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BIOFUEL; A SUSTAINABLE RENEWABLE SOURCE OF ENERGY-A REVIEW

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Abstract: The improvisation of renewable energy sources is of global concern as there is foresight in the depletion of fossil fuels. This is because there is dependence on energy fuel consumers over time and the detriment on the biotic and abiotic component of the environment is alarming. The need for an alternate source of energy source is imperative. Several options have been considered by the scientific community, especially biofuels which hinges primarily on the type of biomass. Agro waste is most considered because of its abundance but it is competed for as feeding purposes in humans and animals. However, Lignocellulose is being utilized recently. The preliminary step in the conversion of the lignocellulose (pre-treatment) stage is the most challenging which is presented in three major methods; physical, chemical, and biological treatment. This review assessed its sustainability and the limitations of each of these methods. The biological pre-treatment poses to be a cost-effective method with a low yield of products. These shortcomings could however be managed by redesigning the procedure to include a partial chemical pre-treatment, optimization of the process parameters such as pressure, temperature, and genetic manipulation of microorganisms of choice.

Keywords: Biofuel; Biodiesel; Biogas; Renewable; Energy; Nanoparticles; Agro waste

1.0 Introduction

In this present time, the global need for petroleum products is on the high side. This is as a result of its utilization as a main source of energy in most engines used in industries and transportation [1]. Petroleum products are obtained from natural products; fossil fuels whose sources are depleting faster than expected. Petroleum products are found to be a major contributor in the discharge of toxic gases most especially greenhouse gases, this is of great concern to the biological and ecological system [2]. Also, the high demand for these petroleum products influences the world's economy such that the prices of crude oil are inflated continually [3].



Therefore, the consistent delving for energy sources apart from petroleum hydrocarbon which is economical, sustainable, cost-effective, renewable, and produced in large quantities is expedient [4]. Several energy sources are been discovered recently, but biofuel has been gaining attention globally because biofuel is being considered a prospective alternate energy source that is readily available, eco-friendly, and sustainable [5]. Some of the reasons biofuel has a higher consideration over the petroleum hydrocarbon include; the ease extraction of biomass, the biodegradability properties, combustion based on the carbon-dioxide cycle, and ecological friendliness [6]. In the next decade, biofuel is expected to incline and gain more influence in the automobile market because of these environmental advantages. Consequently, there will be more development in agriculture products and its associated by-products [7].

1.1 Biofuel

Biofuel is the fuel (solid, liquid, gaseous) extracted from biomass [8]. With reference to the source of their biomass, biofuels are majorly categorised into secondary and primary biofuels. Primary biofuels also called "biomass" are often applied in their natural or raw form without being processed especially for generating heat and electricity [9]. Examples include; firewood, plant materials, excretory discharge from animals, and crop wastes. Secondary biofuels are obtained from biomass and processed into the desired products. Secondary biomass is subdivided into first, second, third, and fourth-generation biofuels which depend solely on the source of the biomass/feedstock [10]. Biomass are living organisms especially plants and microorganisms; these are a natural and cost-effective form of storage device for energy that could be harnessed anytime [11]. Biofuel is categorized into two main forms which are; Bioethanol and Biodiesels

1.1.1 Bioethanol - are alcohols made by fermenting carbohydrates; simple sugars or starch are found in crops such as maize, rice, sugarcane, and sorghum [12]. Cellulose-based biomass could be used as a feedstock for the production of ethanol and is mostly sourced from non-food crops like grasses [13]. Ethanol with 100% purity is used as fuel in vehicles but mostly used as additives in gasoline to enhance the octane and reduce vehicle emissions [14]. Ethanol can be used in petrol engines in place of gasoline; the mixture of ethanol and gasoline to any percentage is common in most recently used petrol engines and it runs on mixtures of approximately 15% bioethanol with petroleum/gasoline [15]. This is because the energy density of gasoline is greater than ethanol and this implies that ethanol can take more (volume and mass) for the operation of a similar amount of work. Also, there is a higher octane rating in ethanol than in gasoline sold at commercial gas stations, this leads to increased thermal efficiency as a result of the engine's compression [16]. The production of ethanol from corn and other similar feedstocks has enhanced the synthesis of cellulose-based ethanol. A joint research agenda survey by the US Department of Energy reported the fossil energy ratios (FER) for gasoline, corn ethanol, cellulosic ethanol, are 0.81, 10.3, and 1.36, respectively [17].

Ethanol is graded is an excellent fuel candidate for newly designed combustion engines in motors [18]. The following attributes of ethanol are accountable for its preference over gasoline in newly designed engines.

- i. Higher octane number in ethanol (98) than in gasoline (80) Coelho and Goldemberg [19] reported that the octane number in ethanol is 98 while that of gasoline is 80.
- ii. Lower evaporation in ethanol compared to gasoline [20].
- iii. Less flammability for ethanol in the air than gasoline, therefore ethanol is more environmentally secured [21].
- iv. Compatibility with motor combustion engines of combustion ratio 10:1 compared to gasoline which is compatible with engines of the compression ratio of 8:1. Goldemberg [23] reported 15% efficiency in ethanol as a result of a higher compression ratio which compensates for its lower energy density. With these features for ethanol, it is a better choice of fuel than gasoline. [24].

1.1.2 Biodiesel. The process in which biodiesel is produced from fats and oils is transesterification which is the most prominent biofuel in Europe. Biodiesel is an oxygenated fuel; it has higher oxygen and hydrogen content than fossil diesel but a lesser amount of carbon [25]. This aids the combustion of biodiesel and minimises the emissions of particles from unburnt carbon. However, using pure biodiesel may increase NO_x-emissions [26]. Biodiesel can be utilized as a fuel in its pure form for vehicles but this could happen occasionally. Biodiesels are not appreciable for use during winter because of their lower viscosity at a higher temperature which may lead to maintenance and performance issues [27]. They are therefore recommended for use as an additive in diesel to minimise the emission of particles, carbon monoxide, and hydrocarbons from diesel-engine vehicles [28].

In most cases, the compatibility of biodiesels with diesel engines produced 1990 and beyond included the electronically monitored 'common rail' and 'unit injector' type systems and they use biodiesel blended with conventional diesel fuel [29]. Nevertheless, vehicles beyond 2014 are not approved for pure biodiesel because emission control protocol was limited before date. The majority of these newly-designed diesel engines run on the pure form of biodiesel without disturbance in the engine itself whose reliance is also on the fuel rail design [30]. Biodiesel is a solvent that works smoothly with the engine and also washes off impurities deposited in mineral diesel. This subsequently leads to the replacement of engine filters because the biofuel helps in the cleaning of the combustion compartments of the engine where there is sufficient carbon deposit; maintaining its efficiency [31]. Biodiesel is environmentally safe and easily transited because it is non-toxic and biodegradable.

1.2 Other types of biofuels are:

1.2.1 Bio-ethers are used for enhancing octane in fuels, minimize the emission of pollutants, and to bloom the quality of fuel [32].

1.2.2 Biogas. Biogas is primarily made up of methane. It is obtained from the fermentation of organic matter via anaerobic microbes. This can be produced by farmers from animal manure by using anaerobic digesters [33]. Mechanical and biological treatment waste processing systems, landfill gas generate a less clean form of biogas by the action of naturally occurring anaerobic microorganisms digesting animal waste [34].

1.2.3 Syngas. This is derived from biomass which has undergone pyrolysis, combustion, and gasification [35]. Syngas may be burned directly in internal combustion engines, turbines, or high-temperature fuel cells [36]. These internal combustion engines can be connected directly to a wood gas generator. Methanol, hydrogen can be produced from syngas or transformed via the Fischer-Tropsch process to produce a diesel substitute, or alcohol blends in which can be distilled into gasoline at temperatures greater than 700 °C [37].

2.0 Generations of Biofuel

There are four generations of biofuel presently known which solely depends on the chemical nature and complexity of the biomass; the first, second, third, and fourth-generation [38].

2.1 First generation biofuels

They can be grouped as one obtained from sugar, starch, vegetable oil, animal fats that are produced using conventional methods [39]. Vegetable oil is processed to biofuels following atomization and reducing the viscosity. These vegetable oils can be synthesized using transesterification methods to form biodiesels [39].

2.2 Second generation biofuel

They are produced from a group of non-food crops and biowastes. Waste biomass which is generally the stalks of agriculture crops such as wheat, corn stover, and wood can serve as raw materials [40]. The feedstock used to generate second-generation biofuel are intermediate products of an actual main crop harvest while some are cultivated on lands that are generally used to grow non-food crops where there is no application of sufficient water or fertilizers. These feedstocks include grasses and other seed crops [40].

2.3 *Third generation biofuel*

They are obtained from algae and these fuels are also termed 'oilgae'. Algae can be characterized as low input biomass which exhibits high yield. Although algal blooms have been reported in Nigeria [42], yet the scientific community is still undergoing strategies for its large scale production. Also, feasibility studies are ongoing to arrive at the expected yield estimate. However, there is a prospect in high yield of algaculture as it does not interfere with a decrease in food production unlike the crop-based raw materials, and no farmland nor freshwater is involved [43].

2.4 *Fourth generation biofuel*

This involves the conversion of biological waste from plants and animals such as carbon iv oxide into energy products. Scientists have been engaged in genetic manipulations of some microorganisms which can synthesize fuel directly from CO₂. Plants crops can also be genetically engineered to accumulate more CO₂ at an optimum rate more than what is released during combustion to acquire what is known as "carbon negative cycle" [44].

2.5 *Biomass for Biofuel Production*

Biomass is reported as the fourth-largest abundant energy resource in the world [33]. Also, the global consumption and production of biofuel have inclined by 7% in 2013 to a level of 116.6 billion liters. In 2012, there is a slight decrease whereas the volume of fuel ethanol increased by 5% to a level of 87.2 billion liters [45]. Biofuel production globally increased to 152 billion liters (40 - billion gallons US) in 2018, up 7% from 2017 [23] and biofuels supplied 3% of the fuels required for road transport globally. The requirement of biofuel as highlighted by the International Energy Agency is to target more than a quarter of world demand for fuel transportation by 2050. However, the production and consumption of biofuels have not yet been achieved as demanded by IEA's sustainable development regulations. From 2020 to 2030 the world's biofuel production is expected to increase by 10% annually to meet up with IEA's goal [25].

Moreover, with regards to the over-dependence on traditional petroleum which is depleting with time, the scientific community is on the hunt for alternate products from renewable raw materials which will not only meet up with the demand globally but reduce the discharge of greenhouse gases [46]. Several methods for the production of these fuels have been researched upon but bulk production is yet to be accomplished [38].

With this in view, raw materials that are not included as food crops are being targeted as great potentials in the commercial production of biofuel [11]. However, the issue of concern in the production of biofuel is carbon emission levels, nitric oxide (NO₂) emissions, energy consumption, and environmental issues [68]. It has been argued that biofuel produced from biomass crops has minimal carbon content. Fisher et al. [28] reported that grasses have high carbon accumulation which can store up to 100 to 507 million tonnes. A study reported by McCalmont et al. [47] discovered that an energy crop; *Miscanthus sp* has a mean accumulation rate of 1.84 tonnes (0.74 tonnes per acre per year), or 20% of total harvested carbon per year and could serve as prospective biofuel crops. In Nigeria, biofuel production is yet to be harnessed intensely, therefore this review focuses on assessing the methods of production of biofuels from lignocellulosic waste, and considering the challenges and most preferred of each method and tackling some of the challenges the preferred method presents [48].

3.0 *Biofuel Production from Agro-waste*

The most viable raw materials for bioethanol production are the starch-based biofuels but are limited due to its utilization for commercial production and animal and human feeds. However, one of the Sustainable Developmental Goals is to overcome famine, which can be impaired by the dependence on starch crops for energy fuels [34]. Therefore there is a need to hunt for alternate abundant agricultural products which are closely related to starch-compounds and could be a potential raw material for bioethanol production and lignocellulosic waste fits considerably [49].

3.1 *Lignocellulose*

Lignocellulose is a highly abounding and cost-effective biomass in nature. It is a prospective and sustainable biomass in the production of bioenergy products [32]. Although other agro wastes such as coconut shells, dried grains, textile wastes, palm kernel shells can also be of consideration as a prospect for bioenergy fuels because of their high polysaccharide content, lignocellulosic biomass is more preferred because of its abundance and its broad evaluation recently [41]. Lignocellulosic waste from the furniture has also been highly abundant recently as a result of urbanisation leading to the discard of larger percentage of their elements in the environment [50].

3.2 *Production of bioethanol from Lignocellulose*

The production of lignocellulosic biomass to bioethanol are primarily three procedures:

- (i) The Lignocellulosic biomass is de-lignified by treating with some compounds to produce cellulose and hemicellulose. This is one of the most challenging tasks in its procedure [51].
- (ii) Cellulose and hemicellulose are hydrolysed to simple sugars such as glucose, xylose, arabinose, galactose, mannose
- (iii) Fermentation of the simple sugars using enzymes to yield ethanol [34].

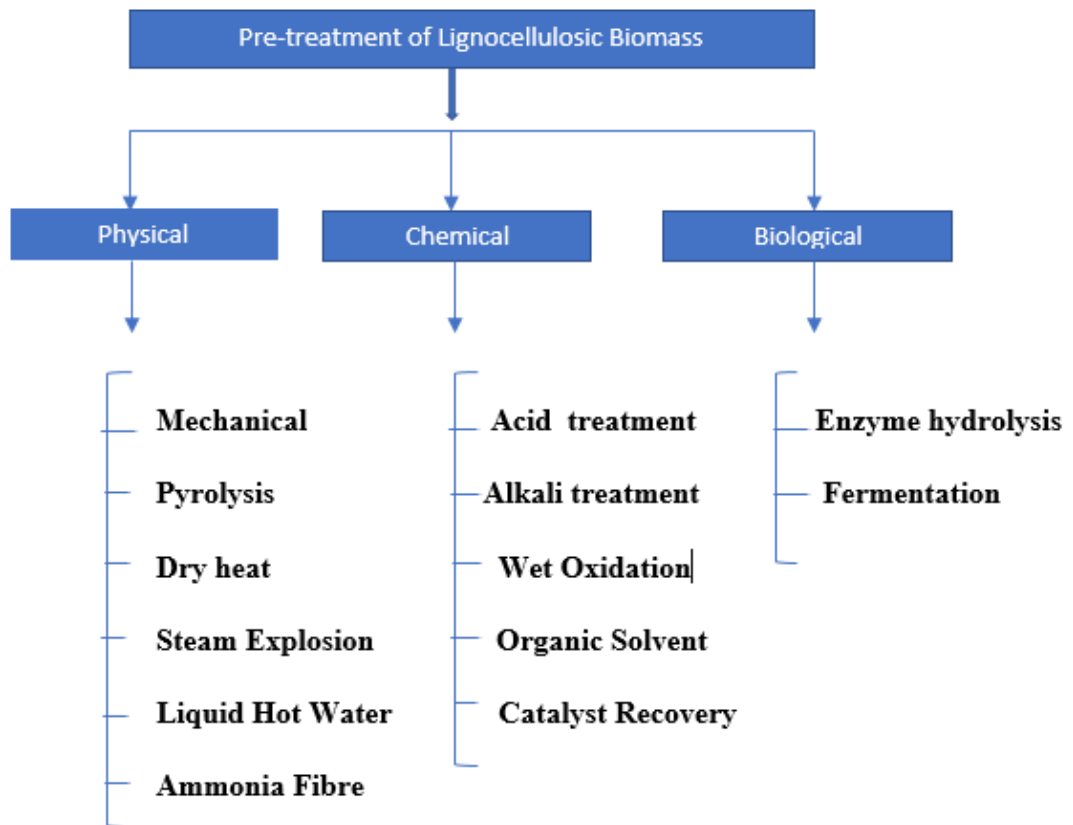


Figure 3.0: Overview of Pre-treatment procedures for Lignocellulosic Biomass

3.3 Pre-treatment of Lignocellulosic Biomass

Pre-treatment of lignocellulosic biomass is done to alternate the microscopic and macroscopic size and chemical composition of the biomass. This involves breaking the crystalline structure of the lignocellulosic compounds to release the cellulose and the hemicellulose [43]. This enhances hydrolysis, enzymatic and microbial interaction of the cellulose and hemicellulose [46]. In pre-treatment lignocellulosic structure is usually destroyed to reduce the crystalline nature of the cellulose and this improves accessibility for enzymatic hydrolysis [52]. Pre-treatment is based on the properties of the substrate and this pre-treatment is of three types; Physical, chemical, and biological treatment and each of the types are summarised in Figure 3.0.

3.3.1 Physical Methods of pre-treatment

3.3.1.1 Mechanical size-reduction. This involves milling, grinding, or chipping to reduce size particles and increase the surface area hence this decreases the crystallinity [43]. The smaller the size the better the production of ethanol [53] Nevertheless, extremely small particles could clump during subsequent processing and result in channeling.

3.3.1.2 Pyrolysis process. A lesser amount of energy is needed (endothermic process). The lignocellulosic biomass is subjected to a temperature of 300°C or more which rapidly degrade the

cellulose for the generation of gases such as hydrogen and carbon monoxide [54]. The products contain primarily glucose (55%) which is a major substrate for the growth of microbes in bioethanol production [47].

3.3.1.3 Dry heat and Electron Beam Radiation. There is a generation of heat in the biomass which is produced by microwave radiation and hotspot. The generated heat leads to the burst among particles and the alteration of the lignocellulose structure [31].

3.3.1.4 Steam Explosion. This is one of the compatible methods that involve the use of steam burst for pre-treatment of lignocellulosic biomass. Thereafter, there is the accessibility of biomass to cellulose hydrolysis [49]. Levulinic acid, xylitol, and alcohol are generated from Lignocellulosic biomass [55]. This involves the use of catalysts and high-pressure steam (20–50 bar, 160–290 °C) for a few minutes [51]. The individual fibres of the lignocellulosic matrix expand and separate as the steam stretches out [5]. In this process, there is 45% of xylose recovery which makes it more economical. [49, 30]

3.3.1.5 Liquid Hot Water Method. This makes use of compress hot liquid water that is compressed for the hydrolysis of the hemicellulose [49] which releases the main part of the oligomeric sugars from the hemicellulose at a pressure of 5MPa, temperature 170–230°C for 20 minutes. This method is safe for the environment as it requires no chemical or acid and there is an 85% recovery of xylose [56].

3.3.1.6 Ammonia Fibre Explosion (AFEX). This method involves high temperature and pressure to lead rapid expulsion to explore the lignocellulosic material [45]. The merits of this method are its simplicity and lesser time-involved while the shortcoming is that it does give a high amount of lignin. Also, the procedure is being inhibited by temperature, increased pressure, moisture content of biomass and the time required. Inhibitors of downstream processing are not released and small particle sizes are not required [57].

3.3.2 Chemical Pre-treatment. These procedures are easy, transformation is more efficient and happens in a shorter time. The chemicals used are less concentrated acid, organic solvent, alkali ammonia, carbon dioxide, and sulfur dioxide. Maleic and acetic acid is used. Monomeric xylose and cellulose are obtained from hemicellulose while the cellulose and lignin remain untransformed [58].

3.3.2.1 Acid Pre-treatment. The pre-treatment using acids is done with acids (usually sulphuric acids; 0.2–2.5% w/w) at temperatures of 130–210°C, then hydrolysis occurs the yielding high amount of sugars [10]. In most cases, by-products of the acid pre-treatment formed which include acetic acid, furfural, and 5-hydroxymethyl furfural inhibits microbial growth so that hydrolysates obtained after acid pre-treatment are detoxified before fermentation [59].

3.3.2.2 Alkaline Pre-treatment. Low temperature and pressure in contrast to the standard are used in this method (Sanchez and Cardona, 2008). The alkali used include sodium hydroxide, potassium hydroxide, calcium hydroxide, and ammonium hydroxide. They break down the cell walls and solubilise the hemicelluloses, lignin, and silica. This pre-treatment decreases the crystallinity of cellulose while the leftover cellulose could be used to manufacture paper [46]. Kumar and Wyman [38] reported that NaOH reduced the lignin composition of hardwood from 24–55 to 20% and improving digestibility from 14 to 55% [59].

3.3.2.3 Wet Oxidation. In wet oxidation, the raw material is treated with water and oxygen at temperatures above 120 °C [39]. Water is added to the biomass at the rate of 1 liter per 6 grams of biomass enhancing the conversion of solid-phase hemicelluloses into the liquid phase. The primary products in this process are sugar oligomers [60].

3.3.2.4 Organic Solvent-Based Pre-treatment. The organic solvent (such as Methanol, ethanol, acetic acid) is used for reducing the lignin composition of lignocellulosic biomass. This process helps the

extraction of lignin from the solvent by [55]. Nguyen et al. [50] used ammonia fiber extraction and ionic pre-treatment which yielded 97% transformation to glucose.

3.3.2.5 Catalyst Recovery. Catalysts are usually acid/base-based. This method is expensive and requires high energy if the catalyst is recovered from wastewater through chemical precipitation and ultrafiltration. Some process may require a very low concentration of catalyst such as dilute sulfuric acid, dilute ammonium hydroxide which does not need recovery [61]

3.3.3 Biological Pre-treatment. The lignocellulose is acted upon by microorganisms most especially fungi which includes brown-rot attacking cellulose, white-rot fungi attacking both cellulose and lignin [55]. This is one of the most cost-effective methods and is environmentally friendly but requires a longer time. However, Biological pre-treatment has not been done on a large scale just because of the minimal hydrolysis rates and low yields [62]. Biological pre-treatment can be obtained through the action of enzyme-producing microorganisms or fermentation by microorganisms.

3.3.3.1 Enzymatic Hydrolysis. There is a preference for enzymatic hydrolysis over acid/alkali hydrolysis because it is less toxic, no toxic by-product is formed, low corrosion, and low energy is required involved [34]. The critical step in bioethanol production is known as “Saccharification” which is converting complex carbohydrates into monomeric units by the action of microorganisms producing these enzymes; these enzymes are called “cellulase /hemicellulose” [63]. Microorganisms implicated in the production of cellulase as reported [56] include; Bacteria- *Cellulomonas*, *Thermomonospora*, *Clostridium*, *Bacillus*, *Bacteriodes*, *Ruminococcus*, *Erwinia*, *Acetovibrio*,

Microbispora, *Streptomyces*; Fungi- *Trichoderma*, *Penicillium*, *Fusarium*, *Phanerochaete*, *humicola*, *Schizophillum*.

However, *Trichoderma* was intensively studied as the best producing cellulase and hemicellulose enzymes [49]. *Trichoderma* is capable of producing two major cellobiohydrolases, five endoglucanases, and three endoxylanases [60]. *Aspergillus* also produces β -glucosidase [64]. The challenge in lignocellulosic biomass-based bioethanol production technology is that the cellulose is expensive and this calls for a need to design pre-treatment technology that could reduce the crystalline nature of the cellulose and remove the lignin [22]. This pre-treatment design could involve the use of chemical and biological processes to better combat the deficiencies at both ends. Also, surfactants have been reported to be an excellent absorbent of lignin by modifying the surface of cellulose and preventing the binding with lignin [11, 24].

3.3.3.2 Fermentation. This is the process in which the product of hydrolysis (sugar) is subjected to fermentation of different microorganisms. There is limited research about the preferred microorganisms that can effectively ferment sugars [65]. However, in selecting the choice of microorganisms for commercial production, it must have an affinity for a broad range of substrate, high yield of ethanol, and throughput must withstand a high quantity of ethanol and temperature. It can survive under a high quantity of ethanol as well and temperature and must resist inhibitors prevailing in hydrolysate with cellulolytic activity [66]. These limitations could be surmounted by the adjustment of some parameters such as optimization of conditions for the process such as elevated temperature and pressure although this can affect the microbes, however, the best condition for their performance could be sought for and thermo-tolerant microorganisms such as *Kluyveromyces marxianus* could be utilized [67]. *Clostridium* sp. and *Thermoanaerobacter* sp. have been implicated to ferment sugars at elevated temperature [68]. Furthermore, using more than one microorganisms known as a consortium could also be considered, this will improve its efficiency more than a particular strain of microorganisms. When using mixed culture for direct microbial conversion, the compatibility of the mixed microbial strain should be observed first. Two different microbes; *Saccharomyces cerevisiae* and *Clostridium shehatae* was used to produce bioethanol using fermentation method, the former fermented hexose at the first phase while the latter fermented pentose sugar with a minimum yield of

ethanol [69]. Indigenous bacteria mostly used in fermentation are *Saccharomyces cerevisiae*, *Escherichia coli*, *Zymomonas mobilis*, *Pachysolen tannophilus*, *Clostridium shehatae*, *Pichia stipitis*, *Candida brassicae*, and *Mucor indicus*. However, *Saccharomyces cerevisiae* has been reported to be the best bacteria for ethanol synthesis from hexose sugars [68]. The best option that could be adopted is the genetic modification of the microorganisms of interest [70]. Reports showed that some genetically modified microorganisms such as recombinant *Escherichia coli* KO11 [71], and *Saccharomyces cerevisiae* ATCC 26603 [44] fermented sugars to bioethanol. Further distillation is carried out on the bioethanol to obtain 95% purity; separation of ethanol from water. Molecular sieves or additives are required to breakdown the sugars to pure ethanol. High energy is required in the distillation procedure with initial ethanol, a concentration of 4% to make it more economical [72]. Moreso, Researchers are on the hunt for utilizing a variety of biofuels that are not solubilized in water to exempt the process of distillation [73].

4.0 Conclusions

Having scope around biofuel and highlights of the process involved in obtaining biofuel from lignocellulose substrate, the pre-treatment procedure which involves the release of the cellulose (the substrate for fermentation to ethanol) from the compact structure of the lignocellulose poses to be the most challenging process [45]. Several methods such as the physical and chemical treatments are mostly expensive and the biological treatments which are relatively cheap are slow and have a low yield. However the biological methods could be most preferred and the limitations can be combated by the redesign of the process; a combination of chemical and biological treatments, optimizing the procedure conditions (temperature and pressure), genetic modification of the microorganisms of interest which should be given maximal consideration.

5.0 Recommendations

Agro-waste conversion for bioenergy production is trending globally. It is expedient to combat environmental problems by transforming to major needs in the environment. Several non-food agro-waste especially the Lignocellulose substrate could be harnessed effectively using biological treatments. Biological treatment will be of great advantage because it is eco-friendly and sustainable and its limitations can however be managed conservatively.

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