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Catalytic Biomass Valorization

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<http://dx.doi.org/10.5772/65826>

Abstract

Biomass is a significant non-conventional energy reserve, which has been considered as a promising alternative over other renewable sources such as solar, wind or hydroelectric storage due to its comparatively ample availability. A variety of biomass types can be converted into useful products via bioenergy technologies. The deep understanding and knowledge of these processes are necessary for optimization and advancement in a cost-effective way. A comprehensive comparison and discussion is conducted with respect to biochemical and thermochemical conversion technology such as microbial digestion and fermentation, pyrolysis, liquefaction and gasification. Pyrolysis is the process of converting biomass into bio oil, charcoal and gaseous fractions by heating anaerobically to above 500°C. Liquefaction is a low temperature (LT) and high-pressure thermochemical process to produce marketable liquid over suitable catalysts under hydrogen or reductive environment. Gasification is the conversion of biomass into preferred combustible gas mixture (syngas) via the partial oxidation at high temperature, typically in the range of 800–900°C. The product gas is more versatile and can be burned in gas turbine for electricity production or synthesis of high-value chemicals. The parametric impact, mechanism, development status and future direction have been summarized for each of these technologies with the aim to pave the way for optimization of future investigation.

Keywords: biomass, pyrolysis, gasification, liquefaction

1. Introduction

The declining reserves and fluctuating prices of fossil fuels necessitate a switch from conventional to renewable power sources, for instance, solar, wind, biomass and hydroelectric generation [1]. Biomass is considered the fourth largest source of energy in the world, currently supplying more than 10% of primary energy. It also provides a potential source of

valuable chemicals, such as reducing sugars, furfural, ethanol and other products by using biochemical or chemical and thermochemical procedures [2, 3]. Due to its widespread availability, renewable nature and neutral relation to global warming, the potential of biomass to meet the need for the world energy has been widely recognized. Furthermore, biomass utilization has an advantage over other renewable sources on account of its topographical independence and easy storage and transportation.

Biomass is the term for all biologically produced matter, including land and water-based vegetation, as well as organic wastes, which can be used directly or indirectly by converting it into liquid or gaseous fuel. As the necessity for a renewable and sustainable energy becomes more significant, research interest in biomass conversion to fuel or high value-added chemicals has increased dramatically. The distinction between the energy carriers originated from biomass can be made based on their ability to provide heat, electricity and engine fuels. The famous *Van Krevelen* diagram is usually used for comparing biomass and fossil fuels in terms of their O/C and H/C ratios. The lower the respective ratios, the greater the energy content of the material. More details about this diagram can be obtained from the literature [4].

Currently, there are a number of different approaches used for biomass conversion, such as direct combustion for heat or electricity, thermochemical conversion to bio-oil, chemicals and syngas, and biochemical transformation of biogas or bioethanol. Combustion can be widely used on various scales to obtain heat or electricity from biomass; however, the energy efficiency of this conversion is low. Co-combustion of biomass in coal fire plants is an attractive option to improve the conversion efficiency. Biochemical processing involves anaerobic digestion, the decomposition of biomass via bacterial activity without oxygen to yield biogas and alcoholic fermentation, which is used commercially on a large scale to produce ethanol from sugar and starch crops. In this chapter, more attention has been concentrated on the thermochemical conversion of biomass, including gasification, pyrolysis and liquefaction, due to the diversity of products and high conversion efficiency in the process. The differences of the three process conditions are shown in **Table 1**.

An in-depth survey is carried out regarding the mechanism, parametric impacts, products, techno-economics, development status and future direction for each of the three thermochemical technologies. There are a wealth of articles regarding biomass conversion, and this chapter provides a comprehensive overview with a direct comparison of the current technologies highlighting the benefits and drawbacks of each with emphasis on catalytic biomass conversion.

Process	Temperature, K	Pressure, MPa	Drying	Catalyst
Pyrolysis	650–800	0.1–0.5	Unnecessary	Yes
Liquefaction	525–600	5–20	Necessary	No
Gasification	873–1273	1–2	Necessary	Yes

Table 1. Comparison of thermochemical process conditions [5].

2. Biomass valorization

2.1. Pyrolysis

2.1.1. Mechanism

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen, as illustrated in **Figure 1**. Slow pyrolysis occurs when there is a slow heating rate over a longer residence time (5–30 min). The extended residence time and slow heating rate facilitate the increased production of char products and have been used throughout history for the production of charcoal. Fast pyrolysis occurs when there is a much faster heating rate with much shorter residence times. Increased heating rates and faster residence time result in greater liquid and gas products, making fast pyrolysis more desirable for the purposes of producing bio-oil and valuable chemicals [7]. Typically, decomposition occurs in just a few seconds at atmospheric pressure and relatively low temperatures between 300 and 600°C [8, 9]. The quick reaction time and mild operating conditions make pyrolysis an attractive option for producing bio-oil and valuable chemicals from the cheap feedstock of biomass.

A mixture of a complex feedstock and multiphase products make it difficult to study the exact mechanism of pyrolysis, but there is a general understanding. Initially upon heating, water is removed, resulting in a dry fuel that undergoes primary pyrolysis. Decomposition occurs upon the transfer of heat from the surrounding area to the biomass particles resulting in solid char, bio-oil, gas and water, constituting the primary stage of pyrolysis [8]. An increased

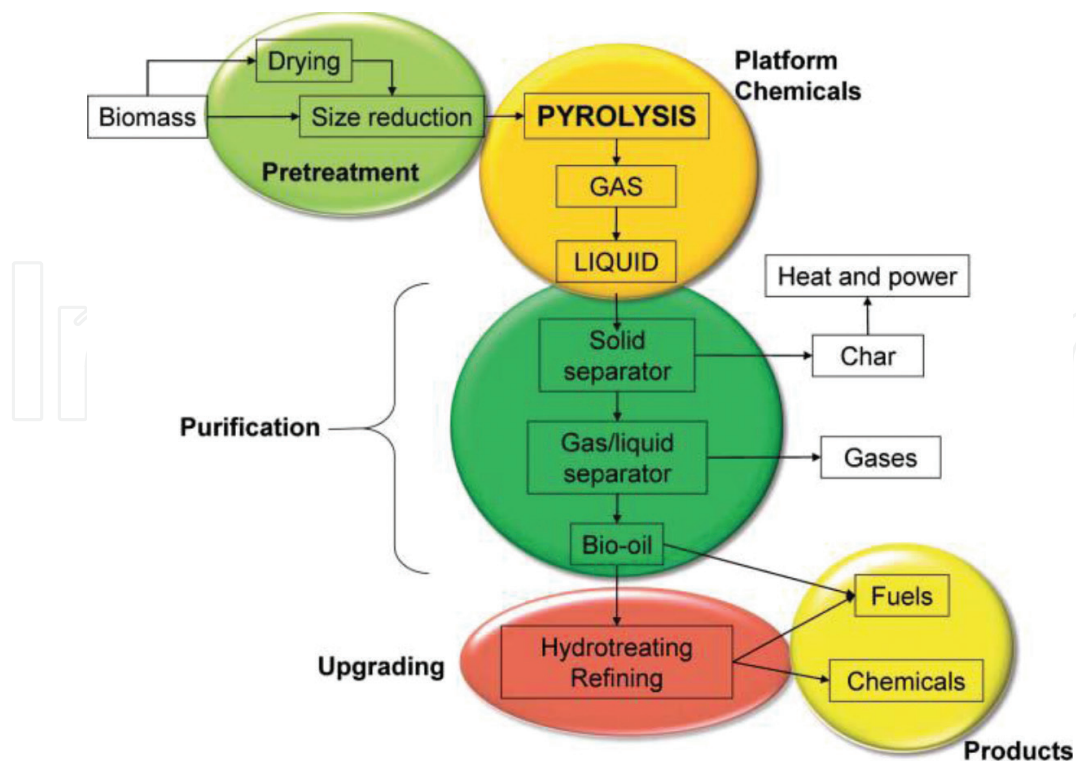


Figure 1. Process schematic of biomass pyrolysis and upgrading [6].

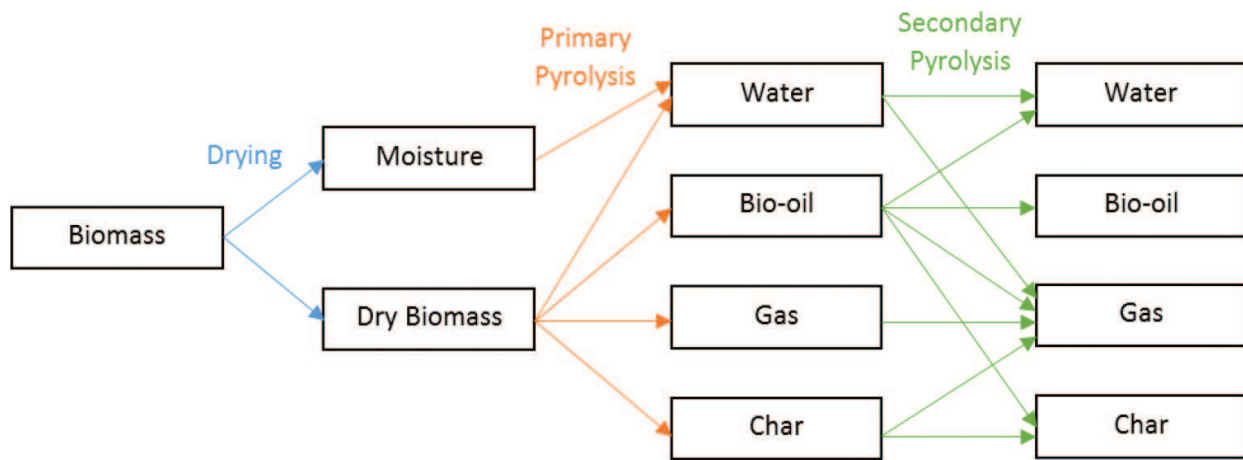


Figure 2. Primary and secondary pyrolysis including arrows indicating reaction pathway [8].

surface area results in better heat transfer, which causes a faster and more complete reaction [9, 10]. For this reason, biomass is typically mechanically ground into a fine powder prior to the reaction. During the secondary stage, further decomposition occurs in addition to various other reactions resulting in an increase in gaseous products. A summary of these processes can be seen in **Figure 2**. Fast pyrolysis can have a biomass to bio-oil conversion of 70–80%. Liquid yield can be maximized by a fast residence time, preventing the secondary decomposition of products. Due to the importance of residence time and heat transfer in pyrolysis, much research has gone into reactor design which is reviewed in reference [9].

2.1.2. Products

Pyrolysis results in a wide range of products that can be divided into the categories of solid char, liquids (water and bio-oil) and gases. Char is the term used for all of the solid products including organic matter (high carbon content) and ash [8]. Water is produced as a product of pyrolysis as well as during the initial drying stage via evaporation [8, 9]. The bio-oil component is a brown, polar liquid comprised of a mix of oxygenated compounds, which differs with feedstock and reaction conditions [9, 10]. At moderate temperatures, gas products are mainly comprised of CO , CO_2 and CH_4 , with H_2 and C_xH_y gases also being produced at higher temperatures [8, 10]. The amount of solid, liquid and gas produced varies greatly depending on the biomass composition as well as the reaction temperature. The temperature has a greater effect on the amount of product in each phase, while the feedstock composition has a greater effect on the bio-oil elemental composition. A higher C/O ratio in the feedstock results in a higher liquid yield and lower gas yield, while the char yield remains relatively unaffected. An increase in hydrogen in the feedstock results in more water formation, more bio-oil and less carbon dioxide and C_xH_y gases [8]. At low temperatures ($<350^\circ\text{C}$) and slow residence times, char is the favoured product [8–10]. Longer residence times allow for the reaction of gas and liquid products to form char [7]. The best yields of liquid product are achieved at moderate temperatures ($400\text{--}550^\circ\text{C}$) and fast residence times. These conditions allow for primary pyrolysis to occur, but the fast residence time allows for products to be collected before secondary reactions can take place [8–10]. At very high temperatures (HT) ($>800^\circ\text{C}$), a higher

yield of gas products is observed due to the presence of secondary reactions, which further break down the liquid and char components into gases.

The liquid product composition generally mimics the biomass carbon, hydrogen and oxygen composition. Due to the high oxygen content in biomass, the liquid product of pyrolysis is made up of a large portion of oxygen-containing compounds. The oxygen-containing compounds including alcohols and acids make the bio-oil reactive and acidic causing issues for storage and transportation through established pipelines [11–14]. As a result, bio-oil must be upgraded before it can be transported or used as a fuel. An increase in temperature leads to a slight decrease in oxygen content and a slight increase of carbon and hydrogen content in the bio-oil. This results in a small increase of aromatic compounds, which marginally improves the oil quality [8].

2.1.3. Developmental status

The majority of research on pyrolysis involves optimizing the upgrading process to acquire a higher quality product. Hydrodeoxygenation and catalytic cracking are the most popular processes currently being utilized for upgradation [12]. Hydrodeoxygenation involves removing oxygen from the liquid product in the form of water through a hydrogen supply [9, 15]. This process is expensive due to the high operating pressures (up to 20 MPa) and the high cost of hydrogen [9, 15]. Catalytic cracking is a fairly new technology, which uses a catalyst to promote a range of reactions including dehydration, decarboxylation, aromatization, alkylation and polymerization [12]. Zeolite catalysts have found to be particularly effective at aromatization and have been found to remove oxygen in the form of carbon dioxide [9, 14]. The addition of metals such as silver or nickel can increase selectivity and allow for optimized products [12]. Catalytic cracking is significantly cheaper than hydrodeoxygenation due to the relatively mild operating conditions and absence of hydrogen; however, the coking of catalysts is a significant concern and due to the lack of hydrogen supply, the product suffers from a low H/C ratio [12, 16].

At the current time, the combination of pyrolysis and catalytic cracking in one process has been attracting more attention [10]. One research group is combining pyrolysis with catalytic cracking under a methane environment, in a novel process called methanolysis [16, 17]. This process is operated at atmospheric pressure and moderate temperatures on a zeolite catalyst with a supply of methane. Methanolysis is economically attractive due to the relatively low operating conditions and the wide availability and low cost of natural gas of which methane is the major component. The aim of this research is to develop a catalyst that will allow pyrolysis to occur in a methane environment, while at the same time upgrading the liquid product. Promising results were found during feasibility studies, where it was shown that not only was the bio-oil produced of greater quality, but the methane was incorporated into the product [16, 17]. **Table 2** compares pyrolysis in inert gas, hydrogen and methane environments with and without catalysts for a sawdust feedstock. An increased oil yield accompanied by a decrease in oxygen content and an increase in H/C ratio can be observed in a methane environment using a catalyst. It is also clear that the metal used in the catalyst can affect both oil yield and quality. These results are very promising for creating a high quality bio-oil in an economical and environmentally friendly way.

Trials	Oil* yield (wt %)	Water formed (mg/g)	Oil quality		
			H/C ratio	O content (wt %)	O/C atomic ratio
Biomass, inert	5.47	97.0	1.62	5.25	0.226
Biomass, inert, Ag/ZSM-5	4.07	135.6	1.29	0.18	0.009
Biomass, 30% H ₂	4.17	73.4	1.46	3.41	0.145
Biomass, 30% H ₂ , Ag/ZSM-5	3.42	100.2	1.45	0.45	0.024
Biomass, 30% CH ₄	4.68	119.0	1.38	0.22	0.009
Biomass, 30% CH ₄ , Ag/ZSM-5	4.85	128.3	1.76	0.07	0.003
Biomass, 30% CH ₄ , Ag/P-Ce-ZSM-5	6.89	110.9	2.26	7.35	0.356
30% CH ₄ , Ag/ZSM-5	0	0	–	–	–

*Moisture-free liquid collections with boiling point less than 150°C.

Table 2. Results of the pyrolysis of sawdust under different environments [16].

2.1.4. Future direction

The next steps of pyrolysis research are optimizing product yield and quality, which can be achieved through the use of catalytic cracking. This involves gaining a better understanding of the complex mechanism involving the catalyst by using model compounds. Once there is a clear understanding of the catalyst's role, an industrially viable catalyst and process can be developed to produce high-quality fuels that are cost competitive with oil-derived alternatives. Methanolysis is considered a promising new technology, which can be a sustainable alternative to traditional fuel sources. In addition to developing an optimal catalyst, work must be done to improve methane conversion and incorporate catalyst regeneration into the reaction.

2.2. Liquefaction

2.2.1. Mechanism

Liquefaction is the thermochemical conversion of biomass to primarily yield liquid fuel at moderate temperature and high pressures. This is a chemical reforming process of organic matters, usually with a high hydrogen partial pressure and catalysts to enhance the rate of reaction and/or to improve the selectivity of the product. This approach is summarized in **Figure 3**. In the process of liquefaction, the carbonaceous materials of biomass are ultimately converted into liquefied products through a series of complex physical and chemical reactions [18, 19]:

- Micellar-like substructures are formed by solvolysis;
- Smaller and soluble molecules are generated via depolymerization;
- New molecular rearrangements occur through thermal decomposition, including dehydration, decarboxylation, C-O and C-C bonds rupture.
- Hydrogenolysis and hydrogenation of functional groups.

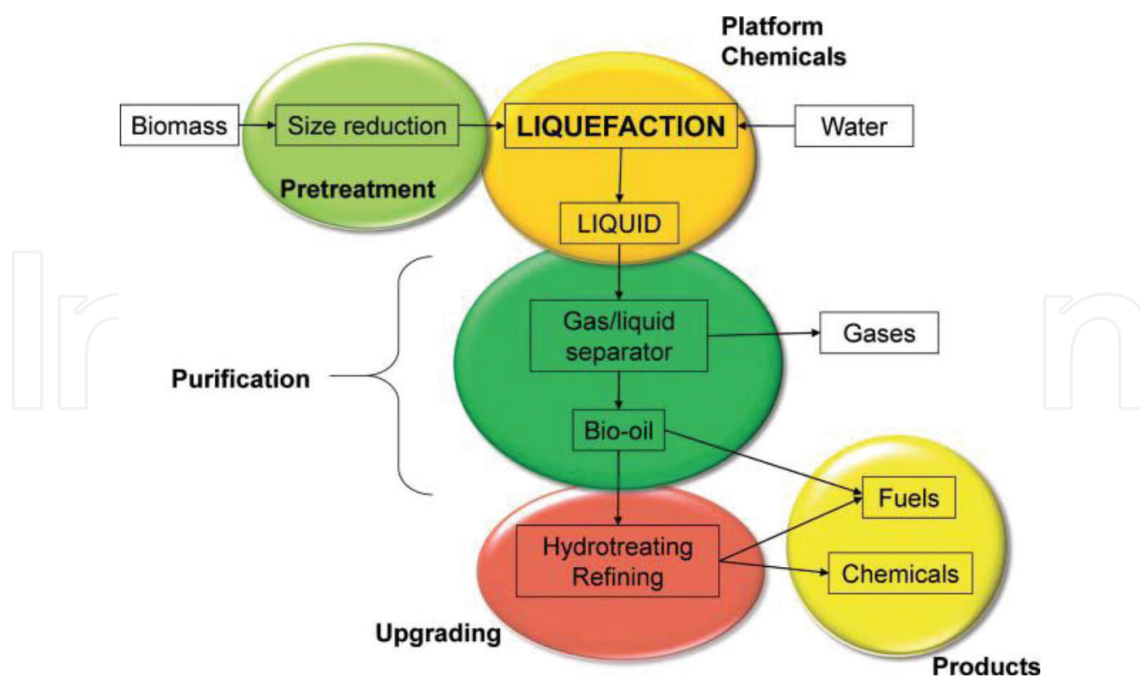
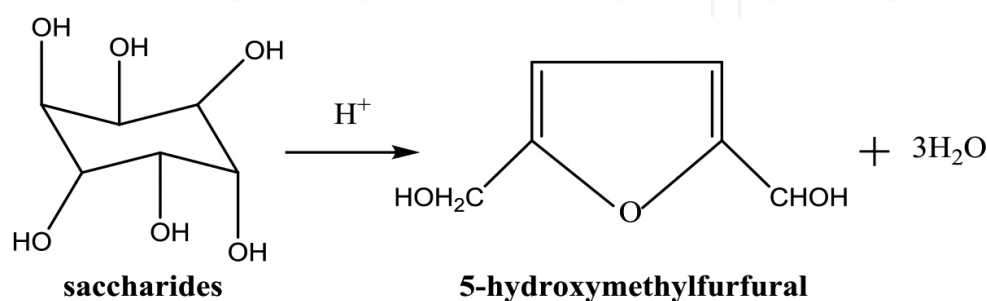
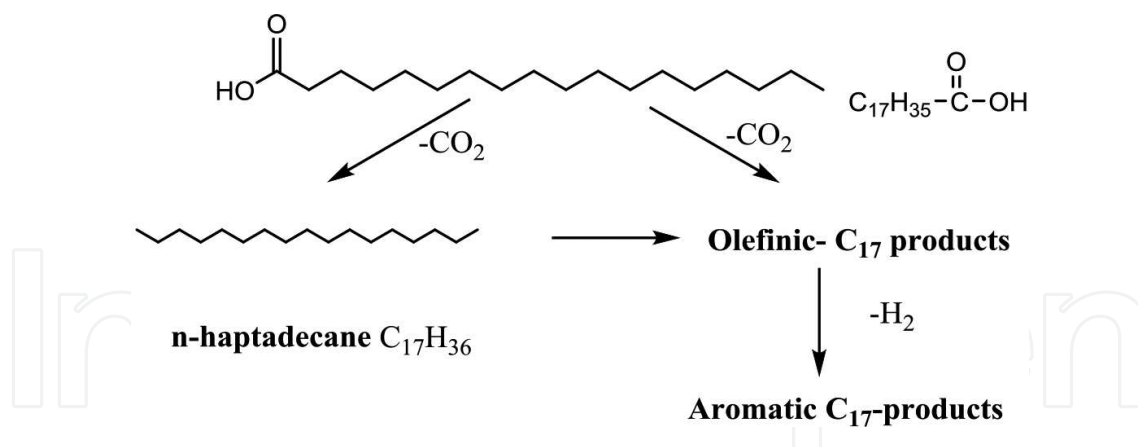


Figure 3. Process schematic of biomass liquefaction and upgrading [6].

Another remarkable feature of liquefaction is that it maximizes the liquid-yields with high quality. One important quality index of product oil is the H/C ratio, which can be increased by removing the oxygen content. The lower oxygen content makes the oil more chemically stable and requires less upgrading to the hydrocarbon product [20]. Generally, biomass contains typically 40–50 wt.% (DAF basis) of oxygen, which can be removed via dehydration and decarboxylation as the form of H_2O and CO_2 , respectively. Thermodynamically, removal of H_2O and CO_2 from biomass can be considered as the best option to reduce the oxygen content. Removal of H_2O ultimately forms carbon as the remaining product such as charcoal while removal as CO_2 is prone to generate the product with high H/C ratio. Under hydrothermal upgrading reaction conditions, the decarboxylation selectivity is almost constant, 0.52 [21]. Dehydration and decarboxylation reactions are conceptually described as follows:



Dehydration of saccharides to 5-hydroxymethylfurfural [22]



Simplified decarboxylation network of stearic acid to diesel products [23]

2.2.2. Conversion of biomass components

As we know, biomass is a broad definition and contains a wide range of substances with different compositions. The main components are categorized four groups: carbohydrates, lignin, protein and lipids. The protein and lipids are prevalent in the dried distiller grains with soluble (DDGS) and slaughterhouse waste [24, 25], which are not further discussed in this chapter. More concerns are focused on the conversion of carbohydrates and lignin.

2.2.2.1. Carbohydrates

The most abundant carbohydrates contained in the biomass are polysaccharides, cellulose, hemicellulose and starch. Carbohydrates first are hydrolyzed to glucose and other saccharides and further degraded into small molecule compounds at higher temperature. The hydrolysis rate varies with the components. Generally, the hydrolysis rate of hemicellulose and starch is much faster than cellulose, since the cellulose has relatively stable crystalline structure. The conversion of cellulose can achieve 100% at 280°C within 2 min. The addition of carbon dioxide increases cellulose hydrolysis rate, and this is most likely attributed to the formation of carbonic acid, acting as an acid catalyst. However, the beneficial effect is insignificant above 260°C [26]. Hemicelluloses are readily soluble and hydrolyzed above 180°C [27] and close to 100% conversion of hemicellulose is obtained for various wood and herbaceous biomass materials at 230°C within 2 min [28]. Several attempts have been made to reveal the general degradation mechanism of carbohydrates. Glucose is commonly chosen as the model compound because it is one of the main hydrolysates. Even though the employed models are different in details, the overall pattern is quite similar [29, 30]. An overall degradation route for glucose is presented in **Figure 4**.

2.2.2.2. Lignin

Lignin is an aromatic heteropolymer, which is relatively difficult to be degraded chemically or enzymatically [27]. The hydrothermal degradation of lignin can occur at high temperature of 350–400°C, and the main products are catechol, phenols and cresols [37, 38]. However, it can be catalytically hydrolyzed into various phenols and methoxy phenols by cleavage

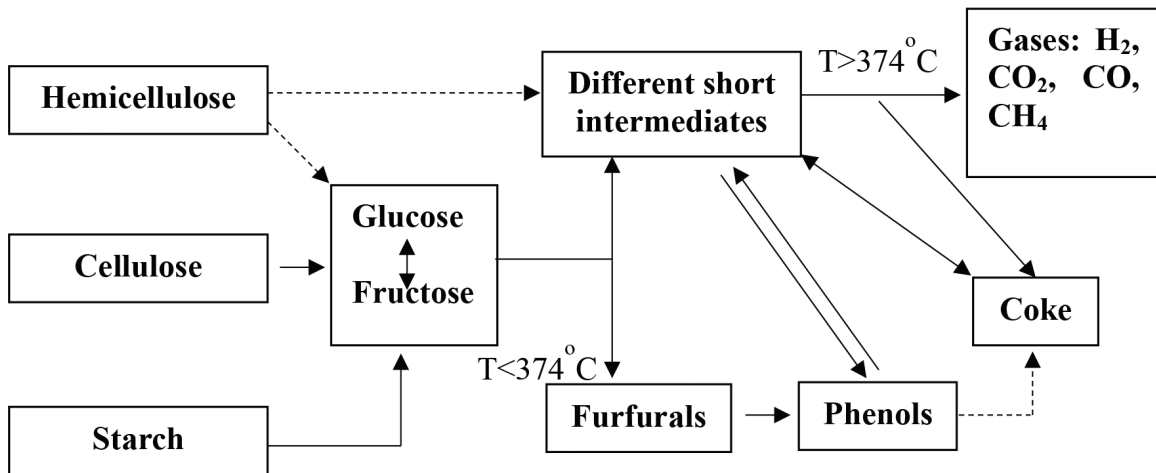


Figure 4. A simplified reaction mechanism for carbohydrate hydrolysis at sub- and supercritical conditions [69].

of ether-bonds under alkaline environment. The reaction temperature for hydrothermal processing of lignin is 200–300°C. The hydrothermal degradation pattern of lignin is shown in Figure 5.

2.2.3. Impact of parameters

Biomass liquefaction can be influenced by numerous parameters, including temperature, pressure, catalyst, residence time, heating rate, particle size, solvent, reducing agent and the type of biomass. In this chapter, the effect of temperature, pressure, catalyst and residence time on biomass liquefaction will be discussed separately.

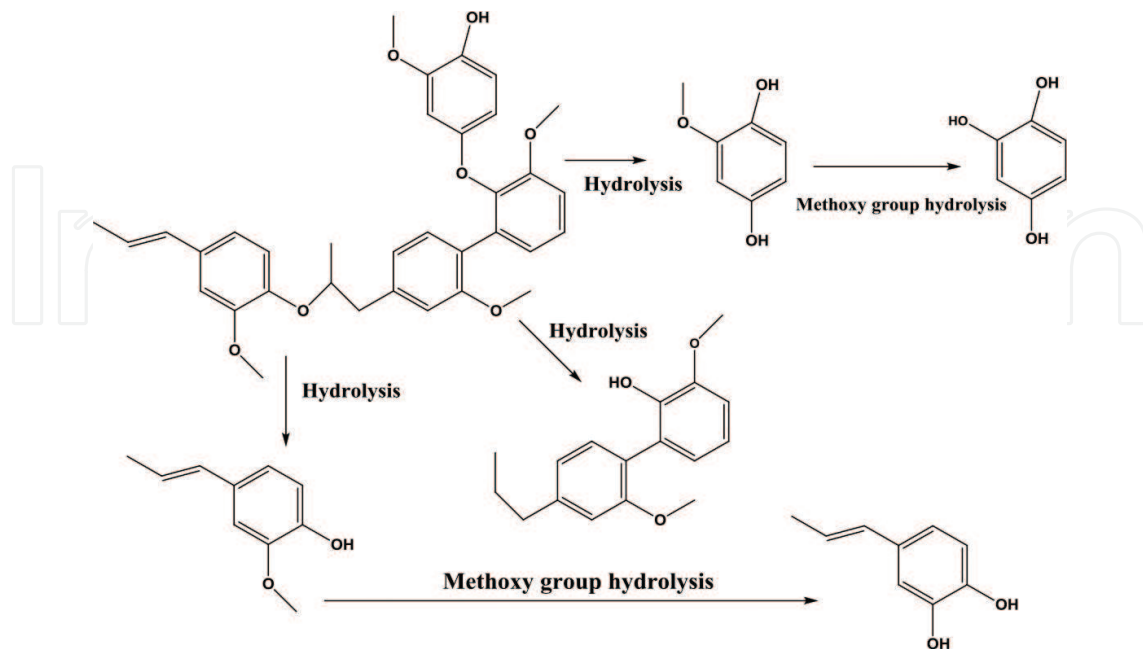


Figure 5. Simplified scheme of lignin degradation [39].

2.2.3.1. Temperature

The influence of temperature on the oil yield has been investigated by many researchers [31–36]. The results are illustrated in **Figure 6**. It is obvious that the maximum oil yield can be achieved in the intermediate temperature range. The reason is that temperature enhances the synergetic effect on the yield of liquids due to more biomass fragmentations generated with temperature. When temperature is sufficiently high to provide the activation energy for bond rupture, depolymerization occurs extensively, increasing more free radicals and fragmented species for further repolymerization at higher temperature. Therefore, the dominant reaction is depolymerization of biomass in initial stage, and repolymerization is prevailing in the later stages, and intermediate temperature is expected to yield higher amounts of bio-oil [40].

2.2.3.2. Pressure

Pressure is another factor affecting hydrothermal liquefaction (HTL). The hydrolysis rate and biomass dissolution are controlled by maintaining the pressure above the critical pressure of medium, which may enhance the favourable reaction pathways thermodynamically for production of liquid fuels or gas yield [40]. In addition, the density of medium solvent can be increased with pressure, which makes the medium more efficiently penetrates into molecules of biomass components, promoting the decomposition and extraction. However, the influence of pressure on the yield of oil or gas is negligible under supercritical conditions [41–44]. It is reported by Sangon et al. [41] that the oil yield was slightly increased with pressure increase from 7 to 12 MPa during the coal liquefaction in supercritical conditions. Kabyemela et al. [43, 44] observed that pressure rise had a certain degree of adverse effect on the degradation of glucose. The same phenomenon was witnessed in the process of hydrolysis and pyrolysis of cellobiose liquefaction at 400°C. This is because under the supercritical conditions, the increase in pressure results in the cage effect for C–C bonds, which inhibits the breakage of

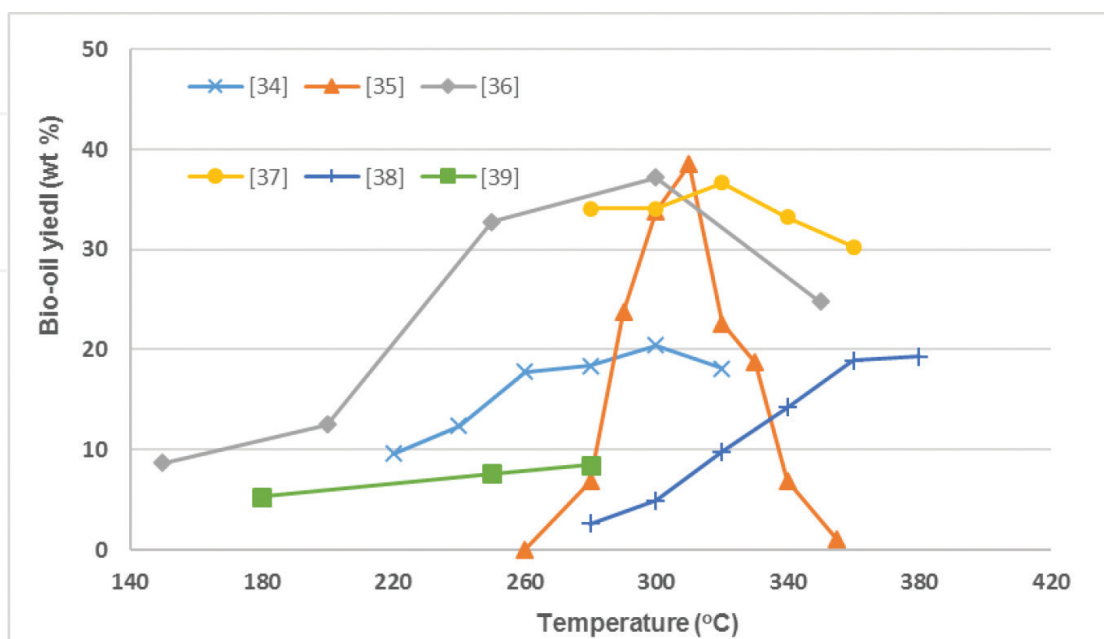


Figure 6. Oil yield dependence of temperature as reported by different research groups [31–36].

bonds and ends up with low degree of biomass fragmentation. Therefore, variation of pressure in supercritical region plays an insignificant role for overall oil yield.

2.2.3.3. Catalyst

Generally, homogeneous catalysts, such as alkali salts, organic and inorganic acids, are significantly more active than heterogeneous catalysts in the process of biomass liquefaction. Heterogeneous catalysts, such as Ni-containing catalysts, are frequently used in low-temperature water gasification of biomass. Homogeneous catalysts in the form of alkali salts have been commonly used in biomass liquefaction. For example, sodium carbonate has the catalytic effect of increasing oil yield and reducing char, and potassium carbonate can promote the water-gas shift reaction and lessen solid residue, while the catalysts sodium hydroxide and potassium hydroxide can enhance decarboxylation and increase isomerization of glucose. The heterogeneous catalysts Ni,Ru have the enhancement of H₂ and CH₄ yield in the hydrothermal conditions. According to the studies [45–48], the organic acid catalysts exhibit better catalytic activity than inorganic acid catalysts with respect to the solid residue content. Salts (phosphates, sulphates, chlorides, acetates, carbonates) don't have as good of catalytic performance as alkali (NaOH, KOH) at typical liquefaction temperatures.

2.2.3.4. Residence time

The effect of residence time on hydrothermal liquefaction is mainly demonstrated in two aspects: the overall conversion of biomass and the composition of products. According to the study of Boocock and Sherman [49], the bio-oil yield was reduced with increase in residence time. Other researchers [33, 36] witnessed the same results. It is observed by Yan et al. [50] that there is no significant increase in liquid yield for longer residence time. Therefore, the short residence time favours more liquid products in the liquefaction. There may be many reasons to explain the effect of residence time. One convincing explanation is that decrease in oil yield may be as a result of secondary and tertiary reactions for longer residence time when biomass conversion reached the saturation point.

In addition, the duration of liquefaction influences the composition of oil product. The significant difference between the decomposition products obtained for longer and shorter residence time was observed by Karagoz et al. [50]. For instance, some furan carboxaldehydes, benzoic acid and phthalate were gained for 60 min, which were not observed in the case of shorter residence time (15 min). Obviously, the preasphaltenes and asphaltene can be decomposed into lighter products for longer residence time, enhancing the yield of light oil and gases. Therefore, it is necessary to inhibit the further disintegration of lighter products in order to obtain high oil yield. One way to prevent oil decomposition is addition of reducing agents like tetraline, hydrogen and syngas. This strategy not only stabilizes the radicals and lighter products but also favours the high oil yield.

2.2.3.5. Feedstock

Theoretically, any biomass can be converted into bio-oil via liquefaction regardless of water content, including forestry, agriculture residues, sewage sludge and food waste. Due to the different behaviours of major biomass components (such as lignin, hemicellulose and cellu-

lose) on the temperature variations, the liquid products and overall yield can be influenced significantly by the heterogeneity of biomass stock. More bio-oil can be obtained from feedstock with a higher content of cellulose and hemicellulose. In addition, the physical properties of bio-oil depend on the feedstock type. The bio-oil produced from liquefaction of the loosely structured biomass usually has poor quality and HHV and a low viscosity. This is because the oxygen and moisture contents are high in the liquid products. Therefore, modifications are necessary before the product can be used in engines, turbines and boilers. It is also unsuitable for long-term storage due to the complexity of the oil [51].

2.3. Gasification

Gasification is a high temperature partial oxidation process to optimize gas production, and it involves the extremely complex catalytic conversion of solid/liquid organic compounds into the gas or solid phase in the presence of a gasifying agent (air, steam, oxygen, CO_2). The gas phase, usually called “syngas”, is a mixture of hydrogen, carbon monoxide, carbon dioxide, methane and small hydrocarbons. The solid phase, called “char”, is actually composed of unconverted organic fraction, fixed carbon as well as ash. Gasification has been considered as a cost-effective way to increase the use of biomass for energy production, allowing widespread biomass utilization [52]. Especially in the beginning of this century, rising oil price and concerns over climate change resulted in the expansion of more advanced biomass gasification projects around the world. One typical biomass gasification process is shown in **Figure 7**.

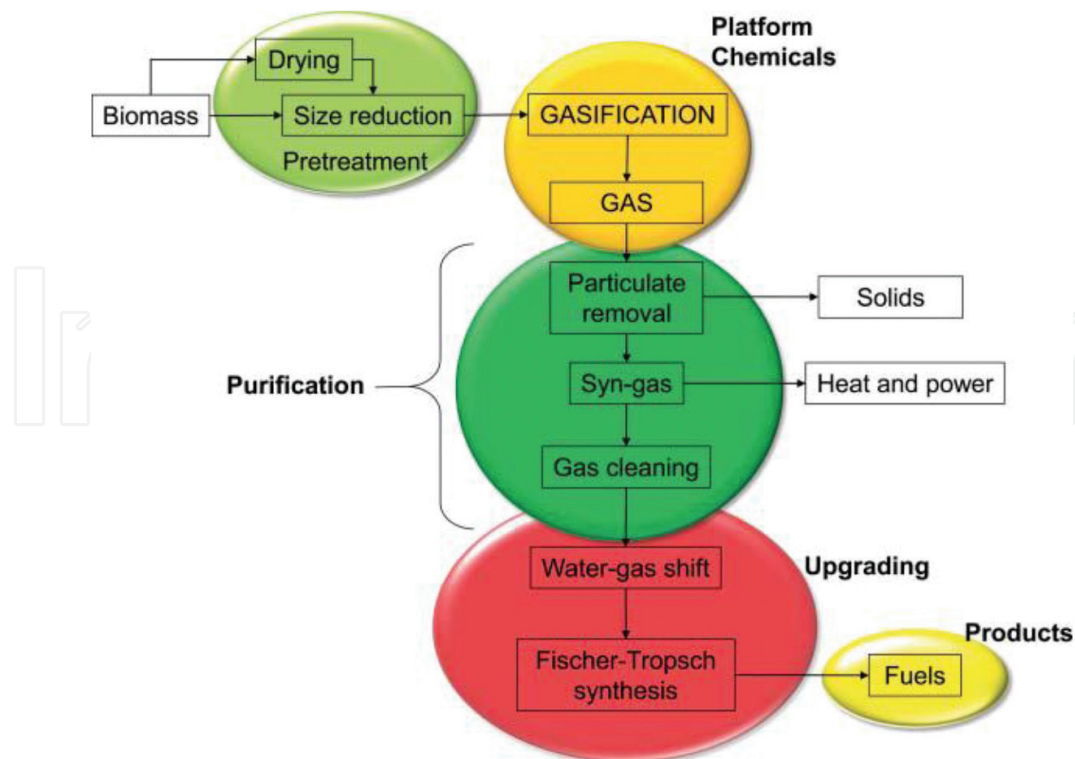


Figure 7. Process schematic of biomass gasification and upgrading [6].

2.3.1. Mechanism

It is believed that gasification involves several sequential and parallel reactions in an oxygen deficient environment. And the primary steps include drying, pyrolysis, reduction and oxidation, shown in **Figure 8**. Initially, the moisture of biomass is evaporated quickly during the drying, and this process is considered complete at 150°C. With the temperature increased, matrix carbonaceous materials, such as cellulose and lignin, are decomposed into small species by cracking of chemical bonds within a temperature range of 250–700°C, which can be simply schematized with the following overall reaction:



Several complex phenomena, such as heat and mass transfer and reaction kinetics, are involved in this stage. The reaction kinetics is the determining step at low temperatures, while the heat or mass transfer becomes the limiting step at higher temperatures. Then the reduction stage comes into play. It involves all the products of the preceding stages. The final syngas is formed through the complicated reactions between gas mixture and char. The principal reactions include carbonation of char, water gas shift reaction, methanation, tar decomposition and steam reforming [1, 52].

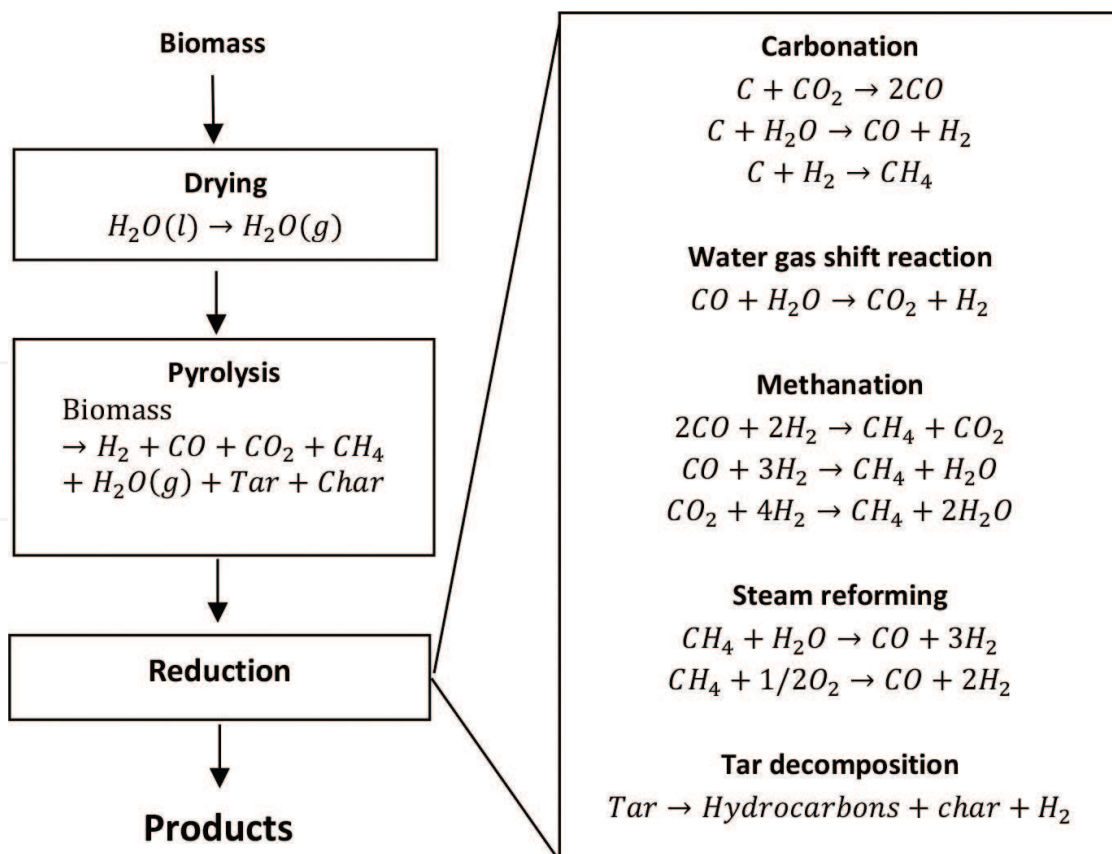


Figure 8. Main stages and the reactions involved in the gasification process [1, 52].

2.3.2. Parametric impact

There are many factors influencing the product distribution of biomass gasification, such as feedstock type, quality and moisture, particle size and density, operative conditions, the ratio of steam (or other gas) to biomass and catalysts.

2.3.2.1. Particle size and density

The smaller the particle size, the better would be the heat diffusion, which can make the temperature uniform throughout the particle, benefiting the reactions. The effect of particle size on reaction rate is more significant when there is a limitation on size above which heat transfer would be controlling [3]. In addition, the reduction in particle dimension can enhance the carbon conversion and hydrogen yield, improve the syngas efficiency and suppress the formation of tar and char [53, 54]. However, the particle size reduction requires intense energy [55].

Biomass is normally of low density due to the porous structure. The presence of the pores facilitates the heat transfer throughout the pellet, which in turn results in the homogeneous gasification and uniform product composition. As for the dense materials, there is a temperature difference between the exterior and interior of particle, leading to the simultaneous drying, pyrolysis and gasification. Accordingly, a non-homogeneous gas composition is produced.

2.3.2.2. Operating conditions

The operating conditions, including pressure, temperature, heating rate and other vital factors, have the potential to affect the gas yield and biomass conversion [54, 55]. The pressure is closely associated with bio-char reactivity and an increase in temperature would involve a faster heating rate, which generates a greater temperature difference over feedstock particles. While the fast and slower heating rate operations largely contribute to the design of gasifier and the desired products. The faster heating rate favours more gas production and less tar yield owing to the volatilization and degradation of the active tars by transforming them to the product gases. The slower heating rate contributes to lower gas yield and higher tar yield because of the recombination of lower-volatility hydrocarbons on the surface of the char particles.

2.3.2.3. Steam-to-biomass ratio

The ratio of steam to biomass (S/B) can determine the input energy requirements, outlet gas quality and yield of products. Increasing S/B ratio can positively enhance the reforming, cracking and water gas shift reactions, leading to higher hydrogen yield and consequently generating the syngas with high calorific content [56, 57]. However, there is a threshold limit beyond which increasing S/B will generate excess steam, resulting in the enthalpy loss and reduction in process efficiency [58]. This issue necessitates optimizing the ratio in steam biomass gasification.

2.3.2.4. Catalysts

Catalysts can provide an alternative lower-energy pathway for the reactions to follow. The catalysts used in the biomass gasification are categorized alkaline (Na, K) metal, alumina and zeolites, dolomites and limestones, Ni-based, Zn-based, as well as some rarer metals such as platinum- and ruthenium-based, specifically in relation with gasifier design or the type of biomass feed. Among them, alkaline metal oxides, dolomite and Ni-based catalysts have been testified to greatly promote the reformation reaction [59], and alumina silicates are found to enhance the char gasification effectively, whereas Ni-based catalysts are identified to facilitate the conversion of lighter hydrocarbons [60]. It is essential to develop more efficient and economical catalysts with the ability of enhancing the quality and yield of the desired product while minimizing the residual char and tar [1].

2.3.2.5. Feedstock.

In the case of gasification, due to the indispensable role these constituents play during the process of gasification, the proportion of cellulose and hemicellulose is closely related to the yield of the gaseous products, while the lignin has significant influence on the production of bio-oil. Generally, the higher the ratio of cellulose (including hemicellulose) to lignin in the feedstock, the higher the gaseous products yields. The moisture content of biomass affects the characteristics of the final gas products significantly. A feedstock with more than 30 wt% moisture would result in less gas production, higher tar content and more energy input. Gasification technology can be a good solution for energy production from renewable sources; however, the water and impurities in the gas products can be problematic in downstream FT processes, where a clean gas feed is required [6].

2.3.3. Application

The versatility of gasification manifests in that it can meet the demand for the electricity or thermal energy and industrial purposes. The products obtained from the biomass gasification are shown in **Figure 9**. The gas products, typically including H_2 , CO, CO_2 , CH_4 , H_2O and other gaseous hydrocarbons, can be used to generate heat or electricity by direct firing in diesel engines, gas turbines and boilers. Alternatively, the gas mixture can be further reformed to produce usable fuels such as methanol or hydrogen, which can be transported with high energy densities, enabling the generation of electricity or heat to be centralized based on disperse gasification systems. Renewable biomass is considered as a potential material for gasification to produce syngas, hydrogen or other liquid fuels; however, the economics of current processes favour the use of light hydrocarbons (in natural gas) and coal owing to the characteristic of high oxygen content in the biomass.

On the other hand, bio-syngas originated from biomass gasification can act as the raw material for Fischer-Tropsch Synthesis (FTS) to produce green liquid fuel (diesel) or high value-added chemicals. It is needed that the ratio of H_2 to CO in syngas is adjusted to an appropriate range through water gas shift reaction prior to FTS, and then the syngas is catalytically converted to liquid fuels

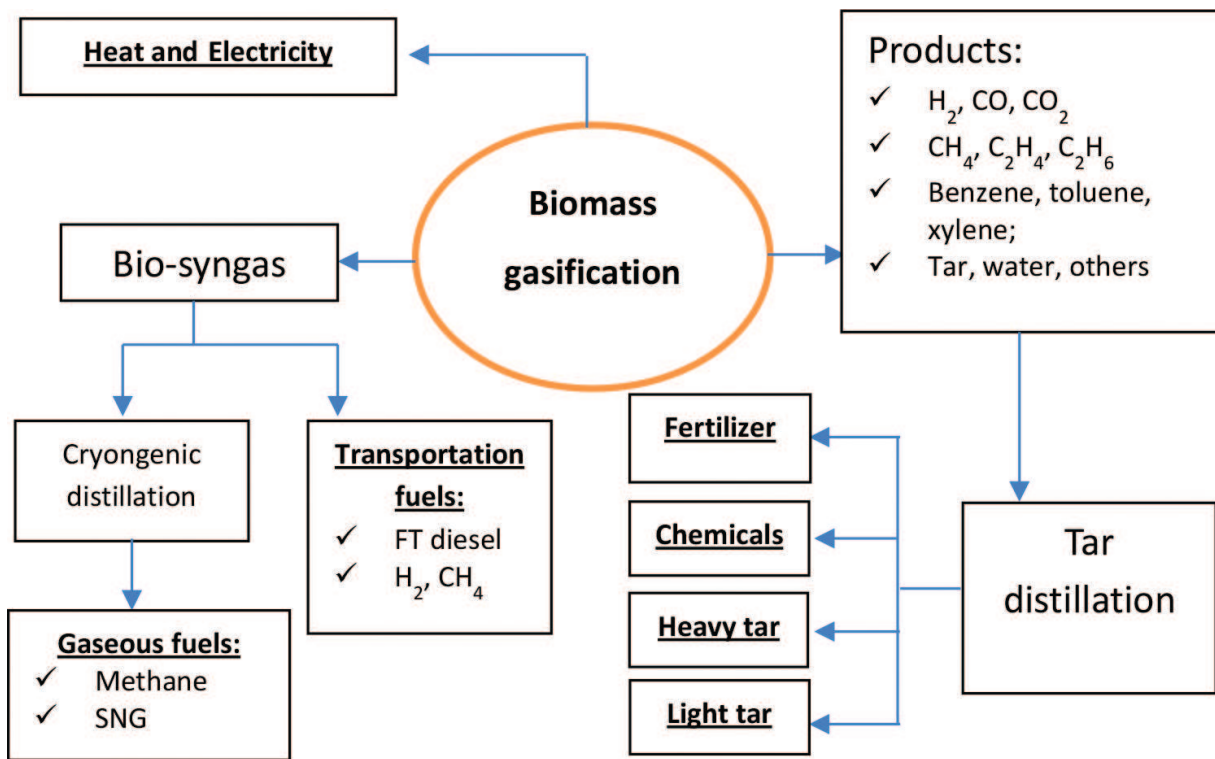


Figure 9. Products from gasification process [61].

and/or chemicals via FT process over Co-based or Fe-based catalysts. This type of synthetic FT diesel fuels has excellent quality. For instance, the emissions can be reduced significantly when fuels are employed in ignition combustion engines because of low content of nitrogenous and aromatic species. In addition, the FT fuels are sulphur-free, which is vital for lowering emissions of exhaust pollutants. Therefore, biomass gasification coupled with FT process provides a promising alternate for mitigating the burden on conventional transportation fuel; however, it requires significant development and scale-up efforts for commercial-scale installations [62].

The poly-generation concept has been developed with advancement in biomass gasification. For instance, co-generation of thermal power with electricity; poly-generation of heat, fertilizer and bio-char; poly-generation of heat, SNG/bio-fuels; and poly-generation of H_2 with heat and electricity. All these approaches not only optimize the thermal efficiency of the process but also provide flexibility and sustainability, thereby enhancing the economic advantage in the long run [3].

2.4. Biochemical transformation

Biochemical conversion of biomass involves the use of bacteria, microorganisms and enzymes to break down biomass into gaseous or liquid fuels, such as biogas or bioethanol. These processes are essentially microbial digestion and fermentation, which are most suitable for the high moisture herbaceous plants, marine crop and manure. The main products in the process are methanol, ethanol and gas mixture (CH_4, CO and CO_2) [63]. This biocatalytic process is considered to be a suitable alternative to chemical catalysis. Some important considerations when selecting the biocatalyst used for the upgrading of biomass are listed in Table 3.

(A) Source of biocatalyst	
Whole cell or free enzyme	Whole cells can also be used in permeabilized form
Wild type or mutant enzyme produced by rDNA technology	Some organisms are frequently used as the source for industrial enzymes
Refolded from IBs or use of IBs itself	Choice of the host is important. For enzymes where activity depends upon post-translational modification, higher organisms are used as host expression systems
(B) Free or immobilized form	
Soluble conjugates	For insoluble substrates (which is often the case with biomass), soluble conjugates or enzymes in membrane reactors are preferred
Carrier free or insoluble support	Enzyme aggregates like CLEA or CLEC have high volumetric activity
(C) Operational stability	This may be different from storage stability
(D) Reaction medium	The use of co-solvents is under exploited
(E) Normal or promiscuous activity	As more enzymes, engineered for better promiscuous activity, become available, this application may increase

Table 3. Summary of important parameters of biocatalysts [64].

2.5. Techno-economic analysis

Techno-economic analyses are essential for determining the economic viability of biomass conversion technologies in the research or development stage. On the basis of current performance and targets established for process improvements, evaluation of the production costs can allow us to assess the potential economic feasibility of a process configuration. These results are significant for investing in the technology with high potential for deployment success.

The economic feasibility of fast pyrolysis and upgrading facilities employing two bio-oil upgrading pathways have been evaluated based on the scale of 2000 metric tons/day and 65% biomass conversion in the literature [65]. The results showed that the hydrotreating followed by fluid catalytic cracking (FCC) pathway with hydrogen production via natural gas reforming is the best option with highest IRR (internal rate of return) of 13.3% when compared with single stage hydrotreating. According to the sensitivity analysis, product yield, fixed capital investment (FCI) and biomass cost have significant impacts on the facility IRR. Variation of 5% bio-oil yield can lead to product value (PV) of \$2.60–3.89/gal [66]. The hydrotreating/FCC pathway is proved to be of relatively low risk for project investment based on the Monte Carlo analysis.

Techno-economic analysis was implemented to assess the feasibility of developing a commercial large-scale woody biomass hydrothermal liquefaction (HTL) and upgrading plant with the scale of 2000 dry metric ton/day in the literature [67]. Two cases were involved: state-of-technology (SOT) and goal case considering future improvements. The annual production rate was estimated to be \$42.9 and \$69.9 million gallon gasoline-equivalent (GGE) for SOT

and goal case, respectively. The minimum fuel-selling price was estimated to be \$4.44/GGE and \$2.52/GGE. Obviously, the liquid fuel cost of current HTL and upgrading technologies (SOT) is not competitive with the conventional petroleum-based gasoline. For advancing SOT to goal case, future improvements of HTL competitiveness should be focused on reducing organic loss to obtain higher final yield and lowering wastewater treatment cost. Based on the sensitivity analysis, the key factors that influence the production cost significantly are plant scale, yield, upgrading equipment cost and feedstock cost. Although the goal case technology is promising for future liquid fuel production via woody biomass HTL, there are still financial risks resulting from lack of knowledge and experience.

The techno-economic analysis of green fuel production via BG-FT (biomass gasification and Fischer Tropsch) with a scale of 2000 metric tons per day of corn stover was conducted in the literature [68]. Two scenarios are considered: high temperature (HT) gasification and low temperature (LT) gasification. The results showed that the total capital investment required for nth plant scenarios are \$610 million and \$500 million for HT and LT, respectively. Product value (PV) for two scenarios were estimated to be \$4.30/GGE and \$4.80/GGE, but the HT scenario was more desirable due to its higher carbon efficiency and subsequent higher fuel yield. Based on the sensitivity analysis, the capital investment and feedstock cost are chiefly responsible for affecting the PV, whereas the conversion of FT process, feedstock moisture and catalyst cost are least influential parameters.

3. Conclusion

Pyrolysis and liquefaction are inclined to obtain more liquid products (bio-oil), but the stability of bio-oil produced in the pyrolysis process is worse than that generated in the liquefaction process. However, the interest in liquefaction is considerably lower due to the reactors and feed systems, which are more complex and expensive than that for the pyrolysis process. Therefore, upgrading bio-oil by lowering the oxygen content, removing alkalis by means of hydrogenation and catalytic cracking are required for further application of pyrolysis conversion. Catalytic cracking pyrolysis gasification has shown promising application, since the syngas can be used for the production of methanol and hydrogen, which may have a future as fuel for transportation. The economic studies show biomass gasification plants can be as economical as conventional coal fired plants. Compared with chemical catalysts in the process of biomass conversion, biocatalysts have higher selectivity to products and cheaper capital investment. However, the practical industrial application of biocatalysts is limited due to slow conversion process, high dependence of environment and feedstock and difficult recycling of the biocatalysts.

It is noteworthy that one novel technology, achieved by a green catalysis research group at the University of Calgary, is catalytic coal or biomass upgrading using natural gas for liquid chemical or fuel productions. This process directly employs methane as reducing agent instead of hydrogen for removing oxygen from biomass under the facilitation of specially developed low-cost supported catalyst, leading to significantly reduced operation cost.

Acknowledgements

We gratefully acknowledge the financial supports from Natural Sciences and Engineering Research Council of Canada (NSERC, RGPIN/04385-2014).

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