitation of syngas, substrate and product inhibition, and cost of products separation and recovery among others. (Yasin and Khanal, 2019).

3. GENERAL ANALYSIS

Since combustion is an exothermic chemical reaction in the presence of an oxidizer, the nature of the combustion greatly depends on whether the fuel is gaseous, liquid, or solid. Gaseous fuels such as natural gas is easy to feed and mix, and are relatively clean burning. Liquid fuels are typically broken into small droplets by being sprayed through a nozzle at high pressures. When heated, liquid fuels vaporize and then burn as a gaseous diffusion flame. Many solid fuels are pulverized or ground before being fed into a burner or combustion chamber. Larger-sized solid fuels combust in a fuel bed with air flowing through the bed. When heated, solid fuels (such as wood, switchgrass, or coal) release gaseous volatiles with the remainder being solid *char*. The char is mostly porous carbon and ash, and burns out as a surface reaction, while the volatiles burn as a diffusion flame. Vaporization of liquid fuel sprays and devolatilization of solid fuels occur much more slowly than gas phase chemical reactions and hence become important aspects of the combustion process. Char burnout, in turn, occurs more slowly than devolatilization.(Ragland and Bryden, 2011).   This section therefore presents the properties of the different types of fuel, the stoichiometry and thermodynamics of combustion

3.1 Nature and Properties of Fuel

3.1.1Gaseous Fuel: Gaseous fuels are fuels that are transported within a combustion device and used in gaseous form. The primary gaseous fuels are natural gas and liquefied petroleum gas (LPG). Thermal gasification of solid fuels such as coal and biomass is used to create a gaseous fuel, called syngas. Hydrogen is a gaseous fuel of increasing interest because it can be combusted without releasing greenhouses gases. Natural gas is part of fossil fuel that is found in reservoir rocks and frequently exists near or above oil deposits. It is a mixture of hydrocarbons and small quantities of various non-hydrocarbons existing in the gaseous phase or in solution with crude oil. Raw natural gas contains methane and lesser amounts of ethane, propane, butane, and pentane. Sulfur and organic nitrogen are typically negligible in natural gas. Carbon dioxide, nitrogen, and helium are sometimes present; however, the amounts of these non-combustible gases are generally low. Prior to distribution and use, natural gas is processed to remove the non-combustible gases and higher molecular weight hydrocarbons. Dry pressurized natural gas is transmitted long distances in pipelines. At some wells natural gas is liquefied (LNG) by cooling it to −164°C, and it is then transported to selected ports around the world in supertankers. The LNG is then transferred to tanks and subjected to heat and pressure to return it to a gaseous state for transport by pipeline. Syngas (synthetic gas) was presented in section 2.4.6 of this work, and just as a recap, syngas is produced through gasification process passing a less than stoichiometric amount of air or oxygen through a hot bed of coal or biomass particles. Using sub stoichiometric oxygen can produce syngas with a higher heat content, but the process is more expensive than using air.

3.1.1.1 Characteristics of Gaseous Fuel

Important characteristics of gaseous fuels that measures the efficiency of combustion include volumetric analysis, density, heating value, and autoignition temperature.

(a) The heating value is the heat released per unit mass when the fuel, initially at 25°C, reacts completely with oxygen, and the products are returned to 25°C. The heating value is reported as the higher heating value (HHV) when the water in the combustion products is condensed or as the lower heating value (LHV) when the water in the combustion products is not condensed. The LHV is obtained from the HHV by subtracting the heat of vaporization of water in the products

$$\mathbf{LHV} = \mathbf{HHV} - \left(\frac{m_{\mathrm{H_2O}}}{m_{\mathrm{f}}} \right) h_{fg} \qquad \text{Equation 1}$$

where mH2O is the mass of water in the products, mf is the mass of fuel, and hfg is the latent heat of vaporization of water at 25°C, which is 2440 kJ/kg water. The mass of water includes the moisture in the fuel as well as water formed from hydrogen in the fuel. The heating value of a gaseous fuel may be obtained experimentally in a flow calorimeter and can also be calculated from thermodynamics if the composition is known.

(b) Autoignition temperature is the lowest temperature at which ignition occurs spontaneously in a standard container with atmospheric air in the absence of a spark or flame and without regard to the ignition delay time. The autoignition temperature of alkanes (hydrocarbons of the form CnH2n+2) decreases with increasing molecular weight. Carbon monoxide has a high autoignition temperature, and hydrogen has a low autoignition temperature. In general, autoignition temperature is an indication of the relative difficulty of combusting a fuel. Autoignition temperature varies with the geometry of the hot surface and other factors such as pressure

3.1.2 LIQUID FUELS

Liquid fuels are fuels that are transported within the combustion device as a liquid, and because liquid fuels cannot be used directly, they are generally vaporized and then combusted. The vaporization process may occur as a part of the combustion process, such as in a diesel engine, or it may occur upstream in a vaporizer, such as in a liquid fuel cookstove. Because of this need to vaporize and then combust the fuel, clean combustion of liquid fuels is more complicated and challenging than clean combustion of gaseous fuels. Currently, most of liquid fuels are derived primarily from crude oil, with increasing contributions from biomass, oil shale, tar sands, and coal. Crude oil is made up of roughly 84% carbon, up to 3% sulfur, and up to 0.5% nitrogen, and 0.5% oxygen with the remainder being primarily hydrogen. Crude oil is sometimes burned directly; however, because of its wide range of densities, viscosities, and impurities, crude oil is generally refined. The refining processes of fractional distillation, cracking, reforming, and impurity removal are used to produce many products including gasoline, diesel fuels, gas turbine fuels, and fuel oils.
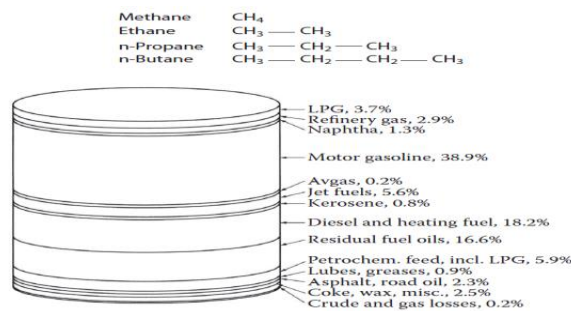

Figure 9: Typical crude oil refinery products. Source: Ragland and Bryden, 2011

3.1.2.1 Characterization of Liquid Fuels

Important properties of liquid fuels that determines combustion efficiency include heating value, specific gravity, viscosity, flash point, distillation curve, sulfur content, vanadium and lead content, octane, number (for gasoline), cetane number (for diesel fuel), and smoke point (for gas turbine fuel). Some of the typical properties of fuel for internal combustion engines and gas turbines, and for fuel oils, are given in table 3.

(a). Volatility is measured by Reid vapor pressure, which is the equilibrium pressure exerted by vapor over liquid at 37.8°C. Generally, liquid fuels are semi-volatile organics, that can be kept and transported in liquid state without pressurized containers but will volatilize upon moderate heating. The boiling ranges of common fossil fuels, HVO/HEFA, and synthetic XTL fuels typically are on the order of 30 to 215 °C (gasoline) and 160 to 370 °C (diesel). Constituents occupying the lower end of the boiling range are critical regarding volatilization losses (gasoline), cold-start behaviour and ignitability (gasoline, diesel), while the highest boiling components influence the efficacy of fuel atomization to achieve proper combustion of cylinder charge. Reid vapor pressure (RVP) for spark-ignition fuels is determined by low-boiling fuel components and has to be adjusted seasonally (front-end volatility), as determined in respective fuel specifications for climate-dependent parameters. (Grope et al 2018).

(b). **Flash point** is an indication of the maximum temperature at which a liquid fuel can be stored and handled without serious fire hazard. Flash point is the minimum temperature at which fuel will rapidly catch fire when exposed to an open flame located above a mixture. An example of a flash point of interest is the ignitability of the mixture above the liquid fuel in a partially full fuel tank. Gasoline, which has a flash point of −43°C, is typically so volatile that the mixture above the liquid fuel is too rich to burn. No. 2 diesel fuel (flash point of 60°C–80°C) is so non-volatile that the mixture above the liquid fuel is too lean to burn. (Ragland and Bryden, 2011).

Table 3: Typical Properties of Automative Fuels

Typical Properties of Automotive Fuels

Property	Automotive Gasoline	No. 2 Diesel Fuel	Ethanol	B100 Biodiesel
Chemical formula	C_4 to C_{12}	C_8 to C_{25}	C_2H_5OH	C_{12} to C_{22}
Molecular weight	100–105	~200	32	~292
Specific gravity at 16°C	0.72–0.78	0.85	0.794	0.88
Kinematic viscosity at 20°C (m²/s)	0.8×10^{-6}	2.5×10^{-6}	1.4×10^{-6}	—
Boiling point range (°C)	30–225	210–235	78	182–338
Reid vapor pressure (kPa)	48–69	<2	148	<0.3
Flash point (°C)	—43	60–80	13	100–170
Autoignition temp (°C)	257	~315	423	—
Octane No. (Research)	88–98	—	109	—
Octane No. (Motor)	80–88	—	90	—
Cetane No.	<15	40–55	—	48–65
Stoichiometric air-fuel ratio by weight	14.7	14.7	9.0	13.8
Carbon content (wt %)	85–88	87	52.2	77
Hydrogen content (wt %)	12–15	13	13.1	12
Oxygen content (wt %)	2.7–3.5	0	34.7	11
Heat of vaporization (kJ/kg)	380	375	920	—
LHV (MJ/kg)	43.5	45	28	42

Source: Ragland and Bryden, 2011.

(c) The Autoignition temperature is the lowest temperature required to initiate selfsustained

combustion in a standard container in atmospheric air in the absence of a spark or flame. For example, the autoignition temperature of gasoline is 257°C. In general, autoignition temperatures are an indication of the relative difficulty of combusting a fuel. Because the autoignition temperature varies with the geometry of the hot surface and various factors such as pressure, other tests—octane number and cetane number for instance are used for engine fuels. (Ragland and Bryden, 2011).

(d) The Octane number (ON) indicates the tendency of gasoline to knock (onset of autoignition) when the compression ratio in a spark ignition engine is raised. The octane number of a fuel is measured by comparing the performance of the fuel with the performance of mixtures of isooctane and n-heptane in a standardized spark ignition engine. Isooctane is arbitrarily set at 100, and n-heptane, which is more prone to knock, is arbitrarily set at zero. The octane number is the percentage of isooctane in the isooctane-heptane mixture that most closely matches the performance of the test fuel. (Ragland and Bryden, 2011).

(e) The **Cetane number (CN)** ranks fuels according to their ignition delay when undergoing

compression ignition. Because cetane (n-hexadecane) is one of the fastest igniting hydrocarbons in fuel, it is assigned a cetane number of 100. Isocetane (heptamethylnonane) ignites slowly and is arbitrarily assigned a cetane number of 15. A diesel fuel is compared to mixtures of the reference fuels in a standardized diesel engine and rated by the mixture that most closely matches the ignition delay of the test fuel. Ignition delay in an engine is the time between the start of injection and the onset of combustion. The cetane number of the reference mixture is defined by

$$CN = \% \text{ n-cetane} + 0.15 \left(\% \text{ heptane} \right) \qquad \text{Equation 2}$$

(f) Density and Viscosity, are closely related to proper action of fuel system components

like pumps, valves and filters. Exceeding specified parameter limits would negatively affect fuel injection timing and amount. Large differences in density and/or viscosity among fuels would be unfavorable in everyday practice after refilling events, since inhomogeneities from incomplete mixing introduce uncontrolled variability in the quality of fuel being delivered to injectors. Local inhomogeneity also increases risks for phase separations in the case of falling temperatures or increasing water content.

(g) Fuel lubricity relates directly to durability of mechanical parts of fuel pumps.

Additionally, enhanced wear and abrasion due to insufficient lubricity will subsequently contribute to fuel deterioration, which especially affects fuel circulating in common rail systems

(h) Fuel stability and chemical fuel reactions - among organic combustible chemicals,

engine fuels show comparatively moderate to low reactivity at normal ambient conditions. Nevertheless, since fuel components come with structural moieties that are susceptible to chemical modification and degradative attack, fuel

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quality deterioration and reduced shelf life may occur. Accelerating factors are elevated temperature, irradiation, oxygen or oxidizing agents, radicalic species and catalytically active trace metals. Changes in chemical nature of fuels become evident in several ways, such as changes in color, formation of opaque, amorphous or crystalline deposits, and measurable modifications of physical or chemical parameters that not necessarily are perceivable macroscopically. Resulting negative impacts from such processes may be poor operation or malfunction of pumps, filters, injectors, valves, pistons and exhaust equipment, but also impairing of engine combustion, emission levels and engine oil quality. Fuel types most often associated with deterioration and deposit formation are biodiesel and diesel-biodiesel blends, provoked by unsaturated esters as specific structural elements. Microorganisms especially reside and grow at fuel-water interfaces, build up biofilms, produce and excrete reactive metabolic products which promotes further degradation and corrosion. The resulting biofilm microcosm is a viscous sludge that plugs filters, injectors etc. and finally causes instrumental failure. A broad spectrum of aerobic and anaerobic microorganisms is involved. Therefore, it is common practice to spike biodiesels (and fossil fuels, too) with specific amounts of synthetic stabilizers which act as radical scavengers (primary stabilizers), like 2,6-di-tert-butyl-4-hydroxytoluene (BHT). Secondary stabilizers like tris-nonylphenyl phosphite act as peroxide decomposers; application of both stabilizer types may prove beneficial in terms of fuel stability. (Grope et al 20018).

3.1.3 SOLID FUELS: Solid fuels include wood and other forms of biomass, peat, lignite, coal, and refuse- derived fuels. Solid fuels are more challenging to transport, handle, and combust than gaseous or liquid fuels. Solid fuels come in a variety of sizes and shapes and for most uses they need to be processed to reduce their size and moisture content. In addition to carbon and hydrogen constituents, solid fuels contain significant amounts of oxygen, water, and mineral matter, as well as nitrogen and sulfur. Table 4 shows some relevant properties of solid fuels. The oxygen is chemically bound in the fuel and varies by weight from 45% for wood to 2% for anthracite coal on a dry, ash-free basis. Moisture content is a significant issue in biomass and low-ranked coals. Within the solid fuel matrix, water exists as water vapor, liquid water chemically bound to the fuel (adsorbed or bound water), and free liquid water within the pores of the solid fuel. Bound water is held by physical adsorption and exhibits a small heat of sorption. This heat of sorption is a function of moisture content and is in addition to the heat of vaporization. Green wood typically consists of 50% water on an as-received basis. After being air-dried for 1 year, the moisture content of wood typically falls to 15%–20% on an as-received basis. Lignite coals contain 20%–40% moisture on an as-received basis, most of which is free water, whereas bituminous coals contain about 5% moisture on an as-received basis that is bound water. Fuel moisture significantly influences the rate of combustion and the overall efficiency of the combustion system. (Ragland and Bryden, 2011)

Table 4. Relevant properties of solid fuels.

Typical Percent Oxygen, Water, and Ash (wt) in Solid Fuels

Fuel	Oxygen (Dry, Ash-free)	Moisture (Ash-free)	Ash (Dry)
Wood	45%	15%–50%	0.1%–1.0%
Peat	35%	90%	1%–10%
Lignite coal	25%	30%	>5%
Bituminous coal	5%	5%	>5%
Anthracite coal	2%	4%	>5%
Refuse-derived fuel	40%	24%	10%–15%

**Source: (Ragland and Bryden, 2011)**

The inorganic residue remaining after the fuel is completely burned is called ash. Depending on how it was handled and transported, wood usually has less than 1% ash, while coal has 3%–10% or more of ash. Typically, the ash begins to soften at 1200°C and becomes fluid at 1300°C, although this varies significantly between fuels and even between coals of the same rank or biofuels from similar crops. Ash characteristics play an important role in system design in order to minimize slagging, fouling, erosion, and corrosion

**3.2 Stoichiometry and Thermodynamics of Combustion**

Combustion as earlier defined is an energy-evolving (exothermic) chemical transformation, whose final product and how much energy can be extracted from a fuel/air mixture under a specified process, are restricted by the laws of thermodynamics. (Janbozorgi et al 2010). The laws of thermodynamics deal with conservation of mass, species, and energy, and the equilibrium states and chemical composition of the reactants and products. Technically, the reactant atoms

under any chemical reactions are rearranged to form new combinations, under the laws of conservation of mass. This means that the mass of the reactants equals the mass of the products, although the moles of the reactants are not the same as the moles of the products. This is also applicable to reactions of ideal gases that changes in volumes at constant temperature and pressure. Consequently, in a typical combustion process, the fuel reacts with Stoichimetric air rather than oxygen, since air is composed of 21% O2, 79% N2, and small amounts of argon, carbon dioxide and hydrogen. Stoichiometric air is the amount of air required to burn a fuel completely to products with no dissociation. Stoichiometric calculations are done by performing an atom balance for each of the elements in the mixture. For example, consider the combustion of methane (CH4) with air. This can be written as

$$1(CH_4) + a(O_2 + 3.76 N_2) \rightarrow b(CO_2) + c(H_2O) + 3.76a(N_2)$$
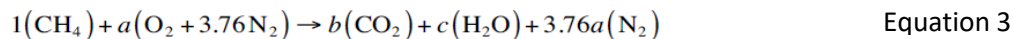
Equation 3

Which upon making relevant element balances for the various components, the stoichiometric equation for the combustion of CH4 is

Equation 4

$$CH_4 + 2(O_2 + 3.76 N_2) \rightarrow CO_2 + 2 H_2O + 7.52 N_2$$
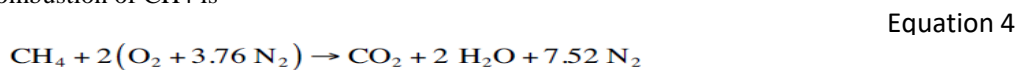
In this calculation, dry air as a mixture is approximated as consisting of 79% (vol) N2 and 21% (vol) O2 or 3.764 moles of N2 per mole O2. Using $M_{O_2} = 32.00$ and $M_{N_2} = 28.01$ yields $M_{air} = 28.85$; however, the molecular weight of pure air is 28.96 because of the small amounts of other gases. The most straightforward way to correct for this difference is to use an apparent molecular weight of N2 of 28.16 as shown by Ragland and Bryden, 2011:

$$M_{air} = \sum_i x_i M_i = x_{N_2} M_{N_2} + x_{O_2} M_{O_2}$$

Equation 5

rearranging and simplifying,

$$M_{N_2} = \frac{(M_{air} - x_{O_2} M_{O_2})}{x_{N_2}} = \frac{(28.96 - 0.21 \times 32)}{0.79} = 28.16$$

Equation 6

As exothermic reactions, the absorption or evolution of energy, which usually manifests itself as heat, temperature and the product composition during combustion, can be estimated through thermodynamics processes. (Yetter, 2008). This is where we now deal with the concepts of heat of reaction at constant pressure and constant volume, heat of formation, and enthalpy of combustion. Heat of reaction is the chemical energy released when a fuel reacts with air to form products. (Ragland and Bryden, 2011).   The heat of reaction, Q_p thus depend on the temperature T at which the reaction and product enthalpies are evaluated. The heat of reaction at one temperature T_0 can thus be related to that at another temperature T_1. Consider the reaction configuration shown in Figure 10. According to the First Law of Thermodynamics, the heat changes that proceed from reactants at temperature T_0 to products at temperature T_1, by either path A or path B must be the same. Path A raises the reactants from temperature T_0 to T_1, and reacts at T_1. Path B reacts at T_0 and raises the products from T_0 to T_1 . This energy equality, which relates the heats of reaction at the two different temperatures, is written as

$$\left\{ \sum_{j,\text{react}} n_j \left[\left(H_{T_1}^\circ - H_0^\circ \right) - \left(H_{T_0}^\circ - H_0^\circ \right) \right]_j \right\} + \Delta H_{T_1}$$
$$= \Delta H_{T_0} + \left\{ \sum_{i,\text{prod}} n_i \left[\left(H_{T_1}^\circ - H_0^\circ \right) - \left(H_{T_0}^\circ - H_0^\circ \right) \right]_i \right\}$$

Equation 7

where n specifies the number of moles of the i th product or j th reactant. Any phase changes can be included in the heat content terms. Thus, by knowing the difference in energy content at the different temperatures for the products and
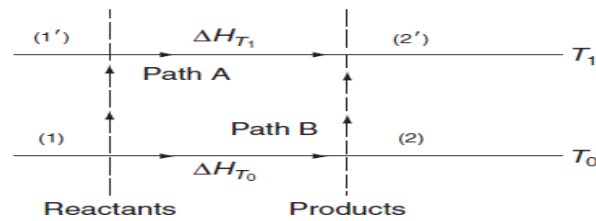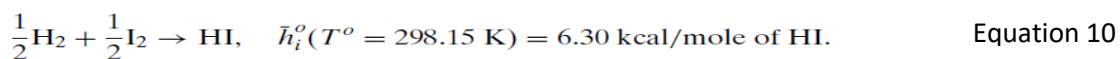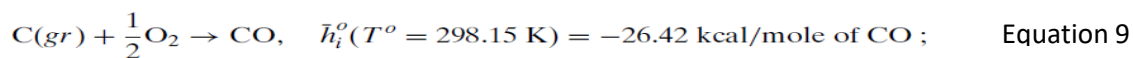
Figure 10. Heats of reactions at different base temperatures.

Source: Yetter, 2008.

Thus for each species a heat of formation at constant volume (e^-oi) and a heat of formation at constant pressure (^-hoi) can be defined as the amount of heat needed to form one mole of the substance from its elements in their standard states, with the reaction taking place in a closed system, either at constant volume or constant pressure, and with the initial and final temperatures, To, being the same. The chemical reaction representing such a process is the forward reaction of as shown by Chung, 2006:

$$\sum_{j=1}^{L} v'_{i,j} M^o_{i,j} \rightarrow M_i .$$

Equation 8

By definition, the heat of formation is zero for elements in their standard states. For a given substance, ^-hoi is positive if heat is absorbed by the system, and negative if heat is released. As examples, we have

$$C(gr) + \frac{1}{2}O_2 \rightarrow CO, \quad \bar{h}^o_i(T^o = 298.15 \text{ K}) = -26.42 \text{ kcal/mole of CO} ;$$

Equation 9

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightarrow HI, \quad \bar{h}^o_i(T^o = 298.15 \text{ K}) = 6.30 \text{ kcal/mole of HI}.$$

Equation 10

The negative and positive signs indicate that the formation reactions of CO and HI are exothermic and endothermic respectively. We also note that the reaction

CO + 12O2 → CO2 evolves−67.63 kcal/mole of CO2. This is not the heat of formation of CO2 because CO is not an element.

The relation between e^-oi (To) and ^-hoi (To) is the following.

Equation 11

Since $E = H - pV = H - NRoT$,

for reaction, we have

Equation 12

$$\bar{e}^o_i = \bar{h}^o_i - R^o T^o \left(1 - \sum_j v'_{i,j}\right),$$

where the summation is performed over all gaseous elements. For example, for the

formation of CO2(g) from C(gr) + O2(g) → CO2(g), (1 −j v_i, j) is zero while for

the CO(g) formation it is 12 according to C(gr) + 12 O2(g)→ CO(g).

Enthalpy of reaction or enthalpy of combustion is defined as the net change of enthalpy due to a chemical reaction. This quantity takes a positive value for an endothermic reaction, and a negative value for an exothermic reaction. This means that in the former reaction the energy is absorbed by the reacting system, whereas in the latter reaction it evolves as a result of the reaction. (Janbozorgi et al 2010).

4. ACTUALIZATION

Bioenergy is a complex energy system that consist of a multitude of feedstocks, technology pathways and end products that provides varying energy streams as thermal energy, electricity and fuels for transport (biofuels). While many bioenergy conversion pathways are well established and fully commercial, others are still at the early stages of development, demonstration and commercialisation. According to the Renewables 2019, Global Status Report (REN 21. 2019), Bioenergy makes the largest renewable contribution to global energy supply in 2018. Including the traditional use of biomass, bioenergy contributed an estimated 12.4% – or 46.0 exajoules (EJ) – to final energy consumption as of the end of 2017. Modern sustainable bioenergy (excluding the traditional use of biomass) provides around half of all renewable energy in final energy consumption. Figure 11 shows the chart of Estimated Shares of Bioenergy in Total Final Energy Consumption, Overall and by End-Use Sector, 2017.
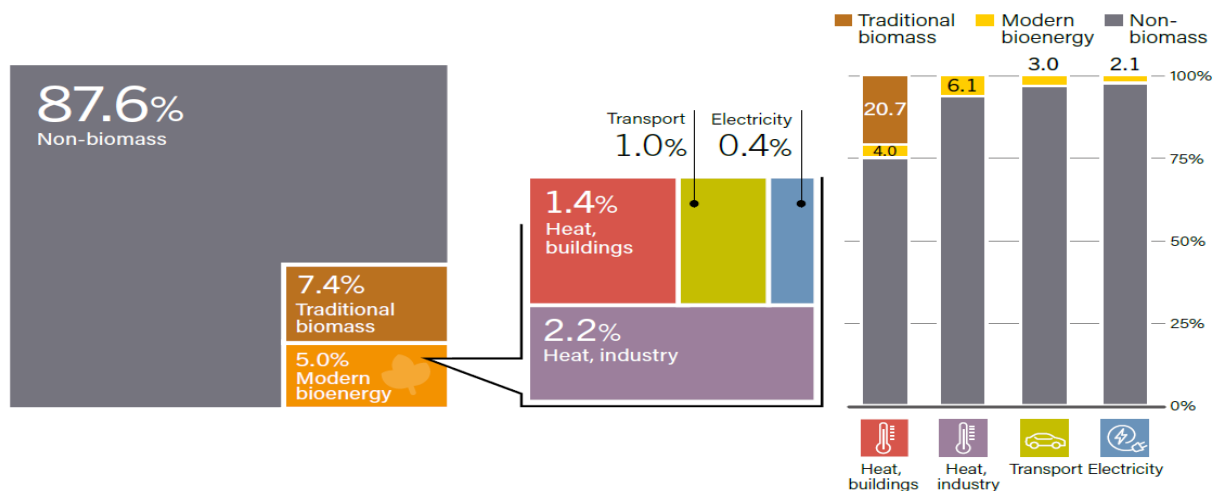

Figure 11: Estimated Shares of Bioenergy in Total Final Energy Consumption, Overall and by End-Use Sector, 2017.

The traditional biomass use for home heating, though less efficient is still the largest use of Bioenergy. On the other hand, the modern bioenergy use is also growing most quickly in the electricity sector (at around 9% per year), compared to around 7% in the transport sector; its use for heating is growing more slowly, at around 1.8%. Globally, modern bioenergy provided around 4.0% of the energy used for heating buildings in 2017. Modern use of bioenergy for heating in the buildings sector is concentrated in the EU. In 2016, the region accounted for some 46% of all bioenergy used for heat in individual buildings, and for an even higher share of global bioenergy use in the residential sector (54%); together, Italy, France and Germany accounted for 44% of the global total. North America followed the EU for bioenergy consumption in buildings. In 2017, more than 2 million US households (2% of the total) used wood or wood pellets as their primary heating fuel, and a further 8% of households used wood as a secondary heat source. In the industry sector, heat supplied from bioenergy accounted for some 6.1% of all heat consumption. In terms of global bio-power, Global bio-power capacity increased an estimated 6.5% in 2018 to 130 gigawatts (GW), up from 121 GW in 2017. Total bioelectricity generation rose 9%, from 532 terawatt-hours (TWh) in 2017 to 581 TWh in 2018. The EU remained the largest generator by region, with generation growing 6% in 2018, stimulated by the Renewable Energy Directive.31 Other trends of previous years continued: generation grew most rapidly in China – up 14% in 2018 – and in the rest of Asia (16%), while generation in North America remained essentially stable.
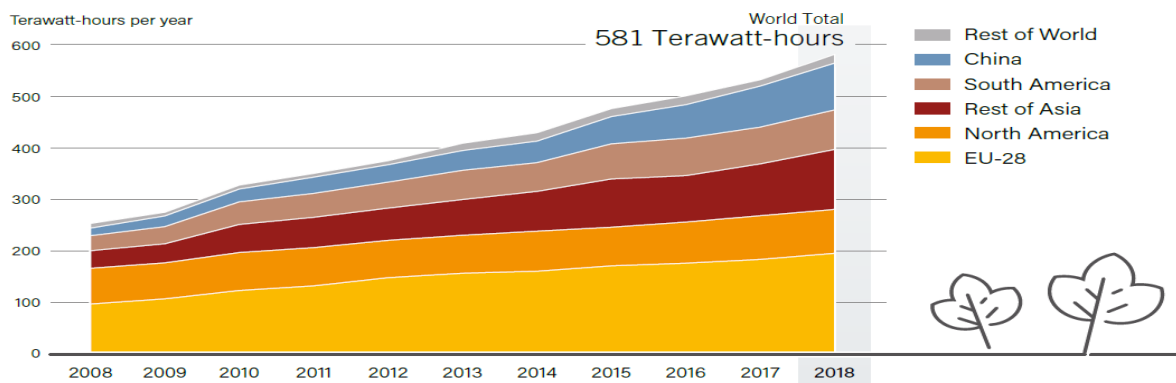
Figure 12. Global Bioelectricity Generation, by Region, 2008-2018

According to the RN21, 2019, the use of Bioenergy in transportation increased by 7% from 2017 number in 2018, with ethanol (produced mostly from corn, sugar cane and other crops) and biodiesel (fatty acid methyl ester, or FAME, fuels produced from vegetable oils and fats, including wastes such as used cooking oil) as the major biofuels produced in 2018. In addition, the production and use of diesel substitute fuels – made by treating animal and vegetable oils and fats with hydrogen (hydrotreated vegetable oil (HVO) and hydrotreated esters and fatty acids (HEFA)) – is growing. In 2018, ethanol accounted for an estimated 63% of biofuel production (in energy terms), FAME biodiesel for 31% and HVO/HEFA for 6%. The contribution from biomethane is also increasing rapidly in some countries. Nevertheless, it represented less than 1% of the biofuel total in 2018, and other advanced biofuels had shares below 0.5%.   Figure 13 show the distribution of the types of biofuel production between 2008- 2018.
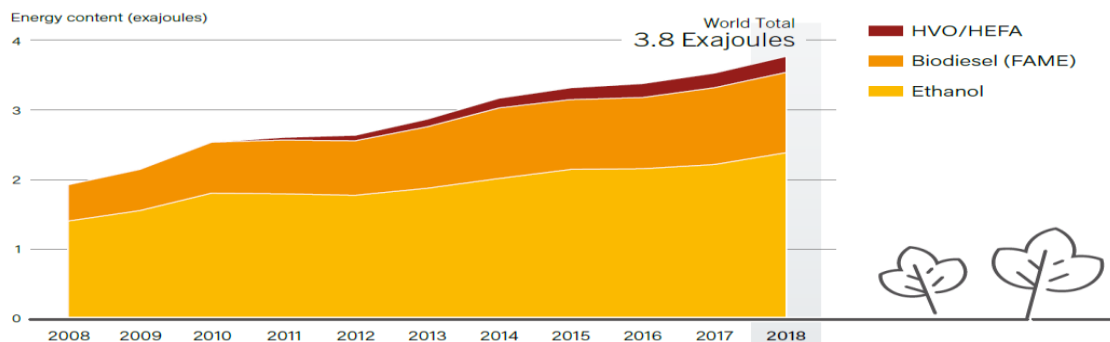
Figure 13. Global Ethanol, Biodiesel and HVO/HEFA Fuel Production by Energy Content,   2008-2018

In terms of country, the United States and Brazil dominated biofuel production – together producing 69% of all biofuels in 2018 – followed by China (3.4%), Germany (2.9%) and Indonesia (2.7%). Global production of biodiesel based on the REN21, 2019 report, also increased in 2018, up around 5% to 41.3 billion litres. Biodiesel production is more geographically diverse than ethanol production (due to policy priorities) and is spread among many countries. The top five countries in 2018 accounted for 53% of global production. Europe was the largest biodiesel producer by region, and the leading country producers were the United States (17%), Brazil (13%), Indonesia (10%), Germany (8%) and Argentina (5%).   The global increase in biodiesel production was due mainly to growth in the United States, where production rose 14% to a record 6.9 billion litres.83 Factors behind this growth included a good soya crop, increased opportunities for biodiesel in the RFS, and the impact of US anti-dumping duties, which constrained imports from Argentina and Indonesia. On Green Diesel, Douvartzides et al 2019 reported that the global market is also growing in great volumes, from 330×106 gallons in 2011 to 2.1×109 gallons in 2017 . A list of the main green diesel producers is given in Table 5 . Most of the producers have developed proprietary technologies (Neste NExBTL, UOP/Eni EcofiningTM, UPM BioVerno etc.) and standalone plants comprised by the biomass cleanup and pretreatment section, the deoxygenation (hydrotreatment) section, a hydroisemarization reactor and a separation column. Given that green diesel can be mixed with conventional petroleum diesel to satisfy the automotive fuel specifications, some oil refineries have developed methods for the simultaneous co-processing of triglyceride feedstocks with petroleum intermediates such as straight run gas oil and/or vacuum gas oil.

**Table 5. List of the main green diesel producers currently in operation.**

Company Name	Location	Feedstocks	Capacity	Technology
Neste	The Netherlands	Vegetable oil and waste animal fat	1,000,000 tn/year	NExBTL
Neste	Singapore	Vegetable oil and waste animal fat	1,000,000 tn/year	NExBTL
Diamond Green Diesel	USA	Non-edible vegetable oils and animal fats	900,000 tn/year	Ecofining™
UOP/Eni	Italy	Vegetable oils, animal fats and used cooking oils	780,000 tn/year	Ecofining™
Neste	Finland	Vegetable oil and waste animal fat	380,000 tn/year	NExBTL
Renewable Energy Group (REG) Inc.	USA	High and low free fatty acid feedstocks	250,000 tn/year	Dynamic Fuels LLC
AltAir Fuels	USA	Non-edible natural oils and agricultural waste	130,000 tn/year	Ecofining™
UPM Biofuels	Finland	Crude tall oil	100,000 tn/year	UPM BioVerno

NOTES: Also, there are a number of companies co-processing vegetable oils with petroleum distillates such as Petrobras (Brazil), Cepsa (with several refineries in Spain), Preem (Sweden), Repsol (with several refineries in Spain) and British Petroleum (Australia).

5. DISCUSSIONS

There is no doubt that Clean energy is the cornerstone of the better future for humanity, as according to the UN Report on Global Trend in Renewable Energy Investment, report, 2019, neither the Paris Agreement nor the 2030 Agenda for Sustainable Development will be able to fulfill their full potential unless renewable energy replaces fossil fuel generation. Renewable energy avoids the greenhouse gas emissions that warm our planet. It improves air quality and therefore human health. It brings new opportunities to energy-poor communities. The report showed that global investment in renewable energy capacity hit $272.9 billion in 2018, far outstripping investments in new fossil fuel generation. And that the year 2018 was the fifth successive year renewables capacity investment exceeded $250 billion. That looking across 2010-2019, the report estimates that a total of $2.6 trillion will have been invested in renewable capacity (excluding large hydro) over that period. This corresponds to an estimated 1.2 terawatts of new renewable energy capacity over this decade. Despite these obvious benefits associated with renewable energies, and especially bioenergy in heat and electricity, and transportation services, there are also documented challenges and concerns about the use of renewables, and especially the combustion of biofluids. This section therefore discusses some of the pros and cons of the combustion of biofluids as a source of bioenergy.

5.1. Combustion of Biofluids: Biofluids in this context include biofuels, biodiesel, and green diesels, which were presented in detail in section 2 of this work. This section now presents the pros and cons of the applications of these fuels in various combustion devices. For the purpose of this work, we have limited our combustion devices to Compression-Ignition (CI) and Spark Ignition (SI) and the Homogeneous Charge Compression Ignition (HCCI) engines. Figure 14 shows pictorial representations of the three types of Internal Combusion Engines. Generally, internal combustion engines (ICE) burn a mixture of fuel and air (oxygen), in an appropriate ratio, in order to produce mechanical power. Besides the mechanical power, ICE also produces by-product, or exhaust gases, where in an ideal condition, if the combustion process is complete, the exhaust gases should only be carbon dioxide (CO_2) and water vapour (H_2O). However, in reality, mainly due to incomplete combustion, the exhaust gases also contain pollutant emissions: oxides of nitrogen (NO_x), unburnt hydrocarbons (HC), carbon monoxide (CO), soots/particles (PM), polyaromatics, aldehydes ketones and nitro-olefins.
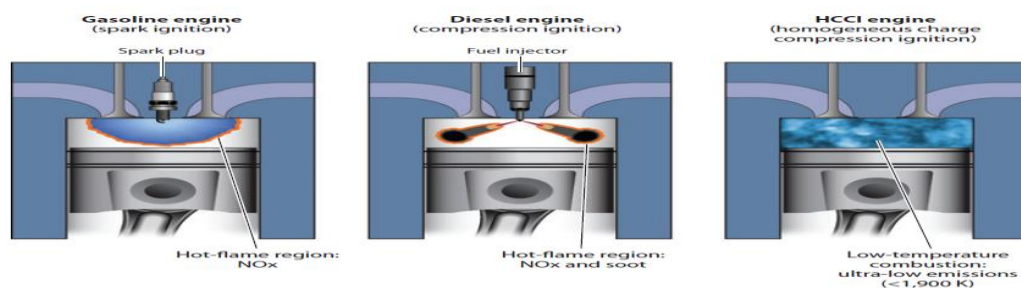
Figure 14: Three types of internal combustion engine in common use. Source: Westbrook, 2013.

The generation of pollutant exhaust gas emissions also depends on the sequence of engine phases (engine cycle), and this is where Compression-Ignition or Diesel Engine and Spark Ignition or Petrol Engines differ especially regarding how the air-fuel mixture is created and how the combustion process is triggered. Also, the properties of the fuel determine how the combustion is initiated, how the flame is propagated and the content of the exhaust gas. Typically, in a gasoline

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(petrol) internal combustion engine, before the spark is generated, the air-fuel mixture must be homogeneous. This is critical for the flame to appear around the spark and propagate into the cylinder, for a quasi-complete combustion. The electric arc (plasma) generated by the spark plug reaches temperatures of 10000 °C and triggers the combustion process. The air motion is also important since the higher the turbulence into the cylinder, the faster the combustion and flame propagation. In a normal combustion process, the speed of the flame into the cylinder, during combustion, is between 25 – 50 m/s.

On the other hand, in a diesel internal combustion engine, the air-fuel mixture is not homogeneous but stratified. Compared with a gasoline/petrol engine, the time allowed for the fuel to mix with air is much shorter, between 5-8 times. If for the gasoline engine the air and fuel are mixed for nearly two piston strokes (intake and compression), for a diesel engine the mixture forms in around 40 – 80 ° of crankshaft rotation. The flame is generated when the fuel is vaporised (during injection) and comes into contact with the hot compressed air. (X-Engineer.org-2020)
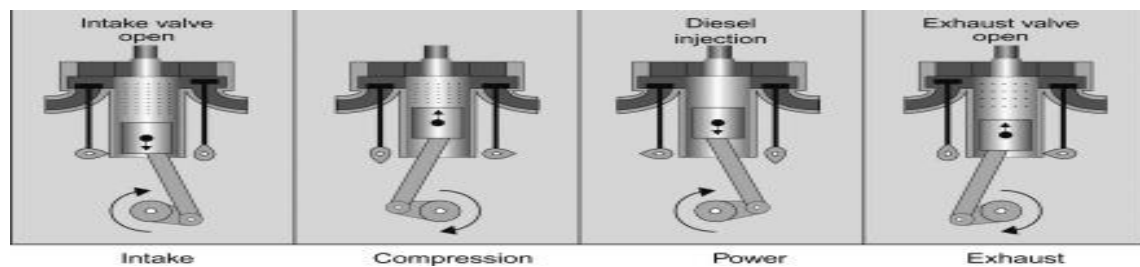

Figure 15: Typical 4-stroke diesel engine cycle. Source: Breeze, 2019

5.1.1 Compression Ignition (CI) Engines with Various Fuels.

(a) **Green diesel** : According to Douvartzides et al 2019, green diesel decreases both the maximum

cylinder pressure and the rate of pressure increase, mainly due to its higher cetane number which shortens the ignition delay period and the premixed combustion phase in CI engines. Again, its lower viscosity allows for better mixing of the liquid fuel droplets with air and reduces the ignition delay. Green diesel also increases the crankshaft interval of the combustion process by approximately 0.5–2°, and was also observed to reduce the brake specific fuel consumption (bsfc) of the engine when comprised by either normal or branched saturated hydrocarbons. This is very significant since bsfc is the ratio of the mass of the fuel consumed per brake power output, as lower bsfc values translate into higher fuel economy during engine operation and also to lower emissions, since less fuel is burned for the same power output. Finally, green diesel was able to increase the brake thermal efficiency of the engine defined as the ratio of the brake power output to the rate of fuel energy consumption of the engine, by 10%. Several test runs indicated that green diesel reduced the emissions of CO, CO2, unburned hydrocarbons (HC), nitrogen oxides (NOx) and solid particulates, and this was attributed to (i) the mixing of green diesel with air is better since the fuel is comprised by hydrocarbons in narrow carbon atom (C15–C18) and narrow molecular length chain ranges. This reduces the emissions of CO, HC and smoke by promoting more complete combustion. Secondly, the higher cetane number of green diesel reduces the heat release rate and the maximum flame temperature in the cylinder. Technically, The reduction of NOx emissions is an advantage of green diesel over biodiesel and petroleum diesel. (Douvartzides et al 2019).

(b) **Biodiesel:** Bergthorson and Thomson, 2015 reported that biodiesels have shown to reduce engine

deposits and coking compared to petroleum-derived fuels, which is directly linked to the observed decrease in soot emissions for biodiesel compared to petro-diesel fuels. This can be explained by (i) the reduced local fuel-to-air ratio at the time of the initial fuel-rich flame ignition event, caused by the oxygen already present within the fuel, (ii) changes in the fuel–air mixing process due to the fuel physical properties; and (iii) the changes in the ignition propensity, or cetane number, of the fuel blend. The reduction in soot for biodiesel blends is also a result of the lower content of aromatic hydrocarbons in the biodiesel/diesel blend com pared to neat diesel, since aromatic hydrocarbons are known to produce higher soot emissions than other fuel components. NOx emissions have been observed to increase for biodiesel compared to petro-diesel for many engine tests. Use of exhaust-gas recirculation can greatly reduce NOx emissions for FAME-diesel blends , but this can slightly increase soot emissions. (Bergthorson and Thomson, 2015). Biodiesel also causes higher peak cylinder pressure than petro-diesel and this was attributed to the advanced combustion process initiated by easy flow-ability of biodiesel due to its enhanced physical properties. Also, due to the presence of oxygen molecule in

biodiesel, the hydrocarbons achieve complete combustion resulting in higher in-cylinder pressure. For a CI engine, the cylinder pressure depends upon the fuel-burning rate during the premixed burning phase, and since the blend quantity increases causes the amount of fuel taking part in the uncontrolled combustion stage of the mixture to increase, this eventually results in a higher pressure raise. Biodiesel also showed shorter ignition delay and lower maximum heat release rate than that of diesel, this is attributed to less intense premix combustion phase due to the shorter ignition delay of biodiesel. Finally, Biodiesel also showed slightly higher mass fraction burnt than that of diesel at full load and is due to the oxygen content of biodiesel that enhanced the combustion process. At crank angle before 360°, the mass fraction burnt for the fuel biodiesel is higher than the standard diesel. But at crank angle after 360°the mass fraction burnt is slightly closer to each other. The efficient rate of combustion is shown by the highest rate of burning. (Kale, 2017).

(C) **Biofuels:** Smaller oxygenated fuels, such as alcohols (e.g.,ethanol or butanol), are not applicable as alternative diesel fuels in a pure form due to their high octane rating, which corresponds to a low cetane number, typically less than10. The poor ignition properties of these fuels delay ignition and results in higher unburned hydrocarbon emissions. Ethanol–diesel blends have been used, typically only upto a maximum of 15% due to solubility issues at low temperatures, and generally show reductions in sulfur-oxide and particulate-matter(soot) emissions, no change or slight reductions/increases in NOx and CO emissions, and increases in unburned hydrocarbon emissions. Droplet combustion experiments of n-butanol showed very low soot levels due to less acetylene production during the combustion process. Blends of n-butanol with n-dodecane show a reduced sooting propensity for butanol, but also a lower rate of soot oxidation after it is formed that can slow soot burn out before exhaust, which could lead to higher net PM emissions. Alcohols are ignition-retarding compounds when added to diesel fuel. The reduction in low-temperature ignition propensity (lower cetane numbers) when alcohols are blended with petroleum fuels is caused by the alcohol acting as a sink of reactive species that reduces the overall chain-branching reaction rates and, thus, slows ignition. The high-octane tert-butanol has a highly branched structure that results in it having the lowest reactivity, and hence smallest cetane number, of the butanol isomers, as well as a lower cetane number than ethanol. Interestingly, even though it has the lowest pure-component cetane number with the largest variation from petroleum diesel, it has the least effect in retarding the ignition process of alcohol– diesel fuel blends. This is because the highly branched tert-butanol molecule acts like an inert compound, rather than an ignition retarder, in the mixture. The combustion properties of alcohol fuels, or their blends with diesel, can be improved by adding ignition promoters, such as alkyl nitrates. (Bergthorson and Thomson, 2015).

5.1.2 Spark Ignition (SI) Engines: The SI engine uses lighter constituents in petroleum, those with about 4 to 10 carbon atoms per molecule; jet fuel uses those with about 10–14 carbon atoms; and diesel uses the larger molecules with about 15–22 carbon atoms. Each type of engine exploits the physical and chemical properties of the fuel it burns, consequently, SI engines require fuel that vaporizes easily and mixes rapidly with air, and the small oxygenated biofuels such as alcohol (ethanol, methanol, *n*-butanol, and iso-pentanol) with molecular weights and other properties like gasolines fits into that specification. Their general combustion properties are similar to those of gasoline, and the most common obstacles to converting gasoline engines for ethanol or methanol use have been the corrosion of fuel lines, filters, and gaskets by the alcohol fuel, problems that have usually been solved by using different materials for those engine and fuel-system components. Again, SI engine fuels must have acceptable resistance to knocking behavior that occurs if end-gas fuel autoignition occurs before the flame can consume all the fuel/air mixture in the combustion chamber. Knocking behavior is measured by the octane number (ON), and fuels with high values of ON resist knock better than fuels with low ON values. All these biofuel alcohols, similar to gasoline components, have relatively high ON values and therefore are not likely to produce engine knock. Ethanol has an ON of approximately 100 and strongly resists knocking behavior. The knock resistance of ethanol permits the use of compression ratios significantly higher than those commonly used in gasoline engines, producing better overall combustion efficiencies because of the positive dependence of combustion efficiency on the compression ratio, although NOx aftertreatment or high levels of exhaust gas recirculation are sometimes needed. (Westbrook, 2013).

5.1.3 Homogeneous Charge Compression Ignition (HCCI) Engines: The two dominating engine

concepts commonly used today are the diesel and SI engines. A comparison between the two engines shows that the SI engine equipped with a catalytic converter provides low emissions but lacks in efficiency, while the diesel engine on the other hand provides high efficiency but also produces high emissions of and particles. Over the last decade, an alternative combustion technology, commonly known as homogeneous charge compression ignition (HCCI), has emerged, with an engine concept capable of combining the efficiency of a diesel engine with the tailpipe emissions level of an SI engine.

The HCCI thus is a clean and high efficiency technology for combustion engines that can be scaled to any size-class of transportation engines as well as used for stationary applications. In other words, it is is the autoignition of a homogeneous mixture by compression and has the potential to decrease emissions and fuel consumption in transportation. HCCI. (Izadi and Aziz, 2013). According to Westbrook, 2013, the HCCI combines the advantages of SI and diesel engines without the problems of either. The basic concept, the HCCI engine as shown in Figure 14, is a premixed, spatially homogeneous charge that is fuel lean and is ignited by piston compression. Because HCCI combustion is premixed and lean and takes place entirely in the gas phase, it avoids the soot production seen in diesel engines, but it uses a high compression ratio that provides high fuel efficiency. By operating very fuel lean, the product temperatures remain relatively low, so production of the nitrogen oxides that lead to photochemical smog is sharply reduced. In fact, the basic form of HCCI uses fuel/air mixtures that are too fuel-lean to be able to support a flame, but because most of the charge ignites and burns nearly simultaneously, there is no flame propagation and therefore no opportunity for knocking operation to occur in HCCI combustion. The most significant difficulty with HCCI and other extremely lean combustion systems is that they are usually subject to unacceptably high emissions of unburned hydrocarbons and CO. This is a common problem related to the low NOx emissions. If combustion temperatures are kept low to limit the production of NOx, then the same low temperatures slow the overall consumption of hydrocarbons and CO. If the combustion temperature is increased, often by increasing the rate of fuel addition, then the temperatures rise and increase NOx production. (Westbrook, 2013). In the experimental study by Ramavathu and Kota, 2019, they obtained the combustion results to be of 39.69 % higher Rate of Heat Release (RoHR) for biodiesel HCCI as compared with diesel HCCI. Higher brake thermal efficiency (BTE) was found 37 % without exhaust gas recirculation (EGR) at WPPO 20 % biodiesel blend. They also found 50 % and 65 % reduction in NOx emission and 18 % and 28 % reduction in smoke opacity for biodiesel vapour induction without EGR and biodiesel vapour induction with 15 % EGR as compared with diesel fuel. The CO (0.34 %), and UHC (2.15 %) emissions increases with 15 % EGR, but the emissions are within the standard limits specified by the emissions standards. Westbrook, 2013, further reported that the HCCI engines have the attractive feature of being suitable for almost any type of fuel, from diesel fuel to gasolines, and they are capable of burning virtually any biofuel with high efficiency and low NOx emissions. An interesting extension of this concept is to use two fuels in the same engine, first injecting a small portion of a fuel that ignites easily (i.e., with high CN), such as a diesel fuel, followed by a second injection of another, more difficult to ignite fuel (i.e., high ON). The earlier injected fuel will already be burning when the second injection occurs, which produces a reliable, quite rapid ignition of the second fuel. This strategy is called reactivity-controlled compression ignition (RCCI), and the second fuel in many studies has been natural gas or ethanol. The earlier injected, more ignitable fuel can be conventional diesel or biodiesel fuel. The use of multiple injections and the flexibility provided by adjusting the timing of the injections, combined with operation at high compression ratios, can produce very low emissions and high combustion efficiency. The RCCI engine, with its excellent performance characteristics and unusually broad fuel tolerance, is a concept that is likely to grow steadily in importance in the coming years.

5.2 Challenges with the combustion of Biofluids: Studies have shown that some challenges exist

with the use of biofluids, and this section presents some of those findings. Kenward, 2010 in his work, reported that while biofuel combustion produces many of the same chemicals released during fossil fuel burning, it also generates a complicated mixture of additional chemicals that are potentially harmful to humans and the environment. Chauhan and Shukla, 2011, also reported that with ethanol fuel combustion, emission of the toxic air pollutants acetaldehyde, formaldehyde, peroxyacetyl nitrate (PAN) increase relative to straight gasoline. Most is emitted as acetaldehyde, a less reactive and less toxic pollutant than formaldehyde, which are created as by product of incomplete combustion. PAN is an eye irritant that is harmful to plants, is also formed as by product.

Furthermore, Kenward, 2010 reported that nitrogen and phosphorus from fertilizers, which are used to grow biofuel crops, can remain in biofuels, and their presence can introduce an even broader spectrum of possible chemicals into the burning process. In the case of heavier biodiesel made from vegetable and soybean oils, the higher oxygen content and residual nitrogen from fertilizers further increases the complexity of combustion products. In their contributions to the challenges with the combustion of biofluids, Kumar et al, 2014 stated that some of the problems (primarily cold-weather problems) are not due to poor fuel quality but are related to the biodiesel fuel properties. The diesel engines face the problem of filter clogging or coking of the injectors when operated on biodiesel, and this can be solved by the addition /use of cold flow improvers and blends of biodiesel with kerosene, as it has been found to extend the range of operating temperature of

biodiesels. That use of B100 tends to operate well at temp below 5°C which varies from the biodiesel to biodiesel, however, the use of additives can lower this temperature by 5° – 8°C while the winter blends (mixture of biodiesel with kerosene) can be effective at temperature as low as -20°C and below. Biodiesels are also more prone to atmospheric oxidation than diesel, thereby, making the bio fuels acidic and forming insoluble gums and sediments that plug the fuel filters and impact of the engine performances. Kumar et al 2014, further noted engine starting problems under cold weather conditions where engine run only a few seconds, engine stops after operation for few second, and the problems of Fuel filter clogging due to: Poor biodiesel quality due to formation of resins or gels in the fuel supply system. The fuel clogging has been attributed to the relatively high viscosity (about 11–17 times greater than diesel fuel) because of the large molecular mass and chemical structure of vegetable oils. The clogging also leads to problems in pumping, combustion and atomization in the injector systems of a diesel engine, causes excessive engine wear, and form coking of injectors on piston and head of engine. Finally, Biodiesel lower engine speed and power as they on the average decrease power by 5% compared to that of diesel at rated load. (Hassan and Kalam, 2013).

5.3 Technological Innovations to enhance combustion: Besides the move to renewables, there has

also been efforts to re-engineer existing combustion systems to reduce the harmful emissions, and this has motivated vehicle manufacturers to see how to decrease the exhaust emissions produced by diesel-engine vehicles down within legal limits. They thus use systems such as high-pressure fuel injection, multi-stage injection, three way catalytic converter, exhaust gas recycling, particle filters and injection start control through diesel engine management with an effort to meet the Euro norms. In addition to the reduction of harmful exhaust gas emissions, there has also been evolution of various bio engineering to create more enhanced biofuels; biofuels have already moved from the traditional First Generation Biofuels (2000-2010), to Second Generation Biofuels (2010-2030), to Third Generation Biofuels (after 2030), and finally to Fourth Generation Biofuels (after 2030). (Aydogan et al, 2014

5.3.1The Green Engine: The Green Engine is one of the most important discoveries in combustion

engines with some excellent features than the typical internal combustion engines. For instance, the Engine does not contain the typical piston but has features like sequential variable compression ratio, direct air intake, direct fuel injection, Multi fuel usage etc. It also has very high efficiency when compared to the traditional IC Engines with nearly zero exhaust emissions. Compared to the conventional internal combustion engine with 4 phases, the Green Engine is a six-phase internal combustion engine with much higher expansion ratio. The six phases are INTAKE, COMPRESSION, MIXING, COMBUSTION, POWER AND EXAUST, with high air charge rate, satisfactory air-fuel mixing, complete burning, high combustion efficiency, full expansion, as the main features. Other main features are the sequential variable compression ratio, which can provide the most suitable compression ratio for the engine whatever operation mode it works on with burning variety of fuels. The most important characteristic is the expansion ratio being much bigger than the compression ratio. Due to the six phases of working principle, super air fuel mixing process and constant volume combustion with controllable time, the Green engine becomes the only real multi-fuel engine on our planet; any liquid or gas fuels can be burnt well. (Mubashir, 2016).

5.3.2 Flexible-fuel vehicles (FFV): Flexible fuel vehicles (FFVs) have an internal combustion

engine and are capable of operating on gasoline and any blend of gasoline and ethanol up to 83%. FFVs have one fuel system, and most components are the same as those found in a conventional gasoline car. Some special ethanol-compatible components are required to compensate for the different chemical properties and energy content in ethanol, such as modifications to the fuel pump and fuel injection system. The engine control module (ECM) is also calibrated to accommodate the higher oxygen content of ethanol. (AFDC). However, according to Chauhan and Shukla, 2011, tests to date have found that the use of FFVs results in higher air emission than new gasoline vehicles. Because it is not possible to tune the combustion controls of vehicles so that it is optimized for all conditions, controls are compromised somewhat to allow for different mixes. It is possible that vehicles dedicated to specific blends, operated on those blends level, would achieve lower emissions than conventional vehicles.

5.3.3 Co-Optimization of Fuel and Engine: Efforts to improve the fuel economy of vehicles with internal combustion engines (ICE) over the drive cycle has led to downsizing and downspeeding of the engines. Downsizing represents the reduction of displacement of the engine, and to retain the required performance, a proper boosting device, ensuring higher intake pressure, must be added to the ICE. Downspeeding refers to the reduction of engine speed (RPM), which in turn

further reduces friction losses of the engine and allows the engine to run at higher load at the same power output. Again this can be enabled by a suitable boosting device which allows sufficient boost pressure to be supplied at low engine speed. The boosting system represents a new device or devices coupled with the engine, and its features also influence the engine itself such as low power demand, fast pressure build-up during transients, a wide range of operation with high isentropic efficiency, lightweight and easy packaging, fast warmup of after-treatment systems and their control, minimum NVH issues and cost. (Bolehovsky and Macek, 2016). Maximizing the efficiency of Boost Spark Ignition (BSI) engine (Spark ignition systems with the capability of providing spark event with either higher current level or longer discharge duration) requires fuels with higher octane number, higheroctane sensitivity, and increased heat of vaporization, along with low particulate matter index (PMI < 2 leads to no merit function score decrease). Daniel, 2019 reported the work carried out by Co-Optima in screening more than 400 blendstocks, including single components, simple mixtures and complex mixtures derived from a broad range of production pathways, including biofuels, and in the process, found only two of the mixtures, the fusel alcohol blend and the mixed furans, that are fitting into such fuel specification. According to Daniel, 2019, the aim of Co-Optima was to identify bioblendstocks across a wide range of oxygenates and hydrocarbons, that confer advantageous fuel properties for BSI, a high-performance fuel blendstocks that can boost engine efficiency and cut emissions when combined with advanced combustion approaches.

6.   GENERAL RECOMMENDATIONS:

This work has presented the prospects and challenges of biofulids combustion as part of the efforts at reducing the emissions associated with fossil fuel combustion. While in general, biofluids produce much less emissions than fossil fuel in the same engine systems, there are areas that require further work as pointed out by Oliveira and Brojo, 2017. More attention is required in fuel nozzle design for multifuel capability, and in fuel/air management for minimum soot and gaseous emissions for more efficient biofuel combustion in order to reduce emissions of nitrogen oxides (NOx), unburned hydrocarbons (UHC), carbon monoxide (CO), Particulate Matter (PM) and sulfur oxides (SOx). Carbon dioxide (CO2) and water vapor (H2O) are also products of the combustion process, but they are not regarded as pollutants because they are a natural consequence of the complete combustion of a hydrocarbon fuel. However, these two contribute to global warming and the only way to reduce them, is to burn less fuel. Without doubt, there has been several efforts at adjusting the internal combustion engines primarily for fuel economy and to reduce emissions, but there has been very little efforts towards coming out with engine systems that can run solely on biofluids, which eventually will become the fuel for the future. This was the case when automobiles were first designed to run on biofuels, and when fossil fuel became the main source, the engine systems were also configured to run on fossil fuel. It is thereofore time that the industry also develops engines that will run solely on biofluids. Ofcourse, the technological innovations on the engines will run side by side with the biofuel enhancement technologies to produce more adaptable fuels that will for the "Biofuel Engines".   In pursuant to these two main goals, it is also important that none of these must compromise safety and environmental effects of these innovations. Attention must also be given to the potential life-cycle effects associated with the production and use of an alternative fuel, and the safe and reliable operations of the engines must not be compromised. Finally, given that this transition is a global project, it is also important that there is a shift towards a more consistent and collaborative global policies in the entire life cycle of biofuel production to combustion, and also standards for the engines, for mass production if this energy transition to renewables by 2040 will be of any consequence.

7.   CONCLUSION -A NEW PERSPECTIVE

The current transition to biofuels no doubt will reduce greenhouse gas effect and other pollutants into the atmosphere. However, today's road transport still almost completely relies on vehicles powered by combustion engines, with fossil fuels being the main energy carrier, and this is why there has to be concerted global efforts at speeding up the use of biofuels and coming out with engines that will complement the new fuel system. . The remarkable progress achieved to date regarding engine and fuel issues has been accomplished by performing and evaluating an enormous number of engine tests and calibration experiments complemented by mathematical modeling. Engine tests, in this context means a single combination of combustion instrument (engine) and fuel. Results will change using a different engine or combustion apparatus, or by modifying driving or ambient conditions, and of course using a different fuel. (Grope et al, 2018). These efforts are progressive and the results are that biofluids combustion has produced better quality exhausts compared to combustion of traditional fossil fuel, and this has also encouraged continuous investments in research and development to develop innovative technologies that covers the entire life cycle of biofuel production and combustion, and also in the areas of the engine systems. Regardless of these progress, Bioenergy is still way behind fossil fuel in the

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total energy mix, which makes it imperative for more work to be done if it is to fully replace fossil fuel in the areas of heating, electric power, and transportation. Though companies have made significant adjustments to existing internal combustion engines in order to produce better efficiency and cleaner emissions, given the global trend in the transition, the question should rather be " what engine system will fit biofuel blends" and not " "What fuel properties do engines want?". Just as the beginning of the automotive industry when engines were designed to be run fully on biofuel, before the advent of fossil fuel, the time is ripe for such 100% biofuel engines to come out from the assembly lines. More researches are required on biofluids technology to continuously produce finer fuel qualities as stand-alones or blended within the biofuel family. Finally, as in every global pursuit, the current efforts to transit into renewables for cleaner and more enhanced combustion products requires the collective decisions of every country to evolve some standards that will cut across every sector of the entire life cycle of biofuel production and combustion. (Mubashir, 2016).

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