



Progress in biofuel production from gasification



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ABSTRACT

Biofuels from biomass gasification are reviewed here, and demonstrated to be an attractive option. Recent progress in gasification techniques and key generation pathways for biofuels production, process design and integration and socio-environmental impacts of biofuel generation are discussed, with the goal of investigating gasification-to-biofuels' credentials as a sustainable and eco-friendly technology. The synthesis of important biofuels such as bio-methanol, bio-ethanol and higher alcohols, bio-dimethyl ether, Fischer Tropsch fuels, bio-methane, bio-hydrogen and algae-based fuels is reviewed, together with recent technologies, catalysts and reactors. Significant thermodynamic studies for each biofuel are also examined. Syngas cleaning is demonstrated to be a critical issue for biofuel production, and innovative pathways such as those employed by Choren Industrietechnik, Germany, and BioMCN, the Netherlands, are shown to allow efficient methanol generation. The conversion of syngas to FT transportation fuels such as gasoline and diesel over Co or Fe catalysts is reviewed and demonstrated to be a promising option for the future of biofuels. Bio-methane has emerged as a lucrative alternative for conventional transportation fuel with all the advantages of natural gas including a dense distribution, trade and supply network. Routes to produce H₂ are discussed, though critical issues such as storage, expensive production routes with low efficiencies remain. Algae-based fuels are in the research and development stage, but are shown to have immense potential to become commercially important because of their capability to fix large amounts of CO₂, to rapidly grow in many environments and versatile end uses. However, suitable process configurations resulting in optimal plant designs are crucial, so detailed process integration is a powerful tool to optimize current and develop new processes. LCA and ethical issues are also discussed in brief. It is clear that the use of food crops, as opposed to food wastes represents an area fraught with challenges, which must be resolved on a case by case basis.

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1. Introduction

The twenty-first century has been marked by an exemplary advancement in the fields of information, technology, research and development (R&D) coupled with an enhancement in standards of living. However, the other side of the coin is rising population and increasing energy demand. A large amount of energy (104.67 PWh on primary energy basis) was utilised by around 7.18 billion people around the globe in 2013 and this consumption will rise to 262.8 PWh in the near to medium term future (2050) [1,2]. In 2011, almost 85% of the energy demand was satisfied by the fossil fuels [1,2]. In the light of their non-replenishable nature and their contribution to greenhouse gas (GHG) emissions, researchers are searching for sustainable green fuels. A significant growth in energy demand calls for non-polluting renewable energy sources such as solar, wind and biomass.

Biomass is a renewable energy resource which comprises carbon, hydrogen, oxygen, traces of nitrogen and some minerals. Biomass utilization has an advantage over other renewable sources such as solar energy, wind energy and hydroelectric power because of its low dependence on site and climate as diverse biomasses can grow in varied conditions. Moreover, biomass can be easily stored and transported (albeit with a lower energy density than fossil fuels). Rural areas in under-developed countries are dependent upon biomass for essential activities such as cooking and heating. For example, India has considerable coal reserves of around 223 billion tonnes, but they are located in specific areas such as north-east India, unlike biomass, which is evenly and broadly spread over the whole country [3]. Furthermore, easy availability of waste biomass as a low-cost fuel make it a promising global energy source. Developed nations are also focusing on biomass as a sustainable energy option because of these benefits.

Plant biomass was the first fuel used by humans. The nineteenth century saw fossil fuels allow industrialization and biomass was to a significant extent displaced. On the other hand, fossil fuels have created grave environmental issues such as climate change, due to CO₂ emissions [4], and major pollution problems worldwide. In the light of depleting easily accessible and cheap coal resources and oil reservoirs, it is imperative to shift our focus back to biomass, although underground gasification might help extend the use of coal. Currently biomass provides more than 10% of the global energy supply making it one of the leading potential viable renewable energy resources [5–7].

The carbon cycle associated with biomass production and end use must match up the longer time scales (annual for agricultural residues and grassy energy crops and of the order of three years for woody short rotation energy crops) of carbon absorption in the growing phase with the rapid production of CO₂ during the combustion phase. This is essentially the same requirement as ensuring a secure and sustainable feedstock supply. Much can be learnt from the sustainable timber and pulp and paper industries which have been managing exactly this problem for many decades. This issue is elaborated on further in Section 11.4 on lifecycle assessment.

An extensively explored research area is the development of clean and sustainable technologies to utilize biomass feedstocks to produce biofuels [8]. Biofuels are liquid or gaseous fuels produced

from biomasses which are predominantly employed in the transportation sector. They are also used to generate heat and electricity or can be used as the feedstock to synthesise important chemicals. Gaseous biofuels are normally used for heat and power production, whereas liquid biofuels are generally employed in the transportation sector. Biofuels, in general, include bio-methanol (MeOH), bio-ethanol (EtOH), bio-dimethyl ether (DME), synthetic natural gas (bio-methane), Fischer Tropsch (FT) fuels and H₂.

Biofuels can be classified as first generation, second generation, third generation and fourth generation biofuels [9]. Their composition and calorific content are dependent upon the type of biomass and process employed [10]. First generation biofuels such as bio-methanol, bio-ethanol, bio-propanol, bio-butanol, fatty acid esters, etc., are derived from simple sugars, starch, fats and vegetable oils [11]. Inderwildi et al. [12] stated that second generation biofuels, such as EtOH are produced by the 'biomass-to-liquid' (BtL) route employing lignocellulosic biomass. The third and fourth generation of biofuels products use the 'algae-to-biofuel' strategy. In third generation technologies, algal biomass is treated for biofuel production, whereas the fourth generation approach utilises metabolic engineering of algae for generating biofuels from oxygenic photosynthetic microbes and creating artificial carbon sinks [13]. All the generations of biofuels technologies are discussed briefly in Section 3.

Lignocellulosic biomass can be converted to chemical feedstocks and biofuels via thermochemical or biochemical routes as depicted in Fig. 1. In biochemical processing of biomass, using hydrolysis, sugars and lignin are extracted from biomass and selectively processed via biological and/or chemical routes for the production of chemical intermediates or desired liquid fuels for transportation. It offers selective processing alternatives which are not available in the other pathways [14]. However, it is a more expensive and intricate technique than thermochemical processing. Conversion of biomass to biofuels via biochemical pathways has been extensively discussed elsewhere [15–22].

Pyrolysis, gasification and liquefaction are commonly employed approaches in thermochemical processing of lignocellulosic biomass to biofuels [24]. Among the dominant thermochemical technologies, biomass gasification (BG) is considered as most cost-effective and efficient for lignocellulosic biomass conversion to bio-energy [25]. In gasification, thermal degradation of lignocellulose at high temperature takes place and results in intermediates such as bio-oil and final products such as syngas. The thermochemical unit is usually coupled with a chemical and/or catalytic upgrading unit to convert bio-oil and/or syngas to a wide range of potential biofuels [26].

Gasification technology is almost 100 years old. In the 1920s, cars in Sweden were powered by wood gasifiers owing to ample wood biomass and lack of petroleum resources. During the Second World War (1939–1945), numerous studies were conducted to optimize the design of wood gasifiers and enhance their performance [27]. In the 1970s and 80s, about 40 companies around the globe proposed to build gasification plants based on biomass, to generate heat and power. Indicative yields of important biofuels via both pathways are shown in Table 1.

Advances in gasification technologies and multiple uses of syngas have permitted gasification to integrate with several industrial processes to produce chemical feedstocks and generate power [29,30].

Abbreviations

ASF	Anderson Schulz Flory
ASU	Air Separation Unit
BFB	Bubbling Fluidised Bed (Gasifier)
BG	Biomass Gasification
BtL	Biomass-to-liquid
BTX	Benzene Toluene Xylene
CAE	Cyclo-hexyl Alcohols and Ethers
CFB	Circulating Fluidised Bed (Gasifier)
CGC	Cold Gas Clean-up
CHP	Combined Heat and Power
CI	Compression Ignition
CLR	Chemical Looping Reforming
COP	Conference of the Parties
CREC	Chemical Reactor Engineering Centre
DFB	Dual Fluidised Bed (Gasifier)
DME	Bio-Dimethyl Ether
ER	Equivalence Ratio
EtOH	Bio-Ethanol
FB	Fluidised Bed (Gasifier)
FCV	Fuel Cell Vehicle
FT	Fischer Tropsch
FXB	Fixed Bed (Gasifier)
ΔG	Change in Gibbs Free Energy
GHG	Green House Gas
GT	Gas Turbine
ΔH	Change in Enthalpy
HAE	Higher Alcohols and Ethers
HC	Hydrocarbon
HGC	Hot Gas Clean-up
IC	Internal Combustion
IGCC	Integrated Gasification Combined Cycle
LCA	Life cycle assessment
LHHW	Langmuir-Hinshelwood-Hougen-Watson
MeOH	Bio-Methanol
m-GT	Micro Gas Turbine
MILP	Mixed Integer Linear Programming
MINLP	Mixed Integer Non Linear Programming
MSW	Municipal Solid Waste
MTBE	Methyl Tert-butyl Ether
NPV	Net Present Value
NREL	National Renewable Energy Laboratory USA
OT	Once-Through
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
PMO	Porous Metal Oxide
PSA	Pressure Swing Adsorption
PEMFC	Proton Exchange Membrane Fuel Cell
RC	Recycling
R&D	Research and Development
RDF	Refuse Derived Fuel
RF	Radio Frequency
RTFO	Renewable Transport Fuel Obligation (UK)
S/B	Steam-to-Biomass Ratio
SCWG	Supercritical Water Gasification
SI	Spark Ignition
SNG	Synthetic Natural Gas
STP	Standard Temperature and Pressure
UCSB	University of California Santa Barbara
UNFCCC	United Nations Framework Convention on Climate Change
WGS	Water Gas Shift
WtE	Waste-To-Energy
η	Efficiency.

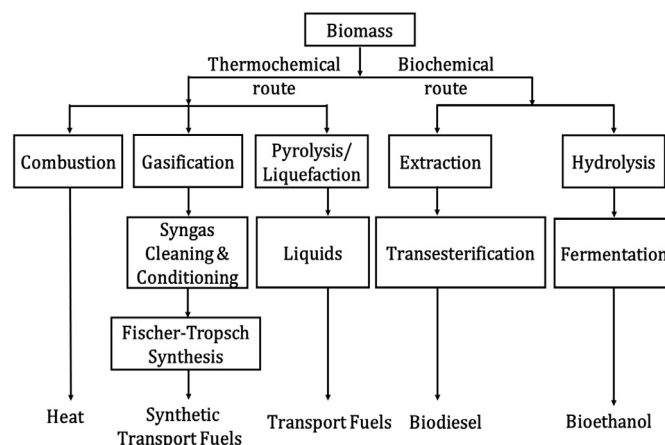


Fig. 1. Thermochemical and biochemical conversion routes for biomass to biofuels [23].

In addition, this progress has allowed the chemical efficiency of gasification to exceed 70% and electrical efficiency to exceed 40% in high-pressure gasification combined with fuel cell power production [25]. Furthermore, waste-to-energy (WtE) in rural areas is a promising approach for energy security development and landfill avoidance [31]. This work briefly reviews pyrolysis and liquefaction thermochemical routes for biofuel synthesis. In addition, biomass gasification along with operational variables such as raw materials, gasifying media, steam-to-biomass ratio, temperature and pressure inside the gasifier, gasifier design and residence time are discussed thoroughly in Section 3.

Biomass-derived syngas, which acts as a raw material for different biofuels production, contains many contaminants such as tars, particulates (PM), alkalis, nitrogen, sulphur, halides and traces of some other elements. Cleaning of these contaminants prior to their feeding in catalytic reactors for biofuel generation is a crucial step. Traditional and advanced cold and hot syngas cleaning technologies are also reviewed in this article.

In the current age, biomass gasification employing steam as gasifying medium has attracted much attention as it produces H_2 -rich syngas, which can be used as a feedstock to produce multiple biofuels via catalytic chemical synthesis [25]. In this work, engineering dimensions such as reactor design, catalysts and pilot plant projects for the production of bio-methanol, bio-ethanol, bio-dimethyl ether, bio-methane, Fischer Tropsch fuels and bio-hydrogen via BG are discussed in detail along with algae-derived biofuels, with an objective to promote their sustainable synthesis and to scale up their production.

Numerous studies comprising thermodynamic analyses of biomass gasification have provided significant guidance to predict the impact of operational variables on the composition and calorific content of produced syngas. These equilibrium models provide satisfactory information vis-à-vis syngas which is a raw material for further catalytic chemical processing to produce hydrocarbon (HC) fuels. Many times, the information regarding syngas composition deviates from chemical equilibrium predictions on account of kinetic constraints [32]. We have reviewed various thermodynamic studies about gasification and biofuel production to show how equilibrium modelling advances the technology.

A bio-refinery combines different processes and equipment to transform biomass to biofuels and other valuable products. In other words, bio-refineries are 'a multiple product production system' employed to maximize the overall economic value. Gasification-based bio-refineries use syngas produced via gasification for the integrated production of chemicals, materials and fuels. Understanding of diverse areas is important for successful operation of a

Table 1

Yield ranges of important biofuels per dry tonne of feedstock from biochemical and thermo-chemical pathways [28].

Process	Biofuel	Biofuel yields (L dry-t ⁻¹)		Energy content (MJ L ⁻¹)	Energy yields (GJ t ⁻¹)	
		Low	High	Lower heat value	Low	High
Biochemical (Enzymatic hydrolysis)	Ethanol	110	300	21.1	2.3	6.3
Thermochemical	Syngas-to-Fischer-Tropsch diesel	75	200	34.4	2.6	6.9
	Syngas-to-ethanol	120	160	21.1	2.5	3.4

refinery, including the biomass logistics and conversion kinetics, and process energetics [33]. Theoretically, a bio-refinery can use a huge array of biomass feedstocks, ranging from forestry waste to sewage sludge to aquatic plants, for the production of worthwhile products and energy [28]. Although the idea of a bio-refinery is comparable to an oil refinery, the diversity in various biomass feedstocks necessitates a variance in the approaches employed to convert feedstocks into useful products [34]. Here, current research is reviewed and discussed in an attempt to promote the concept of process integration via innovative designs, to exploit the variability in biomass components and to increase the derived value.

Liquid biofuels can potentially substitute for fuels produced from existing coal and petroleum reserves. The high-temperature combustion properties of both oxygenated and synthetic hydrocarbon biofuels are quite similar to non-renewable transportation fuels and, therefore, few alterations are needed in internal combustion (IC) engine design or in the present transportation infrastructure [24,35]. In fact, bio-ethanol and bio-diesel are currently blended with conventional fuels in spark ignition (SI) and compression ignition (CI) engines, respectively, in many countries around the world. Production of biofuels via sustainable pathways (e.g., by means of gasification-derived syngas), can not only release pressure to supply or import conventional petro-fuels, but also aid in the reduction in GHG emissions and other pollutants. In spite of the huge volume of research and development conducted in the aforementioned areas, there is no all-inclusive review on biomass-to-biofuel production via biomass gasification with an emphasis on associated areas. This article will assist R&D efforts into the scale-up of biofuel production via gasification plants.

2. Bioenergy around the globe

Biomass has a very high potential among all the renewable sources to help satisfy world energy requirements in the future. As a result of R&D and a push by governments around the world, the application of bioenergy in the transport sector and for combined heat and power (CHP) has risen in the past decade. In the 1990 s, around 50 EJ of energy was obtained from biomass, which is around 9% of the total energy utilization around the globe, and approximately 3 EJ out of this was employed as transport fuels [1]. This biomass utilization has increased every year and is projected to significantly increase in coming years [28]. Favourable policies and legislation by different governments and organizations have resulted in increasing deployment of biomass for heat and power and bio-fuels for transportation [36]. Investigations predict that the potential share of bioenergy by 2050 will be around 100 EJ a⁻¹, which will further increase to 190 EJ a⁻¹ by 2085, as depicted in Fig. 2 [28]. This reflects the vast potential of biomass-derived bioenergy, which can not only contribute to alleviate the requirement for fossil fuels but also lead the development of rural areas with lesser adverse environmental impact.

Conventionally, biomass was directly combusted to obtain energy and this practice is still the main route for using biomass in many regions, especially the rural areas of under-developed nations. Biomass has the potential to be transformed to other energy vectors, such as liquids (biofuels), gases (syngas, H₂, etc.) and electricity, by

using modern technology and processes [37]. The use of such vectors is frequently more convenient, economical and environment-friendly than the direct combustion pathway. Sugar-cane conversion to bio-ethanol (EtOH) in Brazil, CHP generation in Scandinavian countries and co-combustion of coal and biomass in the Netherlands are a few examples of advanced and efficient bioenergy generation from conventional biomass [38]. Currently, in industrialized nations, the focus is to design and develop technologies to produce biofuels for transportation, heat and power generation employing raw biomass, in an efficient and cost-effective manner.

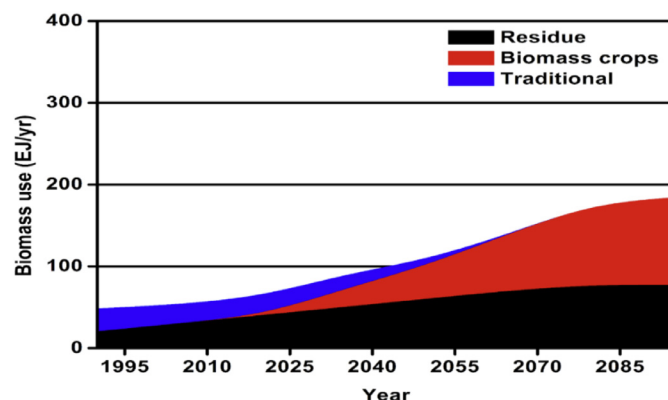
2.1. GHG emissions vs. biofuels

Net GHG emissions from biofuels are significantly lower than the combustion of conventional petroleum-derived fuels [39]. However, biofuel synthesis also generates GHGs in every step in the supply chain, from the raw feedstock production, to transport, conversion, to biofuels distribution and end application, as depicted in Fig. 3. Therefore, lifecycle assessment (LCA) should be considered a vital factor that needs to be addressed by further research.

A few researchers [28] conducted an important study employing a net energy balance approach on a life cycle basis to compare the GHG emissions by gasoline and EtOH produced from a variety of feedstocks. It can be clearly seen from Fig. 4 that the GHG emissions by lignocellulosic biomass- and sugarcane-derived EtOH are on the lower side. Production of biofuels from cellulosic biomass decreases the burden on energy/food crops. In addition, it offers a cheaper and ample feedstock for the generation of a variety of biofuels as discussed later in this article.

2.2. Energy security and rural development vs. biofuels

Oil demand is increasing worldwide, necessitating a suitable substitute for conventional fossil fuels [40]. Production of energy via biomass at local, national and global levels can allay the dependence on politically and socially unstable international energy transactions. Apart from this, there is a direct positive influence of biomass-to-biofuel production on the development of rural areas. Rural areas,

**Fig. 2.** Past, present and future of bioenergy [28].

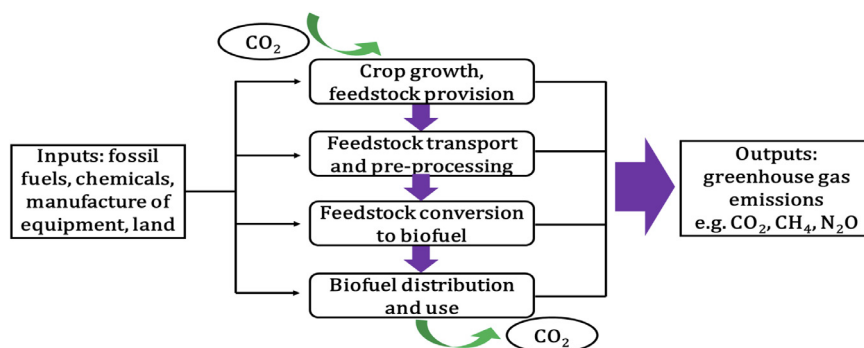


Fig. 3. GHG emissions in biofuel synthesis supply chain.

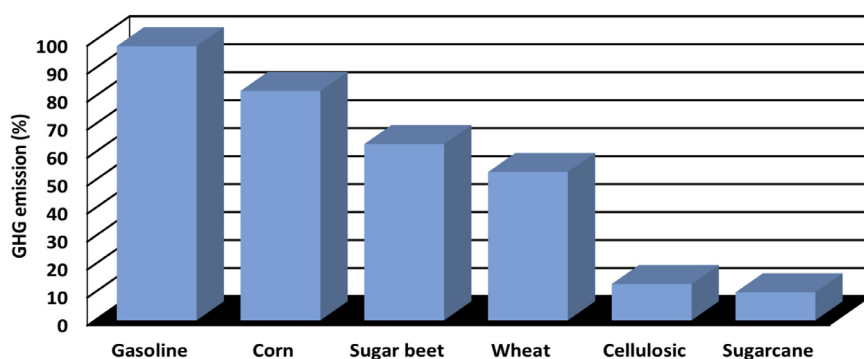


Fig. 4. GHG emissions comparison between gasoline and EtOH derived from different feedstocks [28].

especially in developing nations, traditionally suffer from poverty and are deprived of even the basic amenities. Establishment of biomass conversion plants and bio-refineries, which are labor-intensive in nature, can provide job opportunities to a large number of unemployed people [41], improving the economy locally and assisting in development.

3. Thermochemical conversion of biomass to 2nd and 3rd generation biofuels

According to Luque et al. [40] and Naqvi et al. [42], first generation biofuels are synthesised from edible crops such as wheat, sugarcane, soya bean, rapeseed, etc., using traditional technologies available for biochemical conversion routes (fermentation/hydrolysis). Biodiesel, bioethanol, bio-butanol, 2,5-dimethylfuran along with the biofuels obtained via catalytic cracking are examples of this category. They are derived from food feedstocks, and cultivated in arable land, which potentially increases upwards pressure on food prices [40].

Non-edible feedstocks such as wood, agricultural residues, forestry waste and municipal and industrial wastes are the

raw materials for second generation biofuels. They contain lignin and cellulose and are known as lignocellulosic biomass. A few examples of second generation biofuels are bio-ethanol, bio-methanol, FT-diesel, DME, bio-hydrogen, etc. [43,44]. They overcome the shortcomings of first generation biofuel synthesis such as the usage of arable land and food crops. They are produced using either thermochemical or biochemical pathways. The use of wastes, etc. as feedstocks leads to processes which are more sustainable, with lower negative environmental impacts as compared to first generation biofuels [45]. Second generation biofuel plants around the globe are shown in Table 2.

The third and fourth generation biofuels are derived from algae, which is the most abundantly available potential feedstock. Chen et al. [46] noted that algae does not require arable land for cultivation and is not an edible crop. In addition, it is fast growing with an inherent benefit of producing oils which can easily be refined to diesel and a few components of gasoline. To produce third generation biofuels, such as biodiesel, butanol, gasoline, methane, bio-ethanol and jet fuel, biochemical and/or thermochemical methods are employed [47]. According to Lu et al. [13], fourth generation biofuels will be synthesised from algae which is genetically modified to

Table 2
Second generation biofuel plants worldwide [23].

Company/Institute Name	Location	Type	Start-up	Output
Forschungszentrum Karlsruhe GmbH	Karlsruhe (Germany)	Pilot	Under-construction	608 t a ⁻¹
CHOREN Tech. GmbH	Freiberg (Germany)	Pilot	2003	100 L day ⁻¹
CHOREN Tech. GmbH	Schwedt (Germany)	Commercial	2010	200,000 t a ⁻¹
ECN	Petten (Netherlands)	Pilot	2011	346 t a ⁻¹
ECN	Alkmaar (Netherlands)	Demo	Planned	28,800 t a ⁻¹
NSE Biofuels, NESTE Oil and Stora Enso JV	Varkaus (Finland)	Demo	2009	656 t a ⁻¹
Research Triangle Institute	N. Carolina (USA)	Pilot	Planned	22 t a ⁻¹
GTI Gas Technology Institute	Illinois (USA)	Pilot	2009	26 t a ⁻¹
Flambeau River Biofuels LLC	Wisconsin (USA)	Pilot	2011	51,000 t a ⁻¹

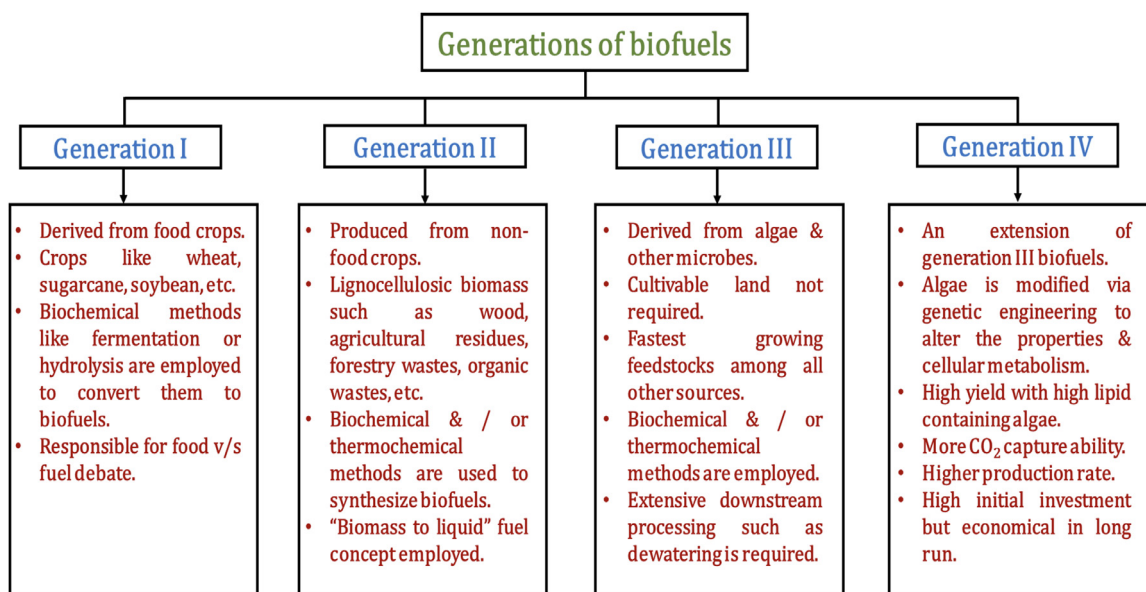


Fig. 5. Different generations of biofuels with their characteristics.

enhance desired HC yields along with creating an artificial carbon sink to make it a carbon-negative energy source. This approach is at a very early stage of research [13,48,49]. Fig. 5 represents different generations of biofuels with their characteristics.

Pyrolysis, liquefaction and gasification are prime thermochemical conversion technologies to synthesise biofuels from biomass feedstocks, employing high temperature and in many cases high pressure [11]. The underlying principle of thermal processing is to reduce the oxygen content of the biomass raw material in order to enhance the energy density and to create carbon-carbon bonds to increase the molecular weight of the final HC fuel [24]. Upgradeable intermediate products such as bio-oils (by pyrolysis/liquefaction) and syngas (by gasification) are obtained by thermal degradation of lignocellulose (for second generation biofuels) and algae (for third generation biofuels). Generally, the thermal processing unit is combined with a biofuel production (for example, FT synthesis) unit. Bio-oils and syngas act as feedstocks for wide-ranging hydrocarbon fuel generation [12].

Pyrolysis is the thermal degradation of a material in the temperature range of approximately 350–550 °C in the absence of oxygen. A short residence time at these high temperatures generates vapour phase products which condense when cooled, to form a blend of compounds including acids, alcohols, ketones, aldehydes, esters,

etc., collectively called bio-oil [50]. Hayes et al. [51] found the yield of bio-oil could be as high as 70% on a mass basis. It is a cost-effective process which does not require comprehensive pre-treatment of input raw biomass [24]. However, the low energy density due to high oxygen content, and the corrosive nature of bio-oil render it unsuitable for fuel applications prior to extensive treatment [52].

According to Alonso [24], thermal degradation of large molecules of biomass in the presence of catalysts, with longer residence time, at a comparatively lower temperature range of 250–450 °C and high pressures (5–20 bar) during liquefaction, produces unstable smaller species, which form polymers, again known as bio-oil. Bio-oil produced by liquefaction has a lower oxygen content of 12 to 14% as compared to bio-oil by pyrolysis and, therefore, less extensive processing is needed prior to biofuel synthesis [24]. However, this is an expensive process on account of catalyst cost and high pressure requirements [29,53].

Biomass gasification is carried out in the presence of a gasifying medium to produce syngas [29]. Syngas can then be upgraded to HC fuels or chemicals via chemical/catalytic upgrading [54]. A detailed sketch of biomass gasification is discussed in the next section. Biomass gasification, pyrolysis, liquefaction and hydrolysis pathways to produce fuels and chemicals are shown in Fig. 6.

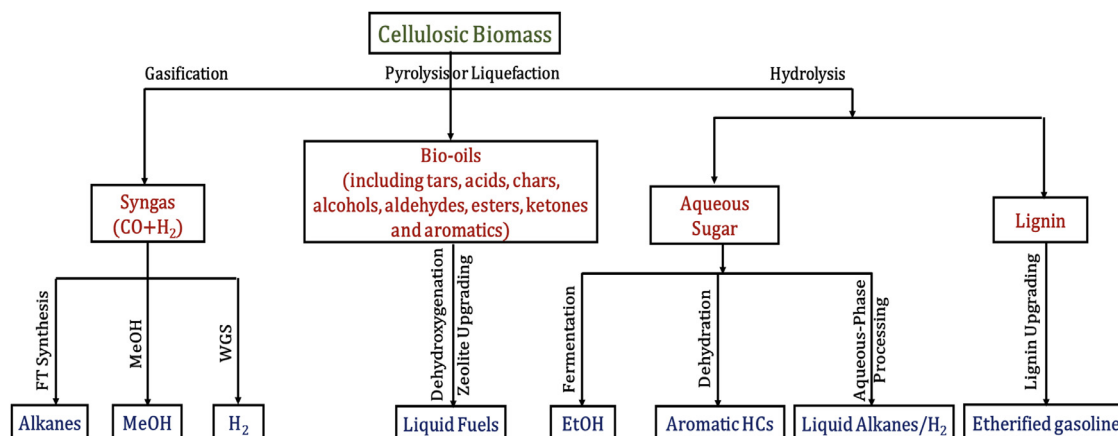
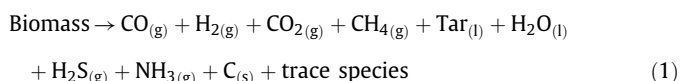


Fig. 6. Cellulosic biomass conversion to fuels and chemicals [29].

3.1. Biomass gasification

3.1.1. Gasification chemistry

Gasification is the thermochemical transformation of solid or liquid biomass into a mixture of carbon monoxide, hydrogen, carbon dioxide, methane, tar, water vapour, hydrogen sulphide and other trace species whose fractions are determined by operational variables such as raw material characteristics, gasifying media (steam, air, O₂, CO₂), temperature and pressure inside the gasifier, and catalysts (if used). According to Bridgwater et al. [55] and de Lasa et al. [25], gasification consists of many overlapping sub-processes, such as drying, pyrolysis and partial oxidation and, therefore, comprises complicated combinations of numerous reactions which are depicted in Table 3. Drying of the feedstocks takes place until 120 °C and volatile species are generated below 500 °C. Gasification of char can begin at around 350 °C. The heat supplied can be intrinsically produced via exothermic combustion reactions or can be supplied from outside sources [56,57]. A simplified gasification reaction can be represented in Eq. (1) as below:



The entire gasification process is divided into primary, secondary and tertiary reaction stages according to the reaction chemistry and temperature ranges [58]. In the primary reaction regime, biomass feedstock is converted to oxygenated vapour and liquid species along with the production of H₂O and CO₂ below 500 °C. Fu et al. [59] observed that primary pyrolysis vapours are monomers and, therefore, have low molecular weight. During primary pyrolysis, no chemical reactions take place among the organic species, and they are significantly free of secondary gaseous cracking products. In the secondary reaction regime, CO, H₂, CO₂, water vapour, gaseous olefins, phenols and aromatics are produced from primary vapour and liquid species in the temperature range of 700 to 850 °C. Tar produced during this stage generally consists of mixed oxygenates, alkyl phenols, phenolic ethers, heterocyclic ethers and polynuclear aromatic hydrocarbons [29]. The remaining tars and gases undergo methanation, steam reforming, water gas shift and cracking reactions. During the tertiary reaction regime, CO, H₂ and CO₂ are formed along with water vapour, polynuclear aromatics and liquid tar, from 850 to 1000 °C [60]. Huber et al. [29] reported that tar composition is a function of temperature. It alters from mixed oxygenates to phenolic species to polyaromatic species with rising temperature. Secondary and tertiary reaction regimes yield soot and coke [61]. It should be noted that the thermolysis of liquid and organic vapours forms coke, whereas uniform nucleation of intermediates formed at elevated temperature produces soot.

Yung et al. [62] and Goyal et al. [63] reported that water loss and condensation during crosslinking reactions result in char formation,

which retains the structure of the original lignocellulose. The amount of char produced is an inverse function of the rising temperature until 400 °C. Elimination of hydroxyl and aliphatic C—H bonds, and the removal of carbonyl and olefinic carbon groups enhance carbon density in char and result in its aromatization with increasing temperature. Simultaneously with the aromatization process, contraction in the carbon structure also occurs beyond 500 °C [59]. Elevated temperatures during gasification not only open pores in the char morphology due to the release of volatiles, but also result in char melting and fusion.

Liao and co-authors [64] demonstrated that ash is formed during gasification on account of the presence of inorganic species in the biomass feedstock. Oxides of aluminium, calcium, iron, potassium, phosphorus, magnesium, silicon and sodium along with residual carbon form the major constituents of fly ash and bottom ash. The proportions of these oxides are dependent upon the quantity and nature of the inorganic matter present in the raw material. Silicon, nickel, lead, zinc, chromium, cadmium, potassium, sulphur, manganese and copper are found in the ash separator exit. Volatile halogens and alkali metals are present in flyash and wet scrubber ash. The presence of these inorganics, therefore, decreases process efficiency and should be taken into account.

3.1.2. Raw material

Raw biomass of all types can be used for gasification. Vassilev et al. [65] classify biomass based on its biological diversity, as follows:

- i. Wood – Numerous wood species including angiospermous, coniferous, softwood, hardwood, barks, stems, chips, pellets, sawdust, etc., come under this category. They form one of the most commonly used biomass groups for transformation into usable products via combustion, gasification, cogeneration and co-firing due to the minimal presence of sulphur and heavy metals.
- ii. Agricultural and herbaceous biomass – These biomasses are further sub-classified into three types, namely grasses and flowers (bamboo, cane, switchgrass, etc.), straws (barley, corn, rice, wheat, etc.) and other residues (grains, seeds, shells, husks, bagasse, pulp, etc.). Agricultural residues such as rice husks and bagasse are highly used biomass feedstocks owing to their year-round availability and cost-effectiveness.
- iii. Marine biomass – Aquatic plants and microorganisms such as marine algae, macro and micro algae, weed, water hyacinth, etc., are potential raw materials for different kinds of thermochemical and biochemical conversion processes. Presently, numerous research investigations (as summarised in Table 19) are carried out to generate third and fourth generation biofuels from algae on account of their fast growth, and intrinsic ability to produce oils which have similar properties to biodiesel. Moreover, such

Table 3
Chemical reactions involved in biomass gasification (gasifying agent: steam) [25].

Name of reaction	Chemical equation	$\Delta H_{f(298)}^0$ [kJ mol ⁻¹]	$\Delta G_{f(298)}^0$ [kJ/mol]
Hydrogenating gasification	$\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$	123.7	168.6
Boudouard equilibrium	$\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$	205.3	140.1
Water gas shift (WGS)	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	-41.47	-28.5
Heterogeneous WGS	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	130.4	89.8
Steam reforming of methane	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$	172.6	118.4
Dry reforming of methane	$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$	-74.9	-50.3
Ethylene	$2\text{CO} + 4\text{H}_2 \leftrightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	-104.3	-111.6
Ethane	$2\text{CO} + 5\text{H}_2 \leftrightarrow \text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	-172.7	-212.7
Propane	$3\text{CO} + 7\text{H}_2 \leftrightarrow \text{C}_3\text{H}_8 + 3\text{H}_2\text{O}$	-165.1	-293.2
Butane	$4\text{CO} + 9\text{H}_2 \leftrightarrow \text{C}_4\text{H}_{10} + 4\text{H}_2\text{O}$	-161.9	-376.7
Pentane	$5\text{CO} + 11\text{H}_2 \leftrightarrow \text{C}_5\text{H}_{12} + 5\text{H}_2\text{O}$	-159.7	-457.9
Hexane	$6\text{CO} + 13\text{H}_2 \leftrightarrow \text{C}_6\text{H}_{14} + 6\text{H}_2\text{O}$	-158.3	-539.6

biomass has the ability to be genetically engineered to yield desired biofuel with negative-C emissions.

- iv. Human and animal waste – Wastes including bones, meat, chicken litter, pig manure, etc., form this category. A significant volume of research has been conducted into the potential for these wastes to be used to produce usable chemicals or energy. For example, Heidenreich et al. [7] reported that pig manure was used as a biomass feedstock to produce syngas via gasification and the maximum calorific value was found to be 7 MJ Nm^{-3} in a 6 MW_{th} capacity plant, employing a low-temperature circulating fluidised bed (CFB) gasifier, which is quite encouraging.
- v. Contaminated and industrial waste biomass – Municipal solid waste (MSW), refuse-derived fuel (RDF), plywood, sewage sludge, paper-pulp sludge, railway sleepers, hospital waste, etc., are examples of this kind of biomass. Numerous researchers [66–70] have successfully demonstrated the production of syngas using these wastes in biomass gasification units.
- vi. Biomass mixtures – These aforementioned biomass categories can be blended in any ratio to get a new biomass variety, which can be employed for different conversion processes.

Biomass feedstocks can also be classified based on their source and origin as shown in Table 4 [28]. Numerous research studies on gasification of biomass employing diverse feedstocks demonstrated that reactivity, thermal decomposition kinetics, and product gas composition and calorific value are functions of the biomass feedstock [71]. Tar and char yields and characteristics are also dependent upon the kind of biomass used and the cracking routes [72]. For instance, it was found in experiments that the maximum tar production was around 60% for paper, 35% for wood and only 30% for sawdust during the thermal degradation process [73]. This demonstrates that the gasification products are heavily influenced by the biomass material's chemical makeup, moisture and inorganic species [74].

The choice of a gasification system is a function of biomass feedstock character such as moisture, particle size or density, inorganic content (ash) and toxicity. In addition, the amount of biomass to be processed is also taken into account, for example, fixed bed systems are suitable for small capacities whereas fluidized and entrained bed systems are appropriate for medium size and large scale capacities, respectively. Every gasification system has its pros and cons and, therefore, feedstock with a character appropriate for a particular gasifier should be employed to ensure high-quality syngas, cost effective and efficient operation, and minimum environmental impact.

Table 4
Classification of biomass feedstock [28].

Biomass type	Examples
Forest products	Wood, logging residues, trees, shrubs and wood residues, sawdust, bark
Biorenewable wastes	Agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes
Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, miscanthus
Aquatic plants	Algae, water weed, water hyacinth, reed and rushes
Food crops	Grains, oil crops
Sugar crops	Sugar cane, sugar beets, molasses, sorghum
Landfill	Hazardous waste, nonhazardous waste, inert waste, liquid waste
Organic wastes	Municipal solid waste, industrial organic wastes, municipal sewage and sludge
Algae	Prokaryotic algae, eukaryotic algae, kelps
Mosses	Bryophyta, polytrichales
Lichens	Crustose lichens, foliose lichens, fruticose lichens

Water content in the biomass feedstock is the most vital parameter as every kilogram of moisture needs around 2260 kJ of unrecoverable energy to evaporate it [50]. In general, wood and low-moisture herbaceous biomass with less than 15% water are suitable for conventional gasification systems. Updraft fixed bed gasifiers (FXB) can function efficiently with higher-moisture (up to 60% wet basis) biomass as compared to downdraft FXB (25% wet basis). However, an open top fixed bed gasifier developed by the researchers of Indian Institute of Science is capable of using biomasses with high moisture. Normally, a decrease in gasifier temperature and gas yield is observed with an increase in tar content if the feedstock contains more than 30 wt. % water [75]. Supercritical water gasification (SCWG) is a potential gasification pathway for high-moisture-containing biomasses such as algae, sludge, manure, olive mill water, etc. High H_2 yield coupled with high gasification efficiency (η) and low tar is obtained via this route. However, high installation costs owing to the necessity of elevated temperature-pressure and rust-resistant materials, and very significant energy requirements are the limitations for this approach [76]. While this is a promising technique for wet feedstocks further investigation is required to bring it to commercial scale. Plasma gasification can also be employed for these kinds of biomasses, although it shares the same drawbacks as SCWG.

Particle size or particle density of the biomass raw material is another significant factor in choosing a gasification system and lies between 0.15 mm to 51 mm for conventional gasifiers [77]. Agricultural wastes such as rice husk, coir pith, bagasse in loose or powdery form are commonly used as feedstock after pulverization, which reduces the bulk density to 200 kg m^{-3} [78]. Owing to a longer residence time for the fuel, fixed bed gasifiers are less prone to be influenced by the particle size of the feedstock provided it is less than 51 mm, in comparison to entrained flow gasifiers. Entrained flow gasification can tolerate up to 0.15 mm diameter particles and, therefore, requires pulverization of fuel prior to gasification [77]. On the other hand, this technology produces high quality syngas with very low tar content. It is, therefore, normally employed for coal gasification. The tolerance for particle size for FBG lies in the middle ($< 6 \text{ mm}$) [50]. It should be noted that although pulverization enhances the flexibility to use a diverse variety of biomasses it also increases the cost as well as being an energy intensive process.

Biomass raw material with low ash content ($< 2\%$) such as wood, is suitable for fixed bed gasifiers. High ash content results in a decrease in conversion efficiency owing to ash agglomeration [79]. Herbaceous biomass such as bamboo, switchgrass, etc., and contaminated biomass such as sludge have high ash content and cause slagging issues in downdraft FXBs, which are dependent upon low ash melting temperature [80]. Ideally, a gasifier should operate either below the flow temperature of ash to decrease slagging, or above its melting point. Only a few gasifier designs (British Gas/Lurgi) encourage slagging where the slag forms a protective layer on the walls of the reactor [77]. Moreover, the generated ash can be employed as a pozzolanic material and can be blended with cement when producing concrete [81], reducing the requirement for cement and thus decreasing the requirement for land fill.

Developments in gasification systems in the past few decades have made it possible to employ even hazardous or high-water-containing feedstocks such as MSW, sludge, rubber, plastics RDF, etc. Plasma gasification is one such pathway, which was developed to destroy these kinds of wastes. Later, research and development efforts improved the technology to generate usable energy through syngas and electricity production. A high quality product gas with low tar and CO_2 content is obtained via plasma gasification. An exemplary example of power generation from a toxic feedstock is the Utashinai plant, Japan. It was installed in 2002 to treat MSW and generate power. As of 2014, it takes 268 tonnes of MSW per day and generates 7.9 MWh electricity [77].

Torrefaction is one route to enhance the potential of some biomasses for gasification. It is a form of mild pyrolysis [82] which significantly enhances the heating value and resistance to moisture of the biomass. Heating at 200–300 °C under an inert atmosphere leads to preferential loss of moisture, hydrogen and oxygenated species [83] and more “coal-like” material, potentially more suitable for entrained flow gasification [83] is formed. The torrefaction of a large number of different types of biomass materials has been investigated; first of woody biomasses, but later of a much wider range of biomass types [84]. The hemicellulose fraction of the biomass is initially converted, and higher fractions of hemicellulose lead to greater mass changes. The mass yield of biomass after torrefaction ranges from 24–95%, with the energy density ranging between 1 and 58% [HHV] higher after torrefaction, in one review [84] (the energy yield ranged between 30 and 98%). Owing to their lower fraction of hemicelluloses, woody biomasses exhibit smaller changes in mass than other types of biomass, with mass yields with few exceptions > 95% [84]. Process integration can yield high energy efficiency for an overall process; simulations indicate upwards of 90% for the integration of a steam cycle with a torrefaction plant, if the gases from the torrefaction process are subsequently burned [85]. It is clear that this is a promising technology that may enhance the potential of biomass for use in subsequent gasifiers.

3.1.3. Gasifying media

The operating conditions which are preferable for different biomass types depend upon the type of gasifier used and the desired quality of the final product, with the amount of tar in the product gas being a primary concern. Gasification is carried out in the presence of a gasifying medium inside the gasifier. The gasifying medium or environment can be air, oxygen, steam or carbon dioxide. The heat content of the product gas is a function of the gasifier environment. The product gas from air gasification gives a heating value of around 4–7 MJ Nm⁻³ on account of the presence of N₂ in the air which dilutes syngas and results in low calorific content [50,86–88]. When the gasifying atmosphere is pure O₂, the heating value can be as high as 28 MJ Nm⁻³ [89]. Steam or a combination of steam and O₂ produces syngas of intermediate calorific value (10–18 MJ Nm⁻³) [50,90–92]. Furthermore, the blend of air and steam yields higher quantities of H₂ than air alone and also aids in decreasing the process energy requirements. The gasifying atmosphere also plays a significant role in transforming solid char and heavy hydrocarbons to carbon monoxide and hydrogen [93].

3.1.4. Equivalence ratio (ER) and steam-to-biomass ratio (S/B)

The equivalence ratio represents the actual air-to-biomass ratio with respect to the stoichiometric requirement for complete conversion and plays a key role in biomass gasification [94]. Studies [95] showed that H₂ and CO fractions in syngas were enhanced when ER values were decreased. However, the yield of gaseous products will decrease too when the ER is reduced below the threshold, which is the initiation of pyrolysis. Higher ER results in lower H₂ and CO yields, with an increase in CO₂, which in turn decreases the heat content of the syngas. By contrast, a higher ER improves tar cracking due to higher O₂ availability for volatile species to react with. However, an insignificant influence of ER was found on nitrogenous products, during gasification. Zhou et al. [96] reported a small increase in ammonia (NH₃) yield at 800 °C, using sawdust as the raw material when the ER was raised from 0.25 to 0.37. In a fluidised bed, the solid bed material (particles) along with gasifying agent forms a solid-fluid mixture which behaves like a fluid and provides a platform for heterogeneous and homogeneous chemical interactions to occur. The temperature of the bed is a significant variable which influences the gasification process. Bed temperature is a function of ER and rises linearly with it, provided the feed rate is kept constant as the increase in feed air enhances the extent of combustion which results

in higher heat release. However, an increase in feeding rates decreases bed temperature keeping ER constant [25]. Some work [95] has examined (among other parameters) the effect of increasing the amount of steam at a fixed equivalence ratio (0.3) during gasification of sawdust. Increasing steam amount led to more H₂, better LHV for the gas and lower tar; however, the authors did not consider the increased energy requirements for raising the steam in their analysis. ER is also impacted by the presence of moisture and volatiles in the feedstock material [97,98]. Water content up to 15% results in an increase in ER and gas amount, but above 15% causes irregular temperature fluctuations. High volatile fractions in the biomass feedstock produce higher tar yields. Biomass with a high proportion of moisture or ash benefits from either co-gasification with a higher heating value fuel if a syngas with a high heating value is required or potentially from the use of oxygen enrichment. Roy et al. [99] considered the co-gasification of cow dung (as an exemplar of a low-quality fuel with a high ash content) and found an approximately 50:50 ratio of dung to biomass to be optimal in a downdraft gasifier.

Numerous research investigations [100–104] have shown that the ratio S/B is a key parameter in BG on account of its influence on the syngas yield and heat content. Increasing the S/B results in more H₂ yield and, therefore, syngas with higher heat content. It also produces lower amounts of tar, due to water gas shift, reforming and cracking reactions [95]. Sharma et al. [105] reported the existence of a limit beyond which any increase in S/B produces excess steam in the syngas. Energy contained in the excess steam along with the enthalpy losses in generating this steam, result in low process efficiency. Such issues demand an optimal S/B in steam biomass gasification. The advantages and disadvantages of the various gasification media have been explored by Wang et al. [106]; amongst those highlighted above, the use of CO₂ as a gasifying agent, similarly to steam, requires an external heat supply.

3.1.5. Gasifier temperature and pressure

Several experimental and modelling studies have reported the effects of temperature on char conversion, gas yield and composition, and tar production. A temperature greater than 800 °C results in higher char transformation and lower tar yield on account of higher conversion of carbon, volatile species and high molecular weight HCs into gaseous products [107]. From this point of view, it is desirable to have a higher gasification temperature [97,108,109]. Optimal ranges of temperatures were reported between 750 and 850 °C for gasification of agricultural waste fuels, 800 and 900 °C for RDF and 850–950 °C for woody biomass (in comparison to ~1000 °C for coal) [110]. However, the desire for lower ash accumulation necessitates lower temperatures which practically restrict the temperatures up to 750 °C during BG [32]. It is found that H₂ yield at equilibrium initially increases to a limit, then decreases, with a rise in temperature [111]. Therefore, the optimal operational gasifier temperature can only be determined after evaluating several key parameters such as desired gas composition and calorific content, tar yield and char conversion. Pressurized gasification of biomass was studied by Knight et al. [112] and Wang et al. [113]. Higher pressures with larger ERs result in the decrease of light hydrocarbons and tar yield along with complete conversion of carbon. The quantity of polycyclic aromatic hydrocarbons (PAH) increases with a rise in gasifier pressure, although an overall decrease in the tar was observed.

3.1.6. Residence time

Residence time has an important impact on tar make-up and yield and, therefore, on syngas quality. Milne et al. [114] and Zhang et al. [61] reported extra production of gases, formic and acetic acids, and water as a result of supplementary degradation of secondary vapour phase species, which occurs due to longer vapour residence time during pyrolysis. Furthermore, the quantity of tar reduces by a

significant extent when the space time was increased for a dolomite bed during gasification [115]. Kinoshita et al. [116] observed that yield of O₂-containing species is an inverse function of residence time. Moreover, except benzene and naphthalene, fractions of all 1- and 2-aromatic ring species reduced with residence time while 3- and 4-aromatic ring compounds increased, which in turn has a significant influence on the outlet gas quality and composition.

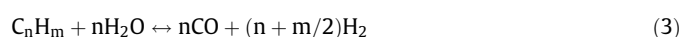
3.1.7. Catalysts

A significant number of investigations have been conducted over the past few decades to develop biomass gasification and ensure its successful installation and operation at commercial and industrial scales. Banowetz et al. [117] reported the major barrier to achieving this objective is the production of undesirable species, such as tar, nitrogenous complexes, PM, alkali metals and carbon deposition on catalysts. Tar is a blend of condensable aromatic and oxygen containing HCs, which is responsible for downstream blockage and corrosion along with the degradation in syngas quality [114]. Tar can be cracked at elevated temperatures. However, an increase in the operating temperature also enhances ash agglomeration with a decrease in process efficiency [118]. It should be noted that ash is a cause of corrosion and alkaline metals are accountable for bed sintering and defluidisation of fluidised bed gasifiers [119–121].

Previous research [60,110,114,117,122,123] has demonstrated the importance of catalytic tar cracking with respect to the process cost and efficiency. Employing suitable catalysts (including any dopants) not only reforms tar but also increases char gasification which, in turn, results in higher and cleaner gas yield with improved calorific content [124]. Presently, a number of investigations are being carried out to develop more stable and active catalysts for gasification, using Ni-based formulations, noble metal catalysts, olivine, dolomite, etc. [122,125–129].

Catalysts can be used in the gasifier directly or may be employed in another reactor placed downstream. The former method is called primary catalysis, and some catalysts used here included, e.g., alumina-supported Ni, olivine and dolomite, responsible for enhancing steam reforming and water gas shift reactions [110,130–136]. They reduce tar yields and increase H₂ and CO yields. In addition, they prevent choking of the bed by reducing agglomeration. However, Ni-based catalysts suffer from deactivation due to carbon deposition [60,137]. Alternatively, product gases can also be processed by secondary catalysts (e.g., Ni-based catalysts, dolomite) placed in a catalytic reactor downstream of the gasifier [123]. They can crack tar in the temperature range of 750 to 900 °C and are, therefore, promising for hot gas cleaning [125,137–140]. However, employing secondary catalysts enhances the syngas production cost considerably. On account of cost effectiveness and reduction in process complexity in downstream treatment of the product gas, primary catalysts are seen as more promising and are attracting more attention for research investigations [110].

3.1.7.1. Ni-based catalysts. Catalysts based on Ni are extensively used in commercial-scale steam and dry reforming processes [141]. As a matter of fact, they are the most commonly used catalysts for gasification processes on account of their tar cracking properties and their potential to improve the water gas shift reaction as shown in Eq. (2). They decrease tar amount and enhance desired product gas yield and quality. They are about 10 times more reactive than calcined dolomite [136]. However, these catalysts are more active for the steam reforming of heavy HC species (Eq. (3)) than lighter ones (Eq. (4)), during catalytic gasification of biomass [125].



Biomasse Kraftwerk Gussing GmbH & Co. operates a biomass gasification facility based on dual fluidised bed gasifier (DFB) where Ni-based catalytic filters are employed in the gasifier freeboard to reform tar at elevated temperatures and remove particulate species from syngas [142]. Ni is undoubtedly a promising choice for biomass gasification; however, it suffers from deactivation due to coking, sintering, attrition and alkali metal and sulphur poisoning [143].

Coke formation is an intrinsic characteristic of steam reforming of biomass for hydrogen production. The elevated temperature during reforming not only results in higher amounts of hydrogen but also in coking. Carbon poisons the catalyst by forming bulky phases of nickel carbides and by condensing nickel crystallites via inactive carbonaceous layers of material [129,144–147]. Moreover, higher molecular weight aromatic biomass raw material can also lead to coking. One of the solutions for coke formation is auto-thermal gasification, where the rate of coke formation on catalyst equalizes the coke removal rate by combustion [148,149]. Here, air fluidises the biomass bed and catalyst and keeps it clean. Coking can also be minimized to a significant extent by enhancing S/B with respect to gasification stoichiometry. However, it increases the energy penalty making the syngas or H₂ generation process expensive. A threshold limit of steam-to-carbon ratio which should be sufficient to avoid coke formation with minimal excess energy [150] is an important parameter to be determined.

Ni catalysts suffer from attrition, in fluidised bed environments due to severe process conditions as compared to fixed bed gasification systems. The mechanical strength can be enhanced by impregnating supports such as olivine [151]. However, even when using Ni catalysts with a carrier material, some attrition is inevitable, since Ni is present as a layer on the carrier [143]. Mechanical deactivation via attrition is irreversible but can be eliminated by using appropriate reactors such as fixed beds.

The overall catalytic activity of Ni-based catalysts is improved by the use of a dopant or promoter along with a support phase. The resultant nickel formulation is mechanically stronger and has a higher resistance to coking and attrition [143]. Nickel-support interaction, pore structure of support and acidity-basicity of support can have positive impacts on metal dispersion, crystallite size and coking [152,153]. Lower nickel concentrations have better interaction with the support phase, along with proper dispersion of metal [145]. This dispersion is enhanced by adding a dopant to the formulation. It should be noted that the presence of promoters and supports in nickel catalysts lead to reduction of their deactivation during BG. A detailed review concerning supports and dopants and their influence on process variables for biomass gasification has been published by de Lasa and co-authors [25].

3.1.7.2. Other catalysts. Usage of olivine (magnesium iron silicate), dolomite (calcium magnesium carbonate) and alkali-based catalysts is considered promising in biomass gasification and has garnered much attention in past years. Some research investigations have been conducted for olivine and dolomite vis-à-vis tar cracking. Catalytic activities of calcined olivine and dolomite were evaluated in moving bed reactors by Hu et al. [127] and it was found that calcined catalysts are more efficient than non-calcined ones. Using a similar set-up, Devi et al. [154] demonstrated an increase in tar cracking between 800 and 900 °C, employing calcined dolomite and non-calcined olivine. These researchers observed that at a temperature of 900 °C, all heterocyclic species are converted. Moreover, tar yield of 4 g m⁻³ decreased to 1.5 g m⁻³ employing calcined dolomite and 2.2 g m⁻³ using olivine.

Olivine and limestone occur freely in nature and, therefore, have been employed widely for biomass gasification due to their cost

effectiveness. They are commonly used as bed materials in fluidized beds where they suffer from attrition on account of intense process conditions. Normally, limestones have shown higher attrition than olivine or silica [151]. The attrition taking place during gasification is dependent on the hardness factor measured according to Moh's scale. However, the attrition of the bed material in a DFB is also a function of the kind of particle separator after the riser as well as the gas velocity [123,143].

Dolomite as a primary or secondary catalyst in catalytic biomass gasification is a good choice on account of its efficient tar removal capacity and cost effectiveness. However, it is mechanically weak and prone to attrition [110]. A mixture of coal, pinewood sawdust and plastic wastes was used as feedstock material by Aznar et al. [126] to investigate the effect of dolomite as a tar reducing agent. The flow rate was kept at $1\text{--}4\text{ kg h}^{-1}$, ER at 0.3 to 0.46 and bed temperature between 750 and 880°C . These authors obtained a product gas with 15% (dry basis) hydrogen yield and tar content less than 0.5 g m^{-3} . This emphatically demonstrates the potential of dolomite as an effective catalyst for gasification.

Alkali metals such as potassium and sodium are normally present in all kinds of biomass feedstock along with other inorganics and are found in the bottom ash of gasifiers. During pyrolysis, these metals can form a reactive char that can have an important influence on BG. If ash is employed as a catalyst during gasification, then it can not only aid in resolving the ash disposal issue but can also enhance the gasification resulting in the generation of cleaner gas [128,155,156]. However, these metals when used as catalysts eventually lose their effectiveness on account of particle agglomeration. Furthermore, costly and complex recovery of catalyst coupled with ash handling problems and enhanced char content post gasification, cause other challenges when alkali metals are directly added as catalysts [123]. Interestingly, when a nickel catalyst was added with sodium carbonate in rice straw gasification, generation of permanent gases were considerably enhanced [157]. These researchers reported that the generation of permanent gases is a function of the alkali metal carbonate employed.

3.1.8. Gasifier design

Gasification of biomass is usually performed in one of two types of gasifier, namely fixed bed (FXB) and fluidised bed (FB) gasifiers. The FXB gasifier is again sub-classified as updraft, downdraft and cross-draft, based on the flow direction of air [158]. Bubbling

fluidised bed (BFB), CFB and DFB are the principal types of FB gasifiers. Another gasifier type is the external circulating concurrent moving bed, which is a relatively new design and is currently under investigation. A final type, called an entrained flow gasifier, was developed for gasification of finely refined coal and is not appropriate for fibrous biomass [29].

3.1.8.1. Fixed bed gasifiers. Fixed bed gasifiers are the oldest and most commonly employed reactors for the gasification of biomass feedstocks on account of their simple design, easy operation, high thermal efficiency and minimal required pre-treatment of raw materials. In commercial markets, FXB gasifiers are considered as the first choice for small-scale gasification plants of less than 10 MW for local power generation [50]. In the updraft gasifier, fuel enters from the top end and gasifying agent from the bottom, and in downdraft both fuel and gasification agent enter from the top with the fuel coming in from a lock-hopper. In updraft gasification, the char at the bottom of the bed meets the gasifying agent first, and total combustion occurs, producing H_2O and CO_2 and raising the temperature to $\sim 1000^\circ\text{C}$. The hot gases flow upward, conducting endothermic reactions with unreacted char to form H_2 and CO , with consequent cooling to $\sim 750^\circ\text{C}$. The gases pyrolyse the dry biomass which is descending, and also dry the incoming biomass near the top of the reactor. Updraft gasifiers typically produce 10–20 wt. % tar in syn-gas, which renders it unsuitable for many advanced applications [50]. In the downdraft gasifier, gas flows co-currently with the fuel. A throated downdraft gasifier has a restriction part-way down the gasifier within which air or O_2 is added, and where the temperature rises to $1200\text{--}1400^\circ\text{C}$, and the biomass fuel is burned/pyrolysed. The combustion gases then pass down over the hot char at the bottom of the bed, where they are reduced to H_2 and CO . The high temperature within the throat ensures that the tars formed during pyrolysis are significantly cracked (homogeneous cracking), with further cracking occurring as the gas meets the hot char on the way out of the bed (heterogeneous cracking), leading to a less tarry off-gas. According to Gordillo et al. [159] typical gas compositions of H_2 , CO , CH_4 and CO_2 in updraft and downdraft gasifiers are found to be 5 to 15%, 20 to 30%, 1 to 3% and 5 to 15%, respectively. A comparative schematic of updraft and downdraft FXB gasifiers is shown in Fig. 7.

In the cross-draft gasifier, feedstock is fed from the top of the reactor whereas air is fed from the side of the reactor [25]. Product gas exits the gasifier unit at the same level as the air inlet, but from

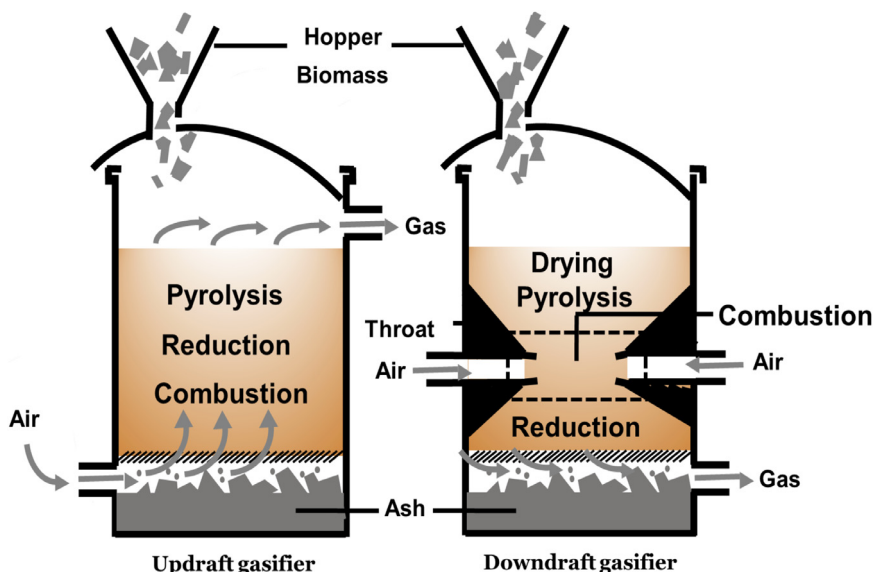


Fig. 7. Comparative schematic of updraft and downdraft fixed bed gasifiers [77].

the other side of the unit. Combustion and gasification take place in the area of the air entrance with pyrolysis and drying zones toward the top of the reactor. Ash is removed from the bottom and exit product gas temperature is around 800 to 900 °C with higher tar content.

3.1.8.2. Fluidised bed gasifiers. Fluidised bed gasifiers are highly efficient and hence form the first choice for very large scale biomass gasification. Air is circulated through a bed of fine particles, for example, sand, resulting in bed fluidisation. This ensures uniform heat and mass transfer among bed material, biomass fuel and hot gases during the gasification. It also enables the gasifier to tolerate diversified feedstock. This flexibility with different biomass raw material is a crucial advantage with FB gasifiers [160]. In addition, around 10 g Nm⁻³ is the commonly observed tar level, which is generated from secondary and tertiary tars [29].

Tasaka et al. [161], used a BFB gasifier which regulated the ER to ensure a bed temperature between 700 to 900 °C. Pyrolysis and gasification of biomass feedstock took place in the hot bed, forming char, tar and gaseous species. Tar was cracked to a significant extent and, as a result, only around 1 to 3 g Nm⁻³ of tar was present in the exit syngas. The tar yield was around 12 wt. % of the cellulose in the fed biomass (in steam gasification) without employing any catalyst.

CFB gasifiers are able to gasify large quantities of biomass and can be operated at high pressures. One application is for them to gasify bark and other forestry wastes in paper mills. This type of gasifier consists of a reaction vessel and a cyclone separator and the bed material is circulated between them. Ash is removed in the latter and char and bed material granules are returned to the former. Gases produced are sent to the gas turbine (GT) for power generation. Corrella et al. [162] and Osowski et al. [163] discussed the major issues related to this kind of gasifier. They stated that the tar formation in the outlet gas is higher than for the fixed bed while the particulate fraction is similar. Secondly, installation and operational expenses are much higher than for FXB gasifiers. A comparative schematic of BFB and CFB is depicted in Fig. 8.

The DFB gasifier was first developed in Austria for biomass steam gasification [164]. It separates the gasification and combustion parts of the process by employing two separate fluidised beds. The biomass is fed into the base of the gasifier bed, usually fluidised by steam. The second bed acts as a char combustor using air in a fast fluidised bed which heats the bed material to around 850 to 900 °C. The bed material acts as the heat transfer medium between beds. This avoids gas transfer, allowing a N₂-free syngas; it is separated from the combustion flue gases in a cyclone and recirculated to the gasifier via loop seal [165]. This technology is successfully demonstrated at commercial scale in coal-fired power plants [166,167].

Recently, a new technology called an external circulating concurrent moving bed gasifier is under investigation, where combustion of produced char and steam gasification of biomass feedstock take place at the same time. It consists of a moving bed with the regions where combustion and gasification take place. There is a loop between these zones, where bed material is circulated, along with heat transfer. Char combustion occurs in the combustion zone and serves two purposes: (a) provides energy for endothermic steam reforming reactions in gasification zone (b) regenerates catalyst by burning off the char deposited over the catalyst. Wei et al. [168] demonstrated hydrogen and tar yields of 53.3 mol. %, 0.7 g Nm⁻³, respectively, with S/B of 0.4 and temperature of 800 °C, employing calcined olivine catalyst in a lab-scale facility. These results demonstrate the potential of this technology for the production of low-tar H₂-rich gas.

One of the critical benefits of FB gasifiers is the possibility to employ a low-cost bed material which can simultaneously act as a catalyst for gasification reactions and tar cracking. This material should have high selectivity for product gas and should not be prone to attrition and formation of carbon [7]. On the other hand, the phenomenon of defluidisation reduces the ability of these reactors to operate above 800 °C. Feedstocks, especially herbaceous biomasses, often contains considerable fractions of Si, K and Ca which can form viscous mixtures that adhere to the surface of the bed particles and bind them to form agglomerates, preventing fluidisation [169,170]. This is the prime limitation of FB gasifiers, although many solutions have been suggested for this problem. One feasible solution is regulating the bed temperature to avoid melting of silicates and alumino-silicates present in bed particles [27].

It should be noted that the installation and operational costs, robust design and the requirement or otherwise of feedstock pre-treatment are significant factors when choosing a gasifier. Physical and chemical properties of biomass raw material, desired product gas composition and calorific content and other operating variables are other key parameters [171]. A reported discussion about fixed and fluidised bed gasifiers based on material, technology, energy and environment demonstrates that there are specific applications for these two gasification systems [172]. Major gasifier designs along with their main advantages and limitations are shown in Table 5.

3.2. Gasification thermodynamics and kinetics

Biomass gasification is a complex process of many overlapping steps. In addition, the physical and chemical characteristics of biomass feedstock are highly variable in nature, which in turn influence syngas calorific content and composition. Here, thermodynamic

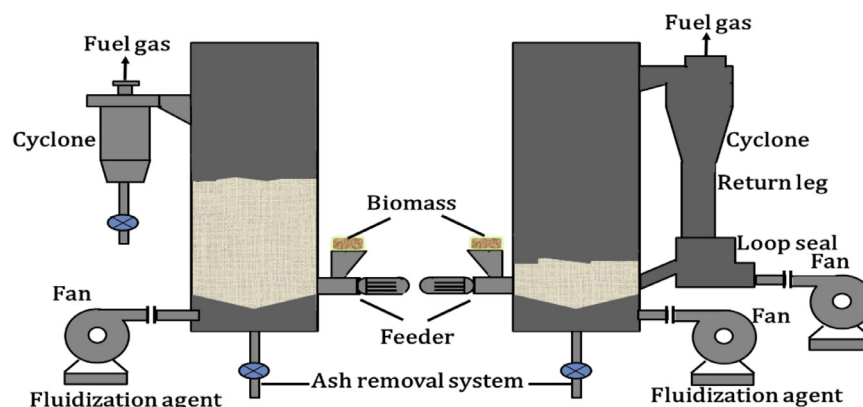


Fig. 8. Comparative schematic of bubbling and circulating fluidised bed gasifiers.

Table 5
Advantages and limitations of major gasifier designs.

Gasifier design	Major advantages	Major limitations
Fixed bed/moving bed gasifier	<ul style="list-style-type: none"> Simplest and robust design Economical at small scale Tolerant for large range of biomasses 	<ul style="list-style-type: none"> Non uniformity in temperature High tar and char yields Poor cold gas η
Fluidized bed gasifier	<ul style="list-style-type: none"> Uniformity in temperature distribution Low tar and char yields Shorter residence time High capacity for raw material processing 	<ul style="list-style-type: none"> Uneconomical for small scale High PM fraction in syngas
Entrained flow gasifier	<ul style="list-style-type: none"> Very low tar yield Economical for large scale High quality syngas 	<ul style="list-style-type: none"> Unsuitable for biomass Non-tolerant for coarse particles Issue with raw gas cooling
Unique gasifier (integration of gasification and gas clean-up in single reactor)	<ul style="list-style-type: none"> Robust design Economical 	<ul style="list-style-type: none"> More R&D is needed to upscale to commercial level
Plasma gasifier	<ul style="list-style-type: none"> Capable to treat hazardous and toxic waste 	<ul style="list-style-type: none"> High energy requirements High installation and maintenance costs Low η

modelling can be an efficient tool to evaluate the impact of operational variables such as feedstock composition, temperature, pressure and steam-to-biomass ratio on the overall gasification process and on the product gas quality.

Employing a thermodynamic modelling approach, theoretical boundaries of various chemical species can be evaluated, at equilibrium. Furthermore, optimum operating parameters and available work contained in biomass fuel can also be determined by developing an equilibrium model [173]. In principle, thermodynamic predictions are independent of reactor type, reaction time and reaction network [174]. However, in practical situations, thermodynamic results are only appropriate for gasification with longer reaction times on account of the key role played by kinetics in these conditions [175].

In real life scenarios, chemical interactions inside the gasifier take place for a finite time and, therefore, predictions by equilibrium models have mixed success depending on reaction temperature and residence time. The equilibrium models work fairly well in high-temperature entrained flow gasifiers but much less well in fluidized bed systems for instance [176]. This necessitates the development of kinetic models which account for reaction rates, gasifier hydrodynamics and residence time of particles. For specific operational conditions and gasifier design, kinetic models can forecast product gas composition, temperature inside the gasifier and gasifier performance to a greater degree of accuracy.

3.2.1. Thermodynamic modelling approaches

Thermodynamic modelling can be done by employing a stoichiometric or non-stoichiometric method. The former necessitates the selection of only the dominant reactions, whereas the latter employs the feed elemental composition (C, O, H, S, N) of biomass feedstock obtained from ultimate analysis. Models developed by the stoichiometric method can result in significant deviations from real life scenarios if important reactions are neglected. On the other hand, the non-stoichiometric approach is more suitable for processes such as biomass gasification where precise chemical composition is unknown or is highly variable and whose reaction mechanisms are often uncertain.

Numerous books, book chapters and large volumes of research and review articles have been published hitherto on thermodynamic models to predict syngas quality and quantity [174,175,177–182]. These models provide acceptable estimates of syngas composition and alterations in chemical species vis-à-vis operational variables. However, in a large number of cases, experimentally observed values deviate from the predicted values on account of the following inappropriate assumptions: (i) tar and char are considered as solid carbon; (ii) ash is considered as an inert species; and (iii) inadequate

equilibrium assumptions are provided for some important reactions [32]. It should be noted that during actual gasification, many reactions do not attain chemical equilibrium and the aforementioned deviations are influenced by different interactions of char and tar. In addition, syngas quality can be affected by the catalytic activity of ash during pyrolysis.

3.2.2. Equilibrium model developed by CREC

In order to counter the above-mentioned limitations, Salaices and co-authors [32] at the Chemical Reactor Engineering Centre (CREC), University of Western Ontario, Canada, have developed a non-stoichiometric model based on the elemental composition of biomass feedstock. They investigated the impact of biomass composition and other operating parameters on product gas generation, employing a Gibbs free energy minimization approach. CO, H₂, CO₂, CH₄, H₂O, C₂H₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂, C₆H₁₄ and char were considered as the product species. Tar was not taken into account because of its low concentration. Moreover, concentrations of N₂ and S were negligible vis-à-vis equilibrium calculations and, therefore, were neglected [179,183]. Nine independent non-linear equations were constructed taking 12 different variables. Calculations were also verified applying the ASPEN HYSYS software package.

Salaices and co-workers [32] studied the effect of varying biomass composition on product gas constituents. They varied C:H (in wt. %) and also C:O content over a diverse range of biomass feedstock, at 800 °C and 1 atm. For example, C:H was varied from 1:2.11 for jute stick to 1:0.69 for coal, whereas C:O changed from 1:1 for glucose to 1:0.111 for heterotrophic (organic carbon). For various biomass compositions, H₂ yield was reported to be dependent upon S/B. It was found that H₂ yield in the product gas is enhanced with an increase in S/B from 0 to 2 and is proportional to C:H fraction. Moreover, a significant rise in H₂ concentration in the product gas was found, when S/B was increased above 1 g/g. All these results were in the agreement with the experimental data.

These investigators also reported that CH₄ reforming reactions, interactions with higher HCs and water gas shift reactions do not attain equilibrium at short reaction times of 5 to 30 s. Therefore, it was concluded that thermodynamic models can predict the product gas compositions, for longer reaction times (greater than 30 s). However, experimental studies demonstrated a significant deviation in the trends of individual species present in the product gas from the equilibrium modelling predictions when reaction time is shorter than 10 s. This necessitates the need of a non-equilibrium model to completely understand the interconversion of chemical species during gasification of biomass.

3.2.3. Thermodynamic models for biomass gasification

Numerous researchers have developed thermodynamic models for moving bed gasifiers, FB gasifiers and specially-designed gasifiers as summarised in Table 6. Many studies were performed to evaluate the system performance for integrated and hybrid biomass gasification systems as well. As noted above, biomass gasification consists of numerous stages, one of which is pyrolysis. As pyrolysis influences syngas yield and quality, its accurate description can lead to more precise forecasts by the equilibrium model [184].

Gao and co-authors [203] investigated the impact of heat rate and temperature during pyrolysis on product gas composition. They modelled the reduction zone and pyrolysis zone simultaneously in a fixed bed gasifier. With rising temperature, H₂ and CO yields were enhanced whereas N₂ and CO₂ were reduced for constant heating rate of the pyrolysis zone. Fractions of CH₄ and H₂O increased during reaction and dropped at the end. When the temperature of pyrolysis was kept constant, H₂, CH₄, CO and H₂O concentrations increased while CO₂ and N₂ concentrations decreased. This study demonstrated the importance of pyrolysis temperature and heating rate on end gas quantity and quality.

The law of conservation of atomic species, law of conservation of energy and principles of chemical equilibrium were employed by Melgar and co-workers [189] to evaluate optimal reaction temperature and syngas composition in a fixed bed downdraft gasifier. The effects of feedstock moisture and fuel-to-air ratio were investigated for a wide range of feedstocks. The modelling predictions were in close agreement with the experimental results.

Numerous important chemical interactions including biomass feedstock, gasifying agent, evolved gases, etc., take place in the reduction zone of the reactor. Therefore, detailed and precise models

can lead to a better understanding of the gasification process. A few studies were also conducted to model the reduction zone of downdraft gasifiers. Sharma et al. [190] developed an equilibrium model considering char-gas and gas-gas reactions which occur in the reduction zone, to forecast residual char yield, temperature and distribution of gas species. The model was able to represent the real conditions closely and, therefore, demonstrated that the predictive ability of an equilibrium model can be enhanced by considering initial reduction zone temperature and char bed length.

Predictions regarding tar generated during biomass gasification are a difficult issue on account of varying tar composition and yield. Typical tar species were taken by Barman and co-workers [186] as input variables to develop a model for a moving bed gasifier. It was demonstrated that predictions of gasification products were close to real values provided that tar yield was considered in the mass balance equation. However, some deviation from equilibrium was observed on account of CH₄ reactions.

Combined theoretical and experimental investigations were carried out by Balu and co-authors [177] to evaluate the performance of woody biomass feedstock in steam allothermal gasification employing a bench-scale steam reactor. High-quality, high-calorific product gas (9–10 MJ/m³) was produced with high-temperature steam (1000 °C) as the gasifying medium. Trends of syngas composition were found to be a function of unconverted char. For high-temperature steam gasification, H₂ concentrations were between 50 to 60%. The lower calorific value of the exit gas was reported to be 85% higher than that for air-blown gasification. The results were in close accordance with the experimental findings. It can be clearly shown from the investigations that for high-temperature steam gasification (~1000 °C), the S/B ratio should be between 1.3 and 10, as lower

Table 6
Important equilibrium modelling investigations regarding parametric impact on biomass gasification.

Type of gasifier	Operational variables investigated	Biomass feedstock
Downdraft gasifier	Char reactivity factor	CH _{3.03} O _{1.17} [185]
	Air-fuel ratios, moles of moisture/mole of biomass	CH _{1.54} O _{0.62} N _{0.0017} [186]
	Reactor temperature, moisture content in feedstock	Olive wood, miscanthus and cardoon [187]
	Pressure, temperature, humidity in feedstock, oxidant composition	Corn stalks, sunflower stalks, and rapeseed stalks [188]
	Air-fuel ratio, moisture content	Rubber wood [189]
	Moisture, pressure, equivalence ratio, initial temperature in reduction zone	Douglas fir bark [190]
	Temperature in pyrolysis zone	CH _{3.03} O _{1.17} [108]
Fluidised bed gasifier	Average temperature of bed material, steam-to-biomass ratio, moisture content, mixing of devolatilized gas	Wood chips [191]
	S/B ratio, temperature	Rice husk, bagasse, rice straw and ground nut shell [192]
	S/B ratio, equivalence ratio, reactor temperature (Eulerian approach for fluid phase and discrete particle approach for solid phase)	Pine wood [193]
	Temperature, ER, level of preheating, steam infection, moisture (Gibbs free energy minimization)	Hemlock wood [194]
	Bed operational velocity, ER, temperature, S/B ratio, particle size (1-D isothermal, steady state model with 2-phase theory of fluidisation)	Biomass [195]
	Pressure, steam-to-oxygen ratio, heat loss, reforming temperature, drying %, filtration temperature (equilibrium model employing ASPEN PLUS)	Crushed wood pellets and forest residues [196]
	S/B ratio, temperature (empirical model considering gas-char reactions, gas-phase reactions and pyrolysis)	Pine wood chips [197]
Traveling bed gasifier	Air-fuel ratio for drying and gasification	Coal, wood and grass [198]
Oxygen-blown gasifier coupled with H ₂ O gas shift reactor	ER, amount of H ₂ O introduced in shift reactor for complete conversion of CO	Wood [199]
Indirectly heated batch reactor	Amount of char produced	Spruce wood [200]
Standalone fluidised bed gasifier (3-stage system)	Steam-to-O ₂ ratio, ER, temperature	Dried sewage sludge [201]
Universal gasifier	Wood type, moisture content in wood, temperature of exit syngas, oxidant	Different biomass varieties [202]

than 1.3 produces residual char while more than 10 generates no usable fuel gas in the product gas composition.

Equilibrium models do not work very precisely with FB reactors on account of their inability to predict some kinetic and hydrodynamic phenomena such as generation of unconverted char and gaseous hydrocarbon species and poor lateral mixing [196]. This issue is countered by modifying the models using correlations and empirical variables, to match the measured data from gasifiers. FB reactors show complicated hydrodynamic behaviour on account of non-linear interactions between the fluid and the particles, and are, therefore, modelled employing a stoichiometric 1-D or 3-D approach or by linking a Gibbs free energy minimization approach to a 2-phase fluidisation hydrodynamic model [191–197].

A quasi-equilibrium formulation was employed by Lim et al. [180] to create an air-steam BG model for FB reactors, to analyse gasification process performance with ER, temperature and S/B ratio as studied variables. Three empirical equations were generated and two non-equilibrium factors were incorporated to adjust the deviation with respect to experimental data. These equations enable flexibility of the model to adjust to specified experimental conditions. Syngas yield was evaluated by employing a carbon conversion fraction. This model precisely calculated the distribution of product gases, calorific content of syngas and thermal efficiency for varied feedstocks and different reactors. The model was valid in the temperature range of 700 to 830 °C, ER between 0.2 and 0.6, and S/B ratio of 0 to 1.5. It should be noted that this model can provide a general guideline about the operation of air-steam blown fluidised bed gasifiers. However, it could not *a priori* forecast the syngas composition to a very precise extent on account of the inclusion of empirical factors such as carbon conversion fraction and non-equilibrium factors. Therefore, adjustment in empirical parameters was required to increase the accuracy of model prediction.

Thermal losses should be carefully considered, as the autothermal zone in a reactor is a function of gasifier design. Various modelling studies have been performed to calculate an optimum ER for biomass gasification in FB reactors. It was reported that ER utilised varies from 0.1 to 0.3 in fluidised beds [193–195].

Influence of moisture content in the feedstocks on the gasification process have also been studied by a few researchers. Kaushal et al. [191] and Gungor et al. [195] performed investigations in FB reactors and demonstrated that high-moisture-content feedstock decreases average gasifier temperature and results in slower kinetics, which in turn generates low quality syngas. Moisture content can also be decreased by pretreatment of the feedstock via drying. However, this increases the overall cost of syngas generation.

A few thermodynamic models were also developed for specifically-designed reactors. Baggio and co-authors [200] performed modelling and experimental investigations on an indirectly heated batch reactor coupled with an external furnace. Unconverted char, CO, H₂ and CO₂ concentrations at 800 °C found during experiments were in close agreement with the predicted values. However, the value for CH₄ yield deviated considerably. They concluded that equilibrium models are accurate only in the cases where thermodynamic equilibrium is attained through longer residence times.

Bhattacharya et al. [199] designed a mathematical model to investigate H₂ yield, impact of ER and amount of H₂O required in a shift reactor for complete conversion of CO, and O₂ fraction in gasifying media. They employed an O₂-blown biomass gasifier coupled with a water gas shift reactor. It was found that the H₂ purification process is easier when a higher O₂ fraction in the gasifying agent is used, on account of lower N₂ concentration. However, the percentage of O₂ employed has negligible effect on the H₂ yield. It should be noted that the higher the purity of O₂, the higher will be the H₂ production cost.

Recently, a detailed validated equilibrium model was generated by the researchers [182] of Delft University of Technology, The

Netherlands, to evaluate the plant performance, future plant operations and scale-up possibilities of the 253 MW Willem-Alexander Centrale Integrated Gasification Combined Cycle (IGCC) power plant situated at Buggenum. Experimental model validation was performed on high percentage (~70%) biomass co-gasification employing steam-exploded wood pellets and torrefied wood pellets. A net power output of 173 MW and net plant efficiency of about 37% were predicted using steam-exploded wood pellets. However, the former increased to 240 MW and latter to about 42% with 70% co-gasification using torrefied wood pellets. It was found in the exergy calculations that maximum thermal losses occurred in the reactor and during combustion. Model predictions vis-à-vis plant performance and operating variables were reasonably accurate. This kind of real scenario-based model formulation is highly useful in the future development of carbon-neutral plants and also to plan real plant operation with various biofuels. Furthermore, they also help in carrying out investigations to integrate carbon capture technologies.

It is clearly seen that thermodynamic modelling has proved to be an efficient engineering tool to evaluate theoretical limits of end product distribution. Furthermore, the influence of numerous operating parameters can be evaluated on syngas composition and calorific content for different gasifier designs. It is seen that equilibrium models are not very effective in predicting the gasification process in FB gasifiers. However, this limitation can be overcome by adjusting the models according to empirical correlations based on experimental data.

3.2.4. Kinetic studies

As mentioned earlier, many reactions taking place inside the reactor proceed at a limited rate (i.e., they occur in a finite volume in a flowing medium) and to a finite extent which necessitates the kinetic studies of the gasification process [50]. A number of experimental and modelling investigations have been carried out with different types of gasifiers employing diverse feedstocks, with an objective to evaluate and find an efficient and cost effective gasification system for given operating conditions.

Gao and co-authors [204] have carried out rice husk gasification employing CO₂ as gasifying agent via thermogravimetric experiments to find the intrinsic kinetic parameters for the process. In addition, they evaluated the conversion profiles for CO₂-rice husk gasification based on intrinsic parameters found in a random pore model. They assessed the influence of gasifier temperature and CO₂ partial pressure on gasification. The activation energy and reaction order were found to be in the range of ~ 226 – 232 kJ mol⁻¹ and 0.28 – 0.35, respectively, whereas the pre-exponential factor was in the range of 2.38×10^5 – 2.82×10^5 s⁻¹ for the temperature range of 700 – 900 °C. The values of overall rate constants varied from 3.5 to 6 for the same temperature range and were found to be unaffected by CO₂ partial pressure and gasification temperature. They reported an enhancement in rate constant from 7.36 to 7.64 when gasification temperature was raised from 850 °C to 950 °C. On the other hand, the rate constant increased in the range of 1.48 – 1.63 times when CO₂ concentration was raised from 25–100%. As all the correlation coefficients between the model and experiments were more than 0.9, they concluded that the random pore model was precise enough to assess intrinsic reactivities of rice-husk chars.

A few researchers [205] have performed biomass gasification in a conical spouted bed reactor in the presence of steam, to evaluate the impact of temperature, partial pressure of steam and feedstock particle size, on the gasification kinetics. The choice of the reactor was made to ensure high heat and mass transfer rates coupled with isothermal conditions in bed. The temperature was varied from 800 – 900 °C whereas steam partial pressure was varied from 0.2 to 1. Pine saw dust was employed as the feedstock with diverse particle size distribution (0.3–1, 1–2 and 2–4 mm). They concluded that temperature is the most important parameter as a slight increase in temperature

from 800 to 900 °C drops the char conversion time to one-sixth. Particle size below 2 mm and gasifying agent partial pressure were not found to have any considerable effects on the rates of reactions. A homogeneous model, shrinking core model, nth order model and random pore model were assessed for the fitting of experimental results. The latter two models were found to be most precise.

Sreejith et al. [206] investigated the effect of calcium oxide for in-situ CO₂ capture during fluidized bed gasification, by developing a kinetic model. The researchers employed wood as the biomass feedstock and a combination of air and steam as the gasifying media. They reported an increase in the LHV of syngas from 5.58 to 6.12 MJ Nm⁻³ (ER = 0.25, S/B = 1) when sorbent-to-biomass ratio was enhanced to 1.5 from 0.75. In addition, H₂ yield was enhanced by 16% when CaO was introduced in the gasifier. At 727 °C with S/B of 1.5, ER of 0.25 and sorbent-to-biomass ratio of 0.27, a maximum H₂ fraction of 53% was obtained in the product gas. They also concluded that air-steam gasification is more energy efficient than gasification with steam alone. It can be clearly deduced that the application of a cheap sorbent such as CaO is advantageous in biomass gasification to yield a H₂ rich syngas.

A significant quantity of tar is generated in the gasification of biomass and is considered as a major factor for downstream blockage and reduction in efficiency. Researchers have performed experimental [207–209] and modelling [210–212] studies to understand the tar production and removal mechanisms. Kinetic models have been developed comprising numerous reactions and attempted more specifically to include gas phase reactions vis-à-vis aromatic growth [213]. Norinaga and co-authors [214] generated a kinetic model employing 500 species and 8000 reactions for the gas phase reactions during secondary pyrolysis of cellulose. Elementary reactions were combined and simulated, followed by comparison with experimental data. Forecasts about inorganic gases, acetylene and acetic acid along with predictions of minor products were quite accurate. However, predictions about propylene and propane (at 700 °C) and

regarding methanol and C3 HCs were not so good. Possible reaction routes leading to benzene were also predicted, thus reducing the yield of feedstock to syngas and, therefore, to fuels.

Modelling of tar is a useful tool to understand tar formation and destruction inside a biomass gasifier. However, detailed kinetic modelling involves numerous species and reactions and, therefore, the model development becomes too complex; this is a key area for future investigation.

4. Syngas processing

Synthesis gas or syngas is the key product of biomass gasification and contains carbon monoxide, hydrogen, carbon dioxide and methane with traces of some other elements. Since its first usage in the early nineteenth century by London Gas, Light and Coke Company, it has become a significant fuel [215]. It serves as a raw material for biofuels and chemicals synthesis and for power generation [215]. Globally, the largest proportion of syngas produced is utilized in ammonia synthesis (50%) followed by bio-hydrogen production (25%), with the rest used in bio-methanol generation, FT synthesis and other processes [216]. Several syngas transformation routes and applications are depicted in Fig. 9.

According to Woolcock and co-authors [218], impurities in biomass feedstocks and partial gasification lead to contaminants in syngas, which are mainly classified as tars, PM, alkali, nitrogen (NH₃, HCN), sulphur (H₂S, COS), halides and trace elements. These contaminants are responsible for the previously mentioned downstream problems in the gasifier such as corrosion, clogging and catalyst deactivation. They also render syngas unsuitable for bio-methanol production, FT synthesis, fuel cells and other applications. Syngas cleaning requirements are a function of end applications and are shown in Table 7. They necessitate syngas processing prior to its usage, via cold gas or hot gas processing techniques.

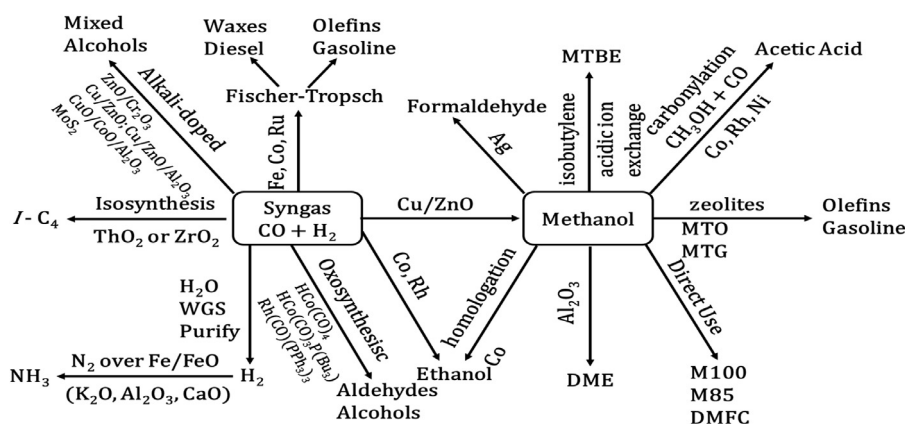


Fig. 9. Different syngas transformation routes to synthesise fuels and chemicals [217].

Table 7
Syngas cleaning requirements for some typical end applications [218].

Contaminants	Applications			
	Methanol synthesis (mg m ⁻³)	FT synthesis (μL L ⁻¹)	Gas turbine (μL L ⁻¹)	IC engine (mg m ⁻³)
Tars (condensable)	– ^a	< 0.01 ^b	–	–
Tars (heteroatoms, BTX)	< 0.1	< 1	–	< 100
Particulate (soot, dust, char, ash)	< 0.02	Not-detectable	< 0.03 (PM ₅)	< 50 (PM ₁₀)
Alkali	–	< 0.01	< 0.024	–
Nitrogen (NH ₃ , HCN)	< 0.1	< 0.02	< 50	–
Sulphur (H ₂ S, COS)	< 1	< 0.01	< 20	–
Halides (primarily HCl)	< 0.1	< 0.01	1	–

^a Data are not available in the original literature

^b All values are at STP unless explicitly specified

It is not possible to prescribe the precise syngas clean-up strategy in each case. The way in which the clean-up strategy should be devised requires the integration of three different factors:

- (i) The nature of the biomass to be processed and the likely nature of minor constituents and the tars formed depending on the type of gasification technology employed – this gives an indication of the window of possible syngas compositions that the clean-up technology will have to deal with.
- (ii) The nature of the downstream processing of the syngas – is the process aiming to produce, e.g., hydrogen, methanol or FT liquids? The purity requirements for the catalytic conversions and separations will differ in terms of tars and minor constituents.
- (iii) Integrating (i) and (ii), the performance in terms of removal percentage of different clean-up technologies and their sequencing (e.g., early removal or cracking of tars followed by syngas polishing) can be optimised to meet the downstream requirements while respecting the expected impurity profile window.

Syngas cleaning technologies are classified as hot gas clean-up or cold gas clean-up based on the condensation temperatures of various species present in the syngas. Usually, cold gas cleaning uses water sprays where contaminants are absorbed in water droplets and condense with water at the exit where temperature is low ($< \sim 100^\circ\text{C}$). Hot gas cleaning techniques take place at elevated temperatures ($> 300^\circ\text{C}$), where many alkalis condense. Other hot gas technologies occur at very high temperatures of 1000°C or above. Significant contaminants and relevant cleaning technologies are discussed in the subsequent sections and are also summarised in Table 8.

4.1. Tars

Tars are condensable organics ranging from heterocyclic aromatics to multi-ring (1 to 7) PAH species [74,219]. They are considered to be the key challenge in the gasification process on account of their ability to clog downstream equipment, deactivate catalysts and degrade syngas quality [220]. Practically, it is impossible to completely avoid tar generation during gasification, although it can be reduced to a considerable extent by employing suitable technologies.

In practice, tar is cracked by employing any of three strategies: elevated temperatures, catalysts or non-thermal plasma. All of the strategies enhance the tar degradation rate and try to enhance the rate at which chemical equilibrium is attained, thereby reducing the quantity of tar (a non-equilibrated species) leaving the reactor. They may be employed in-situ or post-gasification, depending upon the end application of syngas and gasifier design. They can crack tar to as low as 50 mg m^{-3} , if applied in-situ, which is a reasonable limit for certain uses such as direct burning [221,222]. Downstream treatment can decompose tar to the limits of detection and is, therefore, employed for high-purity uses of product gas such as fuel cells or biofuels synthesis.

Thermal decomposition of tar usually employs a temperature between 1100°C and 1300°C , where lower temperatures require high residence time and vice versa [223,224]. Fjellerup et al. [225] and Houben et al. [226] observed that at 1075°C naphthalene in tar is degraded to about 80% in 5 s whereas the same results are obtained in just 1 s when the temperature is raised to 1150°C . Brandt and co-authors [227] have demonstrated that effective tar cracking requires only 0.5 s at 1250°C . The initial tar amount is also a deciding factor for the reduction of tar employing this strategy [222,227]. Downstream thermal decomposition of tar enhances the soot and particulate fractions in the product gas [226,228,229].

Houben et al. [228] have reported the formation of soot and heavy PAH in an FB reactor using thermal cracking downstream of the gasifier. However, an optimal methane-to-hydrogen ratio (low CH_4 and high H_2) in the product gas can be determined to crack tar instead of soot formation. At lower ERs and higher H_2 , the tar yield decreases to a significant extent on account of naphthalene cracking; this is converted into lighter tars and permanent gases. Furthermore, tar can also be removed as soot but this decreases the calorific value and purity of the syngas. Thermal decomposition is relatively simple and effective, but expensive on account of high energy demands.

Decomposition of tar using catalysts requires relatively low temperatures but at the cost of operating problems owing to catalyst deactivation through sintering, coking and/or poisoning [230]. Sutton and co-workers [123] suggested tar cracking potential, ability to regulate carbon monoxide and hydrogen fractions in syngas, methane reforming potential, resistance to coking and sintering, high mechanical strength and cost-effectiveness as some of the desirable characteristics of a catalyst employed in hot gas cleaning. Ni-based catalysts are most commonly employed in commercial applications although they suffer from coking and sintering. Recently, researchers are becoming more interested in transition metal-based catalysts on account of their better potential for tar cracking and enhanced resistance to carbon formation [220,231]. Detailed discussion on catalysts and catalytic cracking is provided in Section 3.1.5.

Plasmas are highly reactive in nature with a potential to decompose tar compounds [232]. A very high temperature can produce thermal plasma whereas non-thermal plasma is generated by molecule-electron collisions at high energy. Pulsed corona, direct current (DC) corona and radio frequency (RF) plasma are a few examples of typically used non-thermal plasma for tar cracking. Pulsed corona plasma degrades tar at a very low temperature of about 400°C [233,234]. Despite their effectiveness, these techniques are not used in large-scale operations because of the operating intricacies and high energy requirements [233–235].

Wet scrubbing is the cold gas cleaning technique employed to remove tar species from product gas. A large fraction of tar compounds is directly absorbed in water. The remaining tar vapours are converted to fine aerosols when syngas temperature falls significantly while scrubbing and are easily absorbed in water. Class II and III tars such as phenols, cresols, toluene, etc., are absorbed by water droplets in the vapour form. This is efficient and cost-effective technology; however, it necessitates waste water treatment of a stream containing toxic tar compounds, which is challenging. Waste water treatment via biological or chemical pathways is the key issue with this strategy and a relatively new area of research called 'syngas fermentation' has provided a platform for relevant investigations [236].

4.2. Particulate matter (PM)

Residual solid carbon and inorganic species form particulates during gasification, which range in size from 1 to $100\text{ }\mu\text{m}$. The inorganic fraction of these contaminants is comprised of potassium, sodium, calcium, silica, iron and traces of arsenic, selenium, lead and zinc [237–239]. The composition and size of PM are the functions of type of gasification technology employed and biomass raw material [240]. Corrosion, erosion and fouling can result from the presence of PM in syngas. Even direct burning of syngas necessitates the particulate fraction to be lower than 50 mg m^{-3} . Numerous researchers have studied its effect on erosion of turbine blades in IGCC power plants and pressurized FB combustion power facilities [235,241,242].

Investigations in the past three decades have developed promising advancements in hot gas cleaning technologies for PM [173]. Inertial separations using cyclones, barrier filtration employing granular filters and electrostatic precipitation are typically used techniques at hot gas temperatures. Cyclones are devices which

Table 8

Syngas contaminants and relevant cleaning technologies [74, 215–219].

Contaminant	Technique employed	Process	Principle	T (°C)	Removal η (%)	Comments
Tar	Hot Gas Cleaning Technique (HGC)	Thermal Cracking	Employing high T to crack tar	1100–1300	~80	Expensive, results in low process η
		Catalytic cracking	Employing catalyst to crack tar at comparatively low T	Vary	Vary	Operational challenges vis-a-vis catalytic activity due to coking, sintering and poisoning
		Non-thermal plasma	Decomposition of tar by plasma	~400 (pulsed corona plasma)	Vary	Complex, high energy demand
	Cold gas cleaning technique (CGC)	Wet scrubbing	Absorption of tar components in H ₂ O	< 100	Vary	Waste H ₂ O needs treatment prior to discharge
Particulates	HGC	Cyclones	Inertial separation	> 1000	90	e.g. – conventional and enhanced cyclones
		Filtration	Diffusion, inertial impaction, gravitational settling	~250 (fabric) ~600 (panel bed) ~1000 (metal barrier)	~99	e.g. – fabric filter, panel bed filter, metal barrier filter & rigid filter
		Electro-static separations	Difference in dielectric properties under electric field	~400	– ^a	e.g. – parallel plate precipitator, tube type
	CGC	Wet scrubbing	(i) separation by inertial force (ii) electrostatic force (iii) T gradient (iv) liquid vapour pressure	< 100	~95 (PM5) ~70 (submicron) (dynamic scrubber)	e.g.- spray (scrubber, wet dynamic scrubber, cyclonic scrubber, impact wet scrubber)
Alkalis	HGC	Condensation	Condensation and agglomeration of alkali vapours	~600	–	–
		Adsorption	Adsorption by sorbents	~840	98 (activated Al ₂ O ₃) 99 (Bauxite)	Removal η & T range are function of nature of SO ₂ sorbent
	CGC	Wet scrubbing	Condensation of alkali vapours	< 300	–	Most alkalis are removed along with tars and particulates
N	HGC	Thermal catalytic decomposition	Cracking of NH ₃ in the presence of catalyst to N ₂ and H ₂	500–800	80 (WC, WZ catalysts) 92 (Ni/MnO ₃ / Al ₂ O ₃)	Different catalysts have different removal η at different T
	CGC	Wet scrubbing	Absorption in H ₂ O	<100	Vary with NH ₃ concentrations	Other cold gas methods such as adsorption and biological treatments are not feasible on account of cost and CO ₂ generation issues
S	HGC	Physical and chemical adsorption	Physical absorption is based on Vander Waal's inter-molecular dipole interactions whereas chemisorption employs covalent bonding of adsorbate molecules	400–600 (Z-sorbIII) > 600 (Mn mixed with V and Cu)	99	S adsorption occurs in 3 stages – reduction, sulphidation and regeneration
		Chemical solvent methods	Absorption by amines	< 100	–	COS can't be removed. Continuous solvent replacement is needed.
		Physical absorption	Absorption by methanol and DME	<100	–	COS/H ₂ S can be removed. High energy requirement.
	CGC	Liquid redox process	Wet scrubbing in the presence of catalyst	< 100	100	Non-toxic reactions. Process flexibility. Elemental regeneration
Halides	HGC	Adsorption	Adsorption by sorbents	500–550	80 (Ca-based powders at 600 – 1000 °C)	Activated carbon, alumina, trona, Ca-based powders are commonly employed sorbents
	CGC	Wet scrubbing	Removal of HCl and NH ₄ Cl via absorption	<100	–	Reduction in process η because of acidic compounds and filter coke formation

^a Data are not available in the original literature

remove heavier solids from lighter gases by employing the principle of separation by inertia. They decrease the time required by light particles to settle by gravity, by using centripetal acceleration. They are available in numerous designs. Choice of a specific design is dependent upon the nature of the PM and gas [240,243–245]. They are highly efficient with particle size PM_{10} (particle diameter less than or equal to $10\ \mu\text{m}$) and above. Removal of smaller particulates is also possible ($PM_{0.5}$ with an efficiency of 90%) with the incorporation of multiple stages for large gas volume, though this is expensive and complex [240]. A relatively new design known as a 'reverse flow gas cyclone' has an efficiency of 99.6% in pilot and commercial-scale plants for $1\ \mu\text{m}$ particles [246]. These are promising technologies on account of high efficiencies and robust nature. However, design advancements are needed to reduce process complexity and cost for particulates removal of less than PM_{10} .

Barrier filtration is another commonly used hot gas clean-up strategy for PM. It employs the principles of diffusion, impaction by inertia and gravity settlement [235]. Filter media which are made up of fibres or granules of different materials such as fabric, ceramic, metal, alumina, etc., collect PM. The fabric filter is one of the oldest devices which can decrease the particulates ($\sim > 1\ \mu\text{m}$) quantity to less than $1\ \mu\text{g m}^{-3}$, although its operational temperature is limited to about $250\ ^\circ\text{C}$ on account of its construction material [235,247].

The kind of cleaning strategy employed and the maximum allowable drop in pressure prior to the removal of filter cake is the most crucial design factor for a system employing a fabric filter [218]. Compressed gas pulses, rapping, mechanical shaking and reverse flow are commonly employed cleaning techniques. Optimal filtration velocity which is defined as flow rate per area of fabric, is the other important design parameter. It reflects total effective fabric area of the filter. Lastly, material of the cleaning medium is the key design consideration. The temperature and composition of the gas are the deciding factors for the material employed. Synthetic polymers (e.g., polyvinyl chloride, etc.) with low crystallinity can function only at low temperatures ($< 250\ ^\circ\text{C}$) whereas metallic composites (Nextel's 3 M material) can work efficiently at elevated temperatures as high as $700\ ^\circ\text{C}$ [235]. High temperatures and presence of alkali particulates and acidic gases such as HCl and H_2S enhance the probability of corrosion in fabric filters. The minimum inlet temperature is kept above the acid dew point of the gas to avoid acid/moisture condensation, which in turn prevents corrosion [248]. In addition, common materials such as poly-peptide, silicate glass, etc., are corrosion-resistant and cost effective vis-à-vis composites.

Progress in rigid filter design has enabled them to function at high temperatures of $400\ ^\circ\text{C}$ with a removal efficiency of 99.99% for a particle size of $100\ \mu\text{m}$ and above [249]. Advancements in design and granular media materials for moving bed granular filters, in recent years, have enhanced removal efficiency and operational temperature ranges. Smid et al. [250,251] showed removal efficiencies of 99% and 93%, respectively, for $4\ \mu\text{m}$ and $0.3\ \mu\text{m}$ particulates at $840\ ^\circ\text{C}$. The same authors have demonstrated an efficiency of 99.99% up to $870\ ^\circ\text{C}$ employing a stand-leg moving granular bed filter system. These filters are highly promising on account of high-temperature operation with efficient operation and minimal maintenance. The major limitations with filter devices are the low lifetime of the filter due to elevated temperatures and frequent downtime because of stress and shock. Although many strategies have attained a removal efficiency of 99% at $400\ ^\circ\text{C}$ or above, non-stop operation before failure hardly goes beyond 2700 h [249]. New materials for filters and better designs are needed to improve filter life and reduce downtime frequency.

Electrostatic precipitators exploit electrical properties of the gas stream (gas+particulates) to remove particles. Particulates are charged under the influence of an electric field and separated from the gas stream on account of differences in dielectric properties

[252]. Tube type and parallel plate are commonly used designs. Device design, electrical resistivity of the gas stream, voltage applied, and particulate geometry are some of the parameters which define device performance. Electrical resistivity of the particulate phase has a profound influence on the working of ESP. Charge dissipation effects prevent the effective removal of the solid particle with very high or very low resistivity, when it comes in contact with the collector element. Particulates such as carbon black have low resistivity ($< 100\ \Omega\ \text{m}$) which make them lose charge rapidly when they reach the collection electrode [235]. Consequently, they acquire the same charge as the electrode and are repelled back to the stream. Particulates (e.g., elemental sulphur) with high resistivity of greater than $10\ \text{G}\Omega\ \text{m}$ suffer from the undesirable phenomenon of 'back corona' on account of slow discharge at the electrode leading to excessive accumulation of charge [252]. In addition, collection electrodes are unable to trap solid particles with a very high resistivity of more than $100\ \text{G}\Omega\ \text{m}$ due to their extremely slow migration velocity ($\sim 2\ \text{cm s}^{-1}$) [252]. It has been found that significant improvements in ESP efficiency can be achieved by decreasing the resistivity of the particles by employing temperatures above $150\ ^\circ\text{C}$. For example, an increase in industrial ESP η from 81% to 98% was reported, when the dust resistivity was reduced from $5\ \text{G}\Omega\ \text{m}$ to $0.1\ \text{G}\Omega\ \text{m}$ [218]. It should be noted that particle resistivity should not be reduced beyond a threshold to prevent particle re-entrainment via high rate of charge dissipation.

ESPs are typically employed at $200\ ^\circ\text{C}$ for fly ash removal in thermal power plants, and between 300 and $450\ ^\circ\text{C}$ in synthetic fuel plants for oil vapour separation [235,253,254]. Their efficiency decreases with an increase in temperature, although few research investigations have employed temperatures as high as $1000\ ^\circ\text{C}$ [235]. These systems are efficient; however, elevated temperature and pressure result in decreased mechanical strength and induction of stress, respectively, in materials.

Wet scrubbing using water as the scrubbing agent is a commonly used cold gas cleaning technique. Spray scrubbers, wet dynamic scrubbers and electrostatic scrubbers are a few examples of wet scrubbers employed for particulates removal [255]. Inertial separation is the implied principle behind all the methods used to separate particles of size $3\ \mu\text{m}$ and above [218]. However, with smaller particulates removal, temperature gradient, liquid-vapour pressure and electrostatic forces also play significant roles. Spray scrubbers have high efficiencies of about 90% for PM_5 particles which reduces to 40% for submicron particles [255]. Wet dynamic scrubbers have a higher efficiency of 95% for $5\ \mu\text{m}$ particle size and 60 to 75% for submicron particles [218]. Wet electrostatic scrubbers are most promising on account of their high efficiencies, low energy consumption and comparatively lower pressure drops. Bologna and co-authors [256] have observed an efficiency of 99% in removing submicron aerosols of ammonium sulphate, hydrochloric acid and ammonium chloride in lab- and pilot-scale investigations employing a two-field wet electrostatic precipitator. These authors have reported a power drop of $0.2\ \text{kWh}$ for every $1000\ \text{m}^3$ of syngas in industrial tests with an efficiency of 95% for sulphuric acid removal. Progress in the research work is needed to reduce its complexity and waste water treatment issues to make it the most promising option at commercial-scale facilities.

4.3. Alkalies

Raw biomass inherently contains alkali and alkaline earth metals in variable quantities. Herbaceous biomass has larger amounts of alkalis than woody biomass, whereas the latter contains larger fractions of alkaline earth metals [27]. They can also be inadvertently added to the syngas via some catalysts which are employed for other contaminant removal [257–259]. The presence of alkali metals such as sodium and potassium in gasification-derived syngas is

considered a serious issue on account of their reactive and volatile nature. They are responsible for ash fouling and corrosion in boilers and gasification power plants [260, 261]. They can also cause catalyst poisoning during and after gasification. Therefore, a decrease in their concentration is required from a few g kg^{-1} to a few $\mu\text{g kg}^{-1}$, depending upon the application [262].

Condensation, and adsorption by sorbents, are two normally used hot gas clean-up strategies for alkali metals removal from syngas. Alkali vapours nucleate and agglomerate when the gas temperature drops below their condensation temperatures. In order to decrease the vapour phase alkalis that pass through the equipment, the temperature is kept below 600°C [173,258]. Adsorption is a better choice on account of its capacity to remove alkalis (in any phase) at almost any temperature [218]. Tolerance for elevated temperature, high and irreversible adsorptions, and regeneration capacity with high loading potential are some basic required characteristics of a sorbent [263]. The temperature range and presence of other contaminants in the syngas are the deciding factors for the sorbent life. Silica, clay, activated alumina, etc., are typically employed hot gas sorbents [235, 264,265]. Minerals such as kaolinite chemisorb alkalis even at very high temperatures of around 1000°C and may be employed in-situ or post-gasifier [263]. Bauxite effectively removes alkali metals via physisorption, in 0.2 s with an efficiency of 99% [266]. It can be employed at elevated temperatures and can easily be regenerated with boiling water. Activated alumina is another good choice for hot gas removal of alkalis. At 840°C , it outperformed kaolinite, bauxite and second grade alumina with sodium loading of 6.2 mg g^{-1} and efficiency of 98.2% [267]. These sorbents not only eradicate alkali species but also get rid of chlorine from syngas. Therefore, adsorption via sorbents is a cost-effective and efficient method. However, trials with new sorbents are required which can eliminate other contaminants as well, inside the gasifier and downstream.

Alkali vapours condense and agglomerate with other materials to form small solid lumps or fuse with tars around 300°C , during wet scrubbing [268]. Wet scrubbers, therefore, remove alkalis along with tar and other particulates. Biomass pretreatment (low-temperature preventive technique) prior to gasification can also be done to reduce alkali fractions in syngas. One of the strategies is to choose low alkali-content biomass for syngas generation via gasification. Almost 95% of the biomass feedstock contains alkalis either in water soluble or ion exchangeable form, which can easily be washed or mechanically dewatered [266,269]. Biomass raw material can also be treated by acid to reduce alkali amounts. In one investigation, high reductions in alkalis and other contaminants (sodium $\sim 68\%$, potassium $\sim 90\%$, magnesium $\sim 68\%$, phosphorus $\sim 72\%$, chlorine $\sim 98\%$, sulphur $\sim 55\%$) were observed with an overall ash decrease by 45%, during gasification [270]. Another study on pyrolysis of wheat straw and wood showed that acid treatment can reduce alkali discharges by 70%, whereas water wash was only found to reduce it by 30% [271]. Employing biomass pretreatment depends upon the nature of feedstock, operational variables and desired cost of syngas.

4.4. Nitrogen

During the pyrolysis phase of BG, nitrogen leaves the feedstock in the form of ammonia or hydrogen cyanide [272]. The intrinsic characteristics of the raw biomass along with operational parameters decide the quantities of nitrogen generated. Normally, ammonia is the dominant nitrogen species and is produced during primary reactions (from biomass) or in the secondary gas phase reactions (from HCN). With increasing temperature, fractions of ammonia and HCN rise considerably during secondary reactions. Eventually HCN also reacts with hydrogen to form ammonia [273–275]. However, almost 75% of ammonia produced during gasification is converted to elemental nitrogen at operational temperature. Almost all applications

demand its removal to a significant degree; e.g., GTs require ammonia volume to be less than 0.05 mL L^{-1} , to prevent nitrogen oxides release [275]. In addition, its reduction is also essential to avoid catalyst poisoning.

Hot gas cleaning of nitrogen (present in the form of ammonia) in syngas is carried out via selective oxidation or thermal degradation in the presence of catalysts. If chemical equilibrium is obtained during gasification, a very small amount of ammonia is present in the syngas; however, it still renders syngas unusable in many applications, which necessitates clean-up [218]. Tar cracking catalysts such as nickel-based, iron-based, dolomite, etc., are also effective in ammonia cracking. They are cost-effective and, therefore, suitable substitutes to Ru, W, nitrides, oxynitrides and carbides [220,276]. Thermal cracking of ammonia typically takes place around 500°C but elevated temperatures ($700\text{--}800^\circ\text{C}$) are recommended to prevent coking [220]. Commonly employed nickel-based catalysts decompose ammonia up to 75%, but they suffer from sulphur poisoning within about 60 h of operation; moreover, this issue would be even more severe at increasing process pressures due to the formation of NiS, although the higher the pressure the more efficient is NH_3 cracking [277].

Removal of ammonia via its absorption in water is one of the typical cold gas cleaning strategies used for nitrogen removal from syngas. Pröll et al. [278] and Pinto et al. [279] found that nitrogen compounds are removed to a significant extent, even when water in the syngas condenses. In wet scrubbing of tar compounds, employing organic solvent (rape oil methyl ester) at 50°C , syngas with 400 mL L^{-1} of water vapour partially condensed. The initial concentration of ammonia was 2 mL L^{-1} [278]. An increase in efficiency to 50% was observed with a decrease in initial ammonia amounts. Furthermore, addition of more water while wet scrubbing can enhance removal efficiencies and bring down the ammonia level to pL L^{-1} ; however, it is also dependent upon biomass feedstock and upstream treatment [280].

4.5. Sulphur

Sulphur is present as hydrogen sulphide, carbonyl sulphide and carbon disulphide in syngas and sulphur dioxide (in combustion by-products). The percentage of this contaminant is dependent upon the composition of the biomass feedstock [281]. Usually biomass contains low amounts of sulphur (0.1 to 0.5 g kg^{-1}) as compared to coal (50 g kg^{-1}), except for a few feedstocks such as black liquor ($> 1 \text{ g kg}^{-1}$) and some types of grasses [220,276,282,283]. Even a small quantity of sulphur is considered detrimental. It corrodes metal surfaces and causes catalyst poisoning [284,285]. Moreover, it forms oxides when syngas is combusted, which are regulated toxins.

Numerous syngas applications require very low sulphur levels (pL L^{-1}) to prevent catalyst poisoning and equipment failure. Even direct combustion applications require negligible amounts of sulphur in the gas fuel to follow stringent emission norms for SO_x . This necessitates sulphur removal from syngas prior to its utilization in biofuel synthesis and other applications [218]. Physical or chemical adsorption via sorbents is the hot gas clean up technology most widely used for sulphur removal. Metal oxides are the most promising sorbents on account of their high removal efficiency, high thermal tolerance and regeneration potential. Westmoreland and co-authors [286] have presented a comprehensive evaluation of potential metals vis-à-vis desulphurization potential and free energy minimization. Vamvuka et al. [287] have reduced their list to Fe, Zn, Mn, Cu, Co, Mo, V as most effective oxides for sulphur removal.

A blend of metal oxides was found have better characteristics for desulphurization than individual metal oxides in terms of removal efficiency, regeneration capacity, heat tolerance and other contaminant removal potential. For example, a blend of Mn, V and Cu displayed high sulphur removal even at elevated temperatures of

600 °C and above [220]. In addition, a mixture of CuO and ZnO had very high removal efficiency of above 99%. ZnO is readily available and is one of the most prevalent regenerable sorbents [288]. Conoco-Phillips has developed a new sorbent called ZsorbIII which is a mixture of ZnO (500 g kg⁻¹) and NiO (100 g kg⁻¹) for commercial applications [289]. ZsorbIII eliminated an initial concentration of 10 mL/L of hydrogen sulphide with a removal efficiency of more than 99%. During testing, optimal performance of the sorbent was reported at temperatures between 400 °C and 600 °C and a pressure of 2026.5 kPa, with syngas. Elevated pressures and temperatures with repetitive regenerations caused no loss in activity or morphology. Good performance of mixed oxides coupled with long lifetimes makes them an attractive area for future research.

Low-temperature sulphur removal techniques can be classified as chemical absorption, physical absorption and a combination of both processes. Where sulphur recovery is necessary, chemical redox and biological techniques are also employed. Chemical absorption processes employ a solvent (primary, secondary or tertiary amines) to generate bonding between hydrogen sulphide and amine [218]. Acidic gases such as hydrogen sulphide are absorbed in an absorber unit. The sorbent is recycled to the absorber division by stripper division with the production of a strong acid gas stream. However, sulphur in the form of carbonyl sulphide cannot be removed from syngas employing this technique. Therefore, hydrogenation of COS to H₂S is needed. This increases the cost and complexity of the entire sulphur removal process. Furthermore, liquid solvents need to be replaced continuously during operation.

Physical absorption processes employ the simplest alcohol (MeOH) or ethers such as DME. These solvents are excellent choices on account of their capability to remove both H₂S and COS at low temperatures coupled with high loading capacity and minimum solvent degradation. For example, the Rectisol process is generally used for desulphurization of syngas, for ammonia and hydrogen synthesis, employing methanol at -62 °C as solvent [290]. Acid gas scrubbing processes for desulphurization are very selective with high efficiency. However, they are responsible for over 10% of the overall cost of the plant because of multiple columns and absorbents [291].

Liquid redox techniques for cold gas cleaning of sulphur are generally employed at commercial scale for acetic acid synthesis and FT fuels production and have high capabilities to remove sulphur from 100 kg d⁻¹ to 36 t d⁻¹. In these strategies, varied feedstocks ranging from coal to municipal solid waste were used under pressurized conditions and almost 100% desulphurization was attained [292]. In addition, improved catalyst activity, process flexibility, absence of tail gas and regeneration of sulphur (via sulphate) were other observed benefits. It should be noted that improper process management may cause plugging problems which necessitate proper administration.

Recovery of sulphur during syngas cleaning is the key consideration for all the removal techniques. Sulphur is usually recovered as elemental sulphur or as sulphuric acid via previously discussed physical and chemical processes. The acid is usually employed as a reagent in catalytic processes such as petroleum alkylation, methyl methacrylate synthesis, etc. or in leaching processes such as mining or synthesis of hydrofluoric acid, phosphate, etc. [293]. Many industries dispose sulphur as a waste after neutralizing sulphuric acid by its salt formation. Elemental sulphur generated via the Claus process is either stored in the form of blocks or sold to the market. These blocks are very large and every block containing sulphur weighs more than a million tons. Storing sulphur in blocks prevents its exposure to dust and also avoids oxidation. This strategy is normally deployed in remote regions. Many industries prefer to dispose of the acid gas (H₂S) underground directly than to stockpile the elemental sulphur. Generally, industries co-inject CO₂ with H₂S for geological storage in order to save cost and avoid carbon emissions.

Sulphur recovered in the form of sulphate via liquid redox techniques is hydrophilic with fast soil adsorption rates [292]. It is often employed as an additive to regulate the pH of soil. Proper management coupled with efficient technology can make this noxious element useful and beneficial. Moreover, stringent laws are required to restrict sulphur emissions and disposal, especially in developing nations to prevent environmental hazards.

4.6. Halides

Chlorine, present as hydrochloric acid, is the prime halide contaminant in syngas. Chlorine in the form of alkali metal salt vaporises at elevated temperature inside the gasifier and reacts with water vapour to form hydrochloric acid [173,235,264,294]. Even minute concentrations such as 0.024 µL L⁻¹ and 20 µL L⁻¹, are responsible for corrosion in GTs and deactivation of nickel anodes in solid oxide fuel cells, respectively [264,294,295]. Furthermore, HCl can be converted to chlorides of ammonia and sodium after its reactions in the gas phase. These species can cause clogging and fouling in downstream piping and equipment.

HCl is removed from syngas via adsorption by sorbents at elevated temperatures [296]. A salt is produced because of chemisorption when gaseous HCl is adsorbed on the solid surface of a sorbent. A chemical equilibrium is attained around 500 - 550 °C between gaseous and solid species involved in the process and, therefore, this is the optimum temperature range for maximum removal of HCl [297]. Alkali oxides, alumina and activated carbon are widely used sorbents in fixed bed applications. Alkali-based mixed oxides are also used on account of better efficiencies, but are more expensive [264,298].

At commercial scale, cold gas cleaning is normally applied for chlorine removal from syngas. Gaseous HCl and/or solid ammonium chloride is removed via wet scrubbing of the gas through deposition of ammonium chloride and absorption of HCl. This strategy not only eliminates chlorine from the syngas, but tars, PM and alkalis are also removed [218]. This technology is very efficient and commonly employed; however, loss in process efficiency and equipment failures are observed on account of acidic compounds and filter cake generation. Equipment damage due to corrosion may be avoided by choosing suitable non-reactive materials such as glass, ceramic, tantalum, etc. [299]. Research is in progress to mitigate these concerns associated with de-chlorination of syngas.

4.7. Other trace contaminants

Trace elements such as mercury, arsenic, cadmium, zinc and selenium are present in variable amounts in biomass feedstocks. Their fractions are less than 0.1%. However, because they are highly toxic, their emissions are heavily controlled. Mercury is highly corrosive to aluminium and has been responsible for equipment failures in natural gas applications. Due to health concerns, it is the most highlighted toxin among all trace elements [290].

Adsorption by sorbents is commercially employed technology for the removal from gas streams of mercury and other aforementioned contaminants. Kaolinite, bauxite, zeolite, lime, silica, activated carbon and blends of other compounds are widely used sorbents in IGCC and other combustion applications. In some investigations, metal oxides, limestone and fly ash have demonstrated high removal efficiency for Se and As. Cd and Zn can also be eliminated by using fly ash as a sorbent [300]. Activated carbon is used in natural gas applications for mercury removal. Korens et al. [290] reported that a blend of silver and activated carbon has a very high efficiency for trace contaminants removal; however, it cannot be regenerated and, therefore, is not suitable for commercial-scale applications.

5. Alcohols

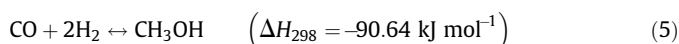
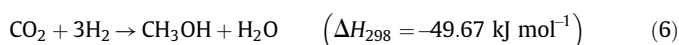
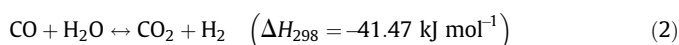
5.1. Bio-methanol (MeOH) and derivatives

MeOH is one of the highly synthesised chemicals around the globe. It is seen as a promising substitute for existing automotive fuels. Prior to the introduction of gasoline as a cost-effective motor fuel, MeOH was widely used for the same purpose. During World War II, it was extensively employed to power automobiles in Germany [43]. MeOH came back into the picture in the 1970s during the oil crisis on account of its easy availability and reasonable cost. It can be employed directly as clean automotive fuel or can be mixed with other conventional fuels. Furthermore, numerous important chemicals (derivatives) can be produced using MeOH as an intermediate, such as formaldehyde, methyl tertiary butyl ether (MTBE), acetic acid, gasoline, DME, to name a few [217]. Various important investigations vis-à-vis process design, engineering aspects and recent projects for MeOH and synthesis of its derivatives are discussed in subsequent sections.

5.1.1. Bio-methanol (MeOH)

MeOH is a commodity chemical whose production initiated back in the nineteenth century when wood alcohol was extracted during wood pyrolysis [217]. The early twentieth century saw the development of the MeOH production process, which is now employed commercially, after numerous R&D efforts. MeOH can also be obtained as the by-product in FT synthesis, provided alkali metal-promoted catalysts are used. Natural gas reforming is the primary method of MeOH synthesis. However, developments in BG have enabled the usage of a variety of biomass feedstocks to produce syngas, which in turn can be converted to MeOH. BG-derived syngas is fed to a methanol reactor, where MeOH is synthesised along with H₂O vapour in the presence of a catalyst. Crude MeOH is a blend of numerous chemical species such as water, alcohols, ketones, etc., and is directed to a distillation unit for separation. Very high conversion efficiency of greater than 99% is achieved, as unreacted syngas is sent back to the reactor [217].

Rostrup and Nielsen [301] suggested that MeOH production employing syngas takes place best at elevated temperature (350 °C) and pressure (250–350 bar), and is highly exothermic in nature as depicted in Eqs. (5), (6) and (2).



A stoichiometric ratio (H₂—CO₂/CO+CO₂) of around 2 is recommended for MeOH synthesis; however, it is generally kept a little above 2 to regulate by-products and also for kinetic reasons [302]. This reflects that there should be just the stoichiometric amount of H₂ required for MeOH synthesis. It should be noted that the presence of CO₂ enhances the rate by 100 times [303]. Moreover, isotopic investigations have conclusively demonstrated that the carbon in MeOH was provided by CO₂ [303,304]. Carbon dioxide keeps the Cu catalyst in an intermediate oxidation state Cu⁰/Cu⁺ preventing ZnO reduction followed by brass formation. The proposed mechanism for MeOH generation proceeds through a formate intermediate. CO₂ is adsorbed on a partially oxidized metal surface as a carbonate, and hydrogenated. This intermediate is then hydrogenated in the rate-limiting step. The sites of Cu have high activity for splitting the first C—O bond in CO₂ that aid in maintaining the oxidation state of the active copper sites [304]. However, catalyst activity is hampered when CO₂ is in larger amounts. Therefore, syngas composition is

regulated to contain 4 to 8% of CO₂, for maximum activity and selectivity of the process [305].

Catalysts have the most significant role to play in MeOH synthesis from syngas. ZnO/Cr₂O₃ were the earliest employed catalysts while producing MeOH from coal gasification [217]. They have high activity and selectivity along with high tolerance for sulphur poisoning. Copper (Cu) catalysts which are easily poisoned, became a better choice as gas cleanup technologies advanced. A new era of low-temperature (220–275 °C) and low-pressure (50–100 bar) MeOH production began in the late 1960s, with the advent of Cu/ZnO/Al₂O₃. After closure of the last high-temperature/pressure MeOH production plant in the 1980s, every commercial production plant now works at low-temperature/pressure employing Cu catalysts [306]. Many other catalysts formulations were used to increase per-pass MeOH production [307]. For example, when Cu/ZnO is embedded with Cs, MeOH yields are enhanced. However, this is applicable only for the heavier alkali metals, as the addition of potassium diverts the products towards the higher alcohol range [307]. For commercial MeOH synthesis, catalysts usually have a lifetime of 3 to 5 years under normal operating conditions, with a selectivity of more than 95%.

Longer lifetime along with high selectivity of catalysts necessitates stringent syngas cleaning. Catalyst poisoning and sintering are considered as prominent reasons for catalyst deactivation in MeOH synthesis [308]. Cu catalysts undergo reductions in surface area due to sintering. Furthermore, sulphur present in syngas blocks the active sites and reduces activity. It is, therefore, highly recommended to keep sulphur below 1 ppm and preferably below 0.1 ppm. However, when ZnO is present in the catalyst formulation with Cu, it keeps S away from Cu active sites by forming ZnS and ZnSO₄. Commercial Cu-ZnO catalysts have an activity of 70% by absorbing up to 0.4% S [309]. The presence of chlorine in syngas is also a major nuisance in MeOH synthesis on account of its ability to form volatile copper chloride compounds and enhance sintering of Cu [308]. In addition, it also increases S poisoning by forming Zn chlorides and removing the previously available S capture sites. This makes Cl more detrimental and hence, the limit for HCl is 1 ppb. Metal carbonyls (especially Ni and Fe) are other syngas contaminants which affect catalyst performance [303]. They block active sites and considerably reduce catalyst selectivity. Their concentrations should be less than 5 ppb. Apart from gas contaminants, reactor temperature is also an important parameter which influences the catalyst. MeOH synthesis is a highly exothermic process which necessitates continuous removal of the reaction heat. Elevated temperature (> 300 °C) in the MeOH reactor causes sintering of Cu crystallites [217]. Moreover, by-product (methane, DME, higher alcohols, etc.) yields also increase at higher temperatures on account of other competing reactions [310]. Therefore, proper regulation of operating temperature is imperative for longer catalyst lifetime and desired product yield.

A major challenge for commercial MeOH generation is to overcome thermodynamic limitations. Around 25% of syngas is converted to MeOH in every pass, which is quite low [303]. This conversion efficiency can be enhanced by lowering the operational temperature, which shifts the equilibrium toward the products. However, a decrease in temperature reduces catalyst activity. This issue can be handled by removing MeOH as soon as it is produced, after every pass. Methanol can either be physically removed via physisorption or can be converted to some useful derivative such as DME, acetic acid, etc.

The methanol reactor, commonly known as methanol converter is designed based on the aforementioned considerations, namely, regulating and removing high heat of reaction, and overcoming thermodynamic limitations to maximize per-pass conversion efficiency [217]. Numerous designs were developed over the past decades and are employed for commercial MeOH production. Basically, they are of 2 types: (1) Isothermal MeOH converters – They are designed to

behave like a heat exchanger by constantly removing the heat of reaction. They have an isothermal axial temperature profile. Some commonly employed designs are Lurgi MeOH converter, Variobar converter, MGC/MHI superconverter, etc. (2) Adiabatic MeOH converters – They are designed to contain numerous catalyst beds separated by gas cooling devices. Either fresh (or recycled) syngas is fed or direct heat exchange is employed in these reactors. The axial temperature profile contains a saw tooth pattern which is low at the point of heat removal and increases linearly in heat exchange regions. The ICI low-pressure quench converter and CMD converter are some of the commercially used designs. As mentioned earlier, MeOH in itself is a source for many useful chemicals such as DME, acetic acid and many others which are discussed briefly in later sections.

5.1.1.1. Recent projects for MeOH generation. Choren Industrietechnik, Germany, invented a novel concept for air-blown gasification of biomass called 'Carbo-V' where the biomass raw material undergoes slow pyrolysis as a pre-treatment step and releases gases and char [311]. The gases undergo gasification at elevated temperatures of about 1300 °C to yield syngas whereas the char goes through pulverization and is fed downstream of the high-temperature reactor to cool the syngas by endothermic char gasification reactions. This so-called chemical quench decreases the temperature of syngas to about 1000 °C. The concept has been tested in the 1 MW_{th} alpha pilot plant in Freiberg from April 2003 to May 2003 and generated 11,000 L of MeOH [312].

BioMCN in the Netherlands has used an innovative process to synthesise MeOH employing the gasification of crude glycerine [313]. The crude glycerine from biodiesel plants is transported to the BioMCN plant. It is stored in the tanks as feedstock for further processing. It is then purified, evaporated and cracked to obtain syngas, which is further employed to generate MeOH. Produced MeOH is purified via distillation. A BioMCN commercial plant is producing 200,000 t of MeOH every year. Prior to the installation of the large-scale plant, the viability of the process was evaluated by a pilot plant study in March 2008. The major advantage of this route is that the feedstock is available in abundance as a by-product of a bio-diesel production process. Therefore, using glycerine as raw material reduces the problem of surplus glycerine disposal which in turn makes bio-diesel synthesis more sustainable. BioMCN has also optimized the logistics in the supply chain by using the same tankers delivering the raw glycerine to deliver MeOH.

The National Renewable Energy Laboratory (NREL) under the Biofuels Systems Division of United States Department of Energy ran a biomass-to-methanol generation pilot project [314]. Sugarcane waste, called bagasse, which is produced during the milling of sugarcane, was employed as the biomass feedstock. The project was focused on developing new catalysts to ensure cleaner syngas generation during BG as well as to get the desired syngas composition and to demonstrate the feasibility of a biomass-to-methanol pilot plant. The primary objective of the study was to produce cheaper MeOH from renewable resources such as biomass to make it competitive with the conventional gasoline. These type of projects aid researchers in industry and academia to explore the possibility to enhance MeOH utilization as alternative fuel. Existing and planned MeOH generation plants are illustrated in Table 9.

5.1.1.2. Energy and exergy studies for MeOH production. The significance of thermodynamics in MeOH synthesis has already been discussed. Thermodynamic investigations are performed to evaluate the optimum process conditions with an objective to increase the overall process efficiency and per-pass conversion efficiency for biomass gasification-coupled MeOH production plants and for poly-generation of MeOH and heat and/or electricity.

Researchers [327] modelled a 2-stage gasifier with an input of 5 MW_{th} biomass, for the poly-generation of MeOH/DME, heat and electricity, employing commercial software such as DNA and ASPEN. Models of both recycling plants (RC plants) and once-through plants (OT plants) were developed with an aim to compare efficiency differences, when MeOH yield is maximized, as shown in Fig. 10. In the RC plant model, around 76 to 79% of the unused gas is recirculated back to the MeOH/DME converter, whereas the residual 21 to 24% is employed for power generation. Energy efficiencies for biomass to MeOH/DME synthesis were found to be 56–58% and 51–53%, respectively, for RC and OT, taking LHV as reference. This efficiency is enhanced to 87 to 88% (LHV) if district heating is also counted as one of the products. This study proved that the MeOH production plant is more appropriate and less complex in design for small-scale generation than a similar BIO-DME production plant.

Sues et al. [328] carried out a detailed modelling investigation with five different bio-wastes, namely (a) wood and forest wastes, (b) grass and organic fraction wastes, (c) agricultural wastes, (d) manure and sludge and (e) MSW, to produce MeOH via biomass

Table 9
Worldwide existing and planned bio-MeOH production plants [315].

Company and location	Start-up year	Product	Capacity (kt yr ⁻¹)	Feedstock	Status	Source
BioMCN, The Netherlands	2010	MeOH	200	Glycerin	Operational	BioMCN, 2010 [313]
BioDME, Sweden	2011	DME	1.5	Black liquor	Operational	BioDME, 2011 [316]
Enerkem, Canada	2011	Syngas, MeOH	4	Treated wood	Operational	Enerkem, 2011 [317]
Carbon recycling international, Iceland	2011	MeOH	1.6	Flue gas CO ₂	Proposed/under construction	CRI, 2011 [318]
Al-Pac, Canada	2012	Paper pulp	4	Wood	Proposed/under construction	Rabik, 2011 [319], Al-Pac, 2011 [320]
Enerkem, Canada	2012	MeOH, EtOH	29	MSW	Proposed/under construction	Enerkem, 2011 [317]
Chemrec & DomsjöFabriker, Sweden	2012	MeOH, DME	100	Black liquor	Proposed/under construction	Chemrec, 2008 [321]
Varmlands Metanol, Sweden	2014/2015	MeOH	100	Forest residue	Proposed/under construction	Varmlands Metanol, 2011 [322]
Woodspirit, The Netherlands	2015	MeOH	400–900	Wood	Proposed/under construction	CHE, 2011, [323] Biorefining, 2011 [324]
PKE & ZAK, Poland	2015	Heat and power, chemicals	Up to 550	Up to 10% biomass, coal	Proposed/under construction	Zak & PKE, 2009 [325]
DeBioM, Germany	–	MeOH	–	Wood	Proposed/under construction	DeBioM, 2011 [326]

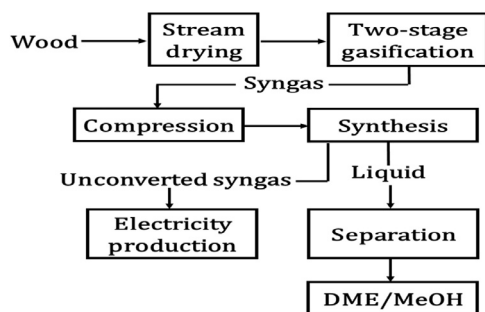


Fig. 10. Concept depicting poly-generation approach using wood biomass [327].

gasification-generated syngas. A CFB gasifier was used with air and oxygen as gasifying agents. Mass conversion yield for MeOH synthesis varied from 15 to 38% for biomass (d) and (a), respectively. The highest exergetic efficiency reported was 45% for biomass (c). This efficiency (45%) dropped 1–2% when exergy losses due to external heat production were taken into account and dropped 5–6% when both heat and electricity production were accounted for. The highest first law efficiency was found to be 53% for biomass (a) and (c) and lowest of 43% for (d) (the sludge). It is again decreased by 2–4% and 8–9%, when external heat (only) and external heat and electricity generation losses are considered, respectively. This study recommended that overall process efficiency could be enhanced further by better heat integration and regulation of operating variables (temperature and pressure).

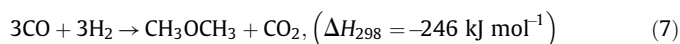
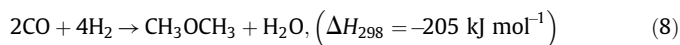
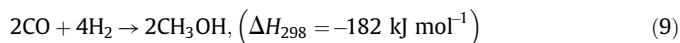
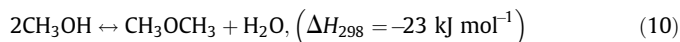
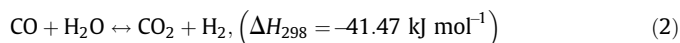
Ptasinski and co-authors [329] developed a model for sludge gasification followed by MeOH synthesis via a modified plant to compare its exergetic efficiency with the traditional sludge treatment process. The plant under consideration had a capacity of 50,000 t dry solids a^{-1} and LHV of the sludge was 12 MJ kg^{-1} (ds). All plant segments such as thermal dryer, gasification reactor, gas clean-up section, compressor, MeOH converter, distillation column and purge gas combustion were considered and their irreversibilities were calculated. It was reported that MeOH produced is a function of gasifier temperature and of dry solid content of the sludge leaving the thermal dryer. Overall exergetic efficiency was found to be higher than the conventional thermal sludge treatment, and reached a maximum at 1000 °C with 80 wt. % dry solids content.

5.1.2. Bio-dimethyl ether (DME)

DME (CH_3OCH_3) is one of the most useful derivatives of MeOH with diverse applications such as paints, agricultural chemicals, cosmetics, etc. [330–332]. It can also be employed as a diesel substitute on account of its high cetane number. In addition, it can be used as a cooking gas with slight modification in existing natural gas cooking ovens.

DME can be produced by two different approaches, namely 2-stage synthesis (via MeOH) and direct synthesis employing syngas as shown in Eqs. (7) and (8) [333]. In 2-stage production of DME as depicted in Eq. (7), first MeOH is produced followed by its dehydration in the presence of an acid catalyst (e.g., γ -alumina) in MeOH production conditions [334,335]. The reaction shown in Eq. (7) is basically made up Eqs. (9), (10) and (2), which are MeOH production, dehydration and water gas shift reactions, respectively. In the absence of water gas shift, Eqs. (9) and (10) can be combined to Eq. (8), which is another direct DME synthesis route and adopted by a few companies including Haldor Topsoe. JFE Corporation, Japan, adopted Eq. (7) to synthesise DME in one stage for their 5 ton DME d^{-1} (5TPD) pilot plant [333]. Bifunctional catalysts are normally used for direct DME synthesis in the gaseous or liquid phase (in slurry reactor). A simple process flow diagram for the JFE 1-stage direct synthesis

of DME is shown in Fig. 11.



In the two-stage production of DME, methanol is produced in the first stage by catalytic conversion of syngas (Eq. 9). In the second stage, the generated methanol is dehydrated to produce DME (Eq. 10). This synergy among the reactions explains the higher total conversion of syngas to DME (~95%) as compared to the conversion of syngas to MeOH (~77%) [332]. In addition, considering reactions in Eqs. (7) and (8), where 6 molecules of reactants give 2 molecules of products, it is evident that higher reaction pressure has a direct positive influence on syngas conversion to DME [333]. In the JFE single-stage DME production process, the standard pressure employed is around 50 bar with a range of 30 to 70 bar.

MeOH production is thermodynamically limited and it has been found that syngas conversion is greatly enhanced when dehydration of MeOH (Eq. 10) occurs simultaneously [333]. Stoichiometric syngas conversion to DME for reactions (Eq. (7) and (8)) under 50 bar, and MeOH production [3] under 50 and 90 bar, are shown in Fig. 12. It can be clearly seen that reaction (Eq. 7) has higher syngas conversion efficiency for all temperatures. Fig. 13. shows synthesis gas conversion with respect to CO/ H_2 molar ratio, for Eqs. (7), (8) and (9). For

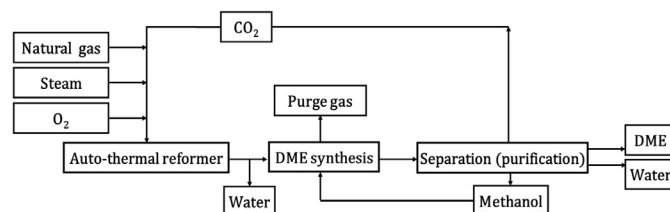


Fig. 11. Direct pathway to synthesise DME [333].

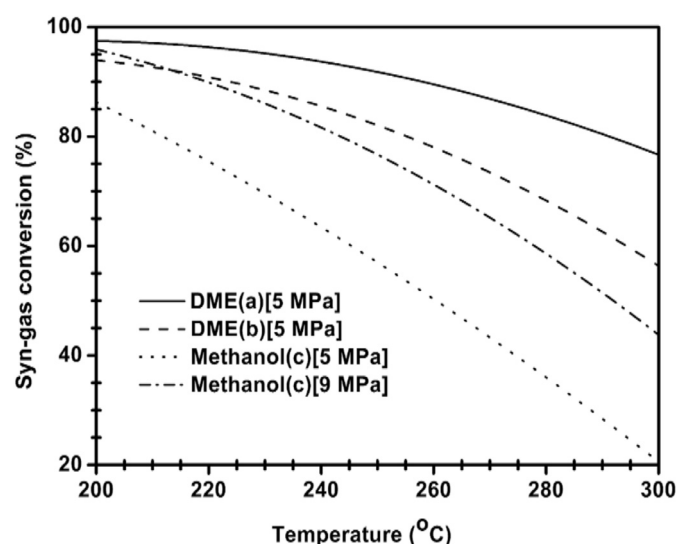


Fig. 12. Analysis of syngas conversion vs. temperature for MeOH and DME synthesis [333].

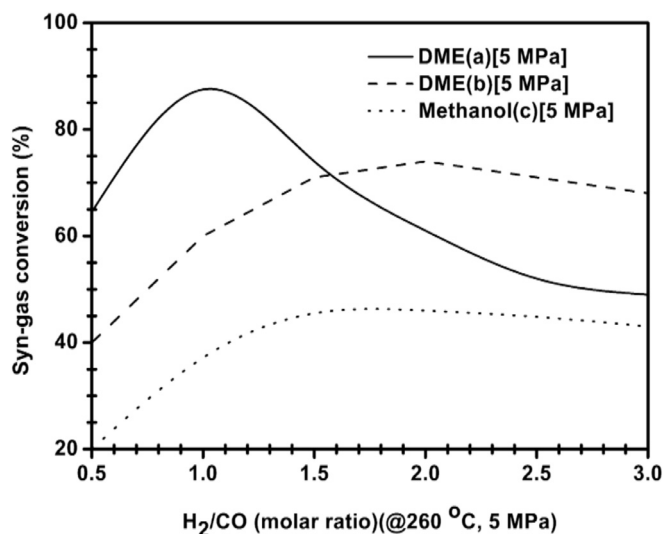


Fig. 13. Analysis of syngas conversion vs. H_2/CO molar ratio for MeOH and DME synthesis [333].

each reaction route, conversion reaches the highest level for a stoichiometric H_2/CO ratio. The stoichiometric H_2/CO is 1 for Eqs. (7) and 2 for Eqs. (8) and (9). Again, the maximum equilibrium conversion of syngas to DME is considerably higher for Eq. (7) than for Eq. (8) [333]. This observation reflects the importance of water gas shift in DME synthesis.

Kansha and co-authors [336] carried out a modelling study for a novel 2-step DME synthesis in order to evaluate its viability and its potential to reduce energy penalties in the thermal and separation processes, employing a commercial simulator – PRO II-Invensys. They employed the so-called ‘self-heat recovery’ approach in which the entire process thermal energy (sensible + latent) is re-circulated among heating and cooling loads. They explore this technology only for a single distillation column, but with excellent results. The reboiler energy requirement was significantly reduced from 44.6 kW to 1.4 kW, which reflects the great potential of this approach for DME synthesis. In addition, this technology can be employed for any biofuel production including MeOH.

Xiang et al. [337] performed an extensive first law and second law investigations for a complete DME production system which was comprised of a biomass torrefaction unit, entrained flow gasifier, single-step DME synthesis and DME purification, coupled with heat recovery and co-generation. The DME generation rate was 0.32 kg^{-1} of biomass feedstock (raw sawdust). Energy and exergy efficiencies were reported to be 55.2 and 46.9%, respectively. The exergetic efficiency was improved to 52.6% when the torrefaction unit worked at 250°C and the gasifier was operated at 1200°C . This study provides some important information vis-à-vis thermodynamic evaluation of the entire DME system and has the potential to aid in future process design modifications and integration.

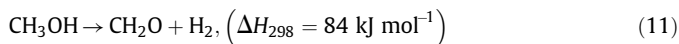
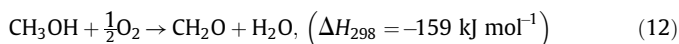
DME generated via BG-derived syngas can be considered to be a “green” fuel. Its calorific content is almost 1.4 times higher than MeOH [333], albeit that studies have proved that it is mildly toxic (like liquid petroleum gas), but less so than MeOH. However, it does not have any corrosive influence on metals and is not an ozone-depleting chemical either. It has a very high potential to be used as cooking gas but can also be employed as a diesel substitute and/or additive on account of its high cetane number. More research is needed to improve engineering aspects of process design to enhance per-pass conversion efficiency and reduce the overall process energy penalty.

The BioDME project to evaluate the large-scale viability of DME production from lignocellulosic biomass was backed by the

European Union’s Seventh Framework Programme and the Swedish Energy Agency [338]. This project involved a consortium of Chemrec, Haldor Topsøe, Volvo, Preem, Total and Delphi. DME was synthesised employing black liquor as the feedstock through the production of clean synthesis gas and a final conditioning step. DME generated was tested in a fleet of Volvo trucks to analyze the engine compatibility, commercial-scale possibility and technical standards. In September 2009, the world’s first Bio-DME production plant at the Smurfit Kappa paper mill in Piteå, Sweden was brought on stream, followed by the inauguration of a pilot plant in 2010 with a capacity of about 3.6 t per day. This pilot plant employed forest residues as biomass raw material and the estimated cost of the plant was around USD 20 million.

5.1.3. Formaldehyde

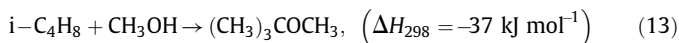
Formaldehyde (CH_2O), or methanal, is one of the most important products from MeOH. It is a precursor to numerous chemical products, and finds its largest application in the production of industrial resins. In the late nineteenth century, it was first produced commercially at atmospheric pressure via partial oxidation of MeOH in the presence of air and Cu catalyst, in Germany [339]. Later, silver and iron/molybdenum/vanadium oxides replaced Cu as catalysts. It is synthesised by dehydrogenating MeOH (Eq. (11)) and partial oxidation (Eq. (12)) over Ag [340,341].



Most of the commercial processes use MeOH mixed with air (1:1) passed through a thin fixed bed over Ag catalysts at slightly above atmospheric pressure and temperature of 600°C . Metallic Ag by itself is not active for MeOH decomposition and, therefore, chemisorbed O_2 is needed to provide sites for MeOH adsorption. Other commercial processes employ iron molybdate as catalyst, requiring a lean blend of MeOH and air. It is more exothermic and hence constant heat removal is a prerequisite to avoid volatilisation of molybdenum oxide which decreases process selectivity [339]. The partial pressure of O_2 should be high and MeOH concentration should be low, to prevent catalyst deactivation.

5.1.4. Methyl tertiary butyl ether (MTBE)

MTBE ($(\text{CH}_3)_3\text{COCH}_3$) is a volatile, flammable and colourless liquid, mildly soluble in water, which raises the octane number of gasoline and, is used as a gasoline additive. Typically, more than 95% of MTBE production ends up as a gasoline additive. It also finds applications in the petrochemical industries for isobutene synthesis and in hydrocarbon industries as solvent [342]. At the commercial level, MTBE production units consist of reaction and refining sections. It is synthesised when isobutene reacts with MeOH over an acidic catalyst, at a temperature range of 30 to 100°C and pressure range of 7 to 14 bar, as shown in Eq. (13) [217].



The reaction takes place in liquid phase and is exothermic. The most commonly employed catalysts are zeolites (H-ZSM-5), solid acids and macroporous sulphonic acid ion exchange resins (Amberlyst-15) [343]. Isobutene conversion is enhanced, and its dimerization and oligomerization are prevented by increasing the amounts of MeOH.

There is debate over the production and usage of MTBE around the globe considering its potential as a human carcinogen, especially in the Americas. Leakage from underground gasoline storage tanks and spillage of MTBE-containing gasoline above ground contaminate groundwater. It imparts an unpleasant taste to water and renders a

large quantity of underground water undrinkable. Many states in USA and provinces in Canada have closed the production units for MTBE and many are planning to do so in the near future [217]. However, its potential as a human carcinogen is not yet proved.

5.1.5. MeOH-to-olefins (MTO)

Olefins such as ethylene, propylene, butane, etc., serve as the raw material for modern chemical manufacturers. They are also employed to produce diverse chemicals (benzene, isopropyl benzene, styrene, etc.), all of which are of high commercial importance [344,345]. The most common route to produce olefins is via steam cracking of diesel, naphtha and ethane [346]. Increasing pressure on petroleum resources and climate change issues, however, have led to a demand for alternative pathways for olefin production. The methanol-to-olefins (MTO) approach can produce renewable olefins via diversified biomass feedstocks. In the past few years, green MeOH synthesis via BG-derived syngas has been developed as a mature technology [347–349]. Therefore, biomass-to-renewable olefins production which includes biomass-to-syngas conversion (via gasification), syngas-to-MeOH conversion and MeOH-to-green-olefins conversion, appear to have opened a new route, with minimal environmental effects.

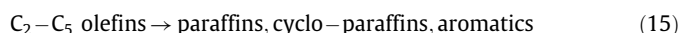
Bio-methanol is converted to olefins by employing zeolite catalysts. Keil et al. [348] suggest elevated temperatures, low pressures and low catalyst activity (acidity) as the optimum conditions for light olefins synthesis. The desired range of products can be produced by regulating the rate of production [303,350]. Norsk Hydro, Norway, employs the MTO process at a commercial scale to synthesise ethylene and propylene [348]. It uses FB reactors at elevated temperature (400–450 °C) and obtains high carbon selectivity (~80%) to olefins. In some cases, operational variables are regulated to get preferred yields.

The most important energetic and exergetic evaluations of 2-stage olefins synthesis, namely, biomass-to-MeOH synthesis and MeOH-to-olefins synthesis are depicted in Fig. 14 [351]. A thermodynamic model was developed using wheat straw as the biomass feedstock and entrained flow gasification as the method to generate syngas. Around 0.25 kg of light olefins was produced per kg of feedstock, which was slightly higher than the previously reported value in the literature, due to the production of high-quality syngas via entrained flow gasification. Energetic efficiency was found to be 54.66% while exergetic efficiency was 47.65%, considering light olefins as the sole product. However, major exergy losses were reported in gasification, steam cycle, MeOH separation, CO₂ extraction and olefins separation. Biomass torrefaction and thermal energy integration were suggested as the ways to enhance available work.

5.1.6. MeOH-to-gasoline (MTG)

The methanol-to-gasoline (MTG) process was developed by Mobil Oil Corporation, USA. It depends on the conversion of MeOH

to HCs in the presence of zeolites [348]. Crude MeOH with around 17% H₂O is superheated at 27 bar and 300 °C and partially dehydrated in the presence of alumina catalyst. This results in about three quarters of the total MeOH conversion and an equilibrium mixture of MeOH, DME and H₂O is produced. From this, HCs (44%) and H₂O (56%) are obtained, when the effluent is blended with high-temperature recycled synthesis gas and fed into a reactor in the presence of ZSM-5 in the temperature range of 350–366 °C and pressure range of 19–23 bar [352]. Multiple gasoline conversion reactors are arranged in parallel in the MTG process to burn off the coke produced during the process by regenerating zeolites [353]. The process chemistry is depicted in Eqs. (10), (14) and (15).



The process has very high selectivity (~85%) for gasoline-range HCs and the residual product is mainly liquefied petroleum gas (LPG) [303]. Around 40% of HCs synthesised are aromatic with 43% xylenes and 26% toluene. One of the major drawbacks of the MTG process is high durene (1,2,4,5-tetramethylbenzene) concentrations in the product [350]. It necessitates gasoline distillation to decrease the durene amount to less than 2%. However, as a consequence of this treatment, high octane gasoline is obtained. Nonetheless, MTG is not a very good option to produce gasoline on account of stringent laws vis-à-vis air toxicity, e.g., US Clean Air Amendment Act 1990 [354].

5.1.7. Acetic acid

Acetic acid is one of the most important chemicals produced from MeOH. Bio-methanol carbonylation is responsible for around 50% of acetic acid synthesis around the globe [355]. It is a precursor to synthesise terephthalic acid, vinyl acetate and acetic anhydride, which are further employed to manufacture latex emulsion resins, adhesives, paper coatings, cellulosic plastics, cellulose acetate fibres, etc. [217]. Acetic acid is synthesised by carbonylation of MeOH by CO in the presence of catalysts (Rh, Co, Ni), promoted by iodine as depicted in Eq. (16) [356]. This is in fact one of the most vital applications of homogeneous catalysis at industrial scale. BASF's and Monsanto's processes are two commonly employed liquid phase routes to synthesise acetic acid.



Spath and co-authors [217] reported that the BASF process is a high-pressure process (500–700 bar) which employs a Co/I catalyst at 250 °C and with around 90% selectivity for acetic acid. On the other hand, the Monsanto process employs relatively low pressure (30–40 bar) at 180 °C in the presence of a Rh/I catalyst, to convert MeOH into acetic acid with very high selectivity (> 99%). Due to less severe operational variables and high selectivity, the Monsanto

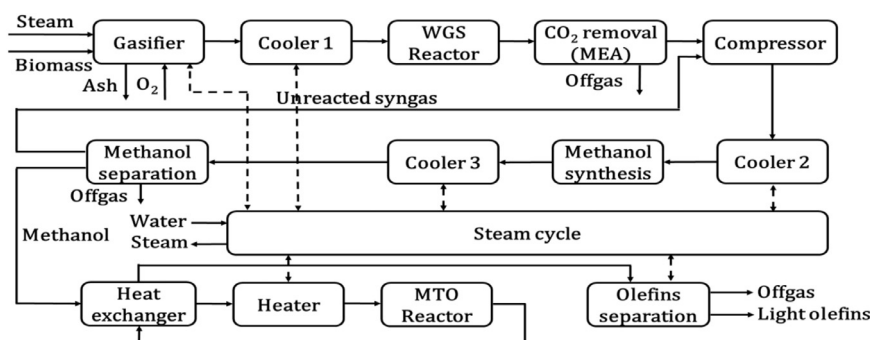


Fig. 14. Model representation of biomass-to-MTO synthesis via MeOH [351].

process has displaced the BASF process since the 1970 s. However, the chemical environment in this process is extremely corrosive and necessitates the use of expensive steels as construction materials. The high cost of Rh catalyst is another issue with this technology [356,357].

5.2. Bio-ethanol (EtOH)

EtOH is one of the oldest fuels derived from biomass. In the past decade, bioethanol received significant attention as a potential alternative for gasoline or as an additive. Currently, it is a common practice to blend gasoline with EtOH, as transportation fuel, in many countries including the USA. Investigations have proved that EtOH-driven engines emit less greenhouse gases (GHG s) along with other pollutants and its use is even more favourable when EtOH is synthesised from cellulosic biomass and not from corn starch [358]. Numerous fuels, chemicals and polymers are also synthesised from EtOH [359,360]. Moreover, this fuel has the potential for application as a precursor to generate green H₂ for fuel cells [361–363]. However, the socio-environmental and economic concerns associated with its use are still under examination [361].

Bio-ethanol is synthesised at the large scale via two commonly employed routes. Biological treatment of feedstock involves extraction of sugars from food or energy crops such as sugarcane or corn, followed by fermentation to obtain EtOH. The second method employs hydration of ethylene which is obtained from petroleum, over solid acid catalyst. Biochemical synthesis of EtOH is now considered to be a conventional process. Table 10 shows countries worldwide which produce high levels of EtOH via the conventional route of using energy crops as feedstock.

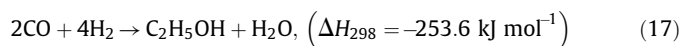
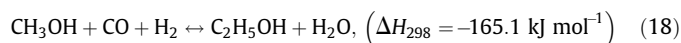
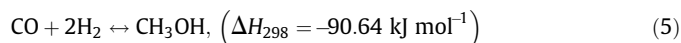
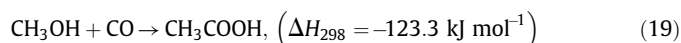
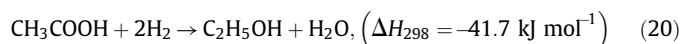
Biological treatment is used to obtain beverage grade liquid with 14% EtOH [364], whereas hydration of ethylene is employed to synthesise industrial grade pure EtOH [365]. The major drawback with the hydration of ethylene route is its dependence upon non-renewable oil. Highly volatile oil prices are another issue with this approach. Fermentation is, therefore, normally practiced to synthesise EtOH at commercial scale, but it is unsuitable for fuel grade EtOH generation on account of its inefficiency and high cost, due to energy-demanding distillation stages [366]. In addition, microbes employed in fermentation are incapable of converting complete lignocellulosic biomass (pentose sugars) to alcohols [217,367]. Thus a constraint is imposed on numerous easily available feedstocks for the process. Research is ongoing to develop novel processes to convert pentose sugars (and syngas as well) via fermentation, but no commercial plant is in operation at present [217,368]. In light of the above issues, thermochemical conversion of BG-derived syngas to bio-ethanol in the presence of catalysts seems a desirable option and the various routes to synthesise EtOH are depicted in Fig. 15.

Table 10

Countries with high bioethanol yields from different energy crops [28].

Country	Bioethanol feedstocks	Bioethanol yield (liters/hectare)
Brazil	Sugarcane, 100%	6641
USA	Corn, 98%	3770
	Sorghum, 2%	1365
China	Corn, 70%	2011
	Wheat, 30%	1730
EU-27	Wheat, 48%	1702
	Sugar beet, 29%	5145
Canada	Corn, 70%	3460
	Wheat, 30%	1075

Synthesis gas obtained as the product of BG serves as the raw material for catalytic conversion of EtOH synthesis via three different pathways [217,369]. It can either be directly converted or used to generate MeOH which in turn can be converted to EtOH, as shown in Fig. 16. Selective hydrogenation of carbon monoxide present in syngas takes place at the catalyst surface, in order to synthesise EtOH directly (Eq. (17)). The second method employs MeOH as intermediate and involves reductive carbonylation in the presence of catalyst. This process yields bio-ethanol by joining C—C bonds over the surface of the catalyst and is known as MeOH homologation (Eq. (18)). The third approach is a 3-stage process called the ENSOL process. Here, MeOH is first synthesised using syngas as raw material. The second step involves acetic acid generation via MeOH carbonylation, followed by EtOH synthesis through hydrogenation of acetic acid (Eqs. (5), (19) and (20)) [369]. All the reactions are represented in Eqs. (17), (18), (5), (19) and (20).



According to Subramani and co-authors [364], MeOH homologation via reductive carbonylation has lower EtOH yields and selectivity vis-à-vis commercial levels. The ENSOL approach has three steps and different catalysts are needed for each, making the process both expensive and complex. These approaches have been tested in pilot-scale plants but neither has been employed commercially. Both

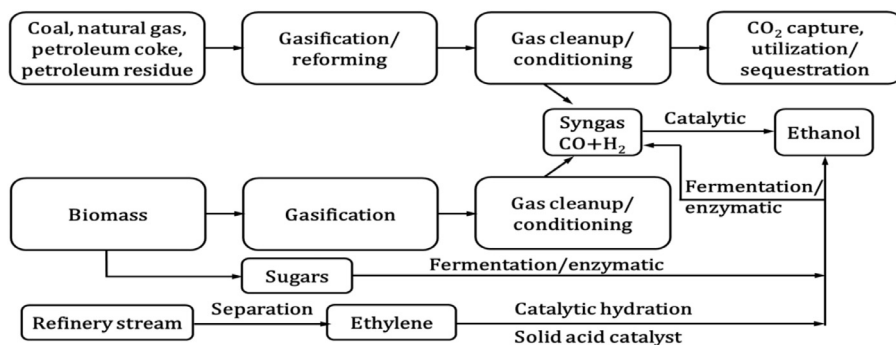


Fig. 15. All possible pathways to synthesise EtOH [364].

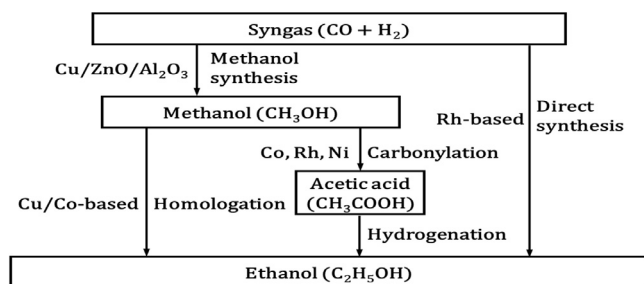
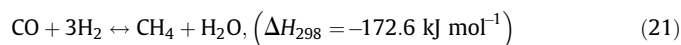


Fig. 16. Typical routes to produce EtOH via syngas.

direct synthesis and production of EtOH via methanol homologation are accompanied by several side reactions. These side reactions are a function of the catalysts used and they produce diversified chemical species such as CH_4 , higher alkanes and olefins ($\text{C}_2\text{--C}_5$), esters, ketones, aldehydes, acetic acid, etc. Among all of these side reactions, the highly exothermic methanation reaction is of prime interest on account of its ability to consume H_2 as shown in Eq. (21).



Higher EtOH yields and selectivity demand the inhibition of the methanation reaction. This can easily be achieved by controlling the operating conditions and the type of catalyst used. Another important side reaction is the water gas shift reaction [370]. This is promoted by almost all the commonly employed catalysts for EtOH generation and is favourable when the feed syngas contains low H_2 . Normally, a ratio of 1 to 2 (H_2/CO) is employed for direct EtOH synthesis.

Crespo and co-authors [371] investigated the impact of MeOH co-feeding in the catalytic reactor to convert BG-derived syngas into EtOH, over MoS_2 catalyst. Methanol was recycled and its influence on EtOH and HC production was evaluated at three different reaction temperatures (280, 290, 300 °C). They reported a linear rise in CO conversion and EtOH generation, and exponential increase in HC production as a result of co-feeding MeOH with syngas. Bio-ethanol and higher alcohols production was found to be more than doubled, when the MeOH molar concentration was enhanced from 0 to 8%. A trade-off needs to be established between enhancement in alcohol generation and selective conversion to EtOH. It should be noted that only lower MeOH concentrations have positive impact on EtOH production.

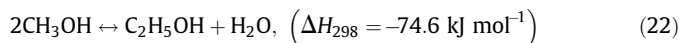
Numerous investigations have been carried out using various homogeneous and heterogeneous catalysts to convert syngas into EtOH via direct synthesis and MeOH homologation. Bio-ethanol and C_2 oxygenates are directly synthesised from syngas over Co, Ru or Rh metal formulations [372–375]. Some oxy-solvents (glymes, sulfolane, etc.), ionic liquids (Bu_4PBr) or iodides are employed as promoters. Heterogeneous catalysts are broadly categorized as noble metal-based and non-noble metal-based catalysts. The former are Rh-based complexes whereas the latter include modified FT catalysts, Mo-S₂-based catalysts and MeOH synthesis catalysts [370]. Extensive studies on the catalysts employed for EtOH production via catalytic syngas conversion can be found elsewhere [364,370,376].

Bio-ethanol production via gasification-generated syngas is a highly exothermic process. Constant heat removal is imperative to ensure optimum catalyst activity and a long catalyst lifetime. Therefore, appropriate reactor design is a key parameter to obtain high product yields with desired selectivity. FXB reactors are most commonly employed for almost all lab- and pilot-scale investigations on account of their good performance and simple design. However, continuous stirred-tank reactors (CSTRs) and slurry bubble column reactors (SBCRs) have also been used in a few demonstrations. Verkerk and co-authors [377] compared the data for EtOH production via direct synthesis and MeOH carbonylation, for FXBs and CSTRs under

the same operational conditions in the presence of $\text{ZrO}_2/\text{ZnO}/\text{MnO}/\text{K}_2\text{O}/\text{Pd}$ and reported that the amount of EtOH produced in both routes is 5 to 10 times higher for CSTRs than for FXBs. In addition, MeOH productivity was found to decrease and EtOH was the major alcohol grade produced in CSTRs, for both routes. Effective heat removal and back-mixing were cited as the reasons for better performance in CSTRs. Currently, SBCRs have also become an attractive choice for commercial establishments on account of numerous reasons such as (1) enhancement in per-pass efficiency due to constant heat removal, (2) elimination of intra-particle mass transfer restrictions by employing smaller catalyst particles, (3) simple reactor design and (4) addition or removal of catalysts without breaking up the operation. Therefore, slurry reactors such as CSTRs and SBCRs are promising options for EtOH synthesis; however, appropriate solvents and their influence on catalytic activity are major concerns and should be considered prior to their installation and operation [364].

5.2.1. Thermodynamics of bio-ethanol synthesis

Bio-ethanol synthesis via syngas in the presence of catalysts consists of a complex reaction network which includes both the main reactions and side reactions, resulting in a diverse product range. The composition and yields of products are significantly influenced by thermodynamic restrictions. Subramani et al. [364] performed comprehensive equilibrium studies to evaluate the alterations in enthalpy (ΔH) and Gibbs free energy (ΔG) between 25 °C and 400 °C, for EtOH production via direct synthesis and MeOH homologation routes. They investigated changes in ΔH and ΔG vis-à-vis temperature by constructing Ellingham diagrams, as shown in Figs. 17 and 18 and it can be seen from Fig. 18 that direct synthesis of EtOH has the highest exothermicity ($\Delta H \sim 260\text{--}270 \text{ kJ mol}^{-1}$). Feeding MeOH along with synthesis gas (MeOH homologation route) decreases ΔH ($\sim 160\text{--}170 \text{ kJ mol}^{-1}$). This further reduces to around 74 kJ mol^{-1} when 2 mol of MeOH reacts to form EtOH, by what appears to be a bimolecular reaction (Eq. (22)). This bimolecular reaction is not firmly established; however, mechanistic investigations employing an isotopic tracer approach suggested the probability of its occurrence during MeOH homologation [378,379].



Subramani and Gangwal [364] predicted the trends of Gibbs free energy change for syngas conversion to CH_4 , MeOH and EtOH (Fig. 19) and concluded that direct synthesis of EtOH is feasible below 280 °C, but that higher pressures are needed to enhance amounts of EtOH. Methane formation is favourable at all

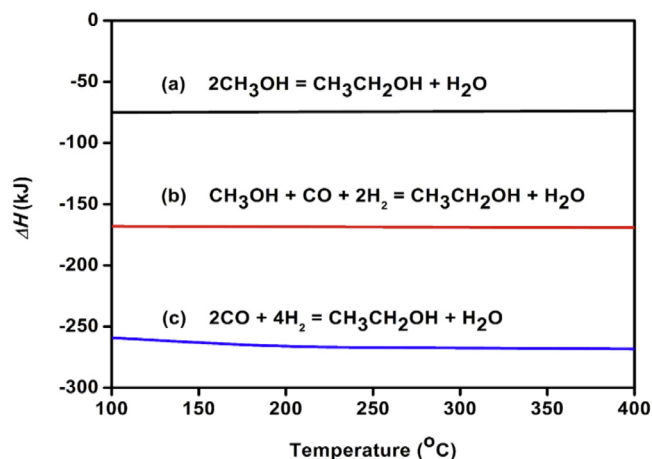


Fig. 17. Analysis of change in enthalpy vs. temperature for EtOH production [364].

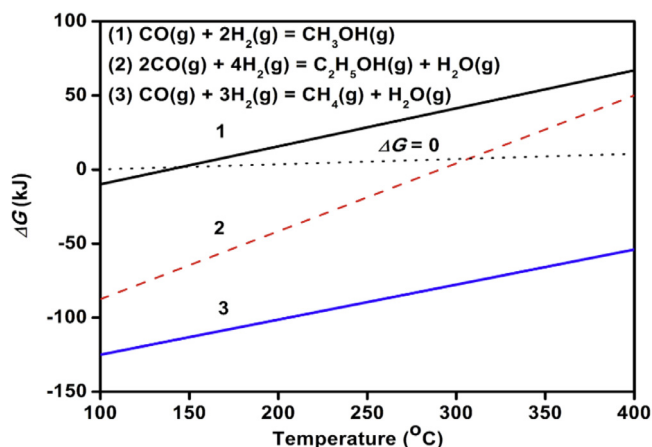


Fig. 18. Analysis of change in Gibbs free energy vs. temperature for EtOH production [364].

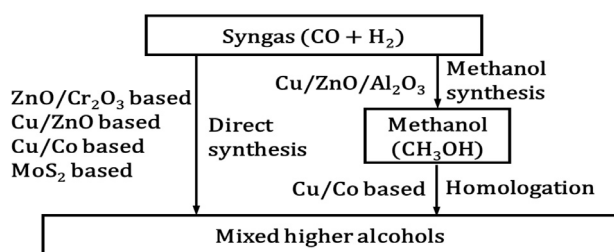


Fig. 19. Main routes for mixed higher alcohols synthesis employing syngas as raw material [364].

temperatures under consideration; however, MeOH synthesis from syngas is only thermodynamically viable below 150 °C. It should also be noted that while CH₄ and MeOH are commercially produced from syngas, C₂ oxygenates (EtOH, acetaldehyde, acetic acid) are not directly synthesised, although the reactions to produce them are thermodynamically favourable. It can be inferred that C–C bonding for EtOH direct synthesis from syngas is thermodynamically possible but kinetically limited.

Heijden and Ptasiński [380] performed second law analysis for EtOH production via steam-blown BG-generated syngas. This included biomass feedstock (wood) drying and gasification, syngas cleaning-conditioning-compression, EtOH production, separation and heat recuperation. They developed the model using commercial software – ASPEN PLUS, employing Rh–Mn/SiO₂ and MoS₂–K₂CO₃–CoS catalysts. They reported that Rh-based catalyst showed reduced CO conversion and higher EtOH selectivity than MoS₂-based catalyst. Taking EtOH as the only product, both catalysts showed almost equal exergetic efficiency of around 44%. However, when EtOH production by-products are taken into account, the efficiency of the MoS₂-based catalyst (65.8%) was higher than the other (58.9%), on account of extra by-products generation. The maximum irreversibilities occurred in the gasifier, EtOH reactor and syngas compressor and it is evident that the overall process exergetic efficiency would improve at lower gasification temperature on account of minimization of irreversibilities. Moreover, catalyst performance was also found to improve with decreasing gasifier temperature. However, the gasifier cannot operate below a threshold temperature (~800 °C) due to kinetic restrictions. This study proves that bio-ethanol production via thermochemical gasification-produced syngas is a promising pathway for green fuel synthesis.

Yan and co-workers [381] investigated the impact of process variables such as temperature, pressure, H₂/(CO+CO₂) molar ratio (in syngas), on CO and CO₂ conversion and EtOH yields. Their

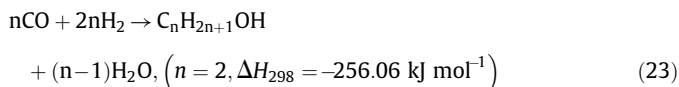
equilibrium reactor was operated at 240 – 400 °C and 20 – 80 bar H₂/(CO+CO₂) ratio was taken as 0.25 to 3 whereas CO₂/CO was taken between 0.2 and 1.5. They observed that low-temperature and high-pressure conditions are favourable for EtOH synthesis. The composition of gasification-derived syngas is one of the deciding factors for EtOH yields. Higher H₂/(CO+CO₂) ratio and lower CO₂/CO result in higher amounts of EtOH. Therefore, syngas composition should be regulated via feedstock composition and gas cleaning to obtain maximum EtOH yields.

5.3. Mixed higher alcohols

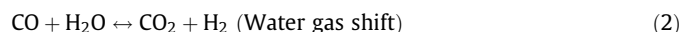
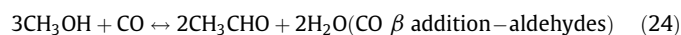
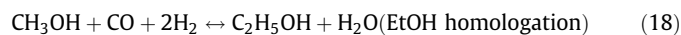
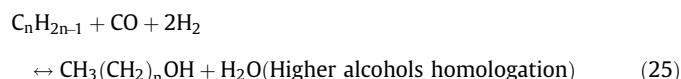
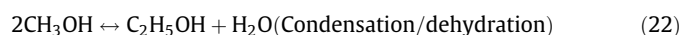
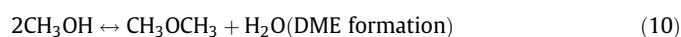
Higher alcohol synthesis from syngas has a long history of more than 100 years. In 1913, BASF obtained a patent to produce a blend of mixed alcohols and other organic compounds such as ketones and aldehydes, from syngas [382]. They carried out the process at elevated temperatures (300–400 °C) and pressures (100–200 bar) in the presence of alkali cobalt oxide catalyst. In 1923, Franz Fischer and Hans Tropsch also developed a process known as ‘Synthol’ for mixed alcohol synthesis from syngas, over Fe catalyst at around 450 °C and pressure more than 100 bar [217]. From 1935 onwards, a few commercial processes synthesised mixed alcohols employing alkali ZnO/Cr₂O₃ catalysts, for about a decade [217]. Mixed alcohol production via syngas reduced to a considerable extent after 1945 on account of increasing demand for neat alcohols (as raw material for chemicals) and easy availability of petroleum [383]. Interested readers can refer to the literature [384] for a comprehensive discussion about earlier work in higher alcohol synthesis.

Interest in mixed alcohols production and applications (such as gasoline blending agents) was revived after the oil embargo in the 1970s. Utilization of mixed alcohols as an additive to increase octane rating is more promising than adding MeOH alone, in gasoline-driven engines [385]. As mentioned earlier, MeOH is also a commonly employed gasoline blending stock. However, it suffers from high volatility and affinity towards phase separation, in the presence of H₂O [217]. In addition, it is not compatible with some engine-fuel system parts. Mixed alcohols (MeOH + higher alcohols) do not suffer from these problems and also offer higher calorific content as compared to MeOH alone. They are equally beneficial for diesel additive as well. When employed as diesel blending agent (~20–30 wt. %), they offer better lubrication properties, improved ignition characteristics and higher heating values than MeOH [386]. Although there are some commercial systems to produce other fuels via syngas, there is currently no large-scale plant which produces higher alcohols (C₂–C₆). Poor selectivity and lower yields are the key factors which make it commercially unviable [387].

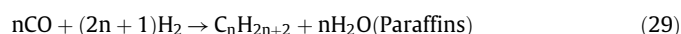
Higher alcohol production consists of various chemical reactions with mainly three routes as depicted in Fig. 19. It results in the synthesis of a wide range of products vis-à-vis equilibrium and kinetic restrictions. Carbon monoxide from syngas reacts with MeOH to form C–C bonds, in the primary stage [217]. Linear chain alcohols are synthesised in a step-wise manner which initiates with the production of MeOH [388]. Subsequently, bio-ethanol, propanol, butanol and other higher alcohols are synthesised, by the homologation of MeOH. It should be noted that the catalyst employed for higher alcohols production should also demonstrate MeOH synthesis activity as MeOH is a recurrent C₁ reactant. Alkali MoS₂ is used for linear alcohols production whereas modified MeOH and FT catalysts are employed for branched chain alcohols synthesis [217]. Wong et al. [389] and Hutchings et al. [390] have provided the following general reaction Eq. (23) for higher alcohol production:



where n normally varies between 1 and 8 [383]. It can be inferred from the reaction stoichiometry that the molar H_2/CO ratio is one-half, although simultaneous water gas shift enhances this ratio to 1. All the key reactions involved in higher alcohol production are shown in Eqs. (5), (2), (24), (18), (25), (22), (10), (26) and (27) [364,391].



As noted above, during alcohol synthesis from syngas, a number of competing reactions (Eqs. (28) and (29)) also occur simultaneously.



Low temperature and elevated pressures inside the reactor are optimum conditions for MeOH synthesis [392]. At higher pressures, with the increase in temperature, the rate of higher alcohols synthesis improves at the cost of MeOH formation and that of other HCs. This rate can further be enhanced by keeping the H_2/CO molar ratio in syngas close to 1, which is favourable for CO induction and carbon-carbon chain growth [217]. However, operating conditions for higher alcohol production are more severe than for MeOH synthesis. If the catalysts employed prove efficient for hydro-carbonylation activity, then MeOH can be recycled for subsequent homologation resulting in higher productivity [388,392]. Chemical dehydration occurs in-situ for mixed compound (higher alcohols, ethers, esters) synthesis on account of the water gas shift [392]. Yields are the function of shift activity of the catalysts used. Secondary reactions are responsible for aldehydes, ketones and CH_4 formation [392–394]. Equilibrium restrictions limit the theoretical amount of higher alcohols produced [393]. It can be clearly seen that lower yields of higher alcohols are produced per mole of CO consumed, more by-products per mole of alcohols are produced and a higher amount of heat is expelled, as compared to MeOH.

Bi-functional-based hydrogenation catalysts are typically employed for higher alcohols synthesis and are classified into the following four groups [382] – (1) modified elevated-pressure MeOH production catalysts (alkali-doped ZnO/Cr_2O_3), (2) modified low-pressure MeOH production catalysts (alkali-doped Cu/ZnO and $Cu/ZnO/Al_2O_3$), (3) modified FT catalysts (alkali-doped $CuO/CoO/Al_2O_3$) and (4) alkali-doped sulphides (MoS_2). It can be noted that alkali metals are added in the formulations for all kinds of catalysts on account of their basicity. They act as a site to catalyse the aldol condensation reaction by stimulating surface-adsorbed CO along with an increase in formate fraction which is an intermediate [217]. Modified MeOH and FT catalysts are found to be more effective in mixed alcohols synthesis with oxide-based catalysts performing better than sulphide-based [395]. Catalysts formulations based on Rh are also employed to synthesise C_2 oxygenates such as acetaldehyde and acetic acid along with enhanced levels of CH_4 [391,396].

However, they have been developed for selective EtOH production. More research on new catalyst formulations is recommended to enhance the activity and selectivity for higher alcohol synthesis processes.

5.3.1. Unique higher alcohol synthesis in single stage

Matson and co-researchers [397] have demonstrated a novel process to synthesise higher aliphatic alcohols (C_2 to C_6) and methylated derivatives from wood and cellulose in the presence of supercritical MeOH and Cu-doped porous metal oxide (PMO) as depicted in Fig. 20. They converted biomass to liquid fuels in one step at a temperature range of 300–320 °C and pressure range of 160–220 bar, with little or no residual char. They employed a stainless steel Swagelok mini-reactor to carry out the investigations and examined woody sawdust, powdered torrefied wood and cellulose fibres and observed the key components (gas and liquid phases) present in the products, for each feedstock employed. Higher alcohols and ethers (HAE) with 2 to 6 carbons, and substituted cyclohexyl alcohols and ethers (CAE) with 9 to 12 carbon atoms, were obtained as liquid yields. Gaseous phase chemical species were mainly comprised of CO , H_2 , CO_2 , CH_4 and other volatiles.

The authors further suggested that significant ring methylation of the final products also occurred when lignin was treated by this process [398,399]. It should be noted that comparable methylation of unsaturated intermediates is a probable source of branched alcohols in HAE products while treating cellulose. Metal oxide/Cu is very effective for carbonyl hydrogenation [308], aryl ether hydrogenolysis and aromatic ring hydrogenations [399] and it was reported that the blend of supercritical MeOH and intrinsically-reduced Cu-doped PMO is ideally suitable to aid the complex network of physical and chemical processes needed to obtain liquid fuels via lignocellulosic biomass.

Transportation cost is a major obstacle in biomass conversion to usable fuels [400]. The novel routes suggested by Matson and co-authors [397] and depicted in Fig. 21 can eliminate the transportation cost from biomass source to processing facility. Medium-sized facilities can be installed near the source (lignocellulose, crops, etc.) to convert them to useful liquid fuels and there are three possible pathways as shown in Fig. 21. The first option (MeOH option) employs MeOH as reaction medium as well as liquid syngas to

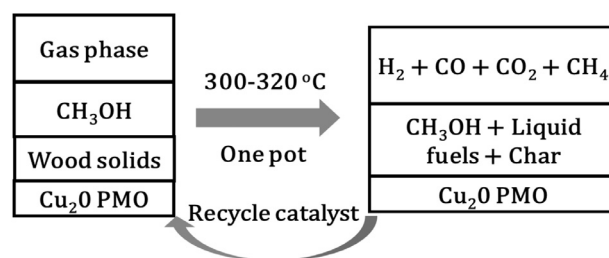


Fig. 20. Novel process to synthesise higher alcohols [397].

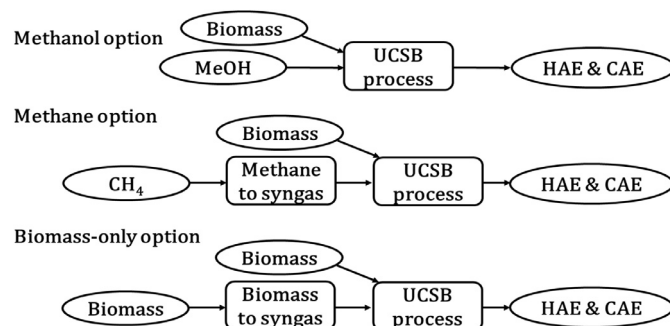


Fig. 21. Three conceptual pathways to produce HAE/CAE [397].

reduce biomass feedstock. The second option employs CH_4 -to-syn-gas conversion to produce essential reducing species.

An existing CH_4 distribution network can be helpful for this route, however, accretion of an additional (CH_4 reforming) process is a limitation. The third option suggested by the researchers [397] uses biomass to generate HAE and CAE, with even lower carbon emissions [401]. In the last two pathways, MeOH can be produced in-situ to be used as the reaction medium. This process seems promising, albeit thermodynamic and kinetic investigations should be carried out to evaluate the feasibility of scale-up to commercial scale.

5.3.2. Pilot plant testing at NREL

Biomass to mixed alcohols synthesis was carried out at National Renewable Energy Laboratory, USA, for a continuous 233 h operation in a pilot plant [402], on MeOH-derived syngas for 81 h and on a biomass-derived syngas for remaining 152 h. The average syngas composition comprised 39% H_2 , 33% CO_2 , 13% CO with some other gases. The plant operated at maximum pressure and temperature of 138 bar and 322 °C, respectively, and generated 20 L of mixed higher alcohols. The system consisted of a solid feeder, FB steam reactor, thermal cracker, char collector, FB steam reformer, packed bed polishing steam reformer, scrubber, pressure-swing adsorption (PSA) unit and gas phase continuously stirred tank gas to liquid reactor. Tars and CH_4 were reformed over a NREL-developed Ni-based catalyst in a FB reactor, followed by pelletized precious metal catalyst in a FXB reactor. Promising results were reported in steady state conditions. Steam reformers converted almost 100% of tars, 97% of benzene and 86% of CH_4 present in the producer gas. More discussion on this subject can be found elsewhere [402].

5.4. Comparison of MeOH, EtOH and gasoline as transportation fuel

Methanol and ethanol both have high octane ratings and, therefore, have the potential to be employed as gasoline substitutes or blending agents in SI engines. Some tests have shown the possibility of using 85–100 vol. % MeOH in automobiles. Prior to the introduction of cost-effective gasoline, MeOH was widely employed to propel vehicles [403]. Interestingly, MeOH is a better fuel for SI engines than conventional gasoline, with higher thermal efficiency and lower emissions. High octane number (106) coupled with lower

flammability makes it a better choice [404]. However, 2.2 L of MeOH is equivalent to 1 L of gasoline due to its lower energy density, necessitating larger fuel tanks.

Ethanol has a long history as an automotive propellant. In 1894, it was employed in France and Germany by the incipient IC engine industry [405]. Wider flammability range coupled with higher heat of vaporisation, higher flame speeds and higher octane rating (108) than gasoline, imbues it with a shorter burn time and higher compression ratio, which in turn results in better efficiency [406]. Table 11 depicts the physical and chemical properties of MeOH, EtOH and gasoline and demonstrates that almost all the properties of these two alcohols are close in value to those of petroleum-derived gasoline, thus making them a promising choice as substitute/blending agent for SI engines, although the heating value of gasoline is higher than these alcohols, necessitating larger tanks to provide the same amount of energy.

6. Fischer Tropsch (FT) fuels

FT synthesis for higher hydrocarbons production was developed by German scientists Franz Fischer, Hans Tropsch and Helmut Pichler in 1923 [408]. Diesel, gasoline and heavy oils were synthesised via syngas in the presence of Co catalysts. The Ruhrchemie atmospheric FXB reactor was the first established for industrial production of FT fuels in 1935. It was used to produce gasoline, diesel, lubrication oils and other chemicals with total production of 0.10 to 0.12 Mt a^{-1} , employing coke-derived syngas [409]. All commercial FT plants around the globe use syngas produced by coal or natural gas reforming, as summarised in Table 12.

Unlike other biofuel production processes, FT is considered to be the most developed and mature technology for liquid transportation fuels synthesis. As mentioned earlier, all large-scale FT plants employ either gasification of coal or reforming of natural gas to generate syngas. Thus, BG-based FT plants should not encounter any serious technical issues. Gasification of biomass feedstock to generate syngas followed by its conversion to long chain HCs and upgrading to liquid transportation fuels such as gasoline and diesel over Co or Fe catalysts is a promising option for the future of biofuels [413]. Although there are numerous commercial-scale BG plants worldwide for thermal and electrical applications, FT fuels generation via BG-derived syngas has not reached that scale as yet. However,

Table 11
Comparative analysis of the properties of ethanol, methanol and gasoline as transportation fuel [407].

Property	Methanol CH_3OH	Ethanol $\text{C}_2\text{H}_5\text{OH}$	Gasoline $\text{C}_4\text{--C}_{12}$
Molecular weight (kg mol^{-1})	0.032	0.046	~0.114
Specific gravity	0.789 (25 °C)	0.788 (25 °C)	0.739 (25 °C)
Vapour density rel. to air	1.10	1.59	3.0 to 4.0
Liquid density (kg m^{-3} at 25 °C)	790	790	400
Boiling point (°C)	65	78	27 to 245
Melting point (°C)	−98	−144	
Vapour pressure @ 38 °C (kPa)	31.72	17.24	~55–69
Heat of evaporation (kJ kg^{-1})	1097.8	953.6	314.1
Heating value (MJ kg^{-1})			
-Lower	20.1	26.9	43.4
-Upper	22.8	29.8	46.5
Tank design pressure (kPa)	103.4	103.4	103.4
Viscosity (Pa-s)	0.00054	0.0012	0.00056
Flash point (°C)	11	14	−45
Flammability/explosion limits			
-(%) Lower (LFL)	6.7	3.3	1.3
-(%) Upper (UFL)	39	19	7.6
Auto-ignition temperature (°C)	460	363	250–460
Solubility in H_2O (%)	Miscible (100%)	Miscible (100%)	Negl. (~0.01)
Azeotrope with H_2O	None	95% EtOH Hygroscopic	Immiscible
Peak flame temperature (°C)	1870	1920	2030
Minimum ignition energy in air (mJ)	0.14		0.23

Table 12
FT synthesis plants at commercial scale [410–412].

Organization	Location	Date of commissioning	Raw material	Capacity (bpd)
Shell	Qatar	2009	Natural gas	140,000
SasolChevron	Escravos	2007	Natural gas	34,000
Sasol/Qatar Petroleum	Qatar	2006	Natural gas	34,000
Shell	Bintulu	1993	Natural gas	12,500
MossGas	Mossel Bay	1992	Natural gas	30,000
Sasol	Secunda	1982	Coal	85,000
Sasol	Secunda	1980	Coal	85,000
Sasol	Sasolburg	1955	Coal	2500

numerous demonstration plants with BG coupled with FT plants have been set up with the same motivation [411,413–419] as summed up in Table 13.

A significant study was conducted by Kim and co-authors [412] to produce FT liquid fuels via BG-derived syngas. This integrated bench-scale system was run for 500 h on a 20 kW_{th} gasifier and produced 0.1 bbl d⁻¹, as a pre-cursor to establish a pilot plant of 200 kW_{th} with a production of 1 bbl d⁻¹. An atmospheric BFB reactor was employed over a temperature range of 700–900 °C, with wood pellets as the feedstock. The gasifier, gas cleaning and processing unit (cyclone, gravitational dust collector, packing type wet scrubber and MeOH absorption tower), acid gas removal unit and FT reactor formed the system. The FT reactor was operated at an elevated temperature of around 300 °C over Fe catalyst. FT diesel was produced at an average rate of 0.037 bbl d⁻¹ which is lower than expected. Elevated temperature, impact of high H₂/CO ratio, non-optimized FT reactor conditions and uncondensed C₅ – C₈ fractions of the

products were cited as the reasons for lower yields. However, stable operational conditions for every individual component were achieved and technical viability was demonstrated.

6.1. Process chemistry and products

6.1.1. Process chemistry and mechanisms

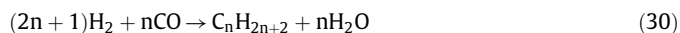
Fischer Tropsch technology offers a significant pathway to utilize synthesis gas and produce higher HCs which can be further hydrocracked to premium-quality gasoline and/or diesel. Renewable biomass feedstock of diverse compositions can be used to generate clean transportation fuel when BG is coupled with FT synthesis, leading to a promising and feasible substitute for fossil-derived liquid fuels. The FT process is basically a surface polymerization reaction which employs Co or Fe catalysts at 200–300 °C temperature and 10–60 bar pressure. CO and H₂ present in syngas interact to form a chain initiator by adsorption and dissociation at the catalyst

Table 13
FT plants based on biomass gasification around the globe [409–412,420,421].

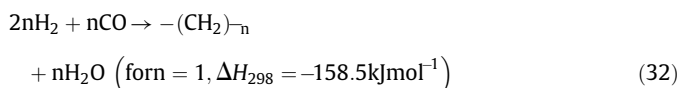
Organization/year	Gasifier/feedstock	FT synthesis	Scale	Duration	Details
Red Rock Biofuels (USA), 2017	TRI steam reformer, forest and saw mill waste	Velocys reactor, Co catalyst	Commercial	— ^a	460 t day ⁻¹ biomass feed, 1100 barrels day ⁻¹ liquid fuel
Sierra Biofuels, Fulcrum Bio-energy (USA), 2016	TRI steam reformer, MSW	Velocys reactor, Co catalyst	Commercial	—	400 t day ⁻¹ MSW feed, 657 barrels day ⁻¹ liquid fuel
Solena Fuels, Green Sky (UK), 2015	Solena plasma gasifier, municipal and commercial waste	Velocys micro-channel reactor, Co catalyst	Commercial	—	1157 barrels day ⁻¹ jet fuel
SYNDIESE (USA), 2015	Entrained flow, oxygen-blown, forest and agricultural waste	—	Commercial	—	205 t day ⁻¹ biomass feed, 530 barrels day ⁻¹ liquid fuel
KITECH/KIER/KRICT (Korea), 2011	BFB (20 kW _{th}), steam-blown, wood pellet	Fixed bed, Fe catalyst	Bench	500 h	No poisoning of catalyst, 2.8 L/d product, over 92% overall CO conversion, C ₅₊ selectivity above 50%
Cearfuels/Rentech (USA), 2011	HEHTRR (8 ton day ⁻¹) (entrained flow gasifier), steam-blown, various wood	Slurry, Fe catalyst	Pilot	—	1600 L d ⁻¹ product
TRI (USA), 2011	BFB (5 t day ⁻¹), steam-blown, black liquor	Fixed bed, Co catalyst	Pilot	Over 1300 h	80 L d ⁻¹ product, 70% CO conversion
CUTEC (Germany), 2010	CFB (400 kW _{th}) steam/oxygen-blown, mainly straw	Fixed bed, Co catalyst	Pilot/lab	900 h	150 mL d ⁻¹ product
Velocys (USA), 2010	DFB (8 kW _{th}) (Gussing gasifier), steam-blown, wood chip	Microchannel, Oxford catalyst	Demo/pilot	Over a month	115 kg day ⁻¹ product, 70% CO conversion
AIST (Japan), 2010	Downdraft (40 kg/h), oxygen-enriched air blown, wood chips	Slurry bed, Co/SiO ₂ catalyst	Bench	—	C ₅₊ selectivity 87.5%, 0.1625 L-hydrocarbon kg-wood ⁻¹
MIUN (Sweden), 2008	DFB (150 kW _{th}), steam-blown, wood pellet	Fixed bed, Fe or Co catalyst	Lab	—	—
CHOREN (Germany), 2007	Carbo-VR (45 MW _{th}) (Entrained flow 3-stage gasifier), oxygen-blown, waste wood/wood chip	Fixed bed, Co catalyst	Commercial	—	43 t day ⁻¹ product
Integrated project RENEW (UN), 2007	DFB (8 kW _{th}) (Gussing gasifier), steam-blown, wood chip	Slurry, Co catalyst	Demon	495 h	C ₅₊ selectivity above 90%, no loss of catalyst activity
TUV (Austria), 2005	DFB (8 kW _{th}) (Gussing gasifier), steam-blown, wood chip	Tubular slurry, Co or Fe catalyst	Demo/lab	—	2.5–5 kg d ⁻¹ product, 90% CO conversion
ECN (Netherlands), 2003	CFB, oxygen-blown, willow	Fixed bed, Co catalyst	Pilot/lab	500 h	C ₅₊ selectivity around 90%, no loss of catalyst activity

^a data are not available in the original literature.

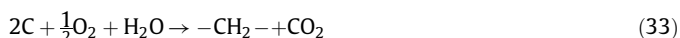
surface [422]. Further steps in the reaction are chain propagation followed by termination and product desorption. FT synthesis is depicted in Eqs. (30) and (31) as overall reactions for alkanes and alkenes production, respectively [423,424].



The addition of CH_2 monomers in a growing chain is shown in Eq. (32) [425]. Water gas shift activity is reflected in Eq. (2) leading to CO_2 generation [426,427].



The stoichiometry of FT synthesis is a function of usage ratio (ratio of consumption of H_2 and CO) and this ratio fluctuates as a function of the extent of other reactions. The WGS alters H_2/CO ratio and thus influences the usage ratio [426,427]. Fe catalysts are highly active for WGS and, therefore, can play an important role in FT process chemistry, in particular for H_2 -deficient syngas [428]. Biomass-derived syngas can have a ratio of $H_2:CO$ as low as 0.7:1 [429], in comparison to that from steam reforming of methane of 3:1. Co catalysts are not active for WGS [430–433]. Taking biomass feedstock as the raw material to produce syngas which is further converted to green fuels via FT process, the overall reaction (Eq. (33)) can be written as:



The composition and variety of products generated by FT synthesis are dependent upon catalysts and process conditions. Therefore, the steps employed during the process along with the mechanistic and kinetic factors directly affect the product quality and yield [434]. This explains the higher FT product yields in comparison to yields calculated by thermodynamic investigations [433]. It is important to note that exothermicity of the reactions is an important feature in FT synthesis. Reactions producing H_2O and CO_2 as products release more heat as the heat of formation of these species is higher [28]. Dissipation of heat of reaction becomes a critical factor to ensure stable reaction conditions, synthesise higher HCs and avoid catalyst deactivation.

Numerous studies [410,426,435–441] [422–424,427,442] have been conducted to examine the kinetics of the FT process. The kinetic models for FT synthesis can be categorized as hydrocarbon selectivity models and detailed Langmuir-Hinshelwood-Hougen-Watson (LHHW) models [427,442]. FT reaction networks form the

basis of selectivity models and can be sub-classified as the double-alpha models or the olefin re-adsorption models. Re-adsorption models are employed often on account of their ability to evaluate selectivity for diverse product species (paraffin and olefin), whereas the former can only calculate the total HC production (lumped paraffin and olefin) [427]. In addition, re-adsorption models can forecast the deviations from Anderson Schulz Flory (ASF) and the alterations of olefin-to-paraffin ratio vis-à-vis carbon number. On the other hand, LHHW kinetic models take into account the complete FT mechanism such as adsorption of reactants, formation of monomer, chain initiation, propagation and termination. It should be noted that these models also incorporate the information such as 1-olefin re-adsorption and/or chain length-dependent olefin desorption which aid in understanding the deviation in product distribution with respect to carbon number [423,427]. Commonly employed mechanisms are alkyl, alkenyl, enol and carbon monoxide insertion mechanism [408], as shown in Table 14.

6.1.2. FT products

The FT process synthesises a diverse range of HCs and oxygenated HCs. The product spectrum is directed by mechanics and kinetics of the reactions as well as by the catalyst type and reaction conditions. Methane generation is considered undesirable and its selectivity can fluctuate from 1 to 100%. Selectivity of long chain waxes can diverge from 0 to 79% whereas yields of the products with an intermediate number of carbon atoms are limited. The number of carbon atoms in the products is a function of various parameters such as operating temperature and pressure, catalyst employed, type of promoter, syngas composition and reactor type [443].

Desired products via FT synthesis include C_{20+} linear HCs, C_{5+} paraffins and medium weight olefins, which are further processed to generate usable liquid transportation fuels. The ideal FT process should have high selectivity towards these products. It should be noted that selectivity during FT synthesis is steered by kinetics during polymerization which controls the chain growth process during the catalytic reaction [444]. FT product spectra obey ASF chain length statistics as depicted in Eq. (34). The reaction mechanism during the FT process is assumed to follow ASF, however, the nature of the catalyst necessitates variations in the ASF model [437].

$$\log(w_i/i) = i \log \alpha + \log((i-\alpha^2)/\alpha) \quad (34)$$

where, w_i is the product weight fraction, i is HC chain length and α is chain growth probability. Generally, typical α values lie between 0.7 and 0.9, where HCs with maximum weight fractions are from C_5 to C_{10} [28]. For industrial processes, only a few carbon chains are desired on account of the fact that they have diverse physical properties and hence, different usage and distribution to the consumers.

Table 14
Different FT mechanisms [410].

Mechanism	Monomer species	Chain initiator	Products	Points to be noted
Alkyl	=CH_2	—CH_3	α -olefins, n-paraffins	Inadequate to account formation of branched HC and oxygenates
Akenyl	=CH_2	—CH=CH_2	α -olefins	Only explains formation of α -olefins as primary products
Enol	$\text{=C} \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$	$\text{=C} \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$	Aldehydes, alcohols, α -olefins	Unable to explain formation of n-paraffins
CO-insertion	$\text{=C} \begin{smallmatrix} \text{CH}_3 \\ \text{OH} \end{smallmatrix}$	—CH_3	α -olefins, n-paraffins, aldehyde, alcohol	Primary pathway for formation of oxygenated FT compounds

Moreover, longer chain groups (diesel, soft wax, hard wax, etc.) can be cracked to smaller C chains, if the desired products involve shorter chains (petroleum fractions). Consequently, it can be deduced that FT process conditions which yield product distributions with longer C chains provide more flexibility to choose saleable fractions. Thus an ASF product distribution model is, therefore, a useful tool on account of its ability to forecast the weight percentage distribution of diverse FT product groups.

Van der Laan [439] has performed extensive studies on the product distribution employing Co, Fe and Ru catalysts. It was reported that FT products with C_1 were highest in concentration. These concentrations reduced steadily with higher C numbers however, a local maximum was observed around C_3 – C_4 . Monomethyl-substituted HCs were produced in minor amounts whereas dimethyl species existed in lesser concentrations. Interestingly, no branched product species were found to contain C_4 atoms. Alcohol amounts were observed to be maximum as C_2 and decreased with increasing C atoms. In the FT product distribution, a deviation in chain growth was reported only for linear paraffins and not for olefins.

6.2. Catalysts and reactors

6.2.1. FT catalysts

Much research has been done on catalysts for the FT process. The ability to catalyse hydrogenation of CO to higher HCs is the key requirement for FT catalysts. Fe, Co, Ni and Ru are four typically used transition metals as FT catalysts on account of their high hydrogenation activities [445]. Ruthenium is the most efficient FT catalyst but it is more costly than others [443]. Ni also has a high hydrogenation activity, although it forms more CH_4 than Fe or Co. In addition, Ni catalysts are liable to constant loss of metal due to the production of volatile carbonyls. On the other hand, Fe and Co are easily available and cost-effective and, therefore, form the primary choices for the FT process. However, Co is preferred over Fe for commercial-scale production as FT fuel production rates with Co are considerably higher than with Fe [446]. The desire for improved FT catalysts has led to research [447] into combinations of metals and supports, for example, Co/ Nb_2O_5 , including promoters such as Pt (in the study cited, increasing the activity of the catalyst by more than a factor of 2). Similar work has shown the promoting effect of CeO_2 on the Co/ ZrO_2 system (in both of these cases the primary effect of the promoter was to enhance the number of active sites, most likely by improving dispersion of the metal). Other workers [448] have shown that the precise nature of catalyst-promoter interactions

(in this case, Fe_2O_3 – MnO_2) can result in significantly different product yields via modification of the physical forms of the materials at the nanoscale. Extensive discussion on FT catalysts can be found in the literature [441,445,446,449–452]. Importantly, work is currently ongoing to improve understanding of the underlying mechanisms of reaction at a molecular scale [453], with better understanding likely to lead to more efficient and rational catalyst design.

The overall FT reaction rate is a function of the following two parameters: (1) diffusion rates of reactants and products through the porous catalyst particles; and (2) rate of FT reaction on the surface of the catalyst. Diffusion rates are functions of porosity and pore size of the catalysts, concentrations of species and the presence of higher HC species within the catalysts particles. It should be noted that intra-particle diffusion plays a vital role in the FT process especially when diameter of FT catalyst particles is greater than 0.5 mm. Therefore, utmost care should be taken while choosing FT catalysts for the FT process using fixed beds [452]. Sulphur is known to poison FT catalysts, most likely by competitive adsorption onto reactive surface sites.

6.2.2. FT reactors

Important relationships with catalysts and catalytic reactors have led to the development of numerous designs for heterogeneous gas-solid catalytic vapour phase reactors for the FT process, which is a multi-product reaction system [451]. Most commonly employed reactors are the multi-tubular FXB reactor, slurry reactor, fixed fluidised reactor and CFB reactor [452], as shown in Fig. 22(a), (b), (c) and (d).

The mode of operation for FT reactors can be classified into high temperature (300–350 °C) or low temperature (200–240 °C). High-molecular-mass linear waxes are produced in low-temperature processes over Fe or Co catalysts. On the other hand, low-molecular-weight olefins and gasoline are generated at high temperature in the presence of Fe catalysts. FB reactors are better as they are more isothermal in nature and can operate at around 320–350 °C, whereas tubular FXB and slurry phase reactors operate at a temperature which is 100 °C lower [454]. A detailed account of the basic designs of FT reactors is available elsewhere [451,452,454–459].

Novel intensified reactors based on micro channel systems have been studied [460]. The main advantage of such a system is that via tight temperature control, both the selectivity towards desired products and the activity of the catalyst can be carefully optimized. A comprehensive review [461] discusses the different array of reactors

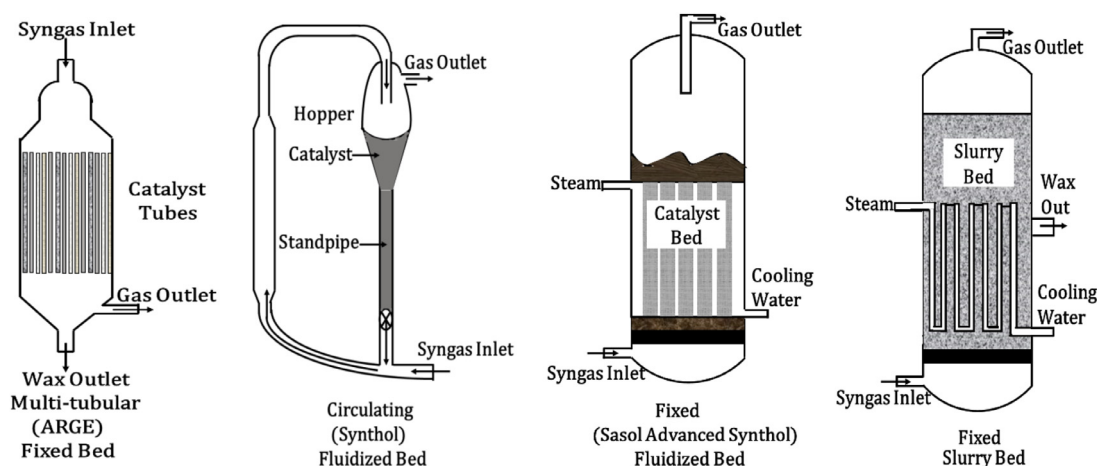


Fig. 22. FT reactors (a) Multi-tubular fixed bed, (b) Circulating fluidised bed, (c) Fixed-fluidised bed and (d) Fixed slurry bed [28].

which can be used. Another novel idea is the use of ionic liquids to suspend FT catalysts [430], which has been shown to be potentially interesting.

6.3. Thermodynamics of FT synthesis, including co-products

Optimizing the overall efficiency of the FT process is compatible with co-production of fuels and electricity (to allow utilization of any unreacted gas) [433]. Such strategies can also improve the economic argument for a process, in particular when the output can be tailored depending upon oil and electricity sale prices at any particular time.

Maximum generation of FT fuels via BG-derived syngas requires optimal usage and understanding of the thermodynamics governing the process. Many researchers have examined the FT process employing the first and second laws of thermodynamics. Ptasiński [462] developed a model to analyse exergetic efficiency for the conversion of syngas to FT green fuels. Syngas ($H_2/CO = 0.8$ to 1.6) was produced by the gasification of sawdust (9.3% carbon, 55% volatile matter, 35% moisture and 0.7% ash) in the presence of air at 900 °C and atmospheric pressure. FT fuels were produced at 260 °C over a Co catalyst along with electricity generation [462]. The single-pass conversion efficiency was found to be 80%. Diesel and wax were reported to be the final liquid products. Low calorific content (3 MJ m^{-3}) gas was recovered as tail gas and was used to produce electricity in a steam Rankine cycle. In the analysis, 51.7 t h^{-1} of feedstock was reported to produce 5.1 t h^{-1} of diesel and wax, and 4 MW of net electricity. The overall exergetic efficiency was found to be 36.4% with maximum losses taking place in the gasifier, and power generation from the tail gas. It should be noted that this efficiency could be enhanced to 46.2% if the operating temperature of the gasifier were reduced to 700 °C, naphtha included among other FT products and a combined cycle were employed for generating electricity. However, in a real case scenario, 700 °C in the gasifier would not yield sufficiently fast reaction kinetics. Another study [463] has compared the environmental impact of producing biodiesel via FT synthesis, with a particular focus on clean-up of the syngas and integration of the process with electricity production. It was found that the higher the fraction of syngas going towards the production of diesel (as opposed to electricity) the higher the NPV (net present value). Maximising an environmental-friendliness index indicated that for a given input flow of biomass, autothermal reforming (adding a small amount of added oxygen to the process to clean up tars, etc.) was superior to not having such a reformer, or the addition of a basic steam reformer, at a gasifier temperature of 1000 °C, FT reactor operating temperature of 200 °C and reactor operating pressure of 60 bar

A recent publication [328] showed the results of carrying out both energy and exergy evaluations for FT fuels generation through BG, using various feedstocks such as wood, grass, agricultural residues, manure, sludge and MSW to generate syngas via gasification in the presence of air, followed by its conversion to green fuel in a FT reactor. The system was composed of pre-treatment, gasification, gas clean-up, WGS, FT reactor and final product upgrading. Mass conversion yield was reported to be 15%, 10%, 12%, 6% and 9%, respectively for wood, grass, agricultural wastes, manure and MSW. Wood and agricultural wastes have the best conversions due to high C and H fractions. First law investigations revealed maximal efficiency for agricultural wastes (44%) and minimal for manure and sludge (36%). Second law examinations exhibited the same trend, with the highest exergetic efficiency of 42% for agricultural residues and 34% for manure, owing to the obvious reasons of less energy penalty (in drying prior to gasification) and high C content. When only external heat production is considered with an efficiency of 60%, exergetic efficiency falls by 1–2% whereas if heat and electricity (generation efficiency = 45%) both are taken into account along with liquid fuels synthesis, the exergy drops by 4–5%. In common with previous investigations, the gasifier is the key source of irreversibilities followed by electricity generation and cleaning, as shown in Fig. 23. However, overall efficiency of the plant can be enhanced to a considerable extent by taking heat integration measures and modifying operating variables.

An interesting perspective for the FT process was demonstrated by Hildebrandt and co-authors [464] to make it more energy efficient. They suggested a pathway to optimize the energy usage for a gasification-coupled FT system, by producing CO_2 and H_2 (and not CO and H_2) and employing them for higher HCs generation. They considered different steps which require large amounts of work and heat inputs as they are the reasons for lowering of efficiencies [465–467]. The model was developed taking coal and water as the input to produce higher alkanes, where each CH_2 monomer needed 58 kJ mol^{-1} of heat input. Moreover, around 41 kJ mol^{-1} of work is required by the reversible process. Therefore, it adds up to a minimum 350 MW of work for a FT plant producing $80,000 \text{ bbl d}^{-1}$ as depicted in Fig. 24. The first step is to gasify the coal and is highly endothermic, whereas the second step of FT synthesis is a low-temperature exothermic process. In the first step, the heat input transfers work, W_{in} , which is equal to or more than the Gibbs free energy change. On the other hand, the second stage emits heat and carries work, W_{out} , which should be equal to Gibbs free energy change of the reaction to make it reversible. Net work obtained for the overall process is the difference between W_{in} and W_{out} and is equal to the Gibbs free energy change of the whole process. These two steps of the coal-to-liquid process can be assumed to be equivalent to a heat engine.

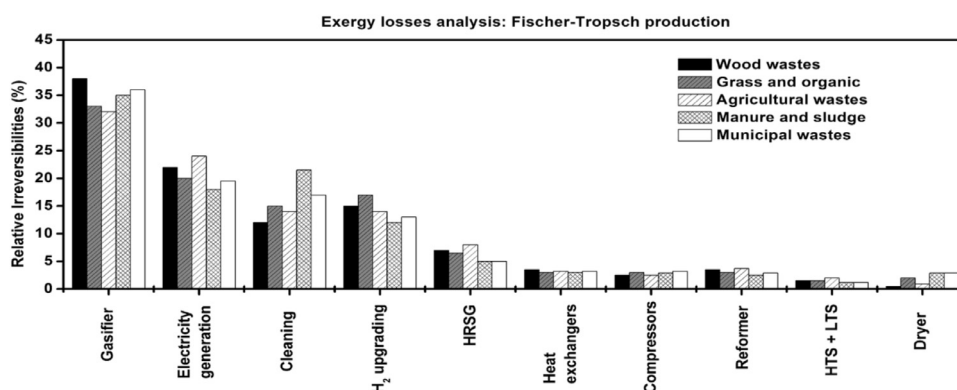


Fig. 23. Model representing irreversibility at various stages in FT fuels synthesis using five different biomass types [328].

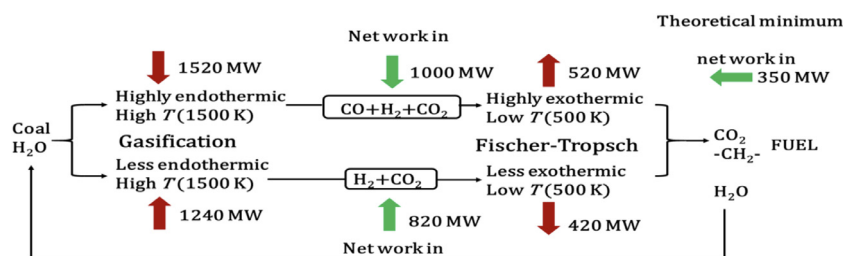
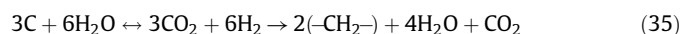


Fig. 24. Schematic of novel perspective for FT fuels synthesis via coal gasification (can be applied to biomass gasification as well) [464].

Conventional gasification-coupled FT plants are not highly efficient on account of significantly more work input into the gasifier and more work output from the FT reactor, than that needed to operate reversibly. It can be made more efficient by decreasing both W_{in} and W_{out} . The gasifier should produce CO_2 and H_2 to achieve this goal (as it is less endothermic). Moreover, employing CO_2 and H_2 for FT fuels synthesis is less exothermic. Although FT synthesis cannot be carried out directly with this feedstock gas composition, it can be made viable by incorporating reverse WGS to produce CO_2 and H_2O as shown in Eq. (35).



Water can be employed to transfer heat back to the gasifier. This model requires at least 20% less work input to the gasification system than the CO pathway. If the work is recuperated in the form of heat from the FT reactors, net work required was reported to be 820 MW for an 80,000 bbl d⁻¹ plant facility. This is closer to the optimum value (350 MW) than the traditional path (1000 MW). Furthermore, the production of CO_2 via this route is around 15% (0.5 MT) less per year. It should be noted that this approach can easily be adapted to natural gas-to-liquid systems, followed by biomass-to-liquid systems. Further research and development is recommended to elucidate the technical challenges related to its implementation in BG-coupled FT synthesis.

7. Bio-methane

Synthetic natural gas or SNG consists mainly of methane (CH_4) and is a promising renewable substitute for natural gas (NG). It is normally called bio-methane to distinguish it from non-renewable natural gas. It is a vital energy carrier for industrial applications and can serve as a transportation fuel, without the environmental implications of hydraulic fracturing [468]. It has all the advantages of natural gas including a dense distribution, trade and supply network. A few decades ago, fossil fuels were the major source of bio-methane. Climate change issues due to GHG emissions and fossil fuel depletion have led to many significant research investigations to generate green SNG (or Bio-methane). This can either be generated biologically with the aid of micro-organisms at around 70 °C in stirred tank or trickle bed reactors, or can be produced through BG followed by methanation (CO or CO_2 methanation) at around 250 °C [469–472]. Thermochemical catalytic generation of bio-methane (at pilot and commercial scale) via biomass (or coal) gasification-derived syngas has been adopted by numerous organizations, as depicted in Table 15.

Paul Sabatier and Jean Baptiste Senderens were French chemists who discovered CO and CO_2 methanation reactions in 1902 [473]. The original application of CO methanation (CO to CH_4) is the removal of CO from syngas, e.g., in ammonia synthesis [474] and in proton exchange membrane fuel cells [470]. CO methanation found application in SNG generation, when researchers tried to find an alternative for NG during the 1970 s oil crisis by utilising coal gasification-derived syngas [475]. CO_2 methanation (CO_2 to CH_4) came into being in the 80 s with an aim to use some other gas; however, it

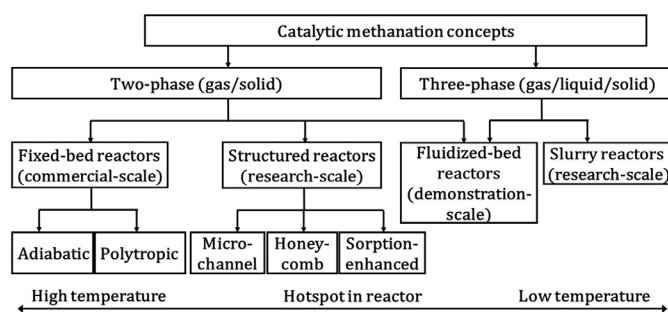
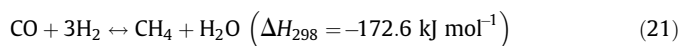
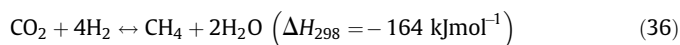


Fig. 25. Advancements in methanation concepts [470].

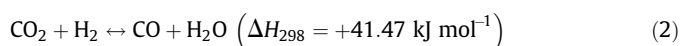
is primarily dependent upon CO methanation [476]. Interest in CO and CO_2 methanation was revived in the twenty-first century on account of climate change mitigation, electricity storage and health consciousness issues. Fig. 25 shows the advancements in methanation concepts over the past five decades and Table 16 reflects carbon oxides technologies adapted by commercial SNG/bio-methane plants.

7.1. Process chemistry

Biomass-derived syngas can be utilized to produce methane in the presence of catalysts and is, therefore, called catalytic generation of bio-methane. CO and H_2 from biomass or coal gasification are employed to synthesise CH_4 with H_2O and heat as by-products in CO methanation whereas CO_2 methanation uses CO_2 and H_2 [470,473,477] as depicted in Fig. 26. Moreover, CO_2 methanation is an attractive option to chemically store electricity, if electrolysis H_2 is employed as an educt [469,478–480]. Carbon oxides conversion to CH_4 is shown in Eqs. (21) and (36).



The heats of reaction mentioned for Eqs. (21) and (36) are at STP. Interestingly, here CO and CO_2 methanation release around 2.3 and 1.8 kW of heat, respectively, for 1 m³ of CH_4 generation [470]. Furthermore, there is a considerable volume contraction in gaseous phase reactants (50% for the former and 40% for latter). Fundamentally, the addition of CO methanation and reverse WGS results in CO_2 methanation (Eq. (2)). CO_2 conversion is dependent upon the CO concentrations and is inhibited when CO volume reaches a certain limit [481,482].



Pressure and temperature are two key operating variables which directly influence these methanation reactions. Elevated pressures and low temperatures are considered favourable for CH_4 production, at thermodynamic equilibrium. Interested readers can find

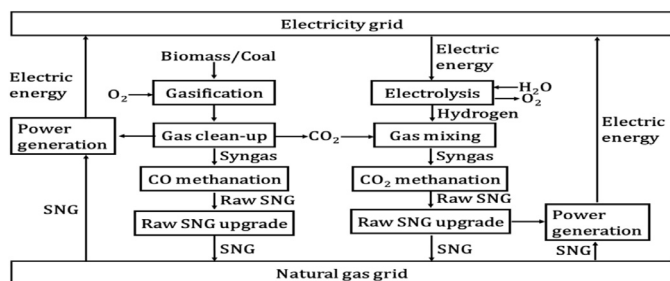
Table 15Methanation projects (CO- and CO₂-based) at pilot and commercial scale [470].

Project	Fuel	Location	Capacity	Methanation approach	Scale
GAYA (Engie)	Biomass	Saint Fons (France)	400 kW bio-methane output	— ^a	Pilot plant (under construction)
GoBiGas (Goteborg Energi)	Biomass	Goteborg (Sweden)	20 MW bio-methane output	TREMP	Commercial plant (in operation)
BioSNG (EU project)	Biomass	Gussing (Austria)	1 MW bio-methane output	PSI (Research institute)	Pilot plant (not in operation)
Great Plains Synfuels Plant (Dakota Gasification Company)	Coal	Beulah (North Dakota, USA)	1500 MW fuel input	Lurgi methanation	Commercial plant (in operation)
DemoSNG (EU project)	Biomass	Köping (Sweden)	50 kW bio-methane output	KIT (honeycomb) (Research institute)	Pilot plant (not in operation)
CPI project (CPI Xingjiang Energy Co.)	Coal	Yili City (Xingjiang, China)	6 billion m ³ /a SNG output	TREMP	Commercial plant (in operation)
Keqi project (Datang)	Coal	Chifeng (Inner Mongolia, China)	4 billion m ³ a ⁻¹ SNG output	HICOM	Commercial plant (in operation)
Fuxin project (Datang)	Coal	Fuxin (Liaoning, China)	4 billion m ³ a ⁻¹ SNG output	HICOM	Commercial plant (under construction)
Huineng project (Huineng Coal Electricity Group)	Coal	Ordos (Inner Mongolia, China)	1.6 billion m ³ a ⁻¹ SNG output	TREMP	Commercial plant (in operation)
Xinwen project (Xinwen Mining Group)	Coal	Yili City (Xingjiang, China)	4 billion m ³ a ⁻¹ SNG output	HICOM	Commercial plant (under construction)
Qinghua project (Qinghua Group)	Coal	Yili City (Xingjiang, China)	5.5 billion m ³ a ⁻¹ SNG output	TREMP	Commercial plant (in operation)
POSCO Project (POSCO)	Coal	Gwangyang (South Korea)	0.7 billion m ³ a ⁻¹ SNG output	TREMP	Commercial plant (under construction)
Hashimoto CO ₂ recycling plant (IMR)	Coal	Sendai (Japan)	—	IMR	Pilot plant 1996 (not in operation)
PtG ALPHA plant Bad Hersfeld (ZSW, IWES)	Raw biomass	Bad Hersfeld (Germany)	25 kW power input	Etogas/ZSW	Pilot plant 2012
PtG ALPHA plant Morbach (Juwi AG, ZSW, Etogas, Etogas)	Raw biomass	Morbach (Germany)	25 kW power input	Etogas/ZSW	Pilot plant 2011
PtG ALPHA plant Stuttgart (ZSW, Etogas)	—	Stuttgart (Germany)	25 kW power input	Etogas/ZSW	Pilot plant 2009
PtG test plant Stuttgart (ZSW, IWES, Etogas)	—	Stuttgart (Germany)	250 kW power input	Etogas/ZSW	Pilot plant 2012
PtG test plant Rapperswil (Erdgas Obersee AG, Etogas, HSR)	—	Rapperswil (Switzerland)	25 kW power input	Etogas/ZSW	Pilot plant 2014
E-Gas/PtG BETA plant (ZSW, Audi, Etogas, EWE, IWES)	Biomass	Werlte (Germany)	6300 kW power input	MAN	Commercial operation 2013

^a Data are not available in the original literature.**Table 16**

Different available methanation technologies [470].

Approach	Supplier	Concept	Technology name
CO methanation	Air Liquide (formerly Lurgi)	2 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	Lurgi methanation
CO methanation	Haldor Topsoe	3–4 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	TREMP
CO methanation	Chariant and Foster Wheeler	3 fixed-bed reactors with steam addition and without gas recycle	Vesta
CO methanation	Johnson Matthey (Davy Technologies)	3 adiabatic fixed-bed reactors with gas recycling and intermediate cooling	HICOM
CO methanation	Linde	1 isothermal fixed-bed reactor with internal contorted heat exchanger	Linde isothermal reactor
CO ₂ methanation	Outotec	Staged fixed-bed reactor with intermediate cooling	Outotec methanation
CO ₂ methanation	Etogas	Fixed-bed reactor or plate reactor with steam cooling	Etogas methanation
CO ₂ methanation	MAN	1 isothermal fixed-bed reactor with molten salt cooling	MAN methanation

**Fig. 26.** Schematic of network representing biomass/coal to SNG/bio-methane and power-to-gas conversion pathways.

comprehensive investigations regarding the impact of pressure and temperature on methanation elsewhere [483–485].

A few researchers have also employed supercritical water gasification technology to study bio-methane generation using different biomass feedstocks. Waldner and Vogel [486] investigated bio-methane production via hydrothermal gasification in a laboratory batch-scale reactor using wood as feedstock in the presence of Raney Ni catalyst. High feed concentrations of about 10–30 wt. % were fed at 300–410 °C and elevated pressures (120–340 bar). Around 0.33 g-CH₄ g-feedstock⁻¹ was observed, close to equilibrium yield (0.34 g-CH₄ g-wood⁻¹). The product gas contained 49% CH₄ at 404 °C and 310 bar. They reported that carbon gasification efficiency was dependent upon reaction times. Complete gasification was obtained

with longer reaction time of about 1.5 h. The liquid phase was demonstrated to be colorless, free of tar and residual char (< 2 wt. % of feed C) at supercritical reaction conditions. This work proves the viability of hydrothermal gasification, especially for wet biomass such as MSW, sludge and manure to produce renewable bio-methane.

UK Department of Transport has funded a £5 million bio-methane project which is operated by a consortium including Advanced Plasma Power, National Grid and Progressive Energy [487]. Advanced Plasma Power has developed a pilot plant which successfully generates CH₄ employing wastes from the homes in Swindon as the feedstock. The pilot plant gasifies RDF which is produced from the mixed household waste, to generate a synthesis gas. This gas is cleaned in an elevated temperature plasma furnace to crack tars and other contaminants, followed by a series of catalyzed reactions to generate CH₄. The first production of methane was achieved in August 2016. This project clearly reflects the technical, commercial and environmental viability and advantages of natural gas generation from the waste.

The Goteborg Biomass Gasification (GoBiGas) project (Table 15) is an exemplary example of bio-methane generation via BG-derived syngas [488]. This project was executed by Goteborg Energi, funded by the Swedish Energy Agency and recognized by the European Commission. The project employs forestry wastes as a raw material to produce syngas via gasification, followed by syngas purification and upgrading to bio-methane in a methanation plant. The quality of bio-methane generated is equivalent to NG and, therefore, both are mixed and fed into the same grid. It is developed in two stages – the first stage which comprises the gasification plant to generate 20 MW gas has been operational since 2013, while the second stage (80–100 MW gas) will be in operation in 2016. By 2020, the project forecasts to deliver bio-methane equivalent to 1 TWh (fuel for ~100,000 cars). Such projects are crucial for the technology development and should be strongly promoted as they generate useful renewable energy without causing any adverse impact on the environment via carbon emissions.

7.2. Catalysts and reactors

7.2.1. Catalysts

Catalysts play an important role in syngas conversion to bio-methane and have a close relationship with reactor design. Reactor design is a function of type of catalysts, their activity and selectivity. They also have a direct impact on upstream and downstream processes. Typically employed catalysts contain active metal, support and promoters. Nickel was the first catalyst employed by the inventors of methanation [473]. Now, even 100 years later, due to its high activity and selectivity coupled with low cost, this is the first choice for commercial-scale bio-methane generation. Ru is the most active catalyst for methanation but is seldom employed for large-scale applications on account of its very high cost (almost 120 times that of Ni) [489,490]. Co, Fe and Mo are other methanation catalysts [439,491–494].

Supports for active metals are also important components to evaluate while choosing a catalyst. They positively affect the activity and selectivity of the process to a considerable extent [481]. Metal oxides with large surface area such as Al₂O₃, SiO₂, TiO₂, etc., form the primary choices for supports [495]. Among these γ -modified Al₂O₃ is mostly employed. Sometimes, a further improvement to supported catalyst is achieved with the aid of promoters. Promoters enhance the characteristics and catalytic performance; e.g., thermal stability and carbon resistance in Ni/Al₂O₃ is increased with the addition of MgO [496]. Ni dispersion and H₂ uptake are increased in Ni/Al₂O₃ by La₂O₃ leading to better activity [497]. The surface morphology of Mo catalysts is improved resulting in the enhancement of S resistance, by adding Co promoters [498].

Catalysts are subject to deactivation due to chemical (catalyst poisoning, formation of Ni carbonyls) [499,500], mechanical (fouling, attrition, crushing) [485,501] and/or thermal (thermal degradation) [501] mechanisms. The presence of contaminants such as sulphur in syngas leads to its chemisorption in catalytic sites and results in poisoning. Ni undergoes vapour-solid interactions with its support or promoters and can form carbonyls below 230 °C in the presence of CO. Catalyst particles also break down due to thermal and/or mechanical stress and lose activity. Moreover, fouling can also be a key reason for catalyst deactivation in which coke or tars are deposited over the Ni surface and render it inactive. These issues can be tackled by employing stringent syngas cleaning and processing. In addition, regulating operational variables such as temperature and pressure can also be beneficial in combating catalyst deactivation.

7.2.2. Reactors

The availability of BG-derived syngas fluctuates on account of the variation in the obtainable biomass feedstock. This calls for continuous optimization of the existing bio-methane production approaches via temperature control, process flexibility and cost effectiveness. R&D work is going on worldwide to achieve these objectives by upgrading the designs of conventional reactors as well as developing new reactor technologies. Bio-methane reactors can be classified as FXB, FB and three-phase reactors [470]. They can also be categorized as adiabatic, isothermal and polytropic reactors, based on their temperature profile.

7.2.2.1. Fixed bed reactors. FXB reactors are the oldest reactor type to be employed for bio-methane generation. Much research has been conducted to upgrade their design in order to achieve better temperature control and process flexibility. Proper temperature control results in high quality bio-methane production. Moreover, it also reduces the requirement for process equipment such as recycle compressors and heat exchangers, which lead to cost-effective production of bio-methane [502]. Investigations are being carried out on adiabatic or polytropic FXB reactors. Temperature hot-spots in beds, high exit temperatures and sharp pressure drops are major limitations associated with these reactor types [470]. In order to overcome these drawbacks, structured reactors (e.g., honeycomb reactor) with modified internal structures have been developed. They have improved heat transfer with reduced pressure drop [503–506].

The micro-reactor is an advanced version of structured reactors with high surface-to-volume ratio, which offers better temperature control. However, placing catalyst on the metallic bed and replacing it on deactivation is tedious [504]. The sorption-enhanced reactor is also one of the improved versions of structured reactors. The thermodynamic restriction of carbon oxide conversion to bio-methane is reduced to a significant extent in this type, by the adsorption of H₂O produced during the process through catalyst support [507,508]. The adsorbent is revived by temperature- or pressure-swing approaches, once it is completely loaded with H₂O. Structured reactors follow polytropic temperature profiles. They have the best performance with only moderate hot spots formation as well as enhanced reaction and conversion rates. However, they are the most costly among all available designs.

7.2.2.2. Fluidised bed reactors. Uniform temperature distribution and effective heat removal are key attributes of FB reactors. This is the reason for using a single reactor rather than reactor cascades (as in the case with FXB). These reactors are isothermal in nature which ensures absolute carbon oxide conversion to bio-methane [470]. However, limited reaction rate and fluidisation of catalysts are key drawbacks. These lead to catalyst attrition and mechanical stress on the walls, which in turn result in shorter reactor life. Several investigations [509,510] are on-going to develop novel catalysts to alleviate this problem. FB reactors are being examined by many research

groups and industries to investigate methanation from BG-derived syngas [485,511]. A power-to-gas demonstration facility employing FB for gasification and bio-methane generation is being commissioned by Engie Gas Company, France [470].

7.2.2.3. Three - phase reactors. The three-phase reactor concept is a type of isothermal reactor with improved reactor temperature control due to its liquid phase with high heat capacity [480]. Also, during high load variations, it can be maintained at isothermal process conditions. It is a modern design with enhanced performance; however, decomposition of heat transfer liquid and additional gas-liquid mass transfer make the operation costly. Researchers are studying the hydrodynamics of the reactor to improve heat transfer fluid stability and to develop specific catalysts [470,512,513].

7.3. Thermodynamic modelling

Equilibrium modelling for bio-methane generation plants is carried out to achieve diverse objectives such as concept comparison, process and heat integration, efficiency evaluation and data collection for economic and ecological assessments. It has proved to be a trustworthy and powerful engineering tool to evaluate vital parameters in a short time with great precision and low cost. Table 17 summarises some important equilibrium modelling investigations for biomass-to-bio-methane production.

Molino and co-authors [517] developed an equilibrium model for bio-methane generation via BG employing different configurations. They reported CH_4 yield of $0.4 \text{ Nm}^3 \text{ Nm}^{-3}$ -syngas with a purity of 65 vol. % and calorific value of 23 MJ Nm^{-3} in single-stage methanation. Inserting a WGS reactor prior to the methanation reactor improved the purity and heat content to 80 vol. % and 26 MJ Nm^{-3} , respectively. This simulation study was carried out using a local biomass, with isothermal conditions for bio-methane production. They proposed the use of an isothermal reactor to enhance process performance; however, its management is more difficult than a conventional adiabatic reactor. It can be inferred from the study that by employing an isothermal configuration for bio-methane generation it is possible to improve the performance and this can be a promising substitute for conventional configurations. However, demonstration plants are required to evaluate the viability of the proposal.

Municipal solid waste generation is inevitable in every civilized society in the world. Therefore, its proper and efficient treatment is indispensable. Various research studies are on-going worldwide to utilize MSW to generate usable fuel/power. Gasification of biomass has turned out to be one of the feasible pathways. Zhu et al. [528]

modelled green bio-methane production via MSW gasification employing different MSW compositions. The impact of operational variables such as ER, steam-to-MSW ratio and methanation pressure on process efficiencies and bio-methane quality were also evaluated. They used paper, wood, textiles and kitchen wastes and found the best results for textile feedstock with a gas yield of $0.406 \text{ Nm}^3 \text{ kg}^{-1}$ and energy conversion of 82%. It was noted that the high volatile content in textiles is able to produce more light gases during reactions. Generated gas contained around 88% bio-methane (average) with a lower heating value of 32 MJ m^{-3} . Carbon conversion, energy conversion and overall efficiencies were reported as around 19%, 39% and 28%, respectively. Moreover, an increase in ER and steam-to-MSW ratio leads to a decrease in bio-methane yield whereas increase in methanation pressure enhances CH_4 concentrations.

A detailed second law analysis of biomass-to-bio-methane generation via wood gasification was carried out by Juraic and co-workers [515]. They performed an exergetic evaluation to assess process performance vis-à-vis conditions in the gasifier and methanation reactors. The system comprised a gasification reactor, gas processing unit, compressor, methanation reactors and bio-methane processing unit. The gasifier, followed by the methanation reactors, were found to be the sources of maximum internal exergy losses. The gasifier was operated at 700°C with a variable pressure from 1 to 15 bar. It was reported that an increase in gasifier pressure enhanced exergetic efficiency whereas increased temperature of the methanation reactors increased irreversibilities. They found a maximum exergetic efficiency of 72.6% with optimum operating conditions (gasifier temperature = 700°C , pressure = 1 bar, first methanation reactor temperature = 580°C , second methanation reactor temperature = 405°C). This kind of study is helpful to examine technical challenges and analyse the economics of the whole system.

8. Bio-hydrogen (H_2)

Considering its avoidance of point source CO_2 emissions, hydrogen is the most promising energy carrier among all the existing fuels. It finds its key applications in fuel cells as well as in the synthesis of numerous useful chemical feedstocks such as MeOH, EtOH, etc., and may find future applications in decarbonisation of heat and industry. A large number of research investigations are proceeding worldwide to use H_2 as an automotive fuel. It has the highest energy density (LHV $\sim 120 \text{ MJ kg}^{-1}$) among all conventional fuels, which is almost 3 times that of gasoline and, therefore, could offer a promising substitute for gasoline as transportation fuel provided storage issues are resolved [529]. Furthermore, there are no toxic emissions from H_2

Table 17
Significant modelling studies for biomass-to-bio-methane.

Authors	Objective	Methanation reactor	Software used
Kohl et al. [514]	Process assessment: efficiency	OD, – ^a , equilibrium	Aspen Plus and MS Excel
Juraic et al. [515]	Process assessment: exergy	OD, – ^a , equilibrium	Aspen Plus
Feng et al. [516]	Concept comparison: efficiency	OD, fluidised-bed, equilibrium	Aspen Plus
Molino et al. [517]	Process optimization: process integration	OD, – ^a , equilibrium	– ^b
Zhu et al. [518]	Process optimization and concept comparison	OD, fluidised-bed, equilibrium	Aspen Plus
Wang et al. [519]	Process assessment and optimization	OD, – ^a , equilibrium	Matlab Simulink
Zwart et al. [502]	Concept comparison: efficiency, costs	OD, fixed-bed, equilibrium	Aspen Plus
van der Meijden et al. [520]	Concept comparison: efficiency	OD, fixed-bed, equilibrium	Aspen Plus
Tremel et al. [521]	Process optimization: process integration	OD, fluidised-bed, equilibrium	Aspen Plus
Swedish Gas Centre [470]	Concept comparison: efficiency	OD, fixed-bed, equilibrium	Aspen Plus
Ronsch et al. [522]	Concept comparison: efficiency, costs, GHG emissions	OD, fluidised-bed, equilibrium	Matlab Simulink
Ronsch et al. [523]	Concept comparison: efficiency	OD, fixed-bed, equilibrium	Aspen Plus
Rehling et al. [524]	Process optimization: heat integration	OD, fluidised-bed, equilibrium	IPSEPro
Nagumo et al. [525]	Process optimization: process integration	OD, – ^a , equilibrium	Aspen Plus
Heyne et al. [526]	Process optimization and concept comparison	OD, fixed-bed, equilibrium	Aspen Plus
Fendt et al. [527]	Concept comparison: efficiency, costs	OD, – ^a , equilibrium	Aspen Plus

^a Type of the reactor was not mentioned in the original literature.

^b software used was not mentioned in the original literature.

combustion unlike gasoline and diesel. In addition, hydrogen can be stored in different forms such as in gas phase, liquid phase or as metal hydrides, albeit given its low density H_2 storage is an issue. However, most of the H_2 generation pathways are expensive with low efficiencies on account of immature technologies [530].

Hydrogen can be generated either via a thermochemical or biological pathway. These routes may employ biomass, fossil fuels and/or water as the raw material, with the application of thermal, electrical or photonic energy [531]. A brief analysis of all the H_2 production technologies along with normalized energy and exergy efficiencies, advantages and limitations is summarised in Table 19. Energy efficiency is given by the ratio of the heating value of syngas to the heating value of feedstock. On the other hand, exergetic efficiency is the ratio of physical and chemical exergy of syngas to the chemical exergy of biomass raw material and is based on the second law of thermodynamics. Among all the prevalent routes, steam methane reforming is most widely used and is responsible for around 50% of worldwide H_2 production, followed by oil reforming (30%) [532]. The major drawback with these methods is significant GHG emissions resulting in adverse environmental change. One of the solutions can be green H_2 (or bio-hydrogen) generation via thermochemical processes such as combustion, pyrolysis and gasification of renewable and abundantly available biomass. It can be seen from Table 18 that among all the H_2 production pathways BG has the highest exergetic efficiency of 60% [531]. A discussion about

different gasification routes employing biomass can be found in the subsequent section.

8.1. H_2 generation pathways via gasification

Bio-hydrogen can be generated by steam reforming of char produced during fast pyrolysis of biomass. It can also be produced via supercritical water gasification; however, this approach is mainly employed for wet biomass. Conventional gasification of biomass employing steam or oxygen as gasifying agents is the commonly applied method to generate H_2 . Both gasifying agents result in a product gas with around 40% H_2 content under normal operating conditions; however, steam is preferred over O_2 for generating H_2 in a gasifier on account of reasons such as (1) higher reactor temperature in case of O_2 (1000–1400 °C) as compared to steam (700–1200 °C) and (2) oxygen-blown gasification is costlier than steam-blown BG [539].

8.1.1. Steam gasification of fast pyrolysis-derived char

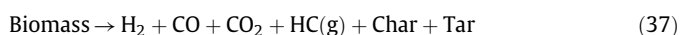
Pyrolysis is the thermochemical conversion of biomass into usable fuels or chemical feedstocks. It takes place in the absence of O_2 . However, some amount of O_2 is provided for partial combustion in cases where heat is required for the process [540]. Biomass conversion via pyrolysis in the absence of O_2 is depicted in its simplest form in Eq. (37). It mainly produces liquid products with a low

Table 18
Analysis of different hydrogen generation pathways [93,530,531,533–539].

Technology	Energy η (Normalized)	Exergy η (Normalized)	Scale	Major advantages	Limitations
Autothermal reforming	8.3	4.6	Large/currently available	Proven technology, lower capital costs	CO_2 by-product, limited methane supply, less efficient than SMR
Biomass gasification	6.5	6	Mid-size/currently available	Renewable, indigenous	Seasonal availability, operational difficulties, transportation problems, varying H_2 content
Biological	1.4	1.3	Under research	Renewable, alternate source	Low efficiency, high capital cost
Biomass pyrolysis	5.6	4.5	Mid-size/currently available	Renewable, indigenous	Seasonal availability, operational difficulties, transportation problems, varying H_2 content
Bio-photolysis of water by algae	0.9	0.8	Under research	Renewable, sustainable, CO_2 consumed	Strong inhibition effect of generated oxygen on hydrogenase enzyme, low H_2 production, no waste utilization
Coal gasification	6.3	4.6	Large/currently available	Established, cost-efficient	CO_2 by-product, low quality hydrogen
Dark fermentative hydrogen production	1.3	1.1	Under research	Renewable, simultaneous waste treatment and generation of H_2	Low energy conversion efficiency
Electrolysis	5.3	2.5	Small/currently available	Proven technology, emission free	Low overall efficiency, high cost
Photo fermentative hydrogen production	1.5	1.4	Under research	High theoretical conversion yield, absence of oxygen which reduces the potential for inhibition (Biological processes for Hydrogen Production from Biomass)	Uses nitrogenase enzyme with high-energy demand, low solar energy conversion efficiency, accommodates large areas for the anaerobic photo bioreactors
Photocatalytic	0.2	0.1	Under research	Renewable, alternate source	Pricy, low efficiency
Partial oxidation	8.3	4.6	Large/available	Established, cost-effective	CO_2 by-product, lower efficiency than SMR, global warming
Steam methane reforming (SMR)	8.3	4.6	Large/currently available	Proven technology, high efficiency, economical	CO_2 by-product, limited methane supply, global warming, dependence of fossil fuel
Ideal process	10.0	10.0	Hypothetical	Zero emission, low cost, 100% efficiency	— ^a

^a Not mentioned in the original literature.

amount of gases. The yield of gaseous products (especially H_2) can be maximized by employing elevated temperature, high heating rate and longer residence time [541].



Bio-oil is a thick viscous liquid containing more than 350 compounds and is obtained as the key product of biomass fast pyrolysis, along with char [25]. The produced char is highly reactive in nature and can be employed to generate H_2 via steam gasification. Product gas generated is a function of char composition and operating variables. A few researchers [539] have performed experimental studies on char and lignin gasification to evaluate H_2 and other bitumen gas yields. Steam was used as the gasifying medium with a flow rate of $10 \text{ g h}^{-1} \text{ g-feedstock}^{-1}$, in a FXB in a temperature range of 600–800 °C. The range of bio-hydrogen yield was reported to be 30–50%. It was an important study to reveal the potential of H_2 recovery from pyrolysis-derived char.

8.1.2. Supercritical water gasification (SCWG)

Supercritical water with co-existing gas and liquid phases can serve as a reactive species employed for the treatment of high-moisture biomass such as sewage and other kinds of sludge, MSW, etc. In the supercritical state (374 °C, 220 bar), it has enhanced transport and solubilisation properties [542]. It behaves as a homogeneous non-polar solvent with exceptional diffusivity and transport characteristics with an ability to dissolve any organic compound [539].

When BG takes place in supercritical water, it acts as an oxidant. Oxygen atoms from supercritical water interact with C atoms of biomass to generate CO, which in turn reacts with steam to produce H_2 and CO_2 via WGS [93]. In terms of H_2 production efficiency, this pathway is a better choice. However, it is more suitable for wet biomass because water present in the wet biomass is not a liability as it is in thermal gasification. On the other hand, this water acts as a reaction medium and a reactant. However, the cost of H_2 production via this route is many times higher than the conventional method of steam methane reforming due to a high energy penalty. Therefore, R&D is still in progress to reduce the cost by recovering energy, prior to scaling up.

8.1.3. Steam gasification of biomass

As discussed earlier, BG is a thermochemical process to convert biomass into a mixture of gases, predominantly CO and H_2 in the presence of air, O_2 or steam. It employs a complex network of reactions with overlapping steps of drying, pyrolysis and partial oxidation. H_2 is the dominant fraction among other gases in the product gas when steam is employed as gasifying agent [25]. This method is considered an efficient route to generate green H_2 without leaving

any carbon footprint [543]. This pathway reduces the limitations of other thermochemical methods to a great extent such as high energy consumption and low H_2 yield [540]. In addition, it generates lower amounts of tars and char as WGS converts them to product gas, thereby enhancing H_2 yields. The key reactions to produce H_2 via steam BG are shown in Table 3.

The fraction of H_2 in the product gas is a function of a number of variables such as biomass feedstock, operating temperature and pressure, S/B ratio, catalyst and sorbent-to-biomass ratio (in the case of sorption-enhanced gasification) [536]. They all have a direct impact on H_2 yield and, therefore, must be taken into account. The influence of various process parameters on H_2 yield during steam BG is depicted in Table 19.

A few researchers [544] have also employed co-gasification of biomass feedstock and coal to evaluate the viability of the process along with the H_2 yields. They carried out experimental investigations using bagasse and coal in a FB gasifier. It was reported that tar and gaseous HC yields were a function of bagasse amount and encountered the formation of increasing tars and HCs by enhancing air flow rate and operating temperature. Maximum H_2 yield of 45% (in total product gas composition) was found at a bed temperature of 885 °C. It should be noted that addition of coal to the feedstock increases S content in the syngas.

Garcia-Labiano and co-authors [545] have evaluated the possibility of employing bio-EtOH as fuel in a chemical looping reforming (CLR) process to generate H_2 with negative CO_2 emissions. They performed experimental investigations in a continuous CLR unit (1 kW_{th}) for more than 50 h in the presence of two different NiO-based oxygen carriers. Hydrogen-rich syngas (61 vol. %) with 32 vol. % CO was obtained in the fuel reactor and pure N_2 was released via the air reactor. The composition of syngas was close to equilibrium values. They reported complete conversion of the fuel coupled with no carbon formation. This study reflects the potential for producing H_2 employing renewable fuel, with an added advantage of negative carbon emissions.

8.2. Thermodynamics of H_2 production

Many thermodynamic modelling studies for BG-coupled H_2 production systems have been carried out either to optimize the system or to evaluate the feasibility of a new system. El-Emam and Dincer [178] developed a model of BG integrated with a SOFC to examine the parametric impact. An atmospheric BFB gasifier was employed to produce H_2 -rich syngas with steam as the gasifying medium, and the generated H_2 was fed to the SOFC to generate power. S/B ratio has a direct influence while operating temperature was found to have an adverse impact on gasification performance. The optimum S/B ratio was found to be 0.677. The authors also reported that SOFC

Table 19
Impact of operating variables on bio-hydrogen yield in biomass gasification [93].

Operating variables	Description	Impact
Biomass types	Different plant species wastes	Product composition largely depends on inherent nature of parent biomass
Particle dimension	Biomass feed particles dimension	Feed size influences heat and mass transfer conditions which in turn influences product constituents and composition
Operating temperature	Gasifier temperature is considered after pyrolysis zone	Low temperatures favour char yield and methane production. Optimal temperatures for hydrogen generation 800–900 °C
Operating pressure	Gasification occurs at constant pressure in the gasifier	Chemical equilibrium indicates that gasification is favoured by low pressures and high temperatures. However, no substantial gain is obtained if the process runs in vacuum.
Catalyst	Small quantity of materials added to the process to speed up the reaction rate	No catalyst: less gas yield and more tar formation
Steam-biomass ratio	Mass of steam/mass of biomass	Low S/B – methane and char; high S/B – syngas
Sorbent-to-biomass ratio	Materials of small amount added to adsorb CO_2 developed during the process	Removal of CO_2 increases syngas yield

fuel utilization has more impact than recirculation ratio, on fuel cell performance. This study reflects the promising nature of the BG-coupled SOFC system for renewable power generation.

Beheshti et al. [546] developed an equilibrium model for a proton exchange membrane fuel cell (PEMFC) coupled with BG. Bio-hydrogen derived from gasification was used as a fuel for the PEMFC. An Aspen Plus simulator and FORTRAN subroutines were employed to simulate the steady state behavior of the entire system. Significant operating variables such as ER, S/B, feedstock moisture, feed gas humidity and current density were investigated vis-à-vis cold gas efficiency and fuel cell potential. Gasification efficiency was reported as 75.85% and cell potential as 752.8 mV keeping optimum values (ER = 0.49, S/B = 0.5, moisture = 5% and feedstock size = 2 mm) for the studied variables. It was demonstrated that feed humidity has a direct influence whereas feedstock moisture has an adverse impact on output voltage. It can be inferred from the study that it is viable to integrate PEMFC with BG and has a potential to generate high voltages provided optimum operating conditions are maintained.

Iribarren and co-authors [547] performed exergetic and LCA analyses for H₂ generation via BG. Poplar was used as the feedstock in a low-pressure indirect gasifier. Catalytic tar cracking, cold gas clean up, syngas conversion and H₂ purification were taken as sub-systems along with gasification. The maximum exergetic efficiency was found to be 48% which is equivalent to H₂ production via coal gasification. In life cycle assessment, the authors considered the steps from poplar cultivation to H₂ purification. Cumulative energy demand, global warming, ozone layer degradation, photochemical oxidant formation, land competition, acidification and eutrophication were taken as impact variables. Poplar cultivation, biomass pretreatment and syngas clean-up were found to have maximum environmental impact. Reduction in poplar demand, improvement in logistics to supply biomass feedstock, reduction in natural gas demand for steam reforming and low consumption of fertilizers were suggested as the solution. These equilibrium studies along with cradle-to-grave LCA investigation give a clear and more realistic picture of renewable H₂ generation, and enable scientists to work on a more practical basis.

Cohce et al. [548] designed an equilibrium model comprising BG followed by steam methane reforming and WGS. They used the Gibbs free energy minimization approach with chemical equilibrium considerations. Oil palm shell material was employed as biomass feedstock to produce H₂. They found energy and exergy efficiencies of 22 and 19%, respectively. The cold gas efficiency was reported to be 18%. They demonstrated a higher H₂ production rate with this system (3700 kg h⁻¹ H₂ from 88,400 kg h⁻¹ oil palm shell) than from the conventional system (17 kg h⁻¹ H₂ from 900 kg h⁻¹ dry bagasse).

Wang and co-authors [549] have employed a distinctive approach to develop a thermodynamic model for co-gasification of biomass and coal to generate H₂ over CaCO₃ catalyst. They divided single FB gasification into two steps, namely, combustion and gasification. The combustion model was generated to evaluate the residual char, whereas the gasification model was developed to examine H₂ yield vis-à-vis CaO catalyst. Parameters such as gasifier temperature, coal-to-biomass ratio, steam-to-coke ratio and calcium-to-coke ratio were found to have a profound influence on H₂ yield. Maximum H₂ yield was reported to be 60% at 800–850 °C. Optimum values for coal-to-biomass ratio, steam-to-coke ratio and calcium-to-coke ratio were suggested as 0.25, 1.8 and 0.5, respectively.

8.3. H₂ as an automotive propellant

Green H₂ generated from a renewable energy source such as biomass has the potential to replace fossil fuels as transportation fuel. It will reduce GHG and other toxic gaseous emissions to a significant extent. Research on H₂ as an automotive fuel has been on-going for almost half a century. It has long been investigated as primary fuel

and also as an additive (supplemental fuel) for gasoline engines. Its ability to extend the combustibility range of the fuel-air mixture, enhance engine efficiency and reduce toxic emissions makes it an attractive option as an automotive propellant [529]. Furthermore, it has the highest energy-mass coefficient among all existing conventional fuels.

Flame travels at a faster speed (2.65–3.25 m s⁻¹) inside the cylinder when H₂ is employed as fuel in an IC engine [550,551]. Flame velocity is a function of the temperature of the H₂-air mixture and increases with temperature. This high velocity coupled with low activation energy of H₂ and wide range of combustibility, results in uncontrolled combustion with sudden rise in pressure inside the cylinder. Consequently, the phenomenon of knocking occurs on account of shock wave generation leading to enhancement in heat discharge to the cylinder walls and an upsurge in mechanical losses [529]. These problems are not found in the case of gasoline-air mixture combustion, to such an extent. Table 20 compares physical and chemical properties of gasoline and H₂.

A blend of H₂ and air is more homogeneous than a mixture of gasoline-air resulting in reduced cyclic fluctuations [529]. In addition, it also ensures uniform distribution of H₂-air in the cylinder. The wide range of combustibility allows 4 to 75% of H₂ presence in the air-fuel ratio (0.13 to 10.2). This eliminates the need of regulating the mixture qualitatively as in the case with diesel, leading to removal of the throttle valve and finally significant reduction in mechanical losses [529]. Furthermore, employing only H₂ eradicates soot, HCs, CO, SO_x and NO_x formations in the emissions.

At stoichiometry, due to the low density of H₂, it occupies 30% of the cylinder volume whereas gasoline occupies only 2–4%. This means that for equal energy, a storage tank for H₂ is almost 30 times in mass and 24 times in volume as compared to gasoline. Consequently, when pure H₂ is employed as automotive fuel, a reduction in engine horse power occurs of 20–25% [553]. Furthermore, work done by a unit volume of H₂ mixture is around 910 kJ m⁻³ while it is 1320 kJ m⁻³ for gasoline. If H₂ is directly fed into the engine cylinder, heat released is 20% more [554]. Therefore, the power factor of the engine is a function of how H₂ is introduced into the cylinder. High reaction ability of H₂ can cause backfiring [529]. Moreover, its low ignition energy causes the appearance of flame in the carburettor. However, such problems can be minimized to a considerable extent by employing a lean mixture or H₂O injection into cylinders.

It is noted that liquid H₂ has a poor heat of combustion of around 25% that of gasoline [529]. It also requires high thermal insulation. The storage of gaseous H₂ is a major challenge as it requires large

Table 20
Comparison of the properties of hydrogen and gasoline [552].

Property	Hydrogen	Gasoline (H/C = 1.87)
Molecular weight (g mol ⁻¹)	2.016	~110
Mass density (kg Nm ⁻³) at P = 0.101 MPa, T = 0 °C	0.09	720–780 (liquid)
Mass density of liquid H ₂ at -253 °C (kg Nm ⁻³)	70.9	— ^a
Boiling point (°C)	–253	57–205
Higher heating value (MJ kg ⁻¹) (assumes water is produced)	142.0	47.3
Lower heating value (MJ kg ⁻¹) (assumes steam is produced)	120.0	44.0
Flammability limits (vol. %)	4.0–75.0	1.0–7.6
Detonability limits (vol. %)	18.3–59.0	1.1–3.3
Diffusion velocity in air (ms ⁻¹)	2.0	0.17
Ignition energy (MJ)		
–At stoichiometric mixture	0.02	0.24
–At lower flammability limit	10	n/a
Flame velocity in air (cms ⁻¹)	265–325	37–43
Toxicity	Nontoxic	Toxic above 50 ppm

^a Not mentioned in the original literature.

volumes and is susceptible to loss via evaporation [550], thus making it a poor choice to be employed as primary transportation fuels. However, H_2 is an excellent blending agent. If added to a blend of air and gasoline in some amounts (5–10%), it improves all vital factors in the engine and reduces liquid fuel consumption by 30–40% [551]. In addition, toxicity of the emissions is significantly reduced. H_2 can also be employed as an intermediate to propel vehicles. Currently, several studies are in progress to develop H_2 -driven fuel cells, which in turn would run vehicles. Thus for instance, Toyota Motor Corporation is about to launch the first fuel cell vehicle (FCV) called Mirai, in the market [555]. Development in fuel cell technology and H_2 storage methods can enable successful deployment of H_2 as transportation fuel. It can potentially bring about a revolutionary reduction in fossil fuel usage and favourable alteration in climate change.

9. Algae-derived biofuels

Algae are unicellular (micro-algae) or multicellular (macro-algae) photosynthetic organisms capable of converting sunlight, CO_2 and H_2O to significant amounts of lipids, proteins, carbohydrates and other bioactive species, in a short duration [556,557]. They are found in fresh and salty water and possess an enormous potential for conversion into usable fuels. They are one of the potentially attractive options to generate renewable and sustainable biofuels, also known as third generation biofuels. They have numerous benefits such as the capability to fix large amounts of CO_2 (1 kg of micro-algae synthesis takes 1.8 kg of CO_2) [558,559], ability to grow in any environment (sea/fresh water, on land) [560], very high growth rate (a doubling rate of 24 h) [47,559], and versatile usage (food, animal feed, fertilizer, waste H_2O treatment).

Conversion of algal biomass to a wide spectrum of biofuels such as EtOH, H_2 , diesel and biogas is possible via biochemical and thermochemical routes. Thermochemical routes are considered better than the former on account of short reaction times, high conversion efficiencies and comparatively low costs [47,561]. All the possible algae-to-fuel and -power conversion processes are depicted in Fig. 27. In the gasification approach to thermochemical processing, algal biomass is typically heated with O_2 , air or steam in deficient conditions (or in the absence of air/ O_2) to generate syngas. This product gas can be directly utilized as fuel for boilers or can be employed as raw material for MeOH or DME production. Direct combustion, liquefaction (hydrothermal processing) and pyrolysis are alternative thermochemical methods to convert algae into usable fuels, power and electricity [556]. A significant number of investigations to exploit unicellular and multicellular algae are reported in the literature. Biofuels generation from macroalgae via liquefaction

[562] and pyrolysis [47,563], and from microalgae via liquefaction [564–566], pyrolysis [6,567–569] and gasification [564,570–572] have all received significant attention.

Gasification process chemistry employing micro-algal biomass has already been discussed in Section 3.1.1. BG is best suited for feedstock up to 15% moisture content [573]; however, researchers have used algae with high moisture content (~40%) as raw material for BG [47]. This has an adverse effect on gasifier performance and calorific content of the product gas. The heat content of product gas with 5 to 30% moisture ranges from 3.45 to 5.9 $MJ\ kg^{-1}$ [194]. The various steps involved in micro-algae gasification are shown in Fig. 28.

Hirano and co-authors [574] investigated gasification of *Spirulina* at different temperatures (850, 950 and 1000 °C) in the presence of O_2 . Algae slurry was fed at a rate of 0.25 $g\ min^{-1}$ and O_2 at 0.39 $mL\ min^{-1}$. The syngas generated was composed of CO , H_2 , CH_4 and CO_2 with traces of O_2 , N_2 and C_2H_4 . An increase in temperature enhanced the H_2 fraction at the cost of CO , CO_2 and CH_4 . It was reported that elevating the temperature from 850 to 1000 °C increased the carbon conversion efficiency from 93 to 100%. It should be noted that the gasifier temperature has a key impact on product gas composition as well as on carbon conversion.

Numerous researchers have employed fresh water micro-algae *Chlorella* as the feedstock for gasification studies. Minowa et al. [571] investigated *C. Vulgaris* gasification over Ni catalyst in a N_2 cycling

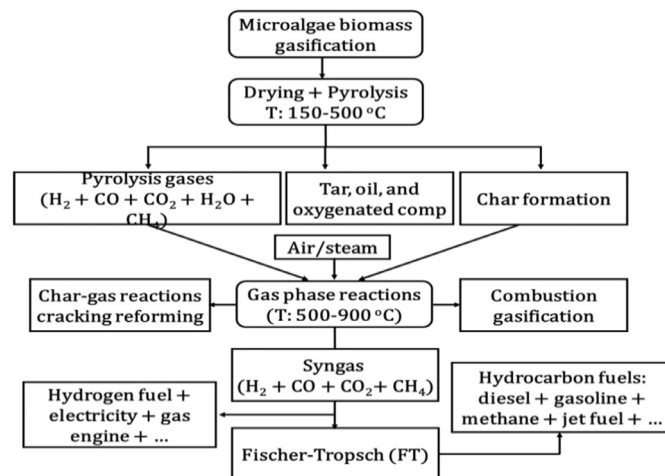


Fig. 28. Algal gasification (step-wise) to produce biofuels and power [47].

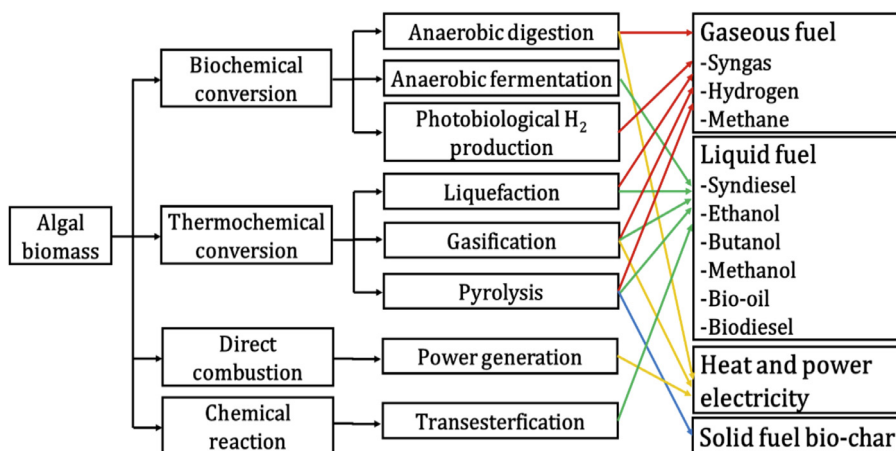


Fig. 27. Possible pathways for algal biomass conversion to usable fuels and power [47].

system at 350 °C to produce CH₄. Higher catalyst amounts resulted in higher CH₄ and lower H₂ concentrations. Moreover, the carbon conversion efficiency and product gas yield were found to increase on account of catalyst loading. An important observation was the conversion of N present in the feedstock to NH₃, which can further be transformed to premium quality fertilizer.

As algal biomass contains a high amount of moisture, it forms an appropriate feedstock material for SCWG. Chakinala and co-workers [570] examined *C. Vulgaris* as raw material for catalytic and non-catalytic SCWG using different catalysts. They found that the use of Ni catalyst at relatively high loadings results in H₂-rich gas on account of improved WGS activity. The gasification efficiency was reported to improve (~84%) at 600 °C with 2 min residence time. The authors also employed excess Ru/TiO₂ catalyst and obtained 100% gasification of the biomass at 700 °C. The investigation proved the significance of elevated process temperatures, lean algae slurry and longer residence times in optimizing gasification to achieve maximum efficiency.

An important investigation using *S. Platensis* was carried out by Stucki and co-authors [572]. They cultivated the algae using CO₂ emissions from fossil fuels followed by their transformation to usable fuels via SCWG with absolute mineralization of nutrient-bearing organics. They obtained a CH₄-rich syngas over Ru catalyst and concentrated CO₂ for storage. Around 60–70% of the calorific content in the algal biomass was recovered as CH₄. Carbon conversion was reported to be 50%. This must be considered to be a key study which explored a viable route for renewable bio-methane generation to counter fossil fuel dependence and climate change, without also competing with food production.

All the investigations prove that catalyst loading and elevated temperatures during algal gasification are vital parameters to enhance H₂ and/or CH₄ yields. Dolomite, Ni and potassium carbonate are typically employed catalysts [123]. Ni-based catalysts are found to decrease tar generation by about 5% in the temperature range of 500–900 °C [575]. The presence of catalysts can increase gasification efficiency by up to 85% [570]. If thermochemical treatment such as gasification of algae is envisaged to occur at scale, then algae need to be cultivated in large amounts to serve as the feedstock. Algae has the potential to remove/degrade organic pollutants in aquatic systems for their own growth apart from generating energy and, therefore, act as a controlling-agent for the pollutants [576,577]. All the investigations reflect the significant potential of algal biomass as a raw material for sustainable biofuels with promising bioremediation capabilities. The high growth rate of algae as compared to all other biomass feedstocks and the avoidance of arable land for its production have the potential to enhance the sustainability of biofuels which in turn can reduce pressure on non-renewable energy sources such as fossil fuels.

The idea of using algae for biofuels is an area which is receiving increasing attention, with over 3900 publications listed in this area by Scopus since the beginning of 2013, and numerous scenarios are being generated for possible applications of biofuel over the next two decades [578]. Currently, algae-based fuels are in the research and development stage and as such they have been classified as third generation fuels in a recent European Union Report [579], with bio-fuels from crops and animal sources being classified as first generation, fuels and lignocellulosic biomass as second generation fuels; moreover it is anticipated that algae-based fuels are likely to need significant innovation if they are to become commercially important [579]. A major concern with one promising development, namely that of genetically modifying algae is the need to keep such a plant clean and free of invasion from natural organisms which is likely to be challenging for large-scale applications [579]. As with biofuels in general, another critical issue is to ensure that the production of algae-based fuels does not compete with agricultural land for food and feed markets, but here algae-based approaches have an obvious

potential advantage. The economics of developing such fuels is also questionable given the high overall potential cost of such fuels, and there is a suggestion that developing them for use in high value processes and applications such as pharmaceuticals might well represent a bridging approach, justifying the expense of developing algae biofuels per se [580].

10. Process design and integration

Biomass has undoubtedly proven itself as a potential renewable energy resource which can meet global energy needs to a significant extent. However, this calls for a suitable biomass-to-energy conversion technology, which in turn necessitates a proper and sustainable process design. Among all the available choices for a given system, not all the options are viable, efficient and cost-effective. Selection of suitable process configurations which result in optimal plant designs is crucial. In addition, decisions regarding production capacity and plant scale are important for efficient and sustainable operation. Prior to installation, a trade-off between large centralized production plants and smaller decentralized plants is required.

Process integration is an all-inclusive approach which considers all the interactions among different steps within a process. The objective is to enhance overall process efficiency by elevated product yields with minimum costs. It is a powerful tool in process design investigations to optimize current processes and develop new processes. Integrating energy streams and process intensification are two commonly employed approaches for process integration [23]. The former is the integration of energy streams within a system, where high-temperature streams with surplus heat provide thermal energy to those with heat deficits, minimizing external heat requirements. The latter is concerned with the design and development of novel technologies to improve chemical processes and aim to operate them closer to fundamental limiting rates. An example is the deployment of advanced process configurations with an aim to reduce equipment volume and decrease energy consumption coupled with an enhancement in production intensity and sustainability.

In this section, the bio-refinery concept is discussed in detail followed by some important process design and integration studies. Moreover, decisive factors related to efficient and economical installation and operation of bio-refineries are elucidated.

10.1. Lignocellulosic biomass-based bio-refinery

A bio-refinery is a facility which integrates conversion processes and equipment to produce biofuels and chemicals employing diverse biomass types. Numerous conversion technologies are combined to produce a variety of products such as transportation fuels and other chemicals from biomass feedstock via gasification and fermentation. Bio-refineries are classified by the nature of the biomass used, e.g., crops such as cereals are employed in crop bio-refineries whereas cellulosic biomass (wood, straw, etc.) is used in a lignocellulosic bio-refinery. A lignocellulosic biomass-based integrated bio-refinery concept is depicted in Fig. 29.

A bio-refinery is analogous to a petroleum refinery where an input feedstock yields diverse usable outputs. However, the difference lies in the input material for the biorefinery due to large variation in biomass properties which necessitates divergence in methods to obtain useful products. Pulp and paper mills can be termed as bio-refineries on account of their ability to produce numerous usable products employing biomass [28,581]. Presently, many research studies are underway to establish large-scale production of multiple products, which are now only obtained by petro-refineries. The basic objective is to generate high-value chemicals as well as high-volume biofuels to cater to energy requirements while ensuring viable process economics.

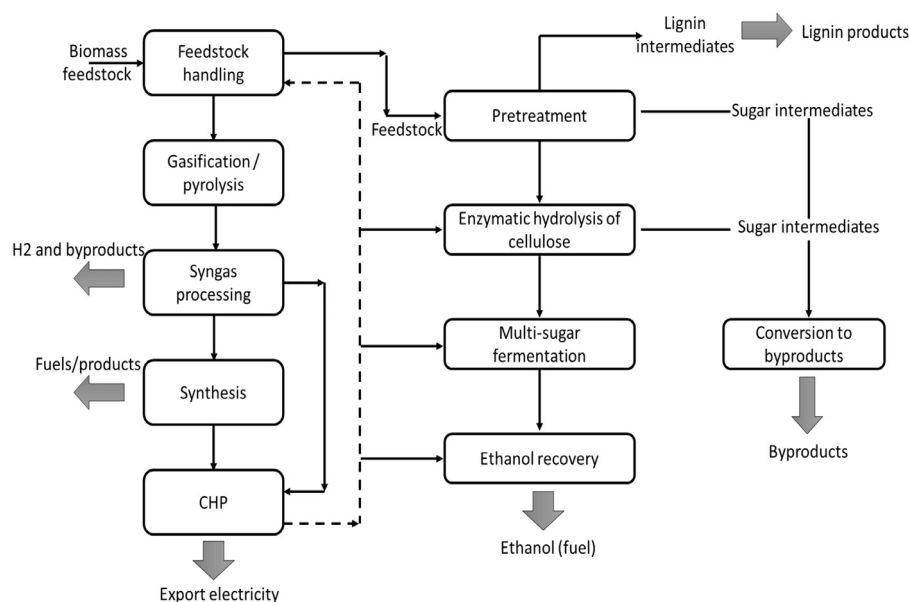


Fig. 29. Schematic of lignocellulosic biomass-based bio-refinery [28].

One of the important challenges for a bio-refinery is to efficiently and economically transform 5- and 6-carbon sugars present in lignocellulosic biomass feedstock into useful products [28]. The thermochemical platform of bio-refineries offers options such as combustion, liquefaction, pyrolysis and gasification to overcome this challenge [582]. They can process the biomass into syngas, chemicals, liquid fuels, heat and electricity. Ample availability coupled with its versatility and renewable nature make biomass a highly promising raw material. However, lower energy density, high fibre, ash (in some feedstocks) and moisture content, and diverse composition are some of the limitations associated with the bio-refinery concept [77]. Installation and successful operation of integrated bio-fuel and renewable chemical production plants establish the potential of non-food crops (lignocellulose) around the globe. Vital technical challenges need to be addressed to reduce the production cost of biomass-based fuels and chemicals from the bio-refinery. Only then can significant switching from petro-derived fuels to biomass-derived fuels take place on a larger scale.

10.2. Some important design and integration investigations

Numerous significant investigations have been performed to design and integrate the biomass-to-biofuels conversion process, with an objective to reduce cost and enhance process efficiency coupled with decreased GHG emissions. Researchers have employed various approaches such as mixed integer linear programming (MILP), mixed integer non-linear programming (MINLP), site-scale approach, fuzzy logic approach, modular optimization approach, etc., to carry out these studies.

Clausen [583] developed a novel design for a gasification-based bio-refinery. Instead of removing CO_2 , H_2 derived via water or steam electrolysis was added to the system. This resulted in almost 96% carbon conversion which in turn doubled biofuels production per unit biomass feedstock input. Two different designs of bio-refineries were made to generate MeOH with integrated H_2O electrolysis for extra H_2 production. Torrefied wood was employed as biomass feedstock in an entrained flow gasifier. In the first design torrefaction was integrated on-site with the gasifier whereas in the second design, torrefaction was done off-site. The biomass-to-MeOH energy ratio was much higher (136%) for the former as compared to the latter (101%). In addition, overall total energy efficiency (MeOH/biomass + net

electricity) was 62% for the integrated torrefaction design while it was 56% for the other. However, more electricity was found to be consumed per unit MeOH produced in the former case. It should be noted that this approach is not highly desirable as H_2 is produced via electrolysis and, therefore, raises the cost of production.

Ng and co-authors [584] synthesised and optimized an integrated bio-refinery employing a fuzzy logic optimization approach. The four parameters under consideration were economic performance, environmental influence, inherent safety and occupational health performance. A palm oil-based bio-refinery was taken as the case study and all four parameters were solved in parallel as they are often incompatible with each other during process synthesis and optimization in a bio-refinery. They reported that despite the inherent contradictory nature of these parameters, they can be optimized via a fuzzy logic scheme to transform biomass into primary or secondary energies. Tay et al. [33] integrated a BG stoichiometric thermodynamic model with the structural models of synthesis processes with an objective to evaluate optimal operational conditions to obtain the maximum amount of syngas with appropriate composition for diverse end-use applications in an integrated bio-refinery. They employed the modular optimization route for the synthesis of a gasification-based bio-refinery with (1) optimum product portfolio and (2) a variety of feedstocks and products. They reported the generation of H_2 -rich syngas with a composition of 42.7 mol. % H_2 and 38.9 mol. % CO for case-I and, 41.6 mol. % H_2 and 39.8 mol. % CO for case-II, on a dry basis. Optimized values of temperature, pressure and S/B were found to be 927 °C, 36.5 bar and, 0.33 (case-I) and 0.36 (case-II), respectively.

Wang et al. [585] developed a MINLP model to optimize a gasification-based HC bio-refinery involving economic and environmental variables and solved it by the ϵ constraint method. All processing steps such as drying, air separation unit (ASU), BG, syngas processing, FT synthesis, hydro-upgrading, power generation and, diesel and gasoline production were taken into account. Superstructures were employed to consider substitute technologies and equipment such as BG routes, H_2 generation sources, cooling options and FT catalysts. The model simultaneously defined technology selection, operational conditions, flow rates of streams, energy required by each sub-system, economic performance, equipment sizes and environmental effects. They reported that gasification at elevated temperatures coupled with direct cooling, inherent H_2 generation and

Co catalyst is the optimal solution for the best economic and environmental performance.

Holmgren and co-authors [347] integrated different steps in a BG-based MeOH production system. They developed and compared energy balances to evaluate the influence of process-integrated drying compared to import of dried biomass as well as the impact on power generation due to heat pump integration or district heating delivery, and influence on MeOH production when H_2 is added, and the effects of adding the MTO process. They reported that the effect of combining the MTO process is very limited. However, when H_2 is added as a replacement for WGS, the production of MeOH is enhanced significantly (by ~35%). Moreover, it was found that heat pumping has a positive impact on power generation by the system. The same authors [586] performed another study where BG-based MeOH generation is integrated with clusters of industries with an objective to examine and reduce life cycle GHG emissions. A rise of 10% in the efficiency was found when H_2 from an industrial cluster was added in the system. Moreover, the presence of a heat sink to use excess heat from the system coupled with technology type has a vital influence on GHG reduction. For example, a rise in GHG emissions was found when the industrial waste heat is placed as a substitute for the system where heat generation technology in the district heating network is natural gas combined cycle CHP and the technology for marginal electricity generation is coal condensing power, whereas GHG advantages are more noticeable when fossil boilers are substituted by industrial excess heat. Furthermore, electricity generation and district heating were also reported to have an important impact on GHG. Damartzis and Zabaniotou [23] developed a fully integrated biomass-to-liquid conversion system where all material and heat streams were combined. Feedstock is fed into an integrated bio-refinery where it undergoes pyrolysis and gasification. Char is obtained as a solid product whereas liquid products are reformed to produce H_2 for further hydro-cracking to FT fuels. Gaseous products undergo processing and are sent for FT synthesis to produce FT fuels. Wax from FT synthesis is hydro-cracked to generate more FT fuels while H_2 from liquid products reforming is fed to the gas processing sub-system. In a nutshell, raw biomass feedstock is transformed to usable second-generation biofuels via FT synthesis, with holistic integration of material and heat streams, as depicted in Fig. 30.

Tock and co-authors [587] have designed a superstructure-based thermo-economic model to generate biofuels from lignocellulose via different pathways, with an objective to examine their effectiveness. Several combinations and technologies were considered for model development. FT generation, MeOH production, DME production via biomass (dried with steam/flue gas) employing directly- or indirectly-heated entrained flow or FB gasifiers, hot or cold gas clean-up and fuel production and upgrading were taken into account. The competitiveness of various process alternatives was evaluated and compared vis-à-vis energy efficiency and economic and environmental performance. Efficiencies for these integrated plants for FT

fuel, MeOH and DME were reported as 59.8%, 52.5% and 53.5%, respectively. This work reflects the potential of process integration enhancing efficiency via waste heat valorisation.

You et al. [588] developed a MILP model for optimal design and planning of EtOH supply chains considering economic, environmental and social variables. Supply dependence on seasons, topographical diversity, feedstock degradation and variety, different conversion pathways and respective by-products, infrastructure compatibility, demand distribution, local economics and governmental incentives were taken into account. After this analysis, an improvement in conversion technology was recommended to commercialize EtOH production. Issaksson et al. [581] integrated BG with pulp and paper mills in order to obtain more valuable products. BG-derived syngas was employed separately in three energy mills to generate electricity (via GT), MeOH and FT fuels, respectively. These energy mills, in three different cases were individually integrated with a thermo-mechanical pulp mill co-located with a saw mill, via the steam cycle. It was found that electricity production requires the smallest gasifier while the FT fuels energy mill needs the largest amount of biomass. Moreover, they reported that the pulp mill acted as a heat sink for excess heat from the energy mills and, therefore, this integration resulted in decreased GHG emissions as compared to stand-alone plants.

Cucek and co-workers [589] employed the MILP route to carry out multi-period synthesis of an integrated biomass and bioenergy network. Different sources of biomass were taken to produce first, second and third generation biofuels such as EtOH, diesel, H_2 , FT and green gasoline with an aim to maximize utilization and sustainability of resources. Seasonality and availability of resources, products recycling and total on-site heat integration were considered as key variables. They observed that the production of second and third generation biofuels is viable. In addition, they suggested that switchgrass and algae are the best raw materials for biofuels production. Most importantly, they found that an integrated bio-refinery network is a potential means to decrease GHG emissions.

Sharifzadeh et al [590] explored alternative biofuel production systems including biomass production, harvesting, processing and transport with a particular interest in centralized versus decentralized systems and quantifying the potential for mobile pyrolysis units coupled with centralized fuel hydro-processing. They demonstrated that such mobile units would, if cost reductions are possible, be useful in pre-processing dispersed feedstocks such as agricultural residues, which could then be moved by tanker to processes which benefit from economies of scale.

10.3. Decisive factors for sustainable bio-refinery

Biomass is the key input raw material in a bio-refinery and its diverse physical and chemical composition offers limitations to design similar biomass supply systems [591]. Moreover, the cost of lignocellulosic biomass differs vis-à-vis types, sources and collection

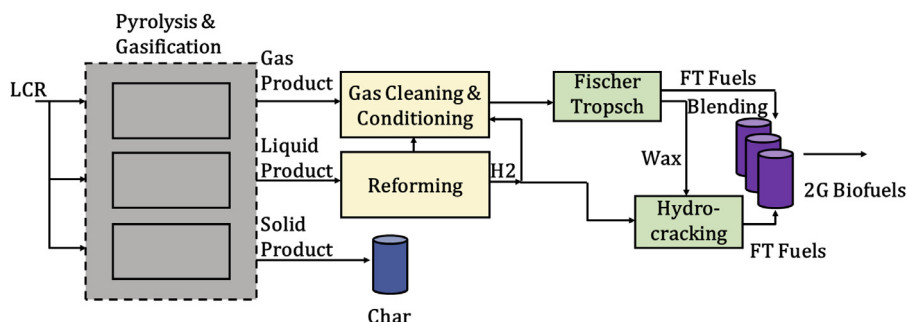


Fig. 30. Schematic of model representing BG-based integrated bio-refinery [23].

logistics. Furthermore, it creates a challenge to develop a common technology to process various kinds of cellulosic biomass. The operational details of a bio-refinery are also a function of seasonal variation in biomass production, especially agricultural feedstock [592]. Storing these biomass types for long durations can serve as one solution. However, space requirements, absorption of moisture and biomass degradation are the outcomes of long-term storage.

Logistics is another key factor which directly influences the successful operation of a bio-refinery. Biomass types from several decentralized sources need to be transported to a centralized bio-refinery, which is usually far away. The collection and transportation costs associated with lighter biomass such as straw, grass, etc., can be significant, making the generation of usable products very expensive and, therefore, unattractive. Novel bio-refining technologies are needed which can be employed at small scale near the source. They can convert low-density low-energy biomass into either highly-dense biomass (via baling for grass) or intermediates (oil-char slurry) [593,594]. The Bioliq concept developed in Germany transforms decentralized biomass into high-energy oil-char slurry in their respective locations, followed by its transportation to centralized gasification plants. It enhances the energy density of biomass from about 2 GJ m^{-3} to an oil-char slurry which has an energy density of about 25 GJ m^{-3} , thereby greatly improving the process economics [77].

The compatibility of bio-refineries with petroleum-based refineries and their infrastructures is also a vital parameter to ensure long term sustainability. Existing infrastructures for petro-refineries took around two centuries to reach the current advanced state [591]. The compatibility of a bio-refinery with the prevailing set-up would drastically reduce time and investment in building a new infrastructure and would definitely have a positive direct impact on its swift growth. Technologies to produce HC fuels and chemicals well suited to current infrastructures (instead of oxygenated biofuels and platform chemicals) should be developed.

In order to completely substitute petro-derived fuels, chemicals and polymers by biomass-derived equivalents, an enormous amount of biomass raw material is needed, which in turn would adversely influence food crop production [595]. Biomass such as forestry waste, agricultural waste, MSW, sewage sludge, etc., should be employed to overcome this challenge. In addition, more R&D to develop technologies to obtain usable fuels and chemicals via algal biomass is required.

Fuels and chemicals obtained from bio-refineries must meet standards in accordance with market requirements and should be economically competitive with fossil fuel-derived products. Currently, petro-refineries produce around 90% fuels and 10% chemicals from crude petroleum [591]. The bio-refinery should follow the same trend to match the market demand, although it may be argued that a higher proportion of chemicals may improve economic viability. In addition, LCA of biomass raw material is recommended to evaluate socio-environmental and economic effects of an integrated bio-refinery and certification schemes such as the UK's renewable transport fuels obligation (RTFO) scheme will prevail [596]. In a nutshell, more research is needed from industry and academia to develop advanced conversion technologies for multiple fuel/chemical large-scale production in a cost-effective manner to replace petroleum-based equivalents.

11. Socio-environmental impact, LCA and ethical issues of biofuel production

Biofuels reduce the burden on conventional fuels and, therefore, should decrease GHG emissions to a considerable extent. They can also enhance the local economy with increased job opportunities and, therefore, have a positive social influence. However, they can have an adverse impact on society and environment too.

Unfortunately, while assessing the biofuel generation route, more emphasis is placed on “positive” subjects such as technology and economics as compared to factors such as social, safety, environmental and health issues [597]. Chemical accidents, e.g., the explosion in the fertilizer industry in Texas in 2013, oil spill in deep water in the Gulf of Mexico in 2010, etc., forced governments to look into these aspects and, therefore, stringent laws came into being vis-à-vis health, safety and environmental methods [598]. These accidents played a key role in raising awareness in society about the significance of so-called unprofitable factors. Under stringent laws coupled with public force, chemical industries are compelled to employ principles to enhance safety, health and environmental performance.

11.1. Social impact

Excessive deployment of coal, petroleum and other fossil fuels has resulted in climate alterations which in turn cause social concerns such as droughts, which further become a root-cause affecting food security and malnutrition, especially in underdeveloped nations [599]. By contrast, the increased demand of agricultural feedstock by biofuels production plants enhances the local economy. In addition, it creates job prospects and higher income generation. This is more evident in rural areas of developing nations where poverty and food insecurity exist on a large scale [600]. These factors may ultimately lead to food supply concerns especially in populous countries such as China and India. Ewing and co-authors [601] demonstrated that poor people from African countries (Mozambique, Tanzania, etc.) are more prone to under-nourishment. In the light of these concerns, rural area development (including upgrading of road networks) via biofuel production seems a significant and viable route in diminishing such social issues to a considerable extent [602]. Kline et al. [603] demonstrate how bioenergy can support agricultural development and improve security.

The development of agriculture and rural economy is a function of suitable biofuel production and usage policy. According to Tirado and co-workers [599] biofuel policy should include factors such as food and nutrition security, poverty reduction planning, land usage strategy, energy security, employment enhancement and markets for new products [599]. Land usage is one of the key concerns for biofuel production especially when lignocellulosic biomass is taken as feedstock. In this regard, biofuel support policies can play a vital role in determining land use strategies which have a direct impact on socio-economic development. Moreover, they should also include technologies for biomass-to-biofuel conversion to decrease adverse socio-environmental impact.

Social acceptance vis-à-vis socio-political, community and market dimensions is also an important factor in biofuel production and application [604]. Diaz-Chavez [605] has developed indicators to assess socio-economic sustainability. Proper assessment of social acceptance can lead to maximization of biofuel development plans. For example, the adoption of new biomass raw materials/technologies coupled with novel plant operation, can have unknown influence on investors and producers. In summary, appropriate biofuel policy as well as understanding of social acceptance issues represents the keys to a positive social influence of biofuels.

11.2. Health impact

The influence of chemical processes on human and animal health is usually serious, especially for long-term exposure. Production and application of biofuels are estimated to have lower health impacts compared to petro-fuel processing and combustion. Still, there are adverse effects which may range from mild problems such as eye and nose irritation to grave health issues such as lung dysfunction, mutation, cancer and respiratory defects. For instance, application of

biodiesel in CI engines has reduced CO, S, PAH, soot and smoke emissions to a significant extent on account of its oxygenated nature. However, NO_x emissions are enhanced considerably, e.g., around 70% increase in NO_x from biodiesel than from conventional petrodiesel [35].

Energy can be directly obtained from raw biomass such as wood or bagasse by combustion. There are several studies which reflect on the influence of biomass combustion on human health [606]. Arbex and co-authors [607,608] found in two different studies, that hypertension and asthma were the outcomes from exposure to total suspended particles (greater than 10 µg m⁻³) due to sugarcane burning. Cancado et al. [609] reported respiratory problems in children due to PM of 2.5 µm size with a density of 10.2 µg m⁻³ or more, while PM₁₀ produces the same problem in adults when they are exposed to 42.9 µg m⁻³. Investigators [610] employed Poisson regression modelling approach to establish a relation between weight of the sediments and the number of hospital visits. The models were controlled for the variables such as season, temperature, day of the week and rainfall. They reported a vital association between the quantity of sediment and the number of visits. People who are exposed to 10 mg or more particle sediment are at a higher risk and are required to be hospitalized for inhalation therapy. Fig. 31 depicts the impact of various steps and different routes associated with biofuels synthesis on human health. To our knowledge, no in-depth and direct epidemiological study has been conducted to evaluate the influence of second and third generation biofuels on human health. It is, therefore, recommended that studies which analyse the advanced biofuels and their production pathways in detail with respect to their influence on human and animal health are needed.

11.3. Environmental impact

The influence of biofuels production and usage on the environment is deep and extensive. A report by Intergovernmental Panel on Climate Change reads that enhancement in GHG emissions due to anthropogenic activities is responsible for global temperature rise [611]. Since the pre-industrial era, CO₂ emissions (35.9 Gt per annum) were found to be maximum in 2014 [612]. In the Paris Agreement, 2015, under United Nations Framework Convention on Climate Change (UNFCCC) (COP 21), it was unanimously decided to limit the world temperature rise by 2 °C with an aspiration to limit it to 1.5 °C [613]. It should be noted that in order to achieve the goal, CO₂ emissions should be decreased by 50 to 85% by 2050 [598]. Application of biofuels to replace petro-fuels can play a key role to reduce CO₂ emissions, in this case. However, it should be noted that the influence of biofuel generation on the environment through GHG emissions, generation of co-products, influence on water resources, biodiversity, land usage, etc., should be properly assessed and analysed for this strategy to be effective.

It is crucial to assess the footprint of the chemicals that have the potential to pose risk on the environment in life cycle analyses. The concentration of a chemical expended or discharged to the environment on account of anthropogenic activities and which has the potential to influence global sustainability is termed its footprint [614]. Cucek and co-authors [615] classify footprints into carbon, nitrogen, water, energy, land, emission, biodiversity and others which include phosphorus, waste, human and fishing grounds.

Some investigations on environmental footprint have been performed in the biofuels arena. Cucek and co-workers [616] combined different operational segments in a so-called total site system and examined the environmental footprints in thermal energy exploitation. A reduction in C, N and H₂O footprints was reported on account of energy integration in a heat-integrated total site system. In another study, the impact of a transition to biodiesel and EtOH in the transport sector, on global water footprint, was investigated [617]. The study demonstrated dramatic results and forecasted a 10-fold rise in water footprint by 2030 causing more pressure on fresh H₂O resources. Hammond et al. [618] suggested that global footprints (especially carbon and land use) would rise as a consequence of biofuel generation. They clearly stated that the carbon footprint for first-generation biofuels is high and this impact can easily be decreased by employing second-generation fuels. Cucek and co-authors [619] compared carbon and nitrogen footprints for both biomass and fossil fuels. They reported that biomass displays higher N footprint and lower C footprint than its counterpart.

In general, biofuels were found to be better than fossil fuels in LCA and footprint studies carried out around the globe. The results in LCA investigations are inconsistent vis-à-vis energy balance and environmental influence. This holds true even when the same biomass raw material is employed but with varied farming and conversion technology for fuel production [620]. These inconsistencies are due to diverse economic and geographical factors, for example, raw material, cost, kind of biofuel, weather, etc. Standardized methodology for analysis coupled with common assumptions can lead to better results in future studies, which in turn can aid in designing and developing sustainable biofuel technologies and applications.

11.4. Life cycle assessment

Life Cycle Assessment (LCA) is a methodology that examines products and services from cradle to grave with a view to understanding the system-wide environmental impacts. A cradle-to-grave LCA study of a product considers all life cycle stages from extraction or primary production of materials and fuels ('cradle') through production and use of the product to its final disposal ('grave'). The framework has been standardised by the International Organization as ISO 14,044:2006 [621]. It comprises four key elements:

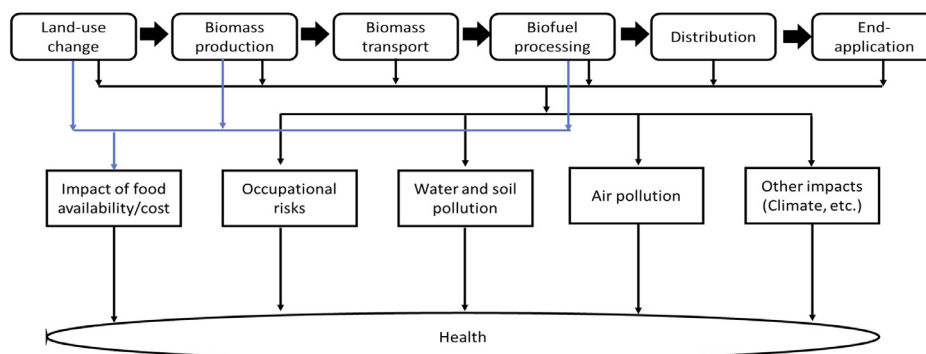


Fig. 31. Impact of various steps and pathways associated with biofuels synthesis on human and animal health [606].

- i. Goal and scope definition: identifying the purpose of the study and the system boundary
- ii. Inventory analysis: essentially establishing the material and energy balances of all stages
- iii. Impact assessment: converting the inventories to environmental impacts using a set of damage categories (e.g., resource depletion, global warming, ozone depletion, ecotoxicity, etc.)
- iv. Interpretation and improvement: generating insights and identifying opportunities for improvement.

Bio-based fuels production has been subject to a large number of life cycle analyses. A large number of factors come into play when undertaking such assessments, in particular understanding land use changes, credits from co-products such as chemicals, heat and power and the degree of carbon sequestration during the biomass growth phase [622]. One of the main sources of uncertainty in undertaking a life cycle assessment for biofuels is the concept of indirect land use change. This arises out of the need to explore what might happen if a biofuel supply chain increases in scale – this change from marginal to system wide analysis is called consequential life cycle assessment and is concerned with how land-based activities displaced by biofuel production will re-establish themselves. Because these analyses tend to be hypotheses-driven, they do give rise to large uncertainties and are strongly affected by underlying assumptions [623,624].

Two key insights arise from life cycle analyses: the use of agricultural residues or non-food crops leads to lower environmental impacts than the use of food crops, and the efficiency of conversion from primary biomass to products should be high because most environmental impacts are incurred in the production stage and hence a higher amount of useful product per unit input is critical. This is where the benefits of effective gasification and downstream conversion can provide significant benefits by maximising the use of all the biomass (lignin, hemicellulose and cellulose) directly. A comprehensive analysis of gasification for power production was performed by NREL [625], who found that the life cycle CO₂ emissions were very sensitive to assumptions on soil carbon accumulation. A study of hydrogen production through biomass gasification and conversion found that the life cycle CO₂ emissions were seven times lower than the incumbent methane steam reforming process and the life cycle acidification impact around half of the SMR process [626]. A benefit of the biomass route was the ability of a process to generate its own power needs from a renewable source.

11.5. Ethical issues

There are ethical issues relating to the use of biofuels based on food crops given a steady population growth, and potential shortages of agricultural land due to urbanization, global warming and other factors. One of the more detailed evaluations of issues relating to biofuels was provided by the Nuffield Council on Bioethics [627], which explored whether 9 billion people could be fed equitably, without putting excessive strains on water use, while adapting to mitigating climate change based on the consideration that by 2030 the world will need to produce 50% more food and energy, together with 30% fresh water [628,629]. The overall conclusion of this work was that any strategy should include protection of human rights, full life cycle assessment of greenhouse gas emissions, the employment of fair trading principles and the use of access and benefit-sharing schemes, but that providing this was done biofuels had a clear role to play in contributing to energy security, especially for transportation fuels and that such developments should be supported providing they met the ethical guidelines laid out in the Nuffield Council of Bioethics study. A significant issue in such developments is how high their cost, which will militate against biofuels in favor of cheaper conventional alternatives [630]. While, there appears to be general support for the concept that biofuels can make an extremely

positive contribution, this must be done in an ethical framework, and the criticism remains that without respecting such a framework, current land-use “reflects the dietary and transportation preferences of wealthier individuals” [630]. What is clear from the literature is that the use of food crops, as opposed to food wastes represents an area fraught with challenges, which must be resolved on a case-by-case basis.

12. Conclusions

Various important investigations in the last century and in this century emphatically reflect the potential of biofuels, especially lignocellulosic biomass-derived biofuels. Second- and third-generation biofuels are considered better alternatives to petro-derived fuels when compared to food crop-derived first-generation biofuels on account of their ability to utilize wastes and other material with low food supply interactions. Numerous advancements in biomass gasification technology have made it a viable route to process diverse biomass feedstock in an efficient and cost-effective manner to generate syngas. Moreover, the latest developments in syngas clean-up and processing techniques have enabled its usage as a raw material for catalytic biofuel generation.

A sense of concern is required among different governments on account of the impact of conventional fuels on climate change due to GHG emissions as well as their contribution to land and water pollution during their extraction, production and transportation. This calls for sustainable substitutes which have the potential for climate change mitigation. In addition, these substitutes should be cost-effective and should not have an adverse influence on society. Syngas-derived biofuels have the potential to include all these characteristics. However, unavailability of the right technology coupled with poor planning, ineffective policies and badly-controlled practices are critical hindrances in the production and usage of biofuels to a greater extent. These issues should not be allowed to distract us from taking the necessary steps to exploit the major potential advantages of biofuels and encourage biomass exploitation more widely.

Biofuels can be a vital contributor to curb energy scarcity, especially by their deployment as transportation fuels. Governments should provide necessary infrastructure and policies to support their development provided they meet the ethical guidelines. It should be noted that the major limitation in such developments is the higher cost of biofuel production against established fuels. It can be emphatically deduced from the previous studies that employing food crops for biofuels instead of wastes and other biomass as raw material for biofuel generation is a complex issue and should be dealt with on an individual basis using sophisticated whole systems analyses.

The challenges should be taken as an encouragement to design and develop advanced technologies for waste processing to generate syngas and to employ it for fuel generation. More studies on LCA and footprint of biofuels combined with systems optimization are needed to ensure holistic and sustainable implementation in diverse areas. Furthermore, scale-up of the existing biofuels production plants should be explored, employing new technologies with favourable governmental policies. In this regard, a collaborative effort by scientists and engineers, environmentalists and policy-makers is critical to ensure the effective incorporation of biofuels in our society for an environmentally-friendly and sustainable future.

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