Chapter 1 Biorefineries: An Analogue to Petroleum Refineries



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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%, NOx 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 $\sim 9\%$ 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 (Invang 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 secondand 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

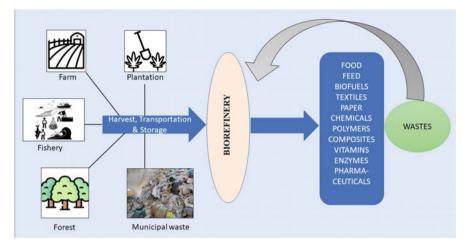


Fig. 1.1 Overview of biorefinery

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 CO₂ 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

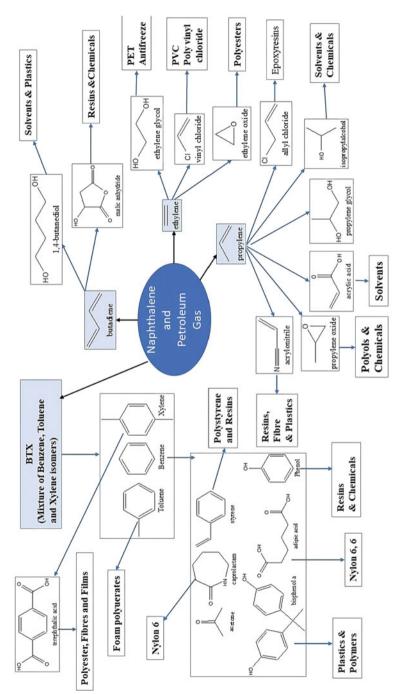
When comparing the manufacturing technologies of biorefineries, it becomes evident that there is a significant and noticeable difference between hydrocarbon-based crude oil and biomass. This disparity in quality can be attributed to the distinct soil varieties from which they are derived, resulting in 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

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 car- bohydrates, 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: eth- ylene, propylene, methane, ben- zene, toluene, and xylene isomers	The fundamental building blocks involved in various bio- logical processes are glucose, xylose, and fatty acids. These building blocks play crucial roles in biochemical pathways and are essential for the syn- thesis of diverse compounds. Examples of fatty acids include oleic acid, stearic acid, and sebacic acid, each serving dis- tinct functions within biologi- cal 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 syn- thesis 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 pro- cesses, such as dehydration, hydrogenation, and fermenta- tion. Through these transfor- mations, the aim is to obtain building blocks that can be fur- ther utilized for the production of desired products. These pro- cesses are essential for converting the feedstock into bioenergy, biofuels, chemicals, and high-value compounds
4	Chemical inter- mediates pro- duced at a commercial scale	Produced in a wide range and huge amount	Produced in fewer amount but its number is increasing with more advancement

 Table 1.1
 Comparison of refineries and biorefineries





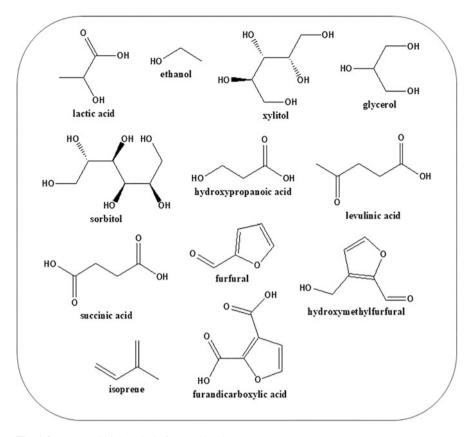


Fig. 1.3 Proposed biobased platform molecule

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

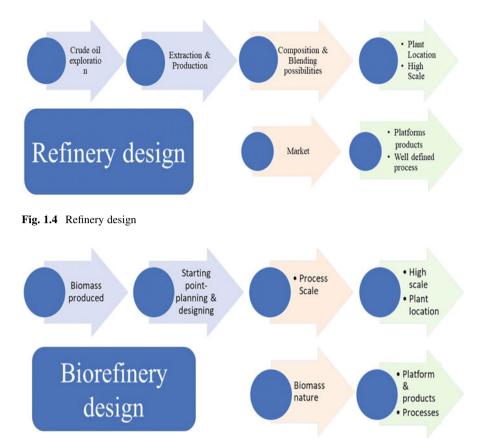


Fig. 1.5 Biorefinery design

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.

S. No.	Refinery design strategy	Biorefinery design strategy	Comments
1	The same quality of crude oils is refined; rather spe- cific crude oils are refined in a specifically designed refinery	Combining the feedstocks. The overall biomass effi- ciency and raw material utilization both rise as inte- gration 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 technol- ogies combine fermenta- tion, 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, multiprocess- ing biorefineries combine various raw materials and products to produce addi- tional 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 comprehen- sive assessment of the fea- sible and practical products that could be obtained from them. The focus was pri- marily on the processing and refining of crude oil to produce conventional petroleum products such as gasoline, diesel, and jet fuel. At that time, the con- cept of integrated refining and petrochemical com- plexes was not extensively explored	The best scenario is always a multiproduct portfolio Technical, economic, environmental, and social process indicators typi- cally rise as the number of goods increases	Any biomass-based pro- ject should take into account the maximum products that can be pro- duced after using all bio- mass, based on preliminary or heuristic analysis
5	For many years, the refin- eries showed little concern for the ecosystems in gen- eral 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, bio- mass, is found in all	In comparison to oil refin- eries, the logistical and social aspects of

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

(continued)

Table 1.2	(continued)
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S. No.	Refinery design strategy	Biorefinery design strategy	Comments
	actual societal impact is minimal	nations. Positive effects may result from effective logistics and a biorefinery, among other factors	biorefineries are more cru- cial. The supply chain will determine the project's true success given the massive amount of bio- mass that can be dispersed throughout many nations or regions
7	Energy usage and extremely complicated by-products and wastes were not a problem in crude oil refineries for a very long time The energy was regarded as being extremely abun- dant, and any leftover oil or by-products were sim- ply dumped in open ponds or landfills	It is necessary to value by-products and reduce energy use during design	Energy consumption and the utilization of by-products are important to consider in the design of biorefineries when assessing the feasibility of a project
8	The development of ther- modynamics, kinetics, mass energy transfer, and other fields was fueled by the crude oil business. The most potent design soft- ware was created and developed by this sector from the start	Designing biorefineries with sustainability in mind is a crucial component. Using Aspen Plus and other specialized software is a thorough technique to examine the processes' convenient scale	Practically every design tool used in the crude oil business is used in the design of biorefineries. To be closer to the actual feedstocks and processes utilized in biomass con- version, specialized soft- ware is required
9	Based on cutting-edge approaches for reliable computations, crude oil refineries were extremely worried about safety even in the early stages	Create safer procedures. A good simulation aims to use chemicals and materials under controllable circum- stances to guarantee the stability of the units	The design of a biorefinery takes safety into account using the same methods as the crude oil sector
10	The past, present, and future scenarios for oil refining (including alloca- tion variables, market goods, etc.) are essentially never taken into account by the crude oil industry or petrochemical facilities The fact that we currently have a steady market for fuels and polymers, for instance, provides a good explanation for this	Sensitivity analysis could be incorporated into the design to better understand the potential uses of the biorefinery	Before implementation, scenarios and optimization techniques can reveal information about the biorefinery's true sustain- ability. This kind of examination is especially necessary for brand-new crude oil refineries because of the genuine risk that biomass poses to them

(continued)

S. No.	Refinery design strategy	Biorefinery design strategy	Comments
11	To stabilize prices, the crude oil industry has implemented quota produc- tion models. This model remains functional even with varying levels of uncertainty	To prevent unanticipated and unfavorable fluctua- tions in the pricing of the energy and raw materials utilized in the biorefinery, hedging techniques should be taken into account. This enables the management of financial risks	In order to ensure stability in the business model regarding biomass prices, it might be necessary to establish an organization similar to the Organization of the Petroleum Exporting Countries (OPEC)

Table 1.2 (continued)

1.4 Classification of Biorefineries

Biorefineries are categorized based on the type of biomass utilized and the resulting products at each stage of biofuel production (de Jong and Jungmeier 2015). Costefficiency plays a crucial role in biofuel production, encompassing both transportation and manufacturing processes. The classification of biorefineries is determined by four main factors: the platform they operate on, the products generated, the feedstocks employed, and the conversion methods utilized (Cherubini et al. 2009b).

1.4.1 Biorefineries Can Be Classified in the Following Ways

1.4.1.1 Technology-Based Classification

This categorization includes conventional and advanced biorefineries, which are further divided into first-, second-, and third-generation technologies.

1.4.1.2 Raw Material-Based Classification

Biorefineries can be classified as whole crop biorefineries (WCBRs), oleochemical biorefineries, lignocellulosic feedstock biorefineries, green biorefineries, and marine biorefineries based on the type of raw materials they utilize.

1.4.1.3 By-product and Intermediate-Based Classification

This classification distinguish between the utilize syngas platforms and sugar platforms, depending upon the by-products.

1.4.1.4 Conversion Process-Based Classification

Biorefineries are further classified as thermochemical biorefineries, biochemical biorefineries, or two-platform concept biorefineries, based on the specific conversion processes employed.

Platforms refer to the intermediate substances generated during biofuel production, which can serve as final products or be utilized as by-products to connect different biorefineries. Examples of platforms include C_5/C_6 sugars, syngas, and biogas (de Jong et al. 2012). The complexity of the biorefinery system increases with the number of intermediates involved. Biorefineries mainly utilize two main feedstock groups: "energy crops" such as starch crops and rotation forestry, which are used to produce "energy products" like bioethanol, biodiesel, and synthetic biofuels. The other group is "biomass residues" such as straw, bark, wood chips, used cooking oils, and waste streams. These residues are used to produce various products including chemicals, materials, food, and feed (Cherubini et al. 2009a).

1.4.2 Examples of Biorefinery Classifications

The biorefineries can be classified into various forms on the basis of different parameters. If we classify them on the basis of material than four major biorefineries are as follows.

1.4.2.1 Oil Biorefinery

This type of biorefinery uses oilseed crops to produce biodiesel, glycerin, and animal feed.

1.4.2.2 C₆ Sugar Platform Biorefinery

These biorefineries produce bioethanol and animal feed using starch crops.

1.4.2.3 Syngas Platform Biorefinery

Utilizing straw, this type of biorefinery produces Fischer-Tropsch (FT) diesel and phenols.

1.4.2.4 Lignin Biorefinery

These biorefineries utilize wood chips to produce C_5 and C_6 sugars, electricity, heat, and phenols for bioethanol production.

The other way to classify the refineries, is on the basis of raw materials used.

1.4.3 Conventional Biorefineries

In 1839 a Dutch businessman Scholten started the industrial manufacture of potato starch which provided the base idea for the beginning of industrial refining which began in the nineteenth century with steam-powered paper machines (de Jong and Jungmeier 2015). In this process, high-quality native proteins were extracted from the potato juice using advanced methods, which improvise the quality of proteins making it suitable to use in food, cosmetics, and medicines as well as it can also be used as feedstock which makes it the best end food product. It also used in the manufacture of "Spiritus" or "Kartoffelsprit in German" which is the vodka or ethanol. Twenty-five percent of this product was incorporated with petrol until the 1950s. The Scholten company produced a variety of goods, including thermoplastic starch-based biopolymers, in addition to (modified) starch (Rahardiyan et al. 2023). Industrial biorefining was revolutionized by the advancement in food production like potato starch, wheat and corn starch, soy oil, proteins, vitamins, etc.

In 1801, Franz Achard of Germany introduced a series of processes including extraction, filtration, evaporation, crystallization, and centrifugation, which are used to produce crystalline sugar from beetroot (De Jong et al. 2010). Following World War II, soybeans gained popularity as a source of edible oil and as a substitute for protein-rich diets. Currently, soy is a major crop in countries like the USA, Brazil, Argentina, and Paraguay, with significant export volumes (Garrett et al. 2013). The process of obtaining soybean oil involves breaking the beans, controlling moisture levels, and rolling them into flakes. Soybeans are utilized in the production of various products such as margarine, butter, vegetarian burgers, oils, soap, cosmetics, inks, and clothes and increasingly as a feedstock for biodiesel (Fig. 1.6).

1.4.4 Advanced Biorefineries

An advanced biorefinery is a type of facility that shares similarities with conventional biorefineries as they both rely on a single feedstock. However, what sets advanced biorefineries apart is their capability to produce a diverse range of goods. Let's explore two specific examples of advanced biorefineries:

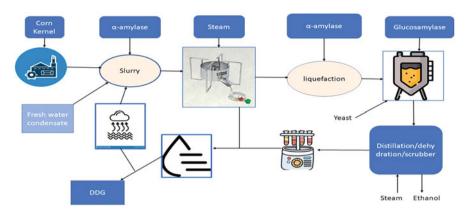


Fig. 1.6 Dry-mill ethanol process plant

1.4.4.1 Starch-Based Chemical Production

An advanced biorefinery of this kind utilizes starch as the primary feedstock. By employing advanced processing techniques, it can generate a wide variety of chemicals as end products. These chemicals find applications in various industries such as pharmaceuticals, textiles, and plastics. The advanced biorefinery's ability to convert starch into multiple valuable chemicals sets it apart from conventional biorefineries.

1.4.4.2 Cereal Grain-Based Carbohydrate Derivatives and Bioethanol Synthesis

Another example of an advanced biorefinery involves the use of cereal grains as the feedstock. Through the implementation of advanced processing methods, this biorefinery produces not only bioethanol but also a range of carbohydrate derivatives. These derivatives have applications in various industries like food, cosmetics, pharmaceuticals, etc. By efficiently converting cereal grains into both bioethanol and carbohydrate derivatives, this advanced biorefinery showcases its capability to produce multiple valuable products.

We can say that advanced biorefineries leverage advanced processing techniques to convert a single feedstock into various valuable products. These examples highlight the versatility and efficiency of advanced biorefineries in meeting the demands of different industries.

1.4.5 Whole Crop Biorefinery

In a WCBR, the fermentation process is used for the processing of grains and straw to obtain the final products, which is followed by dry and wet milling, and after distillation of grains and straw, these are converted into end products (de Jong and Jungmeier 2015). Sulfur dioxide is added to water-soaked grains during wet milling to lose the hull and soften the kernels. The starch, cellulose, oil, and proteins can then be separated from the grains using known processes (Rausch et al. 2019). Before the flour is blended with water and the enzymes are liquefied, whole grains, including the germ and bran, are ground in the dry milling procedure. The starch in the mash is then broken down by boiling it. This hydrolysis phase can be avoided by adding fermenting yeast and saccharifying enzymes to the fermenter at the same time. After fermentation, the alcohol in the mash is concentrated, purified, and dehydrated using a multicolumn distillation system (which is then turned into beer). The remaining mash (stillage), which is composed of both liquid (syrup) and solid (wet grains) phases, is combined, dried, and used as cow feed under the name "distiller's dried grains with solubles" (DDGS). The straw, consisting of chaff, nodes, ears, and leaves, is a lignocellulosic feedstock that can be further processed (Fernando et al. 2006) (Fig. 1.7).

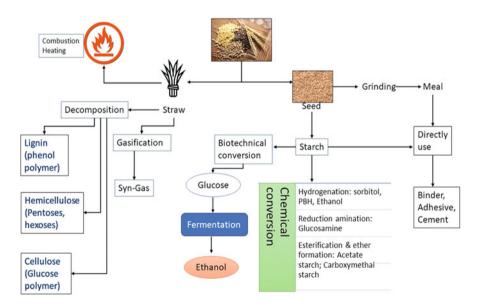


Fig. 1.7 Whole-crop biorefinery process

1.4.6 Oleochemical Biorefinery

An advanced version of Whole Crude Biodiesel Refinery (WCBR) involves the extraction of biodiesel while simultaneously producing high-value vegetable oil-based products. Advanced biorefineries utilize oil crop-derived fatty acids, esters, and glycerol to produce sustainable feedstocks, platform compounds, monomers, lubricants, and surfactants, aiding in the effective replacement of fossil fuel counterparts. An enormous quantity of lignocellulosic biowaste is used in lignocellulosic feedstock biorefineries. This biomass is also present in significant numbers in the precursor feedstocks used to make products based on vegetable oils (Schneider et al. 2016).

1.4.7 Lignocellulosic Feedstock Biorefinery

Lignocellulosic feedstock biorefinery is made up of three fundamental chemical fractions: (i) lignin, phenol polymers, (ii) cellulose, and (iii) hemicellulose. Hard fibrous plant materials obtained from municipal waste are used in LCF. To divide plant matter into its three components, it is first chemically cleaned and digested or hydrolyzed using enzymes (hemicellulose, cellulose, and lignin). Sulfite and alkaline (caustic soda) can produce cellulose and hemicellulose (acidic, bisulfite, alkaline, etc.). Plant-based lignin is broken down by enzymes such as ligninases, lignin peroxidases, laccases, and xylanolytic enzymes, leading to the hydrolysis of sugar components. Hemicellulose, a branched carbohydrate composed of five different sugars including uronic acid, C-5 sugars (D-galactose, D-glucose, D-mannose), and C-6 sugars (D-xylose, L-arabinose), is formed during this process. Xylose, a component of hemicellulose, is particularly valuable as it can be converted into furfural, a key building block for nylon and other applications. Hydrolyzing cellulose using chemical or enzymatic methods yields glucose and produces useful by-products such as ethanol, acetic acid, acetone, butanol, succinic acid, and other fermentation products (Calvo-Flores and Martin-Martinez 2022). While cellulose and hemicellulose have various applications, lignin is currently utilized primarily as an adhesive, binder, or direct combustion fuel. However, the lignin structure holds significant potential for producing additional monoaromatic hydrocarbons, which could greatly enhance the overall lignocellulosic fractionation (LCF) process if feasibly isolated. In Missouri, an LCF facility utilizing 4000 t of feedstock per day produces approximately 180,106 t of ethanol and 323,103 t of furfural annually. Additionally, significant microbial conversion of glucose can yield hydrogen, methane, propanol, and acetone, which are all petrochemical products (Calvo-Flores and Martin-Martinez 2022) (Fig. 1.8).

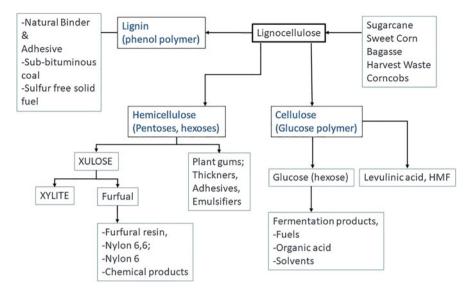


Fig. 1.8 LCF biorefinery process and products

1.4.8 Syngas Platform Biorefinery (Thermochemical Biorefinery)

The initial step in processing lignocellulosic biomass involves subjecting it to high temperature and pressure through size reduction, drying, or torrefaction methods. This treatment results in the production of gas, predominantly composed of carbon monoxide (CO) and hydrogen (H₂). The obtained syngas then undergoes purification in a high-temperature gas cleanup system, where impurities are removed. The composition of the gas is adjusted to meet the specific requirements of downstream synthesis processes.

Following this, a catalytic synthesis method is employed to extract various products from the clean gas. These products can include FT diesel, dimethylether, a range of alcohols, as well as several fundamental chemicals such as ethylene, propylene, butadiene, and others. The catalytic synthesis process enables the conversion of the syngas into these valuable end products, which find applications in industries such as transportation, chemical manufacturing, and energy production (Haro et al. 2013) (Fig. 1.9).

1.4.9 Next-Generation Hydrocarbon Biorefinery

Advancements in nanoscience and technology have introduced various new methods that aid in the development of fuel conversion techniques from biomass. However,

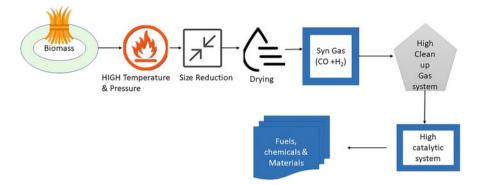


Fig. 1.9 Conceptual of syngas platform-based biorefinery

there remains a need to establish economically viable hydrocarbon biorefineries. One such method is liquid-phase catalytic processing, which involves the production of functionalized hydrocarbons from intermediates derived from biomass, such as hydroxymethylfurfural (HMF). This biorefining technique offers a means to convert biomass into valuable hydrocarbon products (Huber 2008).

Another method involves the utilization of renewable furan derivatives, which can serve as alternative raw materials for fossil fuels and polymers. These derivatives are derived from C_5 and C_6 carbohydrates found in biomass, such as sugars, hemicellulose, and cellulose. This approach enables the production of biofuels. Avantium Chemicals, a company based in the Netherlands, is currently involved in the development of chemical catalytic routes for this purpose. The development and implementation of these innovative methods and technologies are essential in advancing the field of biomass conversion and establishing sustainable and economically viable biorefineries.

1.4.10 Green Biorefinery

It was developed by a Dutch researcher that used grass and other leafy materials in the biorefineries with grass costing more per ton than leaves (\notin 50–70). The mechanical refiner then degrades the leaf material to convert it into pure fiber with less than 11% protein content. The products thus formed are pressed to form juice, and the residual juice thus obtained is evaporated to obtain a concentrated product. This material is used as animal feed, building materials, insulation fiber, nursery pots, packaging material, feedstock for biofuels, etc. This range of greens used in biorefineries can be increased by including a wide variety of biomass. Occasionally, mixed feedstocks, including fresh and silage grass, can be employed in between lignocellulosic and green biorefineries. The majority of European green biorefinery initiatives now being worked on in Austria, Germany, Ireland, and the Netherlands,

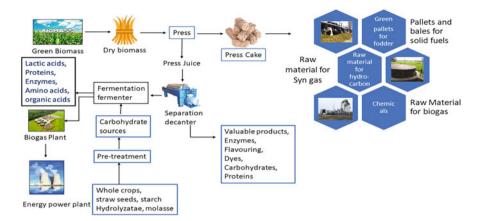


Fig. 1.10 Representation of green biorefinery process and products

center on grass refining. The objective is to extract useful materials with no waste and no emissions and to use all by-products in a biogas plant to make sure the plant can run on its energy (de Jong and Jungmeier 2015 n.d.) (Fig. 1.10).

1.4.11 Marine Biorefinery

Global biomass output is equally distributed between land and sea. Marine sources like microalgae and macroalgae offer potential, yet policies have mainly focused on terrestrial biomass. Diatoms, a type of microalgae, are the most common form of phytoplankton, with an estimated 100,000 species and significant biomass potential. Diatoms are known to accumulate oils and can vary in the production of oil, starch, sugar, and vitamins based on species and growing conditions.

Golden and green algae are capable of producing oils, starch, and carbohydrates; at the same time marine flora have been documented for their superior ability to absorb CO_2 compared to terrestrial species, making them a potential feedstock source for biofuels. However, the cost of biomass production and harvesting in marine biorefineries remains prohibitively expensive for widespread use in bulk chemical and fuel applications at present. Although marine biomass shows promise, further research and technological advancements are needed to make marine biorefineries economically viable and practical for large-scale chemical and fuel production (Antelo et al. 2015).

1.5 Key Challenges

Due to the challenges faced by the government like climate change, food security, and energy availability, more experiments and explorations are done to inquire about the set of biomass feedstock as an alternative for biofuels, bioenergy, and biochemical (Creutzig et al. 2015). These issues can be resolved by particular regional and national government initiatives. Yet, creating policies can be difficult because focusing on one issue may be detrimental to another.

In the absence of specific policies, it is impossible to establish a proper supply chain that ensures the availability of biomass feedstock. Therefore, there is a need to formulate legislation that governs the collection, transportation, and handling of biomass feedstock. Incentives should be provided to farmers to encourage their participation in delivering feedstock to next-generation ethanol plants. The involvement of farmers is crucial for the long-term sustainability of the ethanol industry, and the design of appropriate policies is essential to achieve this objective (Sharma et al. 2020). To mitigate risks to the ethanol industry, a continuous supply chain must be established. India, with its large population advantage, can capitalize on this by implementing special training programs like Skill India to address any skill gaps. Such initiatives will enhance the efficiency of the supply chain, maximize economic potential, and deliver social benefits. Moreover, they will contribute to environmental improvements and reduce the high market risks associated with next-generation ethanol industries.

The major obstacle in the bioethanol industry is the pretreatment of the feedstock. Pretreatment is required so that the carbohydrates present in the lignocellulose can be made available for conversion into the raw materials that are used in the cellulosicbased bioethanol industry. But this pretreatment makes the whole process highly cost-ineffective (Galbe and Zacchi 2007). This process is also important to avoid product degradation as to make the carbohydrates in the lignocellulose available for conversion is a significant obstacle in the manufacture of cellulosic-based bioethanol. In addition to costs, the most important factor in choosing a pretreatment procedure is its effectiveness in preventing product degradation which can prevent the future hydrolysis and enzymatic fermentation of the product (Tian et al. 2012).

1.5.1 Lignocellulosic Biorefinery Commercialization Difficulties

1.5.1.1 Economic and Technical Factors

It is a requirement for lignocellulose-based biorefineries to become industrialized to resolve several fundamental problems that arise at various stages of the processing of biomass. Atypical biomass conversion scheme consists of six main steps: (i) the choice of the biomass and its pre-processing; (ii) efficient pretreatment; (iii) the

creation of a hydrolytic enzyme cocktail on-site or off-site; (iv) enzymatic saccharification; (v) hexose and pentose fermentation; and (vi) downstream processing (Tursi 2019).

1.5.1.2 Biodiesel Production

As biodiesel is made from biomass feedstock, food security is highly compromised during the process, and also practically it is impossible to use edible oil for bioethanol production as most of the edible oil supply in the country is imported. High cultivation costs, low production, and inadequate supply of raw materials also make the bioethanol production process cost-ineffective (Limayem and Ricke 2012). Furthermore, if nonedible oil is used instead of edible oil for bioethanol production, certain limitations arise. For instance, its performance may decrease in colder regions, and there is a possibility of contamination by animal fats or other impurities.

The process of bioethanol production has further challenges like the whole extraction process that needs further filtration which is plant specific and is unsuccessful on a large number of biomass feedstock, which makes the whole process highly expensive. Another limitation is that the production of n-hexane can cause severe effects on the environment as well as human health as it produces large amounts of intoxicants that will be added to water bodies as well as air in the form of volatile organic compound emissions. Thus, noticeable government support is required for the production of biodiesel, and this, the use of bioethanol, should be legalized and incentive support should also be provided by the government to promote the biodiesel program.

1.5.1.3 BioCNG Production

The main reason behind the failure of biogas plants is the reduction in the number of farm animals in rural areas which results in the non-availability of the raw materials used for the production of biogas. Any kind of fluctuation in the raw material supply can alter the plant's productivity as well as performance, and in turn, it results in the loss of the biogas plant.

Individual domestic biogas plants can only produce small-scale biogas which is used only as cooking fuel and a huge amount of monetary investment; however, the large-scale production of biogas is controlled by private industries which are working in partnership to make a huge profit by producing products like heat, power, or transportation fuel. Also, these days agriculture is more inclined toward the use of organic fertilizers in place of chemical fertilizers which reduces the availability of biomass for the production of biogas. In addition to the aforementioned factors, several other reasons contribute to the decline in biogas plants. These include inadequate feedstock supply, as well as a lack of awareness and acceptance regarding the wide range of biomass that can be utilized for biogas production. Certain biomass sources, such as human excreta and dead animal carcasses, are not widely accepted for biogas production. Therefore, it is essential to organize proper training and awareness programs in rural areas to highlight the various environmental benefits associated with biogas production. The lack of transportation and segregation of municipal solid waste in cities has hindered the rapid expansion of the biogas plant industry. Additionally, significant regional variations pose challenges in standardizing the process. Most processes used for treating organic and industrial waste, such as composting, vermicomposting, and waste-to-pellets, require transportation either from rural areas to cities or vice versa. This adds to the overall expenses and bulkiness of the process. In urban areas, industries tend to prefer inexpensive treatment methods like composting, which is a slow process. Furthermore, the cost of the procedure increases due to the additional infrastructure required for biogas cleaning.

1.5.2 Challenges in Third-Generation Biofuels: Algal Biofuel

Third-generation biofuels, such as algal biofuels, face significant threats and challenges that hinder their widespread commercial acceptance compared to other competing biomasses (Lee and Lavoie 2013). The expensive nature of algal biofuels is one major barrier, deterring industries from adopting them. Additionally, the process of algae converting atmospheric CO_2 to carbonic acid leads to a rise in the ecosystem's pH, impacting algal growth and hindering sunlight penetration in large algal blooms (Larsdotter 2006). In addition to these factors, several other reasons contribute to the difficulties faced by algal biofuels in gaining acceptance.

There is a lack of information regarding the effective use of algal biofuels in vehicles and equipment, with limited research in this field. Further exploration is necessary to establish their viability in various applications. Moreover, a high lipid content in the feedstock is crucial for efficient conversion of algae into biofuels. Lipids, which contain oils, can be used for production of biofuels from algae. Extracting and processing these lipids enables the generation of biofuels from algae, making it a valuable renewable energy source (Coma et al. 2017).

The process of converting algal blooms into biofuels is complex, involving multiple stages that make it difficult to implement and adopt (Coma et al. 2017). Another challenge is the high demand for fertilizers to create algal blooms, which consumes significant energy and adversely impacts the environment by increasing CO_2 levels at a rapid rate (Mata et al. 2010). Minimizing algal death caused by pests and pathogens is a significant challenge in algal monocultures. Lack of biodiversity makes them more susceptible to infestations and disease outbreaks, leading to reduced productivity and economic losses. Developing sustainable methods for protecting algal crops from pests and pathogens is crucial for the long-term viability of algal production systems (Smith and Crews 2014). Water demand poses a significant challenge as algae require substantial amounts of water to grow. However, rising temperatures due to global warming accelerate water evaporation, reducing water sources for large-scale algal bloom production. Algal biofuel

production is expensive compared to fossil fuels and other biomass fuels, making it economically uncompetitive (Azar et al. 2006). Quality issues arise as not all species of algal blooms produce the same quantity and quality of oil, posing challenges for large-scale cultivation (Benemann 1992). Meeting the nutrient demands of algae, including CO_2 , iron, phosphorus, sulfate, and nitrogen, along with water and light, presents significant challenges in the current scenario (Ghernaout and Ghernaout 2012). Overall, these challenges collectively hinder the commercial acceptance and widespread adoption of algal biofuels, necessitating further research, technological advancements, and cost-effective solutions to make them a viable and sustainable alternative energy source.

1.6 Conclusion

As the world faces increasing consumption of non-renewable fossil fuels, the need for alternative and environmentally friendly energy sources has become crucial. Biorefineries have emerged as a sustainable solution to produce marketable biobased products, such as petro-based refineries, promoting a greener economy. However, the adoption of biorefineries still faces challenges. Economic efficiency is a key obstacle, requiring researchers to develop new reactions, technologies, and carbon pathways for economically viable synthesis of substances. Additionally, the lignin platform, despite being abundant in nature, lacks effective chemical and biotechnological processes. Scaling up the production of aromatic compounds from lignin is a significant challenge for the next decade. The entire biorefinery production cycle is complex and poses technical, economic, ecological, sociological, and long-term challenges. The dominance of the fossil-based economy in the current market, along with factors like feedstock availability, market demand, resource recovery effectiveness, and sustainability, further complicates the situation. Conducting life cycle assessments can provide valuable insights into the environmental impact of biorefinery projects and guide process optimization.

Biorefineries must optimize biomass utilization to align with market expectations and compete cost-effectively with fossil fuels. Currently, petroleum refineries allocate a large majority of their output to fuel production, with only a small portion dedicated to organic compound production for the petrochemical industry. Biorefineries should strive to replicate this proportion by producing both fuels and organic compounds to meet market demands effectively. To achieve sustainability, biorefineries must reduce their carbon footprint through the use of renewable energy sources. This requires collaboration among stakeholders and integration with other sectors and relevant technologies. By addressing these challenges proactively, biorefineries can enhance sustainability, competitiveness, and successful integration within the broader energy landscape.

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