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Theoretical Considerations for Economics of Second- and Third-Generation Biofuels

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Abstract

Ground is being prepared all over the world for installation of biofuel plants which can govern the sustainable supply of cleaner fuels at affordable prices and predictable amounts. At the dawn of this century biofuels identified low cost feedstocks, their diverse pretreatments, different methods of saccharifications and fermentations and those for cultivation of biodiesel yielding organisms. Bioalcohols, biohydrogen and biogas represent the biofuels which are derived from microbial work on the biowaste-resources. Extensions in this sector have focused the solar energy captured by the microalgae from which oils can be extracted for biodiesel. Undoubtedly, all forms of available energies on this planet earth had/have been derived, directly or indirectly, from the solar inputs. In this chapter pivotal role of solar insolation will be discussed albeit for regeneration as well as processing of lignocellulosic biomass for obtaining biofuels. Conclusively, biofuels' sustainable supplies, role of solar energy has been dreamt at various steps of the process; from the collection of biowaste resources through steps of pretreatment, saccharification / fermentation and purification of the product. This chapter discusses the subject matter into two major sub-headings: 1) Biofuels from lignocellulosic / food industrial wastes and 2) Cultivation of microbes for biodiesel.

Keywords: biodiesel, bioethanol, biohydrogen, economizing biofuel production, lignofuels, second-generation bioenergy, third-generation bioenergy

1. Introduction

The form of life we humans know and understand to some extent is impossible without the sun. The biosphere will not be sustainable without continuous rain of sun energy. Recalling our basic information on energy conversion in and between different systems, efficiencies can

never attain 100% levels. Same is true for biotic components of the biosphere. Food transfer through different trophic levels and metabolites' circulation and their transfer through biochemical pathways all pass through this limitation. Thus, sun energy is pivotal to the existence and sustenance of all forms of energy in the biosphere. The fossil fuels on whom, at present we are dependent to "no return" level had been derived from ancient organisms whose presence at that time was also dependent on the sun energy. Now when the fossil fuels' reservoirs are depleting and further they have polluted our air, soil, and water, we must look for alternatives, which must be sustainable and environment friendly too. Energy from biomass can be condensed into low volume high efficiency fuels through microbial fermentation and/or other routes of bio conversion of abundantly available matter. However, food competing sources of carbohydrates cannot be diverted to biofuels' refineries by ignoring the ever increasing human population. Whereas feedstock for second- and third-generations' biofuels are abundantly available at little or no cost. Biowastes have a great potential in this regard. For instance, it has been estimated that up to 442 billion liters per year of bioethanol could be produced from lignocellulosic materials [1]. But their pretreatments, saccharification, and then fermentation still need a lot of work to be done. Low-cost and environment compatible strategies to render lignocellulosic biomass accessible for enzymatic saccharifications have to be developed. Further for lignocellulosic wastes of different plant origins, different methods may be required for optimum outputs. Liberation of undesired compounds following pretreatments and saccharification is another area demanding more inputs. Inhibitors' resistant saccharifying and/or fermenting microbes and enzymes have to be isolated, developed, characterized, and optimized for select feedstocks and locations. Jumping to third-generation biofuels, biowastes have to be identified to support rapid growth of microalgae and fast fixation of CO_2 . This chapter describes some theoretical considerations which need to be considered through experimental verification to economize the biofuels' production. Although the science of bioenergy, especially for second- and third-generation biofuels is still at its infancy, but taking into account the drastically exhausted fossil fuels' reservoirs, the already polluted biosphere, ever increasing human population, and its elevating demands for more comforts, which need more supply of energy, we are left with limited choices including the fascinating future of biofuels.

2. Biofuels from lignocellulosic/agri/food industrial wastes

Fossil sources of energy are depleting at a very rapid rate and alternative sources of renewable energy are being searched. Agricultural wastes are produced daily and get accumulated into different environments. They pose special problems of solid waste management in urban environments and industrial locations. On the other hand, they are potential source of fermentable carbohydrates. These wastes could be identified as low-cost feedstocks for biofuels' production. For example, bioethanol can be fermented from diverse feedstocks including corn, sugarcane, wood, and fruit and vegetable wastes such as pawpaw and sweet potatoes, etc. In addition to the production of biofuels, utilization of lignocellulosic agriwastes will concomitantly solve the solid waste disposal problem, as the fermentation residues can

be used as solid fertilizers. A number of physical and chemical treatments methods have been reported for the production of bioethanol from diverse categories of plant biomass. However, researchers are continuously describing new methods and techniques for economic yields of bioethanol [2–7]. From the biofuels headings, bioethanol is becoming increasingly popular as fossil fuel additive and for reducing the stress of decline in crude oil availability. Bioethanol productions require sustainable supplies of fermentable sugars, efficient fermenting microbes, a few nutrients (depending upon the nature of feedstock as well as microbes), and optimized culture conditions. Resultantly, bioethanol productions have been described from diverse waste resources such as market vegetable waste, carrot discard, hydrolyzed agricultural wastes, banana peels, and pulp and peels of mango. [8–13].

Interests in the area of bioethanol production from organic waste materials emerged in the late 1980s. Since then lignocellulosic material extraction and enzymatic hydrolysis have been reported extensively, however, for development of technically feasible and economically viable large-scale enzyme-based biomass to ethanol conversion processes addressing diverse waste resources and fermentation conditions a lot of work still has to be done to cover different regions of the world. The success of cellulose to ethanol conversion processes has been described as a function of cellulose fiber pretreatment, enzyme selection, and operating conditions [14]. Nigam and Singh [15] have discussed that researchers have been redirecting their interests in biomass-based fuels for sustainable development in the content of economical and environmental considerations. These researchers further stressed that renewable biore-sources are available globally in the form of residual agricultural biomass and wastes. However, much research has to be done for the development of an effective, economical, and efficient conversion process.

Estimates for bioconversion of globally wasted crop appear promising. For example, Kim and Dale [16] have described that by employing the wasted crops for bioenergy production conflict between human food and industrial use can be avoided. Crops' residues and industrial lignocellulosic wastes can be considered feedstocks for bioethanol productions. Wasted crops have a potential to produce up to 49.1 GL year⁻¹ of bioethanol. These authors further discussed that from the residues and wasted crops potentially 49.1 GL year⁻¹, ethanol production is possible. Accordingly, bioethanol could replace 353 GL of gasoline when used in E85 fuel.

Following unprecedented growth of human population and industrialization, ethanol demand is increasing continuously. Conventional crops of bioethanol production are unable to meet the demand due to their primary value for food and feed. Lignocellulosic substances including agricultural wastes have therefore become attractive feedstocks for bioethanol production. They are cost effective, renewable, and abundant. The promising technology of bioethanol from waste resources has several challenges and limitations such as biomass transport and handling, and efficient pretreatment methods for total delignification of lignocellulosics. Novel pretreatment methods may increase yields of fermentable sugars after enzymatic saccharification [17].

Voluminous work regarding the diversity of lignocellulosic resources dictate for development of diverse methods of pretreatment and to economize further recognition of different categories of saccharifying and fermenting microbes, which might be required for different sorts of

substrates to be processed at different locations in a country. Local sociocultural and economic situations can influence the overall efficiency of biofuels' productions from waste biomass. In this context, cost of transport of raw material from its natural origin or industrial processing units must be considered and if it is profitable then the pretreatment and subsequent concentration/detoxification processes be accomplished at the first place. Alternatively, the small pretreatment as well as fermentation plants might be installed at or near locations of the biowaste resources. Heat for the pretreatment should be secured directly/indirectly from sun rays. Efficient acidic or alkaline pretreatments for different lignocellulosic substrates have to be identified. To reduce the expenditure of neutralizing a substrate pretreated with acid/alkali, respective category of acidophilic or alkaliphilic cellulolytic, and/or ethanologenic microbes must be searched and recruited accordingly. Similarly, a lignocellulosic or a food industrial waste known for higher amounts of certain inhibitors' yield during the initial processes might be attacked with the inhibitor(s)' resistant and/degrading microbes, which must be cellulolytic/ethanologenic too or their enzymes thereof. The points highlighted above will definitely add to the economics of biofuels production from biowaste resources. A layout of schematic thoughts in this regard has been depicted in **Figure 1**, while consideration of different lignocellulosic substrates is summarized in **Table 1**.

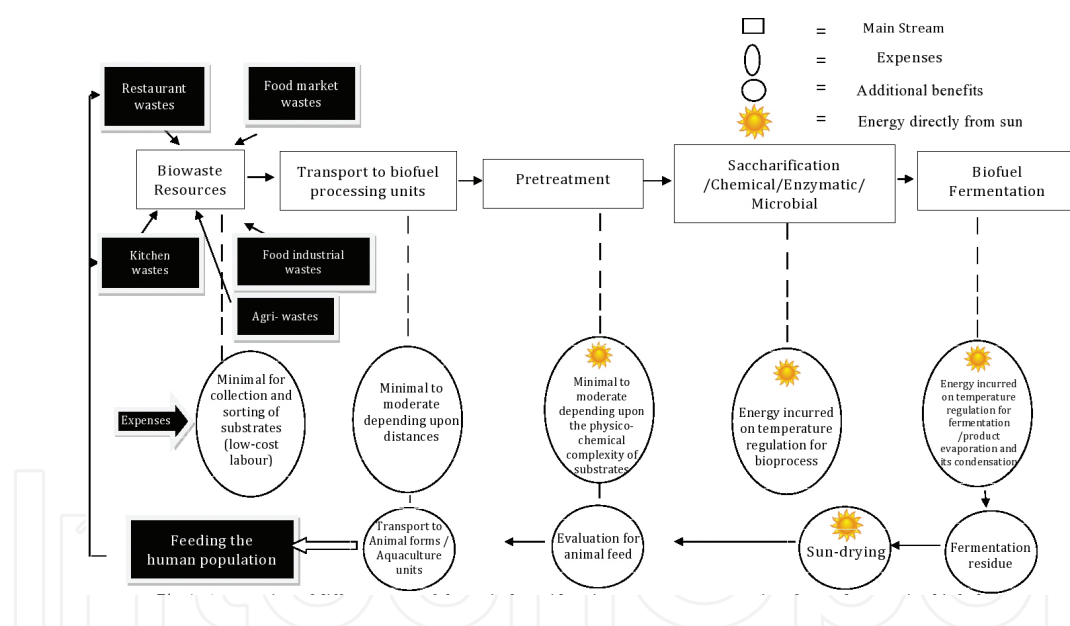


Figure 1. An overview of different steps of theoretical considerations to promote economics of second-generation biofuels deriving from solid wastes.

As can be seen from **Figure 1** that overall conversion of lignocellulosic substrates to low volume high-energy content biofuels involves expenditure of energy at various steps. The raw material processing including washing with hot water, decontaminating or sterilizing, fermentative, and product purification steps need thermal inputs of energy. At least four steps of overall process depicted in **Figure 1** can be accomplished by solar energy inputs. Some other steps to improve economics of lignofuels and their application at present time when the fossil fuels still represent efficient fuels for transport sector, at least, are given below.

Lignocellulosic/ biowaste substrate	Specificity of pretreatment	Microbial requirement	Benefit of specific microbe(s)	Possible locations, e.g., industrial vicinity/ natural habitat	Biofuel/Potential additional benefit(s)	Reference(s)
Sugarcane bagasse/lingo- cellulosic biomass	Ball milling, dilute sulfuric acid, steam explosion, delignification	<i>Pichia stipitis</i> BCC 15191, recombinant <i>Escherichia coli</i> KO11, <i>Paecilomyces</i> <i>variotii</i>	Consumption of both xylose and glucose	Sugar mills/ agro- industrial derivatives	Bioethanol/ Consumption of surplus lignocellulosic material, animal feed from fermentation residue	[17, 19, 20]
Wheat Straw	Knife milling with 0.7– 1.0 mm rejection screen, washed with water and dried	<i>Pichia stipitis</i> NRRL Y-7124 <i>Pichia stipitis</i> A	Adapted at increased concentration of hydrolysate	Agri-waste	Bioethanol/value added product from abundant agriwastes/ sustainable solid waste management	[17]
Rice straw	Chopped to 5–6 mm size range	<i>Candida</i> <i>shehatae</i> NCL-3501	Co-ferment glucose and xylose	Agriwaste	Bioethanol/value added product from abundant agricultural wastes/ sustainable solid waste management	[17]
Corn straw/corn stover	Chopped, steam explosion (3.5 MPa, 275°C, 2 min) 2% NaOH, 80°C, 1 h, ammonia fiber expansion	<i>Saccharomyces</i> <i>cerevisiae</i> ATCC 26603 <i>Pichia stipitis</i> NRRL Y-7124 <i>S. cerevisiae</i>	Ferment only glucose Ferment glucose first and then xylose from the mixture	Agriwaste	Bioethanol/value added product from abundant agricultural wastes/ sustainable solid waste management	[21, 17]
Hard wood	Mechanical communication Steam explosion	Diversity of bacteria and yeasts capable	Vary from substrate to substrate	Forests	Bioethanol/value added product	[22]

Lignocellulosic/ biowaste substrate	Specificity of pretreatment	Microbial requirement	Benefit of specific microbe(s)	Possible locations, e.g., industrial vicinity/ natural habitat	Biofuel/Potential additional benefit(s)	Reference(s)
		of saccharifying fermenting different substrates			from forest residues.	
Kitchen wastes (rich in glucose, starch and cellulose)	Hot water, acid solutions, liquefaction/ saccharification	Enzymatic hydrolysis, <i>Saccharomyces cerevisiae</i>	Easily available	Cafeterias, restaurants, dining halls, food plants and household kitchens	Bioethanol/ reduced ethanol costs/no requirement of fermentation nutrients	[23–25]
Wastewater, agricultural and industrial wastes, animal by- products	Anaerobic digestion	Microbial community	Easy availability from herbivores’ dung	Animal and agricultural farms	Biogas/prevent pollution; stabilized biofertilizer	[26, 27]
Crop residues, livestock waste, food waste Starch-cellulosic- based wastes, dairy wastes, palm oil mill effluent and glycerol	1. Dark fermentation 2. Photofermentation	Bacterial consortia	No need of illumination Light energy inputs required	Agricultural farms	H ₂ /pollution-free fuel; waste treatment; mitigating global warming	[28, 29]
CO ₂	Concentration	Microalgal culture		Cement sector	Biodiesel/ transformation of polluting gas to valuable product; waste water treatment	[30]

Table 1. Compatibility of different pretreatments and fermentative microbes for economic production of biofuels from diverse and abundantly available lignocellulosic and other biowastes.

2.1. Transport of feedstocks

Lignocellulosic feedstocks from agricultural fields and relevant industrial units are required to be transported to pretreatment and/or biofuel's production units. This involves an obvious expenditure; and at present will necessitate consumption of fossil fuels to run the transporting trucks. Important to consider is that biofuels are being attempted/generated to lessen the present burden of fossil fuels' consumption. To reduce the cost of biofuels and render them compatible at present with the fossil fuels' supplies, every step is required to be optimized. In this regard it might prove quite fruitful if the lignocellulosic biowaste feedstocks are pretreated at or near to their generation locations, so that relatively low-volume/mass pretreated material ready for saccharification or biofermentation can be transported at affordable expenses.

To further reduce the feedstock transportation costs, processes of pretreatments and/or saccharification can be accomplished near to the lignocellulosic biowaste origins and the sugar streams can be transported dynamically employing pipe system. Alternatively, sugars syrups can be concentrated into low-volume thick fluids to reduce the cost by usual transport systems. In a country like Pakistan, processes of pretreatments and sugars syrups' concentration can be accomplished by direct solar energy. Another strategy would be installation of those industrial units in one locality whose wastes can be coutilized cost effectively.

2.2. Concept of cluster(s) of industrial units having wastes of mutual interest

Man can achieve maximum efficiency and sustainability of his efforts addressing construction of production units approaching a level and design not superseding natural system(s). In this regard man has been imitating the nature subconsciously in the past. While conferring to the cumulative maturity time has come to recognize/realize that the nature tailored models are best to follow. Exploration of biogeochemical cycles within and among different ecosystems has taught us that sustainability relies upon the utilization of waste of one unit as resource by the other and vice versa. Thus, to save cost presently we have to pay to treat industrial effluents/solid wastes or to transport them to other locations for treatment to utilize them as biowaste resource, industrial units can be managed in the form of different consortia in which for a given set of industrial units, waste(s) from one unit can serve feedstock for another. For instance, sugar industries in Pakistan produce millions of tons of sugarcane bagasse (SCB). Chemical pretreatment of SCB requires the application of dilute acid(s) or alkali. Many other industrial effluents are characterized with considerably high or low pH and are not accompanied with further process interfering chemicals. Coinstallation of such relevant industrial units can solve many problems including low cost pretreatment of SCB and value-added consumption of the otherwise negative-valued acidic/alkaline industrial effluents, for instance.

2.3. Tax relaxation for biofuels' consumers

New trends whose immediate impact on modern human minds reflects reduction in efficiency of desired task(s) are difficult to get acceleration. Their acceptance in the society must be escalated with some incentive. Bioethanol-driven motor cars, especially at the start, might not run with speed comparable to petrol-driven engines. Whereas the environmental friendly

emission from biofuel-driven motor cars might be strengthened with reduction in the motor vehicle taxes.

Waste biomass for biofuels' generation will have to be utilized from different sources for sustainability of the process. The wastes, in general, represent solid wastes while organic content-rich food industrial effluents can also be utilized for the fermentation of different types of biofuels. An overview of different lignocellulosic wastes, their needs of pretreatments, and microbes along with potential biofuels and additional benefits is given in **Table 1**.

Regarding the fluid wastes, continuous and sustainable resources are represented by food, industrial, and domestic sewages, which may contain varying levels of fermentable organic loads. Schemes have been developed and shown in **Figures 2 and 3**, for upgrading the waste effluents into biofuels' generation (**Figures 2 and 3**). Responding to above theoretical notions for improving economics of second-generation liquid biofuels, it appears pertinent here refer to the work of Nigam and Singh [15]. These authors concluded that four challenges are imperative for sustainable biofuel productions:

1. Improvements in enzymatic hydrolysis through the provision of low cost crude enzymes characterized with higher specific activities.
2. The development of such microbial strains which are not only robust fermenting organisms, but must be resistant to inhibitors present in hydrolysates. Further, the developed strains must be able to consume all sugars present in the raw material yielding optimum productivity of alcohols and be resistant to higher concentration of the product too.
3. Development of integration strategies to decrease the number of steps of production process.
4. Useful consumption of any byproducts and wastes generated to reduce the energy demand and protect the environment.

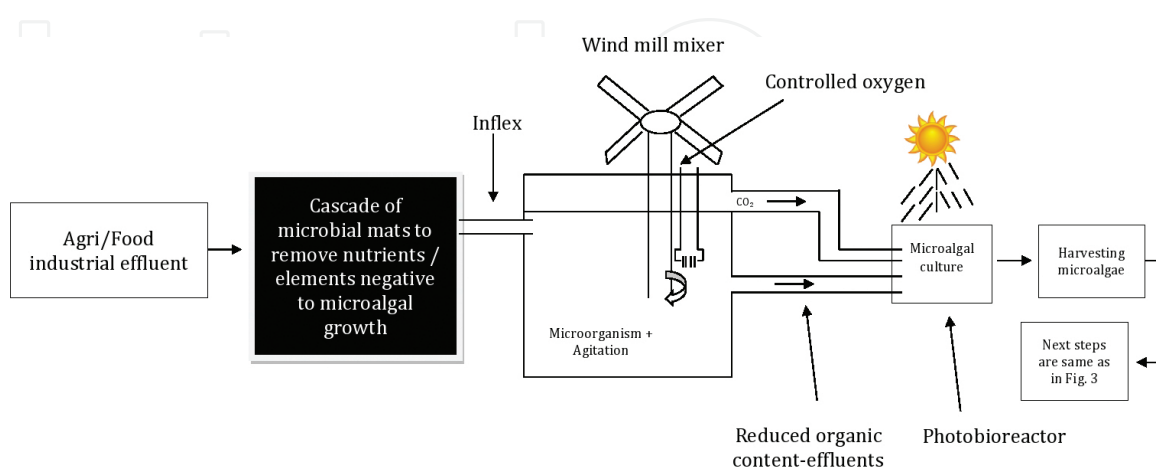


Figure 2. Robust bioreactor for reducing agri/food industrial effluents' BOD with concomitant efficient yield of microalgae for biodiesel production.

Nigam and Singh [15] further added that there is much potential for biofuel market and now it is a matter of time before they compete with petroleum-based fuels. Technological developments, in future, will enhance energy balance and reduce emissions and production cost of biofuels.

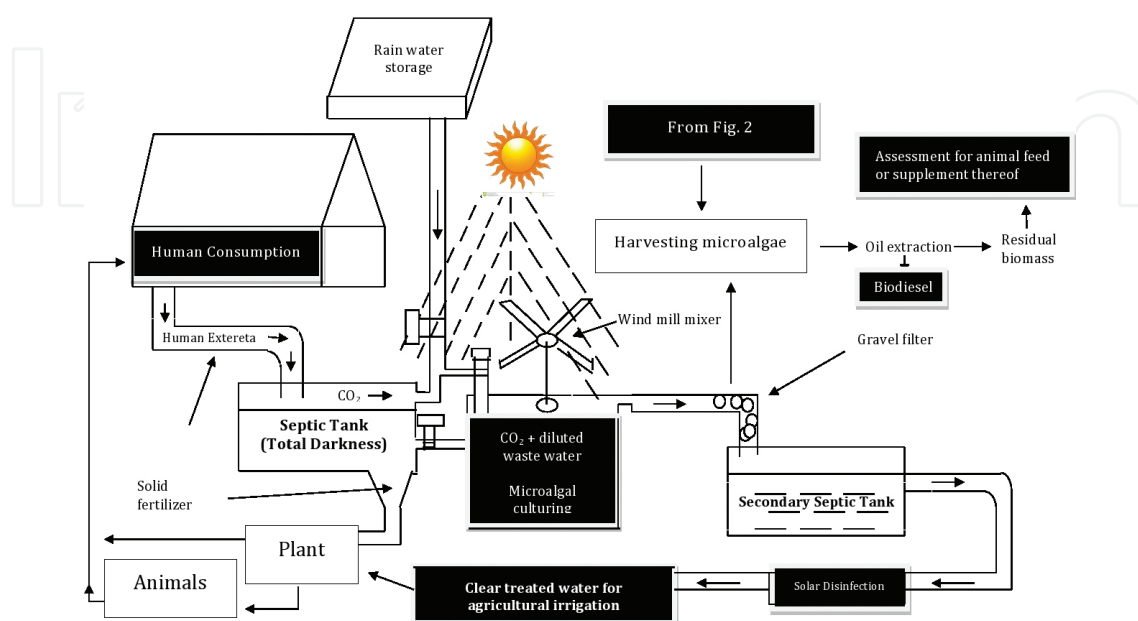


Figure 3. A workable multistep plane for sustainable treatment of domestic/organic content-rich wastewaters with concomitant microalgal yield.

3. Cultivations of microbes for biodiesel (third-generation biofuels)

First-generation biofuels, primarily produced from food crops and mostly oil seeds, will remain far behind to achieve targets of biofuel production, climate change mitigation, and economic growth. Whereas second-generation biofuels from lignocellulosic wastes are still in their infancy. Meanwhile, another bioenergy sector derives from nonfood feedstocks such as microalgae. Different types of photobioreactors and open ponds to cultivate microalgae with additional benefits of wastewater treatment and as food additive for human health and for aquaculture have been described [18].

In an agri-based country like Pakistan, a vast diversity of nutritionally enriched effluents from food industries like corn steep liquor, molasses, and whey are produced in abundant amounts. These can be semipretreated with solar insolation derived heat and fermented for the generation of CO_2 and less BOD effluents. Thus, processed effluents can then be employed for rapid growth of microalgae for biodiesel production. For this particular notion a robust bioreactor has been designed (Figure 2). The food/other industrial effluents pretreated in the bioreactor (Figure 2) and made optimum through dilutions and/or by incorporating essential nutrients for the cultivation of microalgae can then be routed to Figure 3 for obtaining biofuel and ultimate treatment of the effluents.

Domestic sewage can be biotreated specifically designed for the generation of effluents suitable for cultivation of microalgae. Such practices would incur economy of the process as treatment of domestic/industrial effluents will be achieved in a profitable manner. Whereas in the case of water shortage, the fresh water sources will not be affordable for diverse biotechnological processes without involving additional costs. In this context, biofuels' generation from biowastes/effluents would be an appealing field of development for sustainable supplies of biofuels and water for irrigation/other processes (**Figure 3**).

Mata et al. [18] concluded that for algal biodiesel development of strategies for large-scale cultivation and harvesting would be required. Growth conditions and provision of affordable nutrients for large-scale algal cultivations have to be identified for optimum yields. For this oil extraction strategies, provision of light, CO₂, and nutrients and turbulence, temperature, and O₂ levels must be optimized for a given location for conserving efficient oil content and biomass yield. These workers further indicated that using sources of CO₂, nutrient-rich wastewaters, or inexpensive fertilizers are expected to increase algal yields. In addition to biofuel production, considering microalgae biomass for different applications, such as food, agriculture, and medicine, will contribute to the sustainability and market competitiveness of the microalgal industry [18].

Another stream of biodiesel might originate from the identification of such biowastes, whose pretreatments/hydrolyses can lead to the successful cultivation of oleaginous yeasts. Even CO₂ has been claimed as a waste resource for cultivating microalgae to extract biodiesel (**Table 1**). Many other waste resources will hopefully be soon imagined as resources for biotechnological productions of value-added products in the near future.

4. Conclusion

After excessive exploitation of the fossil fuels' reservoirs and rendering the biosphere highly polluted, humans are left to extract/ferment fuels from biomass as we had been obtaining foods directly and/or indirectly from first trophic level. Parts of the plant biomass we preferably consume as food cannot be afforded longer for biofuels' production. Although the lignocellulosic residues and agriwastes represent potential sources of bioenergy productions. Accordingly, low/no cost feedstocks have been identified properly in different countries. Now the challenges of processing the feedstocks in terms of their economical and environmentally sustainable pretreatments, saccharification, and energy productions have been accepted by scientists of different disciplines. It is hoped that collaborative efforts of mechanical engineers, chemical engineers, biologists, and other scientists will bring the human wisdom to the hub of biotechnology for sustainable production of biofuels in the near future. Time is not too far when the humans will intentionally be cultivating specific species of plants and harvesting them or their parts presently considered as wastes to supply the biorefineries. Another business sector will represent biofuel productions from the lignocellulosic residues and industrial wastes.

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