Review

Thermochemical Biomass Gasification: A Review of the Current Status of the Technology

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Abstract: A review was conducted on the use of thermochemical biomass gasification for producing biofuels, biopower and chemicals. The upstream processes for gasification are similar to other biomass processing methods. However, challenges remain in the gasification and downstream processing for viable commercial applications. The challenges with gasification are to understand the effects of operating conditions on gasification reactions for reliably predicting and optimizing the product compositions, and for obtaining maximal efficiencies. Product gases can be converted to biofuels and chemicals such as Fischer-Tropsch fuels, green gasoline, hydrogen, dimethyl ether, ethanol, methanol, and higher alcohols. Processes and challenges for these conversions are also summarized.

1. Bioenergy and the Role of Biomass Gasification

The demand for energy sources to satisfy human energy consumption continues to increase. Prior to the use of fossil fuels, biomass was the primary source of energy for heat via combustion. With the introduction of fossil fuels in the forms of coal, petroleum and natural gas, the world increasingly became dependent on these fossil fuel sources. Currently, the main energy source in the world is fossil fuels. The use of plastics and other chemicals which are derived from these fossil fuels also have increased. These tremendous increases have led to many concerns. Although it is not known how much fossil fuel is still available, it is generally accepted that it is being depleted and is non-renewable. Given these circumstances, searching for other renewable forms of energy sources is reasonable. Other consequences associated with fossil fuel use include the release of the trapped carbon in the fossil fuels to the atmosphere in the form of carbon dioxide which has led to increased concerns about global warming. Also, fossil fuel resources are not distributed evenly around the globe which makes many countries heavily dependent on imports.

Biomass combines solar energy and carbon dioxide into chemical energy in the form of carbohydrates via photosynthesis. The use of biomass as a fuel is a carbon neutral process since the carbon dioxide captured during photosynthesis is released during its combustion. Biomass includes agricultural and forestry residues, wood, byproducts from processing of biological materials, and organic parts of municipal and sludge wastes. Photosynthesis by plants captures around 4,000 EJ/year in the form of energy in biomass and food. The estimates of potential global biomass energy vary widely in literature. The variability arises from the different sources of biomass and the different methods of determining estimates for those biomasses. Fischer and Schrattenholzer estimated the global biomass potential to be 91 to 675 EJ/year for the years 1990 to 2060 [1]. Their biomass included crop and forestry residues, energy crops, and animal and municipal wastes. Hoogwijk estimated these to be 33 to 1135 EJ/year [2]. Biomass included energy crops on marginal and degraded lands, agricultural and forestry residues, animal manure and organic wastes. Parikka estimated the total worldwide energy potential from biomass on a sustainable basis to be 104 EJ/year, of which woody biomass, energy crops and straw constituted 40.1%, 36% and 16.6%, respectively [3]. Only about 40% of potential biomass energy is currently utilized. Only in Asia, does the current biomass usage slightly exceed the sustainable biomass potential. Currently, the total global energy demand is about 470 EJ/year. Perlack estimated that, in the United States, without many changes in land use and without interfering with the production of food grains, 1.3 billion tons of biomass can be harvested each year on a sustainable basis for biofuel production [4]. 1.3 billion tons of biomass is equivalent to 3.8 billion barrels of oil in energy content. US equivalent energy consumption is about 7 billion barrels per year [5]. However, harvesting, collecting and storage of biomass adds another dimension of technical challenges to the use of biomass for production of fuels, chemicals and biopower [6].

Two main ways of converting biomass energy (solid fuel) into biofuels and biopower are biochemical conversion and thermochemical conversion processes. Biochemical conversions convert the biomass into liquid or gaseous fuels by fermentation or anaerobic digestion. Fermentation of the biomass (starch and cellulose) produces primarily ethanol. Anaerobic digestion leads to the production of gaseous fuel primarily containing methane. The details of biochemical conversions are outside the intended scope of this manuscript.

Thermochemical conversion technologies include combustion, gasification and pyrolysis. While combustion of biomass is the most direct and technically easiest process, the overall efficiency of generating heat from biomass energy is low. Gasification has many advantages over combustion. It can use low-value feedstocks and convert them not only into electricity, but also into transportation fuels. In the upcoming years, it will serve as a major technology for complementing the energy needs of the world [7]. Use of advanced technologies such as gas turbines and fuel cells with the syngas generated from gasification results in increased efficiency [8]. For complete combustion of solid fuels, excess air is needed, and high combustion temperatures generate more NO_x and other emissions, as compared with the combustion of products by gasification. During combined cycles for combined heat and power generation, contaminants in the syngas such as sulfur and nitrogen species and trace elements are removed efficiently resulting in much lower emissions [9]. Moreover, liquid and gaseous fuels are more of interest because of their ease of handling and operations, and their applications as transportation fuels.

High oxygen content in biomass reduces the energy density of the biomass. The production of hydrocarbons, similar to petroleum transportation fuels, requires the removal of oxygen from the carbohydrate structure. The oxygen may be removed in the forms of CO_2 and H_2O. Thermochemical conversion of biomass to syngas is an attractive route to extract the oxygen from carbohydrate structures to produce intermediate compounds having C_1 (CO and CH_4), which can be further synthesized into hydrocarbons by catalysis or fermentation. Other thermochemical schemes of decarboxylation (CO_2 removal) and dehydration (H_2O removal) from carbohydrates result in higher hydrocarbons (higher than C_2) having undesired properties which require further conversion to be compatible with transportation fuels [10].

Thermochemical conversion technologies have certain advantages and disadvantages over biochemical conversion technologies. The main advantages are that the feedstock for thermochemical conversion can be any type of biomass including agricultural residues, forestry residues, non-fermentable byproducts from biorefineries, byproducts of food industry, byproducts of any bioprocessing facility and even organic municipal wastes; and the product gases can be converted to a variety of fuels (H_2, Fischer-Tropsch (FT) diesels, synthetic gasoline) and chemicals (methanol, urea) as substitutes for petroleum-based chemicals; the products are more compatible with existing petroleum refining operations. The major disadvantages are the high cost associated with cleaning the product gas from tar and undesirable contaminants like alkali compounds, inefficiency due to the high temperatures required, and the unproven use of products (syngas and bio-oil) as transportation fuels. However, research on the optimization of gasifier operating conditions and heat recovery, syngas cleaning, bio-oil stabilization, and efficient product utilization can make the process important for sustainable production of biofuels. With life cycle assessment, Wu concluded that use of cellulosic biofuels (ethanol via gasification and fermentation, FT diesel and dimethyl ether (DME) from biomass, etc) in light duty locomotives results in significant savings of fossil fuel resources and reduction in green house gases [11]. Co-production of cellulosic biofuels and power generation by GTCC consumes the least fossil fuel resources and results in the greatest reduction in green house gas (GHG) emissions on a per-mile basis, of the thermochemical conversion techniques.

There have been substantial efforts to generate both gaseous and liquid fuels from coal gasification during the 1970s oil embargo. However, after that the continued low price of petroleum resources

halted the major research, development and commercialization of these technologies. Biomass gasification differs from coal gasification. Biomass is a carbon-neutral and sustainable energy source unlike coal. Because biomass is more reactive and has higher volatiles content than coal, biomass gasification occurs at a lower temperature. Lower temperature reduces the extent of heat loss, emissions and material problems associated with high temperatures. Biomass also has low sulfur content, which results in lower SO_x emission. But the high alkali contents in biomass, like sodium and potassium, cause slagging and fouling problems in gasification equipment [12].

The main steps involved in the gasification process can be categorized as upstream processing, gasification and downstream processing (Figure 1).

Figure 1. Processes involved in biomass gasification.
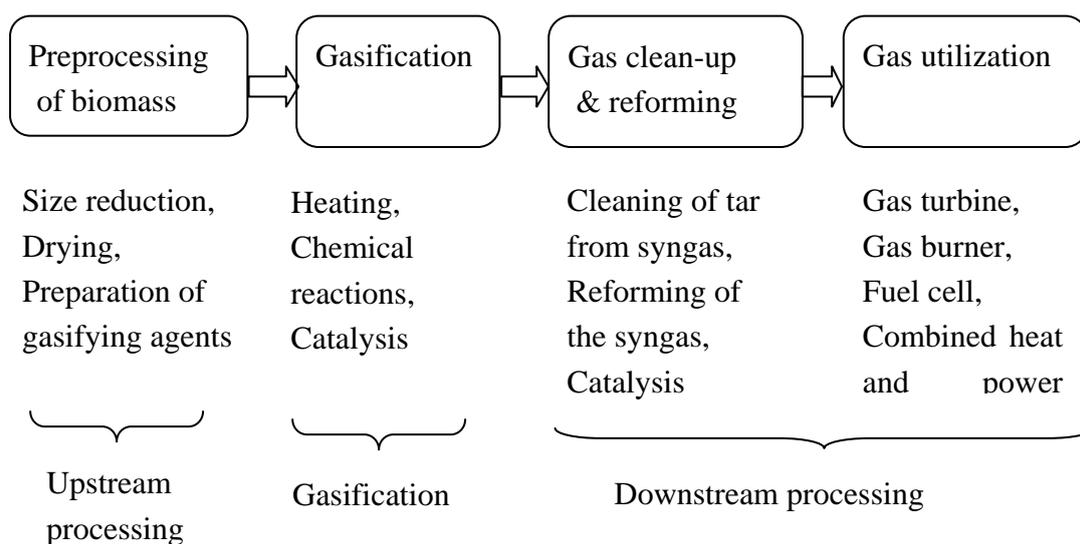
2. Upstream Processing

Upstream processing includes processing of the biomass to make it suitable for gasification operations. Size reduction is needed to obtain appropriate particle sizes. Drying is needed to achieve appropriate moisture so that the process can work efficiently. Densification also may be necessary due to the low density of biomass.

2.1. Size reduction

Smaller particles have larger surface areas per unit mass and larger pore sizes which facilitate faster rates of heat transfer and gasification [13]. Lv observed that smaller particles resulted in more CH_4, CO, C_2H_4 and less CO_2 which led to higher gas yields, gas energy content (LHV) and carbon conversion efficiency (C_{eff}) [14]. Rapagna reported increases in gas yield and gas compositions of CO, CH_4 and CO_2, when the particle size was reduced from largest (1.090 mm) to smallest (0.287 mm) [15]. By decreasing the particle size from 1.2 mm to 0.075 mm, it was observed that H_2 and CO contents as well as gas yield and carbon conversion efficiencies increased whereas the CO_2 decreased [16]. Higher gas yields and energy efficiencies were attributed to the increased heat transfer in smaller size particles due to the larger surface area.

Hammer-mills, knife mills and tub grinders are typical instruments used for reducing the particle sizes of agricultural and forestry residues. Hammer mills are used both for dry agricultural and dry forestry residues. Tub grinders are small, mobile hammer-mills. Screens are used in the mills to assure the ground particles have certain maximum size [17]. Energy consumption during size reduction depends on the moisture content, initial size of biomass, biomass properties, and screen size of the mill and properties of the mill. Mani conducted tests of grinding performance on corn stover, barley straw, wheat straw and switchgrass, and found that the corn stover consumed the least specific energy during hammer mill grinding [18]. On the other hand, switchgrass used the most specific energy probably because of its fibrous nature.

2.2. Drying

Biomass collected from farm and forest lands may contain high moisture. Drying is needed to obtain a desired range of water content for the gasification processes. Drying is an energy intensive process which may decrease the overall energy efficiency of the process. However, in case of gasification, waste heat can be utilized to decrease the moisture content of the biomass which will increase the overall efficiency of the process. Perforated bin dryers, band conveyor dryers and rotary cascade dryers have been used to dry biomass [17]. In the case of generating combined heat and power, biomass moisture should be as low as possible to increase the overall efficiency and decrease the net cost of electricity. However, for low moisture raw biomass (less than 10%) drying stage may not be needed [19].

3. Gasification

Gasification is the heart of the process. The main operating parameters of the gasifier include type and design of gasifier, gasification temperature, flow rates of biomass and oxidizing agents (air or steam), type and amount of catalysts, and biomass type and properties.

3.1. Types of gasifier

Gasifiers are categorized based on types of bed and flow. The gasifier bed can be a fixed-bed or a fluidized bed. Fixed bed gasifier can be classified further as updraft (countercurrent) or downdraft (concurrent). In the updraft gasifier, the feed (biomass) is introduced from the top and moves downwards while gasifying agents (air, steam, etc.) are introduced at the bottom of the grate so the product gas moves upwards. In this case, the combustion takes place at the bottom of the bed which is the hottest part of the gasifier and product gas exits from the top at lower temperature (around 500 ℃). Because of the lower exit temperature, the product gas contains large amounts of tar. In a downdraft gasifier, both the feed and product gas moves downward and the product exits from the bottom at a higher temperature, i.e., around 800 ℃. In this case, most of tars are consumed because the gas flows through a high temperature region. However, heat needs to be recovered from high temperature product gas to increase the energy efficiency. These two types of gasifiers, updraft and downdraft, have been used most extensively in the past.

In the fluidized bed gasifier, the feed is introduced at the bottom, which is fluidized using air, nitrogen and/or steam and the product gas then moves upward. There are more particulates in the product gas from this gasifier [20]. Fluidization of the bed enhances the heat transfer to the biomass particle leading to increases in reaction rates and conversion efficiencies. Fluidized beds also are able to tolerate a wide variation in fuel types and their characteristics. A fluidized bed can be either a bubbling fluidized bed or a circulating fluidized bed. In case of the bubbling fluidized bed gasifier, the flow rate of the fluidizing agent is comparable to the minimum fluidizing velocity. Uniform temperature across the bed can be maintained by fluidization resulting in uniform product gases. The fluidizing mediums used are generally silica or alumina materials which have high specific heat capacity and can operate at high temperature. Catalysts also can be added as fluidizing agents which can increase the conversion efficiency and reduce tar formation. However, fluidized catalysts are more susceptible to attrition and poisoning. There is a need for robust catalysts that are effective at high temperature (800 ℃ or more) in the fluidized medium. Some of the catalysts that have been investigated are discussed in detail in the in-bed catalyst section. Circulating fluidized beds have higher flow rates of the fluidizing agents which move most of the solid and ungasified particles to an attached cyclone separator, from which the solids are re-circulated to the gasifier bed. The higher flow of gasifying agent increases the heat transfer and conversion rate of the biomass.

The advantages and disadvantages of each type of gasifiers have been summarized by Warnecke [21]. Gasifiers also can be categorized by the method of heat source provided for the endothermic gasification reactions. Heat can be supplied to the gasifier indirectly or directly. In a directly-heated gasifier, part of biomass is allowed to combust inside the gasifier. The combustion then raises the temperature and provides the required heat for the endothermic gasification reactions. In the case of an indirectly heated gasifier, biomass or ungasified char is combusted in a separate chamber and heat exchanger tubes conduct the heat from the combustion chamber to the gasification chamber [12].

3.2. Gasification process

Gasification takes place at high temperature in the presence of an oxidizing agent (also called a gasifying agent). Heat is supplied to the gasifier either directly or indirectly which raises the gasification temperature of 600–1,000 ℃. Oxidizing agents are typically air, steam, nitrogen, carbon dioxide, oxygen or a combination of these. In the presence of an oxidizing agent at high temperature, the large polymeric molecules of biomass decompose into lighter molecules and eventually to permanent gases (CO, H_2, CH_4 and lighter hydrocarbons), ash, char, tar and minor contaminants. Char and tar are the result of incomplete conversion of biomass.

The overall reaction in an air and/or steam gasifier can be represented by Equation 1, which proceeds with multiple reactions and pathways. Equations 2–8 are common reactions involved during gasification. Among these, Equations 4–7 occur when steam is available during gasification. Many authors have studied the degradation kinetics of various biomass feedstocks (rice husk, pine chips, wheat straw, rapeseed straw, pigeon pea stalk, etc.) using thermogravimetric analyses (TGA). TGA provides the weight loss of any material with change in temperature. The weight loss (or thermal degradation) in a nitrogen atmosphere occurred in mainly three stages; with the first stage being

dehydration (below 125 °C), the second stage being active pyrolysis (125–500 °C) and the third stage being passive pyrolysis above 500 °C. The dehydration reflects loss of water, the active pyrolysis reflects the loss of the hemicellulose, cellulose and part of lignin, and the passive pyrolysis reflects the slow and continuous loss of residual lignin. The temperature ranges of these stages and the kinetic parameters of the degradations depend primarily on the rate of heat transfer, the composition of the biomass, and the degree of the oxidizing environment [22–25].

$$CH_xO_y \text{ (biomass)} + O_2 \text{ (21\% of air)} + H_2O \text{ (steam)}$$
$$= CH_4 + CO + CO_2 + H_2 + H_2O \text{ (unreacted steam)} + C \text{ (char)} + tar \tag{1}$$

$$2C + O_2 = 2CO \text{ (partial oxidation reaction)} \tag{2}$$

$$C + O_2 = CO_2 \text{ (complete oxidation reaction)} \tag{3}$$

$$C + 2H_2 = CH_4 \text{ (hydrogasification reaction)} \tag{4}$$

$$CO + H_2O = CO_2 + H_2 \text{ (water gas shift reaction)} \tag{5}$$

$$CH_4 + H_2O = CO + 3H_2 \text{ (steam reforming reaction)} \tag{6}$$

$$C + H_2O = CO + H_2 \text{ (water gas reaction)} \tag{7}$$

$$C + CO_2 = 2CO \text{ (Boudourd reaction)} \tag{8}$$
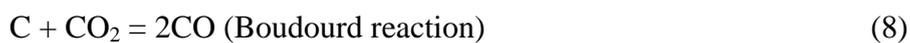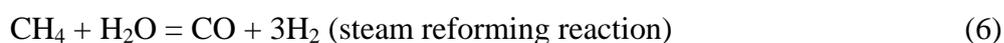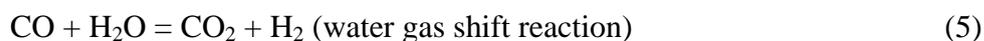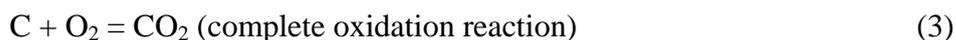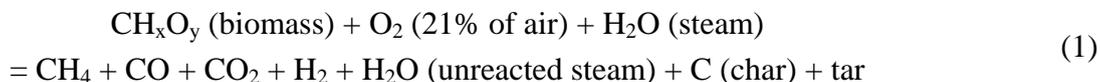
3.3. Effects of gasification operating conditions on the product properties

To obtain the desired product gas composition, the least amount of impurities, and to increase the net energy conversion efficiency, the gasification operating conditions need to be optimized. The following section describes the effects of the main operating conditions on the quantity and composition of the product gas and its impurities.

3.3.1. Biomass flow rate, type and properties

Overfeeding of biomass can lead to plugging and reduced conversion efficiencies whereas starve-feeding results in less gas yield. Hence, an optimum biomass flow rate is desired for the gasification system to maximize energy efficiency. Optimum biomass flow rate is dependent primarily on the design of the gasifier and the properties of the biomass.

The main constituents of lignocellulosic biomass are cellulose, hemicellulose and lignin. Cellulose is a linear polymer of D-glucose (a six-carbon sugar) linked with β-1,4 linkages; hemicellulose is a branched polymer with both five carbon and six-carbon sugars, and lignin is a randomly constructed and highly aromatic cross-linked macromolecule. Herbaceous crops and wood contain 60–80% (db) cellulose and hemicellulose, and 10–25% lignin [5]. The composition of these polymers in the biomass affects the product composition. Hanaoka observed that at 900 °C, carbon conversion efficiencies of cellulose, xylan and lignin were 97.9%, 92.2% and 52.8%, respectively [26]. The product compositions from gasification of xylan and lignin were similar. Cellulose resulted in higher CO

(35 vs. 25 mol %) and CH_4 (6 vs. 5 mol %) but lower CO_2 (27 vs. 36 mol %) and H_2 (29 vs. 33 mol %) yields than those of xylan and lignin. Barneto observed that composting of biomass increased the lignin content in the compost, which resulted in up to 20% increased H_2 production at a slow heating rate as compared to the original biomass at a fast heating rate [27].

Co-firing of biomass with coal also is being studied. Kumabe observed that by varying the ratio of coal to biomass for the gasification, the extent of the water gas shift reaction was maximal at the ratio of 0.5 which they attributed to the synergy between the coal and biomass [28]. With increase in biomass ratio, they observed increases in gas and CO_2 yields, decreases in char, tar and H_2 but CO, and hydrocarbons (HCs) were unchanged. Gasification of coal with biomass reduces problems associated with high ash and sulfur contents of the coal [29].

3.3.2. Air flow rate (equivalence ratio, ER or superficial velocity, SV)

Equivalence ratio (ER) and superficial velocity (SV) are measures of the air (or oxygen) flowrate. ER is the ratio of air flow to the airflow required for stoichiometric combustion of the biomass, which indicates extent of partial combustion. The SV is the ratio of air flow to the cross-sectional area of the gasifier which removes the influence of gasifier dimension by normalization [30]. Hence, both ER and SV are directly proportional to the airflow. Air flow influences the gasification products in different ways. Air supplies the O_2 for combustion (and fluidization in the case of fluidized bed) and effects the residence time. By varying amount of the O_2 supply, air flow rate controls the degree of combustion which in turn, affects the gasification temperature. Higher airflow rate results in higher temperature which leads to higher biomass conversion and a higher quality of fuel. But, an excess degree of combustion, on the other hand, results in decreased energy content of the gas produced because a part of biomass energy is spent during combustion. Higher airflow also shortens the residence time which may decrease the extent of biomass conversion.

With an increase in ER (from 0.20 to 0.45), Narváez observed an increase in gas yield, a decrease in lower heating value (LHV) of the gas and decreased contents of H_2, CO, CH_4 and C_2H_2 and tar [31]. Lv reported that with an increase in ER from 0.19 to 0.27, the H_2 content varied a little but gas yield increased and then decreased with an optimal ER of 0.23 [32]. Wang found that with an increase in ER from 0.16 to 0.26, the bed and freeboard temperatures increased resulting in a higher yield and higher heating value (HHV) of the gas, an increase in cold gas efficiency from 57% to 74%, an increase in H_2 content from 8.5% to 13.9%, and an increase in CO content from 12.3% to 14% [33]. Kumar observed increases in gas yields, carbon conversion and energy efficiencies with an increase in ER from 0.07 to 0.25 [34]. All authors reported increases in gas yields with increases in ER (from 0.0 to 0.45). However, contradictory results of decreases in H_2 and CO yields with increases in ER also have been reported [35]. The increase in gas yield with increase in ER implies that an increased airflow increases conversion rate. Some of the contradictory results on the effects of ER on the contents of H_2, CO and CH_4 (%) is logical because the percentage compositions of individual gases depend on both the yield of individual gases and the overall gas yield. If the increase in overall gas yield is more pronounced than the increase in individual gas yield, then the percentage composition of individual gas decreases, even though the individual gas yield may actually have increased. Effects of ER on the product gas composition also depend upon other factors such as temperature and steam to biomass ratio. During

steam gasification, at high temperature, the H_2 yield is more pronounced than the increase in gas yield which results in an increase in H_2 content.

3.3.3. Steam flow rate (steam to biomass ratio, S/B)

Supplying steam as a gasifying agent increases the partial pressure of H_2O inside the gasification chamber which favors the water gas, water gas shift and methane reforming reactions (Equations 5–7), leading to increased H_2 production. However, the gasification temperature needs to be high enough (above 750–800 ℃) for the steam reforming and water gas reactions to be favorable [34,36,37]. Catalysts can lower the operating temperature needed for the above reactions to occur. Higher S/B also leads to higher biomass conversion efficiency [38].

Reduction in tar also is observed at higher steam to biomass ratios, which is attributed to steam reforming of the tar with an increased partial pressure of steam. Narváez found that with an increase in H/C ratio (H and C from incoming biomass, moisture and steam) from 1.6 to 2.2, H_2 content increased, LHV increased from 4 to 6 MJ/Nm^3 and tar content decreased from 18 to 2 g/Nm^3 [31]. By varying S/B from 0 to 4.04, Lv observed that with S/B higher than 2.7, the gas composition did not change significantly but, with S/B between 0 and 1.35, CO yield decreased, and CH_4, CO_2 and C_2H_4 yields increased [32]. With S/B of 1.35 and 2.70, the CO and CH_4 yields decreased and CO_2 and H_2 yields increased which implied higher steam reforming reactions. Turn observed that increasing S/B from 1.1 to 4.7 decreased CO, CH_4, C_2H_2 yields, and increased H_2 and gas yields [35]. H_2 increased from 46 to 83 g per kg dry and ash-free (daf) biomass. Since the temperature of the steam supplied to the gasifier is lower than the gasification temperature, a significant amount of heat is needed to raise the steam temperature which, in turn, may lower the temperature of the gasifier bed. Hence an S/B ratio above a threshold, steam had negative effects on the product.

Increasing the temperature of the gasifying agents led to an increase in the heating value of the fuel gas, and reduces the tars, soot and char residues [36]. A preheater is recommended before the introduction of gasifying agents (steam and air) to the gasifier to facilitate higher gasification bed temperature.

3.3.4. Gasification temperature profile

Gasification temperature is one of the most influential factors affecting the product gas composition and properties. Higher temperature results in increased gas yield because of higher conversion efficiency. Since, the reactions (Equations 5–8) occur simultaneously, the contents and ratios of H_2, CO, CO_2 and CH_4 in the product gas are affected by temperature and partial pressures of reactants.

At temperatures above 750–800 ℃, the endothermic nature of the H_2 production reactions (steam reforming and water-gas reactions) results in an increase in H_2 content and a decrease in CH_4 content with an increase in temperature. At temperatures above 850–900 ℃, both steam reforming and the Boudouard reactions (Equations 6–8) dominate, resulting in increases in CO content. High temperature also favors destruction and reforming of tar (Equations 9–10) leading to a decrease in tar content and an increase in gas yield [31,34,37,39,40]. Gupta and Cichonski observed significant increases in H_2 above 800 ℃ for S/B between 0.5 and 1.08 [37]. Maximal H_2 yield was obtained at 1,000 ℃ for a feedstock consisting of paper, and 900 ℃ feedstocks consisting of cardboard and wood pellets.

González observed that in air gasification contents of H_2, CO increased from 700 to 900 °C, whereas contents of CH_4 and CO_2 decreased [40]. They also observed that the CO/CO_2 ratio linearly increased from 0.85 at 700 °C to 2.7 at 900 °C in two segments. At 700–800 °C, the slope was 0.0067 and then almost doubled to 0.113 at higher than 800 °C which showed the predominance of the Boudouard reaction at higher temperatures. It was also observed that higher temperatures (700 to 950 °C) increased the gas yield and overall energy content of the gas [38,41]. Kumar observed that an increase in temperature (furnace set point from 750 to 850 °C), led to increases in energy and carbon conversion efficiencies and percent gas compositions of H_2 [34]. Turn found that with an increase from 750 to 950 °C, H_2 increased from 31% to 45%, CH_4 and CO remained fairly constant, CO_2 decreased and gas yield increased [35]. Boateng reported that with an increase in gasification temperature from 700 to 800 °C, gas yield, gas HHV, energy efficiency, carbon conversion efficiency and H_2 content increased and CH_4, CO and CO_2 contents decreased [42]. The decrease in CO content may have been due to the comparatively lower temperature (than 850–900 °C) for the Boudouard reaction to predominate.

$$C_nH_x = nC + x/2 \ H_2 \tag{9}$$

$$C_nH_x + mH_2O = nCO + (m + x)/2 \ H_2 \ (\text{reforming reaction}) \tag{10}$$

4. Downstream Processing

The product gas from biomass gasification needs to be processed further for effective utilization. The processes involved are, overall, termed as downstream processing. Cleaning of tar and other contaminants from product gas, biopower generation, reforming and conversion to biofuels constitute the downstream processing operations. The product gas contains particulates, tar, alkali compounds, and nitrogen and sulfur containing compounds which typically need to be removed before the product gas is used. Reforming reactions change the gas composition of the product gas as desired for the specific syngas utilization. For example, high H_2 content is desired for fuel cell applications, and specific ranges of CO/H_2 are desired for producing other fuels and chemicals from syngas. Tolerable amounts of the contaminants in the syngas depend on the syngas applications. Combustion systems can work with relatively high amounts of tar but hydrocarbon conversion catalysts and fuel cells need syngas with low levels of tar.

4.1. Syngas cleaning

4.1.1. Particulate removal

The product gas stream from the gasifier typically contains particulates. The particulates consist of unconverted biomass material (ash and char) and bed material. Ash materials are the mineral components of the biomass; char is the unconverted portion of the biomass which is less reactive, resulting in decreased carbon conversion efficiency, and the fines from the bed material also are entrained with the gas stream. Particulate deposition in the downstream equipment causes plugging and results in higher wear.

Cyclone separators are widely and routinely used to separate the larger particulates (above 5 μm in diameter) at the initial cleaning stage with little pressure drop. These are inexpensive to build and operate. The design methodology for cyclone separators is available [43–45]. Generally, multiple cyclones are used to increase separation efficiency. Wet scrubbers, various barrier filters and electrostatic precipitators subsequently separate smaller particulates.

Wet scrubbers remove particulates using liquid sprays (usually water) on the gas stream. These can remove 95–99% of over 1 μm particle size and 99% of over 2 μm with pressure across the venturi of 2.5 to 25 kPa [46]. However, wet scrubbers are used at less than 100 ℃ which results in loss of sensible heat. Hotter gas is desired, especially, for many applications such as in gas turbines and reforming reactions.

Electrostatic precipitators (ESP) apply electrical voltage to charge and then separate particulates. The separation efficiency depends on particulate resistivity, and sulfur and alkali contents. Because of its large size and high capital cost, it is suited for large-scale operations.

Barrier filters allow the gas to pass through various porous media collecting the particulates of 0.5 to 100 μm. Because of the smaller pore size, it increases the pressure differential across the filter. Common types of barrier filters are (a) metal or ceramic porous candle filters, (b) bag filters, and (c) packed bed filters. Candle filters can operate at high temperature (ceramic more than metallic) which makes them attractive for hot gas cleaning. Ceramic filters have been tested in a gasifier operated at about 700 ℃ gas temperature. Bag filters are constructed of woven material which collect smaller particles of even sub-micron size, and can operate at temperatures of about 350 ℃. Packed bed filters use bed materials such as ceramic spheres and sawdust to capture the particulates as gas flows through it [47].

4.1.2. Alkali removal

Significant amounts of alkali compounds (CaO, K_2O, P_2O_5, MgO, Na_2O, SiO_2, SO_3) are present in biomass. These alkali compounds can vaporize at temperatures above 700 ℃ during gasification which, when condensed (below about 650 ℃), form particles (<5 μm) in the downstream equipment (gas turbine, heat exchanger), stick to the metal surfaces, and result in corrosion. Moreover, alkali salts inactivate the catalysts used in tar cracking, reforming and converting syngas into hydrocarbons. Removal of alkali can be performed by cooling the gas and then passing it through barrier filters. Hot gas removal of alkali compounds holds promise, particularly for high temperature applications. However, research on hot gas alkali removal is still in the experimental stage [47]. Turn reported that a bauxite filter at 650–725 ℃ removed most of the Na and K compounds [48].

4.1.3. Nitrogen compounds

When gasified, the nitrogen content of the biomass (0.5–3%) results primarily in ammonia (60–65%) and molecular nitrogen. Unlike coal gasification, conversion to hydrogen cyanide is very low in biomass gasification [49]. If not removed, combustion of part of ammonia (occurring at temperatures above 1,000 ℃, typical of combustion) results mostly in NO_x formation. If cold product gas is desired, ammonia can be removed by wet scrubbing. Hot gas cleaning for ammonia can be performed by

destructing ammonia at higher temperature using dolomites, nickel-based catalysts and iron-based catalysts [50].

4.1.4. Sulfur compounds

Most biomass contains very little sulfur (<0.5%), which, during gasification, is converted to H_2S and SO_2. Because of the low sulfur content in biomass, as compared to coal, the gas sulfur content in the gas is low enough to meet the needs of most applications. But for a few applications, such as methanol synthesis, even a low sulfur level can irreversibly inactivate the catalysts. Fuels cells and some tar catalysts also are sensitive to sulfur. SO_2 in syngas can be removed by wet scrubbing. SO_2 and H_2S are the predominant sulfur compounds in the exit gas, in the cases of coal combustion and gasification, respectively. Limestone, dolomite or CaO are used for SO_2 and H_2S removal because of their low cost and wide availability. Calcination processes are advantageous for SO_2 removal whereas cleaning at 600–900 ℃ and regeneration of sorbents is the best scrubbing process for H_2S removal from hot gas [51].

4.1.5. Tar removal

Tar is a generic term used for all organic compounds found in the product gas with the exception of gaseous hydrocarbons. Tar is the part of the biomass which does not decompose completely into lighter gases. Removal of tar is one of the biggest technical challenges facing the commercialization of gasification technology [52]. The high-temperature product gas from a gasifier contains tar. If not removed, the tar condenses on the wall of the downstream equipment such as heat exchangers, combustion engine, reactors or fuel cells [53]. Measurement of tar has been improved over the years to maintain consistency among different tar measurement techniques [54,55].

The primary organic compounds in tar can be grouped as mixed oxygenates, phenolic ethers, alkyl phenolics, heterocyclic ethers, poly-aromatic hydrocarbons (PAH) and larger PAH. The composition shifts from larger molecules (e.g., larger PAH) to smaller molecules (e.g. mixed oxygenates) with increased reaction severity [46,47]. During gasification, reaction severity can be increased by increasing the temperature, flow of oxidizing agents or amount of catalysts.

Tar is less problematic for combustion of product gas because tar also can combust and add to the calorific value of the fuel, although less readily and at higher temperatures. Other applications, wherein the gas stream is cooled, result in condensation of the tar. Tars also are detrimental to catalysts used for conversion of syngas and fuel cell applications.

Tar removal techniques are categorized as: (a) primary removal techniques and (b) secondary removal techniques. Primary removal techniques refer to techniques that reduce the tar content in the syngas and are employed inside the gasifier without the need of a secondary reactor. Primary removal methods include design and optimization of the gasification operating conditions, and addition of catalysts in the gasifier bed (called in-bed catalysts). Secondary tar removal techniques use a separate reactor to destruct and reform the tar content below acceptable level in the product gas. Secondary tar cleaning techniques are divided further into wet and hot gas cleaning. Devi reviewed the methods for removing tar from syngas, with a focus on primary tar removal methodologies [56].

Effects of operating conditions (A primary removal technique)

Numerous studies have shown that the gasification operating parameters, primarily gasification temperature profile, ER, type of gasifying agent, S/B, total gasifying agent to biomass ratio, and feed rate are effective in reducing the amount of tar in the syngas. Effects of the operating conditions on the amount of tar in the product gas have been described in the previous section. In general, higher temperature, ER, and S/B results in product gas with less tar due to their contributions to destruction of tar. Yamazaki found that, in a downdraft gasifier, a higher SV of 0.7 m/s resulted in higher amount of tar as compared to a lower SV of 0.4 m/s [30]. According to them, higher SV resulted in shorter residence time and channeling which may have led to higher amounts of tar. However, a SV of 0.4 to 0.6 m/s were able to produce gas suitable for use in internal combustion engines. Particle yield also increased with increasing SV. Various gasifier designs, such as secondary injection of air or oxygen into the gasifier and two-stage gasification systems, also can result in lower tar contents [56].

In-bed catalyst (A primary removal technique)

The addition of catalysts such as dolomite, limestone, olivine, alkali carbonates, Ni-based catalysts, metal-oxide catalysts, zeolite or char in the gasifier bed, either with or without sand along with the biomass feed, help reduce tar and increase the extent of reforming reactions in the gasifier, thereby increasing overall carbon conversion efficiency.

Rapagna compared the performances of sand, dolomite and olivine particles as bed materials in a bubbling fluidized bed lab-scale gasifier [57]. They observed that the gas yield increased by more than 50%, tar was reduced by 20 times and char was reduced by 30% when dolomite or olivine was used as a bed material as compared to using sand. However, methane content was almost the same which indicated that the olivine and dolomite catalyzed tar destruction, but not methane reforming. Mechanical strengths of olivine and sand were similar but dolomite resulted in more fines. Asadullah found the amount of tar was negligible when using $Rh/CeO_2/SiO_2$ catalysts as compared to 30, 113 and 139 g/m^3 observed for commercial steam reforming catalyst G-91, dolomite and non-catalyst systems, respectively, in the bed for low temperature (823–973 K) fluidized-bed gasification [58,59]. Deactivation was not severe in the 20 h test probably because carbon conversion efficiency was high leaving less char in the bed.

In-bed catalysts reduce tar content but complete tar removal (satisfactory for downstream processing) is not achieved without the use of secondary reactors [52]. Also, it should be noted that the optimized operating conditions, gasifier designs and the application of in-bed catalysts for tar reduction using primary methods may not be optimum conditions for yield, composition, and energy content of the syngas. Therefore, the process efficiencies also need to be considered in determining the best operating conditions and gasifier design for obtaining desired product composition.

Wet cleaning (A secondary removal technique)

Cold gas cleaning uses water scrubbing and venturi scrubbing to condense the tar compounds from the syngas and simultaneously removing the particulates. It has been demonstrated that tar concentrations below 20–40 mg/Nm^3 can be achieved using a venturi scrubbing system [53]. This

technology has been used extensively in coke-oven and gas processing industries, whose details can be found in Baker [46]. The exit gas temperature from wet cleaning methods is 35–60 ℃, which results in loss of sensible heat and water condensate which requires treatment before disposal.

The use of barrier filters and cyclone separators have not been effective for tar removal since tar aerosol particles are less than 1μm in size and are sticky in nature which makes them difficult to remove from walls of the cyclone and filter. Electrostatic precipitator (ESP) wet scrubbers can remove most of the tar up to about 150 ℃ but are more expensive. The tar collected using these physical techniques can be burned to produce heat or re-injected into a gasifier. Bergman developed a wet scrubbing (scrubbing liquid was other than water which was regenerated and recycled) based cleaning technology called "OLGA" [52]. Tar components, which condensed above 25 ℃, were heavy poly-aromatic hydrocarbons (PAH) (≥4 rings), light PAH (2–3 rings) and heterocyclic compounds. By removing these three tar components selectively, based on their dew points, the dew point of the resulting tar was less than normal temperature. Hence, the cleaned syngas can be acceptable for most syngas applications.

The disadvantages of wet cleaning are: (a) that since the product gases are at a high temperature, reducing the temperature, during wet cleaning, decreases the net energy efficiency of the process, (b) that the waste water needs to be treated extensively before discharge which is a capital-intensive process, and (c) if the product gas is used for high temperature applications, there will be a net loss of energy in cooling and heating the product gas stream [53].

Reforming for secondary tar removal and increased H_2 production

The drawbacks of wet cleaning have encouraged extensive research on hot gas cleaning technologies. The aim of hot gas cleaning is to crack the tar using high temperature. Without a catalyst, the temperature required for tar cracking is above 850 ℃ which reduces efficiency, causes material problems and produces soot [12]. Hot gas cleaning also results in increased hydrogen production in the product gas because the destruction of tar yields hydrogen, and the higher temperature and catalysts provide favorable conditions for reforming and shift reactions [53]. Non-catalytic reforming performed by Wang at 800–950 ℃ indicated that supplying air to the reformer decreased the HHV of the product gas by partial combustion and dilution of the reformed gas [33]. With an increased ER from 0.15 to 0.21, tar concentration decreased from 5.7 to 1.0 Ng/m^3. Supplying steam (up to S/B of 0.5) to the reformer increased the HHV and cold gas efficiency of the reformed gas. H_2, and CH_4 contents increased but CO and tar contents decreased with increasing S/B into the reformer. Supplying steam or/and air to the secondary reactor, in presence of catalysts, enables the tar to react and form CO, H_2, CO_2 and CH_4.

Tar removing catalysts are grouped into mineral and synthetic catalysts. The mineral-based catalysts are naturally occurring minerals and inexpensive. They also have fewer disposal problems. Calcined rocks (calcined dolomite, magnesite and calcite), olivine, clay materials and iron ores are mineral-based catalysts. Among these, calcined rocks are the most efficient catalysts. However, calcined rocks are suited only for fixed-bed secondary reactors as they erode in fluidized bed reactors. Olivine has more mechanical strength for attrition but is less efficient than dolomite. Clay materials generally do not withstand temperatures of 800–900 ℃, whereas iron ores are rapidly deactivated.

Fluid catalytic cracking (FCC), char, alkali metal-based, activated alumina, and transition metal-based (Pt, Zr, Rh, Ru, Fe, and Ni) catalysts are synthetic catalysts. Transition metals (Ni, Rh, etc.), as well as other synthetic catalysts, are relatively expensive as compared to the mineral catalysts. FCC deactivate rapidly, alkali metals agglomerate in the bed, and transition metals, although very active (8–10 times than dolomite), need gas with low levels of sulfur, tar and char [60].

Numerous efforts have been made to design catalysts for destructing tar and increasing the extents of reforming reactions at the same time. Using calcined dolomite (120 g per kg/h of biomass) in the gasification fluidized bed and a nickel based catalyst (weight hourly space velocity, WHSV of 2.7 to 10.7 h^{-1}) in a secondary fixed-bed reactor, Lv observed that decreasing WHSV had a positive impact on H$_2$ content and H$_2$/CO. CH$_4$ content decreased by half, H$_2$ content increased up to 49% (v/v), and H$_2$/CO increased up to 3.32 at a WHSV of 2.7 h^{-1} [39]. WHSV was defined as the ratio of biomass flow rate to catalyst mass in the secondary reactor. With an increase in catalytic reactor temperature (650 to 850 ℃), H$_2$ content increased, CH$_4$ CO$_2$, C$_2$ yields decreased but CO content remained the same. Maximal H$_2$ yield was 130.28 g H$_2$/kg biomass.

Wang found that activity of Ni/dolomite catalysts in the secondary catalytic reactor were comparable to commercial steam reforming catalysts [61]. Ni/dolomite catalysts are relatively cheaper than steam reforming catalysts and have anticoking properties. With a space time of 0.02 kg of catalyst (m^3/h) and a temperature of 850 ℃, the catalysts were able to convert 98% of the tar while increasing H$_2$ content. By comparing commercial steam reforming catalysts for naphtha and natural gas, Aznar and Corella concluded that catalysts for naphtha were more effective in destructing tar than catalysts for natural gas reforming [62,63]. A 2 g/m^3 level of tar did not poison the catalysts. Operating conditions such as temperature, space time (mass of catalyst per unit flow rate of product gas), catalyst particle size and gas compositions affected tar conversion efficiencies. Inaba compared two types of supports for production of hydrogen over Ni catalysts [64]. They found that metal oxides produced large quantities of dark-colored tar while zeolite-based support produced carbon deposition without tar formation. Higher temperatures led to higher rates of gasification and H$_2$ production, and decreased depositions of tar and char on the catalysts. Nordgreen reported improved gas yield, decreased tar (most pronounced decline was for toluene), increased CO, CO$_2$, H$_2$ yields and decreased CH$_4$ yield by using elemental iron as a tar removal and reforming catalyst in a secondary reactor [65]. Corella concluded that the performances of expensive Ni-based monoliths were comparable to cheaper dolomite for tar elimination [66]. The development of more robust and efficient catalysts can improve the tar conversion efficiency. Resistance to coking and sulfur poisoning were reported after adding WO$_3$ as sulfur-resistant promoter to Ni/MgO-CaO catalysts supported on dolomite [67]. Kimura found that a co-impregnation method resulted in higher performance of the catalysts for steam reforming of tar (Ni/CeO$_2$/Al$_2$O$_3$) than sequential impregnation (Ni/Al$_2$O$_3$ and Ni/CeO$_2$/Al$_2$O$_3$) due to strong interaction between Ni and CeO$_2$ [68].

4.2. Conversion of syngas to biofuels, bioproducts and biopower

Syngas, primarily a mixture of CO and H$_2$, is a building block for synthesizing a variety of fuels and chemicals [69]. The main routes of converting syngas to fuels and chemicals, and generating biopower follow.

4.2.1. Biopower

The product gas from biomass gasification can be used to produce heat and electricity using a combined heat and power (CHP) system called integrated gasifier combined cycle (IGCC or BIGCC, Biomass-fired IGCC). The main advantages of producing heat and electricity using gasification over direct combustion are (a) fuel-gas based technologies such as gas engines or gas turbines can achieve higher efficiencies than combustion efficiency, (b) the overall efficiency of gasification is higher because gaseous fuels, having improved combustion characteristics, burn more efficiently than solid fuel, and (c) production of gas provides an opportunity to remove contaminants that ultimately produce NO_x and SO_x emissions [9,70,71]. With an overall efficiency of 35%, 7 billion tons of globally available biomass, with an energy content of 124 EJ, could produce 44 EJ of electricity [72].

Several demonstration and commercial CHP plants have been developed around the world as alternatives to the use of fossil fuel for electricity production [72]. Most remarkable and first BIGCC was demonstrated at Varnamo, Sweden producing 6 MW of electricity and 9 MW of heat primarily from wood chips. This facility operated between 1993 and 1999, and was closed due to unfavorable economic conditions. The 8,500 h of gasification runs and about 3,600 h as a fully operational integrated plant provided valuable experiences. The demonstration proved that the producer gas from a high-pressure circulating bed gasifier could be cleaned using hot cleaning technique and could be burned in a gas turbine under stable conditions even with low-energy of 3.8 MJ/kg. More research initiatives are underway to restart the demonstration plant for increased H_2 production using municipal wastes [73]. Yin reported that a circulating fluidized-bed (CFB) gasifier attached to gas engines and a capacity of 150 t/d of rice husk, located in China, reliably provided 1 MW of electricity at a rice mill with an overall electrical efficiency of 18% with a payback period of less than 2 years [74]. Wu reported that after 8,000 h of operation, the overall efficiency improved to 28% for demonstration plant of BIGCC at the scale of 5.5 MWe [75]. The operating and capital costs were estimated to be 0.079 USD/kWh and 1,200 USD/kW with a biomass price of 35.7 USD/ton.

With an increase in size of the gasification system, the cost of electricity production decreases. Brammer and Bridgwater estimated the cost of electricity (coE) was 8.67 Euro c/kWh for a 2 dt/h system at cost of €30/dt with a rotary dryer reducing the moisture from 50% to 10% [18]. Craig and Mann estimated cost of electricity production to be 0.0655 to 0.0820 USD/kWh, depending on the gasifier design, including high or low pressure, and directly or indirectly heated [76]. Uddin and Barreto, and Rhodes and Keith found that biomass-fired cogenerations systems such as BIGCC, with carbon capture, were energy efficient, emission efficient and cost competitive with natural gas cogeneration systems with carbon capture [77,78]. Tiffany concluded that, for ethanol production from corn, the use of biomass (corn stover and fermentation byproduct such as distillers grains and corn syrup) to produce heat and/or electricity might require high capital cost but the profitability of the process was more resilient to the change in prices of commodities (corn, oil, natural gas, electricity), and these were competitive with the conventional natural gas and purchased electricity [79]. However, issues related to biomass collection and utilization, and commercialization of CHP-BIGCC need to be resolved. High capital costs associated with first generation large-scale gasification of biomass, the technical risks involved, and the unproven technologies of tar cleaning are the main hindrance to the

commercialization efforts. The heating value of the product gas needs to be increased, especially in air-blown gasification, to power gas turbines [7,80].

CHP generation from biomass is especially beneficial for rural electrification in developing countries where diesel is the primary fuel. Abe, in a case study of Cambodia, estimated that with the current technology, the cost of electricity from gasification of locally available biomass (agricultural residue, planted trees) was lower than the cost of electricity from diesel engine at the scale of 13.3 kWh electricity usage per household [81]. Gasification has potential to provide electricity to more than 60% of the villages which currently are without electricity. However, the major challenges in the commercialization of small-scale gasification systems are to effectively clean the product gas, at this scale, for proper operation of gas engines; to design the system flexible enough to operate using varying biomass qualities; and to decrease the capital cost [82,83].

4.2.2. Hydrogen

H_2 can be used as a transportation fuel in fuel-cell based automobiles, as a zero-emission fuel. It should be realized that H_2 is not an energy carrier, but rather an energy source. Hence, sources of energy are needed to produce hydrogen. H_2 has the highest energy content on a mass basis. Use of H_2 in fuel cells has gained attention because of its high efficiency (around 60%) as compared to efficiency of IC engines (20–38%). However, more research is needed in the areas of production, storage, transportation and utilization of H_2 for its viable use as an energy carrier [84,85]. Currently, the total production of H_2 is about 9 million tons, 95% of which is produced by steam reforming of natural gas. The H_2 is used for the production of chemicals and intermediate products with 95% being used to produce ammonia (50%), petroleum products (37%), and methanol (8%) [86,87].

Biomass gasification results in H_2 production. As described in the previous sections, changes in gasifier and reformer operating conditions influence the H_2 content of the product gas. Higher temperature, ER, S/R and catalysts all lead to higher H_2 production. However, additional reforming reactions may be needed to further increase the H_2 content in the product gas.

4.2.3. Catalytic synthesis of methanol and higher alcohols

Methanol, produced in large quantity, is used for making various fuels and chemicals. Currently, it is used primarily for making formaldehyde, dimethyether, MTBE (methyl tert-butyl ether, additive for gasoline) and acetic acid. Methanol also is used for converting fats and oil to biodiesel. CO, H_2, CO_2 and H_2O are used to produce methanol using methanol synthesis reactions in the temperature range of 220 to 300 ℃ and pressures of 50 to 100 bars using Cu/ZnO catalysts (Equations 11 and 12) [12].

$$CO + H_2O = H_2 + CO_2 \tag{11}$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \tag{12}$$
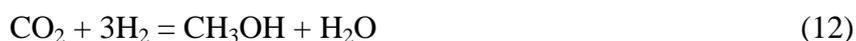
Optimum operating conditions such as temperature, pressure and space velocity (ratio volumetric flow and reactor volume) for the maximal selectivity of methanol from syngas depend heavily on the composition of the syngas. Using a commercial Cu/ZnO/Al$_2$O$_3$ catalyst, Gerber showed that methanol

yield was affected by ratio of H_2 to $CO+CO_2$ but methanol selectivity was more affected by the CO_2/CO ratio [88]. Removal of CO_2 improved both the selectivity and yield of methanol.

In Europe, a number of efforts have been made to produce methanol from biomass. In France and Sweden, methanol production by pressurized biomass gasification was developed and tested [83]. However, the low cost of petroleum-based feedstocks (natural gas and coal) have been detrimental to use of biomass for this application. Recently, increase in the price of fossil fuels and increased awareness about the global warming have led to amplified research efforts for biomass utilization for production of biofuels and chemicals.

Syngas can be converted to higher alcohols using catalysts. After a survey, Gerber reported that catalysts for mixed alcohol synthesis are not commercially available except for one available for methanol synthesis [88]. By comparing 10 catalysts from different classes, they observed that $Rh/Mn/Fe/SiO_2$ catalysts and two modified FT based catalysts had high STY (space-time yields, $g/L_{cat}/h$) of C_{2+} oxygenates (predominantly C_2 to C_5 alcohols, acetic acid, acetaldehyde, and ethyl acetate) with a maximum of 170–400 and 50–830, respectively. Rhodium catalysts seemed to be the best for C_{2+} oxygenate selectivity and STY. Modified FT catalysts were best for best C_2 alcohol selectivity and total liquid STY. Further testing of Rh based catalysts, with different promoters and temperature condition, showed that iridium gave maximum STY of oxygenates of 880 followed by lithium and nickel. Selectivity to C_{2+} alcohols were best by iron and rhenium followed by carbon [89].

4.2.4. Fischer-Tropsch Synthesis (FTS) diesel and gasoline

The Fischer Tropsch (FT) process is a method to produce alkanes from syngas in the presence of Fe, Co and Ru-based catalysts as represented by Equation 13. Co and Fe are more practical to use because of the high cost of Ru. Co also is comparatively more expensive than Fe, but due to its higher activity and longer life, it is the preferred FT catalyst. Co-based catalysts in slurry phase reactors give high wax production from syngas, which is then selectively cracked to diesel fuel [90]. The process takes place at 20 to 40 bars and 180–250 ℃. The FT product needs to be hydrocracked with H_2 to reduce the double bonds of unsaturated hydrocarbons producing hydrocarbons in the diesel fuel range. Larger (higher than C_5) hydrocarbons are desired for use as liquid fuels. FT products are free of sulfur. The yield of FT diesel is estimated to be 120 L/mt biomass with a prediction of ultimately reaching 210 L/mt. The research challenge for the FT synthesis process is to narrow the range of resulting hydrocarbons. The chain lengths of FT products vary from 1 to 50 producing hydrocarbons ranging from methane, gasoline range, diesel range, naphtha, kerosene, to heavy waxes.

$$CO + H_2 = C_nH_m + H_2O \tag{13}$$

During World War II, Germany produced these fuels from coal based syngas. Currently, Sasol in South Africa and Shell in Malaysia produce FT fuels from coal and natural gas, respectively. To date, there is no commercial demonstration of FT fuel production from biomass.

Contaminants in biomass-derived syngas need to be removed to suit the FT synthesis process. Around 2.1:1 H_2/CO ratio is desired for FT synthesis depending on selectivity. As syngas from biomass gasification has less H_2/CO ratio, shift reactions are required to increase the H_2 content suitable for the FT process. Higher partial pressures of CO and H_2 are desired for higher selectivity for

longer chain hydrocarbons. Other gas components also may reduce the partial pressures of CO and H_2, thereby reducing the liquid selectivity. Hot gas cleaning does not seem very beneficial for FT process because this process operates at lower temperature (200 °C) [12,91]. Detailed reviews of the reactors used in FT process can be found elsewhere [90].

Many authors have suggested that by using FT catalysts on zeolite based supports the selectivity of the product can be narrowed to gasoline range hydrocarbons. The bifunctional catalysts allows two simultaneous reactions (syngas to methanol over the metallic function and methanol to hydrocarbons over acidic function) to take place. With Cr_2O_3-ZnO/ZSM5 as bifunctional catalysts, Ereña observed that conversion of CO increased with pressure (10–50 atm), temperature (300–425 °C) and space time (7.23–62.22 h^{-1}) and decreased with CO/H_2 molar ratio (0.33–2.0) [92]. The gasoline fraction (C_{5+}) increased with space time and CO molar ratio and decreased with pressure and temperature. Methanol content was less than 0.01 wt% in the product, which indicated that the reaction rate was limited by methanol synthesis. The product distribution was nearly constant with 70–75 wt% CO, 22–28% hydrocarbons and a small amount of water.

Cr_2O_3-ZnO, with an atomic ratio of 2.0, was the best catalytic mixture for high CO conversion and high gasoline fraction. Cr/Zn > 2.0 decreased CO conversion. Higher Zn gave higher gas production, especially methane and light paraffins because Zn favored hydrogenation reactions over the gasoline formation reactions. Zeolite, with Si/Al ratio of about 154, was most suitable for production of gasoline range hydrocarbons [93].

4.2.5. Fermentation of syngas to ethanol

Fermentation of synthesis gas (Equations 14 and 15) is an attractive process to produce ethanol as a transportation fuel because the biological catalysts are more specific resulting in less side products [94]. Henstra summarized the micro-organisms used for the fermentation of syngas [95]. Since the fermentation takes place at lower temperature as compared to catalytic conversion of the synthesis gas to liquid fuels, the wet gas cleaning can be used for removal of impurities from the product gas. Moreover, ethanol (blended with gasoline) has been used successfully as a transportation fuel in many countries, most notably in US and Brazil with existing transportation infrastructure and automobile engines. As compared to the biochemical conversion with hydrolysis and fermentation processes, gasification and fermentation have potential to use a much wide variety of feedstock producing ethanol.

$$6CO + 3H_2O = C_2H_5OH + 4CO_2 \tag{14}$$

$$6H_2 + 2CO_2 = C_2H_5OH + 3H_2O \tag{15}$$

Datar demonstrated using the producer gas, generated from gasification of switchgrass, to produce ethanol by fermentation [96]. During their 20-day fermentation study, they alternately used bottled gas (clean gases) from days 0 to 8.5 and days 11.4 to 14.5 and producer gas for the rest of the days. They observed that after introducing producer gas, the H_2 utilization stopped but the CO utilization continued forming primarily ethanol. At the end of the run, ethanol concentration reached 5 g/L.

The major challenge with this process was to increase rate and yield of fermentation by increasing gas to liquid mass transfer rate of CO and H_2 [97,98], and to search for a right microbe having increased ethanol yield and high resistance to the contaminants in the syngas [95,99,100]. Sensible

heat from product gas during wet gas cleaning also needs to be recovered to increase the net energy efficiency of the overall process.

5. Conclusions

Biomass gasification is a promising technology to displace use of fossil fuels and to reduce CO_2 emission. Among other alternative energy conversion pathways, it has great potential because of its flexibility to use a wide range of feedstock, and to produce energy and a wide range of fuels and chemicals. Recently, the focus of its application has changed from production of combined heat and power to production of liquid transportation fuel. The technical challenges in commercialization of fuels and chemicals production from biomass gasification include increasing the energy efficiency of the system and developing robust and efficient technologies for cleaning the product gas and its conversion to valuable fuels and chemicals.

Acknowledgements

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