

Review

A Critical Review of the Sustainable Production and Application of Methanol as a Biochemical and Bioenergy Carrier

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Abstract: There is a growing interest in the production of biofuels and biochemicals from renewable biomass. Biomass in the form of woody and agricultural residues, municipal solid waste and other organic refuse is becoming popular as a feedstock for biofuel and biochemical production through thermochemical and biological routes. Methanol, a widely used industrial chemical, also has clean fuel properties due to its high-octane number, low flammability, low emissions and high engine performance. This paper performs a comprehensive review of different thermochemical and biological processes able to sustainably convert waste biomass to methanol. This article also evaluates the techno-economic assessment and lifecycle analysis of different processes used for methanol production. The article discusses the effects of process parameters and biomass properties on methanol production and utilization. Finally, the article concludes with recommendations on the eco-friendly aspects of methanol for use as a clean fuel and chemical derived from renewable organic bioresources.

Keywords: biomass; methanol; techno-economic analysis; lifecycle assessment



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1. Introduction

Methanol production has wide applications for electricity generation and hydrogen transportation. In addition, methanol has many applications including dimethyl carbonate and dimethyl ether production [1]. Recently, methanol production from syngas through catalytic Fischer-Tropsch synthesis, which is not fully carbon-neutral, has raised environmental concerns. Production of methanol from biomass generates many benefits such as sustainability and commercial viability [2]. Green methanol can be generated from different bio-based resources and clean technologies including gasification, reforming, stripper-off gas and power-to-liquid (Figure 1). On the other hand, biomethanol refers to green methanol produced from bio-based sources through bioprocesses with the involvement of microorganisms and enzymes. As shown in Figure 1, e-methanol represents green methanol which is produced from CO₂ capture as a byproduct of the electrolysis process to generate hydrogen. AlNouss et al. [3] developed the gasification of palm wastes for methanol production and investigated a techno-economic and environmental analysis. The focus of the study is CO₂ capture by deploying CaO to maximize methanol production and profit. It is widely acknowledged that fuels derived from biomass resources can reduce CO₂ emissions and partially replace fossil fuels. Regarding the economic aspect, the project life, methanol and dimethyl ether prices affected the economic feasibility of the biomass conversion process [4]. In consideration of the current energy consumption trends, efficient utilization of biomass resources has increased in both the industrial and academic sectors. Galusnyak et al. [5] examined a new membrane process design from secondary biomass for biomethanol production. As the results show, the utilization of exhausted olive pomace as

a biomass source would enhance the detailed distribution of the global warming potential impact category.

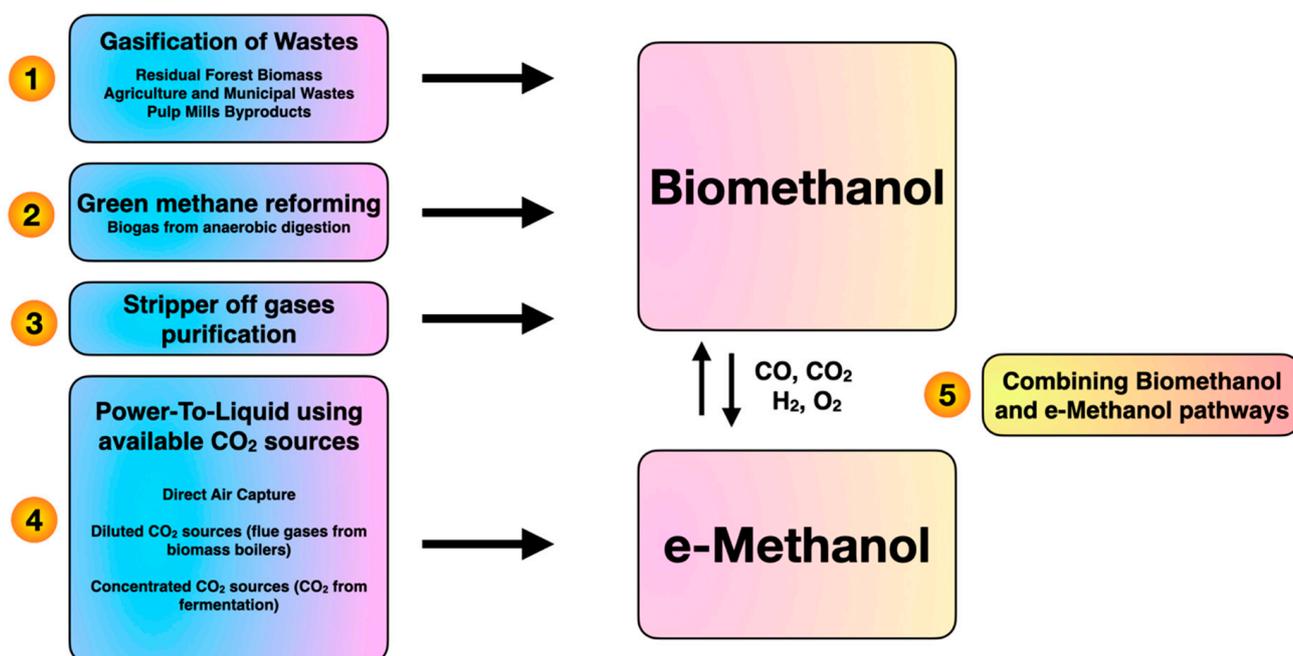


Figure 1. Main pathways for methanol production. (Adapted from Pio et al. [6]).

Commonly, methanol, one of the ‘mega’ industrial platform chemicals, is produced from different feedstocks such as natural gas or coal. From Figure 2, the current worldwide methanol production capacity is 198 Mt/year, which is mostly employed for producing formaldehyde and plastics. Methanol is mainly produced from syngas (H₂ and CO) via steam reforming of natural gas as well as coal gasification. The coal-to-methanol process significantly increases the energy consumption and CO₂ emission to co-produce syngas and hydrogen [7]. The naval industry is also another fast-growing sector to consume methanol. Methanol production is predicted to follow the increasing trend up to 2050 since green methanol is attracting great interest as a sustainable energy carrier [6]. Chen et al. [8] proposed a novel hybrid process of coal gasification and coking to produce methanol. They investigated the effect of the coke gasification reaction and carbon tax on the integrated process economy. According to a detailed techno-economic analysis, the internal rate of return for coal gasification is 22.5% with more economic benefits in comparison with the coal-to-methanol process.

The conventional synthesis of methanol is based on the reforming of fossil sources, which has raised environmental issues due to greenhouse gas emissions. Hence, it is important to generate methanol from biomass feedstocks and thermochemical processes. Kasmuri et al. [9] investigated the production of methanol from renewable sources via a thermochemical reaction. The dynamic control system was employed to maintain a high yield of methanol production in pyrolysis. In this article, an effort has been made to summarize the literature concerning the sustainable production of methanol as a renewable energy carrier. Different applications of methanol are thoroughly discussed together with the different processes that are available for methanol production. The production processes of biomass-derived methanol (referred to as biomethanol or green methanol) and their opportunities and challenges are thoroughly discussed. Recently, the concept of integrating thermochemical and biological processes has been gaining interest. This integration is important to ensure the effective utilization of resources, mitigation of emissions, recycling of wastes, proper recovery of byproducts and a reducing in the energy input [10]. These aspects are critical to ensure a circular economy and a closed-loop biorefinery platform where

the raw materials, products, byproducts and effluents (solid and liquid) are responsibly managed to reduce the carbon footprint and waste generation.

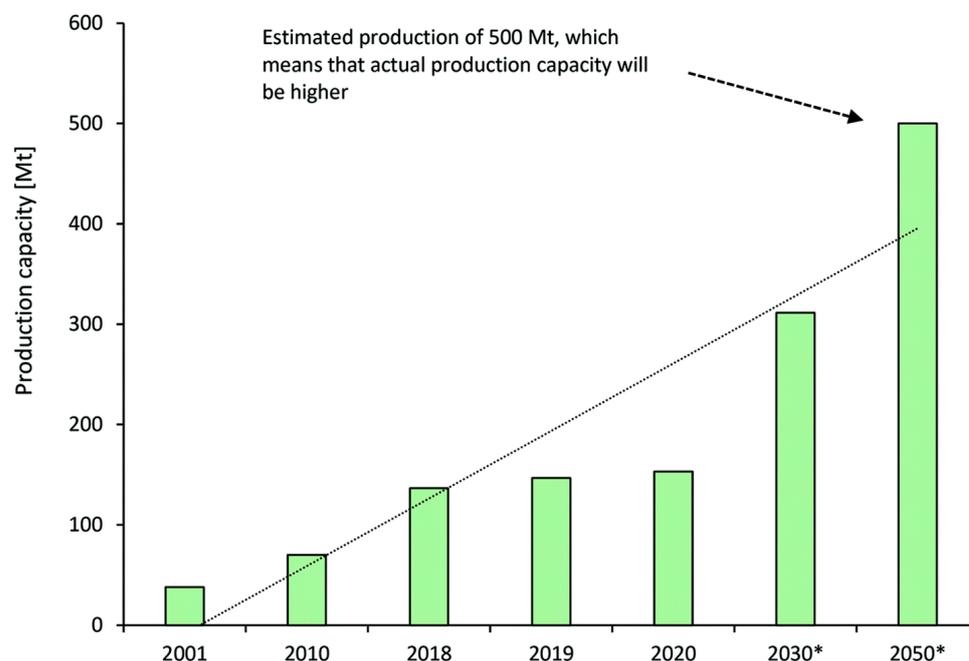


Figure 2. Worldwide production capacity and prediction for methanol in million metric tons (Mt). * Represents predicted production capacity. Reproduced with permission from Pio et al. [6].

2. Potential of Methanol as a Renewable Energy Carrier

2.1. Industrial Applications of Methanol

Methanol has a variety of industrial applications in chemical industries, such as supplementing fuel oil, acting as an antifreeze agent in pipelines, and being used as fuel cells. Moreover, methanol is the simplest organic liquid hydrogen carrier and acts as an energy storage system for a variety of portable power applications. In terms of the transportation sector, Table 1 makes a comparison of biodiesel and gasoline (hydrocarbon fuel) in terms of energy density and average octane numbers. Methanol shows a wide range of downstream applications such as the substrate for producing biodiesel through transesterification and organic solvents. As shown in Figure 3 methanol can be suggested as a promising substrate in various sectors such as the generation of fuel, chemicals and light olefins.

Table 1. Summary of energy density and octane number for different alcohols. Reference: Kasmuri et al. [11] and Kim et al. [12].

Fuel	Energy Density (MJ/L)	Octane Rating
Methanol (CH ₃ OH)	16	98.65/108.7
Ethanol (C ₂ H ₅ OH)	20	99.5/108.6
Propanol (C ₃ H ₇ OH)	24	108/118
Butanol (C ₄ H ₁₀ O)	30	97/103
Dimethyl ether (C ₂ H ₆ O)	18.9	-
C ₈ H ₁₈ (2,2,4-Trimethylpentane)	33	85–96/90–105

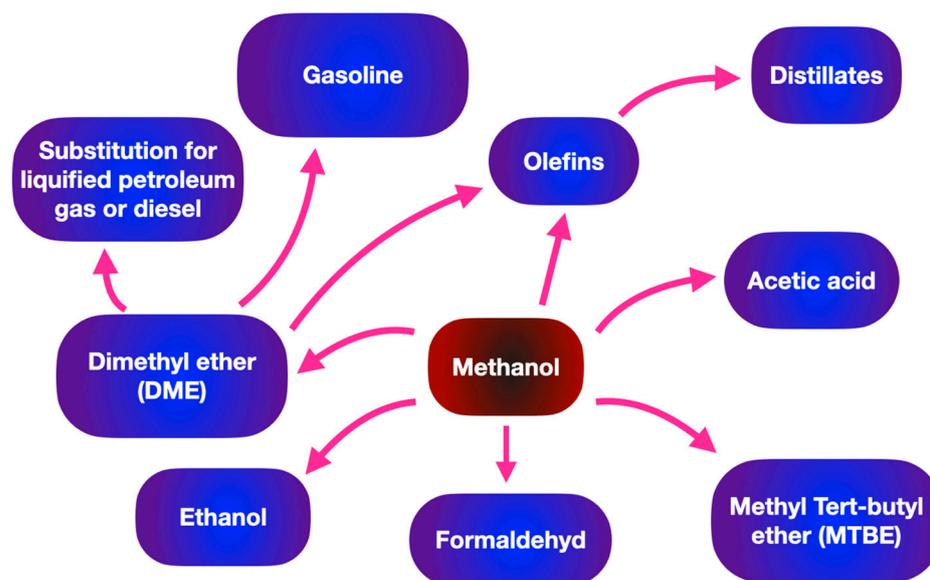


Figure 3. Wide range of applications of methanol in fuel and chemical industries. (Adapted from Sarangi et al. [13]).

2.2. Techno-Economic Analysis of Methanol Production

The current study reviewed the techno-economic assessment and lifecycle analysis of methanol production as a clean fuel using biomass as a renewable resource. It also discusses different thermochemical and biological processes to convert waste biomass to methanol. Table 2 shows a list of some reported thermochemical and biological processes for methanol production.

Table 2. Some reported thermochemical and biological processes of methanol production.

Approach	Concluding Remarks	Future Prospects	Reference
Production of bio-methanol as potential renewable energy	Methanol can be produced from additional reactions of decomposed biomass material. Improvement in the electrolysis process and renewable electricity favors methanol synthesis.	In gasification and methanol synthesis the separation of gas and solid needs to be considered to reduce the environmental impacts.	[14]
Methanol fuel production	Methanol production and techno-economic viability are influenced by feedstock characteristics, initial investment, and plant location.	Dimethyl ether alongside methanol has a huge potential to be a new generation of fuel source owing to its low calorific value, low density, and low viscosity.	[15]
Methanol production from different renewable sources and thermo-economic analysis	The thermo-economic analysis considering different scenarios confirm that the best economic results are obtained with hydroelectric source.	Considering future methanol selling prices of 500 €/ton, the economic performances can be further improved via the European financial incentives for biofuel production.	[16]
Sustainable production and application of methanol	The main advantage of biomass-derived methanol is the eco-friendly aspects of methanol production as a clean fuel.	Biomethanol is a future bioproduct for value-added industries due to its diverse applications.	This study

In developing countries, producing green methanol as a new renewable energy source by using biomass feedstock leads to economic savings. As stated by Zhang et al. [17]

methanol production via steam gasification of lignocellulosic biomass and biochar seems to be the most efficient raw material to produce methanol. The outcome of the techno-economic analysis (TEA) revealed that the internal rate of return obtained in the biochar scenario is higher than using pine biomass at the same plant scales. The authors concluded that methanol produced from waste biomass is unfortunately not commercially competitive with the traditional methods of producing methanol. The detailed distribution of total product costs affected by feedstock at different scales is displayed in Figure 4.

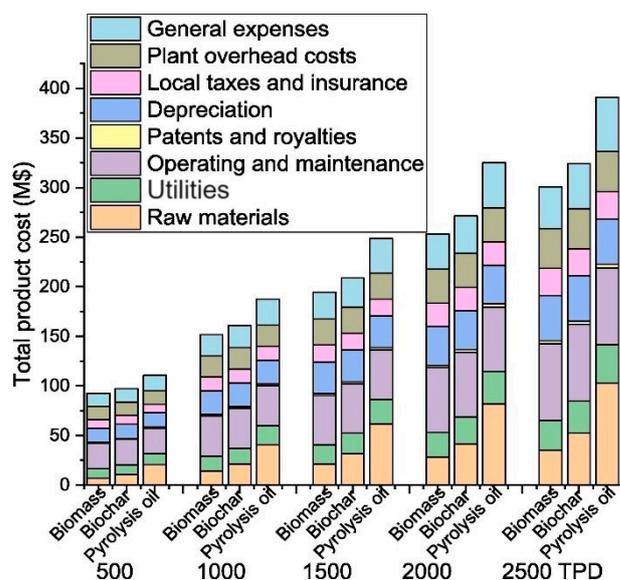


Figure 4. Effects of different feedstocks on the total product costs at various plant scales. TPD represents tons per day. Reproduced with permission from Zhang et al. [17].

Choe et al. [18] investigated the production of methanol by considering different land-fill gas management pathways. TEA was performed to find out the most reliable process for methanol production from an economic perspective. It was proved that the operating expenditure reduction, particularly hydrogen cost and unit electricity price reduction, must be determined to be economically feasible. Table 3 represents current studies about techno-economic assessment for sustainable methanol production. Ramachandran et al. [19] conducted a TEA on the hybrid steam reforming reaction, which involved the co-utilization of glycerol and natural gas to generate synthesis gas under reforming conditions. The resulting compressed synthesis gas was subsequently converted into green methanol, and the capital cost investment was assessed considering the overall equipment expenses. The study concludes that green methanol is not economically competitive with conventional methanol unless specific measures or corrections are implemented.

Table 3. Literature survey of sustainable production of methanol from different biomass wastes.

Technique	Plant Size	Feedstock	End Product	Production Cost	Reference
Biomass torrefaction coupled with gasification	Processing rate of 66.4 tons/h	Bagasse	Electricity and /or methanol production	The annual production cost was estimated at USD 140 M/y	[20]
Sugarcane biorefineries with fossil fuel co-combustion	Processing rate of 421,000 t/y	Lignocellulose	Methanol production of 82,700 t/y and electricity production of 3.5 GWH/y	272.6 USD M/y	[21]

Table 3. Cont.

Technique	Plant Size	Feedstock	End Product	Production Cost	Reference
Tri-reforming of CH ₄ integrated with solid oxide fuel cell	Annual cost of USD 277,742 /y	Methane	Methanol production	5.4 USD M/y	[22]
Synthetic methanol production from H ₂ and CO ₂	243 MT/day H ₂ and 1978 Mt/day CO ₂	CO ₂ and H ₂ feedstocks	Methanol production is 1190 Mt/day	The minimum fuel selling price of methanol was between USD 0.61/kg and USD 0.64/kg	[23]

2.3. Lifecycle Assessment of Methanol

Biofuels are alternatives to fossil fuels and their environmental impacts over the entire production chain are evaluated by lifecycle assessment (LCA). The main objective is to analyze existing LCA studies and highlight key methodological approaches to critically evaluate existing biomass to biofuel pathways. Morales et al. [24] also investigated a consequential LCA of biofuel generation in Denmark considering two cases. The authors concluded that seaweed production was recognized as the most energy-sensitive processing part and the system has the potential for technological development. Mu et al. [25] evaluated a well-to-wheel LCA on algal biofuel production to identify key parameters that determine nutrient use. The authors revealed that most synthetic fertilizer inputs are eventually discharged within wastewater to the environment. LCA of macroalgae cultivation for producing biofuel was studied by Aitken and co-authors [26]. The investigation aims to identify energy conservation and environmental effects of the cultivation and processing of bioethanol production from marine macroalgae and biogas. As the authors point out, the impact of CO₂ emission reduction can be limited unless industrial-scale models are used. Sajid et al. [27] investigated biodiesel production from *Jatropha* oil for damage categories of climate change and ecosystem quality. The authors showed that the production process from *Jatropha* oil has fewer environmental side effects than that from the waste cooking oil process. Sills et al. [28] quantified the environmental performance of algal biofuels to estimate ranges of expected values of LCA metrics. The ranges of reported LCA impact categories showed that global warming potential values aligned with algal biofuel production together with anaerobic digestion are quite uncertain. Table 4 compares biochemical and thermochemical routes in terms of environmental impacts and economic indicators.

Table 4. Economic and environmental aspects of methanol production via biochemical and thermochemical processes.

Process	Environmental Impact Analysis	Economic Evaluation	Reference
Methanol production from wood biomass	Both production processes had a much lower CO ₂ emission compared to fossil fuel-based methanol production.	The rectisol-based acid gas removal unit used for removing sulfur and CO ₂ from syngas corresponds to 20% of the total investment costs.	[29]
Biomethanol production from palm wastes steam gasification	The reduction in CO ₂ using CaO was effective with a slight increase in the total cost of the plant.	The total capital cost is approximately USD 120 M.	[3]

3. Potential of Using Biomass for Methanol Production

3.1. Types of Biomasses

Biomass refers to organic matter derived from carbon structures that can be employed as a renewable energy source. The utilization of biomass as a fuel source has been gaining increasing attention as a sustainable alternative to fossil fuels. There are various types of biomasses, including agricultural residues, wood waste, energy crops, municipal solid

waste, and aquatic biomass. Agricultural residues are residues left after harvesting crops such as corn, wheat, and rice. Wood waste is generated from forestry operations, sawmills, and wood processing industries. Energy crops refer to crops specifically grown for energy production, such as switchgrass and sugarcane. Municipal solid waste is waste generated from households and commercial establishments. Finally, aquatic biomass is derived from plants and animals living in water bodies such as seaweed and algae [30]. Understanding the different types of biomasses is crucial in identifying the most appropriate feedstock for different applications. Alternative energy sources derived from biomass are not only environmentally friendly but also sustainable due to their wide availability across the globe. A range of plant and animal-derived biomasses can be harnessed as sustainable sources to generate gaseous, liquid, and solid fuels [31]. Examples of waste biomass that could be utilized for this purpose include municipal household waste, agricultural waste, forest residues, abattoir waste, bio-industrial waste, and human excreta. Different thermochemical and biochemical processes can be used to modify these waste biomasses to produce high-calorific value gaseous and liquid fuels. However, prior treatment may be required, especially for biomasses rich in lignocellulose, to attain optimal conversion efficiency. Various pretreatment methods, including physical, chemical, biological, and combined approaches, have been developed [32]. Chemical pretreatment is relatively expensive and not environmentally sustainable [33]. Among these pretreatment methods, combined treatments have demonstrated greater success compared to individual pretreatment methods.

Various types of biomasses such as wood waste, agricultural residues, energy crops, and algae, can be transformed into methanol through two main reactions known as thermochemical and biochemical conversion. For instance, during gasification, the biomass is heated under an inert atmosphere to produce a gas mixture consisting of H_2 , CO , and CO_2 [34]. This gas mixture, also known as syngas, could be converted into methanol through a series of catalytic reactions. The use of biomass for methanol production offers several advantages over traditional fossil fuel-based production methods, including lower greenhouse gas emissions and reduced dependence on non-renewable resources.

3.2. Biomass Composition

Most biomass feedstocks consist of cellulose, hemicellulose, and lignin, which exhibit distinct properties and behaviors during biomass conversion. Among these components, cellulose is the most reactive and generally produces more gases and char. On the other hand, lignin is more stable and tends to yield more solid and liquid products. Lignocellulosic biomass, such as natural fibers and agricultural residues, are more economically viable for slow pyrolysis due to their higher lignin content [35]. Lignin has a higher heating value and produces valuable products such as phenols, which contain less oxygen compared to cellulosic biomass and are used as chemical feedstocks [36]. Additionally, lignocellulosic feedstocks require less energy to break down during pyrolysis compared to other biomass feedstocks with lower lignin content, such as algae or municipal solid waste. Furthermore, the high carbon content of lignin-rich biomass makes it an attractive feedstock for biochar production since lignin acts as a glue to hold the lignocellulosic fiber together. Therefore, lignocellulosic feedstocks have significant potential as a potential and cost-effective source of bioenergy and value-added products.

Biomass is primarily composed of hemicellulose, cellulose, lignin, and a small amount of inorganic material. The composition i.e., contents of hemicellulose, cellulose and lignin in biomass can vary. These three components are critical to the stability of biomass [37]. The configuration and transformation of pyrolyzed biomass depend on its composition. When lignin is pyrolyzed, it produces less oil compared to hemicellulose and cellulose. In lignocellulosic biomass, the maximum reduction in cellulose occurs at $400\text{ }^\circ\text{C}$, while for hemicellulose it occurs at $268\text{ }^\circ\text{C}$, and for lignin, it occurs at $900\text{ }^\circ\text{C}$. Lignin adds greatly to the char residue during pyrolysis [38]. The optimal temperature for producing the maximum amount of oil also depends on the composition of the biomass being used. A study conducted by Raveendran et al. [39] demonstrated the comparability of pyrolyzing

lignin, cellulose, rice husk, and bark. The performance of biomass during pyrolysis can be influenced by the presence of oxygen and heteroatoms. Higher oxygen and heteroatom content generally result in increased reactivity. Nevertheless, a separate study has suggested that the oxygen content has a moderate effect on the biomass subjected to pyrolysis [40]. The biochemical composition of the biomass introduced into the biorefinery is crucial for the effective production of biofuels and energy yield, making it a significant driver for biorefinery operations.

3.3. Pretreatment of Biomass for Higher Conversion Yield

Pretreatment is a crucial stage in the biotransformation of lignocellulosic biomass into biofuels including methanol. The pretreatment selection method relies on various parameters, including the composition of the biomass, production cost, and energy demand. The optimization of pretreatment methods and the development of novel ones are essential for enhancing the effectiveness of biotransformation and reducing the production cost of biofuels [41]. Figure 5 illustrates the transformation of complex lignocellulose biomass into simpler forms during pretreatment. Lignin, a complex polymer that provides core strength in tissue structure, is removed during pretreatment. Cellulose crystallinity is also reduced to enhance the accessibility of enzymes and microbes for the effective transformation of biomass. The main objective of pretreatment is to mitigate the inhibitory physicochemical factors that impede the conversion of biomass into biofuels. By doing so, it aims to minimize the energy requirements and production costs associated with biofuel production [42].

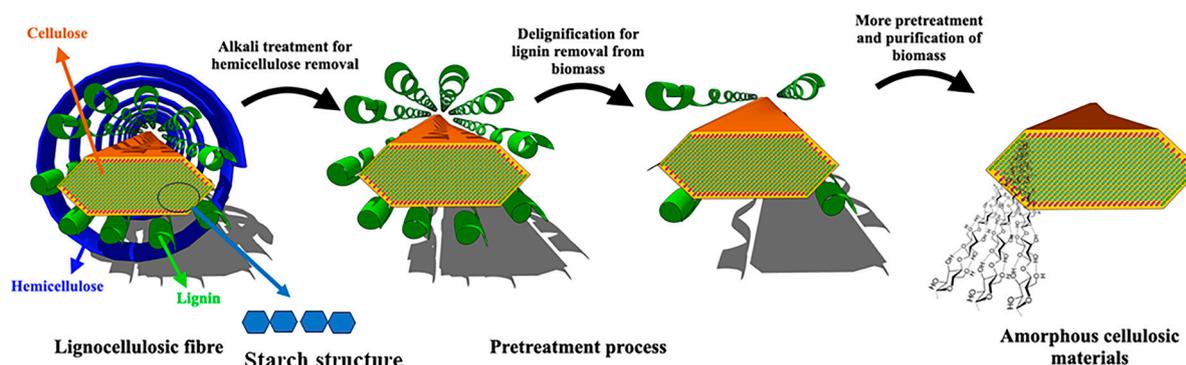


Figure 5. Different phases of biomass decomposition during pretreatment.

Pretreatment techniques can be categorized into various types, including physical, chemical, physicochemical, biological, or a combination thereof. Physical methods encompass milling, ultrasonication, freezing, comminuting, extrusion, and microwaving. Chemical methods involve treating biomass with acids, alkalis, oxidizing agents, ozonation, organic solvents, or chemical catalysts. Physicochemical methods combine physical and chemical processes, such as acid/alkali treatment coupled with ultrasonication. Biological methods involve the pre-incubation of biomass with intact microbial cells or enzymes derived from microorganisms. Combined methods utilize two or more of the aforementioned approaches to achieve synergistic effects and enhanced results [43].

The proportion of lignin and cellulose within lignocellulosic biomass plays a crucial role in determining the suitable biomass for biotransformation processes. Biomass with a lower lignin content is preferred due to the inhibitory effect of lignin on the transformation process. For instance, biomass sources like rice leaves and straw are favored over materials like sawdust or wood chips, which have relatively higher lignin content. Furthermore, the presence of ferulic acid in lignin hydrolysate can impede microbial activity during the biotransformation of such biomass. Therefore, reducing lignin content during pretreatment is crucial for the effective biotransformation of lignocellulosic biomass [33]. High cellulose biomass, such as corn stover, switchgrass, and wood chips, contain more easily accessible sugars and are generally considered more desirable for biofuel production [44]. This is

because cellulose is a polysaccharide that can be broken down into glucose and other sugars using enzymatic processes, which can then be fermented into biofuels [45].

Moreover, the development of novel pretreatment methods and the optimization of existing ones are still ongoing. Researchers have shown that using ionic liquids as solvents for the pretreatment of lignocellulosic biomass can significantly reduce the energy demand and production cost of biofuels. Similarly, using supercritical fluids, such as water and CO₂, for pretreatment has shown promising results [46]. In addition, the use of microwave-assisted pretreatment has been reported as an efficient technique for enhancing the biotransformation of biomass into biofuels [47].

4. Sustainable Production of Methanol

Green methanol can be generated from lignocellulosic biomass via thermochemical and biochemical routes as shown in Figure 6. Among the dominant thermochemical technologies, pyrolysis, gasification and liquefaction are common approaches for lignocellulosic biomass conversion to biofuels which also include methanol as a bioproduct [48]. It should be noted that CO, CO₂, H₂ and CH₄ are some gaseous byproducts obtained from gasification and pyrolysis processes. CO and H₂ (components of syngas) can be further converted into methanol through the catalytic Fischer-Tropsch process. On the other hand, catalytic reforming processes also transform methane into methanol. However, these gas-to-liquid processes are secondary processes that rely on primary biomass conversion processes such as gasification, liquefaction and pyrolysis.

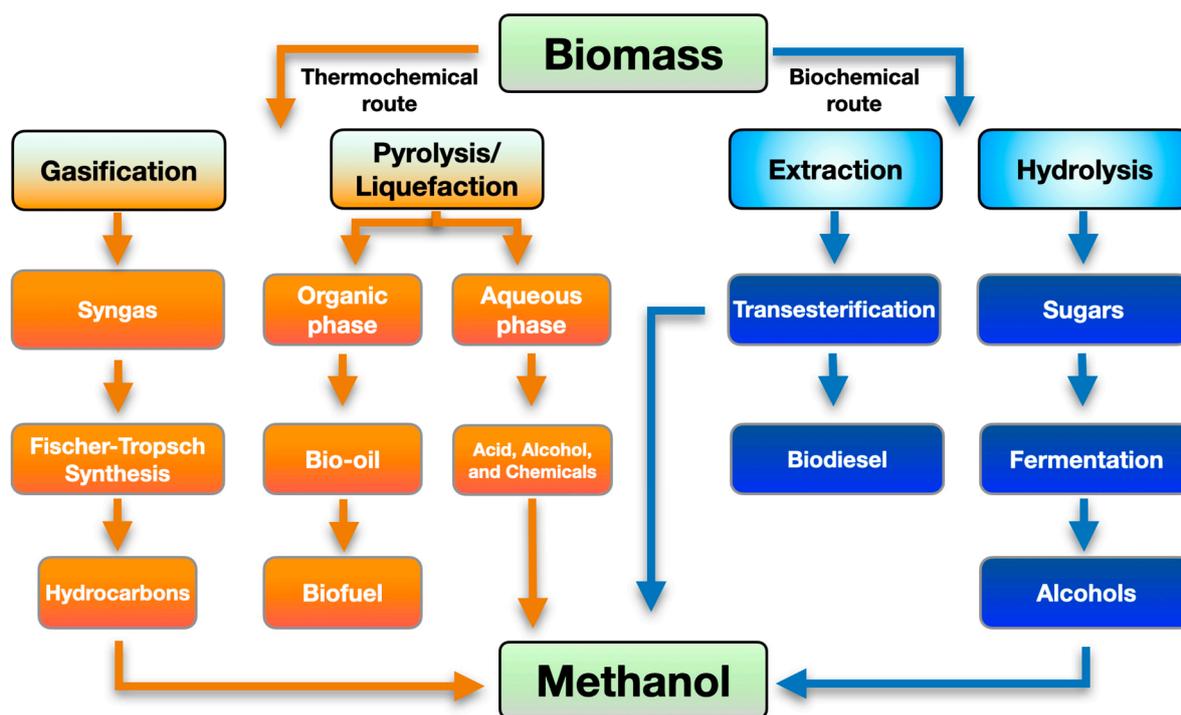


Figure 6. Thermochemical and biochemical processing of biomass to green methanol. (Adapted from Sikarwar et al. [34]).

4.1. Pyrolysis

Bio-alcohol fuels and chemicals including methanol, ethanol and butanol can be produced from the pyrolysis of biomass in the absence of oxygen, especially in the aqueous phase of the liquid product. Table 5 presents the various types of pyrolysis. Kamarudin et al. [49] carried out the production of methanol from biomass waste via pyrolysis. It was observed that to increase the yield of methanol and ethanol, a low temperature and short gas residence time is mandatory in the process.

Table 5. Classification chart for pyrolysis. Reference: Wang et al. [50].

	Slow Pyrolysis	Fast Pyrolysis	Vacuum Pyrolysis
Reaction conditions			
Heating rate (°C/s)	0.2–12	12–300	>1100
Particle size (mm)	7–52	<2	<0.5
Vapor residence time (s)	460–570	0.7–12	<0.7
Product yield (wt% wet basis)			
Liquid	40	68–83	90
Char	40	17–28	18
Gas	37	17	7

4.2. Gasification

Gasification changes carbonaceous biomass materials, which are pretreated into methanol. The pretreatment is due to an increase in the exposed surface area, where the large polymeric molecules are partially oxidized at ultra-high temperatures (800–900 °C). During gasification, the syngas formed mainly consist of CO and H₂ with low concentrations of methane. Various gasifiers have been designed and the generated syngas are influenced by biomass and reactor type. Table 6 lists some characteristics of different gasifier types for different biomass feed. To guarantee minimal impurities and byproducts, different downstream strategies are used to produce pure syngas. The tar and the gaseous impurities are separated by transition metal catalysts through high-temperature barrier filters. The studies on the gasification of biomass for methanol production were summarized in detail (Table 7).

Table 6. Classification chart for gasifiers. Reference: Amigun et al. [51].

Gasifier Reactor	Packed Bed	Fluidized Bed	Entrained Bed
Product temperature	Low (435–620 °C)	Medium (920–1070 °C)	High (1350–1700 °C)
Oxidant demand	Low	Medium	High
Ash properties	Dry ash and slagging	Dry ash and agglomerating	Slagging
Size of coal feed	8–52 mm	7–13 mm	<120 µm
Acceptability of fines	Limited	Good	Unlimited
Other characteristics	Methan, tar, and volatiles present in syngas	Low carbon conversion	Pure syngas High carbon conversion

Table 7. Summary of gasification reactions for methanol production from different feedstocks.

Feedstock	Methanol Yield	Comments	Reference
Forest residues and lignin	62–66%	Catalytic gasification provides operational advantages at production costs.	[52]
Lignite	40–60%	Simulations show the proposed low-carbon methanol synthesis plant is an effective alternative for methanol valorization.	[53]
Rice straw	14.01 g/kg biomass for gasification temperature of 900 °C	It was shown that the methanol yield rises owing to a significant growth in gasification temperature.	[54]
Biomass and plastics (polyethylene terephthalate)	Methane conversion of 98%	Methanol production costs rely on the purity of the syngas as the feed gas.	[55]

4.3. Methane

To develop a platform for methane-to-methanol conversion, Kulkarni et al. [56] reported a key enzyme that participated in natural gas consumption. Cell mass analysis showed a maximum methanol formation of 308.70 mg/L on pure methane. Methane fermentation was carried out in an optimized reaction mixture and resulted in 1.87-fold higher specific methanol productivity. Methanol can be produced biologically through catalytic oxidation. As stated by Sahoo et al. [57] a sequential two-stage integrated process is used for the reduction of CO₂ into methanol. It can be concluded that the maximum methanol production is dependent on the partial pressure of CO₂ in the headspace of a semi-batch stirred tank reactor. Biotransformation approaches have been recognized as a green/clean strategy to produce methanol over methane. Patel et al. [58] reported the immobilized co-culture within polyvinyl alcohol for methanol production using methane. The results indicated that a significant decrease of 90% in residual methanol production might be associated with immobilization methods of methanotrophs. Table 8 summarizes the application of methane as potential feedstock to produce biofuel such as methanol.

Table 8. Summary of the studies on the production of methanol over methane.

Feedstocks	Reaction Conditions	Key Findings	Reference
Glycerol and methane	Gasification at 500 °C under 35 bar Reforming at 900 °C under 20 bar	TEA confirmed that fuel prices and total cost have a significant effect on the average cost of methanol.	[59]
Different feedstock and agricultural residues	Anaerobic digestion at psychrophilic temperature (25 °C)	Methanol yield via anaerobic digestion was strongly dependent on the hydraulic retention time.	[60]
Biowaste-derived sugars and methane	Integration of biogas to biomethanol for up to 120 h at 30 °C	The integration of dark-fermentative and anaerobic digestion yielded 13.8 mmol/L of methanol via methanotrophs.	[61]
<i>Nitrosomonas eutropha</i> cell biomass	Biotransformation reaction at 28 °C under 0.7 bar	The methanol conversion rate was dependent on enzyme activity and its maximum yield was found to be 103 mg/L.	[62]

4.4. Catalytic Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis (FTS) has been investigated through heterogeneous catalytic reactions and as a sustainable process to generate synthetic liquid fuels. It has been estimated that the bioethanol produced by FTS can be much less expensive than the ethanol produced by hydrolysis. Santos et al. [63] conducted TEA of FTS and direct natural gas-to-methanol processes to investigate the effects of tail gas emissions and methane recycling in a compact plant footprint. The simulation results revealed that increasing the tail gas recycle ratio results in an increase in the C₅₊ yield. It should be mentioned that increasing the methane recycle ratio leads to an increase in the yield of methanol.

Khademi et al. [64] employed an optimal design of natural gas tri-reforming to generate appropriate syngas for Fischer-Tropsch and methanol synthesis processes. It is noteworthy that the syngas ratio is almost greater than 1.5, which is proper for application in methanol units. According to the optimization results the methanol conversion and reaction rate increase at high CO/CO₂ ratios. Yue et al. [65] prepared bimetallic Co-Cu supported CeO₂ to produce alcohols under 3 MPa at 180 °C. During the photothermal catalytic reaction, the yields of methanol, ethanol, and isopropanol increased to 33, 15.8 and 6.6 mmol/g_{Co}/h, respectively. At the same time, the in situ Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) indicated that the linearly adsorbed CO is further transformed into side products for C-C coupling. The possible reaction processes over Co-Cu/CeO₂ revealed that light can enhance the production of carrier electrons (Figure 7). The Cu/CeO₂ catalyst under irradiation by visible light can exhibit excellent reverse water gas shift reaction. Localized surface plasmon resonance induces electrons of Cu to promote the

dissociation of formate and regeneration of oxygen vacancies, which promotes the reverse water gas reaction.

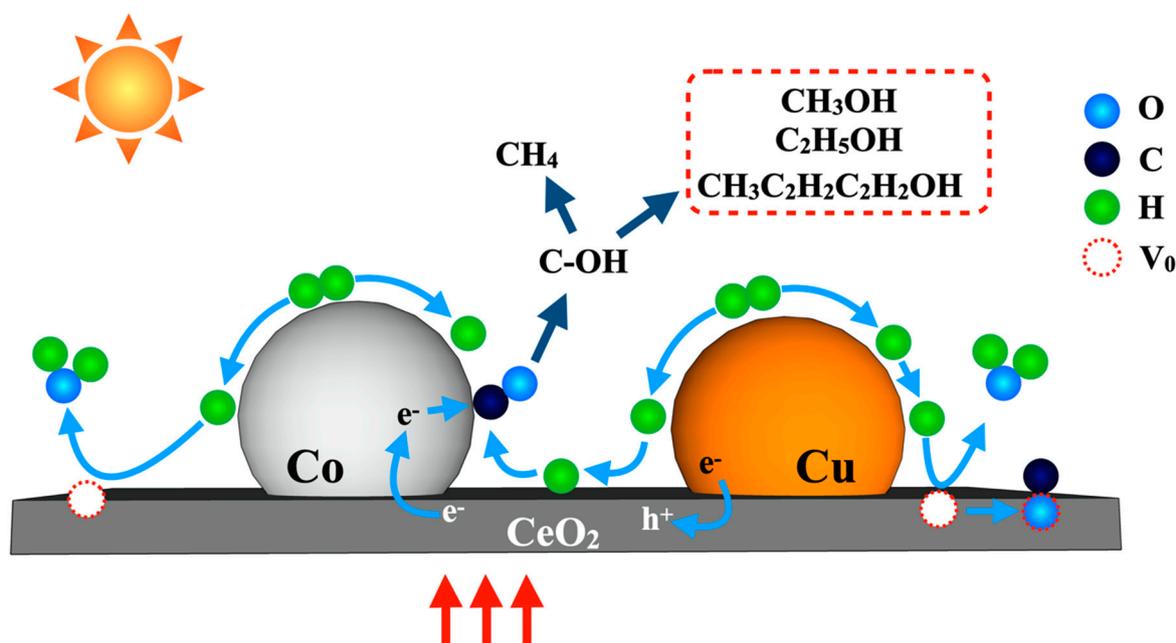


Figure 7. Mechanism of electron transfer from CeO₂ to the surface of Co enhancing catalytic activity.

Marquart et al. [66] studied producing long-chain oxygenates over K/ β -Mo₂C catalysts in the FTS to investigate the effect of synthesis protocols. The selectivity towards oxygenates was reduced to approximately 20 C% upon potassium promotion. Simultaneously, the unpromoted catalysts were mainly reported to form methanol and the chain growth probability confirms this observation. Increasing reaction temperature decreased methanol selectivity while increasing the ethanol content. Zaffran et al. [67] reported the formation mechanism of methanol in FTS at Co₂C surfaces using combined density functional theory and microkinetic modeling. Density functional theory modeling was employed for vibrational calculations, and it suggests that (101) and (111) facets are more favorable to methanol formation. It has been concluded that CH₄ and C₂H₄ share the same determining states at high temperatures. The main challenge for methanol production using syngas is various types of impurities, such as tar, sulfur compounds, and trace contaminants. The level of contaminants that lead to metal corrosion and catalyst deactivation are influenced by gasification conditions and feedstock type. In the FTS, as a heterogeneous polymerization reaction, the hydroxycarbene mechanism explains the condensation reaction between two hydrocarbon reactants and the formation of alcohols by hydrogenation. Additionally, the CO insertion mechanism proposes a C-C coupling reaction and the formation of alcohols [62]. Owing to the current production cost of alcoholic biofuels and their low heat of combustion, the economy of methanol production via FTS is unattractive to entrepreneurs [63]. Replacing conventional feedstocks to produce cheaper syngas for FTS can bring down the production cost of green methanol. Choudhury et al. [68] have investigated the feasibility of the hybrid process of biomass Gasification Integrated FTS to present the possible pathway for its commercial implementation. They concluded that the surplus biomass generation results in considering the hybrid process as a viable method for the generation of liquid transportation fuel and electricity.

4.5. Methanol Production through Fermentation

The production of methanol from biomass through fermentation involves several steps such as biomass pretreatment, fermentation and distillation. Feedstocks such as wood chips or agricultural residues should first be pretreated to break down the complex carbo-

hydrates into simpler sugars. An efficient pretreatment process aims to achieve several goals, including the direct formation of sugars or their subsequent production through hydrolysis, preservation of the formed sugars to prevent any loss or degradation, restriction of the formation of inhibitory substances, reduction in energy consumption, and minimization of costs. The four primary categories of pretreatment techniques used are physical, chemical, physicochemical, and biological improvements, and typically, a mixture of these reactions is employed in the pretreatment step. This is performed through various processes, such as steam explosion, acid hydrolysis, or enzymatic hydrolysis [64–66]. Figure 8 represents a simplified diagram of the process of methanol production from biomass through fermentation.

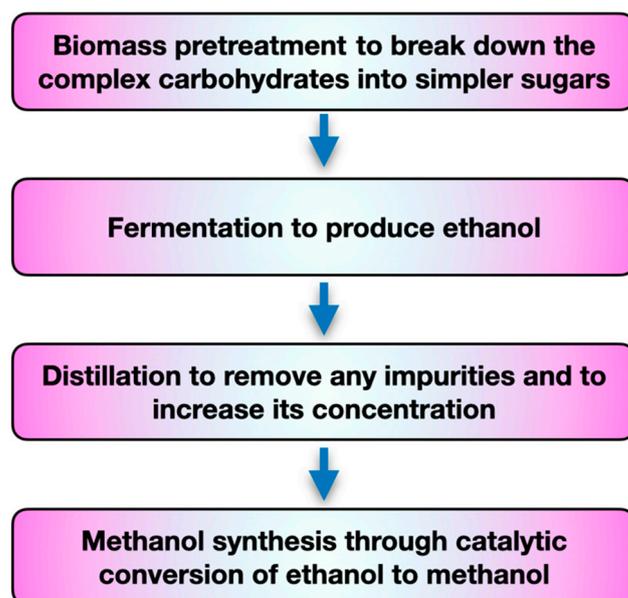


Figure 8. Different steps involved in methanol production from biomass using fermentation.

4.5.1. Acid and Alkaline Pretreatment

Acid pretreatment is a crucial technique to achieve high yields of sugars from lignocellulosic materials. This process involves the application of concentrated or diluted acids (usually between 0.2% and 2.5% w/w) in different temperature ranges. Among various types of acid, sulfuric acid is the most used for acid pretreatment [69]. The acid solution targets the polysaccharides, especially hemicelluloses, which are more easily hydrolyzed than cellulose [69]. Acid pretreatment can be carried out using either dilute or concentrated acids to enhance cellulose hydrolysis [69]. However, acid pretreatment also generates various inhibitors such as acetic acid, furfural, and 5-hydroxymethylfurfural, which can prevent the growth of microorganisms during fermentation [69]. To use the hydrolysates for fermentation, detoxification is necessary. Moiser et al. reported that diluted H_2SO_4 is more effective than other acids in pretreating lignocellulose and achieving higher hydrolysis yield [70]. For example, when wheat straw was subjected to 0.75% vol/vol of H_2SO_4 at 121 °C for 1 h, a saccharification yield of 74% was reached [71]. In addition to sulfuric acid, different types of acid such as carboxylic acids can also be used for acid pretreatment, but sulfuric acid is preferred due to its low price, high efficiency, and easy availability [72]. Furthermore, the use of diluted acids can reduce the production of inhibitory compounds, thereby making the hydrolysates more suitable for fermentation [73]. Overall, acid pretreatment is a promising technique for the efficient generation of sugars from lignocellulosic biomass, but the detoxification of hydrolysates remains a challenge that needs to be addressed to enhance the feasibility of the process [74].

Alkaline pretreatment is an effective technique for digesting the lignin matrix of lignocellulosic materials and making polyose more accessible for enzymatic hydrolysis [75].

Alkali treatment disrupts the porosity and thickness of cellulose, lignin, and SiO₂, hydrolyzing uronic and acetic esters and swelling cellulose, thereby decreasing the crystallinity of (C₆H₁₀O₅)_n [76]. Hence, the compounds can be fractionated into imidazole ionic liquids, hemicelluloses, and residue, making them more suitable for further processing into higher-value products. The end residue, mainly agricultural residues, can be employed for producing paper or cellulose derivatives [76].

Alkaline pretreatment can be conducted using hydroxides of Na, K, Ca, and NH₃. Compared to other pretreatment methods, alkaline pretreatment reactions require lower temperatures and time [76].

Sun et al. (1995) used electrocatalysts in the presence of alkaline solutions for the delignification of lignocellulosic biomass for enhancement of methanol production potential [77]. They suggested that the optimal process conditions were using 1.5% sodium hydroxide for 144 h at 20 °C, which released 65% and 85% lignin and hemicellulose, respectively. Sodium hydroxide has also been reported to increase the digestibility of resulting wood from 17% to 59% by decreasing lignin concentration from 55% to 25% [77].

Alkaline pretreatment has several advantages over other pretreatment techniques. For example, it can efficiently remove water-soluble lignin and hemicellulose, making cellulose more accessible for enzymatic hydrolysis [78]. Additionally, alkaline pretreatment can be performed at lower temperatures and pressures than other pretreatment methods, which reduces energy consumption and process costs [78]. However, alkaline pretreatment also has some limitations, such as high chemical consumption, low selectivity, and difficulty in controlling the degree of delignification [78]. Therefore, further research is needed to optimize the alkaline pretreatment process and develop more efficient and cost-effective methods for lignocellulosic biomass conversion.

4.5.2. Enzymatic Pretreatment

The chemical pretreatment of the biomass makes it suitable for enzymatic pretreatment, which leads to the generation of a wide range of sugars for fermentation. During the process of producing bioethanol, saccharification is a crucial step that involves converting complex carbohydrate polymers into monomer sugars. Compared to acid hydrolysis, enzymatic hydrolysis requires less energy and operates under mild environmental conditions [78]. Cellulase activity is reported to be optimal at temperatures between 40 and 50 °C and pH values between 4–5. In contrast, xylanase activity is reported to be optimal at temperatures between 50 and 60 °C and pH values between four and five [78,79]. In comparison to acidic or alkaline hydrolysis, enzyme hydrolysis offers several advantages, including low toxicity, low utility costs, low corrosion, and the absence of inhibitory byproducts [80,81]. As a result of the substrate-specific nature of cellulase enzymes used in enzymatic hydrolysis, its application may be limited [82,83].

4.5.3. Fermentation

After the saccharification step, the resulting sugars can be used for bioethanol production due to high ethanol fermentation efficiency. However, the efficient commercial production of bioethanol from lignocellulose is currently limited using microorganisms that can effectively ferment both hexose and pentose co-fermenting yeast strains [84]. The ideal microorganism for industrial-scale ethanol production should have the ability to utilize a broad range of substrates, produce high ethanol yields and productivity, tolerate the inhibitors present in hydrolysates, and exhibit cellulolytic activity, enabling it to produce ethanol at high concentrations and temperatures [85]. Unfortunately, no wild-type microorganisms possess all these traits, which necessitates the application of genetically modified microorganisms to achieve optimal ethanol production from lignocellulosic feedstocks [86]. Such modifications can enhance sugar utilization and production efficiency, leading to a more cost-effective and sustainable bioethanol industry.

Two main methods are commonly used for fermenting lignocellulosic hydrolysate: simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermen-

tation (SHF). The traditional approach has been SHF, but in recent years, SSF has gained significant popularity. SSF offers several advantages, including increased ethanol yields by mitigating end-product inhibition and omitting the requirement for separate reactors [87]. SSF is also cost-effective and reduces the risk of microbial contamination, but there are some limitations due to differences in minimum temperature conditions required for enzymatic hydrolysis and fermentation. The use of engineered microorganisms, such as *Saccharomyces cerevisiae*, can help overcome this limitation by improving the ethanol yields and reducing fermentation time in SSF processes [88].

The higher ethanol yield coefficient obtained from SSF is partially attributed to the conversion of xylose to xylitol under SSF conditions. The xylitol formation is a consequence of the higher availability of nicotinamide adenine dinucleotide phosphate (NADPH) and the presence of enzymes that can catalyze the conversion of xylose to xylitol, such as xylose reductase [45,89]. Xylitol can accumulate in the fermentation broth and reduce ethanol productivity and yield. Therefore, to obtain a higher ethanol yield, it is necessary to suppress xylitol formation by regulating the expression of genes involved in xylose metabolism. The use of metabolic engineering techniques can also help minimize xylitol accumulation and increase ethanol production from lignocellulosic hydrolysates in SSF processes [57,90–94].

5. Conclusions and Perspectives

In summary, green methanol has long been used as a platform chemical and precursor for other fine chemicals and base materials. It has many commercial applications in agrochemical, fabric, textile, paint, adhesive, wood processing and pharmaceutical industries. Its applications are currently being recognized as a biofuel or fuel additive due to its low-emission flammability, high octane number and better engine performance. As discussed in this article, biomethanol can be synthesized from waste biomass sources through thermochemical and biological processes. While thermochemical conversion processes such as pyrolysis and gasification of biomass operate at moderate/high temperatures and pressures, biological processes require microorganisms and enzymes for denaturing the polysaccharides (cellulose and hemicellulose) into monomeric sugars for further fermentation to biomethanol. While biological conversion technologies can produce biomethanol as the main product, the thermochemical processes lead to the generation of biomethanol as a byproduct. For example, bio-oil derived from biomass pyrolysis comprises both aqueous and organic phases. While the organic phase contains high molecular weight crude oil, the aqueous phase contains low molecular weight components such as water, acids, aromatics and alcohols (including methanol). The article also reported on Fischer-Tropsch synthesis, which can transform syngas into liquid hydrocarbons such as methanol using selective and high-performance catalysts. Regardless of the production process, the main advantage of biomass-derived methanol is that it is a distributed energy carrier for power generation in methanol fuel cells, which upon combustion generates CO₂ and water. This CO₂ can be further recycled by the fresh plants during photosynthesis leading to its no net accumulation in the atmosphere. With the growing interest in biofuels and biochemicals, biomethanol is steadily emerging as a bioproduct with a high potential for diverse applications in value-added industries at a global scale.

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