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BIOPRODUCTS ROUTE TO SUSTAINABLE ENERGY – THE JOURNEY SO FAR

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Abstract: **A sustainable energy development system that is based on renewable biomass feedstock, an effort on the global scale is now yielding good result. The pilot, demonstration and commercialization of flagship projects on cellulosic biofuel production are on in almost every continent of the world. Despite the technical barriers on the road to the conversion of lignocellulosic biomass, the cellulose bioethanol which was once regarded as the fuel of the future has been moved from promise to reality. Advancement of new and promising technologies to utilize cellulosic resource either through the thermochemical processes that uses heat, pressure and catalysts to produce fuel or through biological processes that uses micro organism to reduce cellulosic material to sugar and then ferment to the desired biofuel product. Now with large investment placements by both governments and the private sectors backed up by sound national energy policies, commercialization and large scale capacity utilization are gradually becoming a realized objective. Bioenergy is now renewable and sustainable without the negative impact on food security. This paper will attempt to review recent updates on lignocellulosic biomass derived biofuels commercialization including the key technical barriers to the commercialization process. This review also presents a survey of some selected commercialized lignocellulosic plants with respect to plant location, statues, technology type, feedstock, products, pretreatment methods etc.**

Keywords: **Biomass; Biorefinery; Conversion Technologies; Fossil fuel, Pretreatment; Green House Gasses.**

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1. INTRODUCTION

The global production and consumption of bioproducts have grown rapidly in the last few years. This rapid growth is also controversial as studies began to emerge linking their production to raising food prices, the combined impacts of these effects have encouraged research efforts to be more focused on the potential of inedible feedstocks alternative for the development of lignocellulosic biofuels known as second-generation biofuels [1].

The social, economic and political impact on the use and depletion of fossil fuel, the concentration of the resultant green house gasses (GHG) in the atmosphere and the world total dependence on the exhaustible fossil source needed to be checked and therefore coordinated efforts to reduce this dependence and emission was urgently necessary.

While the reduction of GHG emissions in the transport sector has been an important driver for biofuel development in the European Union and other Organization for Economic Cooperation and Development (OECD) countries, energy security concerns, coupled with the desire to sustain the agricultural sector and revitalize the rural economy is the primary driver for biofuel development in the USA and much of Asia [2, 3].

For decades efforts to transit from this fossil fuel economy to a renewable biomass economy which holds no negative impact on the environment and was also sustainable brought about the realization that out of the many renewable energy resources (biomass, wind, solar, geothermal, tidal etc) available, biomass was the only renewable resource that can be directly utilized for production of various alternative transportation fuel especially bioethanol and biodiesel [4].

Distinguishing between cellulosic biofuel and conventional biofuel the American Energy Independence and Security Act of 2007, defined Cellulosic biofuel as renewable fuels made from cellulose, hemicellulose or lignin that achieve a 60 percent reduction in greenhouse gas emissions while conventional biofuel is defined as ethanol from corn starch or other edible part of plants that reduces greenhouse gas emissions by 20 percent [5].

In the biochemical processing route, cellulosic biofuel is made when biomass is hydrolyzed to sugar which is then fermented to ethanol while in the thermochemical route, a two step process, biofuel is made when biomass feedstock is gasified into syngas, which is then converted to biofuel by chemical reaction. Yet there is a third pathway which is a hybrid of the thermochemical and the biochemical routes, here, the feedstock is gasified to syngas which is then fermented into the desired biofuels or chemical and finally separated through distillation. Biomass includes agricultural and forest residue as wood and straw, energy crops as switchgrass and miscanthus, cellulosic municipal solid wastes etc.

So many researchers including J. Y. Zhu and colleagues identified the technical barriers such as the recalcitrance of lignocellulose biomass, Lack of low-cost and high-activity cellulose hydrolytic enzymes, the difficulty in fermenting the five carbon sugars produced from biomass hemicelluloses and the cost of distillation of alcohol from the weak fermentation broth as barriers to the economic production and commercialization of transportation fuel from cellulosic biomass. These technological barriers remain despite research progress in the past several decades [6]. Also a reliable supply of biomass feedstock is crucial for the success of a biomass to biofuel enterprise. An all year round supply of biomass feedstock is not guaranteed in most instances [7].

Despite these technical barriers on the road to the conversion of lignocellulosic biomass, the ethanol biofuel which were once regarded as the fuel of the future, and its production from lignocellulosic biomass is now a critical mile stone that has been attained.

According to Aaron J. Whitesel, of DuPont "Cellulosic ethanol is no longer the fuel of the future, it's a fuel that is produced even at commercial scale now – a fuel that is increasingly important in meeting the world's energy needs.

In the search for sustainable alternative to fossil fuel, the first generation biofuel which were food crop based evolved. Biofuels produced from oils, sugars, and starches originating in food crops are known as *first-generation biofuels.* First-generation biofuels are produced through relatively simple and established technologies [8] and all biofuels produced on a commercial scale before now were by these "first generation" technologies.

In the United States of America, corn was the major source of raw material, sugarcane in Brazil, sugar beet in most part of Europe and in Thailand it was the root crop, cassava.

It is important to note that neither the American mode of corn fuel ethanol, Brazilian mode of sugarcane fuel ethanol nor the Thailand mode of cassava fuel ethanol had the potential to provide a major environmental and economic benefit of biofuel rather the mass penetration of economical biofuel only evolved when low cost feedstock like lignocellulosic biomass was used and such technologies that were employed in this conversion process were broadly referred to as "second generation technologies" and the products known as *second-generation biofuel*.

The principle of second generation technology encompasses that of a biorefinery, as a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass.

Lignocellulosic biofuel has the potential to contribute significantly in meeting the challenges of the global energy crisis as they replace fossil fuels and provide a number of environmental and economic benefits [9] and therefore the world's vision of developing technical, political and commercial infrastructure analogous to the oil refinery that will convert lignocellulosic biomass to useful products especially fuel is an effort which must directly impact positively on the Green House Gas emission and will also reduce if not eliminate the world's total dependence on fossil fuel.

Ethanol, one of the products from lignocellulosic biomass conversion is chemically identical to the first generation bioethanol (i.e. CH_3CH_2OH) and is produced from cellulosic biomass through a more extensive and complex processes that releases the polymeric sugar in cellulose and hemicelluloses before they are hydrolyzed and fermented to ethanol.

Second-generation biofuels share the feature of being produced from lignocellulosic biomass which enables the use of lower-cost, non-edible feedstock, that comes in the form of grasses, straw, agricultural and woody residues, energy crops, and wastes. Lignocelluloses are particularly well suited for energy applications because of their large-scale availability, low cost, and environmentally benign production and reducing the risks of competition for land meant for food production [10]. They can be converted to fuels, chemicals, and electricity [11] and in particular, many energy production and utilization cycles based on cellulosic biomass have near-zero greenhouse gas emissions on a life-cycle basis [12, 13, 14]. And their conversion presents a viable option for improving energy security and reducing the negative impact on the environment [15]. Despite their suitability for fuel ethanol production, these biomass (especially those from mixed agricultural and forest sources with varying composition whose processing is more challenging than the bioconversion of corn starch or cane sugar to ethanol [16]) need to be broken down (hydrolyzed) into simple sugars prior to fermentation and distillation which may be achieved using either acid or enzyme hydrolysis, an approaches that have been the subject of continuing research interest and large investments since the 1970s, but now a proven bioethanol production route. It is interesting to note that biochemical process which encompasses hydrolytic treatments is a process of choice among most of the commercialized biomass to fuel business as at now.

Although the economic feasibility of producing large-scale biofuel refineries has been inefficient, several genuine challenges toward achieving efficiency and toward the creation of a sustainable advanced biofuel economy still remains. But the successful demonstration of many conversion technologies has triggered large scale renewed confidence in cellulosic biofuel production process as so many investors are steadily investing in this area. Also many governments have helped to advance these areas through public good research, procurement and by partnering with companies to help share the risk involved with both research and the path to commercialization [17]. This challenge is also being surmounted through the adoption of other technologies and many pretreatment methods that takes care of the variability in feedstock even as other more efficient pretreatment methods are still being researched on.

Despite the enormous potential of biofuels from lignocellulosic biomass, its production at a commercial level took a long time to be proven. As at 2009, there was no commercial cellulosic plant in America and Europe distilling ethanol from the non edible part of the plant such as corn stalk, grasses and wood chip. All ethanol plants were using the edible parts of the plant which were easier to break down. But now countries such as the United States, Brazil, and Canada have initiated major biofuel programs to produce cost-efficient ethanol and other fuels from agricultural and forest lignocellulosic biomass [18].

In 2014, global biofuel production was 127.7 billion litres, 74 percent of which was fuel ethanol. And the top countries responsible for this production were the United States, Brazil, Germany, China, and Argentina [18]. These biofuels were almost entirely first-generation, based mostly on sugarcane and corn, and other agricultural feedstock.
Commercialization of advanced cellulosic biofuel has progressed since then, with construction and commissioning of several commercial scale plants in USA, Brazil, Canada, China, the European Union and some other OECD countries.

Venkatesh Balan et al identified some of the industrial plants that have been designed and built around the world and compares the developments in these areas in the EU and the USA and provides a comprehensive list of the most relevant ongoing development, demonstration, and commercialization activities in various companies, along with the different processing strategies adopted by these projects [19].

These state-of-art conversion technologies represent the first cases of large scale industrial biorefineries [4]. They were classified as Pilot, Demonstration and Commercial of which the basis for the classification is still a matter of public debate and a source of confusion in the industry as no universal acceptable standard for classification are in place even though some may use installed capacity, government protection and subsidy as criteria. Even so there are still several genuine challenges toward achieving this seemly elusive goal of creating a sustainable advanced biofuel economy [20] as commercialization of second-generation biofuels must also overcome uncertainty surrounding feedstock reliability, as supply chains for such feedstocks are relatively new.

Also biomass feedstock pretreatment presents the most practical and an economic challenge in the attempt to commercialize cellulosic bioethanol production since it affects the upstream as well as downstream processes [21]. According to Harmsen and Huijgen, the published pretreatment technologies in public literature are described in terms of the mechanisms involved, advantages and disadvantages, and economic assessment. The choice of the optimum pretreatment process will depends very much on the objective of the biomass pretreatment, its economic viability and environmental impact. [22]. Though only a small number of pretreatment methods have been reported as being potentially cost-effective. However alkaline and dilute acid solutions can effectively remove lignin and reduce cellulose crystallinity [23, 24]. So they are widely employed in many pilot and demonstration plants as they are ideal for low lignin materials [21]. The form of pretreatment adopted by each company depends on the nature of their feedstock and desired products [25]. Other Pretreatment techniques, includes mechanical pretreatment, chemical treatment, biological treatment, ammonia fiber explosion, wet oxidation, steam explosion and ionic liquids. Most of the commercialized pre-treatments processes uses homogeneous rather than mixed feedstocks with enzymatic hydrolysis as a sole route in these demonstrations/commercial scale plants.

2. LIGNOCELLULOSIC FEEDSTOCK AND ITS COMPOSITION

The importance of understanding the cellulosic feedstock structure before processing the biomass to biofuel cannot be overemphasized. Biological feedstock are primarily made up of 3 basic elements, C, H, O and the different combination of these elements will give the biomass its unique composition. Biomass feedstock are derived from plants, microbial cells, wastes and forest residues and they are synthesized when plants through photosynthesis converts carbon dioxide from the atmosphere to sugar which could be stored in the roots as starch, stems as lignocellulose, leaves and fruit as cellulose with forests residue, agricultural wastes, woods, dedicated energy crops and municipal solid wastes being the world's major sources of biomass. However, alternative sources such as agro forestry, conservation lands and algae may grow in importance as demand for bioenergy grows. All forms of biomass have the same major components, cellulose, hemicelluloses and lignin in varying proportion depending on the source. The cellulose is composed of linear polymers of the six-carbon sugar glucose linked by 1,4 glycosidic bonds. Hemicellulose is a complex of primarily five carbon sugars, the majority of which are xylose and arabinose.

Three different arrangements of the basic sugar units are possible, as seen in the three different types of agricultural feedstock available for fermentation: sugar crops, starch crops, and lignocellulosic residues. Sugars and starches are carbohydrates typically found in the edible portions of food crops, such as corn grain and millet. The starch crops and lignocellulosic residues contain six-carbon sugar compounds which must be broken down into simple six-carbon sugar units before fermentation can take place [26]. Although biofuel can be produced from any kind of biomass, recent focus has been on production of second-generation or advanced biofuels from nonfood sources such as cellulosic feedstock, algae, municipal and industrial wastes, wood and agricultural residues. Currently the most promising and abundant cellulosic feedstocks derived from plant residues in the U.S., South America, Asia and Europe are from corn stover, sugarcane bagasse, rice and wheat straws, respectively [27]. In general, lignocellulosic ethanol production feedstocks are grouped as:

- **crop residues** (cane bagasse, corn stover, wheat straw, rice straw, rice hulls, barley straw, sweet sorghum bagasse, olive stones and pulp);
- **Energy crops:** these are crops that are specifically grown for bioenergy production and include herbaceous and woody resources such as alfalfa, miscanthus, switch grass, triticale etc.
- **Woody Biomass** (hardwood/softwood) (aspen, poplar, pine, spruce); A broad category capturing forest logging residues, mill residues, and other woody waste sources.
- **cellulose wastes:** Fibrous cellulose remaining after grain ethanol production in a dry mill (newsprint, waste paper, recycled paper) and
- **Municipal solid wastes:** This refers to solid wastes from residential and business sources that can be converted to produce biofuel and/or electricity.

[28, 29, 30].

Lignocellulosic biomass consists essentially of a network of cellulose and hemicellulose bound by lignin through covalent and hydrogenic bonds [27] that make the structure highly robust and resistant to enzymatic and microbial deconstruction due to cross-linking between the polysaccharides. This protective barrier that makes the biomass highly recalcitrant to enzymatic hydrolysis must be removed before the sugar in the feedstock can be made accessible [31, 32].

The cellulose portion ranges by weight from 35% to 50% of biomass while the hemicelluloses is from 25% to 35% by weight and lignin ranges from 10% to 30% by weight of biomass depending on the feedstock. [33, 34].
Lignin is a complex polymer, the largest non carbohydrate fraction of the biomass [35] that provides structural integrity in plants and remains as residual material after the sugars in the biomass have been converted to ethanol. It contains a lot of energy and can be burned to produce steam and electricity for the biomass to ethanol process. [36, 22]. Lignin is inert for biological conversion processes but can be utilized in thermal conversion processes [37].

Composition of common lignocellulosic raw materials and wastes (wt % on dry biomass):

Table 1. Composition of common lignocellulosic raw materials and wastes (wt % on dry biomass. Adapted from

feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Wheat straw	38–45	20–32	7–10

Miscanthus	35–40	16–20	20–25
Arundo donax	30–38	18–22	8–20
Newspaper	40–55	25–40	15–30
Tobacco chops	22–30	15–20	15–25
Rice straw	35–45	18–25	10–25
Softwood stems	45–50	25–35	25–35
Hardwood stems	40–55	20–40	18–25
Corn stower	45	35	15
Switch grass	45	31.4	12.0`
Leaves	15–20	80–85	0
Nut shells	25–30	25–30	30–40

[28, 12]

A major issue for lignocellulose as a raw material for the bioproducts manufacture is variability (chemical composition of lignocelluloses greatly varies within and in between species) and the conversion yield is dependent on the biomass characteristic at that point in time. A well-functioning system therefore requires the pairing of appropriate feedstock and conversion technologies.

3. THE TECHNOLOGICAL PATH TO BIOFUEL PRODUCTION (PROCESSING OPTIONS & PRODUCTS)

It is a fact that technologies which depends on the vast global resources of non-food cellulosic materials such as forestry and agricultural residues, energy crops, municipal & industrial solid wastes can make a significant contribution in reducing the world dependency on fossil fuel and reduction in atmospheric pollution [38] as a wide variety of conventional and advanced biofuel conversion technologies exists today. With so much money invested in research and development, conversion technology which hitherto was a serious roadblock to realizing this objective is now put to rest as proven technological routes to biofuel production are being demonstrated and commercialized.

Large scale commercial capacity now exists for cellulose biofuel production comparable to the first generation direct sugar and starch fermentation technologies.

Many potential mechanisms for lignocellulosic fractionation such as fermentation, gasification and pyrolysis exist, but there are only two major pathways for cellulosic ethanol production [38, 7] which are grouped as: biochemical and thermochemical [39, 23]. The biochemical process is based on enzymatic hydrolysis of the lignocellulosic material, using a variety of enzymes that break the cellulosic material into fermentable sugars [40]. In the second step of this process, the sugars are fermented into alcohol, which is then distilled into liquid fuels (ethanol, butanol) or gaseous compound (methane) and carbon dioxide.

And the thermochemical liquefaction process, a two-step process where a biomass feedstock is gasified to produce syngas (carbon monoxide and hydrogen) that are then recombined into chemicals and fuels (Fischer–Tropsch synthesis) [41, 42, 43]. The thermochemical process result in higher yields of end products in comparison with the hydrolysis method as lignin, which constitutes a bulk of the feedstock is also employed in the synthesis.

For bioalcohols fuel, biochemical conversion routes appear to be well suited, whereas for hydrocarbon fuels, the chosen production technologies tend to favour the thermochemical conversion routes [44].

Despite the inherent limitation of the two processes, energy analysis calculation and overall economics has shown a close similarity. Nevertheless the comparative live circle assessment suggests that the biochemical conversion process will have a better performance with respect to green house gas (GHG) emission [45].

In recent years, technological advances have given rise to a third pathway called syngas fermentation**,** which combines the elements of biochemical and thermochemical pathways, capturing the benefits of each pathway while mitigating some of their deficiencies. In this process biomass feedstock is gasified to produce syngas. The syngas is then fermented into only the desired biofuel or chemical. The syngas fermentation into fuels or other chemicals is considered by some to be more attractive than the biochemical and thermochemical pathways due to several inherent commercial advantages.

Products From Lignocellulosic Biomass:

Lignocellulosic biomasses are potential sources of several bio-based products according to the biorefinery approach. The goal of the biorefinery approach is the generation of energy and chemicals from different biomass feedstock, through the combination of different technologies [46]. The biorefinery scheme involves a multi-step biomass processing. The first step encompasses the feedstock pretreatment through physical, biological, or chemical methods. The outputs from this step are platform (macro) molecules or streams that can be used for further processing [47].The two most commercially developed bioproducts include biodiesel and bioethanol. The Fisher Tropsch diesel is produced by hydrogenating vegetable oils or animal fats in a two-step process in which biomass is converted to a syngas rich in hydrogen and carbon monoxide. After cleaning, the syngas is catalytically converted through Fischer-Tropsch (FT) synthesis into a broad range hydrocarbon liquid, including synthetic diesel and bio-kerosene.

Cellulosic bioethanol which has the potential to perform better in terms of energy balance than starch and sugar based biofuel, can be produced from lignocellulosic feedstocks through the biochemical conversion of the cellulose and hemicellulose components of biomass feedstocks into fermentable sugars [48]. The sugars are then fermented to ethanol, following the same conversion steps as conventional biofuel.

Bioethanol has higher octane number when compared to gasoline and its use with gasoline reduces the emission of the green house gasses as CO_2, NOx and hydrocarbons. The use of ethanol shows high compression ratio and increased energy production in combustion engines [49, 30].

All oxygenated biofuels are used mostly for road transportation, blended at various percentages with fossil fuel (petrol and diesel) according to regional policies and local climatic conditions [4]. Besides ethanol, several other products can be obtained following the hydrolysis of the carbohydrates in the lignocellulosic materials. Products from biomass conversion can be grouped into two basic categories, energy products (which are produced for the purpose of energy generation) and material products (produced because of their chemical or physical properties). Important energy products include biogas, syngas, pellets, lignin, bioethanol and biodiesel [35].

However, a growing attention is given today to ‘drop-in biofuels’. This term is used to indicate liquid hydrocarbons that are oxygen free and functionally equivalent to petroleum transportation fuel that can be directly blended with petroleum products fuel. Drop-in biofuels are therefore fully compatible with existing transportation fuel infrastructure and engines.

3.1 The Biochemical Pathway:

In contrast to the traditional ethanol production from starch and sugar, production based on lignocellulosic biomass requires additional processing steps. The reason being that the architectural structure of lignocellulosic biomass in which the crystalline cellulose (source of C6 sugar) interacts and entangles with the hemicellulose (source of C5 sugar) and a top protective lignin cover makes it impossible for traditional bioethanol producing enzymes to gain access and hydrolyze the cellulose. It becomes imperative that these components must be separated for hydrolysis to take place.

The separation of the three main components of lignocellulosic biomass is severely limited by many factors, such as the percentage lignin and hemicelluloses content, cellulose crystallinity, degree of polymerization, water content, available surface area and pore volume [28, 50].

Generally, hydrolysis schemes require the feedstock to be pretreated to a state more amenable for polysaccharide breakdown. Without a pretreatment, enzymatic hydrolysis of cellulose is ineffective as native cellulose is well protected by hemicellulose and lignin [51]. The first step toward realizing this objective is to reduce the size of the biomass by milling or chopping, and this is done to increase the surface volume [52]. And then the biomass is treated using any pretreatment method. It is only after breaking the protective lignin cover to the cellulose and hemicelluloses which form the major hindrance to enzymatic hydrolysis that the sugar containing cellulose and hemicellulose become available to the hydrolytic enzymes. Delignification is a sure way to enhance biomass hydrolysis. Pre-treatment and hydrolysis are used to break down the feedstock into sugars, which are then fermented to produce ethanol.

There are many possible means of doing this as pretreatment are classified as physical, chemical and biochemical. Two common methods are dilute acid hydrolysis and concentrated acid hydrolysis, both of which use sulfuric acid, with several drawbacks but yet it is the process of choice for some demonstration and commercialized facilities.

Dilute acid hydrolysis occurs in two stages to take advantage of the differences between hemicellulose and cellulose. The first stage is performed at low temperature to maximize the yield from the hemicellulose, and the second, higher temperature stage is optimized for hydrolysis of the cellulose portion of the feedstock. Once the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol.

The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose [53] even as process improvements now allow Simultaneous saccharification and fermentation (SSF), separate hydrolysis and fermentation (SHF), simultaneous saccharification and co-fermentation (SSCF) of hexose and pentose sugars, and consolidated bioprocessing (CBP), that combines the three main steps in lignocellulosic biomass conversion namely enzymes production, biological hydrolysis of biomass to sugars and oligomers, and fermentation into a single bioprocessing system known as “Direct Microbial Conversion (DMC)” or Consolidated Bioprocessing (CBP) [54, 53, 55].

In the SSF process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step.

3.2 Syngas Platform (Thermochemical Route to Biofuel):

Thermochemical routes include pyrolysis, in which the biomass is thermally decomposed to produce a liquid bio-oil, along with some fuel gas and solid biochar. Fast pyrolysis is carried out at around 400°C - 600°C in the absence of oxygen and maximizes the production of bio-oil (as opposed to slow pyrolysis which maximises bio-char production). and gasification, used to produce long chain liquid hydrocarbons [4]. Basically gasification involves the production of synthesis gas which is cleansed before passing the Fisher Tropysh process, an offshelf process that is available commercially to create a range of liquid fuels.

Biomass gasification is an established route to produce carbondioxide neutral fuels, either as liquid or gaseous. It employs the robust use of known processing techniques which includes 5 different downstream catalytic synthesis steps as:

- ✓ Fischer-Tropsch (FT) synthesis to produce FT diesel, FT jet and naphtha
- ✓ Dimethyl ether (bioDME) synthesis
- ✓ methane synthesis to produce bio-Synthetic Natural Gas (bio-SNG)
- ✓ Mixed alcohols synthesis to produce methanol, ethanol, butanol and higher alcohols
- ✓ Methanol synthesis

These five gasification routes involve thermo-chemically converting lignocellulosic feedstocks into syngas. Cleaned and conditioned syngas is then catalytically converted into different liquid or gaseous fuels depending on the catalytic synthesis process above and can handle many feedstocks, and also will convert all of the organic components of biomass, unlike the biochemical processes, which produce lignin as a by-product and do have difficulty in fermenting the C5 sugars [10, 56] and involves a system that can accommodate the flexibility in feedstock and diversity in products [42] which also addresses seasonal and regional variability issues. The thermochemical process is a two-step process where a biomass feedstock is gasified to produce syngas (carbon monoxide and hydrogen) that is then converted to biofuel by a chemical reaction using chemical catalysis [38].

In this type of biomass conversion platform, lignocellulosic biomass is pretreated to allow high-temperature and high-pressure entrained flow gasification into synthesis gas of mainly CO and H_2. The syngas is cleaned in a high-temperature gas cleanup system, often applying steam reforming to modify its CO/H_2 ratio following downstream synthesis requirements. The clean gas can be used to produce biofuels and/or chemicals (FT diesel, dimethylether), a range of alcohols including bioethanol; and/or a variety of base chemicals (ethylene, propylene, butadiene, etc.) using catalytic synthesis processes [57]. The gasification techniques leverages related commercial experience in production of methanol and F-T liquids from natural gas or coal and the yield of biofuels are high, and the potential for cost reduction is significant. However the barriers for biomass gasification includes such technical barriers as syngas cleanup and conditioning, the removal of tar produced during the gasification process and such commercial barriers as high initial capital cost and lack of demonstrated experience with integrated systems. The thermochemical process results in higher yields of end products in comparison with the hydrolysis method as lignin, which constitutes a bulk of the feedstock, is also processed to produce biofuels [7].

Also the gasification platform is extremely amenable to producing drop-in hydrocarbon fuels and products—as syngas is an ideal feedstock for (chemical and biochemical) catalytic conversion [58].

Gasification can use a wide variety of feedstocks, but the feedstock requirements in terms of size, moisture and ash content are determined by each gasifier type [56].

Hybrid routes (i.e. combined thermochemical and biochemical) are used for producing both bioethanol and long chain liquid hydrocarbons. The hybrid route seems to be a process of choice by some companies like Lanzatech, Coskata, and INEOS Bio. Feedstocks are first thermochemically converted into syngas via gasification before the syngas is anaerobically fermented by micro-organisms into ethanol [4, 56]. Syngas fermentation is very different to the other catalytic fuel synthesis routes, as syngas quality requirements are less strict.

4. THE CURRENT STATUS OF CELLULOSIC BIOFUEL COMMERCIALIZATION

Before the year 2009, the production of second generation biofuel could be rightly defined as laboratory experiments and pilot plants demostration. Although significant progress has been made in terms of deployment of advanced biofuel and despite the fact that the technology for converting any organic matter to biofuel has been in existence for many years before then, however, no cellulosic biofuel production was registered for sale as at 2009 which led to skepticism regarding the commercial viability of the cellulosic biofuel technology. The economic feasibility of producing biofuel in commercial quantity was therefore deemed inefficient.

Even now there are still several genuine challenges toward achieving this seemly elusive goal of creating a sustainable advanced biofuel economy [20]. Most of the cellulosic biofuel productions from second-generation feedstock are still in the demonstration stage and for the commercialized ones; the cost of production is still an uphill task, but with much government support through tax exemption, subsidies, loan guarantees, other financial incentives, as well as the blending mandate (which defines the proportion of biofuel that must be blended with road transport fuel), the future is bright for the commercial biofuel industries.

Overall, tremendous technological progress is occurring around the world to develop, demonstrate and commercialize advanced biofuel technologies. Despite a number of technical, policy and financial factors detrimentally affecting the pace of biofuels development, progress continues with large scale commercialization of technologies for cellulosic ethanol and other advanced biofuel production.

Several advanced biofuel pilot and demonstration plants as well as some commercial facilities are already operating, with the majority of these plants located in North America and the European Union, though an increasing number are being built outside the OECD and some of these facilities began producing cellulosic ethanol as far back as 2009. Such operating companies in the United States were assigned a unique Renewable Identification Number (RIN) in 2014/2015 timeframe.

The US remains the largest biofuel producer in the world, although a variety of factors are creating market and policy uncertainty and posing challenges to accelerating development and commercialization [2]. The commercialization of cellulosic ethanol became a reality in 2013 when INEOS Bio, using numerous feedstocks including vegetative wastes, agricultural wastes, and municipal solid wastes, completed construction and operated its facility in Vero Beach, Florida [59], but was idled in 2015 while working on mechanical improvements though they were expected to resume operations in 2016 [60]. Again the cellulosic ethanol industry witnessed another landmark event when POET-DSM Advanced Biofuels LLC, the first largest commercially operational cellulosic ethanol plant was inaugurated in September, 2014, in Emmetsburg, LA, and dubbed Project Liberty.

According to the United States NREL 29 non starch ethanol operating companies are in operation in the US as at 2015 which includes 27 cellulosic facilities as well as 2 algal derived ethanol facilities [60]. According to the report 11 of the 29 facilities were operational with 3 of the facilities operating at a commercial scale and over 2 million gallons of cellulosic ethanol produced in 2015, a far cry from projection although enough improvement is expected at the end of 2016 as 8 of the surveyed facilities were expected to be operational sometime in 2016/2017. From this same report, the biochemical pathway seems to be the process of choice for 23 of the surveyed facilities with only 2 facilities each utilizing the thermochemical and the hybrid pathways.

With respect to feedstock, of all the 23 biochemical plants surveyed, 7 used crop residue, 4 used woody biomass, 5 used corn kernel cellulose, 4 used dedicated energy crops and 2 plants uses Municipal Solid Waste while the 2 thermochemical plants use either woody biomass or Municipal Solid Waste (MSW) as feedstock [60]. As at 2015 the largest producers of cellulosic ethanol in the U.S. are INEOS Bio, POET, Abengoa, and Quad County Corn Processors.

In Canada, Lignol Innovations adapted the organosolv process to produce fuel ethanol, high purity lignin and co-products (furfural and wood extractives) from lignocellulosic feedstocks (forest, and agricultural residue).

Lignol’s proprietary biorefining process consists of a pretreatment step which utilizes a modified solvent based extraction to fractionate biomass into its principal components as: cellulose, lignin and hemicellulose. This pretreatment system has advanced significantly to produce very pure streams of cellulose, lignin and hemicellulose which can be processed downstream into value added products such as biofuels, after enzymatic processing.

Iogen with large scale pilot plant outside of Ottawa is utilizing its enzymatic hydrolysis and fermentation of wheat straw to produce cellulosic ethanol and electricity (from lignin).

And Enerkem another Canada based company uses a proprietary thermochemical process to convert wastes into biofuels and chemicals. The feedstocks employed are municipal solid wastes, utility poles, and forest residues which are then converted to synthesis gas through the use of catalysts. The synthetis gas is used to produce methanol as a chemical building block for the production of ethanol, or other renewable chemicals. Enerkem has validated its technology over 10 years [61]. The total installed capacity for cellulosic biofuel in Canada is 303.45million litres.

The second-generation biofuel industry in Brazil has had a tendency to develop based on existing infrastructure and feedstock logistics, which are in place for Brazil’s well established first-generation industry.

The commercial potential of cellulosic ethanol in Brazil is substantial due to the great amount of sugarcane bagasse, a fibrous residue of sugarcane production available in that country. Brazil is the world's largest sugarcane producer with an extraction capacity of approximately 600 million tonnes per year, currently yielding over 27 billion liters of bioethanol [62].

Brazil's first commercial-scale cellulosic ethanol plant at São Miguel dos Campos, Alagoas, began production in September 2014, with current production capacity of 22m gallons per annum. In December 2014, production also commenced at the $100 million, 40 MMly Raízen Energia S/Acommercial Cellulosic Ethanol plant at the Costa Pinto sugarcane mill. The 10MMgy plant uses technology developed by Iogen Energy, a joint venture of Raízen and Iogen Corp, to convert sugarcane bagasse into ethanol [59].

In Asia apart from China, where the Fuyiang project, which is a cooperation between Italy-based Beta Renewables and Guozhen Group made a significant inroad causing a rapid growth in the advanced cellulosic ethanol industry. Thailand, India and some other leading economies in that continent have not made much progress on cellulosic ethanol as at 2015. India, currently the world 4th largest emitter of green house gas (GHG) and its transport sector accounts for 13 percent of the country's energy-related CO_2 emissions [63]. An India's tap into the lignocellulosic biomass approach to bioenergy will certainly bring this emission to a minimum [18].

In India, however there is only one second-generation cellulosic ethanol demonstration plant under construction by Praj Industries in Pune, Maharashtra. This demonstration project will use a variety of biomass agricultural residues such as corn stover, cobs, and bagasse. [18] as feedstock.

With regards to the European Union, Chiaramonti and colleagues identified 39 projects in the field of lignocellulosic biofuels production where 16 are based on the thermochemical pathway, 23 on the biochemical process using lignocellulosic feedstock and none on the hybrid process [4]. Here the key actors are Abengoa, STI Cellulonix based in Finland and the Mussi/Chemtex/Beta Renewal industrial partnership in Italy.

Abengoa is operating a demonstration/commercial plant in Spain that utilizes steam explosion pretreatment option and another large demonstration plant with a capacity of 50 ML/yr is coming online in France which is being partially funded by the European Union. The major product from this plant is bioethanol.

Beta Renewables, a $350 million joint venture between Chemtex and TPG using the Proesa™ proprietary technology began shipping fuel from its Crescentino facility in June 2013 and is building a another biofuel facility in North Carolina, USA.

The Beta Renewables commercial scale cellulosic ethanol plant at Crescentino was officially opened on 9th October 2013 and was the first commercial scale plant in the world to be designed and built to produce bioethanol from agricultural residues and energy crops using enzymatic conversion with an annual production capacity of 75 million litres of cellulosic ethanol. The shareholders of Beta Renewables are Biochemtex, TPG Capital, and Novozymes [2, 64].

The plant is based on the patented Proesa™ process, and uses Novozymes enzyme technology to convert local wheat straw, rice straw and Arundo donax to ethanol. Lignin extracted during the production process is used at an attached power plant which generates enough power to meet the facility's energy needs with any excess green electricity sold to the local grid.

In 2014, North European BioTech Oy (NEB) invested €40m in a 10m l/y cellulosic ethanol plant at Kajaani, Finland, using local sawdust as a feedstock. The plant implemented and operated by STI Biofuels Oy as STI Cellulonix. Novozyme is supplying enzymes to the plant, which uses ST1's proprietary Cellunolix® process that incorporates steam explosion and enzymatic hydrolysis. Biofuel production at the plant has commenced already.

The majority of the European commercial plants currently use homogeneous rather than mixed feedstocks such as wheat straw as either the sole feedstock or along with other agricultural residues such as rice straw.

Despite the fact that many developing countries have started realizing the potential economic and social benefits of producing and using biofuels, African countries, Nigeria inclusive and many other developing nations, however, are faced with numerous barriers towards the development of a viable, sustainable biofuel industry. Poor infrastructure, lack of skilled labour, lack of formal land ownership structures and limited financial resources are among the most significant barriers [3].

All the projects discussed above and summarized in the table below illustrate the progress companies have made in bringing the cellulosic technology from pilot and demonstration scaled plants to commercial-scaled facilities [65, 59]. Indeed second generation biofuel has moved from promise to reality. The first full demonstration plant came online in 2013 with several others following in 2014. The current focus is on ethanol production, but very rarely a single item cannot be the output of the plant, more often a range of possible products are typically produced and some players such as Zeachem are on the road to jet fuel, diesel, gasoline and chemical production in their biorefinery. The future is indeed bright for the lignocellulosic biofuel industry.

Summary of commercialized entities and status across selected regions of the world as at 2016:

COUNTRY	*COMPANY*	*LOCATION*	*OPERATIONAL DATE*	*FEEDSTOCK TYPE*	*PRODUCT*	*CONVERSION TECHNOLOGY*	**NOTES**
United States of America	Abenagoa	Hugoton, KS	2015 (idled in 2015	Crop Residues, 350,000 t/y (mixture of agricultural waste, non-feed energy crops and wood waste	23 MMg/y of ethanol	Biochemical	Dilute acid pre-treatment and first-of-its-kind commercial-scale enzymatic hydrolysis conversion of lignocellulosic biomass, www.abengoabioenergy.com/web/en
	Ace Ethanol (Sweetwater Energy, Inc.)	Stanley, WI	[2017]	Corn Kernel Cellulose	3.5MG/Y, Ethanol	Biochemical	
	Beta Renewables Inc.	Clinton, NC	[2017]	Dedicated Energy Crops. (Arundo, Switchgrass, Miscanthus Fiber Sorghum); Ag Residues (Rye Straw)	20MG/Y Bioethanol, Lignin	Biochemical	Proprietary pre-treatment (PROESATM) + Viscosity reduction + enzymatic hydrolysis + Fermentation (C5 and C6) www.chemtex.it
	Canergy	Brawley, CA	[2017]	Dedicated Energy Crops	25 MG/Y, Ethanol	Biochemical	First-of-a-kind Comm Demo plant
	DuPont	Nevada, IA	2015, Commercial operation by Mid-2014	Crop Residues, Agricultural biomass e.g. corn stover, switchgrass	30 MG/Y, Bioethanol	Biochemical	Ammonium hydroxide based pretreatment, enzymatic hydrolysis process (Genencor enzymes) and Zymomonas fermentation http://www2.dupont.com/BioFuel/en_US/index.htm
	Enerkem	Pontotoc, MS	[2020] commercial and Under construction	Municipal solid waste (MSW) and wood residues	10MG/Y Bioethanol, biomethanol, Syngas, acetates	Thermochemical Gasification	Canada based company with proprietary technology focus on syngas to ethanol/chemicals via catalysis route http://www.enerkem.com/en/home.htm

	Front Range Energy (Sweetwater Energy Inc.)	Windsor, CO	[2017]	Cellulosic Sugars	3.6MG/Y	Biochemical	
	INEOS New Planet Bioenergy LLC	Vero Beach, FL	[2016]	MSW, Vegetative, yard and citrus waste ii. mixed lignocellulosic biomass	8 MG/G Bioethanol	Hybrid Biochemical/Thermochemical	Patented bacteria for syngas fermentation http://www.ineos.com/
	Pacific Ethanol (Sweetwater Energy Inc.)	Madera, CA	[2017]	Corn Kernel Cellulose	3.6 MG/Y	Biochemical	
	POET	Emmetsburg, IA	2015, Commercial operation	Crop Residues (Corn crop residue)	25MG/Y Bioethanol, Biogas	Biochemical	Advanced Steam-Ex pre-treatment technology and enzymatic hydrolysis process, pilot plant is running since 2008 http://www.poet.com/biofuels
	Quad County Corn	Galva, IA	2014	Corn Kernel Cellulose	3.8 MG/Y	Biochemical	
	ZeaChem	Boardman, OR	[2017] Commercial operation, was scheduled to have started operation in the beginning of 2015	Woody Biomass, Poplar trees, Wheat straw	22MG/Y, Bioethanol, Biochemicals	Biochemical	Proprietary process, acetic acid via fermentation then converted to ethyl acetate followed by hydrogenation to ethanol. http://www.zeachem.com/
Canada	Enerkem Westbury,	Westbury, Quebec (Canada) Edmonton, Alberta (Canada) Varennes, Québec (Canada)	2014	Sorted municipal solid waste and wood residues	38.02ML/Y, Bioethanol, biomethanol, Syngas, acetates	(Thermochemical)	Proprietary technology focus on syngas to ethanol/chemicals via catalysis route http://www.enerkem.com/en/home.html
	Iogen	Ottawa, Canada	Construction started in mid 2007	Straw	Iogen has been producing ethanol at demonstration facility in Ontario	Biochemical, Acid/steam-explosion pretreatment followed by enzymatic hydrolysis	Iogen uses a modified steam explosion process and separate hydrolysis and fermentation. (www.iogen.ca)
	Core biofuels	Houston BC, Canada	2015	Sawmill waste & roadside residues	67.82ML/Y, Ethanol	Gassification	

	Mascoma	Drayton, Alberta, Canada	2015	Wood pulp and chips	76.20ML/Y, Ethanol	Biochemical	Proprietary consolidated bioprocessing (CBP) technology http://www.mascoma.com/
	Lignol	Vancouver, BC, Canada	2015	Hardwood	76.26ML/Y, Ethanol, Butanol	organosolv enzymatic hydrolysis of cellulose	Lignol utilizes a modified solvent based extraction to fractionate biomass and solubilises lignin. (www.lignol.ca)
Brazil	GranBio / Beta Renewables/ Chemtex	Sao Miguel, AL, Brazil	2014	Sugarcane bagasse and Straw	82.38ML/Y, Ethanol	Biochemical	First-of-its Kind commercial demo
	Raizen Energia	Piracicaba, SP, Brazil	2015	Sugarcane bagasse	40.26ML/Y, Ethanol		
European Union	Abengoa	Seville, Spain	2016	Organic residues / waste streams	28.18ML/Y	steam explosion	EH (Glucose), -operation http://www.abengoa.com
	ST1 - Cellulonix	Kajaani, Finland	2016	sawdust	10.00ML/y, Ethanol		
	Mussi Chemtex / Beta Renewables	Crescentino, Italy	2012 Officially opened on Oct. 9, 2013	Arundo donax, straw (rice, wheat)	75.00ML/Y,	PROESA^{TM} Technology is licensed by Beta Renewables	www.betarenewables.com; www.chemtex.it
China	Beta Renewables - Fuyang Bioproject	Fuyang, China	2016	Wheat straw, corn stover, poplar residues	253.49ML/Y, Ethanol	PROESA^{TM} Technology is licensed by Beta Renewables	www.betarenewables.com; www.chemtex.it
	Longlive Bio-technology Co. Ltd	Yucheng, Shandong, China	2012	Corn cob	63.31ML/Y, Ethanol		

[22, 4, 60, 18, 59]

5. CONCLUDING REMARKS

For those nations that depends wholly or partially on imported fossil fuel as a source of energy to sustain their economic development, one sustainable and renewable solution will be the use of lignocellulosic biomass for the generation of energy. Although biomass itself is cheap, its processing costs are relatively high.

Conversion technology which was the major roadblock to realizing significant production of advanced biofuels is gradually becoming a story of the past.

There are numerous pathways now available for advance biofuels production. The costs and benefits of biofuels vary greatly, depending on the specific pathway taken.

But the portfolio of advanced technologies that can convert biomass to fuels on a large scale which were mostly in the pilot/demonstration stages of development are gradually being scaled up and commercial maturity are being achieved with a dramatic increase in the number of industrial initiatives as supported by both government and public Institutions.

Great numbers of new investments are flowing into the biofuel sector as more facilities are on track towards commercialization even as many plants are still in the process of achieving commercial maturity.

As a result of recent upgrades in the industry a significant number of plants are now addressing production above 20,000 tons/year of feedstock which can be fully considered as real industrial scale demonstration/commercialization plants. With regards to policy framework, which is also crucial and critical as decisions taken by policy makers still influence the market deployment of these commercial plants or otherwise are still hampering the future growth of the industry.

Active involvement of the private sector in the private-public partnerships could help accelerate the process of commercialization of second-generation biofuel technologies.

Even though significant progress has been made in reducing the cost of enzymatic-based technology making it potentially competitive now, yet biomass pretreatment, cellulase production and co-fermentation of the pentose and hexose sugars in bioethanol production is still not economically competitive compared with petroleum-based fuels, making cost reduction the biggest challenge.

A key to a better future in the biomass to fuel industries to achieving higher yields, faster rates, and greater concentrations of biofuels will then be through improved pretreatment technology, development of better cellulase enzymes, and synergistic combination of cellulose hydrolysis and fermentation steps.

As for the developing countries to develop a viable biofuel sector, they may need foreign investment in addition to domestic funding.

In conclusion we will say that biomass to bioenergy industry is on a positive march to a good and foreseeable future, but despite all the good things about biofuels, by redefining a sustainable practice as one that meets the current needs of society without compromising the ability of future generations to meet their own needs we have opined that biofuel can as well be environmentally unsustainable through habitat loss and deforestation, soil degradation, greenhouse gas emissions, pollution of water and air, aquifer depletion etc, therefore if good industrial practices are not employed, biofuels will make limited contributions to our quest for sustainable energy future despite their inherent advantages over the petroleum alternatives.

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