International Journal of Science, Engineering and Technology Research (IJSETR)
Volume 7, Issue 8, August 2018, ISSN: 2278 -7798

Challenges and prospects of using Polysaccharides as a Resource for Bioethanol Production

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ABSTRACT:

This review looks into the challenges encountered in edible polysaccharides and lignocellulose biomass use as feedstock for bioethanol production. The current mandate to blend minimum of 10% bioethanol to gasoline and lower the effect of fossil fuel, has led to an intense search for biomass feedstock or technology that would improve the existing ones. Bioethanol production is characterized with high cost of production and the use of lignocellulose has challenges of low product yield due to complexity of structure and inhibition. Currently, more than 80% of the bioethanol produced globally is centered on the use of edible crops such as sucrose and starch containing biomass and thus hasnegative impact on food security. Cassava is the major raw material used for bioethanol production in Nigeria and its use has a negative impact on the cost of garri which is a major food crop in the country. These issues identified are therefore put into consideration and measures are taken to source for non-edible starch biomass for bioethanol production in order to guarantee sustainability of the industry without effects on food security.

Keywords: Algae, Bioethanol, Biomass, Food security, Lignocellulose, Starch, Polysaccharides .

INTRODUCTION

The necessity for energy due to increase in world population and industrial growth has led to high usage of non-renewable fossil fuels [1][2]. The population the world has been foretold to increase by 50% in 2050 which will in turn cause a rise in demand for more energy [3]. The fossil fuel usage has been proposed to increase to 116 million barrel from current 85 million barrel by 2030, which would result to further depletion of the crude oil reserves around the world [4]. In 2011, renewable energy policy network [REN21], predicted that about 78% of energy consumed globally comes from petroleum, 3% from nuclear energy while 19% came from renewable energy sources such as wind, solar, biomass, hydrothermal andgeothermalenergies.The intensive use of fossil fuels have deleterious effecton the global climate due greenhouse gases emission principally carbon dioxide [5] [6]. In 2013, the global carbon dioxide emission exceeded 11,830 million metric tonnes through an intensive use of petroleum [7]. The transportation sector are the most consumers of energy, consuming over 60% of the entire world oil and consequently emitting more than 60% CO and 19-23% CO_2 globally with emission further predicted to be 80% higher by 2030 [8, 9, 10]. An estimate of 8.908×10^{-3} and 1.015×10^{-2} metric tons of CO_2 are emitted from consumption of a gallon of gasoline and diesel respectively [11]. In this light, Howey [12] predicted that CO_2 emission can only reduce below 8kg whena switch from petroleum fuels to low-carbon alternatives is implemented. The transportation sector currently, depend on petroleum that is mainly produced in the politically unstable countries in the world like Syria, Iran, Libya, Sudan and Nigeria where political instability affects the exploration/ production of petroleum products thus causing fluctuations in both cost and availability of the products [13][14]. The development of an energy system that is renewable, sustainable, efficient, cost-effective and environmentally suitable would help to reduce or replace the reliance on fossil fuels while maintaining the economic security and mitigating the consequences of greenhouse gases and global warming in the world [1][14].

Biofuels have received extensive attention and possess great potential as a suitable alternative to petroleum based fuels and are produced from varieties of biomass [16][17]. Biomass is seen as an interesting energy source for several reasons: a)

Reduction of greenhouse gas emission and subsequent reduction of global warming and climate change. b) Resources are locally available and its conversion is feasible. c) Contributes to sustainable community development and job creation. d) Reduction of agricultural and industrial waste by recycling them into biofuels. e) It is renewable [18][19]. Biofuels are generally expensive, to make them sustainable and cost effective substitute to fossil fuel, it is vital to develop a non-food crop as feedstock and tailor them to grow on marginal land with low agronomic inputs and without putting out of place the agricultural land used for food production [20]. Starch and lignocellulose are abundant natural and renewable resources envisaged to provide a large amount of fuels, chemicals, and materials globally [21]. Lignocellulose based biofuels have been predicted to replace about 30% of the petroleum presently consumed by the USA, if feedstock such as forest residues (sawdust, wood bark), agricultural residues (corn stover), and herbaceous grass (Switch grass) are used [22][23][24]. Other agricultural crops that have been utilized include wheat straw, sugar bagasse, rice hull, corncob,corn fiber and oat hull among other. Lignocellulose biomass is not a food source, thus it offers a potential benefit in ethanol production (no food vs fuel conflict) unlike starch-based biomass. Nevertheless, lignocellulose biomass provide less than 2% of the world over-all bioethanol production as a result of the cost requirement for pretreatment and detoxification tied with product yield when compared to starch-based biomass which made to be less economically viable [25].

Major industrial productions of bioethanol are based on the usage of sucrose containing or starch-based crops such as sugarcane, cocoyam, corn, barley, wheat, cassava and potato. These feedstocks are chief food crops and their use for producing bioethanol poses a great danger to food security, especially when they are fully employed for bioethanol production. In addition, the use of edible biomass accounts for 40-75% of the over-all cost of ethanol production thereby making the product expensive [1][26]. Bioethanol has found use as an oxygenate fuel additive. The presence of ethanol in conventional fuel increases the octane number and reduces methyl tertiary butyl ether (MTBE) which is a toxic, octane-enhancing additive[2][27]. The oxygen content in ethanol molecules also helps in reduction of carbon dioxide emission and non-combusted hydrocarbons [28]. It has been predicted that ethanol is 15% higher in efficiency than gasoline in optimized spark-ignition engines and is almost equal with diesel on the over-all transport efficiency in compression-ignition engines [29]. It is also envisaged that a given volume of ethanol can provide enough energy to drive about 75-80% of the distance as the same amount of gasoline, even though bioethanol only have around two-thirds energy content [22]. The high cost associated with ethanol production has become a factor limiting the intensive utilization of ethanol as an Oxygenate in gasoline in combustion engines. In this regard, several subsidies by governments have been provided to promote development and also meet the global mandate of 10% ethanol blend in gasoline [2].

Thus review summarizes the present challenges encountered in the production of biofuels (bioethanol) from different generation of biofuels. These challenges are in the area of (a) edible feedstock utilization, (b) food security (c) cost of production and (d) conversion technologies. In order to overcome these challenges, non-edible biomass source with higher product yield must be sourced for.

GLOBAL BIOETHANOL PRODUCTION

The Global Renewable Fuels Alliance (GRFA) had in 2013 forecast that global fuel bioethanol production will surpass 90 billion litres in 2014. The global bioethanol output reached 99,6 billion litres in 2016 which shows an improved production from 96.5 and 88.7 billion litres in 2015 and 2013 respectively [30]. Over 80% of global bioethanol is currently produced by fermentation of either corn starch or sucrose (sugarcane), with the U. S.A, Brazil and China toping the chat as the largest producers of bioethanol as presented in figure 1.

U.S.A is the leading producers of ethanol, producing more than 57% of the overall ethanol production globally [28]. Ethanol production hit 15.329 billion gallon in 2016 with an increase of 3.5% when compared with 14.807 billion gallon in 2015 [31]. The U.S. Energy Information Administration’s (EIA) State Energy Data System for ethanol production shows that among the 28 biorefineries, state of Iowa contributed more than 26% of the overall US ethanol with an average of 3.91 billion litres produced between 2015 and 2016 [31]. Other large producers includes Nebraska and Illinois with an average of 1.83 billion gallons and 1.28 billion gallons, representing 13.4%, and 9.4% of U.S. production respectively. While Minisota and Indiana account for an average of 1.12 billion gallons and 0.93 billion gallons representing 8.2% and 6.8% between 2010 to 2014 U.S. ethanol production. In 2016, Iowa together with these four states made up 62.2% (Figure 2) of the estimated ethanol production in the U.S.A [31].

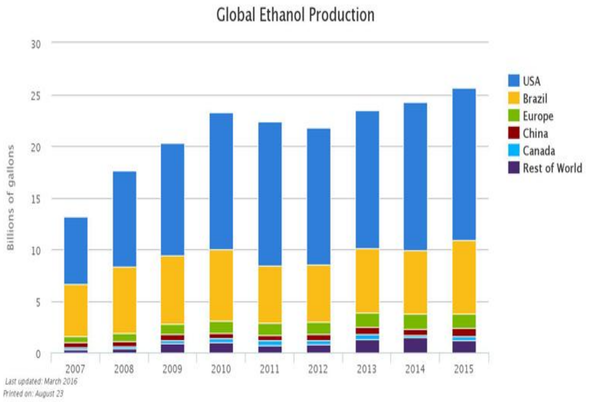

Figure 1: Global Ethanol Production.
Sourse: Renewable Fuel Association, [30]

Gasoline blended with 10% bioethanol (E10) is the major transportation fuel used up in the U.S. E15 and E85 are other avaliable blends but their consumption is limited by infrastructural and other constrains [33]. Corn is the most utilized raw material (feedstock) for ethanol production in the U.S. The primary U.S. staple crops, accounting for over 95% of entire feed grain production and use [34]. Corn as a raw material is processed into various domestic and industrial products which includes beverage, starch, corn oil, industrial alcohol, sweeteners and fuel ethanol. The risk encountered with corn usage for ethanol production includes: a) increased food prices; b) high cost of production due to cost of the feedstock: c) the environmental impact of increased agriculture; d) changes in land use [1].

Inline with the Renewable Fuelstandard(RFS) mandate for the U.S.A, renewable energy mandate of 5% for power and heat energy, 20% for transportation fuel, and 25% for chemicals and materials were made by the US Department of Energy(DOE) in conjunction with US Department of Agriculture (USDA) to be implemented by 2022. This means that approximately 36 billion gallons of liquid bio fuels for transportation are required to meet this goal where 15 billion gallons of these fuels will come from starch-based biomass, where as there maining 21 billion gallons will be produced via lingo cellulose biomass[32].

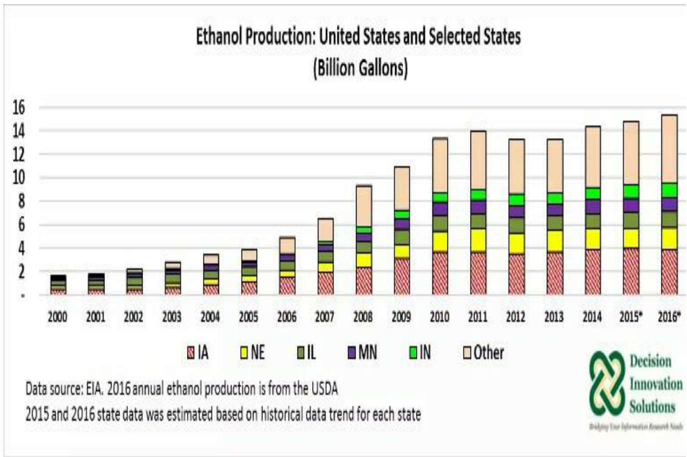

Figure 2. U.S Ethanol Production.
Source: EIA, [31].

Brazil is the second leading producer of ethanol accounting for 28% of the entire ethanol production globally [30]. Since 2010, Brazil ethanol production has gradually increased with an annual production of 7.29 billion gallon in 2016 [30]. Sugar cane is the major feedstock for ethanol production. Sugar bagasses also have been utilized in ethanol production with an annual yield of 1.58 billion gallon (6 billion litres) of the over-all ethanol production in 2016 [35]. In Brazil, ethanol-use mandate remains unchanged at 27 % (E27) after initial ethanol-gasoline average blends of 18% to 25% between 2011 to 2014 [35]. Government policies, such as tax incentives and mass production of flexible flex automobiles (FFAs) have played a vital role in increasing the consumption of ethanol in Brazil. Brazil is the major producers of refined sugar, thus ethanol production as an automotive fuel depends on critical factors such as: i) the world sugar price, ii) the size of sugar cane crop, iii) the exchange rate, iv) tax policies and v) Government controlled price. Thus refined sugar production takes higher priority than ethanol production. These factors influence the total ethanol production as the crop size and price determine the size of the crop that would be utilized for ethanol production [35].

The European bioethanol production accounted for 5% of the over-all ethanol with a production yield of 1.38 billion gallon in 2016 [30]. France is the top producer in Europe with 9.7 billion litres annual production. However Germany is close second with 9.5 billion litres. The main materials for the production of bioethanol are starch-based crops such as wheat, corn and sugar beet. Wheat is frequently used in north Western Europe, while corn is predominantly used in Central Europe. Sugar beet is mainly used in France, Belgium, Germany and the Czech Republic for bioethanol production [36]. In 2015, the European Commission (EC) officially announced a 7% limit on food-based biofuels thereby reducing future production from these first generation biofuels. Incentives have been given to encourage the use of second generation biomass but the rate to commercialize cellulosic ethanol is slow due to issues associated with production [36].

China is the fourth in the order of ethanol producer globally after the United States, Brazil and European Union. China accounted for over 3% of global ethanol production with 0.84 billion gallon (3.19 billion liters) in 2016 [30]. The 2016 ethanol production shows a 2.6% increase from an expected 3.08 billion litres in 2015. Corn and cassava are the major feedstock accounting for 70% and 25% of Chinese ethanol production respectively while Molasses accounts for the remaining 5% [37]. There are seven licensed commercial ethanol plants in China using corn, wheat, cassava, and sweet sorghum, molasses and corn cob. The swift growth of corn-based bioethanol production, coupled with concerns over food security, prompted the government to place strict regulation on corn-based use[37]. Instead non-grain-based biomass feedstock like cassava and sweet sorghum were encouraged. However, feedstock availability is a big challenge as 70% of the cassava is imported from South-east Asia. Increases in the price of cassava imported will result in substantial decreases in the profitability of ethanol produced from the cassava-based plants. The Chinese government also set a goal of producing 300 million tons of ethanol from cellulose by 2020. However, challenges in transporting feedstock combined with limited progress in cellulosic technology are hindering industrial process of cellulosic ethanol [37]. China has an E10 mandate but Subsidy removal from ethanol hampers the implementation and consumption growth in all provinces of China [37].

Africa as a continent is currently producing less than 1% of the whole ethanol production globally as reported by the Renewable Fuel Association, [38]. Though Africa was never a major contributor of greenhouse gases, several ethanol blend mandates are binding on different countries with Angola, Kenya, Malawi, Mozambique, and Nigeria all having an E10 mandate while Ethiopia, South Africa and Zimbabwe have E5, E2 and E15 respectively [39]. Moreover, to meet up with the global ethanol blend mandate, there is need to intensify bioethanol production in Africa.

ETHANOL PRODUCTION AND ENERGY POLICIES IN NIGERIA

Nigeria currently has an E10 blend mandate which is currently sustained by ethanol importation. The National total consumption of gasoline stood at 55million litres daily which are approximately 20 billion litres per annum [40]. The Nigerian Biofuel Policy and Incentive projected an ethanol requirement of 1.3 billion litres per annum to attain the E10 blending rate with further increase to 2 billion litres by 2020 [41]. With a population growth of 3.5% per annum from an estimated national population of 182 million people [42], the continuous ethanol importation therefore has negative impact on the economic development of the country.

The Energy Commission of Nigeria set up a national energy policy with the aim of achieving the following objectives;

i. To steadily reduce the nation's dependence on fossil fuels while creating a commercially sustainable industry that can create sustainable domestic jobs.
ii. To steadily lower environmental pollution.
iii. To firmly establish a blooming biofuel industry usingagricultural products as a way of improving the quality of automotive petroleum-based fuels in Nigeria.
iv. To promote job creation, rural and agricultural development, and technology acquisition and transfer.
v. To offer a framework capable of enticing foreign investment in the biofuels industry.
vi. To reduce the functions of various tiers of government in order to guarantee a well-ordered development of the biofuels industry in Nigeria.
vii. To involve the participation of the oil and gas industries in the development of biofuels in Nigeria [11][43].

The driving Policies to guarantee that the objectives are achieved include;

i. The nation shall improve on the link between the agricultural sector and the energy sector.
ii. The nation shall encourage the blending of ethanol(biofuels) as a component of petroleum-based fuels within the country as requirement for all automotive use. The blends shall include the procedure for upgrading petroleum-based fuels.
iii. The nation shall promote investments in the biofuel industries.

iv. The nation shall grant biofuels pioneer status for an initial 10year period with the possibility of additional 5-year extension.

v. The nation shall encourage the development of an industry of which a sizable portion of raw materials used by biofuel plants will be produced by large – scale investors and out growers.

vi. The nation will make sure that the biofuel industry benefit from carbon credit [11][43].

To develop biofuel in Nigeria and attain the E10 blending target, the government in 2005 established the Automotive Biomass programme (ABP) with a directive to Nigerian National Petroleum Corporation (NNPC) to facilitate the development of two major biofuels; ethanol from edible cassava and sugarcane, and biodiesel from oil palm [11][41]. This directive was meant to integrate the agricultural and petroleum downstream sectors for the sole aim of revenue diversification, job creation, agricultural productivity while meeting the energy need of the nation and addressing the impact of climate change in agreement with the Kyoto protocol [11][41]. The program is anticipated to attract grant from different international organizations with €70,000 already received from Germany Renewable Energy, Energy Efficiency partnership (PEEEP) [11]. Allied Atlantic Distilleries Limited (AADL) is the only major ethanol distillery in Nigeria with a production capacity of 10 million litres per annum (which is 1% of the volume needed in the country) with a projected target of 25% of Nigeria's ethanol need by 2022 [44]. AADL is the first cassava-based bio-refining industry in Africa to commence the production of extra neutral alcohol (ENA). The plant utilizes approximately 240 tons of cassava per day (approximately 87,600 tons per annum) for the production of ethanol which is supplied to pharmaceutical and beverage producing industries [44].

Nigeria is the largest producer of cassava in the world, producing about 50 million tonness per annumfrom around 3.7 million cultivated areas [45]. This figure shows an improved yield of 45 million tons obtained from 3.48million hectare area of cultivated land in 2011 according to the Nigerian bureau of statistics [46]. Cassava is a major food source in Nigeria; its local dishes include garri, fufu, eba, tapioca, cassava cake and other variety of modified cookies. A policy has been put in place for the use of 40% cassava flour in bread making [41]. Apart from its use as a food source, cassava is one of the main commodities used for foreign exchange earning where one million tons of cassava chips were exported in 2012 [46]. To meet up the projected 2 billion volume of ethanol by 2020 in Nigeria, more tons of cassava would have to be used. This will have a direct impact on food security in Nigeria and the global sustainable goal on ending hunger and achieve food security would not be met. Thus to sustain bioethanol production in Nigeria, other non-edible biomass must be used.

GENERATIONS OF BIOFUELS.

First Generation Biofuels.

First generation biofuels (bioethanol) are ethanol produced from sucrose-based feedstock (sugar cane, sweet sorghum and sugar beets) and starch-based feedstock like corn, wheat and cassava [47]. Currently, over 80% of the overall bioethanol production worldwide are from edible crops which includes; corn (USA), sugar cane (Brazil) wheat (European Union) and cassava (Thialand, Nigeria, China) [15]. Corn and sugar cane account for over 75% feedstock used for bioethanol production globally as presented in Figure 3. The increase in the food crops use, such as sugar and starch crops as resource for ethanol production has different global dimensions; on one hand it improves energy safety through high ethanol yield thereby encouraging diversification of energy sources, on the other hand it results in shortages of strategic food resources globally. The utilization of food crops may cause difficulties in balancing the global grain market, feed crops and oil crops. For instance, the higher demand for corn from the bioethanol industry in the US in 2007/2008 season caused the crops to change to the disadvantage of soya bean – the basic fodder crop, which in turn caused the fodder prices to rise and consequently the food prices to rise [48, 49].

An essential factor for the assessment of a biomass(crop) for ethanol production is the availability of the feedstock and land requirement[1].

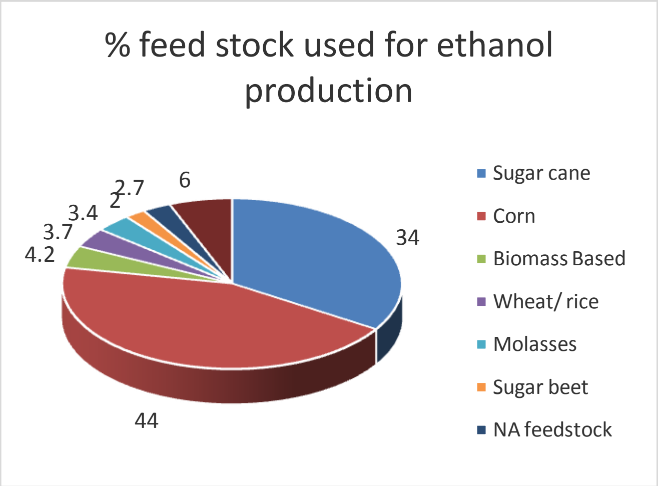

Figure 3. Feedstock used for Ethanol Production
Source: Balan, [15]

Studies carried out shows that sucrose-based biomass have higher production yield on metric tonnes per hectare than starched based biomass with yields of 62 - 122 tons ha^{-1}, 54 - 111 tons ha^{-1} and 25 - 62 tons ha^{-1} for Sugar cane, sugar beet and sweet sorghum respectively while starch-based crops such as corn, wheat and cassava have yield of 6 - 10 tons ha^{-1}, 1.5 - 3.0 tons ha^{-1} and 20 tons ha^{-1} as shown in Table 1 [1][47]. Table 1 shows some parameters for feedstock suitability for ethanol production. The choice of a feedstock especially from edible crops for ethanol production is very vital considering that the price of the raw materials which makes up significant percentage of the over-all production cost. It is estimated that the price of feedstock represents 60–75% of the entire ethanol production cost [1]. Studies have shown that ethanol production from sugar cane (USDollar 0.19-0.23/L) in Brazil is cheaper than dry corn milling (US Dollar 0.23-0.36/L) in the U.S.A [1][50]. The production cost of ethanol from sugar cane is cheaper due to high yield of the crop and less conversion process than corn ethanol [47].

Cassava is the most utilized feedstock for ethanol production in Nigeria. Ogbonna and Okoli [50], evaluated the economic feasibility of ethanol production from cassava tuber in Nigerian rural communities. The findings show that total investment cost of ₦7, 500,000 (US$ 46.875) was utilized for ethanol production with 71.73% of the total cost arising from the cassava tuber which stood at ₦10, 000/ton. The study also shows that the cost of producing ethanol per litre stood at ₦102.5/L (US$0.641/L) which is less profitable when compared to market price of ethanol (US$ 0.597-0.748/L). The process was forecast to be profitable in Nigeria, only if the price of cassava tuber per ton is reduced to ₦5, 000 (US$ 31.25/ton). This prediction was not met as the cost of cassava increased by 150% from ₦10,000 in 2012 to ₦25,000 in 2013 [51]. This is attributed to extraordinary demand for cassava by local industries coupled with cassava chips exportation from the country; without an increased output of cassava from the total 54 million metric ton of 2012 [11][51]. According to Business Day [52] report of March, (2017), the price of garri, an edible food from cassava in Nigeria rose by 28% following the drop in cassava production by 40% of 2016 yield.

Balogun and Salami, [53] carried out a survey on the effect of biofuel activities in three geo-political zones in Nigeria, and various effects were found on local livelihood, food security, land access and use, economic development as well as environmental, infrastructural and population growth. The authors, thus emphasized on the need for government to implement policies that would, (a) ensure that food crops suitable for human consumption is not used for biofuel production. (b) Allotment of land to biofuel investors within communities to grow their feedstock. (c) Communities as well as biophysical environment are positively affected. Ben-Iwo [11] proposed that the transformation of Nigeria to a bio-based economy can be sustained if research gaps, policy shortfalls and sustainable issues are sorted out. Therefore, for E10 blending target for 100% domestic refining to be accomplished by 2020, non-food biomass within the country must be utilized.

Although much of bioethanol is produced from corn, wheat and sugar cane, research is still on going with several starch biomass. Ogali*et al.* [54] evaluated the potential of cocoyam as source for ethanol production. Studies were carried out with four species of cocoyam; (Xanthosoma species and Colocasia species) and the result showed that cocoyam especially the Colocasia specie (edeofe) is a promising feedstock for ethanol production. The authors therefore, encouraged local farmers on cultivating more of the specie since it is mainly use as thickener for soup. Melo*et al.* [55] carried out both acid and enzymatic hydrolysis of castor bean cake (CBC); the result showed that CBC starch was hydrolyzed with 91.4% of efficiency. The authors predicted an ethanol production of 270 L per tonns of processed CBC on dry basis.

Apart from ethanol production, starch-based crops like corn, cassava, and potato are the key source of

Table 1 Parameter for the assessment of feedstock suitability for bioethanol production.

Feedstock	**Annual Yield ton/ha**	**Specific conv.Rate to Ethanol L/ ton**	**Annual Ethanol yield L/ha**	**Output/input rate**	**Cost US$/kg**	**Cost of production of anhydrous Ethanol US$/l**
Sugar cane	70-122	68-70	5345-9381	2.5-10.2	0.010	0.1980
Sugar beet	66-68	80-100	5000-6600	1.9	0.170	0.4910
Corn	6-10	350-460	6600	1.34-1.53	0.076	0.2325
Wheat	1.5-3.0	340-370	1020-3214	2.24-2.84	0.188	0.402
Potato	17-20	100	1700-2000	----------	0.020	1.330
Sorghum	1-6	340	340-2040	----------	0.149	0.386
Sweet sorghum	25-35	68-86	1700-9030	----------	--------	--------
Cassava	20	180	3600	--------	-------	
Straw	1.93-3.86	170-261	------	--------	--------	0.651

Source: Mojovic [1]

Table 2. Non-conventional source of starch (% dry basis)

Popular Name	**Specie**	**Type**	**Starch content (%)**
Amaranthus	*Amaranthuscruentus*	Cereal	57.5
Annalto	*Bixaorellana L*	Seed	40.0
Babassu	*Oribignyaphalerata mart*	Palm	60.5
Breast fruit	*Artocarpusatilis*	Fruit	64,5
Buckwheat	*Fagopyrumtataricumgaertn*	Pseudocereal	80.5
Chayote	*Sechiumedulesw*	Tuber	60.0
Chestnut	*Castaneasativa*	Nut	93.2
Chick pea	*Carer arieinum L*	Legume	34.75
Ginger	*Zinglber officials roscoe*	Rhizome	85.0
Ginkgo Biloba nut	*Ginkgo Biloba L*	Grass	32.0
Horse chestnut	*Aesculusindica*	Nut	38.3
Kudzu	*Puerarialobata*	Root	99.5
Lentils	*Lens culinaris*	Legume	51.7
Lima beans	*Phaseoluslunatus*	Legume	37.5
Mango ginger	*Curcuma amedaroxb*	Rhizome	43.0

Palmirah	*Borassusflabellifer L*	Palm	38.34
Pea	*Pisumsativum L*	Legume	40.00
Peruvian carrot	*Arracariaxanthorrhiza Bancroft*	Root	80.0
Pine nut	*Araucaria angustifolia*	Pine	72.0
Ramon	*BrosimumalicastrumSwartz*	Fruit	92.57
Tef	*Eragrostistef (zucc) trotter*	Grain	75.0
Tumeric	*Curcuma long as L*	Rhizomes	76-86.84

Source: Santana*et al* [56]

industrial starches. In 2012, the cost of starches and their products stood at US$ 51.2 billion and is further projected to reach US$ 77.4 billion by 2018 giving rise to an annual growth of 7.1% [56]. Conventional starches are obtained from cereals (60-80%), tubers (60-90%) and legumes (25-50%) and their use is based on their physicochemical characteristics which depend on the nature and source of the starch [57]. Starches are used as binders in paper and textile industries, drug fillers in pharmaceutical industries and thickeners in food industries. Santana*et al*. [56]evaluated the feasibility of non-conventional starch-based crops as presented in Table 2; which shows appreciable starch content as substitute to conventional starches for various industrial applications.

Therefore, to align with the sustainable development goal of combating climate change and ending hunger through sustained agriculture, the use of cassava and other edible crops as feedstock for ethanol production should be reduced and alternative non-edible crops should be harnessed. The use of non-edible crop will ensure sustainability of the bioethanol industry, reduce cost of production, convert waste to wealth as well as combat climate change and ensure food security.

Second Generation biofuels

Second generation biofuels are biofuels produced from lignocellulose biomass. These biomass are obtained at low cost from variety of resources such as forest residues, municipal or industrial waste. It is made up of about 80% organic matter which consist of polymers; lignin, cellulose and hemicellulose. Cellulose and lignin are the most and second most abundant natural resources respectively and their demands are on the increase due to their environmental friendly and biocompatible nature, making them useful in biomaterial and biomaterials [21]. Llignocellulose is envisaged to provide substantial amount of fuels, chemicals, and materials since they are naturally abundant and renewable raw materials in the world [21]. Annual lignocellulose production worldwide has been predicted to be 10–50 billion dry tonnes, given rise to about half of the world biomass yield [22][26]. Lignocellulose biomass is not a food source, thus it offers an environmental benefit in ethanol production (no food vs fuel conflict) than starch-based biomass like corn. Lignocellulose biomass provides considerable advantage as a feedstock for biorefineries because they are less expensive than starch or sucrose based feedstock [2]. Summarizes in Table 3are some of the major lignocellulose biomass and its components used for bioethanol production.

Nevertheless, the processing of lignocellulose biomassespecially from agricultural residues with differentcompositions, poses greater challenges than the bio-conversion of starch or sugar cane to ethanol [59]. This is attributed to the in-built recalcitrance of the lignocellulose biomass to enzymatic and microbial deconstruction, caused partly by the crystalline nature of cellulose which has close association with lignin and hemicellulose in the plant cell wall [60][61].

Pretreatment is therefore an important step in the conversion of raw lignocellulose biomass to a condition amenable to enzymatic degradation and subsequent fermentation for bioethanol production [60][62]. The importance of the pre-treatment process is to break down the structure of lignin and alters the crystalline structure of cellulose, so that acids catalysts or enzymes can have easy access to hydrolyse the cellulose [23]. Obstacles in most pretreatment route includes;inadequate separation of lignin and cellulose, by-products formationwhichinhibit fermentation of sugars by microorganism, high chemicals and/or energy consumption, and considerable waste production [62]. Physical, physical–chemical, chemical and biological processes are already developed and utilized in the pre-treatment of Lignocellulose biomass [2][58,]. The main pre-treatment methods include;

Table 3 Composition of Lignocellulose biomass on dry bases.

Lignocellulose biomass	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Hard woods stems	40-55	24-40	18-25
Soft word stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Paper	85-99	0	0-15
Grasses	25-40	35-50	10-30
Wheat straw	30	50	15
Switch grass	45	31.4	12
Cotton seed hairs	80-95	5-20	0
Leaves	15-20	80-85	0
Coastal Bermuda grass	25	35.7	6.4
Waste paper from chemical pulp	60-70	10-20	5-10

Source: Sun and Cheng [58]

Physical Method

In this process, the Lignocellulose biomass arecomminuted by chopping, milling or grinding so as to reduce the crystallinity of cellulose [63]. This form of pre-treatment is usually done before subsequent pre-treatment methods. Factors such as scale up, depreciation of equipment capital and operating cost are issues associated with this process and it depends on the particle size and biomass characteristics [62]. Pyrolysis and ultrasonic processes are other kind of physical pre-treatment that are carried out at high temperature and by irradiation which are characterised by high energy (power) consumption thereby increasing the cost of production [62][64].

Physical-Chemical Method.

This method of pre-treatment is considered to be more effective than the physical method. Steam explosion and thermo-hydrolysis or liquid hot water (LHW) are the most investigated methods of this type of pre-treatment [64]. In steam explosion method, the biomass is pre-treated under high pressure saturated steam which leads to conversion of the hemicellulose and lignin fragment into oligomers at a temperature of 160-260^{O}C and pressure of 0.69-4.83MPa [63][64]. This method is envisaged to be one of the most cost-effective for hardwood such as poplar, oak, birch, maple and agricultural residues, but is less efficient for softwood like pine and cedar [64]. Grous*et al*, [65] reported that enzymatic hydrolysis of 90% efficiency was achieved in 24 hours for Poplar chips pre-treated by steam explosion, compared to only 15% hydrolysis of untreated chips. Low energy requirement and no environmental and recycling cost are the benefits of steam-explosion pre-treatment in comparison to mechanical comminution which require 70% more energy than steam explosion method of the same particle size, though factors such as resident time, temperature, moisture content and chip size affect the whole process [63, 64]. Formation of degradation by-products which inhibit fermentation processes is the limitation of steam explosion [66].

Thermo-hydrolysis or liquid hot water (LHW) is one of the most promising method and involve biomass pre-treatment with water at high temperature and pressure [23]. In this method, 40%-60% of the entire biomass is dissolved giving high recovery rate with 4–22% of the cellulose, 35–60% of the lignin and all of the hemicellulose being removed without generation of inhibitors [62][67][68]. Perez *et al*, [68]Studied the effect of LHW process parameters such astemperature (170- 200 °C), solid concentration [5% - 10% (w/v)], residence time (0 - 40 min) and pressure applied in the reactor (30 bar), on wheat straw pretreatment. Pretreatment effectiveness was determined based on the constituents of the liquid and solid fractions achieved after filtration of the pretreated biomass.The solid fraction was subjected to enzymatic hydrolysis using commercial cellulaseand its susceptibility is determined. The research therefore shows thatthe pretreatment time for hemicellulose derived sugar recovery in the hydrolysate depends on temperature; enzyme hydrolysis yield was enhanced as both time and temperature were increased. Maximum enzyme hydrolysis yield was reported to be 96g of glucose per 100g of potential glucose in the pretreated residue.

Ammonia fibre explosion (AFEX) is another form of physical-chemical process, in whichfeedstocks are treated with liquid ammonia at high temperature and pressure [62][64]. A typical AFEX process is carried out with 1-2 kg ammonia/kg dry biomass at 90 °C for 30 min [62]. Greater lignin content is reduced and some hemicellulose are removed while decrystallising cellulose. Limitation of this process is the cost of ammonia, as ammonia recovery drives the cost of the pretreatment [69].

Chemical Method

Chemical Method involves the use of chemicals which includes; acids, alkalis, ozone, organic solvents and peroxide in the pre-treatment of Lignocellulose biomass for ethanol production. Dilute acids are the most investigated method of chemical pre-treatment because it is inexpensive, less corrosive with the ability to effectively remove almost 100% hemicellulose [63][70]. Among all the inorganic acids, sulfuric acid is wildly utilized for biomass pre-treatment. It has been used for corn stover [71], sugar cane bagasse [72] and spruce [73]. Also, nitric acid [74], hydrochloric acid [17] and phosphoric acid [75] have all been utilized for pre-treatment of biomass. The limitation of acid hydrolysis is the degradation of sugars and the formation of undesirable by-products such as 5-hydroxymethylfurfural, furfural, acetic, levulinic and formic acids and phenollic compounds which inhibit fermentation process [2][15][64][76].

Alkali pre-treatment refers to the use of bases such as sodium hydroxide solutions to remove lignin and different uronic acid substitutions on hemicellulose, thereby increasing the accessibility of enzymes to cellulose [77]. The addition of bases causes increase in internal swelling, reduction of the degree of polymerization and crystallinity of the biomass [64]. In alkaline pre-treatment, the efficacy of delignification hinge on the biomass lignin content [58]. Studies have revealed that alkaline pre-treatment is more effective on agricultural residues and herbaceous crops than on wood materials [78]. In organosolvprocess, different types of organic solvents likeacetic acid, peracetic acid, methanol, ethanol and acetone, have found use for the pretreatment of biomass [79]. In organosolv process delignification and prehydrolysis are carried outsimultaneously on the lignocellulose biomass by the organic solvents and, usually, dilute aqueous acids or bases are used as catalysts to break the inner lignin and hemicellulose bond [58][63][80]. Low-molecular-weight alcohols such as methanol and ethanol have been utilized due to ease of recovery and low cost for organosolvpre-treatment [81]. Pan *et al*, [82] carried out an organosolov pre-treatment of Poplar with aqueous ethanol for the conversion of the biomass into ethanol. The Poplar chips was fractionalized into a cellulose-rich solid fraction, an ethanol organosolv lignin (EOL) fraction, and a water-soluble hemicellulosic sugar-rich fraction, as well as sugar by-products, degraded lignin, and other components.

Several pre-treatment methods were carried out to compare the effectiveness of a particular method for biomass conversion. Silverstein *et al*, [83]studied the effectiveness of sulfuric acid, hydrogen peroxide, sodium hydroxide and ozone pre-treatment proceduresfor the conversion of cotton stalks to ethanol. The result reveals that significant lignin degradation and high sugar yield were achieved with H_2SO_4, NaOH, and H_2O_2 pre-treatments than ozone and hence the cotton stalks were hydrolyzed more freely by Celluclast 1.5 L and Novozym 188. Sulfuric acid methodgave the highest xylan reduction with 95.2% (for 2% acid, 90 min, 121 °C/15 psi) and the least cellulose-to-glucose conversion of 23.9% during hydrolysis. Sodium hydroxide pre-treatment gave the highest level of delignification with 65.6% (for 2% NaOH, 90 min, 121 °C/15 psi) and cellulose conversion of 60.8%. Hydrogen peroxide pre-treatment gave a lower delignification of maximum 29.5% (for 2%, 30 min, 121 °C/15 psi) and cellulose conversion of 49.8%. Whereas, Ozone did not produce any significant change in xylan,glucanor lignin content over time. Wyman *et al*, [24]carried out studies on different pre-treatment processes for corn and predicted that different methods yield different results, thus the choice of any technology for anybiomass depends solely on the components of the biomass material that required pre-treatment. The most suitable pre-treatment technology used for a particular lignocellulose biomass depends mainly on its composition and the by-products generated as a result of the pre-treatment method [63]. The cost associated withpre-treatment methods significantly affect the overall costs of ethanol production [63].

Biological Method.

Pre-treatments with microorganisms such as brown, white, and soft rot-fungi are utilized to degrade hemicellulose and lignin. The merit of biological pre-treatments processes are low energy requirement and mild operation conditions. Nevertheless, the rate of biological hydrolysis is usually very slow, and therefore requires long residence times [58][64].

Recent studies show that the biofuels production costs from second generation biofuels (lignocellulose) are two to three times more expensive when compared to fossil fuels on energy equivalent basis [15][84]. The high product cost is attributed to the fact that no efficient process has been established when using lignocellulose biomass as feedstock to overcome the challenges of inhibition in the whole process [15]. To reduce the production cost, several challenges arising from the conversion of the lignocellulose biomass to biofuels and chemicals need to be resolved [85][86]. The challenges of second generation biofuels are categorised in the areas of (a) feedstock production, (b) feedstock logistics, (c) development of energy efficient technologies (pre-treatment, enzyme hydrolysis, and microbial fermentation), (d) co-products development, (e) establishment of biofuel and biochemical standards, (f) biofuel distribution, (g)environmental impact minimization and (h)societal acceptance [15]. To address all these challenges expertise in agronomy, biomass logistics, biomass conversion, process engineering, chemistry, conversion technology, genetic engineering, microbial fermentation, economics, and environmental science are vital to cut the cost of ethanol production when using lignocellulose biomass [15]. Although pre-treatment may account as the most expensive route in biomass-to-fuels conversion, it offer greater potential for improving the efficiency of production and lowering of costs can be achieved through further research and development [22][62][63].

Third Generation biofuels

Algae-based biofuels, known as the third generation biofuels recently are recieving a lot of attention as a new energy source of the future, sustainable, and capable to reduce dependence on fossil fuels [87][88]. Various starch and cellulose containing algae have been predicted to be a potential source for bioethanol production. These algae are characterized with several advantages which include; (i) they are non-food source therefore, no conflict with food crops. (ii) Grows on areas unsuitable for agriculture. (iii) Yield over 30 times more energy per unit area than other biofuels (iv) Characterized with fast growth needing only water, sunlight and carbon dioxide. (v) Consumes huge sum of carbon dioxide thus, reducing greenhouse gases significantly [88][89][90][91]. Carbohydrate content of different percentages of macro-algae has been reported with green algae having 25-50%, red algae (30-60%) and brown algae (30-50%). Algal species with the highest polysaccharide content are Porphyra (40-76%), Ascophyllum (42-70%) and Palmaria (38-74%) [87]. Thepercentage carbohydrate content of some algal species are presented in Table 4. Studies have revealed that macro-algae such as seaweed have very low or no lignin content when compared to lignocellulose biomass [88][92]. The lower lignin content thereby enhances easy conversion of the carbohydrates to ethanol per hectare of cultivated area than other biomass as shown in table 5.Murata*etal*,[92]evaluatedtheethanolproductionofdifferentspeciesofseaweed,theresultshowsthatthereishighconversionratewithredseaweedgiventhehighestyieldof55.0g/Lwhilegreenseaweedgavetheleastyieldof27.5g/L.Theauthorspredictedahigherethanolyieldifallothercarbohydratecomponentsapartfromtheglucanunitscanbeutilizedforethanolproduction.Scholz*etal*,[93]investigatedtheacidhydrolysisofmicro-algalstarch;theresultshowsamaximumethanolproductionrateof44%fromsugarsubstrateof14mL/ghatfermentationperiodofabout24h.Themaximumobservedconcentrationofethanolwas0.87%(m/v)andtheyieldcoefficientofethanolfromglucosewas0.44(g/g).

The most surprising finding of the research was the apparent lack of fermentation inhibitors in the hydrolysis product of the crude extract of algal starches, as demonstrated by the high yield of ethanol from substrate. This therefore, offers a great advantage in comparison to hydrolysis of lignocellulosic feedstock, which produces fermentation inhibitors.

Themajordrawbacktoalgaebiofuelproductionisintheculture ofthebiomass.Theopen-pondsystem,thoughcheapandaccountfor98%ofthecommercialalgaeproductionissusceptibletoothermicrobialattackwhichcanreducethetotalbiofueloutput[91].Theclosedsystemismuchmoreexpensive,andsuffersfromoperatingchallengessuchasoverheatingandcouldnotbescaled-upbeyondhundredsquaremeters.

Inaddition,thecostofalgaeproductionperhectarewasvaluedtobeUS$100,000.Moreover,hundredsofhectaresarerequiredforlargescalebiofuelproductiontherebymakingtheentireprocesslessviable[91].StudieshaveshownthatthecostestimateofabarrelofalgaefuelbasedOn(2010)technologyisUS$300-2600whencomparedwithUS$40-80(foryear2009)forpetroleumfuelstherebymakingalgaebiofuellesscommerciallyviable[94].

Table 4 Carbohydrate content of Algal Species.

Algal Species	**Carbohydrate content (%)**
C. vulgaris	55.5
Chlamydomonasreinhardtii UTEX 90	60.0
Chlorococumsp	32.5
S. obliquus CNW-N	51.8
Tetraselmis so. CS-363	26.0
Ulvalactuca	55-60
Ascophyllum	42-70
Porphyra	40-76
Palmaria	38-74

Source: Ozcimen and Inan, [87]

Table 5 Ethanol Yield from Different Biomass Source.

Feedstock	**Ethanol Yield (gal/acre)**	**EthanolYield (L/ha)**
Corn stover	112-150	1,050-1,400
Wheat	277	2,590
Cassava	354	3,310
Sweet Sorghum	326-435	3,050-4,070
Corn	370-430	3,460-4,020
Sugar beet	536-714	5,010-6,680
Switch grass	1,150	10,760
Micro algae	5,000-15,000	46,760-140,290

Source: Chaudhary et al, [88]

CONCLUSION

This review identified the challenges facing different generations of bioethanol production in the world and especially in Nigeria. Bioethanol production from first generation biomass such as sugar and starch-based crops are by far commercially viable with over 80% of global production than second and third generation biomass. Though the first generation have an advantage of a well-established technology in bioethanol production, the high cost of production as a result of the feedstock price and overall influence on food security are of great concern to the process. Second generation biomass are not food sourcesand provide considerable advantage as feedstock for bio-refineries because they are less expensive than starch or sucrose based biomass. Though the use of lignocellulose biomass such as grasses, agricultural residues, industrial wastes, and other low-cost substrates can significantly lower the cost of the feedstock thanstarch based crops for ethanol production, high cost of production due to high energy requirement and consumption for biomass pretreatment, low product yield as by-products inhibition remain a challenge. Although the future priority of bioethanol production is placed on the use of lignollulosic biomass, which are considered the most promising second-generation biofuel technologies, their utilization for fuel ethanol is still under improvement. The third generation biomass has been receiving a lot of attention as a new energy source of the future capable of reducing use of fossil fuels, the cost of culturing the biomass and issues of microbial attacks in the open-system, operating conditions and limited environment for scale-up in the closed system are the limitations to the process. Thus the choice of suitable and ample raw material is of great significance since the feedstock cost represents a key part in the cost of production. The use of edible crops for ethanol production have received some restrictions as the case of Brazil and China, therefore, cassava is a major food crop in Nigeria, its use for ethanol production will affect the price of cassava and its local dishes such as garri. The use of cassava for bioethanol production in the Nigerian government Automotive Biomass programme (ABP) would not be sustainable, thus the need to diversify on the use of other biomass to meet the biofuel need in the country. Several non-conventional food (starch based) biomass have been identified in this review as reported by Sanatana*et al*,[56] as good sources for ethanol production. For sustainability of biofuel production, cost efficiency, ensuring food security and reduction of greenhouse-gas emissions, the use of non-edible starch crops must be utilized since they offer lower feedstock cost, less cost of production, higher conversion rate and well established technology.

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