Fuels and Chemicals from lignocelluloses: A Short Overview

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Abstract
This paper looked at the potential and available alternative conversion paths for fuels and chemicals production away from the conventional conversion processes of fossil based fuels. Lignocellulosic biomasses are abundant, renewable, and domestically available energy resources. Though with its own attendant challenges, there are achievements and prospects that have been made in developing environmentally friendly processes for small and large scale conversion of lignocelluloses to different fuels and chemicals. With the continuous reliance on fossil fuels, there is the ever increasing climate change caused by the increasing greenhouse gas emissions such as carbon dioxide. Biomass from marine, trees, plants, animal wastes, food and non-food crops, grains, and wood based can produce fuels such as ethanol, butanol, and other chemicals through some promising technologies. Therefore, identifying ways to improving production efficiency of fuels and chemicals during biomass conversion processes to a sustainable level is very crucial.

Keywords: Lignocelluloses, biomass, fuels, chemicals, conversion process

1. Introduction
Materials such as terrestrial and marine plants, trees of different forms store solar energy which by photosynthesis are converted to lignocelluloses. Lignocelluloses are available worldwide and a sizeable number of the world’s population rely on them for energy utilization or generation [1]. Biomass energy is a renewable resource that is not expensive as compared to the fossil energy. Fossil fuels like natural gas, crude oil, and coal, are referred to as biofuels formed due to the decomposition of plants underneath the earth. Fuels and chemicals presently produced from fossil deposits can also be made from lignocelluloses. Three major polymers present in lignocellulosic biomass are the celluloses (between 42-50%w/w), hemicelluloses (about 18-25%w/w), and lignin (21-32%w/w). Other extractable materials that are known as minor constituents are amino acids, proteins, ether, fats, resins, waxes, aliphatic acids, chlorophyll. Ash can also be present as minor constituents. Rapidly depleting oil reserves along with progress made in the processes of biomass conversion to sugars, fuel-alcohols, and other chemical products, have caused the economic significance of biomass conversion to fuels and chemicals to be comparable to that of petroleum based derived products [2].
Africa, forecast by experts showed that petroleum resources (i.e. fossil fuels) might be exhausted in a not too distant future [3]. The continent of Africa has thermal, hydro-electric, petroleum products, fuelwood as her primary energy resources. Leach and Mearns [4] reported that of the traditional energy consumed in the developing countries, 79% is fuelwood. Between 60% and 69% of this amount are located in the sub-Saharan Africa [4]. This article considers products/fuels and chemicals that can be derived from feedstock of sugar, starchy, and lignocellulosic biomass. Common and latest processing routes are also highlighted.

2. Different biomass sources and feedstocks for fuels and biomass production

2.1. Wood Biomass

Biofuels or bioproducts from wood biomass serve as replacements for petroleum derived products. Biofuels or bio-products are fuels or chemicals that can be produced through simple or integrated conversions of precursors, mainly polysaccharides, found in wood or wood processing by-products such as barks, pulps, shavings, sawdust, etc. Energy can be released from wood biomass by a number of processes – burning, pyrolysis, gasification, fermentation, chemical or bacterial breakdown (Figure 1) [5].

- Burning provides heat that can be used directly or to drive turbines to produce electricity.
- Fermentation converts plant sugars into carbon dioxide and ethanol; hence, could be utilized as liquid fuel.
- Chemical breakdown can provide synthetic gases and fuel oils.
- Bacterial processes can be tailored to produce methane, alcohols and a range of other chemicals.

Figure 1 gives a summary of some chemicals that can be produced from wood biomass.

2.2. Marine Biomass

Marine wastes and biomasses are useful feed-stocks for the production of biomethane, a Substituted Natural Gas (SNG). The conversion process involves anaerobic digestion [6]. The technology (algae conversion to biomethane technology) is well developed but most often the process may involve high conversion of energy. Direct use of methane or the conversion to other forms of energy such as electricity, hydrogen exist. The bioenergy concept from marine biomass can involve large, open ocean farms. Some of the macroalgae that could be used is known as Macrocystis pyrifera, otherwise referred to in the United States of America as giant Brown Kelp (U.S.A. National Research Council, 2000) since it has a high growth rates in natural beds. Macrocystis pyrifera has the potential of regular harvest caused by its repeated growth which originates through the holdfast cells. From the giant Brown Kelp, which can be harvested from natural beds, useful chemicals can be extracted. Other micro algal species are Laminaria, Gracillaria, and Sargassum. It is perceived though that marine biomass has a high cost of biomass energy. Some aquatic macrophytes (aquatic plants that grow near or in water whether floating or submerged) such as water hyacinth are efficient for wastewater treatment and the production of value added chemicals, compost and methane.
Figure 1 Potential chemicals from wood biomass [5]
About 90% of the marine algae is made up of moisture. Therefore, processes suited for recovering usable energy from marine algae are those which are compatible with high amounts of moisture. In this category are the anaerobic digestion and fermentation processes for the production of methane and alcohols respectively [6]. In general, marine algae biomass are good raw materials for the anaerobic digestion process because the conversion efficiencies are high, the conversion rate is rapid, and the production process is stable. The acid phase of the anaerobic digestion process of the marine biomass can also be used in producing acetic acid.

2.3. Polyols from Biomass

Polyols (these are alcohols derivatives e. g. glycerol) can be manufactured from biomass with an efficiency of 75% [7]. Several polymer intermediates and plastics are now produced from polyols - renewable raw materials. This technology has been proven to offer reduced costs of operations and more flexible than any other process in existence. By conventional technologies, ethanol and polyols are obtained from food crop fermentation processes or petroleum conversions, from which the target materials are synthesized. Meanwhile, there are processes that rely on agro – dietary wastes and non- food crop (Figure 2), absolutely independent of petroleum [7].

Due to new processing routes from increased research and development, polyols may now be produced through renewable alcohols and directly by means of hydrogenolysis of sugar groups from agricultural wastes and other renewable resources. Through hydrogenolysis, the sugar mined from agricultural residue is converted into glycol and glycerin as shown in Figure 3. There are variations of this process that are used today to render the process economical.

The preparation of bio-fuels and chemicals from lignocelluloses involves thorough feedstock preparations and suitable processing steps or methodologies [8]. Agricultural crops, by conversion and fermentation, yield various products as well as polyols and ethanol (Figure 4). It has been seen in many instances that these by-products have economic significance and it is worthy of getting back at them. As an illustration, glycerol is sold as a raw material and further processed to obtain pure ethanol - a raw material for the manufacturing of biodiesel. In fermentation of corn grain, products and ethanol that can be manufactured on a commercial scale include: antibiotics, lysine, monosodium glutamate, gluconic acid, lactic acid, acetic acid and malic acid.

All the chemicals (Figure 4) are used in applications and for other manufacturing processes. Feedstock like forestry wastes, agro-dietary wastes and farm crops, suitable for use in ethanol and polyols manufacture must contain carbohydrate such as sugars, cellulose or , starches that are readily fermented into glucose. These feedstock can approximately be categorised into;

1. Sugar crops; likesugar cane, sugar beets, fruits and sweet sorghum.
2. Starch such as potatoes, cassava and grains.
3. Cellulose: such as grass-like crops (non-food crops, hemp etc.), sugar cane bagasse and wood, wood wastes and corn stover.

The processing procedures for sugar-based feedstock vary in comparison to starch and cellulose-based feedstock materials. However, apart from the disparities in producing sugar from the feedstock; the subsequent stages are principally similar [7]. It should be noted that biomass products such as hydrocarbons and other derivatives are excellent sources that can be processed into other chemicals and [9],has shown that we are currently only converting about 5% of available biomass-wastes into hydrocarbon products.
Addition of soy bean oil to ethanol

Figure 2 A Simple pathway to convert biomass to polyols, ethanol and other products.

Figure 3 Polyols from agricultural wastes through hydrogenolysis.
In general, most biomass conversion to chemicals or fuels involve 3 main unit operations: pretreatment and hydrolysis; fermentation and product purification. Pretreatment step/hydrolysis arises by changing the macroscopic and microscopic size and structure of the biomass followed by its sub-microscopic chemical compositions and structures for the hydrolysis of the carbohydrate fractions to monomeric sugars could be obtained at a faster pace and resulting to an elevated harvests. This is the important area in the transformation of biomass to usable fuels and chemicals products. Fermenting the biomass medium employing biocatalysts to make the liquid fuel or chemical in a moderately dilute aqueous solutions. The last operation, product separation/purification involve processing the fermentation product to the desired level e. g. a concentrated form of denatured alcohol.

![Diagram of biomass conversion](image)

**Figure 4** Ethanol, Polyols and other derivatives from sugar, starchy and other agricultural wastes.

### 2.4. Advantages of biomass based fuels and chemicals

1. Biofuels sources are geographically uniformly dispersed compared to fossil fuels; hence, at a greater extent energy sources will be domestic and offer security of supply.
2. Biomass raw materials most are not expensive; hence, produced with lesser contribution of fertilizers, pesticides and energy.

3. Biomasses generally have non-polluting features

4. Biofuels and chemicals from lignocellulosic materials and other related feed stocks produce little net greenhouse gas emissions, decreasing ecological effects, principally climatic change. Therefore, they have limited polluting features compared to the fossil fuel feedstocks [10].

5. Biofuels have the capacity to offer employment in rural regions which limits movement of people to the urban communities. Mostly the sources of the raw materials for fuel and chemicals are of rural origins.

2.5. Economics of conversion processes

The vital economic mechanism in the transformation of biomass to fuels and chemicals is greater product yields for the purpose of improving revenues and decreasing the budget of waste treatment. It should also be noted that the resulting composition of any pretreated biomass is independent on the source of the biomass, and the kind of pretreatment method used. Expansion of the biomass industry as against or complimenting the oil and gas industries has great economic advantages. For example, if we assume a 2% annual increase in oil consumptions the world oil reserves may perhaps been exhausted by 2019 [11]. Also the enlargement of the biomass industry will create employment in agriculture, forestry and industries associated to producing biomass feedstock. The biomass energy industry would be extensively dispersed in rural communities contrasting the petroleum refineries, whose products has to be conveyed over long distances to get the consumers in the market. This engenders reduced plant sites, enough rural job opportunities, and reduced conveyance budget.

3. Types of Conversion Process for Biomass

As a result of the difficulty of the biomass dissolved via pretreatment processes, it is important to select the right conversion method beginning from the material to the anticipated product based. In addition, the criteria to be considered in order to attain efficient pretreatment are preservation of hemicelluloses fractions, for the purpose of achieving elevated yield of fermentable sugars; reducing the accumulation of inhibitors as a result of degradation; reducing the utilization of elevated energy in the process and the reducing the budget for the pretreatment processes [12]. This sub-section reviews different conversion processes.

3.1 Chemical Based Conversion

It was discussed in section 2.3 that biomass conversion to chemicals or fuels involve 3 main unit operations; pretreatment and hydrolysis, fermentation, and product separation; however, the type of processes involved in this type of conversion were not discussed. Chemical based conversion involves chemical interactions to transform biomass to liquid fuel. It is well known that cellulose in a raw biomass have the properties responsible for the transformation to biofuel using a chemical based conversion. Typically, the initial stage in biomass chemical transformation contains the cellulose or hemicellulose depolymerisation by acid catalyzed hydrolysis into the equivalent monosaccharides. These are well-known conventional and recognized processes [13]. The conversion of such monosaccharides in chemicals start with dehydration, oxidation or reduction reactions. Hence, the acid catalyzed dehydration is well investigated and well-established process. With proper acid settings, glucose is parched to 5-
hydroxymethylfurfural (HMF), this have the capacity to later hydrolyzed to levulinic acid (LA) and formic acid. Xylose together with some usual pentoses are parched by acid catalysis to furfural [14].

A process was introduced in the year 2002 to convert cellulose to chemical 5-hydroxymethylfurfural and catalyst at 120°C also exist. Cellulose, via catalytic transformation, has the capacity to be transformed to HMF; as the degradation transformation of cellulose with the existence a catalytic quantity of LaCl3 attained 80.3%, 3 min later. This matched up to the throughput of 83, however the reaction barely progress without the catalyst [15]. In 2010, a new modest and stress-free chemical process was developed employing a very less expensive C9H6CrO3 together with reduced catalyst heaping to transform cellulose to HMF at lower temperature (<120°C) in ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl). Solid acid possessing adequate acidic characteristics was utilized to encourage cellulose hydrolysis [16]. Such a technology can be interested in transforming cellulosic biomass to several chemicals and fuels. Another new process was developed in year 2014 for high performance transformation of cellulose in HMF through utilizing AlCl3 as the catalyst in DMSO–ionic liquid ([BMIM] Cl) mixtures. However, this new process was developed at higher temperature. An elevated yield of HMF at 54.9% was attained from cellulose at 150 °C, just subsequently the processing time of 32400 sec in a composite solvent of DMSO–[BMIM]Cl (10 wt.%). It is worth noting that, catalytic scheme have capacity to be used again for numerous times in spite of the minor loss of its catalytic action [17]. In addition, it is imperative to analyze catalyst potential and shortcomings in the chemical conversion of biomass feedstock.

3.2 Thermal based conversion

The application of heat plays a vital role in biomass thermal conversion to biofuel. Biomass thermal conversion is divided into (i) combustion, (ii) gasification and (iii) pyrolysis. Up till date, the most of biomass conversion technologies are made of combustion of biomass; however, combustion process has low efficiency. Furthermore, the process had environmental and health concerns. Combustion takes place with sufficient oxygen to entirely oxidize fuel such as converting the whole carbon to carbon dioxide, the whole of the H2 to H2O, and whole of the S to SO2. Gasification takes place with inadequate oxygen in a way that total oxidation will seize to happen. Pyrolysis takes place without an oxidizing agent; such as air, O2. As a transitional procedure amid combustion and pyrolysis, gasification can also be called partial oxidizationl or partial pyrolysis [18].

Biomass gasification involves heating the biomass at elevated temperatures with controlled quantity of oxygen. The subsequent syngas either use for production of fuels. This technology employs efficient syngas than the direct combustion of the original fuel. Gasification procedures offer an economical path for the transformation of numerous, extremely dispersed and lesser-quality lignocellulosic biomass resources to synthetically produced gas for the purpose of generating of a wide-ranging kind of harvests such as liquid fuels, electricity, heat, power and synthetic chemicals and hydrogen production (H2) [19]. Biomass gasification have the capacity to attain greater throughputs in producing electricity and reducing emissions when likened to combustion processes. In addition, gasification upsurges the likely usages of biomass because the product gas possess value apart from been a fuel in its nature, nonetheless
it is also employed as a feedstock utilized in producing additional fuels, like C₂H₅OH and H₂ [18]. In order words, the gasification products primarily comprise of hydrogen, CO, CO₂, methane, and H₂O. In gasification process, some portion of the bio-mass is transformed to tars, char particles and ash in place of synthetic gas. The decline and transformation of char and tar is considered prime subject of matter with reverence to biomass gasification. This upsurge the syngas produce and overall transformation effectiveness. The produced syngas quality is dependent on properties like heating rate, raw composition, temperature, water content, the kind of gasifier, and pyrolysis products to be oxidized [19].

Pyrolysis technology involves the heating of biomass at elevated temperature in the absent of O₂. Utilization of pyrolysis to decompose wood and grass biomass via heat has a prospect in the pretreatment for the synthesis of biofuels using lignocellulosic resources [20]. Generally, pyrolysis uses cellulose and hemicellulose component transformation; however much is not known regarding the influence of such technique to lignin fraction [12]. The lignin is simply transformed to lesser concentration of phenolics and char. This technology harvests three kinds of products which are gases, bio-oil and char. Bio-oil, sometimes called “tar or pyrolytic oil”, is corrosive, viscous, moderately not stable and very intricate chemically, it does not have the capacity to be directly employed as transportation fuel, as consequence of its elevated oxygen content (40-50 wt%), more water content (15-30 wt%) together with lesser Hydrogen-Carbon ratios [19]. The capability of pyrolysis technology producing bio-fuel with elevated fuel-to-feed ratios is very high. Hence, pyrolysis has attracted attention with reference to effective technique in transforming biomass to bio-fuel in past two decades [21]. The main aim of such technique was to harvest elevated-quality bio-oil for the purpose of contending with non-renewable fossil fuels and subsequently replacing the non-renewable fossil fuels. Furthermore, advancement of pyrolysis technology is in continuous progress as pyrolysis bio-oil is the liquid manufactured from the condensation of vapour of a pyrolysis reaction [22]. Classification of pyrolysis can be grouped into slow pyrolysis, fast pyrolysis and flash pyrolysis; this is dependent on reaction temperature, heating rate and residence time [23].

3.3 Thermochemical Conversion
Thermochemical conversion equipments for different biomass exist and it can transform agricultural biomass into biofuels/bioenergy [24, 25]. However, selecting the best option as a result of the high achievement of these technologies for envisioned application still remain a challenge. In addition, the transformation of agricultural biomass using thermochemical technology is an exceedingly established technology developed for petroleum and several chemical products. Nonetheless, complication in agricultural biomass and elements like wetness, O₂, S, N₂, and metal substances give room for it difficulties [26, 27]. The yields of the thermo-chemical procedures can be grouped into a volatile fraction made of gases, vapors and tar components and a carbon rich solid residue [28]. The diverse techniques have a tendency of highlighting the diverse instrumental sub-sets in the enormous cluster of prospective chemical mechanisms whereby biomass is transformed to principal harvests, subsequently get transformed by altering the extent of finishing products [29].

Biomass is thermo-chemically treated in the temperature range amid 200 to 315°C in the absence of O₂, for carbonization [30]. Carbonization is attained by total transformation of biomass to biochar. Hence, yield achieved ample elevated energy density when likened to raw
biomass, this reduces the budget for the transportation of the carbonized biomass [26]. Carbonized/torrefied biomass usually possess favourable characteristics like hydrophobic nature, associated characteristics as coal, it is easy to crush and pulverized. The final yields are made of condensable gases like water vapor, formic acid, methanol, lactic acid, phenol, acetic acid and furfural. Hence, carbonization and torrefaction procedures are employed for transforming biomass to a better effective forms of energy source for the purpose of lessening the accompanying cost of conveyance.

3.4 Physical Based conversion
The physical conversion of biomass is essentially a process of mechanical pressing of crops such as soybean and sunflower, with high oil content, and the biomass is densified into solid briquettes. For physical based conversion, pretreatment for some biomass is not usually needed. Here, the preliminary combustion produces steam at elevated pressure and the steam is finally employed to trigger the turbine plant which will subsequently produce electricity. Another method is directly heated the biomass to break it down to flammable gas. The gas sometimes known as biogas would be taken into filtration system in order to clean and improve it before subjecting it for the employment of electricity generation [12].

3.5 Biological Based Conversion
Biological transformation comprises cellulosic or hemicellulosic sugar conversion to fuel [12]. Biofuel such as bioethanol production is utmost popular biofuel that employs microorganism(s) to be the catalyst in the bioconversion process. The two step processes of biological based conversion are fermentation and pretreatment. These processes are used to obtain the primary sugars [31]. Several natural gas can be converted to liquid fuel via biological based conversion. Biological based conversion technique for active transformation of natural gas to fuels in liquid state or other chemical components has capability of converting the natural gas industrial sector employing the important part of the global deposits of natural gas in isolated areas [32]. In addition, bio-technological production of biofuel and chemical products is principally dependent on an elevated cost of sugars, like glucose, as a source of energy and carbon. This cost is estimated to be in the neighbourhood of 50% of the final expected products [33, 34]. Hence, substantial efforts are in progress to find alternative sources carbon, intended to lessen the production cost of fuels as well as chemicals [35]. Schamphelaire and Verstraete [36] explored the utilization of algae for the production of energy in an isolated, closed system. Such system consists of an algal growth unit for manufacturing of biomass. This unit is anaerobic digestion, which transform the biomass to biogas and a microbial fuel cell which helps polishing the effluent of the digester. Subsequently, nutrients that are release in the process of digestion could be reverted to the algal growth unit for a continued algal growth. Therefore, a system presented has the capability to continuously convert solar energy to energy-rich biogas and electricity.

4. Conclusions
For the purpose of making biomass become a sustainable industry, numerous obstacles must be lessened. There is necessity to construct substantial, large scale energy plantations which have the capacity to supply sustainable quantities of low cost feedstocks. It is important to
make the economy conducive for the investors to come into the industry (currently returns on investments are very low, and thus unrewarding for investors to come in). In addition, there implementation is needed for an integrated biomass energy dispersal system to simplify consumer’s access. Several conversion process have been discussed. It is hence, important to providing conducive home grown researches in this area of alternative energy source especially in research institutes and universities.

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