

Techno-economic analysis of biochemical conversion of biomass to biofuels and platform chemicals

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Abstract: Biomass is the most versatile feedstock for renewable energy and chemical production. Biochemical techniques such as fermentation and biomethanation have been developed extensively for converting biomass into bioethanol, biogas, and high-value platform chemicals. However, the techno-economic feasibility of the various biochemical techniques for the production of a range of biofuels and chemicals has not been fully consolidated in a review. This paper reviews the techno-economic studies of biochemical conversion of biomass in a comparative fashion between feedstocks, treatment methods, and product types. The review starts with an overview of various biomass treatment approaches and the need for pre-treatment for processing second-generation feedstocks. This is followed by a review of the main biochemical conversion processes, offering insights into process stages, product yields and quality, as well as commercialization prospects and challenges. The various techno-economic aspects of biomass conversion via biochemical techniques, such as conversion efficiency, production capacity, minimum selling price, capital cost, unit production cost, and profitability metrics, are critically reviewed. It was found that bioethanol and biogas are the most commercially viable products from the biochemical processing of biomass. The production of other biofuels and chemicals such as biobutanol, biohydrogen, furfural, volatile fatty acids, succinate, levulinic acid, and sugar alcohols via biochemical techniques is still largely limited by low conversion, frail microbial strains, cost of enzymes, and separation, and refining challenges. Overcoming these technical bottlenecks, and addressing the issues of feedstock price and supply security, are crucial for enhancing the overall techno-economic attractiveness of biochemical

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processes for fuels and chemical production from biomass resources. © 2022 Society of Industrial Chemistry and John Wiley & Sons Ltd.

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Introduction

Biomass resources are versatile and are the most promising feedstocks for the production of fuels and chemicals akin to fossil-derived fuels and chemicals. The global biomass supply potential by 2030 is projected to range from 97 to 147 EJ per year, cutting across agricultural residues, forestry wastes, specially grown energy crops, and organic municipal wastes.¹ Despite the huge reserves, biomass feedstock variability, availability, and affordability pose a significant threat to their sustainable utilization for fuels and chemicals synthesis in biorefinery plants.² To date, biomass resources are underutilized, with a substantial volume still deployed as low-grade heating fuel and animal fodder, particularly in developing countries.³ Non-food biomass such as specially grown energy crops, forests and agricultural residues represent a sustainable and renewable source of fuel and are the most effective feedstock to explore for bioenergy and biofuel generation.⁴ Biofuels have negligible emissions of SO_x and NO_x, making them a preferable choice for the development of transport range fuels.^{5,6} The inherent threat of depletion of fossil fuels, unstable supply, and increasing prices, together with the realization of the growing importance of a circular economy, has led to intense research on biofuel production from biomass. The prospects of biomass for the sustainable production of biofuels and

valuable chemicals are highlighted in Fig. 1. Most biomass conversion techniques are well-suited for biofuels and bioenergy production, for which bioethanol, biodiesel, biogas, syngas, and bio-oil are the most attractive. Thermochemical conversion techniques can rapidly convert biomass components into biochar/hydrochar, bio-oil/biocrude, and syngas with promising potential for co-producing high-value chemicals. However, the biochemical conversion of biomass to valuable products remains challenging due to the highly heterogeneous nature of biomass resources, complex metabolic pathways of microbial agents, as well as technical bottlenecks with product separation and purification.

Several treatment technologies, broadly classified into thermochemical and biochemical, are available for biomass processing into a range of fuels and chemicals (Fig. 1). Biochemical processes such as fermentation and biomethanation are generally considered environmentally sustainable, with low energy requirements and milder operating conditions than thermochemical processes. However, biological processes are generally slow with complex conversion mechanisms. Notwithstanding, there has been consistent improvement in biochemical conversion techniques to co-produce valuable fuels and chemicals using engineered microbial agents, toxicity resilient and robust microorganisms, as well as aided bioconversion processes.^{7–9} For instance, the anaerobic digestion (AD) of

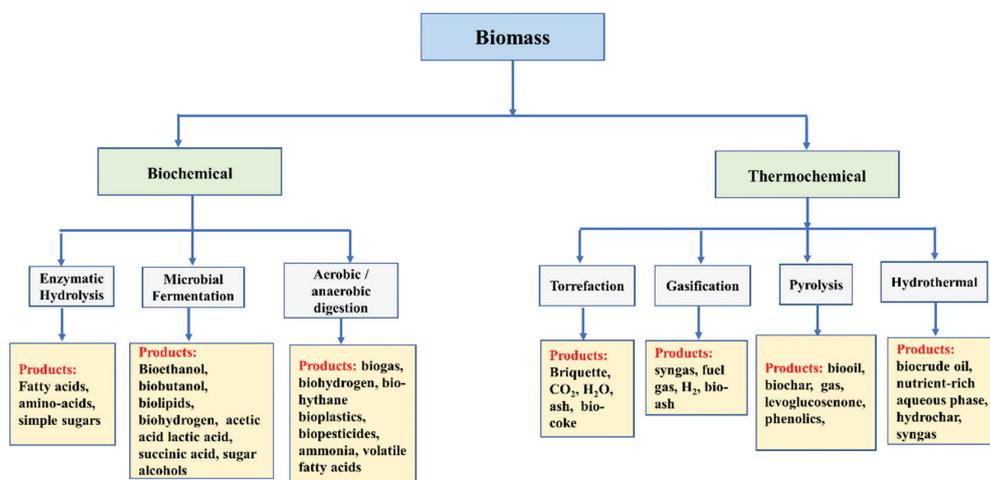


Figure 1. Biomass conversion technologies and their products.

difficult organic substrates such as chicken manure, algal biomass, food wastes, and sewage sludge can be aided by the addition of biochar to mitigate ammonia inhibition, neutralize toxic components release, regulate pH, as well as provide extra nutrient and shelter for the microorganism.^{10,11} Similarly, integrating thermal/chemical hydrolysis to AD and fermentation can reduce biodegradation recalcitrance of biomass organics, thereby improving conversion kinetics and product yield.^{12,13} Co-processing (co-digestion and co-fermentation) is another strategy to intensify the biochemical process performance and increase product output via beneficial synergistic interactions of two or more feedstocks.^{14,15}

Thus, the techno-economic analysis (TEA) of biochemical processes for converting biomass to bioproducts is of interest to researchers and industrial experts in the biorefining industry. Thermochemical techniques and their techno-economic analyses have been documented in our previous review.¹⁶ There are also some recent reviews on the techno-economic assessment of biochemical and thermochemical conversion techniques of biomass to drop-in fuels and chemicals.^{17–21} These works have critically reviewed the influence of feedstock type, compositions and logistics, and process-related conditions on product yields and implications on the techno-economic viability of such conversion processes. Similarly, the techno-commercial perspectives, sustainability approach, and life-cycle assessments of biochemical processes for biofuels and chemicals production from biomass have been reviewed in the previous reports.^{19,20,22} However, in existing reviews, there is limited coverage of the techno-economic analyses of traditional biochemical processes, mainly fermentation and anaerobic digestion and their hybrid, for producing single and multiple fuels and chemical products in a biorefinery context.

The current review therefore focuses on the biochemical processes of synthesizing biofuels and commodity chemicals and comparative techno-economic analyses. The review starts with an overview of biochemical conversion processes with emphasis on biomethanation and fermentation for producing biogas and bioethanol as well as valuable co-products such as biobutanol, volatile fatty acids, furfural, succinate, and organic acids. The commercial prospects and technical challenges confronting the widespread installations of biogas and cellulosic ethanol plants were critically examined. The techno-economic analyses of biochemical processes for a range of single and multiple products were explored. It involves the assessment of cash flows over the plant's lifetime, along with the scale of technology application and its economic benefits. Lastly, critical challenges and perspectives for future research were provided.

Biochemical conversion processes

The biochemical degradation of plant-based biomass (lignocellulosic) is a major challenge due to the complex building matrix of the plants. Lignocellulosic biomass has a typical composition of 40%–80% cellulose, 15%–30% hemicellulose, and 10%–25% lignin with different amenability for bioconversion.²³ However, their physical structure and complex chemical composition have presented barriers to the easy accessibility of the rich fermentable sugars for significant industrial exploration. Biochemical methods of biomass conversion, such as fermentation and aerobic/AD, use the diverse metabolic action of microorganisms to decompose organics components in biomass into a range of valuable products. For example, the biochemical conversion of lignocellulosic biomass to bioethanol involves the breakdown of the complex carbohydrates to simple sugars (saccharification) by enzymes and then the conversion of sugar to ethanol (fermentation) by special microorganisms and/or catalysts. The products formed include renewable fuels like biogas and bioethanol and platform chemicals like sugar alcohols, acetate, and volatile fatty acids. Biochemical techniques have inherent advantages and disadvantages, as elucidated in previous works.^{24–27} The different steps involved in the biochemical conversion of biomass are shown in Fig. 2.

There are various mechanical, biological, chemical, hydrothermal, and physicochemical pre-treatments and their combinations with different levels of technical and economical attractiveness.²⁸ Table 1 highlights common pre-treatment techniques used in biomass integrated processing. The process performance and comparisons of the TEA of the various pre-treatment strategies are documented elsewhere.^{35,36} The pre-treatment step is critical for the biochemical conversion of lignocellulosic biomass. The type of biomass material plays a crucial role in the selection of the pre-treatment technique as well as the formation of the final products (see Table 1). Generally, lignocellulosic biomass requires harsh chemical or thermal or thermochemical pre-treatment strategies to effectively deconstruct the biopolymers constituents into bio-amenable fractions. The fractionation of the recalcitrant biomass matrix into major constituents is the goal of many pre-treatments; however, pre-treatment, if not carefully controlled, may produce undesired by-products and microbial inhibitor components that interfere with the downstream conversion processes (Fig. 2). It is, therefore, crucial that the mechanism of the different pre-treatment processes is understood to prevent/reduce the formation of inhibitors and unwanted co-products. Designing a pre-treatment process for lignocellulosic biomass is a critical

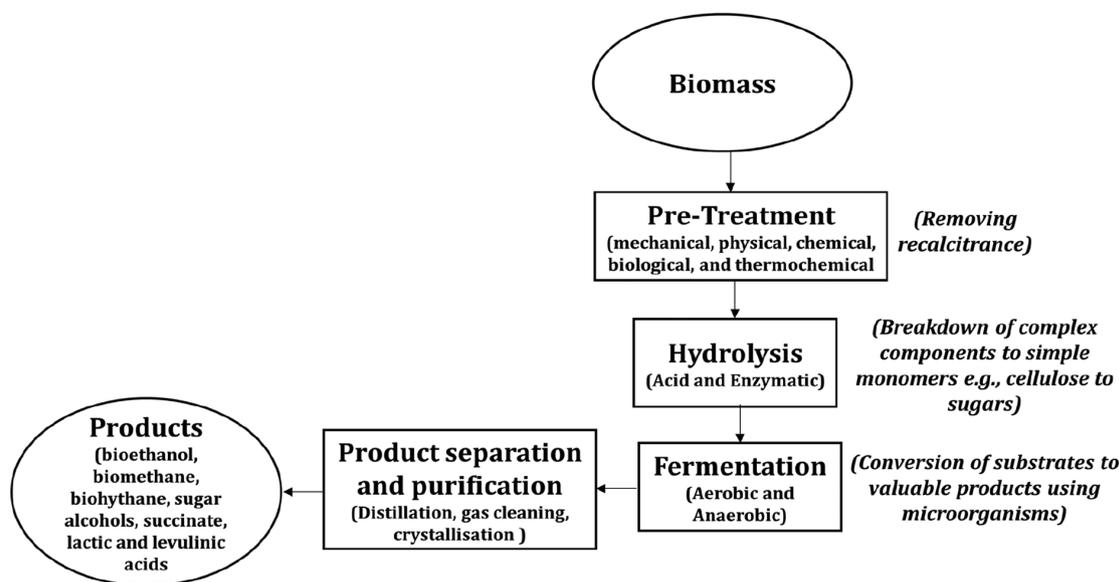


Figure 2. Various steps involved in biochemical conversion of biomass.

challenge that demands a substantial proportion of lignin removal without affecting the fermentable sugar precursor, mainly cellulose and hemicellulose.

The subsequent breakdown of the lignocellulosic components obtained via pretreatment into simple molecules is referred to as hydrolysis. Depending on the choice of pre-treatment technology and severity conditions, the pre-treatment and hydrolysis steps can be combined in a single process. Generally, using chemical solvents like acid and alkali can achieve the objectives of pre-treatment and hydrolysis. The pre-treatment breaks the lignin protection around the cellulose, allowing the acid to depolymerize the cellulose and solubilize its sugars. In terms of efficiency, acid hydrolysis can retain the maximum amount of sugar, yielding up to 90% glucose.³⁷ The use of dilute acids (<5 vol.%) produces a mild reaction catalyzed at higher temperatures (>100 °C). This process causes glucose degradation to hydroxyl methyl furfural (HMF), a toxic compound affecting microbial cell growth and respiration during downstream operation. Figure 3 shows the various chain products obtained during the acid hydrolysis of cellulose. The chemical hydrolysis process needs to be controlled carefully to minimize the formation of HMF and the subsequent formation of organic acids, mainly levulinic and formic acid (Fig. 3). Concentrated acid gives higher saccharide yields at moderate temperatures but at the cost of inhibitor compound formation, which will interfere with microbial activity and increase corrosiveness. The use of highly concentrated acids for hydrolysis also has negative environmental influences and high investment and

maintenance costs, limiting its use.³⁸ Figure 4 illustrates several aspects of the acid pre-treatment/hydrolysis process, including variables, process design, impact on sustainability, and main industrial products.

Traditional methods involving acid hydrolysis did not consider the recycling of acids and the huge quantity of salt precipitates formed following neutralization. However, recent technology and advances in the recycling and recovery of acids can improve the process efficiency and favor techno-economics as a promising alternative to enzymatic hydrolysis. Enzymatic hydrolysis requires controlled temperature and pressure in the reactor to allow the enzymes to work efficiently. However, the use of enzymes incurs large costs. Enzymatic hydrolysis is negatively influenced by biomass structural features such as cellulose crystallinity, degree of cellulose polymerization, and lignin content. Overall, feedstock processing through pre-treatment and hydrolysis makes the production of second-generation cellulosic ethanol expensive in comparison with the production of ethanol from first-generation feedstocks.⁴⁰

Fermentation is required for the final step of producing value-added products. Fermentation is the main process used to convert fermentable sugars produced from the previous hydrolysis step into ethanol, higher alcohols (e.g. butanol), solvents (e.g. acetone) or biohydrogen. The fermentation of biomass depends on three important factors (1) the type of substrate and microorganisms, (2) how the substrate is fed, that is, batch, semi-batch, or continuous, and (3) the type of aeration required. Liquid-phase and solid-phase fermentation can be carried out in the presence of

Table 1. Overview of pre-treatment techniques for various biochemical conversion strategies

Feedstock	Pre-treatment technique	Targeted bio-product(s)	Remarks	References
Switchgrass	Deep eutectic solvent	2,3-butanediol, lignin, furfural	<ul style="list-style-type: none"> At 20% solids loading, cellulose, xylan, and lignin removal were 1.8%, 77%, and 74%, respectively At 27% solids loading, cellulose, xylan, and lignin removal were 3.3%, 70%, and 69%, respectively. Pre-treatment accounts for about 13% of the total capital investment and 30% of the total variable operating costs. 	29
Corn stover	Dilute alkali deacetylation pre-dilute acid	Bioethanol	<ul style="list-style-type: none"> The removal of acetyl groups by alkali pre-treatment reduced biomass recalcitrance and hydrolysate toxicity The feedstock was 20% more digestible Xylose monomer yields and conversion increased by >10% Ethanol yield increased by 10% 	30
Poplar wood	Pressurized lime (Ca(OH) ₂)	Monomeric sugars	<ul style="list-style-type: none"> Delignification increased with increasing lime consumption and pressure At mild conditions, glucan and xylan yields were >70% Recommended lime consumption at optimum condition was $\approx 0.2 \text{ gg}^{-1}$ wood 	31
Wheat straw	Mechanical comminution and hot water (90–120 °C)	Biomethane	<ul style="list-style-type: none"> Volatile solids (VS) of all feedstocks increased by at least 10%, irrespective of the treatment methods. Biomethane yield increased in barley and wheat straw by 20–84%, while there was no significant improvement for corn stalks and rice straw Mechanical treatment gave higher improvements in methane yields compared to thermal treatment 	32
Barley straw				
Rice straw				
Corn stalks				
Sewage sludge	Hot water (120 °C)	Volatile fatty acids	<ul style="list-style-type: none"> Thermal pre-treatment influenced the degree of acidification up to 45% Slight increase in soluble COD, and N-NH₄⁺ increased by 45% Volatile fatty acid production increased by at least 10% Volatile fatty acid profile was influenced by pre-treatment 	33
Rice straw	Dilute acidified steam explosion	Acetone, butanol, ethanol	<ul style="list-style-type: none"> Reducing sugar concentration increased to 32 gL^{-1}, for which glucose was about 72% in the hydrolysate 78% reducing sugar and 55% glucose conversion were observed Product yields are 0.15, 0.33, and 0.02 gg^{-1} total sugar for acetone, butanol, and ethanol, respectively, with max conc. Of 6.4, 13.5, and 0.8 gL^{-1} 	34

Abbreviation: COD, Chemical oxygen demand; VFA, volatile fatty acids

air or under inert conditions. The processes can be aerobic fermentation or anaerobic fermentation, depending on the nature of the product to be obtained. The specific processes

employed depend upon the type of feed, space availability, and product requirement. The processes are discussed in detail below.

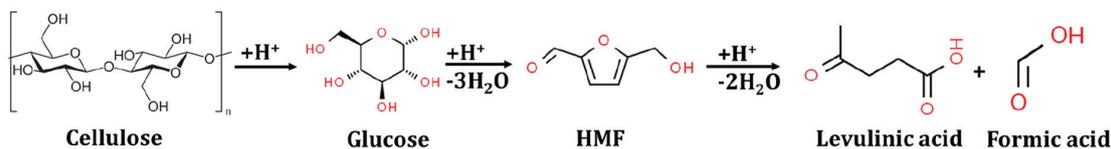


Figure 3. Products of acid hydrolysis of cellulose. HMF, hydroxyl methyl furfural.

	Main process variables	Reactor configuration & process design	Environmental & sustainability concerns	Valuable Industrial products
Acid pre-treatment/hydrolysis	Temperature	Batch	Energy needs	Bioethanol
	Acid concentration	CSTR	Water needs	Biogas
	Stirring speed	Plug flow	Toxic releases	Furfural
	Residence time	Staged process	Wastewater disposal	5-HMF
	Pressure	Countercurrent/co-current acid extraction	Reactor corrosion	Formic acid
	Solid to liquid ratio	Helically agitated mixing	Productivity	Levulinic acid
			Economics	Oligomers

Figure 4. Advantages and disadvantages of acid pre-treatment/hydrolysis of lignocellulosic biomass.³⁹ CSTR, Continuous stirred tank reactor; HMF, hydroxyl methyl furfural

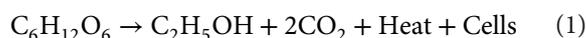
Aerobic bioconversion process

The aerobic process involves the metabolization of organic substrates through microorganisms that utilize oxygen as the energy source for their activity. Hence, the aerobic process requires dissolved oxygen content at a specified minimum level to oxidize organic matter to CO₂ and H₂O. The aerobic process uses different stages, including glycolysis, the Krebs cycle and electron transport. The amount of heat generated in the case of the aerobic process is comparatively higher than in anaerobic fermentation. Usually, industrial fermenters are mostly bioreactors, closed vessels with controlled conditions of temperature, pressure, agitation, aeration, and pH. There are various industrial applications of the aerobic fermentation process, mostly used in food processing, waste treatment, antibiotic production, organic acid formation and ethanol fermentation.

Anaerobic bioconversion process

Anaerobic processes are carried out under inert conditions in which a series of chemical reactions occur,

which decompose the organic materials through the metabolic pathways of microorganisms. It can be suitably used to treat wet organic wastes as it is less energy-intensive than aerobic digestion of biomass. Hydrolysis of complex organics is the rate-limiting step; thus, anaerobic fermentation can be enhanced by improving the process kinetics through biomass pre-treatment operations. A general reaction bioethanol and biogas via anaerobic processes is shown in Eqn (1) and Eqn (2), respectively. The glucose obtained after the saccharification process can be converted into ethanol (Eqn 1) or methane (Eqn 2), depending on the microorganism strain used. The production process of biomethane and bioethanol is discussed in detail in Sections 2.2.1 and 2.2.2, respectively.



Biomethanation

Biomethanation is a process by which methanogens microbiologically convert organic substrates to biogas under anaerobic conditions. In this process, three groups of microorganisms are involved – fermenting bacteria, organic acid-oxidizing bacteria, and methanogenic archaea. Methane formation from the decomposition of acetic acid is the main part of archaea metabolism. The presence of oxygen inhibits the growth of methanogens, and therefore anaerobic conditions need to be maintained. Other than methanogens, acetogens and acetic acid-forming bacteria also affect the AD process. These bacteria stimulate a number of chemical processes in converting biomass to biogas.⁴¹ Anaerobic digestion has four key stages: (1) hydrolysis, (2) acidogenesis, (3) acetogenesis, (4) methanogenesis.⁴² These four stages are described in Fig. 4. The large polymer chains in the organic matter need to be broken down into smaller molecules, for which the first process, hydrolysis, is required.⁴³ The products formed from hydrolysis include sugars, amino acids and fatty acids. Acetate and hydrogen produced in the initial stages can be used directly by methanogens. Acidogenic fermentative bacteria break down the remaining components. Volatile fatty acids (VFAs) are created at this stage, along with ammonia, carbon dioxide, and hydrogen sulfide.⁴⁴ The third stage of AD is acetogenesis, where acetogens digest the molecules created by acidogenic bacteria to produce acetic acid as a major component with a minor quantity of carbon dioxide and hydrogen.⁴⁵ Finally, methanogenic bacteria convert the products of the preceding stage to methane, giving off CO₂ as a by-product.

As seen in Fig. 5, the biomethanation process involves a series of reaction stages, which can be controlled to obtain valuable intermediate products. Under suitable operating conditions, for example, a retention time of 20–30 days, AD can proceed to completion, and the targeted product (biomethane) is produced. However, if the anaerobic process were interrupted, for example, before methanogenesis, many

intermediate compounds, like VFAs, hydrogen, and ethanol, can be generated at acetogenic and acidogenic stages.⁴⁶ Depending on the microbial strains and process conditions, the formation of intermediate products can be promoted or inhibited. For instance, to prevent VFAs consumption, the methanogens can be deactivated by adding chemical inhibitors and co-enzyme.⁴⁶ Table 2 summarizes different types of microbial strains used at each process step to selectively enhance the production of intermediate and final products. The syngas, usually CO and H₂, are used by the acetogenic bacteria as a carbon and energy source.

Biomethanation has a strong potential for the production of energy and commodity chemicals from organic residues and wastes (Table 2). Different process applications have been developed using biomethanation of wastewaters, slurries, and solid wastes. Biogas is the major product of the biomethanation process; however, there is a prospect for co-producing valuable chemicals if appropriate and robust microbial strains are used and process conditions are controlled. Biogas can be used to generate combined heat and power for local energy needs meet the local energy. Typical biogas comprises 55–75 vol.% methane, 20–50 vol.% CO₂, and traces of H₂S and ammonia.⁵⁷ It has been observed that, along with the other process conditions, such as the volatile solids, pH, and inoculant, the carbon-to-nitrogen ratio (C:N) in the feedstock is of utmost importance in determining the quality of the biogas. A typical study by Dioha *et al.* found that a C:N molar ratio between 20–30 parts of carbon to one part of nitrogen was the optimum ratio for a good biogas yield.⁴² The biomass with the highest biogas yield was cow dung, followed by grass silage. This optimum C:N ratio helped maintain a suitable pH, supplement the levels of carbon substrates and mitigate ammonia-nitrogen inhibition, which improved the overall methanogenesis output. Higher carbon content in feedstock yields a high amount of carbon dioxide, thereby lowering the pH, whereas higher nitrogen content stimulates ammonia production, thereby increasing the pH and negatively impacting the methanogens performance.

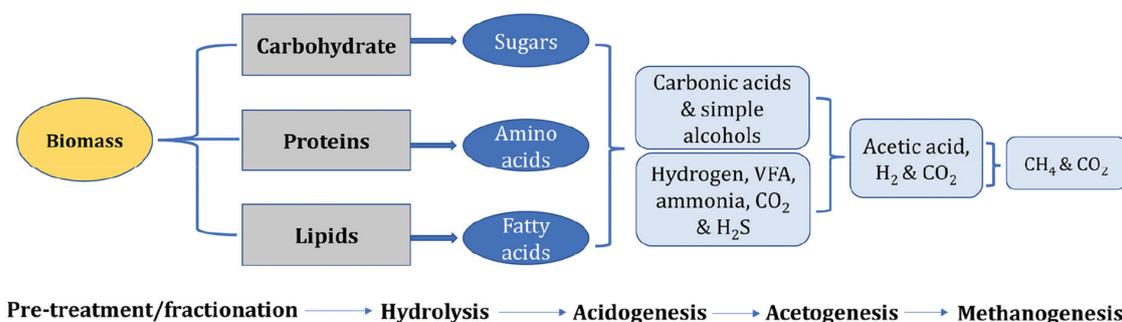


Figure 5. Stages involved in the biomethanation process of biomass to biogas. VFA, Volatile fatty acids

Table 2. Production of fuels and chemicals through anaerobic fermentation stages

Microbial strains	Substrates	Formation pathway	Products formed*	References
<i>Clostridium ljungdahlii</i> , <i>Clostridium autoethanogenum</i>	CO, H ₂ , and CO ₂	Acetogenic	Ethanol ^a and acetic acid ^b	47
P7 novel clostridial strain	CO, CO ₂ , H ₂ , and N ₂	Acetogenic	Ethanol ^a , butanol ^c , and acetic acid ^b	48,49
<i>Clostridium carboxidivorans</i>	CO, H ₂ , and CO ₂	Acetogenic	Butyric acid ^d , hexanoic acid ^e , hexanol ^f	50
<i>Clostridium autoethanogenum</i> , <i>Clostridium ljungdahlii</i> , and <i>Clostridium ragsdalei</i>	CO from industrial waste gas	Acidogenic	2,3-butanediol, ethanol, lactate and acetate	51
<i>Clostridium ragsdalei</i> , <i>Clostridium carboxidivorans</i>	Acetone-scrubbed producer gas (CO, CO ₂ , H ₂ , and N ₂)	Acidogenic	Isopropanol	52
<i>Fibrobacter succinogenes</i> , <i>Prevotella ruminicola</i> , <i>Succiniclasticum ruminis</i>	Lignocellulosic feedstocks	Acidogenic	Volatile fatty acids (propionate, butyrate, acetate)	46
Proteases (Alcalase)	Microalgae biomass	Hydrolysis	Amino acids	53
Cellulases (<i>Trichoderma</i> spp. and <i>Aspergillus</i> spp)	Cellulosic biomass	Hydrolysis	Glucose, xylose	54
Lipases (<i>Geotrichum candidum</i>)	Vegetable oil	Hydrolysis	Free fatty acids	55
<i>Methanobacterium</i> , <i>Methanosaeta</i>	CO ₂ , H ₂ and acetic acid	Methanogenesis	Biomethane	56

*Superscript letters indicate the overall stoichiometry formation of the products.

^a6CO + 3H₂O → CH₃CH₂OH + 4CO₂; 6H₂ + 2CO₂ → CH₃CH₂OH + 3H₂O.

^b4CO + 2H₂O → CH₃COOH + 2CO₂; 4H₂ + 2CO₂ → CH₃COOH + 2H₂O.

^c12CO + 5H₂O → C₄H₉OH + 8CO₂; 12H₂ + 4CO₂ → C₄H₉OH + 7H₂O.

^d10CO + 4H₂O → C₃H₇COOH + 6CO₂; 10H₂ + 4CO₂ → C₃H₇COOH + 6H₂O.

^e16CO + 6H₂O → C₅H₁₁COOH + 10CO₂; 16H₂ + 6CO₂ → C₅H₁₁COOH + 10H₂O.

^f18CO + 7H₂O → C₆H₁₃OH + 12CO₂; 18H₂ + 6CO₂ → C₆H₁₃OH + 11H₂O.

Thus, it was concluded that while designing a biogas plant, it was essential to consider the C:N ratio of the feedstock along with other process parameters. It was also observed that agricultural wastes like sugarcane bagasse and neem leaves were less attractive for biogas production.⁴⁰

Biogas production via AD is a clean method of waste disposal and, at the same time, of generating energy from waste. It can meet the needs of the household and helps to reduce the burden on the state if it is well utilized. It can be used in anaerobic digesters where it can be fed to a gas engine to convert the energy in the gas into electricity and heat.⁵⁸ Biogas can be compressed like natural gas and can be used to power motor vehicles. The rapid degradation of gas turbines by impurities in biogas such as H₂S is a typical drawback. However, the high-end expectation of biogas in meeting local energy needs can only be fulfilled if the biogas plants are designed satisfactorily. Biogas plants utilize different reactor systems, including mixed reactors, plug-flow reactors, and process conditions like retention time, temperature, and feed rate loading, to maximize the energy output from the waste, decrease retention time, and enhance process stability.

There are seven different types of biogas plants that can be designed with respect to desired production volume and intended applications. These are: (1) Fixed dome plants, (2) floating drum plants, (3) low-cost polyethylene tube digesters, (4) balloon plants, (5) horizontal plants, (6) earth pit plants, (7) ferrocement plants. Descriptions of each kind of plant can be found elsewhere.⁵⁹ The design parameters for biomethanation depend on the practical and theoretical methane potential. The methane potential can be defined as the volume of methane formed during anaerobic degradation, in the presence of bacteria, under normal temperature and pressure conditions. This methane generation potential depends on the feedstock and the conditions mentioned above. If methane is to be used as a high-end fuel, it would require processing to remove other gases present in the mainstream, which requires a different set of techno-economic analyses.⁶⁰ Further, according to needs, biogas can be compressed or used directly for heat generation.

An industrial example can be used to explain the commercial scale of a typical biogas-generating unit. Clarke's Energy, a Kohler company, uses energy crops (like maize, grass, wheat, rye, and triticale) and additional feed (manure,

slurry, vegetable waste, and glycerol from a biodiesel plant) for generating large quantities of biogas.⁶¹ Their biogas plants constitute a series of low-digester units built using concrete and steel. They produce electricity through co-generation for combined heat and power (CHP), saving around 40% of costs compared to individual electricity and heat-generation units. The owners state that their agricultural biogas plants generate returns via the sale of electricity alone. Gate fees levied for the acceptance of waste materials may be low or non-existent. If the farmer grows energy crops to feed into the plant, there is a cost associated with producing the feedstock. Thus, it is clear that biogas generation needs to be not only for local use or the generation of a particular kind of product. Multiple usages from the same unit can be economic and yield a significant profit in terms of energy utilization and efficient waste disposal.

In terms of the potential for utilizing this technology in all households or commercial premises, there remain a number of challenges to overcome, including:

- Significant capital investment costs are incurred compared to composting or landfills.
- Additional expenses may be incurred after 1–2 years of plant operation due to the reduced energy efficiency.

Although biogas production technology has developed, further technological development is required to ensure that efficient commercial-scale processes can be sustained. Current biogas units are mainly confined to rural areas where large biomass sources are available. Establishing biogas units in urban areas is difficult as the quantity and quality of biomass are non-uniform. Moreover, designing large-scale commercial biogas plants in areas surrounded by densely populated areas is difficult, requiring careful design.

Fermentation for bioethanol production

The history of biofuel production over the last two centuries has centered on first-generation bioethanol processes. Even though bioethanol has been successfully and favorably used, significant doubt remains around the viability of bioethanol as an energy-intensive and cheaper fuel source. Until 2008, nearly all the ethanol produced was derived from first-generation edible crops such as sugarcane, beet, and corn. However, some reports suggest it takes more energy to make bioethanol than the throughput from it.⁶² Second-generation bioethanol production is considered more favourable in the nexus of food-water-land because it uses inedible portion from agricultural and forestry wastes typically composed of lignocellulosic components. The use of second-generation crops for bioethanol production is still in its infancy. Ethanol can be used in pure form in internal combustion engines but is

more attractive as 10%–15% blends with gasoline. The addition of ethanol to gasoline promotes complete combustion and helps increase the octane number of the fuel, thereby reducing carbon monoxide emissions. Various microorganisms, either bacteria, yeast, or fungi, can ferment carbohydrates to ethanol under oxygen-free conditions.³⁷ Compared to other types of microorganisms, the traditional yeast *Saccharomyces cerevisiae* is commonly used because of its high ethanol productivity and ability to ferment a wide range of sugars.⁶³ The hydrolysis of lignocellulosic components generally yields pentose (from hemicellulose) and hexose (from cellulose) sugars which can be fermented to ethanol according to Eqn (3) and Eqn (4), respectively. According to the reaction stoichiometry, the theoretical maximum yield is 0.51 kg ethanol and 0.49 kg carbon dioxide per kg sugar.³⁷



There are three biochemical approaches commonly used in bioethanol production from lignocellulosic biomass: (1) separate hydrolysis and fermentation (SHF), (2) simultaneous saccharification and fermentation (SSF), and (3) simultaneous saccharification and co-fermentation (SSCF). More recently, a hybrid thermochemical and biochemical process involving the fermentation of pyrolysis-derived bio-oil – thermochemical bio-oil fermentation (TBF) – to bioethanol has been demonstrated. The difference between these methods and the processing steps is illustrated in Fig. 6. Bioethanol production from lignocellulosic biomass requires a pre-treatment or fractionation step before the biochemical or thermochemical conversion process, as shown in Fig. 6. Aside from the requirement for depolymerization of the complex lignocellulosic matrix through pre-treatment, second-generation bioethanol uses crop residues high in minerals that can cause corrosion in the reactors if not treated properly. There is thus a need for pre-treatment of such biomass to remove ash-forming elements as well as to fractionate them into less refractory constituents before further processing (Fig. 6). The other steps that follow for ethanol synthesis remain the same. The final fermentation step produces ethanol, which must be separated from the broth. A distillation process can be employed for the downstream processing recovery of ethanol.

The type of biomass and pre-treatment steps used for bioethanol production impacts the economic feasibility of the process. For example, da Silva *et al.* calculated a minimum ethanol selling price (MESP) of 1.80–5.76 US\$/L when ammonia fiber pre-treatment was used, 1.90–2.46 US\$/L

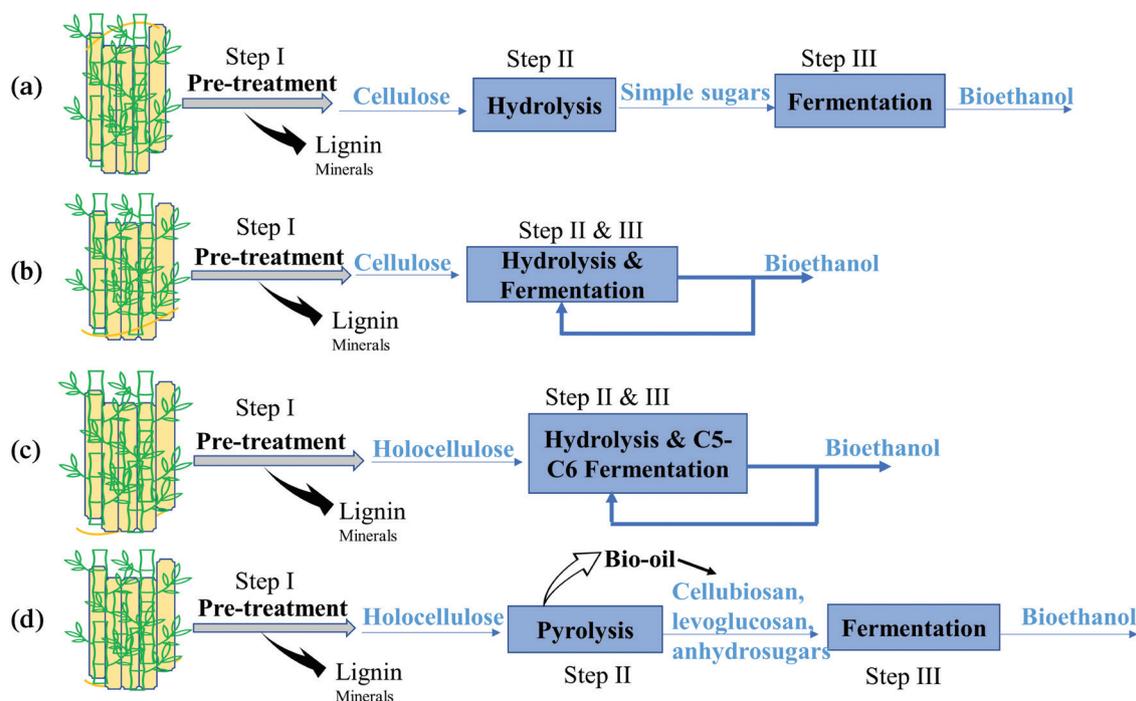


Figure 6. Various lignocellulosic biomass conversion processes for bioethanol production (a) separate hydrolysis and fermentation, (b) simultaneous saccharification and fermentation, (c) simultaneous saccharification and co-fermentation, and (d) thermochemical-derived bio-oil fermentation.

when liquid hot water pre-treatment was used, and 2.55 US\$/L for a dilute acid pre-treatment (DAP) scenario during the economic assessment of lignocellulosic-based ethanol production.⁶⁴ Feedstock selection depends on the local availability, transportation cost, and physical state of the biomass. Agricultural residues and pulp/bagasse generated from the first-generation bioethanol process represent a promising feedstock for second-generation bioethanol production. The different feedstocks used worldwide for second-generation ethanol production include corn stover, soyabean, wheat straw, citrus fruits residues, cassava residues, sugarcane bagasse, sugar beet pulp, rapeseed, jatropha, rice straw, and empty palm fruit bunches.⁶⁵ According to Sarkar *et al.*, four major agro-wastes can be used to produce bioethanol: rice straw, wheat straw, corn straw, and sugarcane bagasse.⁶⁶ It is assessed that the global annual yield of ethanol from rice husks could be 205, 104 billion Litres from wheat straw, 58.6 billion Litres from corn straw, and 51.3 billion Litres from sugarcane bagasse.^{16,67} Rice straw is a major waste with the highest bioethanol product volume potential. These wastes are also used as animal fodder, and the remnant is either discarded or burnt, posing a threat to the environment. The highest amount of ethanol is obtained from rice husk, which is of major interest to commercialize its production.

The production capacity of ethanol plants has generated significant interest in the commercial production of cellulosic

bioethanol. For example, DuPont technology has designed a plant for producing bioethanol from corn stover, the leftover stalks and leaves of corn plants, in Nevada and Iowa.⁶⁸ The plant was designed to produce 120 million Litres of fuel-grade ethanol per year. The start-up was huge, and it was considered to be the largest cellulosic ethanol-producing plant. Things took a negative turn within 2 years of its start-up in 2015. The plant was shut down as it could not produce the estimated ethanol capacity. The technology was not mature enough to sustain the increasing demands for ethanol, and storage for the corn residues was soon inadequate. Another such plant set up by the Spanish company, Abengoa Bioenergy, had seven plants in the US to produce bioethanol from mixed agricultural wastes, including non-food energy crops and wood waste, with a maximum capacity of 360 million Litres per year and a minimum of 100 million Litres per year.⁶⁹ The company could not satisfy the growing fuel needs due to lower plant efficiency.⁷⁰ These failures confirmed a lack of mature technologies, effective government policies encouraging bioethanol use, and a lack of sound market understanding.

Techno-economic analysis

Techno-economic analysis (TEA) is a tool used to assess the economic performance of an industrially viable process or product. This analysis is used at a stage where there is a

commercial prospect for developing the process technology at the pilot scale. Techno-economic analysis typically involves software modeling to estimate the capital and operating cost of a process/product and project revenue based on stipulated technical and financial input parameters. The value thus obtained can be further used to predict future cash flows and the likely return on investment. Several economic and profitability indicators of a project include net present value (NPV), internal rate of return (IRR), unit cost of production (COP), payback period, and minimum product selling price, among others. For a project to be commercially attractive, IRR > 10% is generally acceptable; a net positive NPV with a shorter payback of <5 years is attractive, and unit COP should be as low as possible.⁷¹

Various studies have been conducted to evaluate the techno-economic feasibility of the biochemical conversion of biomass to bioproducts. These studies explored various value extraction methods from biomass, such as (i) biofuel production, (ii) direct energy recovery via combined heat and power, and (iii) value-added chemical isolation to maximize the economic and environmental viability of the process. Generally, certain assumptions are made to simplify and define the process boundaries when conducting TEA. The wide disparity in the scope covered by each TEA study and associated assumptions can bring about significant differences in the results even for similar processes and plant capacity. The assumptions can be process-related, such as conversion, selectivity, yield, design basis, mass and energy requirements, product throughput, and product purity. Economics-related assumptions include tax rate, interest rate, plant life, depreciation parameters, installed equipment costs, and scaling factors. A list of commonly taken assumptions and typical values for TEA study, particularly for bioethanol production, has been highlighted in the NREL report by Humbird *et al.* and a recent review.^{21,72} Many uncertainties come with each assumption and may have various implications on the reliability of the TEA. As a result, it is a common practice to perform uncertainty and sensitivity analyses of selected variables on the cost and profitability metrics.⁷³ However, in many sensitivity analyses, one parameter is usually varied at a time by keeping other variables constant (single-point sensitivity analysis). This approach may not reveal practical realities as the combined effects of strongly dependent process variables cannot be assessed. Multivariate sensitivity analysis using advanced tools such as Monte Carlo simulation and material flow analysis can therefore be used to provide more insight into the TEA results.

Nevertheless, TEA remains a rational way to make meaningful economic assessments of various processes and products at a given scale. The two main biochemical

conversion strategies are fermentation and AD, which can yield a plethora of bioproducts via a series of process configurations. The TEA of the various conversion pathways and product formation are extensively reviewed in this section.

Pre-treatment technologies

The efficacy of biomass pre-treatment technology is often evaluated by the degree of component fractionation and separation. This is because the degree of isolation of the lignocellulosic constituents in the process allows for further chemical transformation of the basic biopolymers to value-added compounds such as cellulose to ethanol, hemicellulose to furfural, and lignin to phenolics. A study by Wooley *et al.* optimized the conversion process of hemicellulose and cellulose to fermentable sugars to minimize the capital and operating cost for corn stover utilization.⁷⁴ The authors found that co-current dilute acid pre-hydrolysis and enzymatic hydrolysis technology were the most optimum pre-treatment configuration. Similarly, an enzymatic hydrolysis process preceded by an organo-cat process was explored for rice straw feed by Morone *et al.* A maximum cellulose recovery of 98.99%, hemicellulose solubilization of 88.79% and lignin removal of 71.46% was reported.⁷⁵ Several benefits, such as improved cellulose accessibility and effective fractionating and cell-wall breakdown, improved the efficiency of the process.

Due to high cellulose crystallinity and low biodegradability, lignocellulosic biomass requires pre-treatment prior to fermentation.⁷⁶ Studies on pre-treatment steps have therefore been the focus of research communities aimed at improving the bioconversion of biomass resources, thereby lowering the production cost of biofuels and chemicals. These pre-treatment steps include ammonia fiber expansion pre-treatment (AFEX), DAP, alkali/lime pre-treatment, hot water pre-treatment, steam explosion, and solvent-based pre-treatment, for example *N*-methylmorpholine oxide (NMMO), ionic liquid, organic solvent, and deep eutectic solvent. The effect of AFEX pre-treatment conditions such as ammonia loading, water loading, reaction temperature, and residence time on ethanol production in a bio-refinery model was explored by Bals *et al.* It was found that ammonia loading and residence time had much influence on the COP than water loading and reaction temperature.⁷⁷ Moreover, it was found that the pre-treatment conditions can vary ethanol COP by ~0.09 US\$/L for an 850 MT per day refinery. A similar process intensification study was performed by Sendich *et al.*⁷⁸ to understand the influence of the AFEX process on the MESP. A net reduction from 0.26 to 0.21 US\$/L was observed by optimizing variables such as overall ammonia requirements, ammonia concentrations, ammonia recovery and enzyme

loadings while maintaining high conversions of glucan and xylan to monomeric sugars.

So and Brown compared three different routes for bioethanol production (6.6 million Litres/year).⁷⁹ The MESP via SSF was 0.41, 0.34 US\$/L for the fast pyrolysis bio-oil fermentation route, and 0.36 US\$/L for the dilute sulfuric acid hydrolysis and fermentation route. Based on the costs above, the study suggests that acid hydrolysis or pyrolysis before fermentation can significantly reduce ethanol costs. Similarly, one study focusing on future advancements and their economics for ethanol production was performed by Dwivedi *et al.* With advancements in hydrolysis and thermochemical-based technologies, the economics of bioethanol production can be greatly improved.⁸⁰ A simulation-based assessment of the economic feasibility of NMMO pre-treated forest residue and organic municipal solid waste followed by anaerobic co-digestion was proposed by Teghammar *et al.*⁸¹ An IRR of 24.14% (pre-tax) resulted in a feed of 100 000 MT of forest residues and 200 000 dry MT of organic fraction of municipal solid waste (OFMSW) per year. The study revealed that the minimum feed for financial viability was 50 000 MT of forest residues per year. Several other scenarios were evaluated, such as the co-digestion of forest residues with sewage sludge instead of OFMSW and the digestion of forest residues (unfeasibly low IRR). A wide range of process variables and their correlation was performed via sensitivity analysis to identify the most influential variables on the process profitability. Steam explosion pre-treatment-based biogas production from wheat straw and paper tube residuals was explored by Shafiei *et al.*⁸² Net projected investment

of paper tube and wheat straw was 85 and 82 MUS\$, respectively. The COP of raw biogas from the same process was estimated as 0.27 US\$/m³ for paper tube and 0.36 US\$/m³ for wheat straw. Because of the steam explosion, the total capital investment (TCI) cost increased by 13%; however, the improved biomethane yield reduced the overall COP by 36%. Furthermore, improving methane yield by 5% decreased the COP by 5.5%, while a 20% decrease in raw material costs decreased methane COP by 8%.

A brief overview of how the choice of pre-treatment technologies can affect the unit production cost of ethanol is shown in Table 3. Dilute sulfuric acid, and ammonia fiber explosion are the most viable option to commercialize cellulosic ethanol production. However, with respect to the capital and operating costs of the pre-treatment methods, liquid hot water appears economically and environmentally attractive compared to chemical-based and microbial-based pre-treatment options. For example, Kazi *et al.* estimated 376 MUS\$ as the TCI for DAP and 361 MUS\$ for liquid hot water.⁸⁴ Similarly, Eggeman and Elander estimated 208.6 MUS\$ as the total fixed capital for dilute acid and 200.9 MUS\$ for hot water.⁸³ The requirement of a special reactor vessel for acid pre-treatment might have contributed to high capital costs. However, in hot water pre-treatment, less hemicellulose is solubilized, which lowers the sugar yield of the feedstock and consequently lowers ethanol yields.³⁵ Lastly, there is a large difference in the estimated MESP values shown in Table 3 despite using similar feedstocks and plant capacity. Therefore, more dominant factors, such as feedstock costs, sugar cleaning and ethanol purification

Table 3. Overview of pre-treatment methods on the unit production of ethanol

Feedstock	Plant capacity	Pre-treatment methods	Cost parameter MESP (US\$/L)	References
Corn stover	2000 MT/day dry feed	Dilute sulfuric acid	0.35	83
		Liquid hot water	0.44	
		Ammonia fiber explosion	0.38	
		Lime	0.45	
MESP (US\$/L)				
Corn stover	2000 MT/day (25% moisture)	Dilute sulfuric acid	0.90	84
		Two-stage acid	1.16	
		Liquid hot water	1.17	
		Ammonia fiber explosion	0.97	
Sugar production costs (US\$/kg)				
Corn stover	5750 MT/day (20% moisture)	Steam explosion	0.43	35
		Dilute sulfuric acid	0.42	
		Ammonia fiber explosion	0.65	
		Biological	1.41	

techniques, could be responsible for the observed discrepancies.

Bioethanol production

Bioethanol production using SSF and SHF (Fig. 6) has been studied extensively for commercial applications. For example, the feasibility of bioethanol production from *Miscanthus × giganteus* was evaluated by Boakye-Boaten *et al.*⁸⁵ The MESP was calculated from discounted cash flow analysis as 0.65 US\$/L. The plant's installation cost (in 2007) was calculated to be 281 MUS\$ (for 701 000 MT/year feed capacity), out of which 40% was the feedstock cost. The TCI of the plant was 464 MUS\$, equivalent to US\$2.01/L of ethanol annually. The variable operating cost of the plant ranged between 79–93 MUS\$ per year, depending on the feedstock cost. Changing the feedstock cost from 0.08 to 0.10 US\$/kg increased the MESP from 0.65 to 0.71 US\$/L. The study also evaluated the MESP for corn stover, grass straw, and hybrid poplar. The study provided a benchmark for future investigation of the economic feasibility of alternative lignocellulosic feedstocks against each other as well as against conventional gasoline and diesel fuels. Figure 7a shows the major cost variables and their percentage shares to the unit production cost of ethanol. Raw materials and utilities are the highest contributing factor to ethanol production cost (accounting for more than two-thirds of the overall cost). The cost of feedstock and enzymes has the largest share of raw materials costs, while the cost of electricity takes the bulk of utility costs. Figure 7b shows energy consumption across the four key stages of bioethanol production: (i) pre-treatment, (ii) hydrolysate detoxification and sugar concentration, (iii)

hydrolysis and fermentation, and (iv) separation and ethanol purification. Sugar cleaning and concentration is the most energy-intensive process, followed by ethanol purification, usually through distillation. The pre-treatment process also incurs high energy costs depending on the pre-treatment methods and conditions. Meanwhile, hydrolysis and fermentation have the lowest energy consumption as they are usually performed at ambient to low temperatures (<50 °C).

A comparison between the economic feasibility of thermochemical and biochemical processes for bioethanol production has been conducted. Carlos *et al.* assessed the indirect and direct production of bioethanol via biochemical process and syngas via thermochemical gasification using *Pinus patula* as feedstock.^{89,90} They performed process simulation with extensive feed composition study data and determined the profitability of both processes by performing differential energy content analysis of the feed and product. They used a cradle-to-gate approach and performed a life-cycle assessment of seedlings production, feed cultivation, harvesting, and collection. It was concluded that the biochemical process could result in an ethanol yield with lower production cost and higher energy efficiency than syngas production via gasification. Technologies, such as the dark fermentation process and the separation of the remaining metabolites, were studied for improved economic feasibility. Such bio-refineries can further boost profitability owing to the production of value-added compounds. A similar study conducted by Seabra *et al.* aimed to convert surplus bagasse from a sugar mill to biofuel using a biochemical and a thermochemical process.⁹¹ Integrating the conversion technology into the mill yielded an additional ethanol production of 33 L/MT of sugarcane

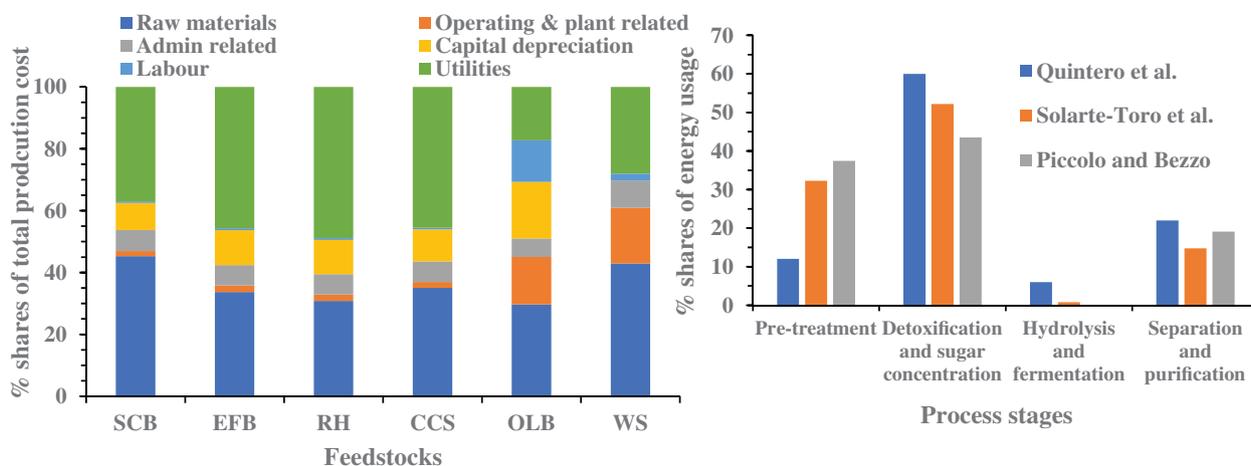


Figure 7. Cost variables and their percent, (b) energy consumption of various process stages in bioethanol production; CCS, coffee cut-stems; EFB, empty fruit bunches; OLB, olive biomass; RH, rice husks; SCB, sugarcane bagasse; WS, wheat straw. Data obtained from various publications.^{39,86–88}

for the biochemical process and 25 L/MT of sugarcane for the thermochemical process. The two technologies produced ethanol with similar MESP, that is, 0.318 US\$/L for biochemical and 0.329 US\$/L for thermochemical conversion.

An extensive comparative process efficiency study between 14 bio-refining technologies based on biological and thermochemical processes for the co-production of fuel, power, and animal feed was conducted by Laser *et al.*⁹² They reported that at a scale of 4535 MT/day feedstock capacity, an overall process efficiency of 49% can be achieved, which can reduce greenhouse gas (GHG) emissions by 1359 kg CO₂-equivalent yielding electricity COP of 0.0575 US\$/kWh (16 US\$/GJ). Furthermore, a 12% IRR, 35% debt fraction, and 7% loan rate were estimated for the process. At a similar scale, efficiencies between 55% and 64% can lower GHG emissions by 1000–1179 kg CO₂-equivalent per MT dry feed with costs between 0.36–0.57 US\$/L gasoline-equivalents were obtained. Biochemical production of ethanol with thermochemical production of fuels and/or power resulted in a process efficiency ranging between 61%–80%, reduced GHG emissions from 965 to 1258 kg CO₂-equivalent per MT dry feed with COP from 0.25 to 0.33 US\$/L gasoline-equivalent.

Several combinations of processes and technologies for hydrolysis-fermentation-based ethanol production with increasing sugar conversion efficiencies have also been investigated. One such study was performed by Hamelinck *et al.*³⁷ An increase in sugar conversion efficiency from 60% to 68% increased the overall process efficiency from 35% to 48%. The investment cost in this scenario was 2500 US\$/kW_t (at 400 MW_t energy input (HHV- Higher heating value), that is, a nominal 2000 dry MT/day input), while larger facilities require 1.07 MUS\$/kW_t feed input for a five times larger operation (2 GW_t). It was estimated that the combined effect of higher process efficiency, lower specific capital investments, higher production scale, and cheaper feedstock costs could reduce ethanol COP from 26.2 US\$/GJ_{HHV} in 5 years timeline to 15.5 US\$/GJ_{HHV} in a 10–15 year timescale, and down to 10.4 US\$/GJ_{HHV} in 20 or more years. TEA by Gnansounou *et al.* revealed that biomass cost significantly affects the production cost of bioethanol.⁹³ Strategies were also proposed to enhance the feasibility of such projects, including promoting the integration of second-generation with first-generation bioethanol and thus using existing residues and shared equipment. Sugarcane bagasse was a particular focus of such a strategy. It is also suggested that risk aversion via advanced technologies and optimization be implemented to attract funding to such projects in the future.

Various papers have explored the economics of consolidated bioprocessing, where a single step is used to

produce enzymes, hydrolysis of cellulose, and fermentation.⁹⁴ One such study was performed by Lynd *et al.*, suggesting that consolidated bioprocessing could potentially be the cheapest route for biomass conversion among all the hydrolysis-based processes.⁹⁵ Another such techno-economic study was performed by Barta *et al.* using Aspen Plus and Icarus Process Evaluator software.⁹⁶ It investigated on-site cellulose enzyme fermentation in a softwood-to-ethanol process based on SO₂-catalyzed steam pre-treatment followed by SSF. The effect of varying the carbon source of enzyme fermentation at constant protein and mycelium yields was monitored throughout the process. The enzyme production step decreased the overall ethanol yield (270 L/MT of dry raw material in the case of purchased enzymes) by 5–16 L/MT. Capital cost was the main cost contributor to enzyme fermentation was the main cost contributor to overall capital cost, constituting 60%–78% of the enzyme production cost, which was equivalent to 0.065–0.082 US\$/L ethanol. The lowest MESP of 0.725 and 0.742 US\$/L were obtained in those scenarios, where the pre-treated liquid fraction supplemented with molasses was used as a carbon source. Another such case is a comparative study for bio-ethanol production on a 5–8 year time frame of implementation focusing on the short-term commercial viability of the process, conducted by Kazi *et al.*⁹⁷ They modeled multiple pre-treatment and downstream process technologies to obtain the TCI and product value (PV) which was equal to (COP + 10% return on investment [ROI]). The DAP process has the lowest PV of around 1.36 US\$/L gasoline-equivalent among all process scenarios. According to the sensitivity analysis, feedstock, enzyme, and installed equipment costs were the most influential on the PV. In similar studies, a key variable in the production cost was found to be feedstock cost, more so in the case of decreasing conversion technology costs as indicated by Bohlmann for corn stover and Leistritz *et al.* for wheat straw (0.412 US\$/L).^{98,99}

Similarly, co-fermentation technology for ethanol production based on simultaneous saccharification was explored by Huang *et al.* for cost optimization.¹⁰⁰ The results indicate COP decrement with increasing plant capacity within 1000 to 4000 dry MT/day, while the increment for hybrid polar in case plant size increased beyond 4000 dry MT/day. However, production cost was affected by plant capacity but was found to be almost independent of feedstock variety. Another important study by Aden *et al.* indicated a total selling price of ethanol produced via SSF technique at 0.64 US\$/L.¹⁰¹ Using corn stover, a steady COP for ethanol of 0.34 US\$/L was estimated for a plant size above 6000 MT. A summary of the data elaborated in these sections and other relevant work has been tabulated and adjusted for inflation in Table 4.

Table 4. Summary of techno-economic studies for bioethanol production.

Processing steps	Plant capacity MT/day	Biomass feedstock	Products	Feed cost* US\$/MT	TCI* Million US\$	Operating cost* Million US\$/year	IRR %	Remarks	Product cost* US\$/L	References
<ul style="list-style-type: none"> DAP EH and co-fermentation 	97.304	Surplus bagasse from sugarcane mill and cane trash	Ethanol Steam Electricity	Bagasse: 0 Cane trash: 18.37	186.15	6.74			0.39	69
<ul style="list-style-type: none"> DAP EH C5 & C6 fermentation 	2000	Miscanthus x giganteus	Ethanol	79.06	505.22	Variable operating cost: 86 Fixed operating cost: 3.05	10	-	0.71	66
<ul style="list-style-type: none"> Biomass pre-treatment EH Fermentation Ethanol recovery Wastewater treatment & Co-generation 	12.06	<i>Pinus patula</i>	Ethanol Hydrogen	10.01	-	26			Ethanol: 2.34 Hydrogen: 2.15	67
<ul style="list-style-type: none"> Pre-treatment and conditioning EH and fermentation Cellulase enzyme production Product, solids and water recovery 	2000	Corn stover	Ethanol	6	501.6	90.23	10%	-	0.66	72
<ul style="list-style-type: none"> Pre-treatment Hydrolysis Fermentation Distillation 	2000	Corn stover	Ethanol	101.65	For various process variations: a 460.5 b 476.4 c 478.9 d 400.5 e 472.7 f 613.6 g 472.7 h 531.5		10% (for base case)	Process variations: a Dilute-acid pre-treatment (base case) b Dilute-acid pre-treatment (high solids) c 2-stage dilute-acid pre-treatment d Hot water pre-treatment e AFEX pre-treatment f Pervaporation-distillation g Separate C5 and C6 fermentation h On-site enzyme production	4.16–5.44	82

(Continues)

Table 4. (Continued)

Processing steps	Plant capacity	Biomass feedstock	Products	Feed cost*	TCI*	Operating cost*	IRR	Remarks	Product cost*	References
<ul style="list-style-type: none"> DAP Fermentation Ethanol recovery 	(a) 1960 (b) 1680 (c) 1636 (d) 1818	(a) Straw (b) Eucalyptus (c) Poplar (d) Switchgrass	Ethanol	(a) 133.43 (b) 76.4 (c) 171.94 (d) 160.8	(a) 378.5 (b) 355.2 (c) 344.14 (d) 362.5	a 178.8 b 137.17 c 186.15 d 188.6		Effect of feedstocks on techno-economics was assessed	a 2.6 b 3.38 c 3.53 d 3.56	72
<ul style="list-style-type: none"> DAP and EH Fermentation Separation, processing and recycling 	2000	Corn stover	Ethanol	73.5	a 412.8 b 412.4 c 410.6 d 386.4 e 450.3 f 409.9 g 414.1 h 409.7	a 169.6 b 170.2 c 163.1 d 165.8 e 181.87 f 169.6 g 171.1 h 169		a Base case b Reducing acetate content of feed c Increasing cellulolytic enzyme activity d Reducing lignin content of feed e Reducing lignin content of feed and increased xylose fermentation by yeast f Increasing the rate of yeast g Increasing the tolerance of yeast to acetic acid h Increasing the tolerance of yeast to ethanol	a 1.47 b 1.32 c 1.43 d 1.29 e 1.14 f 1.3 g 1.25 h 1.45	102
<ul style="list-style-type: none"> Feedstock storage and handling, Pre-treatment and hydrolysate conditioning, Saccharification and co-fermentation, Product separation and purification, Wastewater treatment, Product storage, Lignin combustion for production of electricity and steam 	2000	a Corn stover b Switchgrass (croplands) c Switchgrass (grasslands) d Hybrid polar (croplands) e Aspen wood	Ethanol	a 79.17 b 103 c 117.4 d 129.8 e 137.27	a 250.8 b 263.1 c 263.1 d 252.04 e 232	a 122.42 b 137.3 c 147.5 d 155.2 e 166.46	10	The excess electricity generated: Aspen < corn Stover < hybrid poplar/ switchgrass high Ethanol annual production: Aspen wood > corn Stover > hybrid poplar > switchgrass Ethanol production costs: Corn Stover < aspen wood < switchgrass in grasslands < switchgrass in croplands or hybrid poplar. Linear increase in excess electricity generated with increasing plant size. Suitable plant size as per economics: 2000 to 4000 MT/day	a 0.47 b 0.57 c 0.62 d 0.61 e 0.52	85

(Continued)

Table 4. (Continued)

Processing steps	Plant capacity	Biomass feedstock	Products	Feed cost*	TCI*	Operating cost*	IRR	Remarks	Product cost*	References
<ul style="list-style-type: none"> • Pre-treatment and hydrolysate conditioning • SSF and Co-fermentation • Enzyme production • Product recovery and water recovery 	3840	Corn stover and Switchgrass	Ethanol	40.07	374.8	58.3			0.61	90
<ul style="list-style-type: none"> • Hydrolysis • Neutralization • Na₂SO₃ treatment • Fermentation 	500	Wood chips	Ethanol	70	68.2	48.3			0.82	103
<ul style="list-style-type: none"> • Pre-treatment • Hydrolysis • Fermentation • Downstream processing 	75	Grass straw	Ethanol	56.5	(a) 129.31 (b) 115.93 (c) 114.94 (d) 103.06	(a) 56.47 (b) 59.45 (c) 54.26 (d) 51.7		Different pre-treatment processes (a) Dilute acid (b) Dilute alkali (c) Hot water (d) Steam explosion	(a) 0.95 (b) 1.0 (c) 0.91 (d) 0.97	104
<ul style="list-style-type: none"> • Acid pre-hydrolysis • Cellulose SSF and pentose • Fermentation • Ethanol extraction 	821	Raw wood	Ethanol	67.3	102.6	62.85			0.66	95

Abbreviations: DAP, dilute acid pre-treatment; EH, Enzymatic hydrolysis; IRR, internal rate of return; SSF, simultaneous saccharification and fermentation; TCI, total capital investment.

*All costs have been converted to 2021 equivalent.

Biogas production

Biogas production via AD is viable for biomass conversion and treatment of organic waste streams. Several models and simulations have been developed, and reports show a lucrative opportunity in both economic and environmental aspects. For example, biogas production was modeled using Aspen Plus and CapdetWorks by Bhatt *et al.* for a feasibility study analyzing key variables and process optimization.¹⁰⁵ The TEA results using four types of wet wastes, including wastewater sludge, food waste, swine manure, and fat, oil, and grease, were similar to many literature-reported data with the potential for further reduction for small-scale facilities with technological advancements. The total energy resource for biogas production via the AD process was highest for swine manure, followed by food waste, sludge, and fat, oil, and grease. A similar study with exhaustive and numerical results was performed by Dahunsi *et al.*¹⁰⁶ Mechanical and thermo-alkaline pre-treatment-based biogas production by co-digestion of *Arachis hypogaea* hull and poultry droppings was explored to study the effects of response surface methodology (RSM), and artificial neural network (ANN) based optimization techniques on the COP. The optimized variables were temperature (32 °C), pH (7.62), retention time (30 days), total solids (12 g/kg), and volatile solids (10 g/kg). They suggested that the feed used was good for biogas and bio-fertilizer production due to its high nutrient and mineral content. The models closely determined the biogas generation with very high precision using ANN and suggested that thermo-alkali pre-treatment leads to higher biogas generation.

Along with the use of traditional biomasses such as bagasse and wood, some studies have also focused on the biochemical conversion of algae to produce alcohols and biogas. For example, DeRose *et al.* studied both biochemical and thermochemical conversion of low lipid, high ash content

algae into biofuels.¹⁰⁷ Fermentation-based biochemical conversion for alcohol production, followed by hydrothermal liquefaction (HTL) for biofuel production, was used. They calculated the MESP for biochemical and thermochemical processes as 3.39 and 2.75 US\$/L gasoline-equivalent, making the thermochemical process more economically feasible. Another such study was conducted by Zamolloa *et al.* in which microalgae were grown on non-agricultural land, pre-treated and sent to an anaerobic digester where it was converted to biomethane.¹⁰⁸ They evaluated the costs of biomass for bio-methanation under such conditions to be around 119.6–172.5 US\$/dry MT. The biogas produced was used for heat and power generation at a levelized cost of 0.24–0.12 US\$/kWh, including a carbon credit of around 41.7 US\$/MT CO₂ equivalent.

Several studies also elaborate on technologies and modifications involved in value derivation from biomass, such as carbon capture, pre-treatment steps, feed type, the effect of plant capacity, enzyme cost, and so forth, to draw contrasting conclusions for an optimized plant design both in terms of efficiency of function and minimized cost of plant setup. These studies aim to intensify the process, allowing for variable correlations and optimization of cost production, hence improving efficiency. Carbon capture technologies enable a reduction in pollutant gas emissions. Valencia *et al.* assessed bio-energy with carbon capture and storage systems in a Brazilian sugarcane mill focusing on a steam co-generation system implementation.¹⁰⁹ Carbon capture from fermentation and combustion (amine-based capture) was evaluated via computer simulation. Positive results were obtained, indicating that carbon capture from fermentation should be prioritized over combustion. In the reference case, the cost of avoided CO₂ emissions was 69 US\$/MT CO₂, which can be improved to 66 US\$/MT CO₂ in advanced technologies and 54 US\$/MT CO₂ in the case of larger plants.

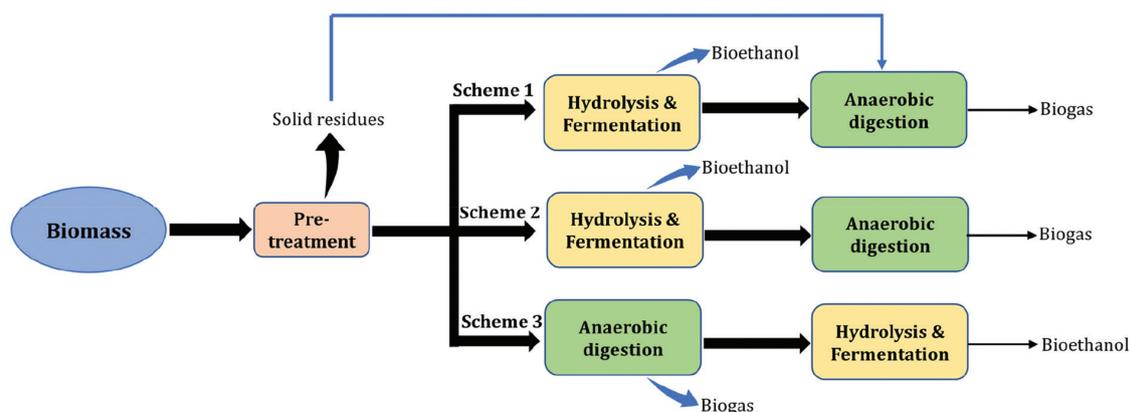


Figure 8. Various process schemes for the co-production of bioethanol and biogas.

Similarly, an exhaustive study for all combinations of biochemical conversion pathways, feed, by-product options and biorefinery siting contexts for bio-sugar production was performed by Reeb *et al.*¹¹⁰ A 15% IRR was obtained at a selling revenue of 150–748 US\$/MT. The lowest minimum selling revenue was given in the case of sugarcane in Asia and South America. Corn grain feed was another optimized scenario in the study. Each of these gave an IRR > 15%, where the major operating cost was due to feedstock cost per MT carbohydrate, sugar yield, capital investment per year MT sugar produced, residue value, and siting context.

Co-producing bioethanol and biogas

The co-production of bioethanol and biogas via hybrid fermentation and the AD process can be achieved through three process schemes illustrated in Fig. 8. The integrated fermentation-AD biorefinery can enhance value recovery from biomass resources and thereby increase the techno-commercial attractiveness of second generation biomass processing. The overall gross bioenergy output from the co-production process can be higher. For example, in the review of Jarunglumlert *et al.*, the average biofuel output from the co-production process was estimated at 8 MJ/T dry biomass, which is equivalent to 250 L gasoline, indicating a 142% increase than producing bioethanol alone and 70% increase than producing biogas alone.¹¹¹ From Fig. 8, schemes 1 and 2, which allow the production of bioethanol prior to biogas, generated an average total bioenergy output of 9.8 and 7.8 MJ/t biomass, respectively. In contrast, scheme 3, where AD comes before fermentation, generated a relatively lower energy output of 6.4 MJ/T.¹¹¹ The observed variation can be tied to the differences in process configuration, including feedstock types, pre-treatment techniques, and process conditions. Demichelis *et al.* observed that potatoes produced more bioethanol and biogas combined than either sugarcane or rice straw.¹¹² The energy content of bioethanol and biogas considerably differs, and depending on the production volume of both products, the overall energy output can be shifted to liquid or gaseous fuel. The process can be optimized to produce more bioethanol or biogas by changing feedstocks and configurations.

Techno-economic assessment of the co-production of bioethanol and biogas in integrated fermentation and AD biorefinery has been reported in many studies. Given the wide range of technical parameters and economic assumptions among studies, minimum selling price (MSP) is a critical indicator to determine the economic feasibility of producing biofuels from biomass to breakeven. Table 5 summarizes techno-economics studies of the production of bioethanol and biogas either as sole or joint products of the process. The MESP from the various studies in Table 5

ranges from 0.34–1.8 US\$/L; the market price of ethanol (US\$ 0.59/L as of August 2021) is at the lower end of the range.¹¹¹ The wide scatter in the MSEP results from different studies is largely attributed to feedstock and pre-treatment method variation. Demichelis *et al.* reported that using different substrates influenced the economics of the co-production of bioethanol and biogas.¹¹² Utilizing sugar-based feedstock (sugarcane) was more profitable than using starch-based feedstock (rice straw), with about 89% and 50% reduction in NPV and ROI from rice straw than sugarcane.

Production of other biofuels

Another common biofuel besides bioethanol is biobutanol which can be obtained through the acetone-butanol-ethanol (ABE) fermentation route using the *Clostridium* species. The techno-economics of the ABE fermentation process for the production of *n*-butanol has been reported in many works. Qureshi *et al.* assessed the techno-economics of 2G ABE fermentation technology to produce *n*-butanol from wheat straw using *Clostridium beijerinckii* P260 strain.¹¹³ The separation and recovery of butanol from the product stream involve an intensive operation; the authors combined pervaporation, distillation, and distillation-membrane separation. At a production rate of 150 kT/year butanol, 78.1 kT/year acetone, and 28.5 kT/year ethanol, the final MSP of butanol being the dominant product was 0.85 US\$/L, and the TCI for the plant was 193 MUS\$. The choice of product recovery technologies impacted the unit production cost significantly. In another work, Kumar *et al.* assessed the techno-economic feasibility of biobutanol production via ABE fermentation using cellulosic (bagasse, barley straw, wheat straw, corn stover, and switch grass) and non-cellulosic (glucose, sugarcane, corn, and sago).¹¹⁴ A production capacity of 10 kT/year butanol, equivalent to 39 wt% of the total ABE products per unit of sugar, was considered. As expected, using glucose as the fermentation substrates required about 37% less fixed capital cost than using other feedstocks. However, the unit production cost of butanol from glucose was fourfold higher than other feed materials due to the high cost of glucose, similar to sago feed limiting the economic attractiveness of biobutanol plants. The authors observed that sugarcane and cellulosic feedstocks were economically feasible with a production cost range of 0.48–0.61 US\$/L butanol. The cheapest option based on unit production cost (US\$/L butanol) was bagasse and corn stover (0.48), followed by switch grass and sugarcane (0.51), wheat straw (0.56), and barley straw (0.61). Enhancing the plant capacity from 5 to 25 kT/year decreased the biobutanol unit production cost by 9% for corn and 3% for sago, while it was a 15%–18% decrease for sugarcane and cellulosic feedstocks.

Table 5. Variation in minimum ethanol selling price (MESP) for the sole and co-production of ethanol and biogas (data presented in this table are obtained from the review by Jarungluert and Prommuak)¹¹¹

Substrate	Pre-treatment	Energy cost-saving approach	MESP (US\$/L)
Ethanol production			
Sugarcane bagasse	Dilute acid + steam explosion	Solid residues were burnt as combustion fuel and liquid residues were sold as fertilizer	0.63
Sweet sorghum			0.34
Rice husk	Dilute acid	Solid residues were used as combustion fuel to generate electricity	0.53
Sugarcane bagasse			0.68
Empty fruit bunch			0.49
Coffee cut-stem			0.59
Miscanthus giganteus	Liquid hot water	Solid residues were burnt as combustion fuel	0.65
Corn stover	Dilute acid	Solid residues were burnt as combustion fuel	1.36
Lignocellulosic biomass	Liquid hot water	Solid residues were used as combustion fuel	1.78
	Ammonia fiber explosion		1.8
Ethanol + biogas production			
Red oak	Solvent liquefaction	Produced biogas from liquid residues and solid residues were used as combustion fuel	0.79
Sugarcane bagasse	Steam explosion	Produced biogas was used as combustion fuel	0.5
Wheat straw	Steam explosion	Produced biogas and solid residues were sold as by-products	0.86
Corn stover	Dilute acid	Produced biogas and solid residues were used as combustion fuel	1.24
Spruce wood	<i>N</i> -methyl morpholine- <i>N</i> -oxide solvent	Produced biogas and solid residues were sold as by-products	0.52
Switchgrass	Ammonia fiber explosion	Produced biogas and solid residues were used as combustion fuel	0.72
	Soaking in aqueous ammonia		1.08

Mariano *et al.* assessed the techno-economics of integrating butanol plant versus biogas plant using 2G feedstock (sugarcane straw) with bioethanol plant using 1G feedstock (sugarcane).¹¹⁵ Regarding energy, feed consumption, and amount of CHP generated, integrating 2G biogas or biobutanol plant with 1G bioethanol did not make a significant difference. The IRR of the investment in biogas production is 11.3%, while the IRR varied between 13.1% and 15.2% for biobutanol plant depending on the microbial strain and target market. When regular fermentation strain was replaced with engineered strain, biobutanol yield increased by 69%, which increased the annual gross revenue to 8.1 MUS\$ for the chemical use scenario compared to 5.0 MUS\$ for the fuel use scenario. Tao *et al.* compared the techno-economic feasibility of cellulosic isobutanol with cellulosic ethanol and *n*-butanol from corn stover.¹¹⁶ The cellulosic plant yielded 330 L ethanol/dry MT feed, 242 L iso-butanol/dry MT feed, and the *n*-butanol plant yielded 200 L *n*-butanol/MT feed, 8.1 L acetone/MT feed, and 35.8 L ethanol/MT feed. The electricity export from these three plants was similar, ~0.023 kWh/MJ, with the lowest coming from the isobutanol plant and highest from the *n*-butanol plant. The TCI of *n*-

butanol was highest at 433 MUS\$ followed by isobutanol at 428 MUS\$ and ethanol at 423 MUS\$. The MSP (US\$/L) was 0.57 for cellulosic ethanol, 0.78 for cellulosic isobutanol and 0.80 for cellulosic *n*-butanol. The cost of butanol was higher than that of ethanol due to the relatively lower fuel yield and complex co-product portfolio which requires more intensive separation operations. The techno-economic comparison of various extracting solvents for ABE products separation was studied by Dalle Ave *et al.*¹¹⁷ It was observed that the choice of extractants affected the ABE product distribution, CAPEX (capital expenditure) and OPEX (operating expenditure) as well as unit production cost. The pure-distillation base case resulted in an MSP of 2.15 US\$/L of butanol produced. Four of the tested solvent had a lower MBSP than this: 2-ethylhexanol (1.57 US\$/L), Blend 2: 20 wt% decanol and 80 wt% oleyl alcohol (1.89 US\$/L), oleyl alcohol (1.97 US\$/L), and mesitylene (2.13 US\$/L).

Biohydrogen production via biochemical routes such as dark and photo fermentation has attracted much research, and some techno-economic feasibility studies have been reported.¹¹⁸ Abuşoğlu *et al.* assessed the energy and economic analysis of biohydrogen production from biogas-based

electricity and sewage sludge substrate using five models.¹¹⁹ The daily hydrogen production rate was the lowest (56.7 kg) from dark fermentation compared to 594, 625, and 869 kg for alkaline, proton exchange membrane (PEM), and high-temperature water electrolysis, respectively. The total hydrogen production cost through dark fermentation was 0.295 MUS\$/year, for which capital investment cost accounted for 44%. The unit production cost of hydrogen was 15.63 US\$/kg, which was at least 34% higher than other models. Biohydrogen yields from organic substrates can be directly related to the amount of cellulose in the feed; hence, the pre-treatment of the sludge before dark fermentation can enhance hydrogen yield, as it has been reviewed for food waste.¹²⁰ Han *et al.* investigated the techno-economic feasibility of a biohydrogen production plant from waste bread (2 MT/day).¹²¹ The pre-treatment and enzymatic hydrolysis of the feedstock yielded 0.28 g glucose/g waste bread, and 84.5% conversion of glucose to biogas containing 37.6% H₂ and 59.8% CO₂ was achieved. The annual yield of H₂ and CO₂ were 182 060 m³ H₂ and 273 080 m³ CO₂. The TCI of the biohydrogen plant was estimated at 0.93 MUS\$, and the total annual production cost of 0.3 MUS\$ was estimated with labor cost taking 60%, utilities cost taking 25%, and raw materials cost taking 6.5%. The unit production cost of hydrogen was 2.34 US\$/m³ (14.9 US\$/kg H₂), which is comparable to that obtained from Abuşoğlu *et al.*¹¹⁹ Although the production cost of biohydrogen via dark fermentation is still not competitive with other production technologies such as steam methane reforming, water electrolysis, and supercritical water reforming of glycerol, the cost is still much cheaper than hydrogen market unit price (US\$2.7/m³).¹²¹

In another work by Han *et al.*, the TEA of a novel biohydrogen production process from food waste (10 MT/day) combining solid-state enzymatic hydrolysis and dark fermentation was investigated.¹²² An annual H₂ production volume of 191 260 m³, a TCI of 0.71 MUS\$, an annual operating cost of 0.37 MUS\$, and 20.2% IRR were estimated. Unit H₂ production cost was 2.29 US\$/m³, and this cost was driven to a large extent by raw materials (27%), labor, maintenance, and insurance (45.8%), and equipment costs (15.3%). The H₂ market price and operating labor cost were the most important parameters on the NPV of the plant. The techno-economic feasibility of co-producing hydrogen and VFAs from vinasse using two anaerobic microbial consortia was studied by Sydney *et al.*¹²³ The use of consortium LPBAH1 for fermentation of vinasse supplemented with sugarcane juice resulted in a higher H₂ yield of 7.14 mol H₂/mol sucrose and H₂ content in biogas ~31%, while consortium LPBAH2 resulted in 3.66 mol H₂/mol sucrose and 32.7% H₂ content in biogas.

Jet fuel production from biomass biochemical conversion has also been the focus of multiple studies. Diederichs *et al.*, using Aspen Plus® simulations, studied jet fuel production from both 2G and 1G biomass feedstock.¹²⁴ A minimum jet-fuel selling price (MJSP) which is 2–4 times higher than the market jet fuel price, was obtained. The 1G process used vegetable oil and gave the lowest MJSP of 2.22 US\$/kg jet fuel. In contrast, the two most promising 2G processes – the thermochemical (gasification and Fischer–Tropsch synthesis) and hybrid (gasification and biochemical upgrading) processes yielded an MJSP of 2.44 and 2.50 US\$/kg jet fuel, respectively. It was concluded that the feedstock cost and fixed capital investment were key determining variables. A simulation-based study for alcohol-to-jet conversion schemes focusing on ethanol and iso-butanol intermediate use was proposed by Geleynse *et al.*¹²⁵ Major cost spawned from alcohol COP (80%), while iso-butanol use offers a reduced conversion cost of 34%. It was found that feed cost also dominates the overall process economics. Table 6 summarizes key studies on the techno-economics of biofuel production as reviewed in this section.

Platform chemicals

Value-added chemicals production is another lucrative domain to enhance the economic feasibility of biochemical conversion of biomass. Several studies also focus on the techno-economics of the isolation and conversion of biomass to value-added platform chemicals. Biorefinery for lignocellulosic biomass-derived ethanol, succinic acid, acetic acid, and electricity was analyzed for economic and environmental sustainability by Luo *et al.*¹²⁶ It was found that multi-product type biorefineries presented better economic and environmental efficiencies. Several variables were analyzed for their impact on economic feasibility. Similarly, a TEA study on glacial acetic acid (GAC) production via bioconversion using either ethyl acetate or alamine in di-iso-butylkerosene (DIBK) as organic solvents for purification was performed by Morales-Vera *et al.*¹²⁷ A simulation with pre-treatment, enzymatic hydrolysis, acetogen fermentation, and acid purification sequence was developed on Aspen with estimated capital costs ranging from 186–245 MUS\$. An average MSP of 756 and 877 US\$/MT were estimated for GAC production using alamine/DIBK and ethyl acetate solvents, respectively. Hence the recovery of GAC from the fermentation broth using alamine/DIBK was identified as the cheapest process.

Similarly, the techno-economic assessment of 1,4-butanediol production was explored by Satam *et al.*¹²⁸ An estimated MSP of 1.2 US\$/kg compared to the market price of 2.5 US\$/kg was obtained, while major COP contributors were found to be bioconversion equipment costs along with

Table 6. Summary of techno-economic studies on the production of other biofuels

Processing steps	Plant capacity MT/day	Biomass feedstock	Products	Feed cost* US\$/MT	TCI* Million US\$	Operating cost* Million US\$/year	IRR %	Remarks	Product cost* US\$/L	Reference
<ul style="list-style-type: none"> Pre-treatment and conditioning Hydrolysis and fermentation Steam and power plant 	1800	(a) Lignocellulose (LCB) (b) Sugarcane	Ethanol – Jet fuel	(a) LCB: 45.62 (b) Sugarcane: 107	(a) 398.7 (b) 592.7	(a) 158.63 (b) 188.9	10	(a) Sugar cane juice to ethanol by sucrose fermentation with upgrading to jet fuel (b) Lignocellulose biochemical conversion to ethanol with upgrading to jet fuel	(a) 2.83 (b) 3.83	99
<ul style="list-style-type: none"> Biomass pre-treatment Cellulose hydrolysis Fermentation Ethanol recovery Wastewater treatment & Co-generation 	12.06	<i>Pinus patula</i>	Ethanol Hydrogen	10.01	-	26		Ethanol: 2.34 Hydrogen: 2.15	67	
<ul style="list-style-type: none"> Pre-treatment EH ABE fermentation (regular clostridium strain) CHP generation 	1104	(a) Sugarcane (b) Sugarcane straw	Butanol Ethanol Acetone	(a) 27.26 (b) 18.29	405	99	13.1	When mutant strain was used for the ABE fermentation, IRR increased to 13.9. The addition of acetone and ethanol to the product portfolio increased the plant revenue	-	115
<ul style="list-style-type: none"> Acid pretreatment Ammonia conditioning EH Anaerobic fermentation with vacuum stripping CHP generation from waste residues 	2000	Corn stover	(a) Iso-butanol (b) <i>n</i> -butanol (c) Ethanol		(a) 428 (b) 433 (c) 423		10	Sugar yield is the most sensitive parameter to MSP for butanol. Energy consumption per gallon of <i>n</i> -butanol is almost 40% higher than it is for ethanol, and 30% higher than it is for isobutanol,	(a) 0.78 (b) 0.80 (c) 0.57	116

Abbreviations: ABE, Acetone-Butanol-Ethanol; CHP, Combined heat and power; EH, Enzymatic hydrolysis; IRR, internal rate of return; MSP, minimum selling price; TCI, total capital investment.

*All costs have been converted to 2021 equivalent.

other systems, such as membrane filtration for operational costs. An increase in butanediol yield to 20 gL^{-1} resulted in a significant reduction of MSP by 45%. It was found that the process was affected significantly by energy prices but not as much by feedstock prices. Another study focusing on lactic acid production (100 000 MT per annum) from corn grain through several fermentation pathways was conducted by Manandhar and Shah.¹²⁹ The unit production costs were evaluated as 1181 US\$ (bacteria), 1251 US\$ (fungi), and 844 US\$ (yeast). Genetically engineered yeast strains further enhanced the COP by process intensification. By performing a sensitivity analysis of various key parameters, it was suggested that sugar-to-lactic acid conversion rates, grain price, plant size, annual operation hours, and potential use of gypsum significantly impact the COP.

Comparably, itaconic acid (IA) production and techno-economic feasibility from lignocellulosic feedstock was explored by Nieder *et al.*¹³⁰ Several IA bio-refinery scenarios were simulated in AspenPlus®, and it was found that a selling price of 1740 US\$/MT could be achieved in contrast to the standard pricing of 1800 US\$/MT. Factors such as cheaper feedstock and external factors such as coal supplementation lowered the COP. It was also suggested that an integrated wastewater treatment system could further enhance the economic feasibility of the process. Similarly, TEA of an organosolv process using hardwood feed for the production of ethanol (459 MT/day, MESP – 0.811 US\$/L), lignin (310 MT/day – MESP – 0.24 US\$/L), furfural (6.6 MT/day, MESP – 0.0185 US\$/L), and acetic acid (30.3 MT/day, MESP – 0.008 US\$/L) was performed by Kautto *et al.*^{131,132} The effect of lignin price, enzyme dosage, feedstock, and investment costs on MESP were evaluated. It was estimated that if the conversion rate in the enzymatic hydrolysis increases by 6% for cellulose and hemicellulose, the MESP of ethanol would be reduced by 0.15 US\$/L. If this conversion rate were reduced by 10% (cellulose) and 2% (hemicellulose), this would increase the MESP by 0.3 US\$/L. Lastly, bioethanol, bio-lipids, and sugar alcohol production from oligosaccharides such as levoglucosan and cellobiosan have been extensively studied through hybrid pyrolysis and fermentation process.^{133–135} The TEA of the hybrid process is highly sensitive to anhydro-sugars yield from biomass pyrolysis, hydrolysate detoxification and inhibitors-tolerant yeasts. A summary of other techno-economic studies of producing high-value platform chemicals is provided in Table 7.

Co-production of biofuels and chemicals

The techno-economic attractiveness of biomass biorefinery can be enhanced through the co-production of biofuels and high-value platform chemicals. Advanced biorefineries utilize

all biomass fraction streams to produce diverse end products analogous to petrochemical refineries. Generally, bio-based chemicals have a higher market value than biofuels; however, fuel-based biorefineries have high industrial maturity and product output than chemical-based biorefineries. Many works have assessed the techno-economic feasibility of co-producing fuel and chemicals from biomass via biochemical conversion strategies. Hossain *et al.* examined a biochemical conversion of corn stover (658 kT/year) to co-produce bioethanol and furfural, which was separated after acid pre-treatment.¹³⁶ For a production volume of 15.54 million L/year ethanol and 7.9 kT/year furfural, the annual production cost for the joint product was estimated as 164 MUS\$. The total annual revenue of 167.66 MUS\$ was estimated, and about 8% was the contribution from the sales of furfural. The separation of furfural, a fermentation inhibitor, increases the ethanol yield and the NPV of the entire project from the US\$ 1700/MT furfural sales credit. Bbosa *et al.* evaluated the techno-economic feasibility of co-producing bioethanol and lignin-derived chemicals with a yield (wt%) of 28.4 catechol, 7.5 phenol, 11.7 cresols, 39 acetic acid, 0.12 formic acid, 0.02 furfural, and 0.04 acetaldehyde.¹³⁷ Bioethanol production by fermentation was integrated to hydrothermal liquefaction (HTL) to convert the lignin separated from the pre-treatment steps to value-added chemicals. For a 2000 MT/day corn stover producing 16 million Litre/year ethanol and lignin-derived chemicals, the TCI was 624.5 MUS\$, and the MESP was 0.27 US\$/L. The most influential factors on MESP were fixed capital investment, IRR, and feedstock cost. Among the chemical prices, cresols, catechol, and acetic acid were the most influential chemicals on the MESP, probably due to their higher market price and chemical yield. Although the techno-economics looks attractive, ethanol biorefineries adopting this integrated lignin-to-chemical strategy via HTL are still under development and susceptible to greater cost uncertainties. Zang *et al.* assessed the techno-economic feasibility of one-pot fractionation of switchgrass using biphasic solvent for furfural production and *in situ* extraction integrated to ethanol production.¹³⁸ Ionic liquid (choline chloride) fractionation of switchgrass produced cellulose-rich solids and hemicellulose-rich liquid phase following the precipitation of lignin. The solid stream was processed to bioethanol, while the liquid stream was converted *in situ* to furfural. For a production yield of 109 kg furfural, 97 kg lignin, and 124 kg ethanol per MT feed, the TCI was 445.4 MUS\$, and the total annual operating cost was 168.5 MUS\$, for which feedstock handling cost accounted for 38%. Furfural, lignin, and ethanol accounted for 34.7%, 18.1%, and 47.2% of total revenues, respectively. A minimum furfural selling price was estimated at 625 US\$/MT, assuming that the ethanol selling price was 0.67 US\$/L.

Table 7. Summary of techno-economic studies on the production of valuable platform chemicals

Processing steps	Plant capacity MT/day	Biomass type	Products	Feed cost* US\$/ MT	TCI* Million US\$		Operating cost* Million US\$/ annum	IRR %	Sensitivity analysis	Product cost* US\$/L	Reference
					(a)	(b)					
<ul style="list-style-type: none"> Feed preparation Liquefaction Saccharification Fermentation Separation and recover 	303	Corn grain	Lactic acid	180	(a) 130 (b) 147 (c) 113	(a) 118.1 (b) 125.1 (c) 84.4	13%	(a) Bacteria based (b) Fungi based (c) Yeast based	(a) 1.54 (b) 1.63 (c) 1.12	107	
<ul style="list-style-type: none"> Sugar milling Pre-treatment enzymatic hydrolysis Downstream recovery 	717.6	Bagasse+trash	Itaconic acid + electricity	10.44	404.15	23.78	9.7%		3.83	130	
<ul style="list-style-type: none"> Mechanical pre-treatment – Micronizing milling Saccharification 	74.7	Forest residue	Concentrated sugar	60.5	127.98	73.5	10%		\$0.53/kg	100	
<ul style="list-style-type: none"> Pre-treatment Enzymatic hydrolysis Acetogen fermentation Acid purification (4 scenarios) 	120650	Poplar wood	Glacial acetic acid	76.608	For the four scenarios: a 186 b 223 c 197 d 245	For the four scenarios: a 90.09 b 92.38 c 109.05 d 102.65	-	(a) Solvent: Alamine/DIBK, boiler—natural gas used (b) Solvent: Alamine/DIBK, boiler—natural gas and lignin used (c) Solvent: Ethyl acetate, boiler-natural gas used (d) Solvent: Ethyl acetate, boiler—natural gas and lignin used Purification step of GAC using alamine/DIBK was a more economical process and consumed 64% less energy as compared to ethyl acetate	When Alamine/DIBK used for purification –0.79 When ethyl acetate used for purification –0.92	105	

Abbreviations: DIBK, di-isobutylkerosene; GAC, glacial acetic acid; IRR, internal rate of return; TCI, total capital investment.
* All costs have been converted to 2021 equivalent.

Ranganathan studied five process scenarios to evaluate the techno-economic prospects of 100 000 L per day of 2G ethanol and co-products from rice straw.¹³⁹ The base scenario considered separate enzymatic hydrolysis and separate C5 and C6 fermentation where C6 fermentation produced only ethanol. For this case, the MESP was estimated at 0.627 US\$/L. For other scenarios that considered the co-production of chemicals from lignin and/or C5-rich fraction, the MESP range ranges from 0.25 to 0.563 US\$/L. The lowest MESP was observed in scenario 5, which considered the production of furfural from C5 and various biochemicals from lignin valorization via HTL. This shows that for economic viability, the biorefinery must produce non-fuel co-products to reduce the capital cost of the process. Although the TCI was highest in scenario 5 (195 MUS\$) due to the requirement of HTL reactor, the co-product credit from the sales of furfural and lignin-derived chemicals offset the production costs considerably. Among the various parameters tested, xylose conversion, and enzymatic hydrolysis yield are the key parameters found to be the most sensitive on MESP.

Similarly, five process scenarios were assessed for integrated biorefineries for cassava waste to co-produce bioethanol, succinic acid, glucose syrup, and CHP.¹⁴⁰ Scenario I and II co-process bagasse and cassava wastewater for biogas and bioethanol, respectively, while scenarios III–V co-produce bioethanol with either glucose syrup or succinic acid. The TCI was lowest for cases I and II, while it almost doubled for cases III–V due to intensive unit operations for the production and purification of chemicals. However, the total production costs for all cases are quite similar (285.3–331.2 MUS\$/year). The estimated MESP for the scenario producing bioethanol alone was 2.07 US\$/L, and it dropped to 1.67 US\$/L for the scenario co-producing ethanol with glucose syrup, and it further reduced to 0.77 US\$/L for the scenario co-producing ethanol and succinic acid. Klein *et al.* reported similar observations for the co-production of succinic acid with bioethanol from sugarcane bagasse biorefinery.¹⁴¹ Succinic acid production cost was 2.32 US\$/kg and presented a stronger probability of achieving an IRR greater than 12%. The integration of succinic acid production in a biorefinery co-producing bioethanol and CHP therefore has attractive economic returns. A summary of other studies is shown in Table 8.

Conclusions and future research perspectives

- Biofuels have been classified into generations (generation is a widely used indicator for biofuel production in terms of competition with food, arable land, and water), namely first, second, and third generations. First-generation

biofuels are believed to have a fierce impact on the nexus of water-food-land as their feedstocks are edible food matter (such as biodiesel from oil crops and bioethanol from corn and sugarcane). Second-generation feedstocks are considered to have less impact on the water-food chain as they are generally non-edible materials (such as agricultural residues, forestry wastes, energy crops, and municipal solid wastes), but great concern still exists about the use of arable land and the associated ecological consequences.

- Additionally, technical challenges (low yield, product selectivity, product toxicity, and materials recovery) have been identified with the biochemical conversion of second-generation biomass resources. The recalcitrant lignocellulosic structure of the feedstock requires sophisticated processing steps needing severe pre-treatment for depolymerization and amenability to downstream bioprocessing. All these considerations taken together have slowed down the rapid commercialization of second-generation biofuels as cost-competitive fuels cannot be produced without adequate government incentives despite the massive availability of lignocellulosic biomass.
- Biofuels have extensive use; however, the technologies for their production on a commercial scale are yet to be fully matured. The challenges facing the rapid commercialization and cost-competitiveness of biofuels include:
 - a Cheaper available fossil-derived fuels with high cetane and octane numbers.
 - b The hydrophobic nature of fossil-derived fuels makes their transportation and logistics economically attractive. It is difficult and expensive to reproduce for biofuel like ethanol, which can readily absorb water during transportation in pipelines and may require extraction units at the fuel stations, adding to the cost per liter.
 - c The heterogeneous nature of second-generation biomass feedstocks is such that existing bioprocessing technology for first-generation biomass may have to be modified to obtain similar end products and grades. The variation in the processing steps of different biomass materials may require different infrastructure investments, which could impact the product compositions, resulting in higher CAPEX and OPEX.
 - d The major failure in setting up commercial plants may be attributed to the dearth of matured technologies, an underestimation of the total COP, and an overestimation of the efficiency of the process. Poor understanding of the market pathways for biofuels, continuous fluctuations in fossil fuel prices and insufficient government policies in encouraging biofuels has led to

Table 8. Summary of techno-economic studies for the co-production of biofuels and chemicals

Processing steps	Plant capacity	Biomass type	Products	Feed cost*	TCI*	Operating cost*	IRR	Remarks	Product cost*	References
Units	MT/day			US\$/MT	Million US\$	Million US\$/annum	%		US\$/L	
<ul style="list-style-type: none"> Pre-treatment (liquid–solid separation & conditioning) Ethanol fermentation, Ethanol recovery for the liquid stream. Enzyme hydrolysis, acids fermentation, and acid recovery for the solid stream 	18.5	Corn stover	Ethanol Succinic acid Acetic acid	37.34	484	156.8	46%		Ethanol: 0.35 Succinic acid: 1.94	101
<ul style="list-style-type: none"> Pre-processing Organosolv cooking Enzymatic hydrolysis Fermentation Separation 	2350	Hardwood	Ethanol Lignin Furfural Acetic acid		814.5	146.65	10%	Steam and power consumption: +30% leads to +0.2 in MESP, –30% leads to –0.19 in MESP Conversion rate in the enzymatic hydrolysis: +6% cellulose and hemicellulose leads to –0.17 in MESP, –10% (cellulose) and –2% (hemicellulose) leads to +0.34 in MESP Conversion rate of hemicellulose sugars in the fermentation: +85% in C6 sugars leads to –0.21 in MESP, –35% in C5 sugars leads to +0.18 in MESP Total capital investment: +30% leads to +0.53 in MESP Discount rate: +10% leads to +1.23 in MESP	Ethanol (MESP): 0.91 Lignin: 0.27 Furfural: 0.02 Acetic acid: 0.01	110
<ul style="list-style-type: none"> N-methyl morpholine oxide pre-treatment Anaerobic co-digestion Upgrading of biogas 	25	Forest residues + Organic fraction of municipal solid waste	Methane CO ₂ Lignin rich digestate		358.7	256.21	24.14%	Minimum plant capacity of 50000DW tons forest Residues per year is financially viable	Methane (MESP): 1.92/kg CO ₂ – 0.004/kg Lignin rich digestate: 0.04/kg	97

Abbreviations: IRR, internal rate of return; MESP, minimum ethanol selling price; TCI, total capital investment.

*All costs have been converted to 2021 equivalent.

the downfall of the new start-ups. However, the present condition is that slowly, many developing nations like Brazil and parts of China have completely turned to biofuels such as bioethanol for transportation purposes, and other countries are also taking the lead. This type of competitive market must be developed so that the existing technologies show maturity with time. This will ensure a steady decline in the COP and conservation of fossil fuels.

- e The outlook for biomass energy as a business strategy on a local, national, and global scale is promising. The economic viability of bioenergy production largely depends on the existing price of fossil fuels. Process efficiency and biomass supply security and cost drives the economic potential of biofuel/bioenergy production. Technological advancements should be made by understanding the production capability of the biomass, the availability of the biomass, and the homogeneity of the available biomass, to attain stability in biofuel prices at par with present-day fossil fuels.
- Techno-economic analyses for second-generation crops such as rice husks and wheat straw are scarce. These crops contribute substantially to agro-waste, which can be utilized effectively for biofuels. Assessing the technology and economics of these crops can pave the way for understanding the suitability of utilizing this biomass in large-scale operations.
- The TEA analysis in the literature mostly comprises developed nations and a few developing countries like Brazil. The abundance of biomass is mostly found in Asian and African countries, which are still struggling to develop frameworks, technologies, and markets for biofuels and biochemicals. These countries should initiate projects and develop statistical data to help unlock the full potential of the bio-economy.
- Many governments continue to set and expand biofuel mandates and develop roadmaps to achieve bio-economy targets. As such, there are soft tools like carbon credits, tax rebates, and emission trading schemes, besides favorable policies, which can support biomass conversion technology scale-up and sustain the drive on biofuel and commodity chemical production from biomass. If these tools are sustained over a long period, cheaper bioprocess technology can be developed, and more investments in commercial-scale biofuel production can be attractive.
- There appears to be more understanding and knowledge of the factors (both internal and external) critical to the techno-economic sustainability of bioprocesses; hence, new and upcoming investments and technology developers in the biorefining industry can learn from the failures of unsuccessful attempts of previous investments. If we put our learning over the last few decades in the biofuel industry into use, there is the prospect of

developing bioprocesses and bioproducts with attractive production costs and prospects for profitability.

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