

CHAPTER 20

c0020

A chemical approach towards the sustainability of biofuels: Environmental and economic aspects

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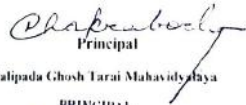
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s0010 1. Introduction

p0010 Considering the global economy, worldwide population, and industrial revolution in the past few years, renewable alternative energy sources such as biofuels, biochemicals, and biomaterials have provided the potential for decreased greenhouse gas (GHG) emissions. Energy security has stimulated the interest in suitable renewable energy sources. Primarily Fossil Fuels were being widely used to cease upraising energy demands and to produce materials for everyday life. Fuels are recently the primary energy source. Starting from transportation, electricity, and industrial advancements, revolutions have significantly increased the energy demands, which directly impact the usage of energy resources (Stoeglehner & Narodslawsky, 2009). The excessive usage of fossil fuels has severe effects on the biodiversity and environment on earth because of the enhancement in daily energy consumption, i.e., an increase in usage of fossil fuels led to an increase in earth's temperature by 1.9°C. Two of the main concerns nowadays are excessive emissions of greenhouse gases, increasing the temperature of the earth, and the depletion of fossil fuel reserves. Due to globalization/industrialization, high demands make fossil fuels highly costly, and the cost increases with time. High fuel cost, decreasing availability, and mitigating the greenhouse effects on the environment have increased demand for alternative or renewable energy sources. Solar, hydropower, wind energy, and geothermal sources can boost power (electricity) and heat generation. However, at the same time, they are largely dependent on seasonal environmental changes and climatic conditions, which are pretty unpredictable, and these cannot produce transportation fuels. On the other hand, organic waste biomass is readily available, cost-effective, and causes less environmental pollution. It has also been considered to be a source of eco-friendly fuel.

p0015 Hence, the global energy market and policymakers are looking toward renewable, sustainable sources of energy. The sustainable energy source options available are solar, wind, hydro, biomass, etc. The problem with these energy sources is they are not well

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suited for usage in transport purposes. Their practical usefulness lies in the successful conversion process into energy carriers, which is also economically beneficial. That is the worldwide concern over biofuels has been observed for the last few years (Stoeglehner & Narodoslowsky, 2009).

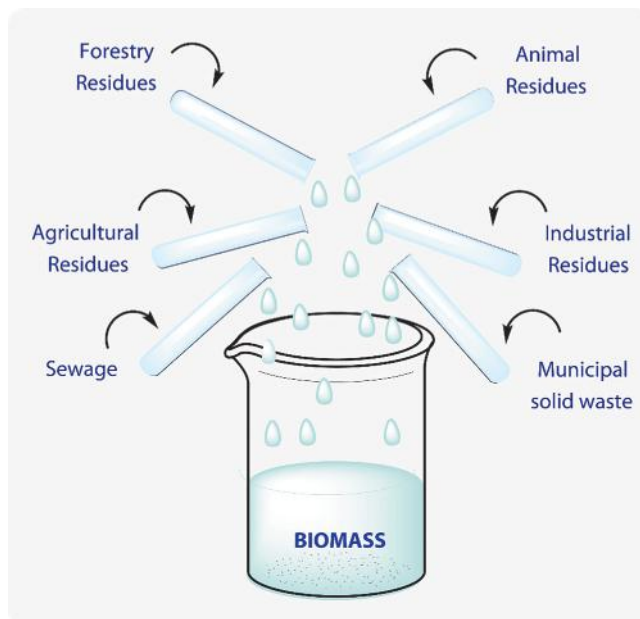
p0020 Hydrogen fuels are considered to be the most efficient of all fuels. However, handling hydrogen fuels is not that easy because of the storage issue, transportation, and the conversion of compounds to hydrogen. These limitations can be overcome by using biofuels and converting them onboard using a catalyst (Petrus & Noordermeer, 2006; Stoeglehner & Narodoslowsky, 2009).

p0025 Developing countries like India suffer from energy malnutrition in two forms—the traditional and high-quality energy resources in short supply. The insufficiency of traditional fuels raises several complications as a door to high-quality forms. Wood fuel is still being considered as pricey as the food in some countries. Hence it can be used as heat for cooking. Such a situation curbs agricultural productivity causing preeminent erosion potential. In this context, it is also absolutely necessary to mention that the more price hike of traditional fuels takes place, the greater dependence on traditional fuels would be there, and the more trapped consumers would arise by shortages. The sustainability of biofuels offers one option to escape the trap and is more convenient for underdeveloped and developing countries than advanced regions. Although converting any biomass feedstock into a liquid or gas fuel using suitable chemical engineering techniques is theoretically feasible, the efficiency of conversion, cost-effectiveness, and the degree of supply and demand have directed to preferred practices. Here in this article, we aim to focus on the sustainability of biofuel from chemical, environmental, and economic aspects.

s0015 **2. Biofuel**

p0030 Biofuels are hydrocarbon fuels obtained from organic matter through biological processes like aerobic digestion. Biomass can be directly used in solid-state as biofuels or converted into liquid or gaseous biofuel and can be burnt subsequently to release energy through combustion. Various biomass materials, such as crops, agriculture residue, etc., can be used to produce biofuel (Fig. 1).

p0035 The presence of carbon is the primary source of energy in biomass. The energy obtained from these biofuels is due to the carbon fixation process in which atmospheric carbon dioxide is converted into various organic compounds like sugar, protein, etc. As the energy demand is increasing day by day, the need for alternative renewable green energy sources, like biofuels, is increasing. Biofuels are generated/obtained from various daily waste products like starch, cellulose-containing foods, grasses, organic municipal waste, fat, vegetable oil, waste from farms, etc. Unlike fossil fuels, the biofuels demands are increasing, and biofuels resources are enormous. Biofuels produced from harvested biomass can be found in different states—liquid (bioethanol, biodiesel), gaseous (biogas),

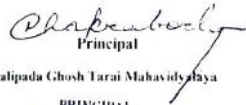


0010 **Fig. 1** Schematic representation of constituents of biomass. (No Permission Required.)

and solid (densified solid biofuel), and different chemical forms (Petrus & Noordermeer, 2006). Anaerobic digestion of biomass produces biosolids (wood pellets) or forestry waste, and biogas are used to generate electricity and heat, whereas liquid biofuels are directly used in the transport sector. Depending on their chemical aspects, biomass feedstock, and conversion techniques, Biofuels are categorized into two main categories—conventional biofuels produced from edible crops, which are also known as first-generation biofuels, and the advanced biofuels, which include second-, third-, and fourth-generation biofuels, are obtained from nonfood, grown feedstock, and agricultural wastes (Ajanovic, 2011; Tsita et al., 2020).

0040 The biofuel market is largely occupied by first-generation biofuels such as ethanol and biodiesel (Araújo et al., 2017). Bioethanol is produced by esterification and transesterification of plant material, animal fats, and plant carbohydrates fermentation. Second-generation biofuels based on nonfood crops include sugar cane bagasse, rice straw, wheat straw, and organic waste (Bhatia et al., 2017). The hydrolysis and fermentation of lignocellulosic material produce second-generation biofuel (Sikarwar et al., 2017). Pyrolysis and gasification generate hydrocarbon-based biofuels, although further catalytic processes are required. Algae and some other microbes are responsible for producing third-generation biofuel via biochemical and thermochemical processes (Pavithra et al., 2020). The algal biomass has an extended application in the production of biobutanol, bioethanol, biofuels, biogas, and bioenergy (Cesário et al., 2018). Enzymatic,

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base-catalyzed, and acid-catalyzed transesterification processes have been introduced with different microalgae (Pavithra et al., 2020; Yusuf et al., 2011). The fourth-generation biofuel is considered an extended form of the third generation and includes the application of advanced biological technologies (Pavithra et al., 2020; Zhang et al., 2020). Apart from these, hydrocarbon generation further requires catalytic steps; bioethanol, biobutanol, and biogas generation require enzymatic, biocatalyzed, and transesterification methods. Even though biofuel generation requires chemical, biological, or thermal methods, biofuels are considered the alternative renewable energy source for the future.

p0045 Hence, increasing interests have been put forward in biofuels as it is considered an alternative to fossil fuels and can be utilized to produce the cleanest hydrogen fuel.

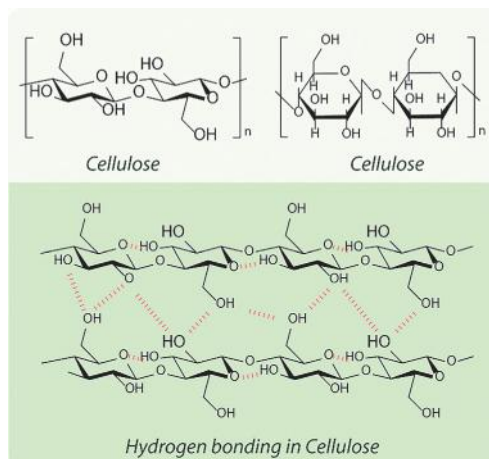
p0050 Now the question is, “how environmentally sustainable are the biofuels?” Various transformation methods/procedures involved in generating biofuels from biomasses are being focused on answering this question from a chemistry approach. The chemical compounds and the main reactions involved are considered for their environmental sustainability.

s0020 3. Biofuels sources: Constituents of biomass

p0055 Because of its renewable nature, biomass is considered to be a starting material for the transportation of fuels. The main components of biomass are cellulose, hemicellulose, and lignin, of varying amounts depending on the source of the biomass. It has a large, diverse composition. The main driving force, though, is the photosynthesis reaction where carbon dioxide (CO₂) and water (H₂O) react in the presence of sunlight to give various components of biomasses. These components are the source of energy. An understanding of the chemistry of these components is important because then only suitable and efficient methods/procedures can be developed for its conversion to biofuels. The understanding will also help recognize whether the process is sustainable. For example, if polysaccharides are the main component, they might require chemical modification or enzymatic degradation. The chemical aspects of such components are described subsequently.

s0025 3.1 Cellulose

p0060 Usually, cellulose is considered the most abundant renewable organic resource available on earth, having an annual production of 7.5×10^{10} tons (approx.) (Habibi et al., 2010). It is commonly available in terrestrial plants, marine algae, and bacteria. Cellulose, a neutral polymer of glucose, comprises various β -1,4-linked D-glucose subunits joined together by glycosidic linkages, van der Waals forces, and hydrogen bonds (Nanda et al., 2015). D-Glucose is the monomeric unit that is linked by β -1,4-glycosidic bonds. The molecular formula (C₆H₁₂O₆)_n shows its degree of polymerization. The structural base of cellulose is 4- α - β -D-glucopyranosyl-D-glucopyranose (Fig. 2). Cellulose consists

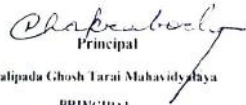


p0015 **Fig. 2** Structure of cellulose. (No Permission Required.)

of both amorphous and crystalline regions with different reactivity of its primary and secondary hydroxyl groups. Due to steric effects, the primary hydroxyl groups are more reactive than the secondary ones. The reactivity of the crystalline regions of cellulose is less reactive due to the regular and orderly arrangements. Celluloses have the chemical formula $-(C_6H_{10}O_5)_n$, where “n” is the number of glucose groups present in a molecule. The degree of polymerization of cellulose falls in the range of 1510–5500 (Hallac & Ragauskas, 2011). Cellulose contains the molecules held together by strong hydrogen bonding, which helps the plant cell walls to preserve their structure (Moon et al., 2011). Cellulose is considered a long-chain polysaccharide composed of 7000–15,000 units of glucose monomers and has a molecular weight of 342.3 g/mol (Gibson, 2012).

p0065 The biosynthesis of cellulose yields individual molecules, followed by spinning in an ordered manner at the site of synthesis. The intermolecular hydrogen bonds between hydroxyl groups and oxygen molecules in closer proximity build up the aggregation of multiple cellulose chains in order to produce fibrils (Moon et al., 2011). Fibrils are further arranged into microfibrils, a larger unit having a diameter of 5–50 nm and length of several microns, and aggregate to form the cellulose fibers. Crystalline linear assemblies of β -(1 \rightarrow 4)-D-glucan chains compose cellulose microfibrils, further stabilizing by hydrogen bonds. The arrangement of the starting and ending points within the plant cell wall differs for each glucan chain. Leading to the extension of their length to several hundred micrometers. The intensity of crystallinity within the fibrils is measured by the extent of hydrogen bonding between the glucan chains. Once all the sites accessible for hydrogen bonding are filled up, only a highly structured three-dimensional lattice is formed. Similarly, if the glucans are cross-linked, they produce para-crystalline structure form a less ordered structure.

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p0070 The cellulose microfibrils collected from plant cell walls have an average diameter ranging between 2 and 4 nm (Martínez-Sanz et al., 2015; Newman et al., 2015). On the other hand, cellulose microfibrils found in bacteria have a relatively large diameter of 4–8 nm (Martínez-Sanz et al., 2015). Some regions within the cellulose fibrils where the chains are highly ordered (crystalline) or disordered (amorphous) (Moon et al., 2011). In the crystalline regions, cellulose chains are strongly packed together in the form of crystallites stabilized by strong intramolecular and intermolecular hydrogen-bonding networks (Habibi et al., 2010). The variation in the molecular arrangement and hydrogen-bonding network in cellulose leads to the formation of cellulose polymorphs. Because of its abundance and critical chemical properties, cellulose has been used for various industrial works.

s0030 3.2 Hemicellulose

p0075 Hemicellulose is another important constituent of the plant. It is also a natural polysaccharide like cellulose. Hemicellulose, biopolymer in lignocellulosic biomass, is made of polysaccharide mixtures. The main constituents of hemicellulose are pentose sugars (e.g., xylose and arabinose), hexose sugars (e.g., glucose, mannose, and galactose), and sugar acids (e.g., glucuronic acid and galacturonic acid) linked by β -1,4-glycosidic bonds. Because of its lower degree of polymerization (50–200) and amorphous structure than cellulose, it can be degraded easily in the acidic or hot aqueous (Chen, 2014).

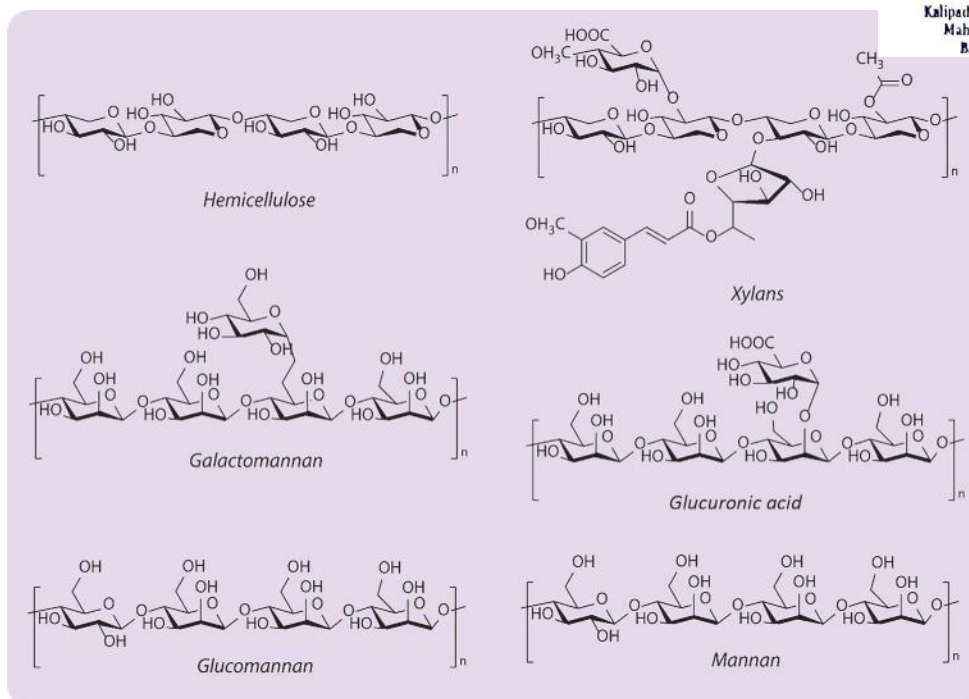
p0080 Several molecules with hemicellulose structures are galactans, mannans, xylans, and arabinogalactans. The main difference between cellulose and hemicellulose structure is the absence of a highly ordered crystalline state and a high degree of polymerization. This eases the easy hydrolysis of hemicellulose compared with cellulose. The diverse types of hemicellulose structures found are shown in Fig. 3.

s0035 3.3 Lignin

p0085 Lignin is another important biopolymer present in biomass. Its amount varies from plant to plant, and its primary function is to support the cell structure. Lignin is a complex aromatic polymer consisting of phenylpropane units (Fig. 4). Unlike cellulose, it is amorphous. The presence of many polar hydroxyl groups allows strong intra and intermolecular hydrogen bonds making it poorly soluble in any solvents.

s0040 3.4 Starch

p0090 Starch is another primary form of carbohydrates in plants. Starch morphology changes with plant species. It has two forms; the water-insoluble form is called amylopectin, and the water-soluble form is called amylose. Amylose is soluble in hot water and constitutes 30% of all starch found in nature; the rest is amylopectin. Starch is a polymer of α -D-glucose where glucose units are linked together in the 4C_1 conformation (Fig. 4).



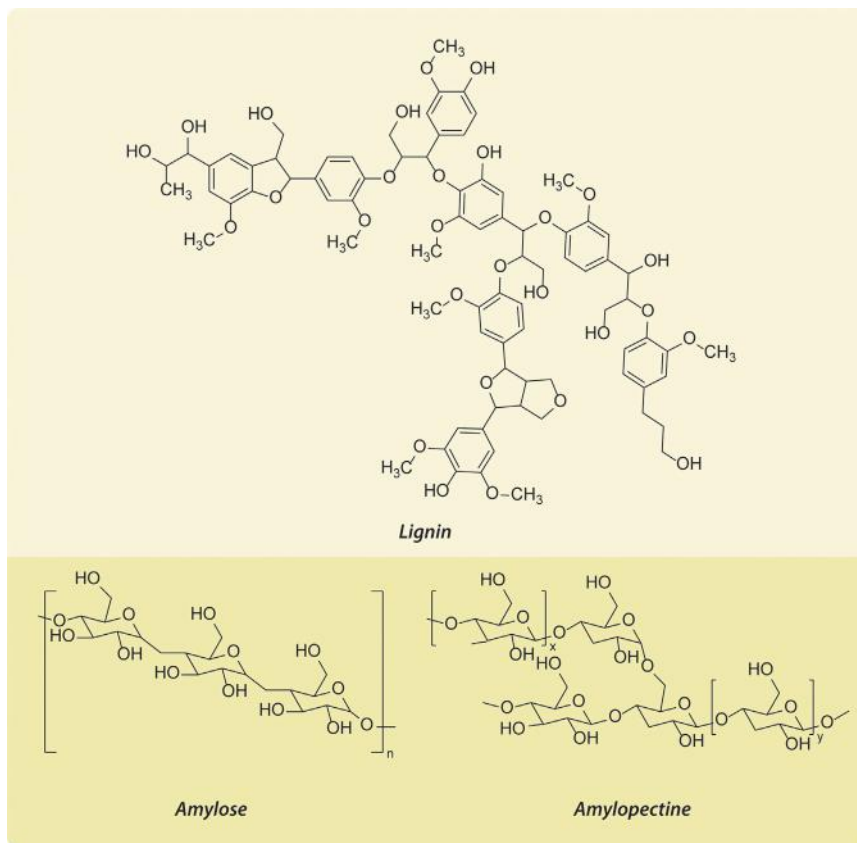
f0020 **Fig. 3** Hemicellulose structures. (No Permission Required.)

Hydrogen bonding among the polymeric chains gives stability to the amylose structures. The main component, amylopectin, is also a polymer made of linear chains of α-D-glucopyranose structures bonded at 1–4 bonds and branched at 1–6 positions.

s0045 **4. Conversion of such components to biofuels**

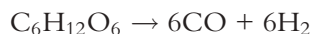
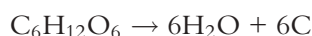
p0095 One of the main utilization of biofuels is for transportation purposes. Instead of the forms, fuels are available; they need to be converted to transport fuels. The current fuels being used for transportation purpose include hydrocarbon molecules ranging from low to high boiling point. To utilize biomass as biofuels, those constituents must be converted to hydrocarbons. We have seen cellulose being the main component of biomass. Cellulose and other carbohydrate compounds are oxygen-rich systems. To convert them to hydrocarbon for the usage as biofuels, elimination of that molecular oxygen would be required (Petrus & Noordermeer, 2006). Now, the elimination of oxygen from the carbohydrate system is highly unfavorable due to the energy demands as the process is an endothermic process. The eliminated oxygen can be of any form like carbon dioxide, water, or carbon monoxide. There are three ways in which the complete elimination of oxygen could

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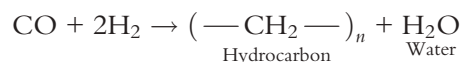
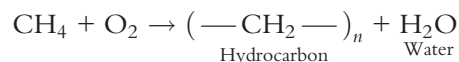
f0025 **Fig. 4** Lignin and starch structures. (No Permission Required.)

happen. (i) Release of oxygen as CO_2 + hydrocarbon (biogas); (ii) release of oxygen as water + Carbon (charcoal); and (iii) $\text{CO} + \text{H}_2$ (synthesis gas) (Petrus & Noordermeer, 2006).

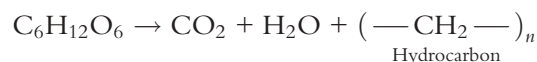


p0100 If the first option of oxygen elimination gives methane as a biogas product, to obtain higher alkane hydrocarbons as biofuels, it will require some kind of coupling reaction. Unfortunately, the coupling process is not feasible because of the lack of a suitable catalyst. Similar is the case with the second option, where oxygen elimination gives charcoal. The third option, where synthesis gas is obtained, is somewhat feasible. There is a reaction named Fischer-Tropsch which synthesizes alkanes from H_2 and CO . Therefore,

the transformation of biomass to biofuels, mainly transportation fuels, through the elimination of all oxygens from biomass resources is mostly not energetically sustainable except only the Fischer-Tropsch reaction that derived higher alkanes from biomass (Petrus & Noordermeer, 2006).

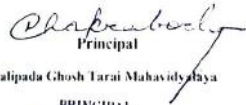


p0105 Another technique to convert biomass to transport fuels is the partial removal of oxygen from the biomass resource instead of complete elimination (Petrus & Noordermeer, 2006). In this process, partial removal could be done instead of full oxygen elimination via a maximum amount of CO₂ and H₂O. For example, if from sugar molecules, C₆H₁₂O₆, two CO₂ molecules are lost, it generates a hypothetical molecule, C₄H₁₂O₂, which is, in another way, a summation of two ethanol, CH₃CH₂OH. Now, ethanol is usually obtained by anaerobic fermentation of sugar molecules. There is another possibility of the formation of another hypothetical molecule, C₄H₁₀O, if two CO₂ along with one molecule of H₂O are eliminated. C₄H₁₀O resembles 1-butanol, which is basically the anaerobic fermentation product of sugars by Clostridia bacteria. Instead of CO₂ removal, sugar molecules can also be broken to give some other arrangements of molecules, e.g., a mixture of succinic acid, ethanediol, lactic acid, and glycolaldehyde molecules. All these products are separately obtainable by various processes from sugar molecules. If instead of these molecules, a larger amount of water is eliminated, the products which can be obtained are maleic acid ester, lactide, or furfural derivative. Thus, linear and saturated carbon structured products are obtained from partial elimination of oxygen.



p0110 Elimination of CO₂ generates structures that may be suitable for gasoline generation, but as the carbon chain length decreases, it becomes a disadvantage for diesel transport fuels. On the other hand, if H₂O is released, the chain length remains fixed, but the resulting compounds become more unsaturated. Such structures are not suitable for diesel production. When both CO₂ and H₂O are eliminated, the resultant compounds are nonpolar, but since oxygens are eliminated, it creates unsaturation. Thus, we see that partial elimination of oxygens from biomass sources is not too helpful for biofuels production as most of the resulting compounds are either too polar or too unsaturated. Thus further modifications are needed to convert them to biofuels (Petrus & Noordermeer, 2006).

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p0115 Apart from the various carbohydrate structures, another critical biomass component is lignin. Lignin having strong cross-linked three-dimensional stable solid structures to be used for the conversion process to biofuels (Petrus & Noordermeer, 2006).

s0050 5. Economic aspect

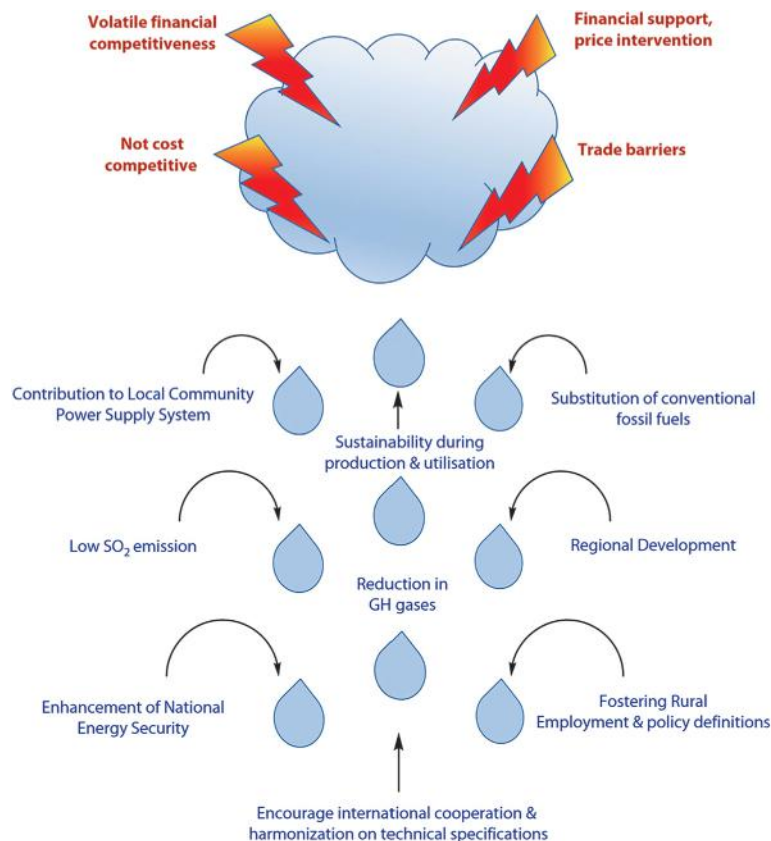
p0120 The chronology of industrial civilization revolves around the records of energy transitions. In ancient times the less developed countries, because of their agriculture-dependent economies, they used cultivation as a method of capturing solar energy for human use. Solar energy stored in firewood or other biomass energy sources is used to fulfill other basic needs for home heating and cooking.

p0125 With the development of socioeconomic structure, the rate of energy consumption has also increased. Now, because of the insufficient supply of firewood and other non-renewable energy sources, the 21st century is already observing the beginning of the next paradigm shift in conventional energy sources—away from fossil fuels toward sustainable biofuels, in order to support the growing economic transition. Such transition is governed by many factors, including environmental issues (particularly climate change), an insufficient supply of fossil fuel, continuous hike in market prices, technological change, and also the recent pandemic situation (Fig. 5).

p0130 Sooner or later, society will find comfort in adopting biofuels since fossil fuels are bound to supply issues and cannot go beyond geologic time. These situations are restricting agricultural productivity, creating more significant erosion potential. In addition to this, the price hike on conventional fuels facilitates greater dependence on traditional fuels and increases the number of trapped consumers. Sustainability offers one way to escape the trap, which is also a well-suited opinion for developing regions. Developing countries like India can finance the manufacturing of biofuels and make adjustments based on the requirement and availability of raw materials.

p0135 After the sudden surge of COVID-19 and its fast proclamation across the world, a sharp drop in economic activity has been observed, which has also been reflected in the decrease in dropping demand for crude oil. It resulted in a striking drop in the market price of oil (Taheripour & Mintert, 2020). and the continuous drop in oil price has been further accelerated by the unethical competition among the major oil producers. According to a recent study, the price of crude oil dropped from \$61.14 on December 31, 2019, to \$40.78 on October 18, 2020, and even reached at a level of \$14.10 during the April 2020 period (<https://markets.businessinsider.com>). As a result of this, numerous case of decline in transport fuel prices has been observed. The influence of the pandemic on the market for biodiesel, which is considered to be one of the most sustainable alternatives to diesel fuel, is expected to be lower than gasoline demand for unavoidable reasons. First, we observed the continuous drop in demand for transportation; diesel fuel consumption could minimize less than gasoline consumption. Diesel fuel is mandatory for heavy-duty

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0030 **Fig. 5** Schematic representation of factors contributing to the sustainability of biofuels. (No Permission Required.)

trucks, agricultural machinery, building equipment, and other manufacturing activities. Hence, although its high demand is predicted to drop due to a decrease in economic activity. In the absence of further reliable documentation, the drop in demand for diesel due to pandemic per month is presumed to be half of the drop in demand for gasoline (Taheripour & Mintert, 2020).

p0140 The restrictions imposed during the COVID-19 pandemic have surely paved the way for the global context of biofuels. Moreover, the suspension of economic activity has led to a reduction in the demand for transportation fuel; as per data received, Global gasoline and diesel demand is declined by 9% and by around 6% by the end of 2020, respectively. Such an absurd drop in demand has also influenced the demand for biofuels badly, as a considerable extent of biofuels is combined with fossil fuels (Agency, 2020). Ethanol production is decreased by 18% (720 million tons), and biodiesel and hydrotreated vegetable oil (HVO) production by 3% (21 million tons). Now on relaxing the restrictions in the

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second quarter of 2020, the demand for biofuels is expected to increase, which also the Indian rural economy and promotes positive growth in GDP (Shah et al., 2021; Najafi, 2021).

p0145 Thus, the question is not whether society will completely shift to sustainable biofuels but when. The production of fossil fuel cannot go beyond required timelines but, at the same time, maybe extended by introducing modern technologies for extraction. However, we must remember the adverse effects of climate change are a more fated issue than fossil fuel depletion. If the worst impacts of continuous rise in temperatures, drastic climatic alteration, and environmental pollution are to be avoided, society needs to switch to more sustainable, environment-friendly, and cost-effective way of fuels, and biofuels are definitely an inevitable alternative of fossil fuels, as most fossil carbon is still safely buried in the earth's crust.

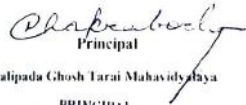
s0055 6. Conclusions

p0150 The interrelatedness of the sustainability, environmental and economic conditions can be well illustrated in the case of biofuels. It is pretty thought-provoking to note that the type of energy used actually plays an important role in determining the economy, economic activities, and environmental aspects of any country. It also indicates that the pattern of biofuel utilization and the existing pattern of producing such fuels under a specific system of socioeconomic pattern determines the economic framework of the system and also provides methods to inhibit the imbalance in a food chain. The use of "Biofuels" results in the development of an agricultural economy or "vegetable civilization." Under such an economic environment, lands are assumed to be valuable assets, which can act as a primary source of vegetal growth. But there are some considerable shortcomings of using biofuels as an alternative source of energy—first, it is quite challenging to obtain the right amount of biofuel in the right place. The isolated nature of the materials used in the production of biofuel poses a little difficulty to sustained use. Second, the production cost is not that much cost-effective if we consider the situation of the developing countries. For the time being, the interest and capital investment being put into biofuel production is adequately low, but somehow it is able to match demand. In contrast, on increasing demand, the supply will be a long-term operation, which will be quite pricey, and such a disadvantage can prevent the use of biofuels from becoming more approved. Third, biofuels are produced mostly from crops that need a good amount of fertilizer for their healthy growth. The downside of using fertilizers is they cause water pollution to a considerable extent. Fourth, a generous amount of water is needed to soak the biofuel crops, imposing unsustainable pressure on local and regional water resources. Finally, biofuels produce carbon dioxide on burning, which contributes to slow global warming. Although it is an undeniable fact that biofuels produce less GHG emissions than fossil fuels, they are incapable of stopping or reversing it.

- p0155 In this article, a primary qualitative explanation of the sustainability of basic discussed. A conclusion can be drawn that biodiesel and bioethanol seem to be they come into a conflict of interest with food production. In contrast, the main aspects of some other biofuels, such as agricultural or forest residues, are considered good because of their contribution to regional and rural development and rebuilding the socioeconomic framework in a sustainable way.
- p0160 Finally, we can say that biofuels may help ease our energy needs, but they cannot be treated as stable conditions to solve all of our problems. With the disappearance of this epidemic, the extent of air pollution is supposed to intensify again, so it can only serve as short-term substitutes in terms of sustainability and any flaws in the future development of sustainable biofuels will have irreversible consequences on the community health and environment.

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Abstract

Nowadays biomass is being treated as the most comprehensive source of renewable energy and a starting material for fuel generation. The abundance and renewable nature of biomass has increased its usefulness as a far-reaching alternative resource of transportation fuel. In order to use biomass as fuels, its major components like carbohydrates, hemicellulose, lignin, and starch require the removal of oxygens, so that oxygen-rich carbohydrates can be transformed into hydrocarbons. Hence, the bio-based economy has been implemented as a prior preference in order to scale down disastrous impacts of Greenhouse gas (GHG) along with fossil fuel consumption. In this connection, an amplification in the production of biofuels has been witnessed in the first decade of this century. This chapter presents a molecular-level understanding of the chemistry involved in the transformation of biomass into hydrocarbons, sustainability and economic aspects of the process. If the chemistry of generation of transportation fuels from biomass is studied minutely, then the global status of biomass can be well scrutinized and in near future it will contribute a lot more toward sustainable developments of biofuels, both from environmental and economic perspectives.

Keywords: Renewable energy source, Greenhouse gas (GHG), Global warming, Sustainability, Biofuel, Green chemistry, Natural resources, Environmental chemical engineering, Energy systems, Bioprocess.