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Seaweed as a Propitious Biomass for the Production of Bioethanol

Mahdi, S.[1], Bichi, B.S. [2], Gwarzo, F.S.[3]

[1]Department of Environmental Science, Cyprus International University, Haspolat-Lefkosa, Via Mersin 10, Turkey

[2, 3]Kano State College of Arts, Science and Remedial Studies, CAS, Kano, Nigeria

Abstract: ***The ability of seaweed to grow in a very short duration, provides it with an advantage over the first generation biomass (edible crops or food stocks) that competes with food stock and grows annually, the second generation biomass (agricultural waste) that are lignocellulosic that were the initial major sources of polysaccharides for bioethanol production. Seaweeds are the third generation biomass that are continuously cultivated and are capable of removing a significant amount of CO_2 (carbon dioxide) from the atmosphere, absorbs a large amount of phosphorus and nitrogen from waste water and at the same time provides biomass for the production of biofuels. This review provides a comprehensive information on the benefits of using seaweeds for the production of bioethanol.***

Keywords: Bioethanol, Seaweed, Biomass.

1. Introduction

The limited availability of fossil fuel and the environmental inference of global warming is increasingly attracting the need for an alternative source of fuel. According to Silva Lora et al., (2011) bioethanol derived from renewable resources (biomass) have the capacity to replace fossil fuel. Bioethanol is produced by the fermentation of monosaccharides (hexose and pentose) obtained from the hydrolysis of polysaccharides (starch, glycogen and cellulose). All these are carbohydrates the major source of energy in living organisms. The biomass utilized for the production of bioethanol can be categorized into three: the first generation bioethanol biomass, second generation bioethanol biomass and third generation bio ethanol biomass (Tan and Lee, 2014). The first generation biomass is composed of sugar and starch, the second generation bioethanol biomass are termed as the lignocellulosic materials composed of: cellulose, hemicellulose and lignin in the following percentages 40-50%, 20-30% and 10-15% respectively (Anwar et al., 2014).

The third generation bioethanol biomass is composed of the polysaccharides (starch or cellulose) of approximately 60% and contains a low lignin or no lignin at all (Chen et al., 2015). Which is an advantage over the first and second generation bio ethanol biomass because lignin present in lignocellulosic materials makes cellulose and hemicellulose resistance to hydrolysis resulting in the requirement for several pretreatments. Therefore seaweeds can be considered a much more suitable biomass for the production of bio ethanol, having the highest percentage of polysaccharides and also presence of low lignin content or no lignin at all (Yanagisawa et al., 2011).

2. Bioethanol

Bioethanol can be considered as a sustainable liquid biofuel that serves as a replacement for fossil fuel (John et al., 2011). Among all biofuels (biodiesel, biogas, bio-oils) (Chen et al., 2015), there is high expectation for bioethanol to be used all over the world as a replacement for fossil fuel because of its ability to be generated from a wide range of biomass i.e. Materials containing cellulose and starch (polysaccharides). The production of bioethanol from biomass containing cellulose and starch have dual benefits (i) the biomass utilizes atmospheric CO_2 for growth (photosynthesis) therefore significantly reducing greenhouse gases (ii) bioethanol is considered to be less harmful to the environment due to its biodegradable property therefore it releases less air-borne pollutant than fossil fuel l(Balat, 2011).

Bioethanol can be produced from the following raw materials: food stocks that contain sugar or starch (corn, sugarcane etc.) (ii) Agricultural waste that are also known as lignocellulosic biomass (crop residues, grasses, sawdust, woodchips, sludge, lives stock manure etc.)(Balat, 2011). (iii) Seaweeds are macro algae that are abundantly found in water composed of cellulose and starch (red, brown and green algae).

(John et al., 2011) stated that even though bioethanol is easily generated from the most common biomass found on earth, the technology is still facing some major challenges. These major challenges are the availability of the biomass required for the production of the biofuel. The availability of the first generation bioethanol biomass is usually seasonal resulting in the high cost of the raw materials, the second generation bioethanol biomass are considerably cheap and available but have a very low yield and the production of bioethanol from such lignocellulosic materials is quite cost due to the presence of lignin that requires additional pretreatment processes (Balat, 2011) and lastly the third generation biomass (seaweeds or macro algae) are always readily available this is because such biomass can be cultivated at all time and have a short growth duration.

Seaweeds (macro algae)

Seaweeds are autotrophs: organisms that are capable of manufacturing the own food by a process called photosynthesis, therefor they are considered as plants placed

in the group "Algae". Algae are divided into two groups based on their visibility, micro and macro algae, seaweeds are termed as macro algae because they are visible to the naked eye.

(Kim et al 2015) explained that seaweed compared to terrestrial plants have a high carbohydrate content and also grow rapidly. They grow in water therefore do not occupy any land for cultivation and during growth they remove a large amount of CO_2 from the atmosphere about 5-7 times higher than that removed by terrestrial plants, this aids in the reduction of greenhouse gases causing global warming.

Seaweeds are characterized by the presence of a pigment that provides them with a color for easy identification and also serve as an energy absorption and storage medium, based on their pigmentation seaweeds are classified into three groups (I) green, (ii) brown and the (iii) red seaweeds botanically termed as Chlorophyceae, Phaeophyceae and Rhodophyceae respectively (McHugh, 2003).

These seaweeds are used in the production of aliginate, agar and carrageenan which are all polysaccharides that can be extracted from algae and are used as raw materials for the production of bioethanol.

Production of bioethanol from variety of biomass

Generation of bioethanol from different types of biomass is feasible provided that the biomass is composed of carbohydrates (polysaccharides, monosaccharides, disaccharides or oligosaccharides). It is easy to convert carbohydrates to ethanol by hydrolysis followed by fermentation (Hamelinck et al., 2005). In some cases the conversion was seen to be quite complicated depending on the type and composition of the biomass in use, some biomass require several pretreatment processes that takes time and results in additional cost for the production of bioethanol. The most commonly used biomass for the production of bioethanol are categorized into 3 (I) the first generation biomass, (ii) the second generation biomass and (iii) the third generation biomass.

First generation biomass

The first generation biomass are food based biomass (Gonela et al., 2015), such as corn, cassava, sugar cane, soybeans, rice, barley, sweet potato all of which are carbohydrate rich biomass. These biomass are significant sources of extracting polysaccharides that can be converted to bioethanol by fermentation and was seen to give a very high yield. The continuous conversion of food to bioethanol resulted in the demand for raw materials which lead to exploitation of lands (deforestation for cultivation) for the production of biomass. This brought about ecosystem destruction because deforestation is the major factor that causes loss in biodiversity and also soil erosion (Khoo, 2015). In addition to this the first generation biomass is highly cost and using it as a raw material for bioethanol production is regarded as a competition with food. Bioethanol production depends on the price of raw materials (crops) therefore the use of the first generation biomass makes very little improvement to the trade balance (Matsuda and Kubota, 1984).

Corn (maize)

Corn is one of the richest cereal crop that serves as a source for ethanol production, botanically termed as (Zea mays) (Pimentel and Patzek, 2005) they grow annually worldwide or by irrigation farming. Corn is composed of 75% starch, 9.4% protein, 1.6% crude fiber, 6.5% moisture and 2.12% ash. Starch are polysaccharides that can be converted to bioethanol, starch are made up of the polysaccharides amylose and amylopectin (A.Meenakshi and Kumaresan, 2014) these polysaccharides when cooked at a high temperature and pressure forms a gel (polymer) that can be digested by enzymes to form monomers that can be fermented to form bioethanol.

Conversion of corn (maize) to bioethanol

According to the study of (A.Meenakshi and Kumaresan, 2014) 15.88g/l ethanol was produced from corn in 72hours (SSF) from 10% substrate concentration under optimum conditions of PH 5.5, and particle size 0.157mm using saccharomyces sp. The method that was used in the conversion involved (I) milling, (II) liquefaction, (III) simultaneous saccharification and fermentation, (IV) centrifugation and (V) distillation.

Brief description of the method

Under optimum conditions of (PH 5.5 and particle size 0.157mm) and thermal pretreatment with (121^{o}C temperature for 30min) and a maintained fermentation temperature of 90^{o}C, 10g or 10% of dry milled corn flour was converted to 15.88g/l ethanol in 48-72hours using 579u/g amylase enzyme and 1364u/ml glucoamylase enzymes for each 0.08g/l and 0.1g/l respectively, baker's yeast was used as the fermentation microorganism. Ethanol produced was separated and collected by centrifugation at 6000rpm for 10min and distillation of the sample at 78^{o}C respectively,A.Meenakshi and Kumaresan, (2014).

Second generation biomass

The second generation biomass are also sugar containing materials made up of 3 major components, a dry biomass of the second generation is composed of about 40-60% cellulose (glucose-glucose or hexose) polymer, 20-40% hemicellulose (xylose-arabinose-galactose-glucose-mannose or pentose-hexose) polymer, a much more complicated polymer and 10-25% of a non-polysaccharide compound known as lignin (Hamelinck et al., 2005). Based on their composition the second generation biomass are referred to as the lignocellulosic biomass. Lignin though in small amount is the most complex component of the lignocellulosic biomass, it of phenyl propane and methoxyl group, and these are compound that binds the cell wall of lignocellulosic biomass together (Anwar et al., 2014). Lignin and hemicellulose combines together to form a protective covering for the cellulose, this is necessary because the lignocellulosic biomass are often exposed to harsh environmental conditions. The lignin containing biomass (lignocellulosic biomass) usually include agricultural waste such as grasses, forestry residue, and woody materials (Anwar et al., 2014).

As stated by (Rogner, 1997), lignocellulosic materials are short time growing plants (perennial plants) based on this their availability can be considered continuous, they are also

cheaper than the first generation biomass and do not require land for their cultivation.

3. Wheat Straw

Wheat straw is the left over (agricultural residue) obtained after harvesting wheat crops, wheat are annual plants botanically known as (Triticumaestivum), these unwanted part of the plants are sometimes left in the soil or on the farm and are eventually burnt, the development of biotechnological technique brought about ways of converting such biomass to bioethanol (Talebnia et al., 2010). According to (Prasad et al., 2007) wheat straw is considered as a lignocellulosic biomass composed of cellulose, hemicellulose and lignin in the given range of percentages 33-40, 20-25 and 15-20% w/w respectively. Based on the presence of lignin in wheat straw and the complexity of the wheat straw several pretreatment processes are required for its conversion to bioethanol (Talebnia et al., 2010).

Conversion of wheat straw to bioethanol

Based on the investigation of (Narra et al., 2015), 21.84g/l of ethanol was produced from 10% concentration of grinded wheat flour at a PH of 4.8 and a particle size less than 5mm in 72hours using an isolated novel yeast strain known as Kluyveromyces sp. The new strain was isolated based on its ability to resist high temperature such strain can be called thermotolerant organisms. The conversion of wheat straw to bioethanol involved three pretreatments processes (I) physical, (II) thermal pretreatment and (III) biochemical pretreatment which was followed by hydrolysis, fermentation and lastly distillation (Talebnia et al., 2010).

Brief description of the method

10% of chipped wheat straw of particle size less than 5mm was placed in 750ml of 4% $H2_SO_4$ and heated at a temperatureof 121^{o}C for 60min with a PH of 4.8, recovered sample by filtration was rinsed with distilled water until it became neutral and dried in sun another pretreatment with 0.5% NaOH at 121^{o}C for 30 minutes took place the recovered and dried sample was placed in a flask and simultaneous saccharification and fermentation was done at 42oC using cellulases enzyme, Kluyveromycessp was added after prehydrolysing the sample at 42oC for 6hours. The sample was then centrifuged 10,000 times for 15min, ethanol was then analyzed from the supernatant using high performance liquid chromatography (Narra et al., 2015).

Third generation biomass

Based on their size algae can be classified as micro or macro algae, the micro algae are usually the unicellular or microscopic algae that can be autotrophs or heterotrophs while the macro algae are the large visible algae and can generally be termed as seaweeds (John et al., 2011), these are known as the third generation biomass and they are considered as an important biomass for the production of bioethanol, this is due to its high carbohydrate content and low lignin content or complete absence of lignin, absence of lignin aids in the easy hydrolysis of the biomass to form bioethanol (Chen et al., 2015). Ethanol can be obtained from such biomass by simply converting the energy storage materials (agar, carrageenan, glucan, cellulose, galactan) of the biomass to fermentable sugar. Algae are photosynthetic organisms that grows rapidly and continuously, this provides them with and advantage over the first and the second generation biomass that are usually annual and perennial plants. Cultivation of macro algae do not require deforestation for provision of space they can be cultivated in water or on unproductive land their byproducts can also help in reviving the soil of the unproductive land(Chen et al., 2015). During their growth macro algae absorbs a great amount of nutrient from waste water and also absorbs CO_2 from the atmosphere 5-7 times greater that the CO_2 absorbed by terrestrial plants there the can be considered as purifiers of waste water and the atmosphere. They are classified into three groups based on their pigmentation (I) brown, (II) red and the (IIII) green algae botanically known as Phaeophyta, Rhodophyta and cholrophyta respectively. Algae are generally composed of 54-84% carbohydrate, 2-6% lipid, 12-31% protein and 3-19% ash(Chen et al., 2015).

Red algae (Gelidiumamansii)

These are marine seaweeds that have high carbohydrate content and no or little lignin content, about 60% of their biomass is made up of the following polysaccharides: cellulose, carrageenan, glucan and galactan(Chen et al., 2015). These polysaccharides can easily be hydrolyzed to form fermentable sugar such as glucose and galactose from which bioethanol can be obtained, galactan is the main component of the red algae Gelidiumamansii from which agar is extracted as it contains two different types of polysaccharides namely: agaran and agaropectin(Kim et al., 2015).

Conversion of Gelidiumamansii to bioethanol

Observing the analyses of (Kim et al., 2015), 51.39g/l of ethanol was produced from 10% dried biomass of Gelidiumamansii in 72hours fermentation process. The method used for the conversion were hydrolysis by autoclaving for 60 minutes followed by fermentation under optimum condition of PH 4.8, temperature maintained at 37oC using the enzymes cellulose and β-glucosidase and Saccharomyces cerevisiae was used as the fermentation microorganism.

Brief description of the process

10g or 10% of washed Gelidiumamansii was placed in a 400ml distilled water in a 1 liter flask and autoclaved at a temperature of 121oC for 20 minutes, this was followed by drying and grinding of the autoclave-treated sample, grinding was achieved using a homogenizer. The enzymes cellulose and β-glucosidase measuring 8.0mg/g/GA and 4.0mg/g/GA respectively were added to 200ml of the sample in a 500ml twin neck round bottom flask. 100mg of the microorganism Saccharomyces cerevisiae was also added, fermentation took place under optimum conditions as follows: PH 4.8, 0.05M citrate buffer at 37oC for 72 hour. The ethanol yield was measured using a high performance liquid chromatography(Kim et al., 2015).

Comparison of ethanol yield

Figure 5 represents the concentration of ethanol produced from three variety of biomass first, second and third generation biomass the used biomass of the groups are corn, wheat straw and seaweed respectively. The ethanol yield

was obtained after 72 hours of fermentation for each biomass under optimum conditions.

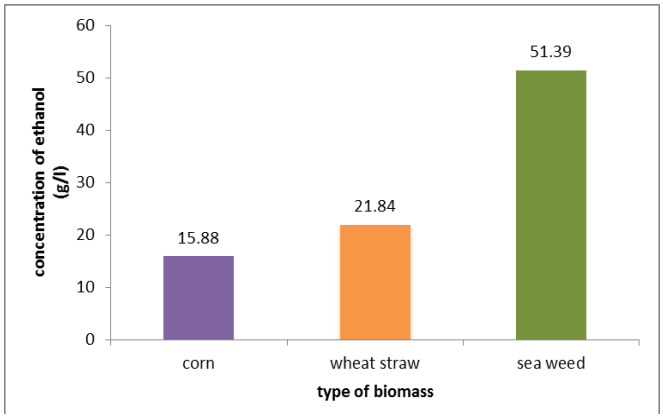

Figure 1: Comparison of ethanol yield after 72hours fermentation of corn, wheat straw and seaweed. (c)

From the result obtained it can be seen that the concentration of ethanol in seaweed is much higher than the concentration of ethanol in wheat straw and corn. This is because seaweeds have a higher carbohydrate content in form of cellulose, glucan, galactan that are easily extracted and converted to simple sugar without difficulty, though the first generation biomass also consist of a high content of carbohydrate in form of starch, conversion of starch to ethanol requires the use of thermal pretreatment and also its fermentation to bioethanol requires a stable temperature of about 90^{o}C, such temperature may hinder the activity of the microorganisms responsible for the fermentation process, therefore resulting in low yield of ethanol, the wheat straw produce is also a biomass with a high carbohydrate content in form of cellulose and hemicellulose incorporated with lignin, lignin inhibits hydrolysis and fermentation of the sugar present in the biomass, therefore for fermentation to take place there is a need for treatment of lignin. Several pretreatment processes are applied for treatment of lignin and this pretreatment processes may directly or indirectly produce other compounds that serve as inhibitors of fermentation, this also result in low yield of ethanol from the second generation biomass.

Pretreatment processes and their effect to ethanol yield

For easy hydrolysis and fermentation of some biomass several pretreatment processes can be applied to enable easy extraction and conversion of carbohydrates to ethanol. The pretreatment processes are required based on the difficulty encountered in converting certain biomass to fermentable sugar, pretreated biomass can easily be converted to sugar by hydrolysis which is followed by fermentation to form ethanol. The pretreatment processes applied are generally termed as (I) biological (II) thermal (III) biochemical and (iv) physical pretreatment process (Bjerre et al., 1996).

Biological pretreatment process

According to (Sánchez, 2009) fungal pretreatment has been antecedently explored to upgrade lignocellulosic materials for feed and paper applications. Recently, this environmentally friendly approach has received revived attention as a pretreatment methodology for enhancing accelerator saccharification of lignocellulosic biomass in alcohol production processes. Biological pretreatments use microorganisms primarily brown, white and soft-rot fungi that degrade polymer and hemicellulose and really very little of polyose, additional resistant than the opposite parts. Non carbohydrate degradation by white-rot fungi, the foremost effective for biological pretreatment of lignocellulosic materials, happens through the action of lignin-degrading enzymes like peroxidases and laccases (Alvira et al., 2010).Phanerochaetechrysosporium, Ceriporialacerata, Cyathusstercolerus, Ceriporiopsissubvermispora, Pycnoporuscinnarbarinus and Pleurotusostreaus are white rot fungi that have been seen to destruct lignin with high efficiency. There the use of fungi especially basidiomycetes for the pretreatment of lignin is more preferable because of its low cost, low energy consumption and also it requires no energy and mild environmental conditions.

Thermal pretreatment process

This is a hydrothermal treatment that doesn't need speedy decompression and doesn't use any catalyst or chemicals. Pressure is applied to keep up water within the liquid state at elevated temperatures (160–240 °C) and stimulate and give rise alterations within the structure of the lignocellulose.

The purpose of the liquid hot water is to solubilize in the main the hemicellulose, to create the polysaccharide a lot of accessible and to avoid the formation of inhibitors. The suspension generated once pretreatment will be filtered to get 2 fractions: one solid cellulose-enriched fraction and a liquid fraction made in hemicellulose derived sugars. To avoid the formation of inhibitors, the pH scale ought to be unbroken between four and seven throughout the pretreatment as a result of at this pH scale hemicellulosic sugars are maintained in oligomeric type and monomers formation is decreased. Thus the formation of degradation product is quiet low (Mosier et al., 2005). It removes about 80% of hemicellulose and promotes enzymatic degradation.

Biochemical pretreatment process

These involves the use of chemicals such as acid and alkaline to soften the biomass for easier hydrolysis and fermentation. According to (Carvalheiro et al., 2008) Alkali pretreatments increase polysaccharide edibility and that they are simpler for polymer solubilization, exhibiting minor polysaccharide and hemicellulose solubilized than acid or hydrothermal processes. Less sugar is seen to be degraded as a result of alkaline pretreatment, the pretreatment can be performed at room temperature and the duration of the treatment depends on the complexity of the biomass (Alvira et al., 2010).

Unlike the alkaline pretreatment acid pretreatment is another biochemical process that degrades sugar along with the degradation of the non-carbohydrate materials. Based on the explanation of (Wyman, 1996) this type of pretreatments may be performed with focused or diluted acid however utilization of focused acid is a smaller amount enticing for grain alcohol production attributable to the formation of inhibiting compounds. What is more, instrumentality corrosion issues and acid recovery area unit vital drawbacks once victimization focused acid pretreatments. The high operational and maintenance prices cut back the interest of applying the focused acid pretreatment at business scale (Alvira et al., 2010).

Physical pretreatment process

This type of pretreatment process is aimed at reducing the particle size for easier conversion t bioethanol and crystallinity of lignocellulosic so as to extend the particular surface and scale back the degree of chemical action. This will be made by a mixture of breakage, chipping, grinding or edge betting on the ultimate particle size of the material that is hammering (Sun and Cheng, 2002).

All these pretreatment processes are applied in other to overcome the main factors limiting the enzymatic hydrolysis, but unfortunately the pretreatment processes or some of the processes contributes in the production of inhibitors of bioethanol production, and also increase the cost of ethanol production. The biological pretreatment process destructs lignin and hemicellulose at a very low energy consumption, on the other hand it cause low rate f hydrolysis, the physical pretreatment process requires high energy consumption if milling method is used, eventually resulting in the production of bioethanol at a very high cost. For the thermal pretreatment process, using heat for the destruction of pathogenic microorganisms present in the biomass usually generates toxic substances that inhibits the activities of the fermentative microorganisms it also denatures protein present in enzymes and the vital microorganisms and degrades hemicellulose. Acid pretreatment process forms substances that hinders the production of bioethanol, brings about corrosive problems in the reactor and also results in the formation of bioethanol at a very high cost, lastly the alkaline pretreatment process produce degradation products resulting in low yield of bioethanol (Alvira et al., 2010)

Table 1: Showing pretreatment processes, time and energy consumption and materials used for the production of ethanol.

Type of biomass	Pretreatment process	Time/energy consumption	Materials used	References
Corn (starch)	Physical pretreatment (grinding) Thermal pretreatment (cooking)	121^{o}C for 30min (cooking) 90^{o}C for 72hours (fermentation)	Amylase and glucoamylase enzymes Saccharomyces cerevisiae	(A.Meenakshi and Kumaresan, 2014)
Wheat straw(cellulose, hemicellulose and lignin)	Physical pretreatment (chipping) Thermal pretreatment (boiling) Biochemical pretreatment (acid and alkaline pretreatment)	121^{o}C for 60min (acid pretreatment) 121^{o}C for 30min (alkaline pretreatment) 42^{o}C for 6hours (prehydrolysis) 42^{o}C for 72hours (fermentation)	4%$H_2SO_4$and 0.5% NaOH Cellulose enzyme Kluveromycessp(thermotolerant isolated strain of yeast)	(Narraet al., 2015)
Gelidiumamansii (galactan)	Thermal pretreatment Physical pretreatment process (grinding)	121^{o}C for 20min (autoclave) 37^{o}C for 72hours (fermentation)	Cellulose an β-glucosidase enzyme Saccharomyces cerevisiae	(Kim et al., 2015)

From the above observation it has been seen that the first generation biomass which is composed of a complex carbohydrate inform of starch requires the application of a thermal pretreatment process for at least 72hours and 30 minutes, and also a physical pretreatment process of grinding (A.Meenakshi and Kumaresan, 2014). Depending on the temperature of the location if cold then thermal pretreatment process required for the second generation biomass would last for 73hours 30 minutes but if the temperature of the area is high the duration would be shorter, for the second generation biomass, there is the need for biochemical pretreatment in addition to the thermal and physical pretreatments which involves the use of chemicals to soften the biomass (Narra et al., 2015). For the third generation biomass only thermal and physical pretreatment processes were applied and the thermal pretreatment process lasted for only 20minutes and based on the softness of the biomass the physical pretreatment process did not require much energy application (Kim et al., 2015).

The application of these pretreatment processes is quite expensive, time consuming and also some of the processes hinders the formation of bioethanol through inhibiting the activities of the microorganism (thermal pretreatment process) or by producing some substances that can also inhibit the activity of the microorganisms, thereby decreasing the yield of bioethanol.

4. Conclusion

Seaweed can be considered as the most beneficial biomass to be used for the production of bioethanol, as it is composed of a high content of easily hydrolyzed carbohydrate (polysaccharides), and also its ability to grow in a very short period of time making seaweed always available for bioethanol production, during its growth seaweed absorbs a large amount of carbon dioxide from the atmosphere about 5-7 times greater than the carbon dioxide absorbed by terrestrial plants, it also have the ability to absorb great amount of Nitrogen and Phosphorus from waste water, , it is considered to have dual benefit, apart from serving as a great source of raw material for the production of bioethanol, seaweed also serve as a purifier of the ecosystem.

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