Chapter 11
Thermochemical Conversion of Biomass to Bioenergy: A Review

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Abstract Increasing global energy demand is being substantially contributed by the bioenergy sector. For the rural communities, bioenergy provides opportunities for social and economic development by improving the waste and other resource management. The contribution of bioenergy proves to be significant in terms of maintaining social, economic as well as environmental health, ensuring energy security. Biomass, when converted to bioenergy, may undergo different suitable processes. Thermochemical conversions are no exception. The process technologies include combustion, torrefaction, pyrolysis, and gasification. All these processes having the common backbone of thermal decomposition are optimized by different factors and yield specific products of different states such as solid, liquid, and gases. The characteristics of generic types of reactors used to carry out such processes are described with their special features, advantages, and disadvantages. Though researches have called for three types of possible biomass for conversion such as lipid, sugar/starch, and lignocellulose in the present chapter, conversion of lignocellulosic biomass feedstock is focused. It has been discussed how the variations in composition of biomass at optimized process flow differ the quality and quantity of potential product yields.

Keywords Thermochemical conversions · Biomass · Bioenergy
Combustion · Torrefaction · Pyrolysis · Gasification · Bio-char
Bio-oil · Syngas

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11.1 Introduction

Long history of civilization had put forward the use of various biomass sources for generating energy and fuel. There is very low utilization of biomass fuels due to exploration of nature’s relatively inexpensive, conventional fossil energy which is easy to handle and convenient to transport and contains high energy content. However, due to the strong energy crisis, need for sustainability, sharp escalating price, environmental issues global interest have been again shifted to renewable alternative sources of fuels. Renewable alternative energy provides many options and different routes for sustainability and freedom in energy sector. Here, bioenergy along with biofuel certainly can solve various societal needs of clean energy and challenges associated with them (Lee et al. 2012).

11.1.1 Biomass

Biomass in a broad sense refers to various materials originated biologically and which can be used for energy content or the chemical counterparts. The word “recent” is of logical significance, as it separates it from fossil fuels from prehistoric origin. Thus, biomass includes all type of biology from agricultural, forestry, algal sectors as well as wastes from manufacturing units including food and beverage effluents, manures, sludge, organic fractions or by-products from industry as well as households as given in Table 11.1. Biomass can also be defined as the solar energy which has been captured and stored from photosynthesis of growing plants. The carbon from the atmosphere is utilized at the time of photosynthesis and is again returned to the atmosphere for decomposition or combustion, thus creating a circle system. This system is also referred as “carbon neutral” system as a balance is maintained leaving zero impact on amount of atmospheric carbon.

According to the report of IEA 2008, biomass played a significant role in global energy consumption, as 285 EJ for the year 2005. Potential biomass supply has also been modeled at regional and national levels under a variety of assumptions, including economic drivers. Thus, Bailey et al. (2011) recommended that the entire

Table 11.1 Biomass sources and types

Types	Sources		
	Forests	Agriculture	Wastes
Woody	– Whole-tree chips – Bole chips – Mill chips	– Short-rotation woody crops	– Industrial – Construction – Municipal
Non-woody	Nil	– Sugar/starch – Lipids – Crop residues – Perennial crops	– Oils, fats, and grease – Livestock waste

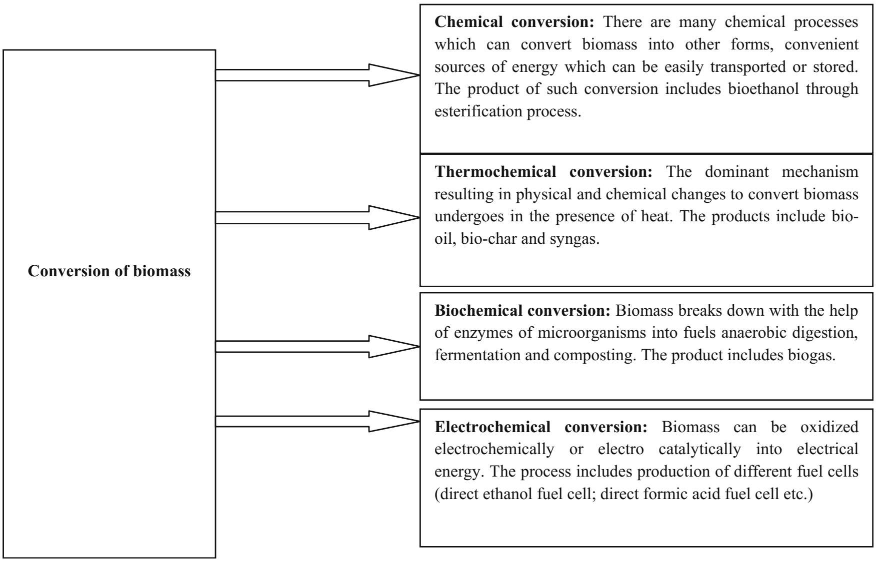
value and supply chain of advanced biofuel need to be carefully planned as well as managed for limited negative impact on human livelihoods.

11.1.2 Bioenergy

The energy derived from biomass fuel along with metabolic by-product yields is termed as bioenergy. Bioenergy has immense potential to meet the renewable energy demands for the future (Ward et al. 2013). India has now shifted much of its concern for the growth of bioenergy to fulfill the demands of improved living standards, economic, and industrial expansions, population growth, etc. Although India is considered as a leading bioenergy sector, still the basic needs for energy for millions of citizens are at high risk. The native resources of energy in India are not enough to meet the demand and that is why the country is still dependent on energy imports, creating a serious imbalance in energy supply demand. Research and development in the field of bioenergy may lead to a permanent solution to the problem and as hoped for.

11.1.3 Conversion Routes of Biomass to Bioenergy

Biomass conversion to bioenergy can be classified into different pathways according to the decomposition reactions and factors relating it. The major types of conversion pathways are shown in Fig. 11.1 with their important features.



Chemical conversion: There are many chemical processes which can convert biomass into other forms, convenient sources of energy which can be easily transported or stored. The product of such conversion includes bioethanol through esterification process.

Thermochemical conversion: The dominant mechanism resulting in physical and chemical changes to convert biomass undergoes in the presence of heat. The products include bio-oil, bio-char and syngas.

Biochemical conversion: Biomass breaks down with the help of enzymes of microorganisms into fuels anaerobic digestion, fermentation and composting. The product includes biogas.

Electrochemical conversion: Biomass can be oxidized electrochemically or electro catalytically into electrical energy. The process includes production of different fuel cells (direct ethanol fuel cell; direct formic acid fuel cell etc.)

Fig. 11.1 Conversion routes of biomass

11.1.4 Thermochemical Conversion

Thermochemical conversions are processes that are carried out in the dominant presence of heat and at times also with a catalyst and higher pressure gradient, much faster than biochemical processes (in the range of a few seconds, minutes, or hours) to produce high-valued hydrocarbons. The process is less feedstock specific or even mixed feedstock can also convert for single pathway. The process involves multiple stages converting a solid biomass into oil or gases. The conversion pathway can be subdivided into four important alternative processes which have been found efficient for conversion of biomass to bioenergy such as combustion, torrefaction, pyrolysis, and gasification. These pathways are further elaborated in the rest part with factors responsible for the entire process flow, the reactors and machineries involved and the products yield at each process.

11.2 Combustion

Combustion or burning or incineration is an exothermic, thermochemical, or redox chemical conversion process taking place in between an oxidant (mostly atmospheric, like oxygen) and reductant (fuel) producing mainly a mixture of gaseous compounds (smoke), flame, and heat. It is often referred to be much complicated sequence of elementary radical reactions It is a common practice to combust biomass and other materials as a commercial basis in order to provide heat and power. Also, new technologies are rising for a wide range of waste incineration to reduce its volume and hazardous characteristics as well as generation of heat and electricity. The reductant or organic fuel when reacts with the atmospheric oxidants, heat is evolved, when the weak double bonds of oxygen break to form carbon dioxide (CO_2) or water as it releases more amount of free energy, though initially heat may be needed to start the reaction. Researchers found that for per mole combustion reaction of oxygen molecule, approximately 418 kJ of heat energy gets evolved. Some industries have been found to incinerate or combust biomass waste by following process shown in Fig. 11.2.

11.2.1 Combustion of Biomass

Around 11% of the world's primary energy is being supplied by combustion of biomass. Combustion is useful in several ways:

- For daily heat consumption
- For community level heating applications
- Industrially for heat as well as electricity production in form of combined heat and power (CHP)
- For pulp and paper industry
- Processing of sugarcane.

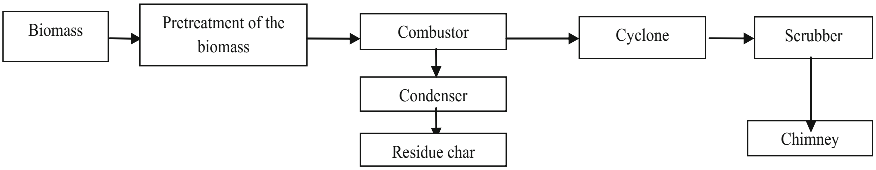


Fig. 11.2 Flow diagram of combustion of biomass

Different variety of biomass is used for each of above application depending on their local availabilities. Preferably, lignocellulosic fiber (straw, wood, nut shells, stalks, etc.) is used as source of biomass. According to Ralph P. Overend 2003 (National Renewable Energy Laboratory, Golden, Colorado, USA), during combustion of biomass released CO_2 is photosynthesized by plants which maintain equilibrium in the atmosphere. However, combusting the fossil fuels increases the CO_2 storage in atmosphere leading to environmental crisis such as global warming. The additional elements present in the harvested or wild biomass sources like nitrogen, potassium, phosphorus, sulfur, chlorine; essential for biological systems for respiration and growth; creates additional challenges for the internal structure of burner and transfer surfaces for heat in form of fouling, deposition, slagging, and corrosion. Depending upon the process quality and emission control system, the biomass as fuel can either be cleaner like natural gas or maybe polluting as coal.

11.2.2 Phases of Combustion

There are mainly three phases by which solid biomass residues (agricultural or forest wastes, etc.) undergoes the reaction of combustion.

11.2.2.1 Preheating Phase

In preheating, biomass is heated first to its flash point and then to the fire point. In this process, flammable gases can also evolve.

11.2.2.2 Gaseous or Distillation Phase

Flammable gas evolved from preheating mixes with oxygen and gets ignited. The energy is produced in form of luminance and heat, with visible flames.

11.2.2.3 Solid or Charcoal Phase

In the end, the gases are no longer capable of causing further ignition of the biomass fuel, and the un-burnt residues form char or charcoal.

Table 11.2 Important features of the common combustors (The Asian biomass handbook 2008)

Methods	Apparatus	Features
Fixed bed combustion	– Dumping grate – Water cooling grate – Inclined or horizontal grate	– Level or sloping grate – Surface combustion of the biomass – For use in batch furnaces of small type to yield ash from biomass
Moving bed combustion	– Step grate – Louver grate – Reverse and forward moving grate	– Grate is divided into two zones as combustion and post-combustion zones – Grate is found moving slowly – Ash deposition can overload the grate thus may be avoided – Applicable to various fuels ranging from chip to block type
Fluidized bed combustion	– Bubbling and circulation fluidized bed	– Sand used as bed material which helps in thermal storage and heat transmission – In a furnace, sand and fuel are kept at boiling state and a high pressure – Suitable for high-moisture fuel
Rotary hearth furnace combustion	– Kiln furnace	– High-moisture fuel combustion preferred – Restricted to fluidity and the size of fuel
Burner combustion	– Burner	– Finly powdered masses are burned mostly

11.2.3 *Types of Combustion*

Combustion can be categorized according to some literature, but these types are still in debates (The Asian biomass handbook 2008). Different types of combustors are used for this process (Table 11.2).

11.2.3.1 Complete Combustion

Reactants burn in oxygen to produce limited products mainly oxides. Though the process involves simple oxidation, it is moreover temperature dependent.

11.2.3.2 Incomplete Combustion

Incomplete combustion of biomass can happen due to insufficient presence of oxygen or an abrupt heat sink in the system. This type of oxidation causes formation of hazardous gaseous particles in atmosphere.

11.2.3.3 Smoldering

Smoldering is a slow form of combustion which is flameless or incomplete. During interaction of oxygen and condensed-phase fuel surface, heat is generated and smoldering is sustained. It occurs as a heat-generated decomposition at a temperature lower than the volatile fuel component's ignition temperature. Some solid matters have the capability to sustain this type of reactions, for example, wood cellulose, coal, tobacco, cotton, humus, synthetic foam, etc.

11.2.3.4 Rapid Combustion

This type of combustion can also be termed as "explosion" accompanied by large amount of heat and light energy release. The general phenomenon of "fire" is the common term used for rapid combustion.

11.2.3.5 Spontaneous Combustion

This type of self-heating process takes place due to heat generation caused by internal exothermic reactions and after that the thermal runaway, rapid temperature rise and finally ignition.

11.2.3.6 Turbulence

Externally fed combustion process used mainly at industrial applications for better mixing of the fuel with oxidizer. The working procedure of gas turbines and gasoline engines is based on this principle.

11.2.3.7 Microgravity

This process is influenced by gravitational state and buoyancy of the reductant. Studies related to microgravity help in understanding the various aspects relevant to the spacecraft environment as well as to the terrestrial conditions.

11.3 Torrefaction

Torrefaction is a thermochemical process which involves drying and incomplete pyrolysis where biomass is subjected to thermal heating in absence of air, typically in temperature range of 200–300 °C at atmospheric pressure, reason why also termed as isothermal pyrolysis (Tumuluru et al. 2011). The term "torrefaction" is derived from roasting process of coffee beans performed at low temperature in oxygenic condition. The similarity lies in the mechanical effect which is same for torrefaction on biomass as for the coffee beans. Torrefaction is also called as mild pyrolysis as it is conducted under similar conditions as pyrolysis which occurs at temperature ranging from 350 to 650 °C. Although, torrefaction differs from pyrolysis process where:

- Purpose of torrefaction is to retain the maximum solid mass yield along with enabling its energy content to be conserved and incomplete removal of volatile matters (Matali et al. 2016).
- Torrefaction reduces the hydrogen and oxygen contents in bio-solids as a result which releases less smoke and water vapor during its combustion (Pimchuai et al. 2010).

11.3.1 Components of Biomass

The process of torrefaction improves the biochemical, physical, and chemical properties of biomass. The thermal treatment temperature and time greatly influence the chemical and physical characteristics of biomass. The variation in formation and functioning of cells, combination of cells to form a tissue and then to a tissue system results in the complex structure of plant body. The plant cell wall is usually flexible, tough and gives support to the structure, which provides protection from stress of thermal and mechanical level. The major components of primary cell wall are—hemicellulose, cellulose, and pectin. The outer part of primary cell wall mainly consists of cutin and wax which together makes the plant cuticle layer. Secondary cell wall mainly consists a wide range of polymers that make up the physical and chemical properties of cell wall. The polymer includes—cellulose, xylan—which is a type of hemicellulose, a complex phenolic polymer named lignin and structural proteins.

11.3.2 Reactions Involved

11.3.2.1 Cells and Tissues

At a temperature range of 100–150 °C, the wall of cell shrinks and the volume of pore size decreases; this leads to changes in structure of cells and tissues.

11.3.2.2 Hemicellulose

Hemicellulose degradation starts at 150 °C, varying with its chemical nature and bond with internal lignin. Major decomposition reactions occur at temperature range of 200–300 °C. This results in a range of non-condensable and condensable products.

11.3.2.3 Cellulose

Cellulose degrades at a temperature between 240 and 350 °C giving levoglucosan and anhydrous cellulose. The crystalline structure resists the thermal depolymerization of cellulose as compared to hemicellulose. The amorphous part of cellulose contains water of hydration which holds free water. Thus, the structure of cellulose is ruptured by vaporization of water when exposed to thermal stress. During depolymerization reaction, polymer restructuring occurs in cellulose but lower than that of hemicellulose. Also, the acids and water released during depolymerization of hemicellulose are responsible for thermal degradation of cellulose.

11.3.2.4 Lignin

Lignin is highly branched, amorphous in nature and is cross-linked polyphenolic resins. It is present in spaces between other components in the cell wall. Lignin is aromatic and hydrophobic character, which degrades at a temperature range between 280 and 500 °C and produces phenols by cleaving the ether bonds and breaking the carbon–carbon bonds. However, since lignin is more difficult to dehydrate, its most of the part gets converted to char.

11.3.2.5 Organic Extractable

Organic extractable includes waxes, proteins, alkaloids, pectins, mucilages, gums, terpenes, phenolics, resins, simple sugars, glycosides, starches, essential oils, and saponins. The amount of these extractables present differs from biomass to biomass. Thus, location and quantity of biomass extractables decide the devolatilization behavior.

11.3.3 Process of Torrefaction

The parameters influencing the process of torrefaction are

• Residence time • Absence of oxygen • Heating rate • Feedstock moisture • Flexible feedstock	• Ambient pressure • Gas flow rate • Reaction temperature • Feedstock particle size

Biomass feedstock is initially dried so that 15–10% of moisture is retained. The mechanism of the reaction, its kinetics, time for the process at a specific heating rate is mainly influenced by the particle size of the feedstock. To obtain the energy dense hydrophobic biomass fuel, the duration of the process is adjusted. The process duration can vary from some minutes to many hours. For example, Felfri et al. (2005) studied that wood briquettes when torrefied for 0.5, 1, and 1.5 h at 250 °C, the higher heating values increased from 20.0 to 21.2, 22.1 and 22.7 kJ kg^{-1}, respectively. The particle heating rate in torrefaction process must be less than 50 °C/min.

Based on Table 11.3, at 50–150 °C, i.e., the nonreactive drying range, the biomass loses moisture and shrinks as a result of which the porosity in biomasses decreases. Although, at this temperature range, cells may have the ability to retain its structure if rewetted and most of the chemical constituents remain intact. At higher range, i.e., 120–150 °C, the biomass becomes suitable for densification by softening of lignin, which acts as a good binder. At 150–200 °C reactive drying range temperature, the bond between carbon and hydrogen breaks and thus lipophilic extractives and compounds are emitted by the degradation due to heat. Then the permanent type of structural deformation occurs. Bergman and Kiel (2005) concluded that the hemicellulose depolymerization produces short-condensed polymers with secondary structures. The higher temperature leads to destructive drying range, i.e., 200–300 °C which represents the range of torrefaction process. As this temperature, maximum inter- and intra-molecular hydrogen bonds and the C–O, C–C bonds are disrupted resulting in formation of hydrophilic extractives, alcohols, ether, carboxylic acids, aldehydes, and gases like carbon monoxide (CO), CO_2. Due to this, the structure of cell is also completely destroyed by destruction of fibrous nature of biomass and it then becomes brittle. Also, during torrefaction, mass loss predominantly results due to the process reactions occurring at the temperature range as mentioned in the table above. Hemicellulosic xylan, however, decomposes at around 250–280 °C. The decomposition of lignin occurs very slowly, but it gradually increases when at about 200 °C. The behavior to thermal decomposition of individual biomass greatly depends on whole integrated structure. According to Bergman (2005), further increase in temperature >300 °C causes extensive carbonization and devolatilization of polymers. Degree of torrefaction can be indicated by the color change in the raw material. It indicates that the biomass turns brown to black at 150–300 °C mainly due to the changes in chemical compositional. By this, even the impurities, namely ash, bark, or other foreign material can also be indicated.

Table 11.3 Parameters affecting torrefaction

Temperature (°C)	Time (minutes)	Reactions	Yield (%)
50–150	30–120	Drying of nonreactive type (moisture is removed and structure changes)	~90–95
150–200	30–120	Reactive drying (removal of moisture and damage of structure due to collapse of cell wall)	~90
200–300	<90	Drying of destructive type a. Depolymerization and devolatilization of cellulose b. Depolymerization and softening of lignin c. Devolatilization and carbonization of hemicellulose	~70

11.3.4 Reactors of Torrefaction

Table 11.4 compares the performances of some common torrefaction reactors available in market, describing their key advantages and disadvantages.

Chemical, physical, and storage-related properties of biomass change due to the release of volatiles. Condensable and non-condensable product emission from biomass depends upon temperature of torrefaction, its rate of heating, time for heating, moisture content of biomass, and composition of biomass. If the moisture content is high, the surfactants like fatty acid, oleic acid, resin acid which are present in the biomass, hydrolyze the monoterpenes, and transport them through matrix of wood. If moisture is low, vapor pressure and the temperature cause emission of different compounds (terpenes). When thermal treatment is applied, there is loss of moisture and other volatiles from the raw biomass which have a low heat value.

Table 11.4 Comparison of different types of reactors (Batidzirai et al. 2013)

Reactor type	Advantages	Disadvantages
Moving type compact bed reactor	– High heat transfer – Relatively simple and low-cost reactor – No moving parts in the reactor – Can process biomass with lower density – High capacity of the reactor is able to support large biomass input	– The dust particles present can cause high pressure drops resulting in automatic reactor shut down – Limited biomass type and size due to pressure drop – Non-uniform temperature distribution – Temperature controlling is difficult – Channel formation between biomass may occur causing unequal torrefaction
Torbed reactor	– Low residence time (<100 s) – The fast heat transfer leads to high throughput capacity – Low maintenance since there is no moving parts	– High utility fuel demand – Higher temperature may lead to increased loss of volatiles – More loss of volatiles leads to higher yield of tar
Belt dryer	– Better temperature control – Can work for a wide range of biomass particle size – Relatively low investment cost – Easy control over residence time through the speed of the belt	– Unequal torrefaction is caused due to clogging of holes of the belt with tar and dust, resulting into inhomogeneous torrefied product – Limited temperature control – High maintenance cost since the system has too many mechanical parts
Rotary drum	– Various methods to control torrefaction process. Both direct and indirect heating can be employed – Uniform heat transfer – It can take different types of biomass and waste size and types	– Lower heat transfer – Poor temperature control – There is more friction between biomass and wall of the drum which accumulates dust – Expensive with large footprint

(continued)

Table 11.4 (continued)

Reactor type	Advantages	Disadvantages
Screw conveyer	– Relatively economical reactor – Better biomass flow – Can take wide range of biomass sizes	– Biomass on the outer wall of reactor is comparatively more heated-causing hot spots and unequal torrefaction – Poor heat exchange capacity
Multiple hearth furnace	– Good heat transfer – Good temperature control – Compatible with wide range of biomass	– Large footprint – The process is less sustainable as the heat is provided by gas consumption, which leads to the production of moisture in flue gas. This results to lower combustion of the flue gas
Fluidized Bed	– Efficient heat transfer	– Selective particle size – Slow temperature response – Excessive biomass attrition and loss of fines – Separation of bed solids and biomass
Microwave	– The heat transfer is based on radiation rather than conduction and convection – Better temperature control – High heat transfer and fast torrefaction – Size of biomass has low effect on the heat transfer	– Electric energy required for the process – Non-uniform heating, for uniformity, it requires integration with other conventional heaters

11.3.4.1 Condensable Products

Among the condensable products of torrefaction, mainly the water is released during moisture evaporation and dehydration within organic molecules. As the temperature increases, the yield of volatiles also increases resulting in the transfer of energy to the volatiles in the form of combustibles (methanol, acetic acid). Other condensable products include acetic acid originated from acetoxy and methoxy groups which are present in xylose sugar units of hemicellulose as side chains. Also according to Ronsse et al. (2013), small amount of furfural, lactic acid, hydroxyl acetone, formic acid, and some phenol are present in volatile emissions.

11.3.4.2 Non-condensable Products

The non-condensable products include CO, CO_2 and small amount of other gases as given in above schematic. CO becomes the source of calorific value in these non-condensable products. The formation of CO_2 occurs due to acid group's decarboxylation in the biomass. CO forms by CO_2 reaction with steam and porous char. Some amount of hydrogen and methane (CH_4) is also present in non-condensable products.

11.3.5 Process Efficiency of Torrefaction

The process of torrefaction increases mainly the energy density, and thus, the fuel properties of the product are improved. The process is considered as technically feasible method, and the products can be used in residential as well as commercial combustion and also in gasification.

11.3.5.1 Moisture Content

A biomass typically contains 10–50% of moisture which gets reduced to 1–3% after the torrefaction process on weight basis. Reduced moisture can be advantageous in three ways: better for conversion process, low-cost transportation due to removal of unwanted water, and easy transportation and storage due to no biomass decomposition and absorption of moisture.

11.3.5.2 Bulk and Energy Density

The biomass becomes more porous after the thermal treatment process as the mass is lost in all the forms like gas, liquid, and solid. As a result, the volumetric density gets reduced to a range typically between 180 and 300 kg/m^3.

11.3.5.3 Calorific Value

During the process of thermal treatment, biomass loses maximum amount of hydrogen and oxygen, and least amount of carbon which results to increase in the calorific value of the product. The torrefied biomass gives an average of 18–23 MJ/kg CV, i.e., low heating value [LHV] and 20–24 MJ/kg, i.e., higher heating value [HHV].

Therefore, due to the above benefits, large amount of torrefied biomass is used in commercial scale for production of:

- For household, commercial, and industrial sector, it provides a good quality smoke-free solid fuel
- Co-firing of solid fuel directly with pulverized coal to be used at electric power plants
- Good quality of feedstock for pellets, fuel briquettes, or other dense biomass fuels.

11.4 Pyrolysis

The Greek word “Pyrolysis”; where “pyro” means fire and “lysis” means separating exactly justifies the primary methods of destruction and removal to remove the contaminants from desired product. The organic contaminants are first broken down into lower molecular weight compounds during destruction; and during the removal, these are separated from the “contaminants” (residual material). Pyrolysis, like other thermochemical conversions, is an alternative where by using heat, the biomass is converted into other chemical forms within a closed-loop system. This process has been separated from the other methods principally by the oxygen concentration and the conversion temperature, which control the extent to which chemical reactions are involved. Higher value products can be obtained by different chemical decompositions of biomass, especially carbon-rich (hydrocarbons) through this technology. It is also one of the most efficient pathways in liquid condensation from dried heated organic matter. Pyrolysis is often considered as the initial step of combustion and gasification. The rate of pyrolysis increases with temperature and the production potential of the process also vary accordingly.

11.4.1 Pyrolytic Products

The products obtained by pyrolysis are:

- Bio-char: Solid residues of carbon and ash
- Bio-oil: Quenched or condensed liquid
- Syngas: Mainly consisting of hydrogen, CO_2, CO, CH_4 along with other carbon species in traces.

Lanzetta and Blasi (1998) showed that at the first step in pyrolysis (250–300 °C), the volatile release is ten times faster than that of the other steps. The relative proportion of the end products may also vary with the composition and the structure of biomass. Based on the temperature advancement, the procedure alters resulting different products with typical compositions (Table 11.5).

The products obtained during the reaction are collected separately and also treated to purify. Like electrostatic precipitators are used in most of the cases for capturing pyrolysis aerosols, but their operations are observed to be tricky and also expensive (Scott et al. 1985). According to Demirbas (2000a, b), products from pyrolysis not only depend on the temperature or the reactor bed at which they had been subjected but also on the water present inside the biomass that can influence the liquid phase product and contributes in extracting some water-soluble products from the gas and tar phases and leads to huge decrease in gaseous and solid products (Arni 2010).

Table 11.5 Features of different products obtained in pyrolysis (Jahirul et al. 2012)

Temperature range	Process reaction	Characteristics of the products
Below 350 °C	Due to depolymerization, some free radicals are formed and water is eliminated	CO and CO_2, carbonyl and carboxyl compound and char residues are formed
350–450 °C	Substitution results in glycosidic bond breakage	Tar fraction is formed by the mixture of oligosaccharides, levoglucosan, and anhydrides
Above 450 °C	Dehydration to form units of sugar	Carbonyl compounds are formed
Above 500 °C	Mixture of all type of reactions	Different types of products are formed
Condensation	Products which are unsaturated gets condensed	Char residue which is very reactive containing trapped free radicals

11.4.1.1 Bio-Char

Char can be described as the intermediate in form of a solid residue which is obtained from the thermal degradations of lignin and hemicelluloses when efficiently separated; as it can act as a catalyst for cracking of vapors and can form some harmful hydrocarbons which can lower the efficiency of the process. According to the investigation of Rocha et al. (2002), the temperature regions were classified into three zones, where the production of bio-char was found to vary dramatically, and it was noted that when there is increase in the temperature, bio-char production rate decreased (Jahirul et al. 2012). The physical characters of char are greatly affected by the pyrolytic characters like—type of biomass, type of reactor, drying, chemical activation, particle size of feedstock, rate of heating, pressure flow of the inert gas, residence time. The char consists of mainly carbon, hydrogen, various inorganic species of both crystalline and amorphous aromatic structures, where elements like hydrogen, oxygen, nitrogen, phosphorus, and sulfur can be incorporated as heteroatoms (Bourke et al. 2007). Bio-char is used in many industries, depending upon the composition, chemical and physical properties, to produce carbon nanotubes, briquettes, hydrogen-rich gas or to be used as simple solid fuels.

11.4.1.2 Bio-Oil

The liquid produced by the condensation of the vapors is called pyrolysis oil. This is found to be much advantageous rather than that of other liquid fuels due to CO_2 balance, possibilities to be used in small-scale power generation, ability to store and transport, and high-energy density (Chiaramonti et al. 2007; Balat et al. 2009). The oil obtained is dark colored with distinctive acrid smoky smell, high density, and viscosity and less volatility and immense miscibility with polar solvents. Lignin content of the biomass affects the high molecular weight of the oil. This oil can be upgraded to the transportation fuel, but it needs further development. New technologies are found to be evolving which not only includes its up-gradation to liquid fuels but also in fields like chemical, heat, and power generations such as for production of resins, fertilizer, flavor, adhesive, acetic acid, industry feedstock.

11.4.1.3 Syngas

High temperature favors tar decomposition and thermal cracking which evolves volatile species capable of undergoing many secondary reactions like dehydrogenation, decarbonylation, decarboxylation, deoxygenation which decrease the yield of char and oil to form syngas. Biomass with very less moisture content is mostly influenced to yield more of syngas. Chemically, syngas is composed of hydrogen and CO. Traces of CO_2, nitrogen, CH_4, tar, ash, etc., are also found to occur depending upon the feedstock type and pyrolysis conditions. These components undergo endothermic reactions affecting the temperature of the reactor as well. Syngas can be used in internal and industrial combustion engines as renewable alternative fuel for and combustion processes. However, they are mostly avoided for economic as well as environmental concerns.

11.4.2 Process Flow of Pyrolysis

Pyrolysis of biomass as schematically represented in Fig. 11.3 is quite complex and includes both successive and simultaneous reactions of organic matters inside nonreactive (inert) atmosphere. The thermal decomposition is carried out at various temperature ranges, starting from 350 to 550 °C finally reaching up to 800–1000 °C. The long chains of carbon, hydrogen, and oxygen are obtained in the form of condensable vapors, gases, and solid residues as stated earlier.

Once the biomass is dried and reduced to the desired size, they are put into the reactor, which undergoes pyrolysis for the optimum residence time, at a particular temperature. The condenser acts as a special quenching unit where the vapors produced are passed and later collected. The remaining gas fraction is flared, whereas the solid char is collected in char cyclone.

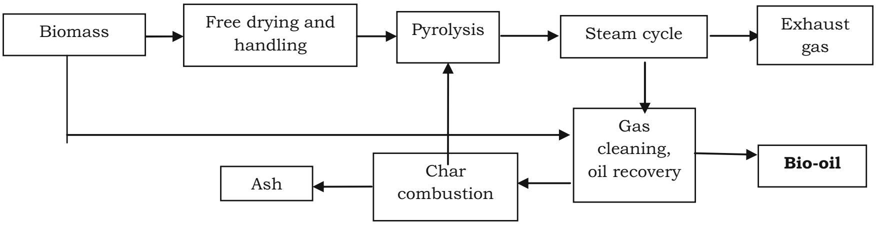


Fig. 11.3 Flow diagram of fast pyrolysis

11.4.3 Suitable Biomass for Pyrolysis and Their Advancement for Maximum Production

According to US Department of Energy, 2011 different factors are taken into account for the production efficiency to produce biofuel and bioenergy. Such factors determine the utility of that particular biomass in terms of sustainability. Similarly, for pyrolysis, the selection of biomass depends on following factors:

- Arable land requirement
- Sustainable feedstock production
- Regional strength
- Feedstock logistics
- Grains or non-grains
- Feedstock properties and compositions
- Pretreatment cost
- Availability of efficient conversion or transformation technology
- Feedstock cost
- Capital investment and operating cost involved
- Environmental benefits
- Desirable products and their values
- Food crops or waste residues

11.4.3.1 Composition of Biomass

The most efficient biomass for pyrolysis is found to be composed of lignocelluloses, i.e., cellulose, hemicellulose, and lignin, whose decomposition at varied temperature gives suitable results on the basis of thermochemical reactions undergone by them, each of which is different in their decomposition behavior. During the process of pyrolysis, all the three components are decomposed at different times. Hemicellulose is first to be pyrolyzed, followed by cellulose, and lignin is decomposed at last. Interestingly, the lignin, as well as hemicellulose, can affect the cellulosic decomposition characteristics but still cannot affect the main overall pyrolysis process (Wang 2008). Yang et al. (2007) observed that cellulose is the main source of bio-oil from the biomass, while the lignin provides the solid residue or bio-char.

11.4.3.2 External Factors of Pyrolysis

During the entire process flow, some of the vital parameters which are specially taken care of are as follows:

- Pressure value inside the reactor
- Screw rotation of the feeder
- Flare operation
- Condenser operation
- Feeding rate

Several experiments are taking place all over the world to optimize the factors for particular biomass varieties to have better process and production efficiencies and immense yield to check the energy crisis faced by all. The international research community has gathered information which carried out researches and put forward the topic to the world to spark interest in the field of Applied Science over a long period of time and now has summed up their attempts into pertinent matters which are very significant for the advancement of pyrolysis. The primary requirement of pyrolysis is to impart high heat flux to increase the rate of heating at desired level. The high temperature splits the bonds of cellulose, hemicellulose, and lignin (Ringer et al. 2006) to produce various oxygenated fragments with diverse ranges of molecular weight. The compounds or fragments with lower molecular weights remain as permanent gases, whereas compounds having higher molecular weights condense to collectively result to "bio-oil" and the others yield as "bio-char" (solid).

11.4.3.3 Requirement of Heat Transfer Mechanisms for Uniform Heating

The thermal degeneration of the lignocelluloses of biomass feedstock requires a lot of heat to cleave the macro-polymeric bonds of the biomass to smaller fragments. When the temperature reaches about 400 °C, the oxygen in these fragments become unstable and various chemical changes take place till they are quenched thermally. The heat flux to the biomass should be maintained with a corresponding high heating rate where the heat transfer from one particle to other takes minimum time. Hence, a short residence time is needed during the reaction which also terminates immediate cooling of vapors and brings "cracking severity" (Ringer et al. 2006). If the vapors are not condensed properly, then the compounds can get fragmented to smaller particles and/or it can also polymerize to large particles. According to Reed et al. (1980), 600–1000 W/cm^2 is the optimum rate of the heat transfer. Many researchers have cited various data for the most appropriate measurement of "heat of pyrolysis" for sublimation of biomass residues to bio-oil vapors. Thus, the exact value is still a debate as because the value does not solely depend on the energy supplied to the reaction vessel but also it is dependent on the quality and quantity of the by-products produced at the time of reaction such as gas and or char.

11.4.4 Classification of Pyrolysis

Pyrolysis can be classified into three types depending on the following factors (Table 11.6).

Table 11.6 Classification and salient features of pyrolysis (Balat et al. 2009)

Types	Temperature (K)	Rate of heating (K/s)	Residence time (s)	Particle size (mm)	Yield (%)		
Slow	550–950	0.1–1	450–550	5–50	30	35	35
Fast	850–1250	10–200	0.5–10	<1	50	20	30
Flash	1050	>1000	<0.5	<0.2	75	12	13

11.4.4.1 Slow Pyrolysis

The process of slow pyrolysis, also known as carbonization, is mainly the process of heating the substrate (biomass/coal) in an anoxic (oxygen-free) or oxygen-limited environment. Slow pyrolysis is basically a traditional application for charcoal production with the main intention to produce smokeless fuel. The process of slow pyrolysis is characterized by long solid and gas residence time along with low temperature and heating rate. Slow pyrolysis process is mainly used for enhanced char production (Jahirul et al. 2012). The process also produces tar and some gaseous components. The main gaseous constituents include CO, NO_x, CO_2, H_2, CH_4, hydrocarbons, and dust. The quantity of products produced from the process greatly depends on the composition of feedstock and process set-up (Jonsson 2016).

The slow pyrolysis process flows as schematically represented in Fig. 11.4 is carried out in a two-chambered apparatus. The inner chamber is filled with solid feedstock. Electronic controllers are set to heat the material with a uniform rise in temperature (~10 °C/min) can be made up to maximum (~500 °C in case of slow pyrolysis) which is to be maintained for defined period (Chhiti et al. 2013). A continuous stream of nitrogen gas flushes the gases and vapors generated during the reaction time through the second chamber. These gases and vapors form the tar portion of the product. This heavy tar portion is condensed and distilled; the distillate is further decanted to obtain settled tar and aqueous phase. The solid residence time ranges from few hours to several days. The solid portion obtained after the completion of the reaction is the char portion of the product.

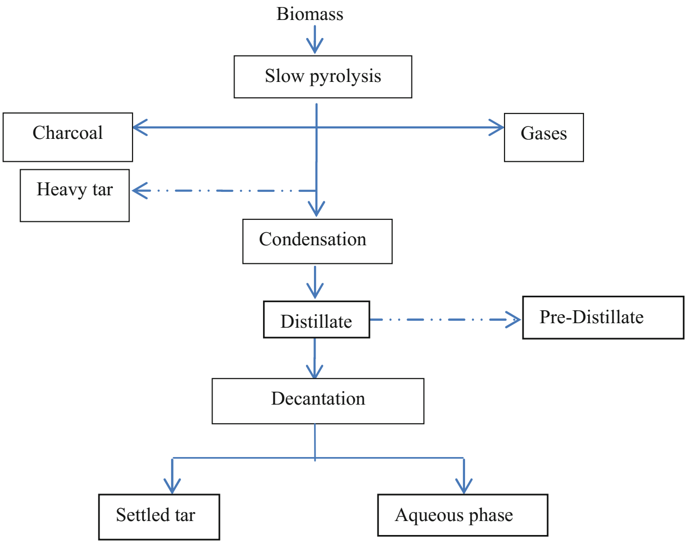


Fig. 11.4 Process flow diagram of slow pyrolysis (Fagernäs et al. 2012)

Benefits of Slow Pyrolysis

- This process can be operated on a wide range of feedstock, also with the biomasses which are hard to handle and are of low quality.
- The feedstock used can be used in larger particle size.
- Slow pyrolysis reactor can handle feedstock having ~50% moisture content.
- The primary product (charcoal/bio-char), can be used for domestic as well as industrial (chemical/pharmaceutical/metallurgical) purpose (Karaosmanoglu et al. 1999).
- Other than energy production, the products can also be used for other purposes in areas like agriculture, fertilizer production, pesticide production (Jonsson 2016).

Limitations of Slow Pyrolysis

- The key product of this process, i.e., char has very less industrial value.
- Since bio-oil is more valuable commodity, this might prove fast pyrolysis to be more competitive.

11.4.4.2 Fast Pyrolysis

Fast pyrolysis is a process that implies very high heat influx on the feedstock in the absence of air (mainly oxygen) so that it gets vaporized and later condensed into dark brown mobile liquid (main product as bio-oil) which may have a heating value alike to the conventional fuels (Ward et al. 2013). Fast pyrolysis differs from traditional charcoal or bio-char yielding slow pyrolysis process in terms of higher heating rates as well as production potential of liquid products. Pyrolysis reactors are having certain criteria for feedstock, and accordingly, feedstock is preprocessed before feeding into the reaction chamber (control panel). Preprocessing may include particle size reduction, grinding, moisture content analysis, and maintaining it to the range of 10%, drying, weighing, etc. Drying is an essential step as it includes removal of water which can be a serious interference in the stability, pH value, calorific value, or corrosiveness of the product yield. As soon as the lignocellulosic feedstock that enters the reaction chamber from the feeder, as shown in the schematic; Fig. 11.5; the intense temperature results in macromolecular depolymerization, and formation of all the three types of products which are collected separately as char, oil, and vapor. Bio-oil is collected after condensation of the vaporized fragments and the rest uncondensed remnants leave the system with the carrier gas, whereas the solid residues are expelled frequently from the system so that it can cause less interference in oil yield.

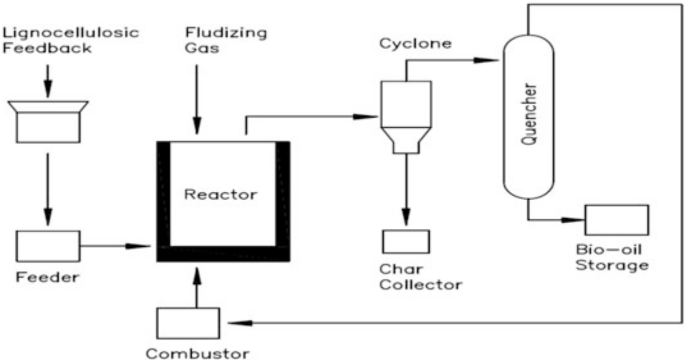


Fig. 11.5 Schematic of fast pyrolysis

Fast Pyrolysis Reactors

In recent studies researches have categorized the reactor beds used for fast pyrolysis process on the basis of the maximum utilization of the machines in an inexpensive way to have the maximum production. Some of the most common reactor beds used worldwide is described in Table 11.7.

11.4.4.3 Flash Pyrolysis

The process is often claimed as an up-gradation of fast pyrolysis with a promising amount of bio-oil yield. It is characterized by reactive flash volatilization method (RFV); converting non-volatile solids and liquids to volatile compounds by thermal decomposition in an anoxic condition, at high heating rates between 400 and 1000 °C and a very short vapor residence time. However, Mohammad I. Jahirul et al. in their work had cited some limitations such as

• Presence of solids in the oil • Inferior thermal stability	• Corrosiveness of the oil • Chemical instability of the oil

11.4.5 Future Challenges of the Process

Commercial production and utilization of bio-oil are still in natal stage. Biomass selection, it is drying, commercial level catalyst development, process optimization, reactor design, separation of oil and gas needs to be studied in terms of laboratory-scale production and up-scaling to industrial model. However, cost of production should be commercially and socially acceptable. Use of bio-oil in different paradigm should be documented and standardized.

Table 11.7 Features, advantages, and disadvantages of different fast pyrolysis reactors

Reactor type	Features	Advantages	Disadvantages
Fixed bed	– Stainless steel, concrete, or firebricks with fuel feed unit, an ash removal unit, etc. – Feedstock enters through simple vertical shaft and the expelled vapors after heating is collected with carrier gas – Cleaning system includes scrubber, cyclones, filters, etc. – Bio-oil yield 35–50%	– Simple design – Independent of biomass particle size – Reliable with gas cooling and self-cleaning system	– Operated with long residence time, high carbon conservation, low ash carry over and low gas velocity – Difficulty in removing the char
Bubbling fluidized bed	– Sand is used frequently as a solid phase to heat the biomass in anoxic condition, and the carrier gas stream conveys the oil vapors out of the reactor – High heat transfer rates and uniform bed temperatures from number of flexible heating sources – The vapor residence time can be manipulated and controlled by the carrier gas flow rate – Bio-oil yield 70–75%	– The simple construction encourages easy operations – Better control in temperature, transfer, and storage of heat	– Particle size not more than 3 mm – Discharging char which accumulates at the upper level of the bed
Circulating fluidized bed	– Much similarity with bubbling fluidized bed – Shorter residence times (0.5–1.0) s – Use of more amount of sand – Flow rate of sand is 10–20 times higher than biomass feeding rate – Bio-oil yield 70–75%	– User-friendly technology – Good control in temperature – Particles of larger size can also be used	– Movement of char and particles causes abrasion of char and forceful interactions between them which can also cause incomplete pyrolysis – High energy cost
Ablative	– Vortex reactor to exploit the phenomena of ablation – Biomass is pressed against the heated	– The particle size can be up to 20 mm – Reactor configuration avoids the basic need of carrier gas which	– Expensive reactor – Less economic – Reaction rate is lower

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
	walls of the control panel, by the high centrifugal force created by the vortex – The materials are found melting to generate both oil (pyrolysis vapors) and residual char – A "solid recycle loop" redirects large incompletely pyrolyzed particles back to the feeder – Bio-oil yield 70%	can dilute the concentration of bio-oil – No excess pressure gradient needed – Temperature to be maintained at 500–700 °C	
Rotating disk reactor	– The reactor enforces the biomass to slide on to the hot disk during rotation under high pressure – Heat transfer results into particle softening, vaporization and collection to separate condensation tank – Bio-oil yield 60%	– No carrier gas needed – Heated sand and biomass are moved by centrifugal force	– Complex process – Small particle size needed
Rotating cone reactor	– Intensive mixing between biomass and hot sand to provide efficient heat and mass transfer – At the time of spinning, it causes centrifugal force to move the solids upward to the lip of the cone – After the reaction, the char and hot sand are recycled to a combustor – Bio-oil yield 65%	– No need of additional heat and inert gas – Undiluted vapor can be obtained	– Complex process – Particle size should be small – Not applicable for large-scale
Vacuum	– Lower heat transfer rates – Induction heater and burner with molten salts are used as heat carrier	– The absence of carrier gas is the primary factor in lowering the aerosol formation	– Slow process – Solid residence time is very high – Heat and mass transfer rates are not adequate

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
	– Biomass is carried by a moving belt into high-temperature (500 °C) vacuum chamber where a mechanized agitator stirs the biomass on the belt with chemically inert quartz as packing material – As prevention for condensing the products in the tube before the cold trap, the tube is warmed with a heating tape at the end of the furnace – Bio-oil yield 35–50%		– Produces liquid effluents as volatile matter which cannot be collected in the scrubbers
PyRos	– It assembles both fast pyrolysis cyclonic reactor and high-temperature gas cleaning system in one unit for production of particle free bio-oil – The temperature should be maintained at the range of 450–550 °C, with a typical gas residence time 0.5–1 s – Hot gas filtration is mainly done by the principle of the rotational particle separator (RPS) – Biomass and the carrier gas are introduced which moves downward by centrifugal force at periphery of the cyclone – Bio-oil yield 70–75%	– Low-cost compact technology – Both small- and medium-scales which make 70–75% oil production in a decentralized way for easy transport of oil	– Reactor is complex compared to other types – Presence of solids in oil (mostly alkali) – High temperature is needed

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
Auger	– Advanced screw assembly – Biomass and hot sand are driven through an anoxic reactor vessel – Space through the tube raises the feedstock to the desired temperature (400–800 °C) – Bio-oil yield 30–50%	– Operating procedure is similar to that of a polymer twin-screw extruder – Influence well mixing and enhance heat and mass transfer efficiency – Residence time can be modified as per convenience	– Heat transfer process is not suitable for large-scale reactors
Plasma	– Cylindrical quartz reactor bed surrounded by two copper electrodes, within which different size of biomass can be inserted by screw-feeder – Inert gas induces production of plasma – Vapors are evacuated from the reactor by vacuum pump – Bio-oil yield 30–40%	– High temperature and energy provide the system of immense potential to generate heavy tarry compound with low productivity of the syngas	– Heavy power consumption – Expensive – Small particle size is needed
Microwave	– Biomass absorbs the microwave radiations effectively at lower initiation time for the reaction. – Microwaves lie between infrared and radio frequencies and cause motion by migration of ionic species or rotation of dipolar species or both to generate heat – Addition of catalyst fastens the reaction rate thus sodium hydroxide, sodium carbonate, aluminum oxide, etc., can be used for higher yield of solids and lower yield of gas – Bio-oil yield 60–70%	– Size of biomass need not be reduced as the uniform microwave heat causes well heat transfer to each particle – Drying of the biomass takes place inside the reactor – Temperature or heat utilizations can be reduced to (150–300 °C)	– High operating cost – High-power requirement

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
Solar	– The reactor bed made up of quartz provides a suitable way of storing solar energy in the form of chemical energy – A parabolic solar concentrator is adhered to the reactor to concentrate the radiation and generate a temperature of nearly 700 °C – Bio-oil yield 40–50%	– Utilization of solar reactor bed overcomes the prolusion problem – Capable of faster start-up and shutdown periods than other reactors	– Weather dependent – Expensive

11.5 Gasification

Gasification is a type of partial oxidation process, a class of thermochemical conversion, carried out in the presence of steam of high pressure and temperature. Volatile matters release as the fuel heated to some extent gets oxidized to produce water, CO_2, CO, hydrogen, CH_4, and other gaseous hydrocarbons along with heat to continue the endothermic gasification process. Water is vaporized, and pyrolysis continues as the fuel is heated. Biomass gasification is a relevant technology which can contribute to develop green energy system which is effective and environment friendly in order to increase the share of renewable energy in all sectors (Chhiti et al. 2013). The syngas generated is found to be directly combustible and can be applied in prime movers such as engines, turbines.

11.5.1 Chemical Reactions of Gasification

The gasification is very complex and includes different chemical reactions such as:

- Decomposition of organics and hydrocarbons such as carbohydrates and cellulose
- Fragmentation of hydrocarbons to other low molecular species
- Recombination of methylene and methyl radicals
- Shift reaction of water gas
- Formation of polycyclic aromatic hydrocarbons
- CO_2 gasification of carbonaceous materials or Boudouard reaction (Sikarwar et al. 2016).

If the biomass is pretreated prior to the reaction, the reaction dynamics have been found varying at equilibrium values.

11.5.2 Routes of Gasification

Research combines all the reactions in five basic steps to understand the process flow of biomass conversion and production of syngas.

11.5.2.1 Dehydration

Drying the biomass at 100 °C, resulting steam which evolves is mixed into the gas flow.

11.5.2.2 Pyrolysis

Pyrolysis is non-oxygenating thermal process which enhances the formation of char (solid residues) and tar (mixed form of liquid and gaseous products). Biomass is found to decompose rapidly at 200–300 °C evolving tar which is more complicated volatiles composed of hydrogen, carbon, and oxygen molecules. The reaction rate is very slow, and the overall reaction is too complicated.

11.5.2.3 Cracking

Decomposition of complex molecules likes tar to lighter gaseous products in the presence of heat. The gaseous products are found to be cleaner and compatible with internal combustion engines. Ensured proper combustion occurs at absolute presence of oxygen and at high temperature.

11.5.2.4 Reduction

This is the process of removing oxygen atoms to form hydrocarbons, water, and heat. The oxygen is drawn toward the bond site on the carbon than to itself, thus no free oxygen can remain in its diatomic form, and the oxygen available will be directed in the same way until number of molecules end up. Combustion and reduction are exactly opposite and equal reactions taking place at the same process flow.

11.5.2.5 Combustion

The heat which is involved in drying, pyrolysis, reduction, etc., comes either directly from combustion or is recovered from heat exchange processes in a gasifier.

11.5.3 Types of Gasifier

The patent literature have mentioned about different types of gasifiers or reactors carrying out gasification of solid and dry biomass. Most of them have been developed and commercialized for generating heat and power from syngas. According to Chhiti et al. (2013), the prime differences between gasifiers are:

• Type of injection • Gasification agents • Type of heating	• Temperature range • Pressure range of operation

Based on the density factor, which is a ratio of the solid matter, a gasifier can burn to the total volume of the biomass. The main two reactor types for such operations are

- Dense phaserReactors
- Lean phase reactors.

Both the types are having special features for individual operations, advantages and disadvantages as given in Table 11.8.

11.5.4 Products of Gasification

11.5.4.1 Syngas

It is basically a mixture of gas released at high temperature followed by a clean-up to remove components like syngas and tar can be used to produce organics like liquid fuel or natural gas. It mainly consists of:

- CO (30–60%)
- Hydrogen (25–30%)
- CO_2 (0–5%)
- Traces of CH_4, water vapor, hydrogen sulfide, ammonia, etc.

Biomass having low ash content is generally used for syngas production, as more ash content result in slagging (Sikarwar et al. 2016). Syngas can be used for following purpose for production of liquid fuels:

Table 11.8 Classification of gasifiers

Types	Features	Advantages	Disadvantages
Dense Phase Reactors			
Updraft	– Simplest and oldest known as countercurrent gasifier – Biomass gets in through the top of the reactor – Steam comes through the bottom of the reactor – Combustion occurs at the bottom of the bed producing water and CO_2	– Effective thermal efficiency – Insignificant pressure drop – Heat production for small-scale applications – Slag formation – Feedstock with high moisture can be used	– Size limit for feedstock – High yield of tar – Poor reaction capability of the syngas cannot be used directly
Downdraft	– Convert biomass or charcoal into fuel – Co-current reactor – Gasification agent and fuel move in the same direction	– Moderate sensitivity to charcoal dust and tar – Flexible adaptation of gas production	– Feedstock drying is required – Syngas exiting at high temperature – Secondary heat recovery system needed
Crossdraft	– Simplest and lightest gasifier – Air enters through a single nozzle at high velocity, induces substantial circulation, and flows across the bed of fuel and char – Production of low tar is noticed – Generates high temperature – Fuel and ash serve as insulation for the walls of the reactor – Air-cooled and water-cooled nozzles and grates are often required	– Very fast response time for loading – Short height – Gas production is flexible	– Severe pressure drop – Very high sensitivity to slag formation
Lean Phase Reactors			
Fluidized bed	– Fine particles of biomass, steam get in the bottom of the reactor – Heat and mass are transported through an inert – Gasification agent blows to lift the bed against gravity – Operating temperature is 700–900 °C and pressure ranges between 0 and 70 bar – It can be classified into three categories	– Temperature distribution is almost uniform – Exhibits high rates of heat transfer – Low tar and unconverted carbon	– Complex design – Limited usage of feedstock having high moisture – Blowers required to inject – Alkali contents form silica

(continued)

Table 11.8 (continued)

Types	Features	Advantages	Disadvantages
	Circulating fluidized bed • Two integrated systems • First unit (riser) is kept fluidized, overall residence time is higher • Second unit differentiates the product gas from bed and sends it back to riser **Bubbling fluidized bed** • Feeding done from side or bottom • The velocity of gasifying agent is controlled • The gas produced, exits from the top • Ash is generally removed using a cyclone **Dual fluidized bed** • Separates gasification and combustion part using two beds • Biomass is fed into the base using steam • The second bed is used as char combustor • The bed mainly acts as a medium for heat transfer to produce nitrogen-free syngas		
Entrained flow	– Sample can be used in powder form – Reaction time is less – Contact surfaces are quite high – Air and feed move together, and reactions occur at more than 1000 °C – It is basically classified into two families: **Top-fed gasifier** • Cylindrical shaped vertical reactors • Refined particles of fuel and gasifying agents are used • Combustion by inverted burner • Product gas is recovered from the side of the lower section and slag remains at the bottom	– Syngas produced is free from tar – Ash is collected at the bottom of the reactor in the form of slag – Conversion is found to be close to 100%	– Slagging, fouling, and corrosion are the most vital issues – Dependent on biomass composition – Generation of acid gas with sulfur and chlorine

(continued)

Table 11.8 (continued)

Types	Features	Advantages	Disadvantages
	Side-fed gasifier • Gasifying agent and feedstock are fed through the nozzles at lower part • Perfect mixing of oxygen and fuel • Product gas is recovered from the top and slag from the bottom		

- Mixed alcohol synthesis (production of a mixture of ethanol, propanol, methanol, butanol, and lesser amounts of heavier alcohols)
- Fischer–Tropsch synthesis (catalytic process used to produce liquid fuel from coal-derived natural gas and syngas)
- Syngas fermentation (biological process which involves anaerobic microorganisms to ferment the syngas to produce alcohol)
- Methanol synthesis (catalytic process of methanol production).

11.5.4.2 Tar

Tar production is an important problem in biomass gasification as it causes blockage in the instruments and makes operation difficult. It is basically a thick dark brown liquid with a low condensation temperature. Light hydrocarbon particles avoid condensation and form tarry aerosols. According to Sikarwar et al. (2016), tar is mainly composed of benzene (38%), toluene (14.5%), single-ring aromatic hydrocarbons (14%), dual-ring aromatic hydrocarbons (8%), heterocyclic compounds (6.5%), phenolic compounds (4.5%), triple-ring aromatic hydrocarbons (3.5%), and quadruple-ring aromatic hydrocarbons (1%). As such, there is no limitation for the amount of tar if the fuel gas is used directly for combustion, provided the gasifier outlet and burner inlet should not allow the gas to cool down below the dew point of tar. Tar minimization and degradation methods to be undertaken for better process efficiencies and better production of syngas.

11.5.5 Benefits of Gasification

Biomass gasification was initially started to utilize organic wastes to produce higher value products to reduce landfill of solid wastes and decrease in CH_4 emission. It also reduces the risk of groundwater contamination. Production of different categories of alcohols or phenolics from non-food sources is one of the prime benefits of the process. Biomass of high moisture content and wastes can be used with ease at the process flow. Some of the important economic benefits of the process are listed below:

- Low-priced or negative-value feedstock can be transformed into higher valued products
- Provides a high range of fuel flexibility
- Reduces the cost of handling wastes
- Provides a source of income from wastes generated at municipal areas
- The by-products can also be consumed like sulfur has utility as fertilizer and slag has usage in construction or as a roofing material
- Reduces dependence on expensive imported natural gas
- Less emission causes reduction in the operation cost of the reactor.

11.6 Conclusion

The utilization of biomass or rather biomass residues as feedstock appears to be an useful solution for producing green energy in future. However, various technical issues remain to be fulfilled,in particular, the recalcitrant nature of the second generation feedstock. The technologies should be analyzed, modeled, and optimized based on a number of factors such as feedstock selection, pretreatment methods, reaction and separation process, water recycling, energy integration, by-products' production, and its utilization to emphasize on economic efficiency as well. Among variety of technologies, thermochemical processing has gained particular attention for converting biomass into more useful and valuable products. Though combustion is the most traditional form of conversion or processing of biomass, torrefaction, pyrolysis, and gasification are still evolving technologies which are creating new blooms in the field of bio-alternative sources of fuel or energy enhancing net usefulness of biomass maintaining the cycle of constituents in nature as well. Not only these processes enhance sustained power or energy generation but also emphasizes on the specificity of bioenergy forms. Products obtained from these thermochemical conversions can be used in various sectors of the society as bioenergy sources which are less polluting as well as have the capability to meet the rising energy demand in a sustainable way. However, systematic research is needed in various aspects starting from feedstock selection, preprocessing, reaction parameters optimization, reactor design, product separation, value addition, utilization, and finally, a business model to make the technology economically viable and socially acceptable.

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