Clean Energy Production Technologies

Series Editors: Neha Srivastava · P. K. Mishra

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Paddy Straw Waste for Biorefinery Applications

Springer

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The consumption of fossil fuels has been continuously increasing around the globe and simultaneously becoming the primary cause of global warming as well as environmental pollution. Due to limited life span of fossil fuels and limited alternate energy options, energy crises is important concern faced by the world. Amidst these complex environmental and economic scenarios, renewable energy alternates such as biodiesel, hydrogen, wind, solar and bioenergy sources, which can produce energy with zero carbon residue are emerging as excellent clean energy source. For maximizing the efficiency and productivity of clean fuels via green & renewable methods, it's crucial to understand the configuration, sustainability and techno-economic feasibility of these promising energy alternates. The book series presents a comprehensive coverage combining the domains of exploring clean sources of energy and ensuring its production in an economical as well as ecologically feasible fashion. Series involves renowned experts and academicians as volume-editors and authors, from all the regions of the world. Series brings forth latest research, approaches and perspectives on clean energy production from both developed and developing parts of world under one umbrella. It is curated and developed by authoritative institutions and experts to serves global readership on this theme.

Neha Srivastava • Bhawna Verma • P. K. Mishra
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Preface

This book entitled, *Paddy Straw Waste for Biorefinery Applications*, provides sustainable value addition of paddy straw and its different roles in biorefinery applications. Additionally, the book explores different large-scale industrial uses of paddy straw for different applications along with biorefinery grounds. Huge production, availability, and advantage of the lignocellulosic waste need mass-scale expansion for extensive industrial utilization as well as for effective environmental management. Biotransformation and value addition of paddy straw also help to resolve the issue of solid waste management around the globe because rice straw is included among the most consumed cereal worldwide and releases huge amounts of waste alongside. Therefore, this book gives the common ground to explore this waste for various important biorefinery roles through its maximum utilization. Based on this fact, this book has been divided into ten targeted chapters based on paddy straw application in biorefinery industries. Chapters 1, 2, and 3 present the basic biorefinery concept, importance, and current scenario with paddy straw utility as promising feedstock. Chapters 4, 5, and 6 explore the sustainable possibility of paddy straw in biofuels production via fabrication of nanomaterials and bioethanol production. On the same pattern, Chaps. 7 and 8 explore the charcoal fabrication and current ethanol production development as well as the challenges in the area. Further, Chaps. 9 and 10 discuss the feasibility and improvement in hydrolytic enzyme production and biochar synthesis using paddy straw as the basic and initiated material. Since the book is exclusively based on the sustainable application of paddy straw in biorefinery industries, it will prove its promising credentials in the area to overcome the existing roadblocks and enrich the biorefinery industries.

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Neha Srivastava has received PhD in Biotechnology from the Department of Molecular and Cellular Engineering, SHIATS, India in the area of bioenergy. She is working as Research Scientist in the Department of Chemical Engineering and Technology, IIT (BHU) Varanasi, India. She has published more than 37 research articles in the in peer-reviewed journals of SCI impact factor and have filed three patents, one technology transfer, and 14 published books and two book series of international renowned publisher. She is working on bioprocess technology and biofuels production (microbial screening and enzymes; production and enhancement, biohydrogen production from waste biomass, bioethanol production).

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Chapter 1
Biorefineries: An Analogue to Petroleum Refineries

Anuja Gupta, Tanvi Sahni, and Sachin Kumar

Abstract This chapter explores the concept of biorefineries as a sustainable and efficient alternative to traditional petroleum refineries. It delves into the increasing global demand for renewable energy resources and the urgent need to transition from fossil fuels to more sustainable options. The abstract begins by highlighting the key objective of the chapter, which is to present biorefineries as a viable solution for the production of various valuable products from biomass feedstocks. It emphasizes the importance of integrating multiple processes in biorefineries to maximize resource utilization and minimize waste generation. The chapter provides an overview of petroleum refineries as a basis for comparison. It highlights the similarities between the two refinery types, such as the conversion of raw materials into valuable products. Additionally, it discusses the significant advantages of biorefineries, including the utilization of renewable biomass resources, reduced greenhouse gas emissions, and the potential for bioproduct diversification. Furthermore the abstract delves into the different conversion technologies employed in biorefineries, such as biochemical, thermochemical, and hybrid processes. It explores various biomass feedstocks, including agricultural residues, energy crops, and algae, and their respective conversion pathways. Moreover, this chapter emphasizes the importance of biorefinery integration with existing industries and infrastructure, highlighting the potential synergies and economic benefits. It also addresses the challenges associated with biorefinery implementation, including feedstock availability, technological advancements, and market competitiveness. Finally, the abstract concludes by summarizing the chapter's key findings and discussing the future prospects of biorefineries. It highlights the role of policy support and research and development in fostering the growth of biorefinery sector and facilitating a sustainable transition toward a biobased economy. Overall, this chapter serves as the comprehensive

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introduction to the concept of biorefineries, showcasing their potential as an analogue to petroleum refineries and as essential component of the renewable energy landscape.

Keywords Biorefineries · Feedstock · Petroleum refineries · Thermochemical and hybrid processes

1.1 Introduction

With the advancement in technology and rise in population growth over the past decades (Alalwan et al. 2019), there is a 64% increased demand for transport and chemical energy with every passing day which results in enhanced usage of biofuels up to ~111 million barrels per day (Mb/d) (Sharma and Singh 2017). Liquid fuels have significant role in the economic development around the globe (Panda et al. 2010). Majorly the global population mainly depends on fossil fuels, which results in the emission of greenhouse gases (Ramachandra et al. 2015). The main energy requirements (80%) are currently fulfilled in the industrial and transport sectors with chemical fuels and petroleum resources (Yusuf et al. 2011). Due to this, carbon dioxide emission over the last 50 years has increased from 200 to 414 ppm (Ballantyne et al. 2012). With this rate, this level can reach up to 500 ppm by 2045, which will cause the melting of the polar ice sheets. This in turn results in the rise of the water levels in the sea to several meters, which gives us a valid reason to shift our focus from the fossil fuels and find some renewable source of fuels for energy production to reduce the carbon footprint on the earth. For example, when we blend 10% bioethanol into gasoline, the emission of greenhouse gases is reduced up to a great extent like reduction in emission of CO_2 by 6–10%, CO by 25–30%, NO_x by 5%, and volatile organic compounds by 7%, respectively (Suarez-Bertoa et al. 2015). Till date, oil is the main source of energy production and transportation. As till date the total daily consumption of oil is about 84 million barrels which is likely to be increased by ~116 million barrels by 2030 (Kjärstad and Johnsson 2009). Studies conducted have shown that lignocellulosic biomass can be used as a good alternative as well as renewable source of fossil fuels and can be efficiently used as transportation fuel (Nanda et al. 2015; Kumar et al. 2023). As biomass availability is also limited, it is necessary to use them efficiently. Thus, biorefineries are thought to play an important part in decarbonizing energy (Stegmann et al. 2020). A noticeably reduced amount of GHG emission can be attained by the use of biomass as biofuels because the carbon dioxide released during the incineration of lignocellulosic plants is balanced by the amount used during plant cultivation (Chen et al. 2021). Thus, the production of bioenergy is proven to be the best alternative till date and contributes ~9% of the entire global energy supply (Gielen et al. 2019). During a research, it was found that there is a significant reduction in GHG emissions in South Africa through the use of advanced biofuels which were prepared from lignocellulosic materials mainly constituting sugarcane bagasse and other biomass resources (Ullah et al. 2015). Several other renewable sources of energy can be used as alternative sources for energy production apart from lignocellulosic biofuels (Ho et al. 2014). Such as heat and electricity are generated from wind, solar, and hydropower energy, the requirement of transportation fuel can be fulfilled from lignocellulosic biofuels (Lange 2007). Biofuels are also helpful in decarbonizing the harmful gases which are the by-products of flight and freight industries (McCollum and Yang 2009). Using biomass for fuel production is a good alternative for the improvement of the environment (Groom et al. 2008). The biomass produced in the form of agricultural, industrial, forestry, aquatic, and municipal solid waste creates environmental pollution by emitting toxic gases as it is decomposing with unstrained methods; thus carbon-based solid wastes can be used as an abundant natural source for biofuels (Inyang et al. 2022). To improve the degrading quality of environment, it is necessary to grow biofuel consumption in automobile industry. It will also prove useful in the growth and advancement of agriculture sector, which in turn will produce more biomass for more biofuel production (Demirbas 2008). In such way, lignocellulosic biomass and biofuel production will slowly dominate the fuel industry in few years.

Over time, different researchers proposed different definitions of a biorefinery based on their demand and usage which kept on changing in due course of time (Borras Jr et al. 2016). “Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy” (Mohan 2016). “A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass” (Béligon et al. 2018). Definitions of biorefineries on the basis of the economic importance of forest industry to the biorefineries: “Full utilization of the incoming biomass and other raw materials for simultaneous and economically optimized production of fibers, chemicals, and energy” (Berntsson et al. 2008). “Maximising the economic value from trees,” need “an improved business model and corporate transformation” (Berntsson et al. 2008). An overview of biorefinery is given below (Fig. 1.1).

Biorefineries are “Facilities that can combine biomass conversion processes and equipment to generate fuels, power, and new materials in an economically, socially and environmentally sustainable way” (Berntsson et al. 2008). Biorefinery is an evolutionary concept in the fuel world; thus, it is defined as “A complex facility (or network) that involves integral biomass conversion processes to produce a range of products, mainly biofuels, power, materials, food, and feed as well as chemicals and biochemicals based on biomass” (Cardona-Alzate et al. 2020).

A huge variety of biowastes are used by the biorefineries to produce a wide spectrum of fuels, for example, glycerol is processed to obtain high-added second- and third-generation fuel (Ferreira et al. 2019). Crop produce is used as potential material in biorefineries to prevent land competition (Cherubini 2010). Due to the above reasons, two different types of biorefineries are required by taking into account the final products used during the manufacturing of biofuels. Energy-focused biorefineries prioritize the production of biofuels, power, and heat as their primary outputs. These biorefineries generate various forms of energy, including biofuels such as biogas, syngas, hydrogen, bio-methane, bioethanol, FT fuels, bio-oil, biodiesel, charcoal, etc. Additionally, they also produce electricity and

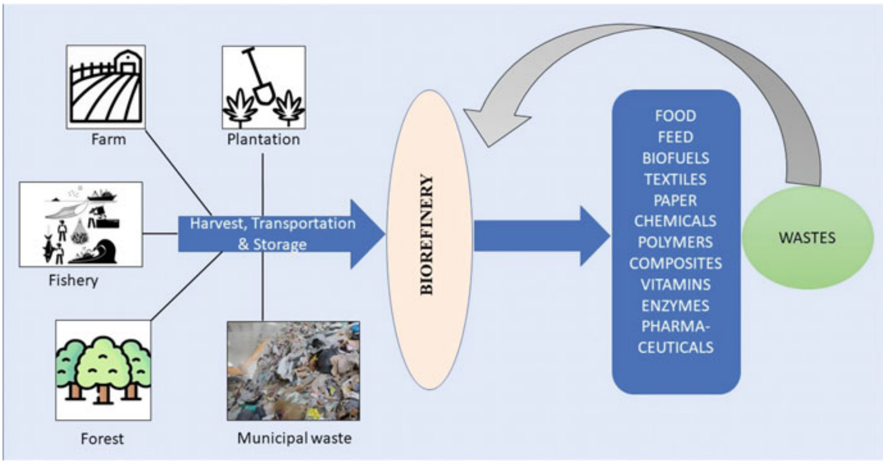

Fig. 1.1 Overview of biorefinery

heat, emphasizing their core purpose of energy generation (Awogbemi et al. 2021), whereas the industries that mainly focus on products are those biorefineries whose main objective is to provide the major products used in energy-driven biorefineries. Such products are:

- Chemicals (fine chemicals, building blocks) (Takkellapati et al. 2018)
- Organic acids (Becker et al. 2015)
- Polymers and resins (Thang and Novalin 2008)
- Biomaterials (Fahd et al. 2012)
- Food and animal feed (Jungmeier 2014)
- Fertilizers (Seghetta et al. 2016)

Bioethanol and biohydrogen have been recognized as beneficial fuels and base chemicals (Gielen et al. 2019; Verma et al. 2023). However, the classification of these products depends on their intended purpose and the demand in the market. In recent times, the concept of biorefineries has emerged, referring to advanced systems that integrate the processing or fractionation of biomass to produce a range of valuable outputs. To achieve this, a comprehensive assessment of the raw materials and the adoption of sustainable design principles are necessary, incorporating the latest advanced technologies and approaches. It is important to note that these considerations align with the three pillars of sustainability, ensuring the viability of the biorefinery in terms of environmental, social, and economic aspects.

1.2 Why Biorefinery Will Replace Oil Refinery?

The industry based on petroleum is unsustainable as the demand for petrochemicals rises day by day due to the finite nature of the fossil fuels from which these chemicals are created, as well as the environmental pollution that results from the overuse of these fossil resources (Bhan et al. 2020). These problems create a need for an alternate sustainable renewable source to meet up the daily energy demands over the globe, which results in an unexpected increase in the development of the biorefinery industry (Kurian et al. 2013). The economy's major material handler in recent years has been the oil industry. Around six billion tons of CO_2 was emitted worldwide as the primary fuel or more than 1000 kg per person (Themelis 2003). In comparison, the global steel industry produces approximately 700 million tons of steel each year, equating to an average of approximately 120 pounds per person. Renewable, photosynthetic biomass should be used as an alternative to oil. Naturally, biomass is preserved in biofuels, and energy is dissipated; oil refineries produce a lot of toxic waste products like phenols, sulfides, and heavy metals, present in crude oil (Wan et al. 2022). During the refining of this crude oil, remaining toxic substances such as cyanide, dioxins, and furans are produced, along with this many other toxic wastes added to the air as well as groundwater, altering their natural composition (Misra and Pandey 2005). The solution to this oil refinery pollution is bioremediation which is one of the methods of biorefinery (Khatiwada et al. 2020). For instance, certain microorganisms are used to break down the pollutants like phenols (Karigar and Rao 2011). The process of refining oil at a petroleum refinery begins with the receipt of crude oil for storage, processing, and shipping of finished products. At the oil refinery, oil corporations utilize catastrophic event risk management (as acceptable risk limits for environmental, public health, and safety). Biomass-based chemicals typically require production procedures with less demanding temperature, pressure, or solvent conditions. Hence the risk is diminished or eliminated via biorefinery (Alfaqiri et al. 2019). In contrast to oil refineries, biomass refineries recycle carbon dioxide. Hence, biorefinery suggests a favorable impact on global warming (Gravitis 1998). The proper functioning of a power plant depends upon how much carbon dioxide is emitted per kWh. Thus the efficiency of electric power plants using wood to generate power is 60% more than the efficiency of the power plants that use coal as the burning material which changes the fossil fuel to plant material ratio to 30:1 (Spliethoff 2010). Several sources of biomass are wasted and disposed of per year in huge amounts, for example, if we talk about the USA, they dispose approximately 350 million tons of agricultural biomass as a waste product every year, and also the biomass production of tropical plantations that is unused is unexpectedly high (Tye et al. 2016). Thus, it is concluded that the world has an enormous amount of residual biomass that can be used as fuel without any harm to the forests and without causing soil erosion. Less than or equal to 40% of the total residual mass from the fields is used for biofuel-ethanol production, and the remaining is again provided back to the fields in the form of organic matter added to the soil which will increase the fertility of the soil, reduce soil erosion, and also remove carbon dioxide in the environment in a noticeable amount (Sinclair and Weiss 2010). Only a 1% rise in the organic matter added to the soil will reduce up to 40 t of carbon dioxide per hectare of land (Winsley 2007). Ethanol transportation reduces up to 46% GHG of the total 25% of greenhouse gas emissions in the USA in place of gasoline (Wang et al. 2011). Thus, to generate full potential from biofuels, the biorefinery industry should be expanded, and engine designs should be improved so that we can take more advantage of the biofuels.

1.3 Refineries vs. Biorefineries

When comparing the manufacturing technologies of biorefineries, it becomes evident that there is a significant and noticeable difference between hydrocarbon-based crude oil and biomass. This disparity in quality can be attributed to the distinct soil varieties from which they are derived, resulting in differing physical and chemical properties of crude oil (Stedile et al. 2015). The properties of biomass, on the other hand, are influenced by factors such as sunlight exposure, maturity duration, and the levels of air and moisture it encounters. These factors contribute to variations in the oxygen content of biomass, which is higher compared to crude oil (Bolan et al. 2021). The potential of biomass as a source for chemical has been extensively studied in various research papers, highlighting its increasing popularity. These biobased products have the potential to generate a significant revenue of more than US$15 billion for the global chemical industry. However, the economic production of transportation biofuels remains a considerable challenge for chemical industries (de Jong et al. 2012). Currently, the fuel industry relies heavily on hydrocarbon products such as LPG and natural gas for transportation, polyester, polyurethane, polymers, glycol, ammonia, synthetic rubber, asphalt, and insecticides (Sudha et al. 2023). Developing biorefineries is aimed at replacing these harmful and finite hydrocarbons with renewable alternatives like biomass-based products. Major differences between refineries and biorefineries are given in Table 1.1.

Figures 1.2 and 1.3 also help in distinguishing between the biorefineries and crude oil based on the different types of products obtained. In crude oil refineries, there is certainty in the composition, technology, and products, but in biorefineries, there is no certainty in the products, technology, location, and composition of the products obtained, although the objective of the biorefinery is the same as that of crude oil refinery (Cardona-Alzate et al. 2020).

In the formation of biorefineries or crude refineries, the location is the main factor for the sustainable operation of the refineries as well as the analysis of the products and their alternatives (DwiPrasetyo et al. 2020). The price of these products is directly influenced by various factors, including the geostrategic policies established by governments and the occurrence of conflicts or wars. Changes in these geopolitical dynamics can disrupt the supply chain, leading to fluctuations in feedstock availability and subsequent price volatility. As a result, the petrochemical industry closely monitors and responds to geopolitical developments as they significantly

Table 1.1 Comparison of refineries and biorefineries

S. No.	Based on	Refinery	Biorefinery
1	Feedstock	Main component of feedstock is typically a hydrocarbon, which contributes to its relative homogeneity	Feedstock is heterogeneous. The bulk components are carbohydrates, lignin, proteins, and oils
		The amount of oxygen content is low	The amount of oxygen content is high
		As processed further the weight of the product is increased	As processed further, the weight of the product is decreased; thus it is important to maintain the amount at the start of the processing to obtain the required quantity of end product
		Sulfur content is high in refinery-based products	Sulfur content is low in biorefinery-based products although it is high in inorganic substances like silica
2	Building block composition	Building blocks of refinery products are hydrocarbons: ethylene, propylene, methane, benzene, toluene, and xylene isomers	The fundamental building blocks involved in various biological processes are glucose, xylose, and fatty acids. These building blocks play crucial roles in biochemical pathways and are essential for the synthesis of diverse compounds. Examples of fatty acids include oleic acid, stearic acid, and sebacic acid, each serving distinct functions within biological systems
3	(Bio)chemical processes	The process primarily involves chemical reactions, particularly the introduction of heteroatoms such as oxygen (O), nitrogen (N), and sulfur (S). This includes techniques like steam cracking and catalytic reforming, which enable a wide range of conversion chemistries to take place. These chemical processes play a significant role in transforming the composition and properties of the substances involved, allowing for the synthesis of various valuable products	Biorefinery operations involve the integration of chemical and biotechnological processes. These processes are employed to remove oxygen from the feedstock and undergo various relative heterogeneous processes, such as dehydration, hydrogenation, and fermentation. Through these transformations, the aim is to obtain building blocks that can be further utilized for the production of desired products. These processes are essential for converting the feedstock into bioenergy, biofuels, chemicals, and high-value compounds
4	Chemical intermediates produced at a commercial scale	Produced in a wide range and huge amount	Produced in fewer amount but its number is increasing with more advancement

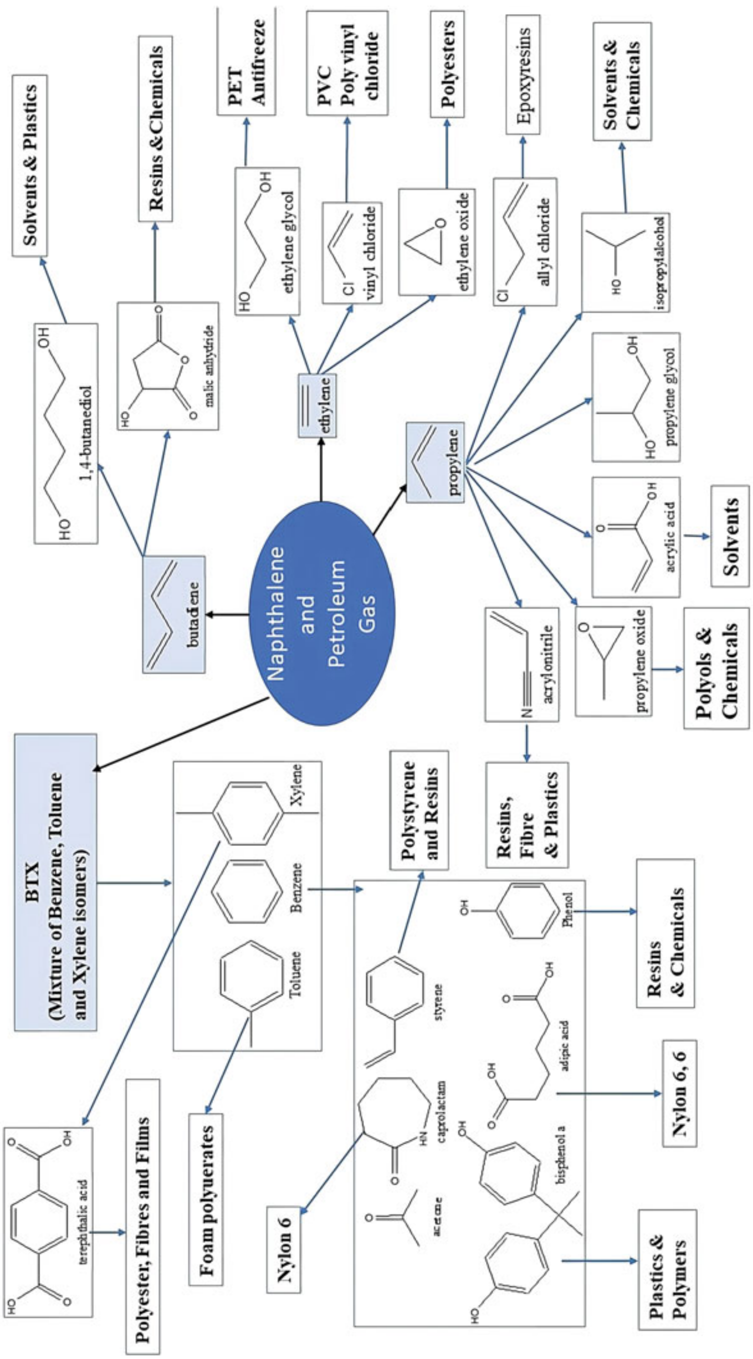

Fig. 1.2 Basic petrochemicals in refinery, and its major applications

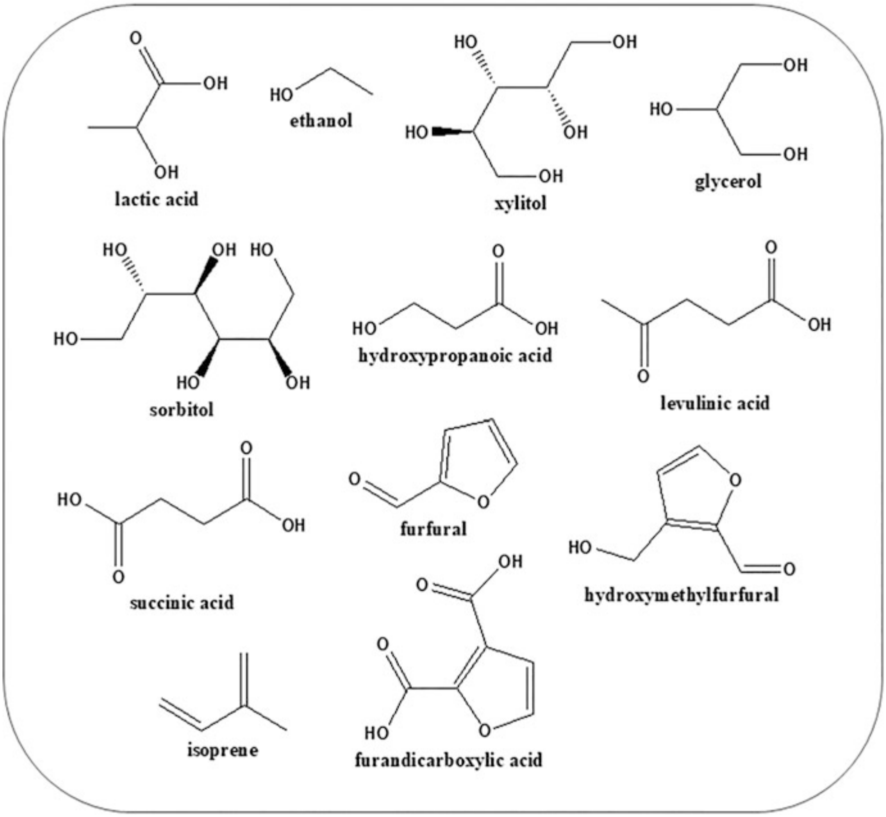

Fig. 1.3 Proposed biobased platform molecule

impact the overall market conditions and profitability (Cardona-Alzate et al. 2020). Thus, with the several factors governing the prices of crude oil refineries, biorefineries have proven to be a great and economic alternative (Figs. 1.4 and 1.5).

There is a need for both the stabilization of biomass pricing and the advancement of technologies to advance and optimize the usage of alternative feedstocks globally. Moreover, biorefineries offset the carbon footprints of fossil fuels because using fossil fuels results in significant CO_2 emissions that are penalized by society (Menon and Rao 2012). The absorption of CO_2 during biomass growth is believed to provide a balance and contribute to the potential benefits of biomass consumption in mitigating climate change. The viability of the hydrocarbons sector was determined by the market development for petrochemicals (Shahbaz et al. 2021). Initially, only a small portion of crude oil was consumed, leading to significant environmental damage due to the leftover waste. However, at that time, environmental concerns were not a priority, and the increase in energy demand facilitated the growth of unsustainable practices (Schnaiberg et al. 2002). With the concurrent development of fractionation and conversion techniques, driven by the demand for novel

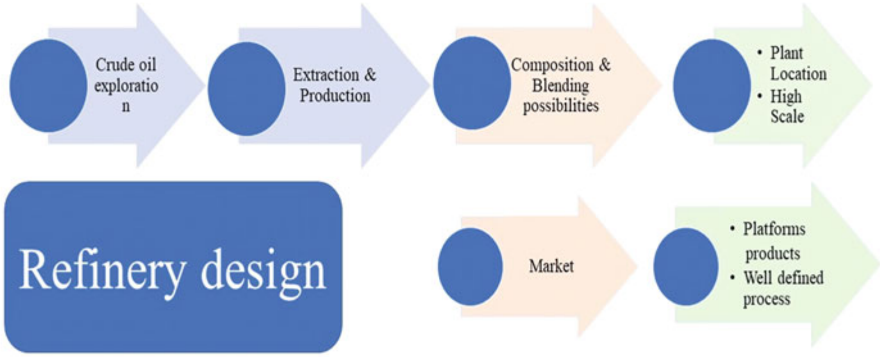

Fig. 1.4 Refinery design

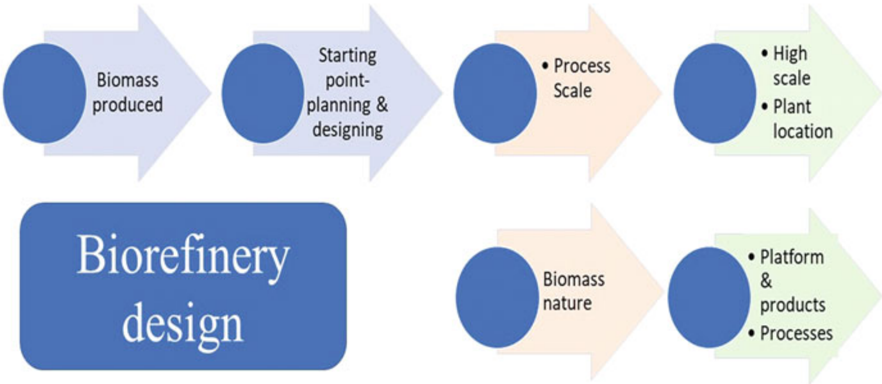

Fig. 1.5 Biorefinery design

products, especially plastics, the petrochemical industry gradually reduced the residues to minimal levels that are widely recognized today. This progress led to an increased reliance on crude oil as a primary raw material. Over time, crude oil gained extensive usage due to its abundance and suitability for the production of various petrochemical compounds. The industry's ability to efficiently process crude oil into different products has contributed to its widespread adoption as a key feedstock in petrochemical manufacturing. Comparing the software and tools available today with those from that era is particularly difficult due to the significantly lower quality and efficiency of the informatics systems back then (Zolfaghar et al. 2013). This method cannot be used using biomass as the basic material. The expansion of biorefineries needs to be examined in the new sustainability context that is now mandated. Although biomass is a complicated system and technology maturity isn't very high, it's still important to incorporate sustainability concepts and techniques, such as those in Table 1.2, during comprehensive design.

Table 1.2 Difference between the biorefineries and crude oil refineries based on sustainability principles as well as design strategies

S. No.	Refinery design strategy	Biorefinery design strategy	Comments
1	The same quality of crude oils is refined; rather specific crude oils are refined in a specifically designed refinery	Combining the feedstocks. The overall biomass efficiency and raw material utilization both rise as integration levels rise	The biorefinery approach should be maintained. New refineries now utilize different feedstocks such as natural and shale gas LEXINNOVA within the facility
2	The best method used in recent decades to produce petrochemicals, such as reactive distillation, was integrated technology	The most effective technologies combine fermentation, saccharification, and separation into one system	Biorefineries incorporated integrated petrochemical industry technologies
3	Refineries did not prioritize reducing waste streams as a primary goal. With time, design techniques such as pinch analysis were added	Based on various levels of integration, multiprocessing biorefineries combine various raw materials and products to produce additional products with added value	The design of biorefineries has always taken cues from the crude oil sector, such as the pinch analysis
4	Refineries were initially designed as independent facilities without conducting a comprehensive assessment of the feasible and practical products that could be obtained from them. The focus was primarily on the processing and refining of crude oil to produce conventional petroleum products such as gasoline, diesel, and jet fuel. At that time, the concept of integrated refining and petrochemical complexes was not extensively explored	The best scenario is always a multiproduct portfolio Technical, economic, environmental, and social process indicators typically rise as the number of goods increases	Any biomass-based project should take into account the maximum products that can be produced after using all biomass, based on preliminary or heuristic analysis
5	For many years, the refineries showed little concern for the ecosystems in general or the environment. The reputation of the crude oil sector today is poor mostly because of this well-known	The usage of other natural resources is decreased because of the preservation of ecosystems by second- and third-generation raw materials	Biorefineries must adopt the concept of life cycle analysis (LCA) and avoid making the same mistakes by giving environmental impact assessments the same weight as economic assessments
6	The most advanced and effective logistics are used in the oil business. The	The most widely used raw material in the world, biomass, is found in all	In comparison to oil refineries, the logistical and social aspects of

(continued)