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Integrated Biorefinery Approach to Lignocellulosic and Algal Biomass Fermentation Processes

Felix Offei

Abstract

Lignocellulosic and algal biomass have been suggested as relatively sustainable alternatives to sugar and starch-based biomass for various fermentation technologies. However, challenges in pretreatment, high production costs and high waste generation remains a drawback to their commercial application. Processing cellulosic and algal biomass using the biorefinery approach has been recommended as an efficient and cost-effective pathway since it involves the recovery of several products from a single biomass using sequential or simultaneous processes. This review explored the developments, prospects and perspectives on the use of this pathway to add more value and increase the techno-economic viability of cellulosic and algal fermentation processes. The composition of lignocellulosic and algal biomass, the conventional ethanol production processes and their related sustainability issues are also discussed in this chapter. Developments in this approach to lignocellulosic and algal biomass has shown that valuable products at high recovery efficiencies can be obtained. Products such as ethanol, xylitol, lipids, organic acids, chitin, hydrogen and various polymers can be recovered from lignocellulosic biomass while ethanol, biogas, biodiesel, hydrocolloids, hydrogen and carotenoids can be recovered from algae. Product recovery efficiencies and biomass utilisation have been so high that zero waste is nearly attainable. These developments indicate that indeed the application of fermentation technologies to cellulosic and algal biomass have tremendous commercial value when used in the integrated biorefinery approach.

Keywords: fermentation, integrated biorefinery, lignocellulosic biomass, algae, ethanol

1. Introduction

Concerns over the depletion and environmental effects of greenhouse gas (GHG) emissions from the use of fossil fuels has led to the extensive search for alternative, renewable and sustainable fuels. Currently, the highest contributor to GHG emissions is the transportation sector through fuel combustion. Biomass is currently the only abundant renewable energy source for the direct production of fuel. Typical fuels currently produced from biomass include bioethanol, biogas, biodiesel, bio-butanol, syngas and bio-oil. Bioethanol is currently the largest alternative fuel produced globally at 106 billion litres per annum [1].

Sugar and starch-based biomass have been the primary choice of raw material for the production of food and fuel grade ethanol for various commercial

applications. They however face enormous competing interests often illustrated with the food-vs.-fuel debate [2]. Lignocellulosic and algal biomass have been suggested as relatively sustainable alternatives. They have been hundreds of extensive research on the factors that influence their efficiency as substrates for ethanol production. The major drawbacks noted in these studies during their application include: the need for pretreatment processes, higher production costs and high waste generation [3]. A processing approach that has potential to maximise the profitability and minimise waste generation from the use of cellulosic and algal biomass as feedstock is the integrated biorefinery approach. The integrated biorefinery concept refers to the use of single or multiple technologies to produce several high value products from a single or multiple biomass [4]. This approach to biomass processing is considered more efficient, economical and sustainable.

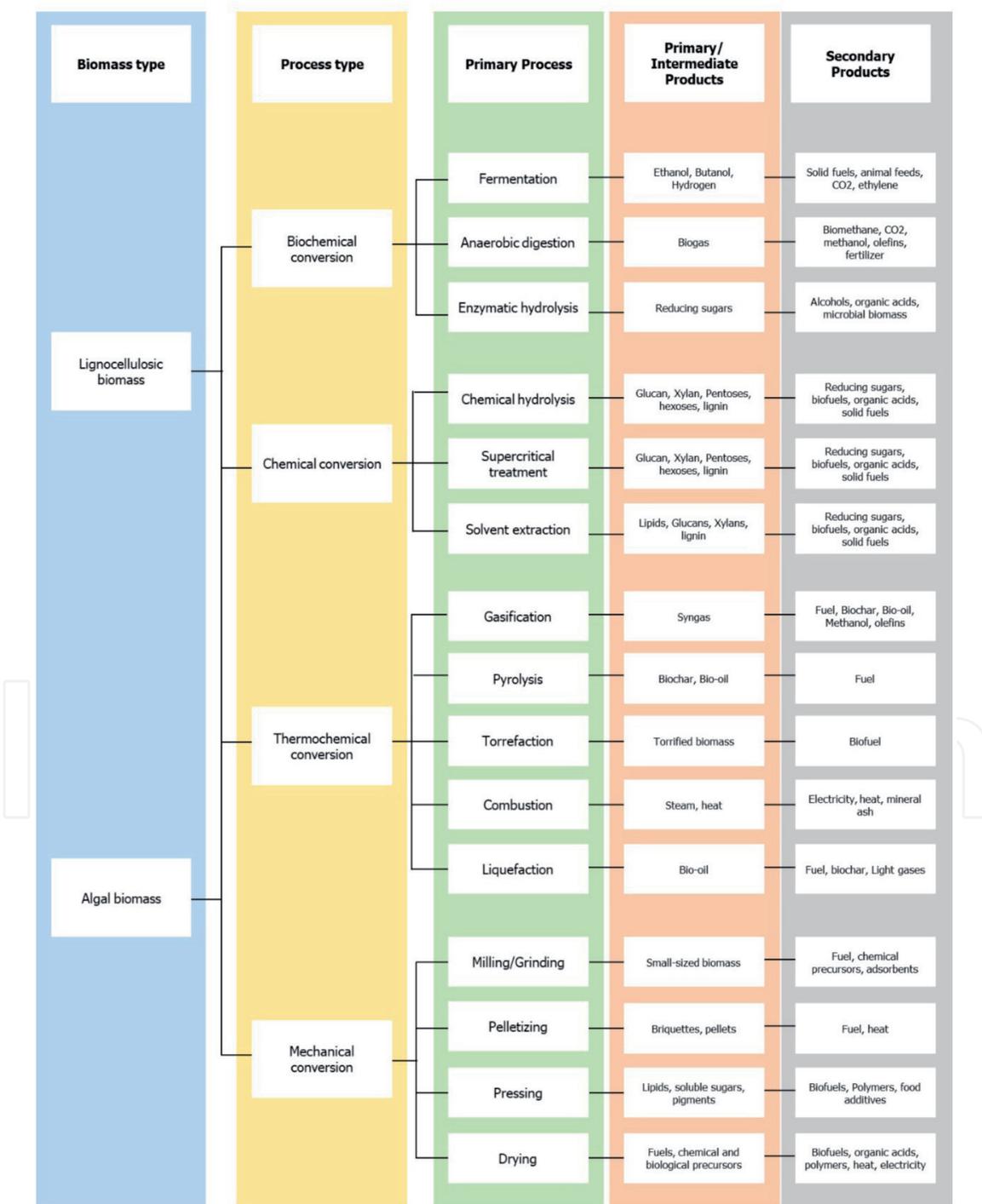


Figure 1. Typical biorefinery conceptual scheme.

Biorefineries generally integrate various biomass conversion technologies to produce fuels, power, heat and other value-added products from biomass. These refineries have evolved over the last two decades in several phases. Phase I biorefineries convert a single raw material to a single product. Phase II converts a single raw material using multiple processing tools to obtain a broad range of products. Phase III biorefineries, commonly referred to as integrated biorefineries use a wide range of raw materials and technologies simultaneously or sequentially to produce a wide range of valuable products [5]. Some integrated biorefineries use various feedstock and technologies to produce biofuels as main products along with co-products such as platform chemicals, heat and power [5].

The International Energy Agency sums up the description of the biorefinery concept as “the sustainable processing of biomass into a spectrum of marketable products and energy” [6]. It expands the concept to include a wide range of technologies that separate biomass resources into their basic polymeric units such as carbohydrates, proteins, lipids and even elementals which can be converted to valuable products including fuels, heat and chemicals. Biorefinery as an entity is described as a facility or network of facilities where various processing technologies are integrated to obtain multiple products from a single or several types of biomass [6]. Bioethanol is currently the leading energy product recovered from biomass using the biorefinery approach.

Sugar and starch-based biomass have been the primary choice of material for the production of food and fuel grade ethanol for various commercial applications but has an enormous competing interest often illustrated with the food-vs.-fuel debate. Lignocellulosic and algal biomass have been suggested as relatively sustainable alternatives. However, difficulties in pretreatment, high waste generation and high processing costs remains a drawback to their commercial application. Processing cellulosic and algal biomass using the biorefinery approach has been recommended as an efficient and cost-effective pathway since several valuable products can be recovered using sequential or simultaneous processes as illustrated in **Figure 1** [4]. This review explored the developments made in the use of this pathway to add more value and increase the techno-economic viability of cellulosic and algal fermentation processes. The composition of lignocellulosic and algal biomass, the conventional ethanol production processes and their related sustainability issues are also discussed in this chapter.

2. Lignocellulosic biomass for biorefinery applications

Lignocellulosic biomass typically refers to plant materials composed primarily of cellulose, hemicellulose and lignin. This type of biomass usually includes forest materials, agricultural residues, wood processing residues and non-edible plant materials usually referred to as energy crops (**Table 1**). In the context of biofuel production, lignocellulosic biomass are referred to as second generation biomass which is used to differentiate them from sugar and starch based biomass (1st generation biomass) and algal biomass (3rd generation biomass). They are typically composed of 40–50% cellulose, 25–30% hemicellulose and 15–20% lignin [30]. The effective use of these three primary components would significantly determine the economic viability of cellulosic ethanol production.

Cellulose refers to the linear polymer made up of glucose monomer units bonded together by β -1,4 glycosidic bonds. Hemicellulose refers to branched heteropolymers of xylose, glucose, galactose, mannose, arabinose and some uronic acids. Lignin is primarily made up of three major phenolic components, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [20]. The ratio of these

Biomass type	Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Agricultural residues	Sugarcane bagasse	49	29.6	27.2	[7]
	Barley straw	37.5	37.1	16.9	[8]
	Rice husk	33.4	30.0	18.3	[9]
	Corn cob	44	36.4	18.0	[10]
	Corn stover	36.5	31.3	13.6	[11]
	Rye straw	42.1	24.4	22.9	[12]
	Rapeseed straw	37.0	24.2	18.0	[13]
	Wheat straw	40.0	33.8	26.8	[14]
	Rice straw	36.6	22.0	14.9	[15]
	Sunflower stalk	33.8	24.3	19.9	[16]
	Sorghum bagasse	45.3	26.3	16.5	[17]
	Barley hull	34.0	36.0	19.0	[18]
	Banana peels	13.0	15.0	14.0	[19]
	Cotton stalk	31.0	11.0	30.0	[20]
	Coffee pulp	36.9	47.5	19.1	[20]
	Wheat bran	14.8	39.2	12.5	[20]
	Sugarcane tops	35.0	32.0	14.0	[21]
	Jute fibres	45.0	18.0	21.0	[20]
	Oat straw	31.0	20.0	10.0	[20]
	Soya stalks	34.5	24.8	9.8	[22]
Municipal and industrial wastes	Newspapers	60.3	16.4	12.4	[23]
	Paper sludge	60.8	14.2	8.4	[24]
	Brewer's spent grain	21.0	32.8	25.6	[25]
Woods and grasses	Softwood stems	44.5	21.9	27.7	[6]
	Switchgrass	35.4	26.5	18.2	[6]
	Bamboo	50.0	20.0	23.0	[20]
	Eucalyptus	51.0	18.0	29.0	[20]
	Hardwood stems	55.0	40.0	25.0	[26]
	Pine	49.0	13.0	23.0	[20]
	Poplar wood	51.0	25.0	10.0	[20]
	Olive tree	25.2	15.8	19.1	[27]
	Water hyacinth	22.1	50.1	5.4	[28]
	Spruce	43.8	20.8	28.3	[29]
Oak	45.2	24.5	21.0	[29]	

Table 1.
Composition of typical lignocellulosic biomass used in biorefinery applications.

components varies between various plant tissues as shown in **Table 1**. The cellulose units are packed into microfibrils which are attached to each other by hemicelluloses and amorphous polymers of different sugars as well as other polymers such as pectin covered by lignin. The units of individual microfibrils in crystalline cellulose are packed so tightly that neither enzymes nor water molecules can enter the complex framework [20]. This high molecular weight and ordered tertiary structure of natural cellulose makes it insoluble in water. However, some parts of the microfibrils have a less ordered, non-crystalline structure referred to as amorphous regions [31]. The crystalline regions of cellulose are more resistant to biodegradation than the amorphous parts while cellulose with low degree of polymerisation will be more susceptible to cellulolytic enzymes. The composition of typical lignocellulosic biomass that have been considered for various biorefinery applications are presented in **Table 1**.

3. Algal biomass for biorefinery applications

Marine biomass accounts for over 50% of primary biomass produced globally but has been the least harnessed for various applications [32]. It is mainly grouped into two, namely macroalgae (commonly known as seaweeds) and microalgae. However, cyanobacteria is conventionally regarded as a form of algae often called blue-green algae [33]. Both groups have been used in the production of various biofuels. Microalgae has been explored predominantly as substrate for bio-oils and biodiesel while macroalgae has been used mainly in bioethanol and biogas production [32].

Marine algae are plant-like multicellular organisms that live attached to hard substrata such as rocks in coastal areas [34]. Their basic structure consists of a thallus, which forms the body of the organism and a holdfast, a structure on its base which allows it to be attached to hard surfaces such as rocks near the shoreline of coastal areas. Brown seaweeds are the largest in size, growing up to 4 m in length for some species. Green and red seaweeds are smaller ranging from a few centimetres in some species to a meter in others [35]. According to the FAO [36], 8.2 and 15.8 million tons of brown and red seaweed respectively were produced in the year 2013. This was valued at USD 1.3 billion and 4.1 billion for the brown and red seaweeds respectively. For the green seaweed 14,800 tons valued at USD 15.7 million was produced globally in the year 2013 [36]. The enormous difference in the production values of the brown and red from the green seaweed can be attributed to the valuable hydrocolloids such as alginate, carrageenan and agar found only in the red and brown seaweeds.

The structural differences found between land-based plants and algae gives algal biomass an advantage of a higher yield per hectare. In comparison to land-based plants, seaweeds have an average yield per hectare per year of 730,000 kg while sugarcane, sugar beet, maize and wheat have 68,260; 47,070; 4,815 and 2,800 kg respectively [37]. The high yields from macroalgae in general is attributed to the low energy required in the formation of its supporting tissue during growth. Seaweeds can also absorb nutrients across its entire surface and can be cultivated three dimensionally in water [37].

Seaweeds are composed of carbohydrates, proteins, lipids and minerals which ranges from 30 to 60%, 10–40%, 0.2–3% and 10–40%, respectively [38]. Besides their unique and varying composition, seaweeds have been grouped into three, based on their pigmentation. They are rhodophyceae (red seaweeds), phaeophyceae (brown seaweeds) and chlorophyceae (green seaweeds) based on their pigments r-phycoerythrin, chlorophyll and xanthophyll, respectively [39].

Biomass type	Species	Carbohydrate	Protein	Lipid	Ash	Ref.
Macroalgae (seaweed)	<i>Chaetomorpha linum</i>	54	—	—	22	[35]
	<i>Caulerpa lentillifera</i>	38.7	10.4	1.1	37.2	[40]
	<i>C. linum</i>	29.8	8.6	2.6	30.5	[41]
	<i>Codium fragile</i>	58.7	15.3	0.9	25.1	[42]
	<i>Ulva fasciata</i>	31.3	14.4	1.5	28.0	[43]
	<i>Ulva lactuca</i>	54.3	20.6	6.2	18.9	[44]
	<i>Ulva pertusa</i>	52.3	25.1	0.1	22.5	[38]
	<i>Ulva rigida</i>	53	23.4	1.2	21.7	[45]
	<i>Chondrus pinnulatus</i>	64.4	22.5	0.2	12.9	[46]
	<i>Cryptonemia crenulata</i>	47	—	—	19	[47]
	<i>Kappaphycus alvarezzi</i>	60.7	17.4	0.8	21.1	[48]
	<i>K. alvarezzi</i>	55	—	—	23	[47]
	<i>Eucheuma cottonii</i>	26.5	9.8	1.1	46.2	[40]
	<i>Gelidium amansii</i>	66.0	20.5	0.2	13.3	[42]
	<i>Gigartina tenella</i>	42.2	27.4	0.9	24.5	[46]
	<i>Hypnea charoides</i>	57.3	18.4	1.5	22.8	[26]
	<i>Hypnea musciformis</i>	39	—	—	22	[47]
	<i>H. musciformis</i>	37	—	—	30	[47]
	<i>Hydropuntia dentata</i>	31.2	10.3	3.2	38.7	[43]
	<i>Lomentaria hakodatensis</i>	40.4	29	0.7	29.9	[46]
	<i>L. digitata</i>	64.2	3.1	1.0	11.9	[49]
	<i>Laminaria japonica</i>	51.9	14.8	1.8	31.5	[44]
	<i>Sargassum fulvellum</i>	39.6	13	1.4	46	[44]
<i>Sargassum polycystum</i>	33.5	5.4	0.3	42.4	[40]	
<i>Sargassum vulgare</i>	32.6	10.3	1.0	27.2	[43]	
<i>Saccharina latissima</i>	16.8	10.1	0.5	34.6	[49]	

Biomass type	Species	Carbohydrate	Protein	Lipid	Ash	Ref.
Microalgae	<i>Scenedesmus acutus</i>	39.0	8.0	41.0	2.0	[50]
	<i>Scenedesmus obliquus</i>	25.0	48.8	22.5	12.9	[51]
	<i>Pseudochoricystis ellipsoidea</i>	19.3	27.5	45.4	2.3	[51]
	<i>Chlorogloeopsis fritschii</i>	37.8	41.8	8.2	4.6	[51]
	<i>Chlorella vulgaris</i>	16.7	41.0	10.0	13.4	[52]
	<i>Chlorella emersonii</i>	37.9	9.0	29.3	2.8	[51]
	<i>Chlorella zofingiensis</i>	11.5	11.2	56.7	4.8	[51]
	<i>Spirulina sp.</i>	15.1	50.1	12.3	7.6	[51]
	<i>Nannochloropsis sp.</i>	37.3	32.2	25.0	5.5	[53]
	<i>Schizochytrium limacinum</i>	25.3	12.4	56.7	5.6	[53]
	<i>Chlorella vulgaris</i>	43.4	28.2	17.9	10.5	[53]
	<i>Scenedesmus sp.</i>	35.4	24.6	10.5	29.5	[53]
	<i>Chlamydomonas reinhardtii</i>	35.5	34.2	24.2	6.1	[53]
	<i>Dunaliella tertiolecta</i>	21.7	61.3	2.9	13.5	[54]
	<i>Botryococcus braunii</i>	2.4	39.6	33.0	7.5	[52]
	<i>Spirulina platensis</i>	11.0	42.3	11.0	7.1	[52]
<i>Chaetoceros muelleri</i>	34.2	16.3	43.4	—	[51]	

Table 2.
Composition of typical algal biomass used in biorefinery applications.

Algal biomass composition has been found to vary based on several factors such as the season, availability of nutrients, water salinity and availability of sunlight (**Table 2**) [55]. The algal component of primary importance to bioethanol production is the carbohydrates (polysaccharides), since they currently form the only fraction that can be fermented to ethanol. Generally, some algae are composed of large fractions of complex sulphated polysaccharides which are uniquely different in each group serving as their cellular storage and structural support tissue [56]. The composition of typical algal biomass that have been considered for various biorefinery applications are presented in **Table 2**.

4. Processes for bioethanol production

The conversion of cellulosic and algal biomass to bioethanol usually involves four major processes excluding biomass selection. They include biomass pretreatment, hydrolysis of pretreated biomass, fermentation of biomass hydrolysates and ethanol recovery from the fermentation broth using distillation and dehydration processes [46]. The various efficiencies of each process will influence the final ethanol yield therefore each process condition and catalyst used is carefully selected and in most cases optimised to maximise the process efficiencies.

One of the most influential processes in bioethanol production from cellulosic and algal biomass is pretreatment. This process is used to render biomass susceptible to further breakdown by separating the cellulose, hemicellulose and lignin fractions. The selection of an efficient and cost effective biomass pretreatment method has been a major hurdle in cellulosic bioethanol production and its commercialisation for several decades. Different pretreatment mechanisms have been developed with varying degrees of efficiency [20]. All these methods have been developed with a common aim of finding a good balance between efficiency, cost, environmental effects and energy use. So far, all the methods developed have come with intrinsic advantages and disadvantages. Some common disadvantages experienced include: degradation of sugars, formation of inhibitors, high energy requirements, catalyst requirements, difficulties in catalyst recovery, challenges in waste treatment and high overall costs [20]. One or more these drawbacks are experienced in the various pretreatment processes currently developed. Nonetheless, a careful comparison and risk analysis could be used to distinguish and select one from the other. The biomass specificity for particular pretreatments could be explored to see the variations in the interactions between various cellulosic and algal biomass and various pretreatment methods as a solution.

The hydrolysis process in bioethanol production is one of the most limiting stages in the entire production process since it is the stage where the sugars to be converted to ethanol is obtained. Hydrolysis simply refers to cleavage or division through the addition of water molecules. In the context of complex sugars (polysaccharides), it involves the use of a water molecule by a catalyst to break the glycosidic linkages within their polymeric form (di-, tri-, oligo- or polysaccharide) to their monomeric form (monosaccharides or reducing sugars). During the cleavage of sugars, a hydrogen atom (H^+) is gained by one part of the polymeric structure while the other gains a hydroxyl group (OH^-). Thus, the separation continues until all polymeric units are reduced to their individual monomeric form [46].

The hydrolysis of cellulosic biomass for bioethanol production involves the breakdown of polymeric units such as cellulose and hemicellulose while the hydrolysis of algal biomass (particularly macroalgae) involves the breakdown of polymeric units such as laminarin, ulvan, alginate, carrageenan, mannitol, agar and cellulose. The simple sugars (monosaccharides) recovered from both algal and

cellulosic biomass include glucose, galactose, rhamnose, mannose, fucose, xylose and arabinose for fermentation to ethanol [57]. The common methods that have been used in cellulosic and algal biomass hydrolysis includes dilute acid thermal [58], dilute alkaline thermal [59], enzymatic [3] and thermal [58] hydrolysis. All other hydrolysis methods are usually derivatives of these and are usually broadly grouped under physical, chemical, thermal and biological hydrolysis. Two or more of these methods are often combined to improve the efficiency of monomeric sugar recovery.

Enzymatic hydrolysis, particularly the use of cellulases in both cellulosic and algal biomass hydrolysis, has been promoted extensively over all other forms of hydrolysis. This is because enzymes are considered more environmentally friendly in their application and generate no inhibitors as is the case with chemical catalysts. Three major cellulase activity systems have been identified to be involved in cellulosic hydrolysis. The enzymes involved in these systems include endoglucanases, exoglucanases (cellodextrinases) and β -glucosidases [60]. Cellulase synthesis is predominant among fungi such as *Trichoderma reesei*, *Aspergillus niger*, and *Humicola insolens*; and bacteria such as *Bacillus subtilis*, *Streptomyces drozdowiczii*, and *Bacillus pumilus* [20]. Studies in enzymatic hydrolysis have focused on process optimization, improving cellulase activities, optimisation of reaction conditions, enzyme-to-substrate ratios and enzyme recovery and reuse strategies. The ideal final enzyme or enzyme cocktail should have high hydrolytic efficiencies on the preferred biomass, operate at mildly acidic or alkaline pH, be resilient to process stresses and be cost-effective [30].

The fermentation process in bioethanol production is the stage within which the reducing sugars obtained after hydrolysis are converted to ethanol by an organism. This process is always dependent on the overall ethanol production pathway selected. Currently, the ethanol pathways that have been used in cellulosic and algal biomass processing include: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF) and consolidated biomass processing (CBP) [46]. SHF is the most common and most well-developed approach which allows the use of the optimal conditions for both the hydrolysis and fermentation processes [61]. It offers the flexibility of choosing various hydrolysis processes, a feature which cannot be found in the use of the SSF approach. The SSF process involves the co-application of the enzyme for saccharification and the organism for fermentation to the pretreated biomass in the reactor under similar conditions of operation. This process is considered more cost-effective than SHF but comparisons on its process efficiency relative to SHF is currently inconclusive [46].

5. Integrated biorefinery applications to lignocellulosic biomass

Processing of cellulosic biomass using the biorefinery approach has often had its roots in the processing of first generation biomass. Typical first generation biomass such as corn, sugarcane and cassava (mostly in Africa and Asia) are still the most preferred feedstock in commercial fermentation processes. The biorefinery way of processing corn by microbial fermentation often yields ethanol, citric acid, lactic acid or lysine as the main product depending the primary product goal of the biorefinery [62]. Conventionally, the starch fraction of the corn is processed to dextrose via enzymatic pathways before microbial fermentation to the desired product. Corn fibre, gluten meal and corn steep liquor are the usual by-products obtained in a corn biorefinery which are of enormous value. Corn fibre which is lignocellulosic in nature can be further hydrolysed to obtain glucose, xylose and other monomeric

sugars which can be further fermented to products such as ethanol, xylitol and acetate [63]. Gluten meal from corn which is very high in proteins can be used as feed for livestock and poultry or as substrates for various pharmaceutical products and commercial polymers [64]. Corn steep liquor which is also high in proteins is often used as a nitrogen source in various fermentation processes [65].

Sugarcane biorefineries are usually very interesting due to the unique composition of sugarcane which is usually 11–16% sucrose, 70–75% water and 10–16% fibre [63]. Sugarcane processing begins with the extraction of cane juice which immediately leads to the generation of solid residue in the form of sugarcane bagasse. Sugarcane bagasse is very high in fibre and is considered a lignocellulosic biomass. This bagasse can be valorised in a relatively more complex pathway to ethanol and other chemicals using microbial fermentation technologies or simply used as fuel in boilers for the generation of steam and electricity. The latter is the predominant process application of bagasse in industry currently. Sugarcane alone as a single biomass can be processed to obtain first generation ethanol from the cane juice and second generation ethanol from the bagasse. Additionally, sugar processing plants which use sugarcane obtain molasses as a sucrose-rich by-product which can also be used as substrate for ethanol production [63].

The potential co-production of ethanol and xylitol from sugarcane bagasse was examined in a study by Unrean and Ketsub [66]. In the study, cellulose and hemicellulose fractions of the sugarcane bagasse were separated using sulphuric acid and enzymatic hydrolysis processes. The pretreated cellulose was used as substrate for the recovery of ethanol using *Saccharomyces cerevisiae* as the fermenting organism while hemicellulose hydrolysate was used as substrate for the recovery of xylitol with *Candida tropicalis* as the fermenting organism. The product recoveries reported from the use of the bagasse was 0.44 g/g total glucose for ethanol and 0.50 g/g total xylose for xylitol. An economic analysis within the same study revealed a 2.3 fold increase in profitability for the integrated ethanol and xylitol production process over standalone cellulosic ethanol production [66].

Cellulosic pulp and paper mill waste in the form of primary sludge was examined in a study as a substrate for the production of bioethanol and biolipids [67]. In the integrated study, bioethanol and biolipids were both obtained from the hydrolysates of the primary sludge at yields of 9% and 37.8%, respectively. *S. cerevisiae* was used as the fermenting organism for bioethanol while the oleaginous yeast *Cutaneotrichosporon oleaginosum* was used as the organism for the biolipids production. A unique addition to the biorefinery process was the use of the unhydrolysed primary sludge as a cement additive or fibre reinforcement material in comparison with conventional Portland cement. The comparison of the compression load between the two materials indicated that the unhydrolysed paper mill material had 102% higher compressive strength than the Portland cement [67]. This unique application of fermentation based and non-fermentation based processes to harness the use of the pulp and paper residual biomass in a zero waste approach can be explored for other lignocellulosic biomass.

Dairy manure, a nitrogen rich cellulosic biomass has been examined as a substrate for the co-production of fumaric acid and chitin [68]. Fumaric acid is commonly used in food flavouring and preservation while chitin is a natural biopolymer with applications in the water treatment and pharmaceutical industries. In the study by Liao et al. [68], *Rhizopus oryzae* ATCC 20344 was applied as fermenting organism in a one-pot fermentation process to obtain fumaric acid in the liquid medium of the broth while chitin was found in the resulting fungal biomass formed in the broth. A maximum fumaric acid yield of 31% and a chitin yield of 0.21 g/g fungal biomass (from 11.5 g/l fungal biomass concentration) was obtained [68].

Wheat straw and corn stover have been studied as substrates for the co-production of hydrogen and ethanol [69]. In the study, genetically engineered *Escherichia coli* were applied in a dark fermentation process as means to maximise the simultaneous production of the two products. The engineered strain of *E. coli* produced a 30% increase in the co-production yield of hydrogen and ethanol. The yields obtained were 323 ml H₂/g total reducing sugars (TRS) and 3.5 g ethanol/g TRS for wheat straw and; 337.1 ml H₂/g TRS and 2.9 g ethanol/g TRS for corn stover [69].

Lignin utilisation has been a very important part of the goal to maximise the use of lignocellulosic biomass in a biorefinery context. Considerably large quantities of lignin-rich by-products are generated from the conversion of cellulosic biomass to biofuels and various organic compounds. The efficient use of the lignin can improve the overall economics of the commercial use of lignocellulosic biomass [70]. A wide range of polymeric materials which can be used as precursors for even more valuable products have successfully been derived from lignin. They include polyesters, epoxy and phenolic resins, hydrogels, graft polymers, vanillin and polyamides. Vanillin in particular is an important compound used as flavouring agent in the food and pharmaceutical industries. It has also been considered as a precursor to hydrogels, polyester epoxide and polyethylene. Direct lignin recovery from lignocellulosic biomass can be effected using the Kraft process, lignosulfonates process, organosolv process, steam explosion or using ligninolytic enzymes such as lignin peroxidase, manganese peroxidase and laccase [70].

6. Integrated biorefinery applications to algal biomass

Several studies have used the integrated biorefinery approach to maximise the use of algal biomass and improve both their economic and process sustainability. This approach was used in the processing of the green seaweed, *C. linum* to co-produce bioethanol and biogas in a single study [41]. A bioethanol yield of 0.41 g/g reducing sugar (0.093 g/g pretreated seaweed) was obtained after the pretreatment, enzymatic hydrolysis and fermentation of the seaweed biomass. The enzymatic hydrolysis was done with a crude enzyme from *Aspergillus awamori* at 45°C and pH 5 for 30 hours while the fermentation was done with *S. cerevisiae* at 28°C for 48 hours while shaking at 150 rpm. The fermentation broth was then distilled to recover the ethanol while the residue referred to as vinasse was used as the feed for anaerobic digestion. The anaerobic digestion of the vinasse which was done at 38°C in a 0.5 l digester for 30 days yielded 0.26 l/g VS of biomethane [41]. The final waste generated was 0.3 g/g biomass which represents a substrate utilisation of up to 70%. This approach did indeed enhance the use of the substrate.

Ashokkumar *et al.* [71] also made a similar attempt with the biorefinery approach. They considered the integrated conversion of the brown seaweed *Padina tetrastromatica* to both biodiesel and bioethanol. The crude lipids content was first extracted from the biomass using various solvents to obtain a yield of 8.15% w/w biomass. This was processed further through transesterification (the process of exchanging the organic group R' of an ester with the organic group R' of an alcohol) to obtain a final biodiesel yield of 78 mg/g biomass. The residual biomass after lipids extraction was hydrolysed and fermented using baker's yeast to obtain a bioethanol yield of 161 mg/g residual biomass [71]. This study demonstrated that the integration of biodiesel and bioethanol production processes on a single seaweed biomass can efficiently harness both the lipid and carbohydrate fraction which could form up to 70% of the entire biomass.

A unique application of the biorefinery approach was used by Xu *et al.* [72]. In their study, mannitol was first removed from the brown seaweed *L. japonica* leaving

behind an alginate rich suspension. The alginate suspension was used as substrate for volatile fatty acid (VFA) production via fermentation. The VFAs produced were recombined with the mannitol to produce lipids through fermentation with the oleaginous yeast, *Cryptococcus curvatus*. During the alginate fermentation process several by-products were obtained including; acetate, succinate, lactate, formate, propionate, butyrate and ethanol. A maximum lipids yield of 48.3% was achieved. The lipids obtained were very high in oleic acid (48.7%), palmitic acid (18.2%) and linoleic acid (17.5%) which indicates a fatty acids composition similar to vegetable oil [72]. The lipids can therefore be used for a myriad of applications including culinary processes and biodiesel production.

Dong *et al.* [50] were able to effectively hydrolyze the microalgae *S. acutus* to obtain reducing sugars while making the lipids more easily extractable. An ethanol concentration of 22.7 g/l was obtained from the algae while the recovery of lipids was in the range of 82–87% of total lipids after ethanol removal [50]. There was no adverse effect observed on lipids recovery due to either the acid pretreatment or the fermentation of soluble sugar processes which preceded the lipids extraction. The fatty acid methyl esters concentration was also found to be high for the lipids recovered which makes it a good substrate for biodiesel production. Lee *et al.* [73] also recovered similar products of lipids and ethanol from the microalgae, *D. tertiolecta*. In their study, 48 g lipids were extracted from 220 g of the microalgae while the residual biomass after lipid extraction was found to have a carbohydrates content of 51.9%. Upon fermentation with *S. cerevisiae*, 0.14 g ethanol/g residual biomass (0.44 g ethanol/g glucose) was obtained from the residual biomass [73]. The successful demonstration of potential biodiesel and bioethanol co-production from microalgae indicates high potential improvements in the economic feasibility of microalgal biorefineries.

The red macroalgae, *Gracilaria verrucosa* was used a substrate for the co-production of agar (a hydrocolloid) and ethanol [74]. In the study, 33% agar was extracted from the biomass while the residual pulp was enzymatically hydrolysed to obtain 0.87 g reducing sugars/g cellulose. The hydrolysate obtained from the pulp was fermented with *S. cerevisiae* to produce ethanol with a yield of 0.43 g/g reducing sugars. A mass balance assessment in the study indicated that for every 1000 kg of dried algal biomass, 280 kg of agar can be obtained together with 38 kg of ethanol. Additionally, 20 and 25 kg of lipid and protein, respectively can be obtained from the residual pulp after agar extraction [74]. In a similar approach, the hydrocolloid, carrageenan was first extracted from the seaweed *E. cottonii* before the application of the residual pulp in ethanol production [3]. The carrageenan extraction led to an increase in the cellulose fraction to 64% in the residual seaweed pulp. Ethanol yields of 0.25–0.27 g/g residual seaweed pulp were obtained using *S. cerevisiae* as the fermenting organism [3].

Co-production of biosolar hydrogen and biogas was explored on the microalgae *C. reinhardtii* as a means to evaluate the integrated biorefinery approach to processing the biomass [75]. Hydrogen was first produced using the sulphur deprivation method. This method involves the cultivation of algal cells in a sulphur-containing medium until the cells reach the stationary growth phase. Cell pellets are then harvested and re-suspended in sulphur-free medium followed by incubation in light at 600 $\mu\text{mol}/\text{m}^2/\text{s}$ under room temperature. The production of hydrogen prior to anaerobic digestion of the microalgae resulted in a 123% increase in biogas generation from an initial 587 ml biogas/g volatile solids with 66% CH_4 content [75].

In another biorefinery process, the microalgae *Nannochloropsis* sp. was used as substrate for the recovery of three different valuable products [76]. Supercritical CO_2 was used to extract 45 g lipids/100 g dry biomass and 70% of pigments which were mainly carotenoids. The residual microalgal biomass after extraction was used

as an efficient substrate to produce hydrogen at a yield of 60.6 ml/g dry biomass through dark fermentation with *Enterobacter aerogenes* [76]. Harnessing these valuable products from a single biomass shows high economic prospects for microalgal biorefineries.

7. Additional prospects for biorefinery applications

Prospects in other biomass conversion pathways such as thermochemical, mechanical and chemical cannot be completely ignored and in some cases entirely replaced with the biochemical processes proposed (**Figure 1**). Thermochemical processes such as gasification which involves the application of heat to biomass at high temperatures (> 700°C) in the presence of low oxygen concentrations can be used to obtain syngas (mixture of methane, hydrogen, carbon dioxide and carbon monoxide) [77]. Syngas can be used as a standalone fuel or a platform chemical for the production of alcohols and organic acids. Alternatively, biomass can be subjected to a pyrolysis process which involves the use of temperatures between 300 and 600°C in the absence of oxygen to convert the biomass to a liquid bio-oil with biochar and light gases as by-products [78]. Such thermochemical processes could be considered as downstream processes after lignocellulosic and algal biomass fermentation where large non-cellulose fractions are generated as side-streams. A variant thermochemical process is hydrothermal treatment or upgradation. It involves the use of high temperature (200–600°C) and pressure (5–40 MPa) liquids often in the form of supercritical water to produce various liquid fuels [33].

Mechanical processes which do not typically change the composition of biomass but tend to reduce sizes or separate impurities or other components are usually applied in most biorefinery processes. It is particularly popular when handling and pre-treating lignocellulosic biomass [79]. However, there are mechanical processes that are considered complete standalone processes which generates their own useful products. A typical example is briquetting. Briquettes are often in the form of relatively evenly sized pellets produced by the compression of carbon-rich biomass. They are known to burn longer and produce a lower net greenhouse gas emissions which promotes their use as good substitutes to coal, charcoal and raw firewood [80]. Such a process could be used as a downstream process after lignocellulosic and algal biomass fermentation to minimise waste generation and add more value to residual materials.

8. Sustainability and circular economy perspectives of cellulosic and algal biorefineries

Circular economies principally emphasise the development of economic systems that eliminate waste and continuously utilise resources. In the context of biomass resources, an alternative term often used is Circular bioeconomy. Biomass is emerging as the primary renewable resource to tackle several challenges especially with regards to greenhouse gas emissions and depleting fossil fuels [6]. Therefore several technologies and multi-technology integration systems are being promulgated as the backbone for a Circular bioeconomy. The European Union describes this Circular bioeconomy as one that encompasses the formation of various renewable biological resources and their conversion to several high-value bio-based products such as food, feed, chemicals, and energy [81]. At the heart of this economic model is the biorefinery concept which has been elaborately described in this review. The biorefinery concept's role especially for algal and lignocellulosic biomass processing

is to optimise the conversion of these biomass to achieve the goals principally set for the circular bioeconomy [82]. Lignocellulosic biomass utilisation will be key to the success of the bioeconomy because they are the primary components of most biological wastes generated especially from crop production and processing. The unique benefits derived from the use of algal biomass in particular includes no arable land requirements, high biomass productivity and no reliance on fresh water and fertiliser sources [2]. This makes it an equally important resource for the circular bioeconomy.

The circular bioeconomy and the circular economy in a broader context have direct positive ripple effects on the social, economic and environmental concerns associated with current economic development models. These three aspects of any development process form the pillars of sustainability. It is therefore nearly impossible to dissociate the circular economy from sustainability. The role of lignocellulosic and algal biorefineries in sustainable development can be found directly in a number of the Sustainability Development Goals (SDGs) proposed by the United Nations. They include: *Zero hunger* (Goal 2) through the provision of affordable feed for livestock farming; *Clean water and sanitation* (Goal 6) through the utilisation of algal blooms which forms a major health hazard for coastal communities; *Affordable and clean energy* (Goal 7) through the conversion of cellulosic and algal biomass to biofuels; *Decent work and economic growth* (Goal 8) through the creation of small and medium scale biorefinery businesses and employment opportunities; *Industry, innovation and infrastructure* (Goal 9) through the creation of new and innovative co-product pathways using the biorefinery approach; *Sustainable cities and communities* (Goal 11) through energy recovery from the biodegradable fractions of municipal solid wastes; *Responsible Consumption and Production* (Goal 12) through the multi-product recovery from the same biomass leading to a reduction in waste fractions and; *Climate Action* (Goal 13) through the reduction in greenhouse gas emissions from crop production residue decay and direct combustion [83].

A reduction or absence of waste streams especially for agro residual biomass which is promoted by Goal 12 of the SDGs is a direct attribute of the zero waste concept. This concept refers to the design and management of products and processes in a systematic form to avoid and eliminate waste, and to recover all resources from the waste stream [84]. Resource recovery from waste streams is the primary point of intersection between the integrated biorefinery concept and the zero waste concept. The utilisation of cellulosic agro residues such stalks from various cereals reduces the apparent greenhouse gas emissions from their decay or direct combustion. This forms a simple yet effective climate change mitigation measure for both developed and developing countries.

9. Conclusions

The studies described in this chapter have highlighted the considerable benefits from the use of integrated processing technologies on lignocellulosic and algal biomass. The most obvious feature is the increased use of the substrate and the minimization of waste generated. The less obvious feature is the improvements in the economic sustainability of commercial cellulosic and algal biorefineries. These studies show that the potential range of products including fuels, chemicals and polymers that current and future biorefineries could produce is currently very extensive. Research and development efforts are adding almost daily to products and co-products of known fermentation-based biorefinery pathways. The most important consideration which has pushed research even further is the importance attached to the sustainability of processes in recent years. Sustainability is now an

equally important consideration in addition to economic feasibility, product yield, process efficiency and selectivity. This is due to the importance of developing climate smart yet cost-effective technologies and processes which will protect and preserve ecosystems for present and future generations. The integrated biorefinery approach has therefore become indispensable to productive and sustainable biomass processing.

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Conflict of interest

The author declares no conflict of interest.

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