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# Advances in Gasification for Biofuel Production

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## X.1 Introduction

Of all of the conversion processes of biomass into fuels, the gasification process gives the widest breadth of potential products, ranging from gaseous fuels, such as hydrogen or syngas, to liquid fuels such as methanol, ethanol, dimethylether (DME), gasoline, or diesel. The gasification process is also one of the most flexible conversion processes in terms of acceptable feed material. Fig. 1 shows a schematic of the predominant process steps and fuel production routes available when gasifying biomass or biomass-derived feedstocks. The key ingredients of this fuel production route include the gasifier, where one or more oxidizing agents are reacted with the biomass feedstock at elevated temperatures in a fuel-rich environment, the syngas cleanup stage, where harmful contaminants of the gasifier product gas are removed or converted to acceptable chemical species, and the fuel synthesis step, where cleaned, compressed syngas is converted to liquid fuels by reacting over an appropriate catalyst.

The fuel synthesis step can be avoided, along with at least some of the need for syngas compression, by producing gaseous fuels, instead of liquids. Cleaned syngas is an appropriate fuel for operating a gas turbine engine, as has been demonstrated for a number of years in integrated gas turbine combined cycle (IGCC) power plants fueled by coal or coal-biomass mixtures.[1-3] Syngas can also be used directly to produce electricity in solid oxide fuel cells.[4] As an alternative, syngas, primarily composed of carbon monoxide and hydrogen, can be converted to high-purity hydrogen by reacting it with steam over one or more shift catalysts and then separating the hydrogen from carbon dioxide.[5-7] Hydrogen can be used to fuel vehicles via internal combustion engines or fuel cells, or can be used to generate electricity through fuel cells or gas turbines.[7-13] Another gaseous fuel possibility is to generate substitute natural gas (SNG) from syngas by passing it over a suitable nickel oxide methanation catalyst.[14] The methanation reactions typically involve 3 or 4 moles of hydrogen reacting with 1 mole of CO or $CO_2$ (yielding methane and water), so the methanation catalyst must also shift the syngas to the appropriate concentrations of CO, $CO_2$, and $H_2$. Coal gasification plants in North Dakota and in South Africa have been generating SNG in this manner for many years.

The generation of liquid fuels from syngas requires that syngas within a certain range of $H_2$/CO ratio be passed over a catalyst operating at a particular temperature and pressure. As such, a shift reactor is often required to tailor the $H_2$/CO ratio for generation of the particular liquid fuel that is desired (assuming the raw syngas has a lower $H_2$/CO ratio than desired). The range of liquid fuels that can be generated from syngas extends from oxygenates such as DME and alcohols to hydrocarbon mixtures such as diesel and gasoline. The simplest synthesis route is undoubtedly to methanol, via reaction over a $Cu/ZnO/Al_2O_3$ catalyst at 35–55 bar and 200–300 °C.[15,16] The ideal $H_2$/CO ratio for generating methanol is ~ 2, as suggested by the overall stoichiometry of the simplified reaction step of $CO + 2H_2 \rightarrow CH_3OH$. Methanol is suitable as an automotive fuel in internal combustion engines or molten carbonate fuel cells, but its corrosiveness and affinity for water pose additional costs associated with its storage and handling. Methanol itself can act as a base material for generation of a variety of fuels and chemical feedstocks.[17,18] For application to liquid transportation, the primary products from methanol include olefins (a component of gasoline), via the commercial methanol-to-olefins (MTO) process,[17,18] DME, via catalytic dehydration of methanol according to $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$,[19] and even gasoline, via the commercial methanol-to-gasoline (MTG) process.[17,18]

Direct synthesis of DME from syngas is optimized for a $H_2$/CO ratio of one, according to the reaction $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$.[20] As suggested by the reaction stoichiometry, this reaction is more difficult to achieve than methanol synthesis and also results in lost carbon (manifest as a $CO_2$ byproduct). DME synthesis reactors are typically operated at 50 bar and 250–260 °C.[20-22] DME is an attractive fuel because its properties are similar to those of liquefied petroleum gas (LPG), and therefore it can be distributed and stored using familiar LPG technology. DME has favorable ignition characteristics (its cetane number is approximately 60) and is therefore appropriate for use in diesel engines, once one makes suitable modifications to the fuel injection system.[23,24] In fact, soot emissions are greatly reduced and NOx emissions can also usually be reduced when operating a diesel engine on DME. It also is an appropriate fuel for use in gas turbines for power generation. [25]

This chapter summarizes the current status and prospective areas for improvements in the biomass gasification process itself. As discussed above and illustrated in Fig. 1, the gasification process is a key component of a wide range of production routes for both gaseous and liquid biofuels. Improvements in the efficiency, capital effectiveness, and availability of the gasification process will have important impacts on the overall cost effectiveness of these thermochemical routes of biofuels production and may therefore play a significant role in the anticipated expansion of biofuels production in the future. The chapter begins with a discussion of the diverse range of biomass feedstocks appropriate for use in gasification processes and then progresses to the core topic: the current state-of-the-art in biomass gasification. Implications of the different gasification approaches on gas cleanup requirements are then discussed, before summarizing the topics that have been covered and forecasting the expected areas of improvements in gasification technology in the future.

## X.2 Biomass feedstocks for use in gasifiers

As suggested by the wide range of biomass-derived feedstocks entering the biofuels production process layout in Fig. 1, many different feedstocks are suitable for use in gasifiers. In fact, because most biomass sources have very similar atomic ratios of carbon, hydrogen, and oxygen and because the gasification process reacts the fuel source down to the smallest possible molecular units (CO and $H_2$, with some $CH_4$ for certain gasification processes), the syngas composition leaving the gasifier is itself fairly insensitive to the type of biomass feedstock that is being gasified. This “feedstock-neutrality” is a significant advantage of gasification-based conversion (as well as other thermochemical processing routes, such as pyrolysis) relative to biochemical conversion, which typically is most effective for starch or cellulose and has difficulty converting hemicellulose, lignin, and protein components of biomass.

The two primary limitations to acceptable feedstocks for gasification are the water and ash contents of the feed. Excessive water in the feedstock lowers the system efficiency because of heat losses associated with first vaporizing and then recondensing the water that is fed with the fuel into the gasifier. Similarly, excessive ash components act as a heat sink in the gasification process and can lead to bed material agglomeration and slag management problems, as will be discussed in more detail in Section 3. The feedstock water content can be minimized by applying feedstock drying practices, including the use of low-quality waste heat that is generated at the biofuels plant, particularly in the syngas cooling, compression, and biofuels synthesis steps. The ash content of the feedstock can also be minimized by applying stone removal and density fractionation steps to remove extraneous mineral matter.

Pre-processed biomass streams, including black liquor (a byproduct of pulpmaking), glycerin (a byproduct of biodiesel production), lignin residues from cellulosic ethanol production, pyrolysis oil, and algae or algal oils, are particularly suitable for use in gasification-based biofuels production because they are generally liquids and can be readily injected into a pressurized gasifier. Pressurizing the gasifier can have substantial benefits to the overall process efficiency and economics, as will be discussed below. Unfortunately, for most of these pre-processed biomass streams, at least part of their fluidity results from their water content, which, as mentioned previously, results in a less efficient gasification process.

## X.3 Gasification Technologies

Fundamentally, the word “gasification” refers to the overall conversion of a solid or liquid fuel feedstock into gaseous fuel. For non-charring fuels, however, simple liquid spray evaporation or simple solid fuel thermal devolatilization is generally not considered to be a gasification process. Rather, chemical reactions that convert the solid fuel to gaseous form are an essential component of gasification. Most biomass fuels, in contrast to coal, undergo extensive devolatilization as they are heated to high temperatures (typically losing 70 – 80% of their mass), which means that the amount of char remaining that needs to be chemically gasified is relatively low. In fact, the extent of biomass devolatilization is a strong function of the heating rate, final temperature, and pressure of the process,[26] so different approaches to biomass gasification can have considerably different biomass char yields within the gasifiers. Because of this strong role of devolatilization in the conversion of the biomass in gasifiers, the pyrolysis and steam reforming reactions of the biomass volatiles play an important role in the overall chemical composition of the gasifier product gas.

A wide variety of gasification technologies have been developed over the years for biomass, owing to the wide variations in feed size, moisture, particle density, etc. for different sources of biomass, as well as wide variations in the desired reactor throughput, based on the magnitude of the available biomass resource. Most of these technologies have involved air-blown gasification, which is relatively simple and low-cost, but which produces a low-energy content and highly diluted 'producer gas' that is inappropriate for subsequent fuel synthesis. To produce a fuel synthesis-quality product gas, or 'syngas', three general approaches for biomass gasification have been developed. One of these approaches uses steam and an external source of heat (typically generated in an adjacent combustion reactor that is fueled by residual char) to gasify the biomass, in a moderate temperature fluidized bed.[27] A second approach uses a sub-stoichiometric quantity of oxygen, produced via cryogenic air separation or a pressure swing adsorption technique, to gasify the biomass. This approach is usually performed at high temperatures, in an entrained flow process that requires significant communition of the biomass feed source,[28-30] but can also be applied in a fluidized bed, if the oxygen is sufficiently diluted with steam before injection.[29,30] A third approach, originally developed for application to waste treatment that has seen considerable interest recently, involves the use of high-temperature plasma sources.[31] After a discussion of the important operational criteria of gasifiers, these three different approaches to biomass gasification will be described in some detail below, before progressing to a discussion of the syngas cleanup processes, as the required cleanup processes are closely linked to the type of gasification process employed. It should be noted that hydrothermal gasification, which occurs at low-temperatures and high pressures in an aqueous-phase reactor, produces a product gas which is predominantly composed of $CO_2$ and methane and is not appropriate for use for fuel synthesis.[32]

### X.3.1 Operational characteristics of gasifiers

Important considerations in the operation of gasifiers include the gasifier pressure, temperature, and energy balance. The pressure is an important factor with regards to feeding the biomass stream into the reactor, the required size of the reactor, and the required size of the subsequent gas cleanup equipment. For fuel synthesis applications, the syngas ultimately needs to be compressed (usually to quite high pressures) for catalytic synthesis, so it is beneficial to operate the gasifier at an elevated pressure, because the introduction of the solid fuel at pressure does not require the compression cost that is entailed for the gaseous products of the gasification process. Also, the sorbent-based and catalytic gas cleanup processes can be reduced in size and are less expensive when operating at pressure. The gasifier size can probably be reduced in size when operating at pressure, because the gasification reactions themselves progress more rapidly at higher pressures (because the collision rate of gas reactants with the solid char increases with pressure, for a given temperature). However, the amount of volatiles produced decreases with increasing pressure (and therefore the amount of char remaining to be gasified increases). The competition between these two competing factors has not been extensively investigated for the different gasification processes. Finally, the gasifier pressure plays an important role in the ease with which a given biomass feedstock can be fed into the gasifier, specifically in the extent of communition of the feedstock and appropriate moisture level for consistent feeding. As the gasifier pressure increases, greater size reduction and uniformity of the biomass feed is required, and at high enough pressures the biomass may need to be introduced as a fuel slurry in water.

The gasifier temperature dictates the rate of devolatilization and char gasification reactions, the overall extent of devolatilization, the degree of softening of the inorganic elements in the biomass (particularly for the alkali metals and their associated salts), and the extent of corrosive attack of refractory and metal surfaces. Gasification processes generally operate above or below the temperature range where the primary inorganic components of the fuel transition from hard solids to molten liquids (slag). This transition generally occurs over a temperature range of approximately 100 – 200°C for most types of biomass, but the actual beginning and endpoint temperatures of the slag transitions vary substantially, particularly as a function of the alkali and chlorine content of the biomass (most biomass sources have slag transitions falling within the range of 850 – 1200 °C)[33-35]. If operating below this temperature, the biomass devolatilization process is less effective at generating volatiles and the char gasification reactions proceed very slowly. Consequently, long residence times are required to yield acceptable conversion of the char, implying the use of some type of bed-based gasifier. Fixed bed gasifiers are relatively simple to operate and can be operated in either an upflow or downflow configuration. Upflow, or countercurrent, gasifiers do a good job of minimizing energy loss through the produced gas, but suffer from high concentrations of methane and tars produced from pyrolysis of the fuel volatiles. Downflow, concurrent gasifiers have much lower concentrations of methane and tars in the produced gas, but suffer from extensive heat loss through the sensible heat of the produced gas. For both types of fixed bed reactors, the temperatures and stoichiometries can vary significantly throughout the bed, making it difficult to have a consistent product gas composition.[36] The use of moving beds and, especially, a fluidized bed, improves the mixing throughout the bed and enhances the fuel heating and devolatilization processes, but at the cost of increased complexity and flow control requirements. Also, the feedstock needs to be processed to an appropriate, fairly uniform particle size for use in a fluidized bed. As fluidized beds necessarily operate in an upflow, countercurrent geometry, tar levels are quite high in the produced gas.

Slagging gasifiers operate at temperatures above the flow point of the mineral constituents of the fuel, such that the minerals predominately flow out of the gasifier as molten slag (unfortunately, some of the alkali metals vaporize and exit the gasifier as an alkali fume at these process conditions). Under these conditions, the introduced particles usually are gasified in an entrained flow process and therefore they must be processed to be sufficiently small to be carried by the gas flow and to be gasified within the available esidence time within the reactor. At these temperatures the tar components formed by the biomass volatiles rapidly undergo pyrolytic reactions that result in production of small gas compounds and soot, and the hydrocarbon species and soot particles rapidly react with steam and $CO_2$ to yield the desired syngas components, $H_2$ and CO. Unfortunately, vaporized and liquid alkali constituents actively attack traditional refractory materials at these temperatures, making refractory repair and replacement a regular occurrence in this type of gasifier. It should be noted that most commercial coal gasifiers are oxygen-driven entrained flow gasifiers, with a wealth of operating experience.

A critical operational variable in gasification is the energy balance. For a steady-state process, the energy losses from the gasifier must be balanced by the energy inputs. The biomass introduced to the process must first be heated and undergo devolatilization (a slightly endothermic process) and then have its char at least partly converted through gasification reactions with steam and $CO_2$. The gasification reactions are strongly endothermic, as shown in Eqs. 1-2.

$$CO_2 + C(s) \rightarrow 2CO \quad (\Delta\text{H} = +172 \text{ kJ/mole C}) \tag{1}$$

$$H_2O + C(s) \rightarrow H_2 + CO \quad (\Delta\text{H} = +130 \text{ kJ/mole C}) \tag{2}$$

Furthermore, the reactor itself loses heat through its walls and through the sensible enthalpy of the hot gas stream and ash leaving the reactor. There are two methods to provide these heat requirements, which lead to the characterization of the process as either direct gasification or indirect gasification. In direct (or autothermal) gasification, the necessary heat is provided internal to the gasifier by using air or oxygen to the reactor and relying on the localized combustion heat release to drive the gasification process, as shown in Eqs. 3-4 (depending on the temperature and pressure, the char will tend to oxidize more to CO or to $CO_2$).

$$O_2 + 2C(s) \rightarrow 2CO \quad (\Delta\mathrm{H} = \text{ -110 kJ/mole C}) \tag{3}$$

$$O_2 + C(s) \rightarrow CO_2 \quad (\Delta\mathrm{H} = \text{ -394 kJ/mole C}) \tag{4}$$

Another option is to provide the necessary heat energy through the transfer of one or more hot mediums (e.g. steam and sand) introduced to the reactor. This process is known as indirect (or allothermal) gasification. An advantage of indirect gasification is the complete absence of diluent gas and combustion products in the produced syngas, as are found in direct gasification, especially for air-blown direct gasification. Plasma gasification is generally applied as a combination of allothermal and autothermal approaches, wherein the electrically generated plasma heat is introduced to the reactor, together with some autothermal oxygen.

### X.3.2 Moderate-Temperature, Indirect Gasification

The indirect, dual-bed biomass gasification process was derived by analogy to the fluidized catalytic cracking (FCC) process that was developed in the late 1930's in the petroleum refining industry.[27,37] This biomass gasification process has seen the most extensive development by far of the three characteristic approaches to generating biomass syngas. In the FCC process, catalytic material reacts with fuel vapors, resulting in coking of the catalyst. To regenerate the spent catalyst, it is removed from the main reactor and the coke layer is burned off in a regenerator reactor (with an air feed), before mixing with the fresh hydrocarbon feed going into the main reactor. The extra heat of the regenerated catalyst is used to vaporize the fresh feed and maintain the temperature in the main reactor.[37] In the indirect gasification system, biomass feed is partially gasified with steam and a solid heat transfer medium (typically some form of sand) in the main reactor to produce syngas and char. The char and sand is then separated from the syngas and fed into an air-blown combustion unit that burns off the char to heat the sand and produce steam, with the steam and hot sand returned to the main reactor (see Fig. 2). The details of the operation of the two linked reactors have varied considerably over the nearly 30 years of implementation of this approach by various groups around the world, as detailed in a recent review article by Corella et al.[27] In some cases circulating fluidized beds have been used for both the gasification and combustion reactors (as in the Battelle and Battelle/FERCO designs)[38], whereas in other cases bubbling fluidized beds or risers have been used for one or for both reactors. In general, the gasification reactor has been operated at a temperature of 700–800 °C, whereas the combustion reactor has been operated at 850–950 °C. Both reactors are generally operated at pressures just slightly above atmospheric pressure (considered 'low pressure' operation, in comparison to most other gasification technologies). Under these conditions, the conversion of the biomass feed in the gasifier is dominated by devolatilization, and actual heterogeneous reaction of the resultant biomass char with steam is very slow.[39,40] Tar production also tends to be strong under these gasification conditions, so many different reactor configurations and bed additives have been investigated in attempts to improve char conversion and reduce tar formation.[39-43] The largest indirect gasification plant built to-date has been the Battelle/FERCO gasifier that was installed and briefly operated in Vermont, which had a capacity of nearly 200 tonnes per day (tpd) of dry wood feed.[38]

Table 1 lists a typical syngas composition produced through indirect gasification.[27,30,42,44,45] The composition shown here is most reflective of the operation of the Battelle gasifier, as this one appears to have the most thoroughly documented experimental results and has been scaled to the largest size. In fact, in indirect gasification a wide range of $H_2/CO$ ratios, in particular, can be generated, depending on the steam content in the gasifier and the gasifier temperature, pressure, and residence time. This is because of the important role of the water-gas shift reaction in determining the balance of the major species:

$$H_2O + CO \leftrightarrow CO_2 + H_2 \tag{5}$$

At higher temperatures, CO and steam are favored at the expense of $CO_2$ and $H_2$, and vice versa at lower temperatures. As is evident in Table 1, the indirect gasification approach produces a good quality synthesis gas, at least on a dry basis, if one can effectively convert the abundant hydrocarbons that are produced in the process and either convert or remove the abundant tar. The high moisture level that necessarily accompanies the syngas in this process represents a significant efficiency loss in the gasification system.[27] For fuel synthesis applications, this moisture will be mostly removed through successive compression and cooling stages before fuel synthesis, but most of this low-quality heat from steam condensation cannot be effectively recovered.

In addition to the traditional dual-bed approach to indirect gasification, a couple of approaches have also been developed that aim to simplify heat and mass transfer through the insertion of hot tubes that pass through the gasifier bed. In one case, the tubes contain the hot flue gas from char combustion, while in another the tubes act as pulse combustors that consume a portion of the syngas exiting the gasifier.[30] In this latter case, effective gasification of the char is required in the gasifier, so the requisite bed depth is much larger than in traditional indirect gasifiers. Neither of these approaches appears to have any active development activity at this time.

Several approaches to indirect gasification have been recently developed which have focused on better process thermal integration, to reduce the heat losses and attendant efficiency loss associated with transfer of hot solids between two separate reactors. One approach uses concentric fluid beds and another uses neighboring fluid beds with a common wall and internal solids circulation.[27,46] As emphasized by Corella et al.[27], such systems with internal solids circulation tend to suffer from gas leakage between the oxidizing and reducing zones. A third approach is to use a central riser within a fluidized bed. Xu et al.[42] compared the performance of gasification in the riser surrounded by char combustion in a fluid bed and the converse, and found improved performance when char combustion occurs in the high velocity riser, as one would expect, based on the much faster char oxidation process. Based on both measurements and process analysis, cold gas efficiencies of 70–75% are attainable with this approach.[39,42] Xu has also been investigating the implementation of a two-stage gasification approach in which the hot sand particles leaving the char combustor are conveyed first to a secondary fluid bed in which the hydrocarbon-laden gas exiting the primary gasifier stage is partially reformed, thereby increasing the cold gas efficiency and lowering the tar yield.[43] A variant of the riser-in-bed approach has been developed at the Energy Research Center of the Netherlands (ECN) and is known as the Milena gasification technology.[14,29] In this approach the biomass is gasified in a central riser that is contained within a bubbling fluid bed combustor that converts the char particles and recycles the sand. Recently, this technology was scaled up to a level of 4 tpd.[14] Finally, Iliuta et al.[47] have proposed a multi-compartment integrated gasifier/combustor concept that benefits from increased wall heat transfer associated with larger surface-to-volume ratios of smaller fluidized bed compartments and from periodic cycling from oxidating to reducing environments in each compartment (eliminating the need to physically move the char from one bed to another). While philosophically appealing, the challenges associated with practical implementation of this approach, particularly regarding biomass feeding and segregation of syngas and oxidizing flue gas, appear formidable.

In summary, in comparison to other gasification technologies for producing synthesis gas, the indirect gasification approach is fairly mature and robust. It can be scaled relatively easily to high processing volumes and has no difficulty with biomass feed. However, application of this technology to fuel synthesis has not been demonstrated, and there are strong concerns with respect to its low-pressure operation (requiring syngas compression), its capital-intensive nature, with two interconnected bed reactor systems, and the high concentrations of hydrocarbons and tars in the syngas, requiring secondary upgrading.

### X.3.3 Oxygen-Blown, Direct Gasification

In comparison to indirect gasification, there has been little historical experience in the oxygen-blown direct (autothermal) gasification process, mostly because the high cost of oxygen production has made application of this technology for heat and power production (the traditional end-products of biomass gasification) untenable. However, the current interest in synthetic liquid fuel generation and the promise of future cost reductions in the cost of oxygen generation make this gasification approach of significant interest.

As mentioned previously, there are two basic variants of direct gasification with oxygen. The moderate temperature approach is modeled after traditional air-blown bubbling fluid bed or circulating fluid bed gasifiers and simply uses steam-diluted oxygen to simulate air as the gasifying agent. In this application the steam must be at least partially premixed with the oxygen before injection into the bed, to avoid the creation of local hot-spots and clinker formation from partially molten inorganic material. Because this gasification process takes place in a single reactor vessel and uses oxygen, which is available at pressure, it can be easily operated at pressure and has been demonstrated up to a pressure of ~ 20 bar. Pressurizing the gasifier reduces the costs of subsequent gas cleanup and syngas compression. Production of hydrocarbons and tar is still significant, because of the moderate temperature of the process, so secondary reforming and/or cracking of the product gas is necessary. Table 1 shows a typical gas composition exiting this type of gasifier.[30] Note that the autothermal nature of the gasification process results in a significant concentration of $CO_2$ in the product gas, on account of partial oxidation of the fuel (to release the energy needed to drive the gasification reactions). This is the primary difference in composition of the direct gasification syngas in comparison to syngas generated from indirect gasification. The carbon conversion in these systems approaches 90%.[29]

The second approach for direct gasification with oxygen is known as entrained flow gasification. This type of gasifier has, in fact, seen the widest commercial utilization, though primarily for application to pulverized coal and/or petroleum coke.[48] In an entrained flow gasifier the fuel particles are carried along (i.e. entrained) in a high temperature gasifying medium and must be gasified during their short residence time being carried through the reactor. As a consequence, the fuel particles must be small (less than 0.1 μm in size, for coal particles), though not necessarily dry – both dry-feed and liquid-slurry feed systems have been employed for coal particle feeding. High temperatures are required to accelerate the gasification reactions to consume the fuel particles within the available residence time. Consequently, these gasifiers are generally operated as slagging gasifiers, wherein the mineral components of the fuel melt, flow along the walls and bottom of the reactor, and leave the reactor as molten slag. The slag layer also acts to insulate and protect the gasifier refractory wall from corrosion. The entrained flow gasification of biomass, with a significant fraction of its inorganics composed of low-melting point alkali metals, can potentially be conducted at somewhat lower temperatures than have traditionally been applied for coal, 1300 – 1500 °C, which would help to reduce refractory corrosion. Entrained flow gasifiers are typically operated under pressurized conditions of 20 – 80 bar.

Entrained flow gasification of biomass has only been demonstrated at a commercial level by co-gasifying biomass with coal in existing coal gasifiers. A small percentage of biomass (5%) has been co-gasified with coal in the slurry-fed Tampa Electric Polk Power Station (220 $MW_e$) in Florida and a significant fraction (30%) of biomass has been co-gasified with coal in the dry-feed Nuon Buggenum plant (250 $MW_e$) in the Netherlands. Slurry feeding of biomass is constrained by the hygroscopic and hydrophilic nature of the biomass constituents, which limits the solids loading in slurries.[49]

For applications to co-gasification, the biomass has been reduced to sufficiently small sizes by mixing the biomass together with the coal before sending it through the coal pulverizers. While the biomass is not reduced down to the same size range as the coal, its high volatile content (which results in strong particle shrinkage upon devolatilization) and the relatively high reactivity of biomass chars means that the biomass only needs to be reduced down to a characteristic size of ~ 1 mm. For a dedicated biomass entrained flow gasifier, traditional biomass milling equipment cannot reduce the particle size down to this level without extensive feed recycling and unacceptable costs. This has posed one of the major barriers (the other being the cost of oxygen) to commercial implementation of entrained flow gasification of biomass. However, during the last few years some concepts have arisen to address this shortcoming. One approach is to pyrolyze the biomass as a preprocessing step and then to use the pyrolysis oil that is generated as a liquid carrier for pulverized pyrolysis char. In this way the biomass can be introduced into the gasifier much as heavy oil (or slurried coal) is in the Texaco gasifier design. Alternatively, if there is sufficient value in other use of the pyrolysis-generated char (for example, as a filtration medium or as a soil amendment), one can simply spray the raw bio-oil into the gasifier. The other approach to biomass preprocessing that shows some promise is to torrefy the biomass and then feed the pulverized torrefied biomass (and the volatiles released during torrefaction) into the gasifier.[50]

A typical syngas composition associated with entrained flow gasification of biomass is shown in Table 1. As with the other direct gasification syngas, a significant amount of $CO_2$ is in the product gas. Unlike all of the previously considered (bed-based) gasification techniques, the production of hydrocarbons and tar is negligible in syngas from entrained flow gasification, because of the high temperature of the process, which results in complete reforming of the biomass volatiles into CO and hydrogen. Also, with the high temperatures in entrained flow gasification, carbon conversion can exceed 99%.

All of the direct gasification approaches described in this section rely on the use of oxygen. For a large-scale coal gasifier, the high capital cost associated with cryogenic air separation units (which liquefy air and then distill out the oxygen) can be recovered in a reasonably short time. Smaller, biomass-based gasification systems cannot afford to have such a high capital cost, and the energy efficiency of air separation with cryogenic methods decreases significantly with smaller plant sizes. Consequently, one can use liquid oxygen, carried by truck or rail to the gasification facility (and presumably produced by cryogenic air separation at a major gas handling facility), or use smaller-scale, lower capital approaches to on-site oxygen production. Membrane-based approaches to oxygen production (e.g. the high temperature ion transport membrane approach) have been in development for a number of years, but still seem to be far away from commercial readiness. Therefore, the most logical approach at this time is to use a pressure swing adsorption (PSA) technique for oxygen production. In this approach, compressed air is passed over an adsorption column that preferentially adsorbs nitrogen, especially, and argon, allowing a fairly pure stream of oxygen to pass through and exit the bed. Once the adsorption media is saturated, the airflow is shut off and the trapped gases are vented before initiating another cycle. By using multiple adsorption columns operating in parallel and, occasionally, in series, a continuous flow of high purity oxygen (typ. 95% pure) is produced.[51] Further efficiency improvements have recently been achieved with this technology by venting the trapped gas to a vacuum, in a process known as vacuum PSA (VPSA).

### X.3.4 Plasma Gasification

The thermal plasma gasification process has been developed over a number of years for treatment of carbonaceous waste streams.[52-54] Essentially this is the same technology as thermal plasma pyrolysis, except it is conducted in the presence of steam, allowing for rapid steam-reforming reactions of the hot pyrolysis products and gasification reactions of the steam with char. In this sense, the thermal plasma gasification process combines the allothermal characteristic of indirect gasification (except the thermal source is externally supplied electricity) and the high temperature volatiles yield and active char gasification characteristic of oxygen-blown entrained flow reactor gasification. Because of the high temperatures associated with thermal plasmas, there is the possibility of producing a product gas with negligible tar content. The high power densities and high temperatures associated with thermal plasmas also offer the possibility of a large reactor throughput in a small volume. The key tradeoffs for these positive aspects of plasma gasification are the high electricity costs and electrode wear and replacement.

It should be noted that non-equilibrium (or 'cold') plasma processes have seen substantial development in recent years for various solid etching or other surface modification processes. These types of plasmas can be generated at relatively low temperatures and generally have lower electrical power consumption than thermal (equilibrium) plasma sources. However, to keep the plasma in non-equilibrium, it must necessarily operate at low gas density, implying reduced pressure. The large amount of residual char produced under these conditions[55,56] and the additional compression of the product gas required before gas cleanup would appear to make this approach to plasma gasification uneconomical.

While a large amount of research and development has taken place in the development of cost-effective waste treatment using thermal plasma techniques, research on production of syngas from biomass fuel sources using this technology is in its infancy. The plasma sources considered are typically directed plasma torches, with associated thermal losses from water cooling of the electrodes.[54] However, it is also possible to construct a gasifier using a plasma arc source maintained between uncooled graphite electrodes.[57] In contrast to most approaches to waste processing, which have used inert gases (usually argon or nitrogen) in the plasma torch and have not been unduly concerned with the gas flow rate from the torch, the production of high-quality syngas from plasma processing requires a minimal use of plasma gas (if a traditional inert gas is used) or else operation of the plasma torch on steam[58] or on a steam-syngas mixture.[59] Many designs, including the well-known Westinghouse plasma gasifier[60] and the Solena gasifier[61] use oxygen to assist in char conversion, but this entails a potentially significant cost, as discussed in the last section. When using an inert plasma gas, the flow of plasma gas is minimized by generating a very high temperature plasma and then mixing steam into the plasma column.[31,48,62,63]

The means by which the biomass feedstocks are coupled to the plasma source(s) vary significantly for different process configurations and have important implications for both the requisite preparation of the biomass feed and the quality of the syngas produced. Some approaches are based on direct-feed of the solid feedstock into the plasma stream, necessitating fairly small particle sizes to attain the requisite conversion in a limited plasma exposure time. This type of process requires fuel preparation that is similar to that required for entrained flow gasification. On the other hand, in both the Westinghouse plasma gasifier and the Solena gasifier the biomass is fed on top of a moving bed that has impinging plasma torches.[60,61] In this case, no special feed preparation is necessary, but the hot syngas flows upwards through the raw biomass feed, generating significant quantities of hydrocarbons and tar, similar to the indirect gasification process. Consequently, secondary tar cracking and/or reforming or tar capture and reinjection is necessary in this approach.

The thermal plasma gasification technology has only been developed for pressures near 1 atm., so significant compression of the syngas is necessary before liquid fuel synthesis can occur. On the other hand, the usable syngas yield (i.e. $CO + H_2$) for plasma gasification far exceeds that from the other gasification technologies, because in the other approaches some of the biomass feedstock is consumed (through combustion reactions) to provide the heat necessary to sustain the gasification process. Whether this primary advantage of plasma gasification can truly offset the cost of electricity consumed in generating the plasma has yet to be practically determined.

### X.4 Gas Cleanup

Synthesis catalysts are sensitive to various impurities that may exist in the gas stream exiting the gasification process. These catalysts can be poisoned by ammonia ($NH_3$), hydrogen cyanide (HCN), hydrogen sulfide ($H_2S$), and carbonyl sulfide (COS). Hydrochloric acid (HCl) and hydrofluoric acid (HF) can corrode the catalysts, while $CO_2$ can inhibit the synthesis process. Hydrocarbons and tars result in catalyst coking, reducing catalyst activity over time. Particles, such as dust, soot, or alkali fume, will deposit on catalysts and reduce their effectiveness. Consequently, all of these contaminants must be reduced to acceptably low levels (typ. from 10 ppb to 1 ppm, depending on the contaminant) before passing the syngas to the synthesis unit.[30,64-66]

Significant effort has been devoted to the development of hot-gas cleanup approaches that can remove all of the contaminants from gasifier syngas.[64,67-70] Removal of contaminants at elevated temperatures reduces heat transfer losses associated with syngas cooling and also eliminates the production of wastewater from the gas cleaning process. However, only some of the cleanup steps have been successfully applied at high temperatures, so current practice is to cool the syngas and conduct most of the gas cleaning at low temperatures.

The concentration of nitrogen- and sulfur-containing contaminants is primarily a function of the biomass feedstock and is fairly independent of the type of gasification technology that is employed. Chlorine species are also carried by the biomass source, and can vary widely, depending on the proximity of the biomass source to the ocean, for example, but the concentration of HCl in the syngas is also somewhat dependent on the gasification technology. Moderate temperature bed-based processes tend to have lower HCl content in the syngas because a larger fraction of the chlorine binds to the ash.

The primary differences in syngas contaminants as a function of gasification technology lie in the areas of hydrocarbons and tar, dust loading, and alkali fume. The lower temperature processes produce much higher levels of hydrocarbons and tar, as has been previously discussed. Bed-based processes also tend to produce some fine dust in the product gas, particularly for circulating fluidized beds. High temperature gasification processes, such as entrained flow and thermal plasma gasifiers, produce alkali fume.

Figure 3 shows a schematic of a typical, multi-step biomass syngas cleanup process. The first step in gas cleanup usually addresses the syngas tar, for those gasification processes that produce a significant tar loading. This is because cooling the raw syngas below 400 °C will begin to condense out the tars, leading to wall deposits and downstream deposition issues. In some designs, the tars are removed by condensation (also removing the dust) and then reinjected into the gasifier.[29,61] In other designs, the hydrocarbons and tar are steam reformed in a catalyst bed. A large amount of research has been conducted on catalysts for tar reforming.[71] Most of this work has focused on nickel catalysts on an alumina substrate, often with a metallic promoter (such as Mg). These catalysts tend to be much more effective at reforming tars than at reforming hydrocarbons, particularly methane. As the sulfur has not been removed at this point in the clean-up process, sulfur poisoning of the tar reforming catalyst is a concern, in addition to catalyst coking. Research is ongoing to discover effective sulfur-tolerant, coke-inhibiting catalysts for tar reforming.

After the tars have been removed, the syngas is dried and the entrained particles are removed through a syngas quench and wet scrubbing system. In most cases the alkali fume particles are also effectively captured in wet scrubbing systems. This process also removes any water-soluble gas species such as HCN, $NH_3$, HCl, and HF. The quench and wet scrubbing system necessarily entails the loss of much of the sensible heat of the hot syngas that enters the process. An alternative approach to capturing particles while maintaining elevated temperatures is to use hot barrier filters, such as ceramic candle filters,[64] but then other approaches are needed to remove the other species usually captured in wet scrubbing, such as the nitrogen-containing species, HCl, and HF.

Acid gas removal is strongly facilitated by operation at pressure. Therefore, for those gasifier designs operating near 1 atm., it is useful to compress the syngas that has otherwise been cleaned and is suitable for use within a compressor. Gasifier designs that can operate at pressure avoid this costly step. Once compressed, the acid gases can be removed, either together, as suggested in Fig. 3, or in series operations. One of the most common means of acid gas removal for biomass gasification systems is to employ an amine scrubber, using a solvent such as monoethanolamine (MEA). This solvent effectively adsorbs both $H_2S$ and $CO_2$ at a temperature of approximately 40 °C and then releases these gases when heated in an adjacent regenerator vessel to 120 °C. For hot-gas cleanup, metal oxide systems, particularly involving zinc oxide (ZnO), have been shown to be effective for capture of sulfur-containing species.[29,70]

## X.5 Conclusions

Gasification is a very flexible process for utilizing a wide variety of biomass feedstocks and generating any number of gaseous or liquid fuels, including synthetic natural gas, hydrogen, methanol, ethanol, gasoline, diesel, or DME. Historically, most operating experience for biomass gasification has either involved air-blown gasification, producing a highly diluted product gas that is unsuitable for fuel synthesis, or steam-blown indirect (allothermal) gasification.

The allothermal gasification process has been actively investigated by a number of researchers and technology developers over the years and has been scaled up to a size that can process 200 tpd. Unfortunately, this process produces large quantities of tars and hydrocarbons, requiring secondary reforming of the produced syngas, and thus far has only been operated at low pressures. Recent advances in this technology have centered on improved thermal integration of the steam gasification/char combustion chambers, to reduce thermal losses in the system. There is also a significant amount of research currently focused on the development of effective tar reforming catalysts. If cost-effective catalysts can be developed that reform small hydrocarbon species, in addition to tars, and which are sulfur-tolerant, the allothermal gasification approach will be much more promising for syngas applications. However, the low-pressure nature of this process, as currently implemented, still creates significant limitations to its use for liquid fuel synthesis.

Direct (autothermal) gasification of biomass has only been commercially employed to-date as a co-feed with coal or petroleum coke into large-scale entrained flow coal gasifiers. The capital and operating costs of oxygen production, especially at the moderate scales required for dedicated biomass gasifiers, have historically restricted the introduction of this technology, though it has the distinct advantage, for purposes of liquid fuel synthesis, of easily being employed at elevated pressure. Also, high temperature entrained flow gasifiers produce negligible char. When operating at pressure, the main difficulty stems from processing the biomass source to a size and consistency to allow feeding against the pressure gradient. Small fuel particle sizes are also required to assure sufficient conversion in entrained flow gasifiers. Recent improvements in production of oxygen via pressure swing adsorption (PSA), especially the implementation of the vacuum PSA technique, offer the promise of lower oxygen production costs at the appropriate scale. Such reductions in oxygen production costs may make autothermal gasification, specifically in the form of entrained flow gasifiers, the preferred gasification route for biomass for liquid fuel synthesis (as it already is for coal gasification).

Thermal plasma gasification was originally developed for application to waste streams, with the high temperature plasma source guaranteeing complete destruction of the waste. As applied to biomass gasification for liquid fuel synthesis, plasma gasification offers the advantage of higher yields of fuels from the biomass source than any other type of gasification approach. However, significant constraints to the practical implementation of plasma gasification lie in the high cost of electricity use (in the plasma source), oxygen use (if needed), electrode replacement, and subsequent syngas compression (because of low-pressure operation of the plasma sources). Furthermore, some designs create significant hydrocarbon and tar loading, necessitating subsequent syngas reforming.

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## TABLE HEADINGS

Table 1 Characteristics of Biomass Gasifier Product Gas

## FIGURE CAPTIONS

Figure 1 Primary process steps and potential fuel products arising from gasification of biomass feedstocks.

Figure 2 Schematic of a basic dual-bed, indirect gasifier.

Figure 3 Schematic of a typical gas cleanup configuration for treating gasifier syngas before passing the syngas to a fuels synthesis unit. The process steps surrounded by dashed boxes are only required when treating the syngas from certain types of gasifiers, as described in the text.

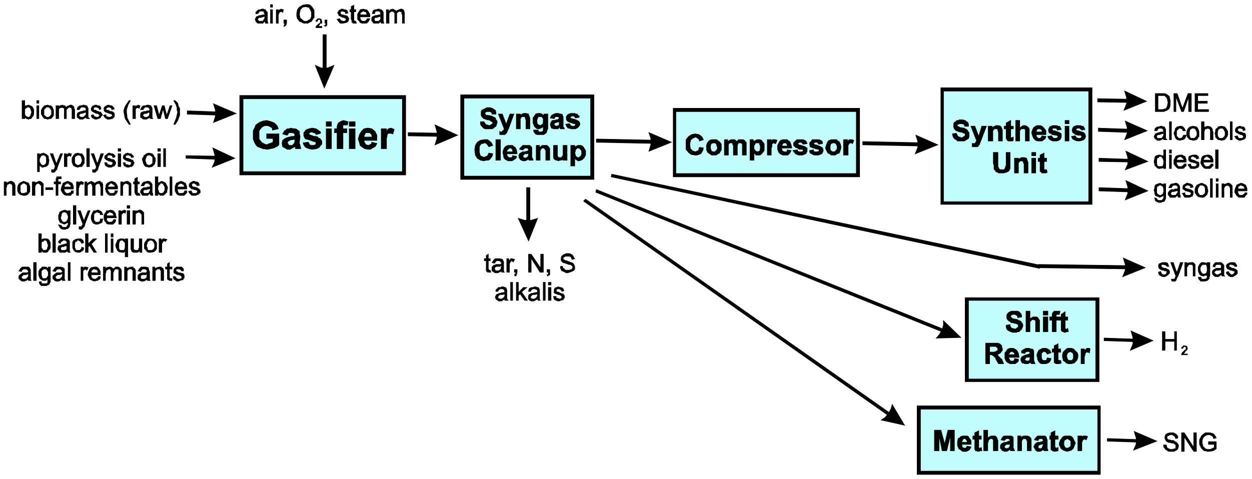
Table 1. Characteristics of Biomass Gasifier Product Gas

| **Gasifier Type** | **Product Gas Composition (vol-%, dry)** | | | | | | | **$H_2$/CO** | **LHV** | **Efficiency** |
|---|---|---|---|---|---|---|---|---|---|---|
| | $CH_4$ | $C_2$ | $H_2$ | CO | $N_2$ | $CO_2$ | tar | | MJ/Nm$^{3*}$ | |
| Indirect, dual-bed | 14 | 5 | 24 | 40 | 1 | 16 | 0.1[†] | 0.6 | 16 | 0.70 |
| Direct, $O_2$-blown bed | 13 | 3 | 29 | 22 | 3 | 30 | 0.05 | 1.3 | 12 | ‡ |
| Direct, $O_2$-blown entrained flow | 0.1 | 0 | 34 | 37 | 3 | 26 | 0 | 0.9 | 10 | ‡ |
| Thermal plasma | 0.5 | 0 | 37 | 60 | 0 | 2 | 0 | 0.6 | 12 | ‡ |

[*] units of mega-joules per normal cubic meter, with normal conditions defined to be 1 atm pressure and 298 K

[†] 0.1% tar corresponds to ~ 30 g/Nm$^3$

[‡] gasifier efficiency cannot be meaningfully defined for those processes that utilize oxygen and/or plasma heating sources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biomass (raw)
pyrolysis oil
non-fermentables
glycerin
black liquor
algal remnants
Gasifier
Syngas Cleanup
tar, N, S alkalis
Compressor
Synthesis Unit
DME
alcohols
diesel
gasoline
syngas
Shift Reactor
$H_2$
Methanator
SNG

Figure 1

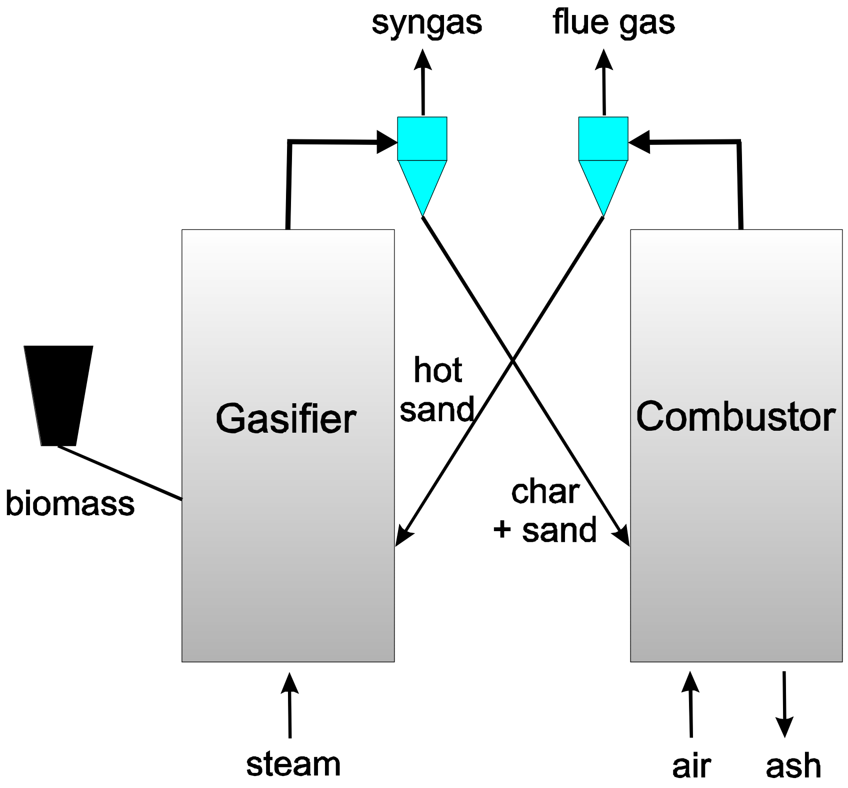
syngas
flue gas
Gasifier
hot
sand
Combustor
biomass
char
+ sand
steam
air
ash

Figure 2

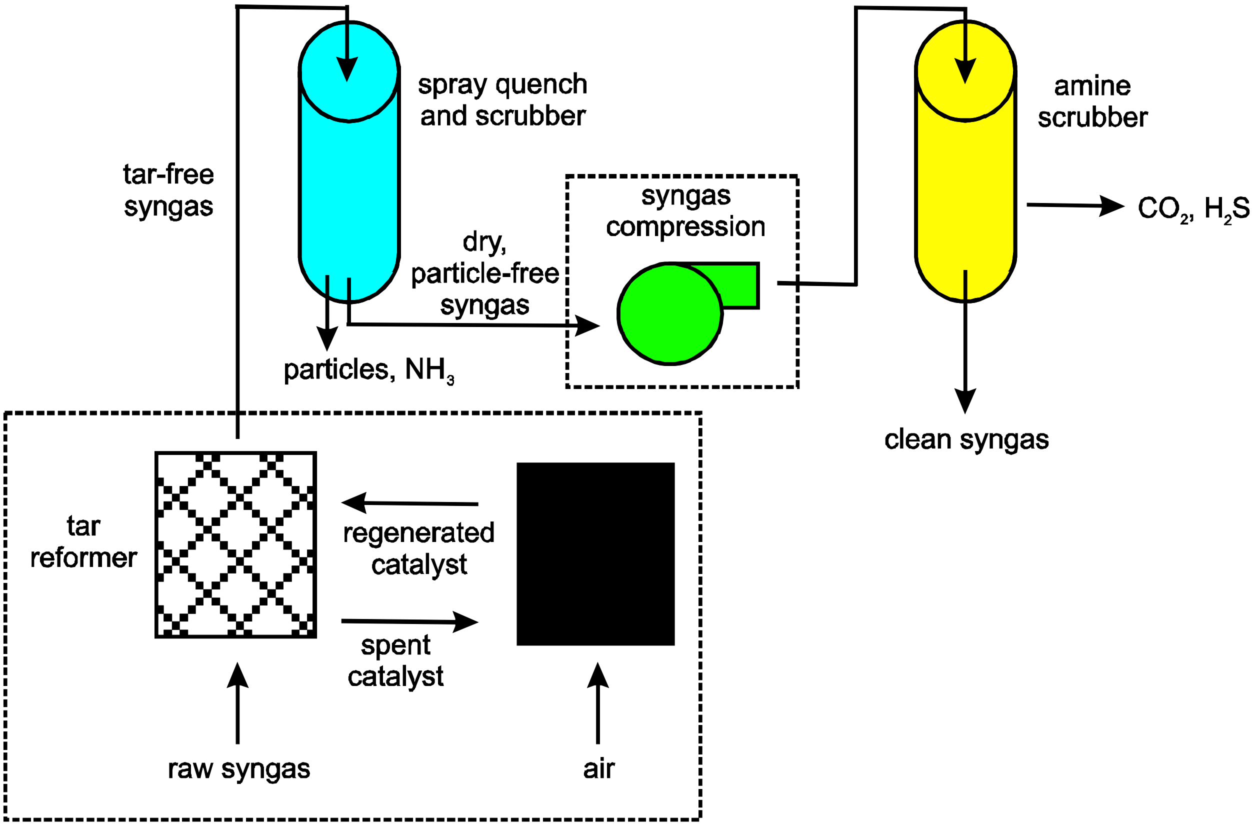
spray quench and scrubber
amine scrubber
tar-free syngas
syngas compression
$CO_2$, $H_2S$
dry, particle-free syngas
particles, $NH_3$
clean syngas
tar reformer
regenerated catalyst
spent catalyst
raw syngas
air

Figure 3