Chapter 1
Biomass Conversion to Energy

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Rapid depletion of fossil fuels, compounded by the accompanying environmental hazards, has prompted the need for alternative sources of energy. Energy from biomass, wind energy, solar energy, and geothermal energy are some of the most promising alternatives which are currently being explored. Among these, biomass is an abundant, renewable, and relatively a clean energy resource which can be used for the generation of different forms of energy, viz. heat, electrical, and chemical energy. There are a number of established methods available for the conversion of biomass into different forms of energy which can be categorized into thermochemical, biochemical, and biotechnological methods. These methods have further been integrated into the concept of a biorefinery wherein, as in a petroleum refinery, a variety of biomass-based raw materials can be processed to obtain a range of products including biofuels, chemicals, and other value-added products. We present here an overview of how biomass can be used for the generation of different forms of energy and useful material products in an efficient and economical manner.

1.1 Introduction

The current major source of energy/fuel is fossil fuel, which, for all practical purposes can be considered to be nonrenewable. Fossil fuels are all petroleum derivatives and the use of these fossil fuels leads to the generation of greenhouse gases such as CO_2, CH_4, N_2O. The transportation sector is responsible for the

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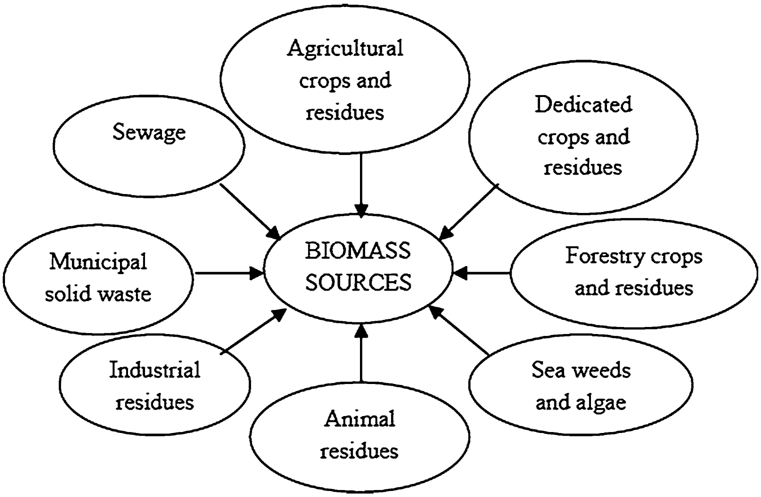


Fig. 1.1 Sources of biomass for conversion to energy

highest rate of growth in greenhouse gas emissions (GHG) among all sectors. This concern as well as the current concern over the rapid depletion of fossil fuel, accompanied by the ongoing price increase of fossil resources and uncertain availability, combined with environmental concerns such as global warming has propelled research efforts toward generating alternative means of energy production using renewable resources. The solution to this problem seems to emerge in the form of bioenergy, i.e., energy generated from biomass.

Biomass is the only renewable organic resource. It is also one of the most abundant resources. It comprises all biological materials including living, or recently living organisms, and is a huge storehouse of energy. The dead biomass or the biological waste can be used as a direct source of energy like heat and electricity or as an indirect source of energy like various types of fuels. The living biomass, or components thereof, like microorganisms, algae, and enzymes can be used to convert one form of energy into another using biofuel cells. Figure 1.1 gives the various sources of biomass which can be used for biomass conversion into energy. In the entire process of conversion of biomass into energy, a dual purpose of energy generation and environmental clean-up is achieved.

Sunlight is an infinitely abundant source of energy on this earth and all energy on this planet, in principle, is renewable. However, considering the factor of time frame, the present sources of energy such as coal, oil, and natural gas take millennia to renew. Therefore, it is imperative that research in the field of energy generation should focus on reducing this time frame by cutting short the time required to turn sunlight into usable energy. Biomass is an excellent source of renewable energy and serves as an effective carbon sink. Plants and trees which constitute biomass can be considered as perpetual powerhouses capable of continuously tapping the energy from sunlight and converting it via photosynthesis

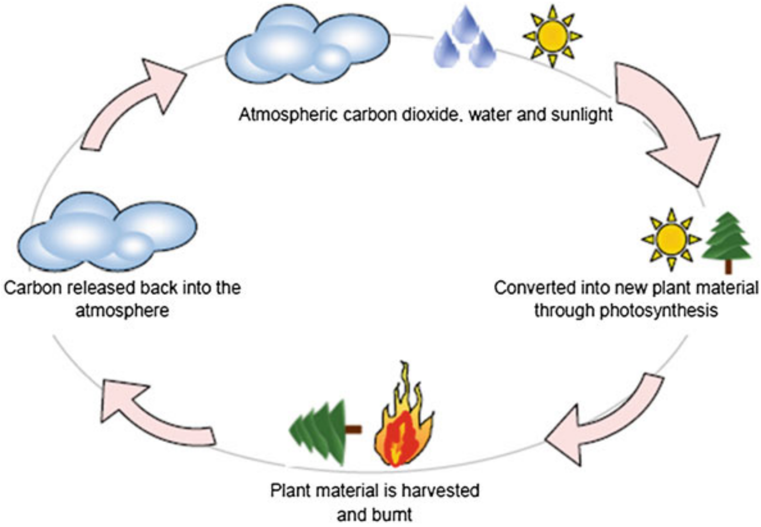


Fig. 1.2 Renewable nature of biomass conversion into energy

into carbon-rich compounds. These carbon-rich compounds which constitute the biomass can then be exploited as and when required to release the energy trapped from sunlight (Fig. 1.2).

It can be seen from Fig. 1.2 that the carbon which is released into the atmosphere as a result of burning biomass, returns to the biomass by way of photosynthesis, which is again converted into carbon-rich compounds for reconversion into energy. This, process can thus be considered to be carbon neutral unlike fossil fuel, which is carbon positive, i.e., burning fossil fuel releases CO_2 into the atmosphere which remains in the atmosphere, thus increasing the amount of CO_2 indefinitely.

The current technology of biomass to energy conversion is at the most, carbon neutral but the amount of CO_2 already present in the atmosphere as a result of use of fossil fuel for so many years, is so high that it cannot be absorbed by conventional sinks such as trees and soils. Thus there is a dire need to reduce the global CO_2 emissions by energy generation technologies that are carbon negative in nature. These technologies, which are commonly termed as “Bioenergy with Carbon Capture and Storage” (BECCS) are expected to achieve the goal of creating a global system of net negative carbon emissions. This carbon capture and storage (CCS) technology, serves to intercept the release of CO_2 into the atmosphere and redirect it into geological storage locations. A similar alternative to achieve carbon negativity lies in fourth-generation fuels which are those fuels based on high solar efficiency cultivation. This chapter gives an overview of conversion of biomass into energy with special reference to the biorefinery concept. The recent developments in the area are also highlighted.

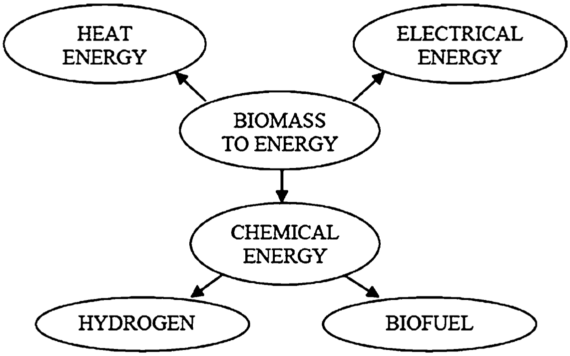


Fig. 1.3 Biomass conversion into different forms of energy

1.2 Biomass and Energy Generation

Biomass can be used to generate different forms of energy (Fig. 1.3). It can be either burnt directly to generate heat, or the flue gases generated during the burning of biomass can be used to provide process heat. The heat generated from biomass can be used to generate steam which can again be used either directly to provide process heat or it can be converted into electricity via steam turbines. As such, biomass is very low in terms of energy density. It can be upgraded into high energy density fuels such as charcoal, liquid fuels (mainly transportation fuels), and gaseous fuels such as hydrogen, producer gas, or biogas. These biofuels form the major, most important product of the bioconversion processes.

Biofuels are classified into four categories depending on the nature of biomass used to produce it. Table 1.1 gives a concise classification of biofuels with representative examples for each category.

First-generation biofuels are already commercially produced, and an established technology is available for their production. However, the major problem with first-generation biofuels is that their production largely depends on raw material feedstock that could otherwise be used for food and feed purposes. This food versus fuel controversy gave rise to the development of second-generation biofuels which are produced from non-feed crops, forest residues, agricultural, industrial, and domestic waste. Second-generation biofuels are produced mainly by thermochemical and biochemical methods. The thermochemical methods are more amenable to commercialization as these are based on technologies established over a number of years. The biochemical methods have not yet been commercialized but these methods have a greater potential for cost reduction. Research efforts toward their optimization are currently ongoing and may soon result in commercialized, low cost alternatives to first-generation biofuels.

Although second-generation biofuels are able to circumvent the food versus fuel controversy, they still need arable land for the generation of feedstock required for their production. Thus land which would otherwise have been used for growing of food crops would still be required. This gave rise to third-

Table 1.1 Classification of transportation-based biofuels

Type of biofuel	Description	Examples
First-generation biofuels	Biofuels produced from raw materials in competition with food and feed industry	• Bioethanol from sugarcane, sugar beet and starch crops(corn and wheat) • Biodiesel from oil-based crops like rapeseed, sunflower, soyabean, palm oil, and waste edible oils • Starch-derived biogas
Second-generation biofuels	Biofuels produced from non-food crops (energy crops), or raw material based on waste residues	• Biogas derived from waste and residues • Biofuels from lignocellulosic materials like residues from agriculture, forestry, and industry • Biofuels from energy crops such as sorghum
Third-generation biofuels	Biofuels produced using aquatic microorganisms like algae	• Biodiesel produced using algae • Algal hydrogen
Fourth-generation biofuels	Biofuels based on high solar efficiency cultivation	• Carbon-negative technology • Technology of the future

generation biofuels such as biofuels produced from seaweeds and algae. This algal biomass is capable of flourishing in marshy land, sea water, and land which is totally unproductive with respect to cultivation of agricultural crops. Concerted efforts are underway to bring out successful technologies which produce biofuels from algae.

Fourth-generation biofuels are still at a conceptual stage and many more years may be required for these types of biofuels to become a reality. These biofuels are produced by technologies which are able to successfully convert biomass into fuel in such a manner that the CO_2 consumed in their generation is much more than that produced as a result of their burning or use. Hence, these biofuels would be instrumental in reducing atmospheric GHGs, thus mitigating the problem of global warming to a significant extent. The technologies for the production of fuels other than first-generation biofuels are yet to prove themselves as commercially viable alternatives to fossil fuels and are under various stages of development. The following section gives an overview of the different biomass conversion technologies developed till date. These are broadly classified as shown in Fig. 1.4.

An important aspect about the use of biomass as an alternative to fossil fuel for generation of energy is that biomass has a high volatility compared to fossil fuels due to the high levels of volatile constituents present in biomass. This reduces the ignition temperature of biomass compared to that of fossil fuel such as coal. However, biomass contains much less carbon and more oxygen. The presence of oxygen reduces the heat content of the molecules and gives them high polarity.

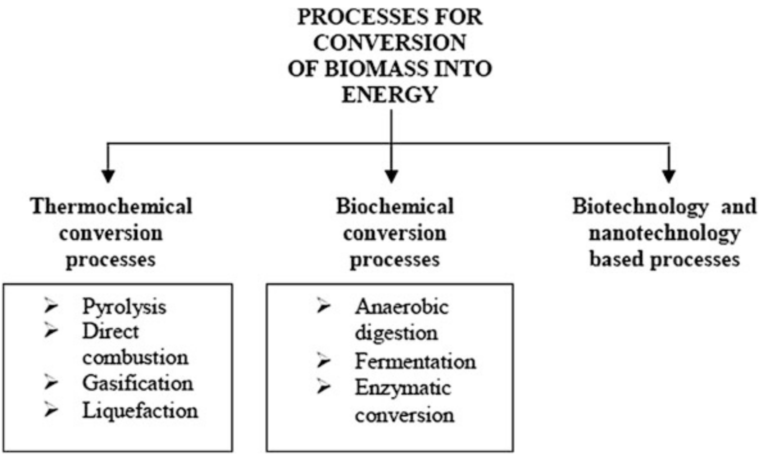


Fig. 1.4 Processes for biomass conversion into energy

Table 1.2 Comparison of physicochemical and fuel properties of biomass and coal

Property	Biomass	Coal
Fuel density (Kg/m^3)	~500	~1,300
Particle size	~3 mm	~100 µm
Carbon content[a]	42–54	65–85
Oxygen content[a]	35–45	2–15
Sulfur content[a]	Max. 0.5	0.5–7.5
Nitrogen content[b]	0.1–0.2	1.5–2.0
SiO_2 content[b]	23–49	40–60
K_2O content[b]	4–48	2–6
Al_2O_3 content[b]	2.4–9.5	15–25
Fe_2O_3 content[b]	1.5–8.5	8–18
Ignition temperature (K)	418–426	490–595
Peak temperature (K)	560–575	–
Friability	Low	High
Dry heating value(MJ/kg)	14–21	23–28

Reproduced with permission from [1]

[a] wt% of dry fuel

[b] wt% of dry ash

Hence, the energy efficiency of biomass is lower than that of coal and the higher polarity of the biofuel which is obtained from biomass causes blending with fossil fuel difficult. Table 1.2 gives a comparison between the physicochemical and fuel properties of biomass and coal.

It can be seen from Table 1.2 that the properties of biomass and fossil fuel vary significantly. Although biomass has a lower heating value, the emission problems especially, emission of CO_2, NO_x, SO_x for biomass are much less than those for coal due to the lower carbon, sulfur,and nitrogen contents of biomass.

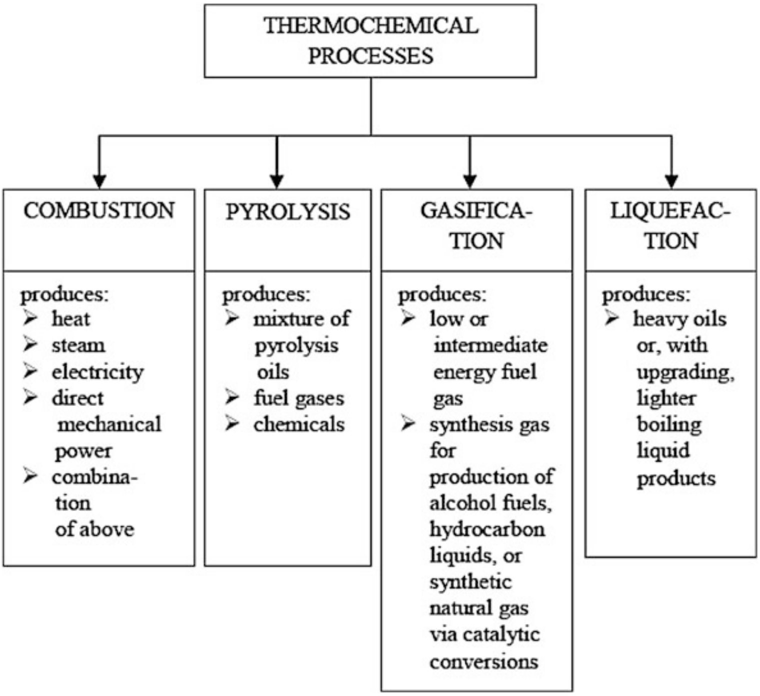


Fig. 1.5 Thermochemical processes for biomass conversion

1.2.1 Methods of Biomass Conversion

1.2.1.1 Thermochemical Processes

Biomass conversion technologies can be broadly classified into primary conversion technologies and secondary conversion technologies. The primary conversion technologies such as combustion, gasification and pyrolysis involve the conversion of biomass either directly into heat, or into a more convenient form which can serve as an energy carrier such as gases like methane and hydrogen, liquid fuels like methanol and ethanol, and solids like char. The secondary technologies convert these products of primary conversion into the desired form which may be an energy product such as transportation fuel or a form of energy such as electricity. The different thermochemical conversion processes are given in Fig. 1.5.

These processes involve high temperature and sometimes high pressure processing of biomass. The combustion process for generation of heat and/or power involves heating the biomass in the presence of excess oxygen. It is responsible for over 97% of the world's bioenergy production [1]. The other processes such as torrefaction, pyrolysis and gasification involve heating in the presence of restricted or controlled oxygen to produce liquid fuels, heat, and power.

The thermochemical processing of biomass produces gas, liquid, and solid. The gas produced primarily comprises carbon monoxide, carbon dioxide, methane, hydrogen, and some impurities such as nitrogen. This gas is called synthesis gas which can be used as fuel, or can be upgraded or converted to more valuable and/or useful products such as methanol or methane. The liquid product contains mainly noxious and a highly complex mixture of oxygenated organic chemicals consisting of volatile components and non-volatile tars. The solid contains ash and carbon or char.

The suitability of biomass for thermal/thermochemical conversion processes, and the products obtained as a result of these biomass conversion processes, depend greatly on the composition and properties of the biomass used. Physicochemical characterization of biomass is therefore an important step in biomass conversion. This involves the determination of particle size and bulk density; proximate analyses such as determination of moisture content, volatile matter, fixed carbon, ash content; ultimate analysis such as determination of carbon, hydrogen and oxygen content; determination of ash deformation and fusion temperature; calorific value; biomass composition; equilibrium and saturation moisture content; and biomass pyrolysis characteristics. There have been a number of projects undertaken the world over, wherein a systematic characterization of different varieties of biomass and species has been undertaken. The output of these systematic studies has, in many cases, resulted in a database on biomass fuel characteristics. Biobank is a set of three databases giving the chemical composition of biomass fuels, ashes, and condensates from flue gas condensers from actual installations. The data set was originally compiled by Biosenergiesysteme GmbH, Graz, Austria. It is continuously expanding, using data inputs from other member countries of IEA Bioenergy Task 32. It currently contains approximately 1,000 biomass samples, 560 ash samples, and 30 condensate samples [2]. Another database—BIOBIB has been developed by the Institute of Chemical Engineering, Fuel and Environmental Technology, Vienna, Austria, which gives similar data for European plants. This database covers different types of biomass such as energy crops, straw, wood, wood waste from wood processing industries, pulp and paper industry, and other cellulosic waste such as that from the food industry. It currently has 331 different biomass fuels listed [3]. Phyllis is yet another database which is designed and maintained by the Netherlands Energy Research Foundation containing information about composition of biomass and waste fuels [4]. Over 250 biomass species from different parts of India have been characterized with respect to the above properties under the MNES sponsored Gasifier Action Research Project at the Biomass Conversion Laboratory of the Chemical Engineering Department at the Indian Institute of Technology Delhi [5]. An overview of the different thermal and thermochemical conversion processes is given in the following sections.

Direct Combustion

The process of combustion can be considered as an interaction between fuel, energy and environment. Fuel is burnt in excess air to produce heat. The excess air

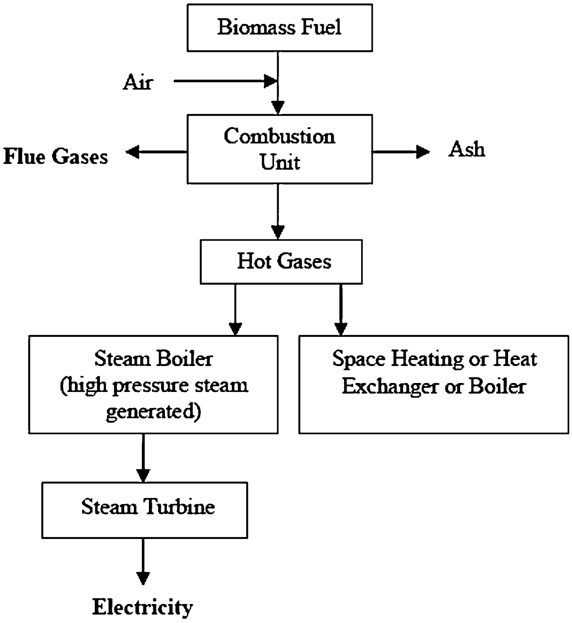


Fig. 1.6 Combustion for heat and power generation

serves as a source of oxygen which initiates a chemical reaction between the fuel and oxygen, as a result of which, energy is liberated. Volatilization of combustible vapors from the biomass occurs which then burns as flames. This volatile degradation product consists of three fractions: gaseous fraction containing CO, CO_2, some hydrocarbons, and H_2; a condensable fraction consisting of water and low molecular weight organic compounds such as aldehydes, ketones, and alcohols; and tar fraction containing higher molecular weight sugar residues, furan derivatives, and phenolic compounds. The proportion of these volatiles and residue is determined by thermal analysis methods. The residual material which remains is the carbon char which is subsequently burnt when more air is added. Demirbas [1] gives some important combustion properties of selected biomass samples. The combustion process can result in production of heat, or by using secondary conversion processes, in generation of electricity (Fig. 1.6).

The open fire at home or the small domestic stove is the simplest example of the use of the combustion process to generate energy/heat. However, this process has an efficiency of only 10–15% as most of the volatile oils released go into the environment along with most heat. More sophisticated combustion technologies have been developed to give increased efficiencies. The use of more efficient wood stove designs results in greatly increased efficiencies of up to 60%. The combustion technologies were originally designed for production of energy from coal or fossil fuel. However, the rapid depletion of fossil fuel and the search for renewable source of energy have directed all efforts toward adapting these technologies to the use of biomass in place of fossil fuels for the generation of energy.

Indeed, the efforts required are enormous as the nature of biomass is radically different from that of fossil fuels. Also, the composition of biomass varies widely depending on its source. In case of biomass, the biomass, directly fed into the combustion furnace, is first converted into a mixture of volatiles and a carbonaceous char which burn with entirely different combustion characteristics as compared to fossil fuels. The heat of combustion ΔH for any combustion process is calculated on the basis of the standard equation:

$$\Delta G = \Delta H - T\Delta S$$

where G is the free energy, H is enthalpy, T is the absolute temperature, and S is the entropy. While using this equation for biomass, the change in entropy or the energy lost in converting the solid fuel into gaseous combustion products must be included [6]. This correction factor may vary greatly depending on the characteristics of the biomass used. When biomass is used as the fuel for the combustion process, there are a number of factors which are responsible for lowering the efficiency of the process and the net usable energy that could be obtained from the process. Some of the important factors are, the variable nature of the biomass, the variable moisture content and ash content present in the biomass, the dissipation of some of the heat of combustion by the combustion products of the biomass, and the incomplete combustion of biomass. The moisture content in biomass varies from an equilibrium moisture content of 10–12% in agricultural residue such as straw to as high as about 50% in biomass such as wood residue and bagasse. This moisture content acts as a heat sink and has to be dried up before it can be used for direct combustion. The extra energy required for this will reduce the net energy output of the process. Therefore the combustion process is best suited for biomass with a moisture content lower than 50%. Biomass containing moisture contents higher than this is better suited for biochemical/biological conversion processes. The proportion of volatile matter and fixed carbon present in the biomass also differs depending on the source [7]. Softwoods contain about 76.6% of volatile matter, whereas hardwood contains 80.2% of volatile matter. As compared to these values, bituminous black coal contains only 37.4% of volatile matter. As most of the combustion process is characterized by the volatile fraction, this difference is of great significance. The mineral content in biomass also varies from 0.5% in woody biomass to 18% in cereal straws. The wood ash mainly consists of alkali and alkali earth cations present as carbonates, carboxylic acids, and some silica crystals. The silica and insoluble organic compounds act as a heat sink, whereas the soluble organic compounds may have a catalytic effect in gasification and combustion of biomass. Complete combustion of biomass releases CO_2 and water which are harmless. However, incomplete combustion leaves carbonaceous residue (fly ash), smoke, and other odorous and noxious gases (containing carbonyl derivatives, unsaturated compounds and CO) which are detrimental to the environment. In addition to this, a considerable amount of biomass is wasted. Figure 1.7 shows a typical combustion plant using municipal solid waste as biomass feed.

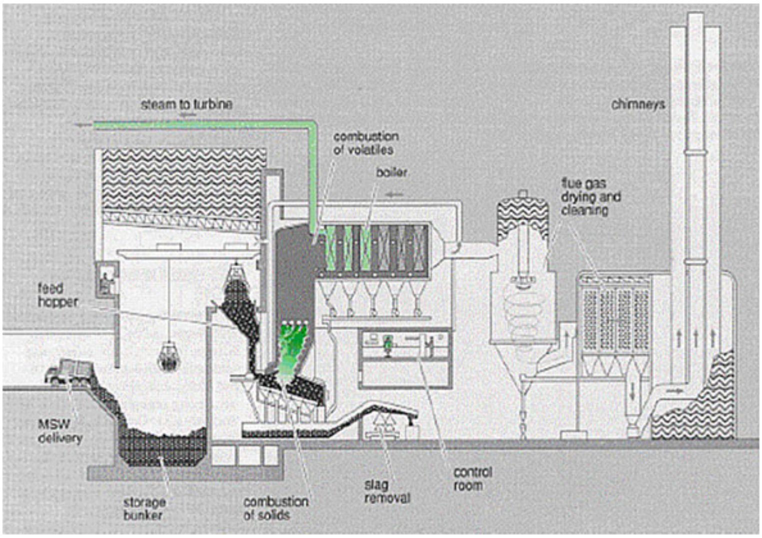


Fig. 1.7 MSW combustion plant (*Source* Open University, UK)

Forms of combustion

Direct combustion of solid biomass occurs through evaporation combustion, decomposition combustion, surface combustion, and smoldering combustion. Components in the biomass which have a relatively simple structure and a low fusion temperature, fuse and evaporate when heated, and burn by reacting with oxygen in the gas phase. This is called evaporation combustion. The heavy oils present in the biomass first decompose due to the high temperatures encountered during combustion. The gas produced from thermal decomposition by heating reacts with oxygen in gas phase, flames, and then burns. This is called decomposition combustion. The char which remains after these forms of combustion, burns by surface combustion. Smoldering combustion is the thermal combustion reaction at temperature lower than the ignition temperature of the volatile components of the reactive fuels such as wood. If the ignition is forced to smoke, or temperature exceeds ignition point, flammable combustion occurs. In industrial direct combustion of biomass, decomposition combustion and surface combustion are the main forms of combustion [8].

The combustion process

The combustion process comprises four basic phases: heating and drying, distillation of volatile gases, combustion of these volatile gases, and combustion of the residual fixed carbon. Prior to the actual combustion process, the biomass is first subjected to pelletizing and/or briquetting in order to increase the density of the biomass and simultaneously reduce the moisture content. This also increases the calorific value of the biomass and increases the easy handling of the biomass during transportation and processing. The following steps are involved in pelletizing of biomass [9]:

1. Drying. The biomass is dried to a moisture content of about 8–12% (weight basis) before pelletizing.
2. Milling. Size reduction of the biomass is done in hammer mills.
3. Conditioning. Conditioning of the biomass is done by addition of steam, whereby the particles are covered with a thin liquid layer to improve adhesion.
4. Pelletizing. Flat die or Ring die pelletizers are used to convert the above material into compact pellets.
5. Cooling. The temperature of the pellets increases during the densification process. Therefore, careful cooling of the pellets is required before the pellets leave the press, to ensure high durability of the pellets.

Pelletization is expensive compared to briquetting where the biomass is compressed and extruded in heavy duty extruders into solid cylinders. This pelletized or briquetted biomass is subjected to heat, which breaks down the plant cells. The volatile matter is driven off from the compacted biomass and instead of being released directly into the atmosphere, it is made to pass through a high temperature zone (above 630°C) in presence of secondary air. Here, the gases are combusted and release more heat. A carbonaceous residue called char, containing the mineral components is left behind.

After briquetting or pelletizing, the biomass is fed into the combustion furnace after which combustion proceeds in four phases [7]:

Phase 1: Heating and drying

Moisture in the biomass varies from 10 to 50% of the total weight (wet basis). This moisture reduces the dry heat value of the biomass and slows down the heating and drying process. It is therefore essential to remove this moisture in order to increase the efficiency of the combustion process. The size of the feed particles is also important because most biomass is woody in nature and wood is a poor conductor of heat. The larger the particle size, the lower the rate of heat transmission through the feed bed. The biomass is hence reduced in size so that the maximum distance from the center of the particle of the feed to the surface does not exceed 20–30 mm. Thus, wood chips, sawdust, shredded straw, and pulverized biomass fuels such as bagasse are preferred.

Phase 2: Distillation of volatiles

After the evaporation of moisture is complete, the heat supplied gets used in volatilization of the liquid constituents present in the biomass. This occurs between 180 and 530°C. Distillation occurs during this phase. The gases released comprise complex saturated and unsaturated organic compounds such as paraffin, phenols, esters, and fatty acids. These distill at different distillation temperatures thus making the concept of “biorefinery” possible.

Phase 3: Combustion of volatiles

Ignition of the volatilized components takes place at temperatures between 630 and 730°C. This involves an exothermic reaction between the volatilized gases and oxygen, as a result of which, heat is produced and CO_2 and water vapor are released. The flame temperature in this phase depends on the amount of excess air present and the amount of moisture initially present in the biomass (because this evaporated moisture is present as water vapor in this gas phase). Here, supply of excess oxygen in the form of secondary air supply is essential because this will maintain high temperatures during this phase. In absence of this, incomplete combustion will result in lower process efficiency . The unburnt carbonaceous part is called soot. This soot absorbs volatile components which condense in the cooler parts of the furnace and form an oily product called tar.

Phase 4: Combustion of residual fixed carbon

After the moisture and volatiles have been removed, the fixed carbon component of the biomass remains as char. This char begins to burn as oxygen is now available, and carbon monoxide is released which, in the presence of oxygen gets converted into CO_2. This CO_2 is finally emitted from the furnace.

Types of combustion systems *[7]*

The design of a combustion system is important for achieving optimum efficiency from the process. During the combustion process, slagging and fouling of the furnace and the boiler occurs. This is more serious when biomass contains a high proportion of alkali metals. The alkalis volatilize during combustion and condense as alkali metal salts on the relatively cool furnace walls. These elements react with other compounds to form a sticky lining on the furnace and boiler wall surface. Regular cleaning of these deposits is required which usually involves process shutdown, reducing the efficiency of the process. The design of the combustion equipment should be such that a minimum of fouling takes place. A number of different designs of combustion systems have evolved in an attempt to get maximum combustion efficiency with minimum fouling. These are summarized along with the salient features of each design in Table 1.3.

Fixed-bed combustion

In this type of combustion system, the biomass is fed in the form of a bed on grates at the bottom of a furnace. The grates may be either inclined or horizontal. Air is passed through the grate (on which the fuel is present) at a restricted rate such that the fuel is not stirred and there is no relative movement of the fuel solids. The stokers used for feeding the fuel may be either overfeed stokers or spreader stokers.

The overfeed stokers were originally designed for firing coal. These feed the fuel by gravity onto the moving grate at one end. The grate travels slowly across the furnace, carrying the fuel along, as combustion takes place. The residual ash and slag are continuously discharged at the opposite end.

Table 1.3 Designs of combustion systems [7, 8]

Combustion method			Salient features
Fixed bed combustion	Horizontal grate: – Forward moving grate – Reverse moving grate – Reciprocating grate – Step grate – Louvre grate	Overfeed stokers	Grate is level and moving in different manners. Biomass is fed by gravity onto the moving grate at one end. It ignites and burns as surface combustion. Residual ash and slag is continuously discharged at the opposite end.
		Spreader stokers	Grate is level and moving in different manners. Stokers distribute the comminuted biomass onto the furnace above an ignited fuel bed on an air cooled travelling grate. Suspension firing occurs partially. Fine particles tend to burn in suspension while larger particles fall onto the travelling grate where they are burnt.
	Inclined grate		Most common design selected for biomass combustion systems. Biomass is fed at the upper part of the grate. Pre-drying of fuel occurs at the upper part of the furnace after which it slowly tumbles down under gravity onto a reciprocating grate lower in the furnace where combustion takes place. The grate is either water cooled or air cooled. Suitable for biomass fuels with lower ash contents.
Fluidized	Bubbling fluidized bed combustion Circulation fluidized bed combustion		Finely comminuted biomass particles fed onto a bed of sand at the bottom of the furnace and subjected to an evenly upward flow of air which fluidizes the biomass. Initial drying followed by ignition takes place.
Rotary hearth furnace combustion	Kiln furnace		Suitable for combustion of high moisture fuel such as liquid organic sludge and food residue.
Burner combustion	Burner		Used for burning wood powder and fine powder such as bagasse and pith.

Spreader stokers distribute the comminuted and dried biomass fuel over an ignited fuel bed on an air cooled traveling grate. These stokers can be made responsive to heat load changes by automatic adjustment of grate travel speed, fuel feed rate, and air intake. A major disadvantage with this type of a system is that an ash layer needs to be maintained on the grate in order to protect it from thermal degradation. Biomass ash may have a high silica content which may cause a greater abrasion of the grate, resulting in a higher maintenance cost of the grate. Another disadvantage with this type of a combustion design is that there can be a significant amount of fly ash and unburned carbon in the flue gas, resulting in lower combustion and boiler efficiencies and higher costs of emission controls.

Inclined grate furnace

This is the most common design used in biomass combustion systems. The biomass fuel is fed at the upper part of the furnace where pre-drying of the biomass takes place. The dried biomass slowly tumbles down over the sloping grate onto a reciprocating grate in the lower portion of the furnace, where combustion takes place. The grate is either water cooled or air cooled which obviates the requirement of an insulating ash layer in order to protect it from abrasion. Thus, this type of a combustion design is suitable for biomass with a lower ash content.

Fluidized-bed combustion

In this type of system, finely comminuted biomass particles are fed onto a bed of coarse sand particles present at the bottom of the furnace. Fluidizing air is passed through this bed in an upward direction through uniformly distributed perforations on which this bed rests. The velocity of this air is critically controlled such that it is just sufficient to fluidize the fuel particles in the air above the bed. The bed appears like a bubbling liquid at this air velocity. The coarse sand particles assist the mixing of the fuel with the air and also increase the heat transfer to the fuel for initial drying and subsequent ignition. Figure 1.8 shows a schematic diagram of a typical fluidized- bed combustion system designed for a boiler. The critical air velocity or the minimum fluidization velocity at which fluidization occurs is a function of the biomass particle size, density and pressure drop across the bed. An increase in air velocity beyond the minimum fluidization velocity causes the bed to become turbulent, and subsequently to circulating. This results in increased recycling rates of the material in suspension. Commercial designs are either bubbling fluidized-bed or (BFB) or, circulating fluidized-bed (CFB). The entire system may operate at atmospheric pressure or may be pressurized. Air or oxygen may be used for fluidization.

BFB system uses air velocities of 1–3 m/s. The primary air supply is through nozzles beneath the bed, whereas the secondary air flow enters the furnace above the bed. The ratio of the primary to secondary air supply controls the bed temperature. The bed temperature can also be controlled by recirculating some of the flue gases that are formed as a result of combustion of the biomass.

In the CFB systems, a higher air velocity of 4–9 m/s is employed. This causes the bed material to circulate within the furnace. As in BFB, here also, there are

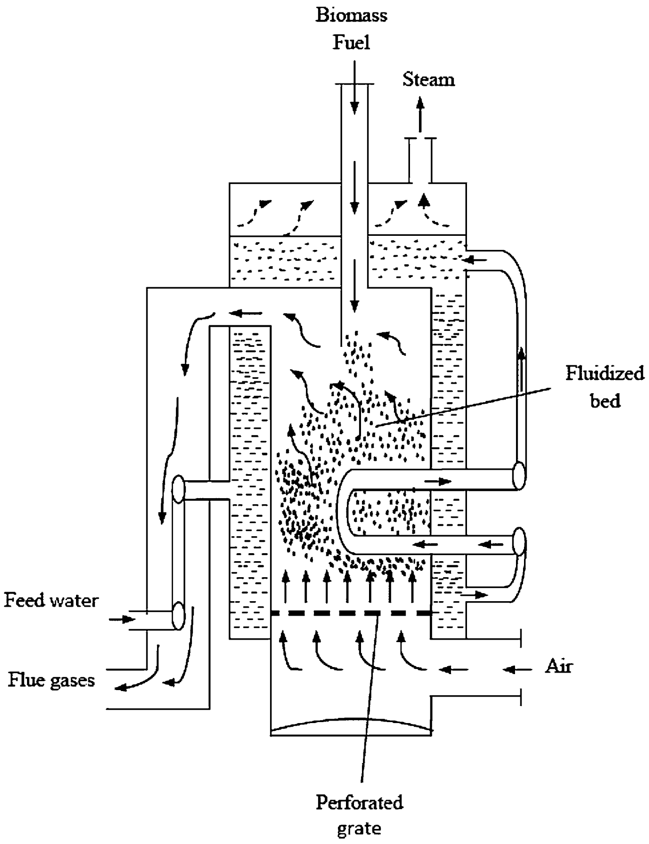


Fig. 1.8 Fluidized-bed combustion system (Adapted from [7])

primary and secondary air supplies. Due to the higher air velocities used, the smaller biomass particles tend to get entrained along with the flue gases generated as a result of combustion. Cyclone separators are provided to collect the biomass and sand particles which are then returned to the feed bed. CFB designs are more expensive than the BFB ones. However, CFBs operate at lower operating temperatures than the BFBs, which reduces the NO_x emissions significantly.

Fluidized-bed combustion systems are much more versatile compared to fixed-bed design systems. A wide range of biomass with varying compositions such as higher moisture contents and varying ash properties can be handled without encountering slagging problems. Varying loads, ranging from full capacity to as low as 35% of full capacity can be handled. At any given time, compared to the fixed-bed design, only a small quantity of fuel is present in the combustion chamber, hence, giving good conversion efficiencies. However, the fluidized-bed designs are costly compared to the fixed-bed designs and are suitable for large-scale operations only.

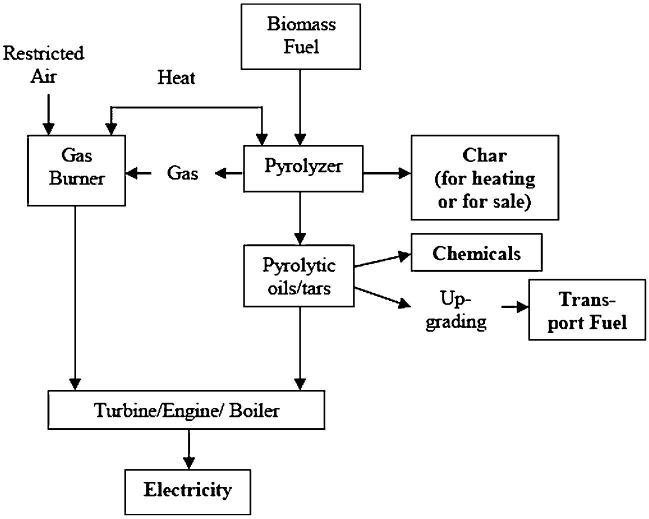


Fig. 1.9 Pyrolysis for biomass conversion

Pyrolysis

Pyrolysis is the thermochemical decomposition of organic material at high temperatures in the absence of oxygen, producing gas and liquid products and leaving behind a carbon-rich residue. It is invariably the first step in combustion and gasification of biomass. If sufficient oxygen is provided subsequent to initial pyrolysis, it can proceed to combustion or gasification. The liquid products obtained from pyrolysis include water and oils, whereas the gaseous products include carbon monoxide, carbon dioxide, and methane. A solid residue that is left behind is a carbonaceous solid, i.e., charcoal. The solid residue can be used as such for heating. The gas produced can be processed through a gas burner and under a restricted air supply can be used as a heat source for the pyrolyzer, or it can be used in gas turbines or gas boilers for production of electricity. The liquid product, bio-oil can have multiple uses: it can be used as such for heating, or for power generation, or it can be upgraded to transportation fuel, or can be used for conversion into suitable chemicals. Figure 1.9 shows the different energy products/forms that can be obtained from pyrolysis. Figure 1.10 shows a general schematic diagram of a pyrolysis process.

The fact that one of the products of pyrolysis is a liquid product (viz. bio-oil) makes this process very important because liquid fuels are easy to transport and hence, it is possible to have the conversion plant remote from the point of use, which is not possible in case of the combustion process. Pyrolysis is not an exothermic process like combustion. It is an endothermic process where heat is required to be supplied for the process. Different types of pyrolysis processes, resulting in different types of products, are possible depending on the temperature and the rate of heating employed. The nature of the biomass also largely affects the

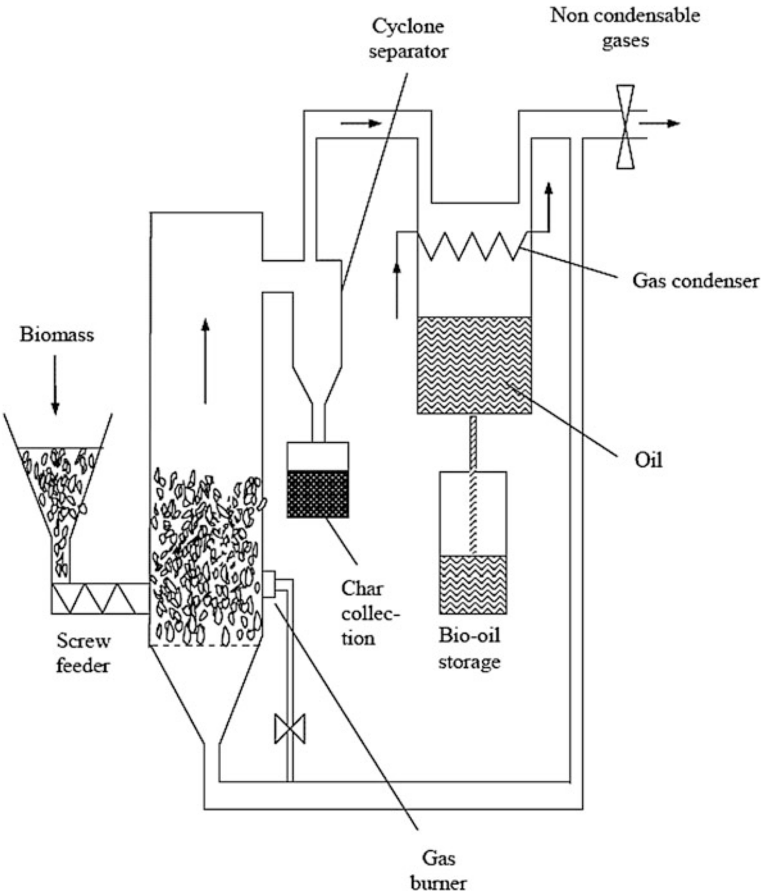


Fig. 1.10 Schematic diagram of a pyrolysis process (Adapted from [11])

yield of pyrolysis, as the rate of heating depends on the nature of biomass. Typically, lignocellulosic materials such as wood, stalks, straw, etc. are poor heat conductors. Hence these materials require pretreatment such as size reduction before they can be used for pyrolysis, so that an acceptable yield can be obtained. Lower processing temperatures and longer vapor residence times are favorable for production of charcoal (solid product); higher processing temperatures and longer vapor residence times favor production of gas, whereas under moderate temperatures and short vapor residence times, a liquid product is obtained. The product dependence on the processing conditions and vapor residence times can be explained on the basis of the composition of the biomass and the chemical nature of pyrolysis [10]. Biomass mainly comprises polymers in which large chains of carbon atoms are linked with each other, or to oxygen atoms, or sometimes to other elements like nitrogen or sulfur, to form macromolecules. The most commonly occurring macromolecules in biomass are hemicelluloses and cellulose.

Table 1.4 Types of pyrolysis processes, processing conditions, and products obtained

Mode/type of pyrolysis process	Residence time of vapor in pyrolysis zone	Rate of heating	Temperature (°C)	Product
Slow pyrolysis Torrefaction	~30 min	Slow	~290	Char, gas (80, 20%) (vapors are burned)
Carbonization	Days	Slow	~400	Char, liquid, gas(35, 30, 35% respectively)
Fast pyrolysis	<2 s	Very high	~500	Char, liquid, gas (12, 75, 13% respectively)
Flash pyrolysis	<1 s	High	<650	Bio-oils, chemicals, gas
Ultra-rapid pyrolysis	<0.5 s	Very high	~1,000	Chemicals, gas
Intermediate pyrolysis	~10–30 s	Medium	~500	Char, liquid-two phases, gas (25, 50, 25% respectively)
Vacuum pyrolysis	~2–30 s	Medium	400	Bio-oil
Hydropyrolysis	<10 s	High	<500	Char, liquid, gas (12, 78, 10% respectively)
Methano-pyrolysis	<10 s	High	>700	Chemicals

Unprocessed biomass consists of a small number of such large polymers or macromolecules. Cellulose is a linear chain polymer, whereas hemicellulose is a branched chain polymer with side chains or branches present at random locations along the chain. As heat is supplied, the chemical bonds linking the monomer units in the large polymer begin to break off. In cellulose, the bonds are broken randomly along the chain whereas in hemicelluloses, first the side chain or branches break off followed by breaking of the straight chains. As more heat is supplied, a large number of smaller molecules are generated i.e. the degree of polymerization (Dp) reduces. When Dp reduces to <10, the polymer is no longer a polymer but an oligomer. These oligomers (especially those having Dp less than around 8), are volatile. These are generated at typical pyrolysis temperatures between 400 and 800°C. These oligomers, comprising anhydro sugars, evaporate from the solid mass as volatiles. These are required to be removed from the solid biomass. If they are not removed, under continued influence of high temperature, they undergo thermal fragmentation to produce highly reactive, small intermediates. These fragments, if removed and quenched immediately, can be used as such as chemicals or as fuels. If, again, these are not removed from the solid biomass, they undergo chemical reaction with the remaining solid material to form new polymers or, accelerate breakdown of original chains. These reactions are exothermic and thus accelerate the overall pyrolysis reaction. Thus, depending on the processing conditions and vapor residence times, different types of pyrolysis processes have been developed, which result in a different product mix. These are summarized in Table 1.4.

A brief description of the different variants of the pyrolysis process is given below.

Types of pyrolysis processes

Pyrolysis processes can be classified on the basis of the rate of heating as: Slow pyrolysis, fast pyrolysis, and intermediate pyrolysis. All these types of pyrolysis processes are carried out in the absence of oxygen. Depending on the medium in which it is carried out, it is classified as either hydrous pyrolysis (carried out in presence of water) or hydropyrolysis (carried out in presence of hydrogen).

Slow pyrolysis

The process of slow pyrolysis is used mainly for production of char and involves slow heating of the biomass over long periods of time (ranging from minutes to days).

Torrefaction is a slow pyrolysis process carried out at low temperatures (230–300°C) in the absence of oxygen. It is a form of pretreatment of biomass to improve its energy density, reduce the oxygen/carbon and hydrogen/carbon ratio, and reduce its hygroscopicity. This pretreatment makes the biomass more suitable for other biomass conversion processes. For example, the high oxygen content of biomass increases thermodynamic losses during the gasification process. Reduction of the oxygen/carbon ratio as a result of torrefaction reduces the thermodynamic losses during the gasification process. The microfibrils in biomass, comprising cellulose, are supported or bound together by hemicellulose. The process of torrefaction depolymerizes this hemicellulose, causing a consequent reduction in binding of cellulose fibrils. This causes the structure to become friable and brittle, reducing the energy requirement for size reduction process which precedes most bioconversion processes. Torrefaction is also accompanied with a color change in most cases. The process of roasting of coffee beans by heating the green beans to 200–300°C over a long period of time is the most popular example of the torrefaction process. During the process of torrefaction, there is some reduction in the energy content of the biomass due to the partial devolatilization occurring during the process. However, this reduction in energy content is compensated by the increase in energy density of the biomass during the process. Basu [11] gives details of the changes in terms of energy density, heating value, etc. in bagasse after torrefaction.

Carbonization

Carbonization is a slow pyrolysis process where biomass is heated slowly to temperatures of around 400°C in the absence of oxygen and maintained for several days. The long heating duration allows adequate time for condensable vapor to be converted into char and non-condensable gases. It is the oldest form of pyrolysis and is generally used as a cheap and inexpensive alternative for making charcoal. Tar, pyroligenous acid, and combustible gases are the by-products of this process. As in torrefaction, here also, dehydration and depolymerization of hemicellulose takes place. The breaking and reforming of intermolecular and intramolecular bonds result in formation of high molecular weight and low molecular weight compounds, where the low molecular weight fragments are cracked into liquid and gaseous products and the high molecular weight fragments formed as a result of re-bonding, char together to form the solid char product. The product distribution depends on the size of feed, heating rate, and temperature at which the process is maintained. The yield of liquid (tar) increases with decrease in size of the feed and a simultaneous increase in the rate of heating. The general scheme of the carbonization process (the Modified Broide-Shafizadeh scheme), and an example of a continuous carbonization process of pine bark and sawdust (the Tech-Air pyrolysis system) is described in the Asian Biomass Handbook [8]. The predominant product of the carbonization process, i.e., charcoal, besides being used as a solid fuel for cooking, has recently acquired new uses such as use of charcoal for soil improvement. The by-products of the process, i.e., the pyroligenous acid has applications in agriculture and as a deodorant. The gas fraction can be used as a supplementary fuel for the process.

Fast pyrolysis

Fast pyrolysis is usually the process of choice for the production of liquid biofuels such as bio-oil. It involves heating of biomass at temperatures of 300–1,300°C under steam or other non-oxidizing gases at pressures ranging from atmospheric pressure to pressures up to 3 MPa, to produce pyrolytic oils and/or medium to high energy value gases. The product of pyrolysis comprises a dark brown homogeneous liquid. This liquid has a heating value which is about half of that of conventional fuel oil. The process of fast pyrolysis thus "concentrates" the biomass to a higher energy density liquid product which can significantly improve the logistics (because liquids can be easily transported from one place to another), and the economics (because energy density of biomass increases) of biomass conversion. The process parameters can be adjusted to give different types of process variants and consequently, different proportions of liquid solid and gas.

In the process of fast pyrolysis, high liquid yields can be obtained under the following process conditions:

- high heating and heat transfer rates
- careful control of pyrolysis reaction temperature of ~500°C and vapor phase temperature of ~400–500°C
- short hot vapor residence time (<2 s)
- rapid cooling of pyrolysis vapors to give liquid bio-fuel.

As can be seen from the above conditions, fast pyrolysis requires rapid heating as well as rapid cooling, i.e., it requires efficient heat transfer. Therefore, the reactor equipment, process, and raw material should be such that efficient heat transfer is possible. Lower temperatures favor formation of charcoal hence, this is to be avoided. Table 1.5 gives the different process variants of fast pyrolysis with respect to their reactor systems and their salient features.

Table 1.5 Variants of fast pyrolysis reactor systems

S.No.	Reactor	Salient features
1.	Bubbling fluid bed reactor	• Simple in construction and operation, good temperature control, efficient heat transfer, good control of vapor residence time. • Liquid yields of 70–75% obtained. • Rate of heating is the rate limiting step therefore, small- (2–3 mm) sized biomass particles are required.
2.	Circulating fluid bed and transported bed reactor system	• Features similar to bubbling fluid bed reactor system, except that it is more complex, and higher char contents are obtained in the bio-oil compared to 1. • Separate process for recovery of char is required. • Suitable for larger throughputs.
3.	Ablative fast pyrolysis reactor	• Mechanism of heat transfer different from 1 and 2. • Heat transfer from hot reactor wall to "melt" wood that is in contact with it under pressure. • Molten wood vaporizes to product similar to that from 1 and 2. • Heat transfer not a rate limiting factor therefore large particles can be used. • Process limited to rate of heat supply to reactor which can be more easily controlled and maintained. • No requirement of fluidizing gas therefore equipment is more compact and reaction system more efficient. • Absence of fluidizing gas increases partial pressure of condensable vapors which increases vapor collection and subsequent condensation efficiency. • Process is surface area controlled therefore scaling is a more serious problem.
4.	Entrained flow reactor system	• Equipment simple but poor heat transfer between hot gas and solid particle. • High gas flows required for efficient heat transfer therefore, larger plant sizes. • Low partial vapor pressure causes liquid collection difficult. • Liquid yield is lower than that in 1 and 2. • 50–60% w/w liquid yield on dry basis reported.
5.	Rotating cone reactor system	• Similar to transported bed reactor system but transport effected by centrifugal forces in a rotating cone. • Recent development. • Carrier gas requirement much less than that in 1 and 2. • Complex integrated operation required. • Liquid yields 60–70% on dry feed basis.

A detailed description of these systems, and the locations where these are operational on an industrial scale, are given by Bridgewater [12]. Pyrolysis, being an endothermic process requires process heat to be provided by some means. A commercial process design typically provides this heat from by-products obtained from within the process. About 50–75% of the energy content of feedstock is required to drive the process. The energy content in char—one of the by-products of fast pyrolysis is about 25% of the energy in the feedstock, whereas gas—the other byproduct, contains only about 5% of the energy in the feed. Thus, the net heat content of the by-products is insufficient to provide the heat of pyrolysis hence, process heat for fast pyrolysis is required to be provided by other external means:

- hot reactor wall
- tubes through which hot char and air are circulated
- hot fluidizing gas
- recycled hot sand
- addition of hot air.

The internal utilization of energy from within the process, i.e., utilization of char, or gas or utilizing energy from fresh biomass, or from the product itself, for providing process heat can be done by the following ways:

- combustion of fresh biomass to provide process heat, instead of using the energy content in the by-product—char (especially where there is a good market for char)
- gasification of the by-product char and subsequent combustion of the resultant synthesis gas
- use of the by-product—gas along with external supplementation (because the energy content of the process by-product gas would be insufficient in itself)
- use of the main product of the process, i.e., bio-oil.

The use of fossil fuel can also be done to supplement the above sources of energy to get by-products with high energy value. A properly designed fast pyrolysis process and process equipment has no waste products other than clean flue gas and ash [12].

The liquid product of the fast pyrolysis process can be obtained by condensing the gaseous products of the process which are in the form of aerosols, true vapors and non-condensable gases, by rapid cooling of the gases. The aerosols may be coalesced or agglomerated to obtain the liquid product. Usually, the char gets entrained in the gaseous product of fast pyrolysis and acts as a vapor-cracking catalyst. This char is removed from the vapor by means of cyclones. In spite of the use of cyclones to remove char from the gases, some char still gets away in the vapor, and on condensation of this vapor, remains in the liquid product. The liquid product of fast pyrolysis is hence a microemulsion, and the char remaining in the liquid product causes destabilization of this microemulsion. The elaborate nature of this liquid microemulsion and its characteristics has been described by Bridgewater [12]. The char remaining in the liquid product is removed by a modified pressure filtration process where the particulates up to <5 μm can be removed. Balat et al. [14] give the chemical composition of fast pyrolysis liquid and list the chemicals obtained from biomass oil produced by a fast pyrolysis process.

Flash pyrolysis

Flash pyrolysis involves heating of biomass rapidly to temperatures around 450–600°C at very high heating rates, in the absence of oxygen. The product obtained depends on the conditions of pyrolysis. Temperatures of around 500°C with high heating rates and short vapor residence times (1 s or 500 ms) maximizes liquid yield at up to 80% on weight basis with minimum gas and char production, whereas very rapid heating to temperatures around 700°C and vapor residence times similar to the above maximize the gas yields (up to 80% on weight basis), with minimum liquid and char production. The liquid produced from the flash pyrolysis process has a relatively low viscosity (51 cp) and a high water miscibility capacity (up to 35–50% w/w water can be mixed). The characteristics of bio-oil obtained from flash pyrolysis process are given by Bridgewater [13]. The conversion efficiency of biomass conversion into crude oil in a flash pyrolysis process can reach up to 70%. However, the quality and stability of the oil produced as a result of pyrolysis is a major problem with the flash pyrolysis process as flash pyrolysis of biomass invariably results in the production of pyrolysis water [14]. The gaseous product obtained from flash pyrolysis has a low to medium heating value (5–15 MJ/Nm^3). This gas has a relatively high oil content. It is either used as such for drying feedstock or as a fluidizing medium in fluid bed reactors (however, its specific energy content is somewhat low). The gas from high temperature flash pyrolysis can also give non-equilibrium products such as alkenes. However, the yields (of around 15%) are not very economical.

Ultra- rapid pyrolysis

In ultra-rapid pyrolysis, very high heating rates and temperatures of around 1,000°C with short vapor residence times gives predominantly a gaseous product. A rapid quenching of the primary product is done following pyrolysis. The heating is done using a heat carrier solid such as sand. A gas–solid separator separates the gas from the heat carrier solid.

Hydrouspyrolysis and Hydropyrolysis

Hydrouspyrolysis and hydropyrolysis involve thermal decomposition of biomass in the presence of water or hydrogen respectively, under high pressure conditions. The process usually takes place in two stages. The first stage involves treating biomass with water or hydrogen at 200–300°C under pressure; the second stage involves cracking of the hydrocarbon produced in the first stage into lighter hydrocarbons at a temperature of around 500°C. The bio-oil produced by this type of pyrolysis method has reduced oxygen content which is a desirable characteristic.

Vacuum pyrolysis
In vacuum pyrolysis, biomass is heated in vacuum in order to decrease the boiling point and avoid undesirable chemical reactions. Vacuum pyrolysis is carried out at temperatures of 400–500°C and at total pressure of 2–20 kPa. Under these conditions, the product of pyrolysis can be rapidly withdrawn from the hot reaction chamber enabling preservation of the primary fragments originating from the thermal decomposition of biomass. Heat transfer, which is a rate limiting factor in pyrolysis, is the major limitation in vacuum pyrolysis. In an actual pilot plant reactor developed by a company called Pyrovac, this has been effected by passing molten salts through hollow heating plates on which the biomass is placed inside the vacuum pyrolysis reactor. The biomass gets heated by conduction as well as radiation thus increasing the heat transfer efficiency. The details of vacuum pyrolysis, with particular reference to the theoretical aspects of heat transfer in vacuum pyrolysis, has been described at length by Roy et al. [15].

The pyrolysis technology is less developed than the combustion or gasification technologies. This is probably due to the fact that the bio-oil obtained from the pyrolysis process costs 10–100% more than fossil fuel and its availability is limited; it is unstable due to the presence of entrained fines of char particles; dedicated liquid handling such as modified pressure filtration is required for removal of these fines; the kinematic viscosity of the pyrolysis oils varies over a wide range depending on the nature of feedstock and temperature of pyrolysis among other factors; bio-oil is acidic in nature with a pH of around 2.5–3.0, making it corrosive to the commonly used construction materials such as carbon, steel, and aluminum. Some of the sealants used may also be affected; bio-oil has a water content of around 15–30% by weight of oil mass, which contributes to the low energy density of the oil—this cannot be removed by conventional methods like distillation. All the above properties of the bio-oil obtained from pyrolysis make it unsuitable for direct application as a transport fuel, as a precursor for generation of chemicals, etc. Upgrading of the bio-oil by methods such as catalytic upgrading, needs to be done before it can be used for the various applications. These are described in detail by Bridgwater [13]. However, fast pyrolysis and flash pyrolysis is advancing very rapidly with a number of commercial level plants being set up across the globe.

Gasification

Gasification of biomass is the thermochemical transformation of biomass at high temperature in the presence of restricted supply of oxygen, which may be supplied as such, or in form of air or steam. It is the latest biomass conversion technology among the thermochemical methods for biomass conversion. The product of gasification is a gaseous product which has applications in electric power generation, manufacturing of liquid fuels, and production of chemicals from biomass. Gasification can be said to be an extension of pyrolysis, and has been optimized to give a maximum of the gas phase at the cost of char or liquid. The gas produced

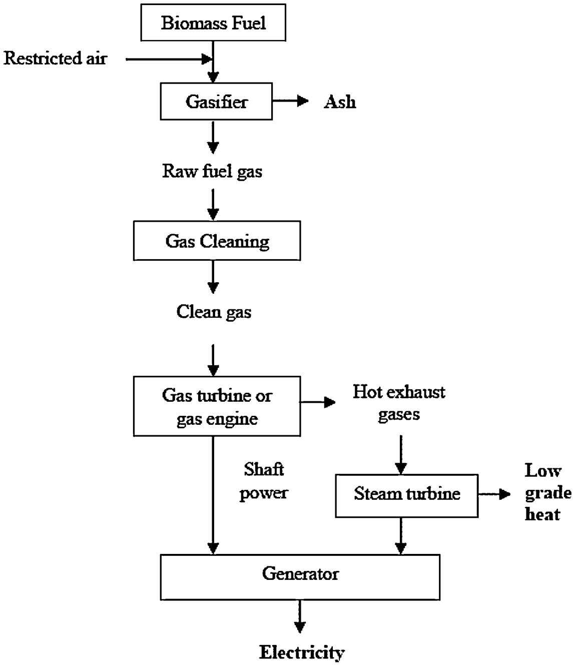


Fig. 1.11 Biomass integrated gasification combined cycle (BIGCC)

from the gasification process is a mixture of carbon monoxide, hydrogen, and methane along with carbon dioxide and nitrogen also produced to some extent, and is called producer gas as it can be used as synthesis gas to produce ammonia or methanol, which, in turn, are used to produce synthetic fuel (synthetic petrol) or as a source of hydrogen. It can also be used as such as a heat source, or to generate electricity through gas turbines. Up to 50% efficiency with respect to electricity generation can be obtained if the gas turbine is integrated with a steam turbine in combined cycle gas turbine system (also called biomass integrated gasification combined cycle—BIGCC). In this system the waste gas from the gas turbine is recovered and used to generate steam in a steam turbine. Figure 1.11 shows a schematic flow sheet for such a system. With such a type of integration, biomass gasification plants can be as economical as coal-fired plants for electricity generation.

However, the power output is limited by economic supply of biomass and is generally limited to around 80 MW of electricity [16]. The medium used for gasification, i.e., oxygen, air, steam, etc. greatly affects the heating value of the product obtained. Gasification in the presence of steam has the highest heating value, followed by oxygen and air in that order. Although the product of gasification in the presence of steam has the highest heating value, higher operating temperatures are required for vaporization of water, increasing the cost of the process. Usually, a mixture of air and steam, with variable inlet ratio is employed. Commercial gasifiers are available in a wide range of sizes and a variety of types which are capable of using a variety of biomass feedstock such as charcoal, wood, rice husk, and coconut shells. The newer gasification processes such as plasma gasification and hydrothermal gasification are also capable of processing municipal solid waste (MSW). The following sections describe the mechanisms and chemistry of the biomass gasification process and the various types of gasifier designs developed for getting optimum product yields for a given biomass feedstock.

The gasification process increases the H/C ratio of the biomass by adding hydrogen to and removing carbon from the biomass.

Gasification consists of four main stages: preheating and drying, pyrolysis, char gasification, and combustion (also called flaming pyrolysis). These stages may take place either in specific regions or zones of the gasifier equipment (especially in moving bed gasifier designs), or these may take place at a microscopic level, within a particle (especially in the fluidized-bed gasifier designs). As in all thermochemical conversion methods, drying of the biomass is a very important step in the gasification process. Moisture contents in biomass vary over a very wide range (from 30 to 60%, and in some cases, even up to 90%). Every kilogram of moisture in the biomass can consume a minimum of 2,260 kJ of extra energy from the gasifier to vaporize the water, which is not recoverable [11]. Hence, pre-heating of biomass is done where the moisture content of the biomass is brought down to about 25%. The pre-heated biomass further dries in the gasifier when temperatures in the range of 100–200°C are encountered. The surface moisture as well as the inherent moisture present in the biomass is removed. The stage of drying is followed by pyrolysis as the temperature increases to 200–700°C. Pyrolysis is the first step in the gasification of biomass. In this stage, large molecules are broken down to smaller gas molecules (condensable as well as non-condensable), carbon char, and tars/oils. This stage is endothermic and does not involve reactions with oxygen or air or any medium. Following the initial pyrolysis of biomass, a number of secondary reactions occur where the products of pyrolysis react with each other and with the medium used for pyrolysis (oxygen, air, or steam), to give CO, CO_2, H_2, H_2O and CH_4. The carbon char is further gasified in the presence of restricted air, oxygen or steam to produce additional combustible gases, giving producer gas. The updraft gasifier and the downdraft gasifier designs (Fig. 1.12, 1.13) illustrate the different stages in a gasification process.

The overall reactions occurring after the initial pyrolysis of biomass in the gasification process are shown below (*source* Ref. [11]):
Carbon reactions:

$$\begin{aligned} &C + CO_2 \leftrightarrow 2CO && \Delta H_r^o = +172\,\mathrm{kJ/mol} \\ &C + H_2O \leftrightarrow CO + H_2 && \Delta H_r^o = +131\,\mathrm{kJ/mol} \\ &C + 2H_2 \leftrightarrow CH_4 && \Delta H_r^o = -74.8\,\mathrm{kJ/mol} \\ &C + \tfrac{1}{2}O_2 \rightarrow CO && \Delta H_r^o = -111\,\mathrm{kJ/mol} \end{aligned}$$

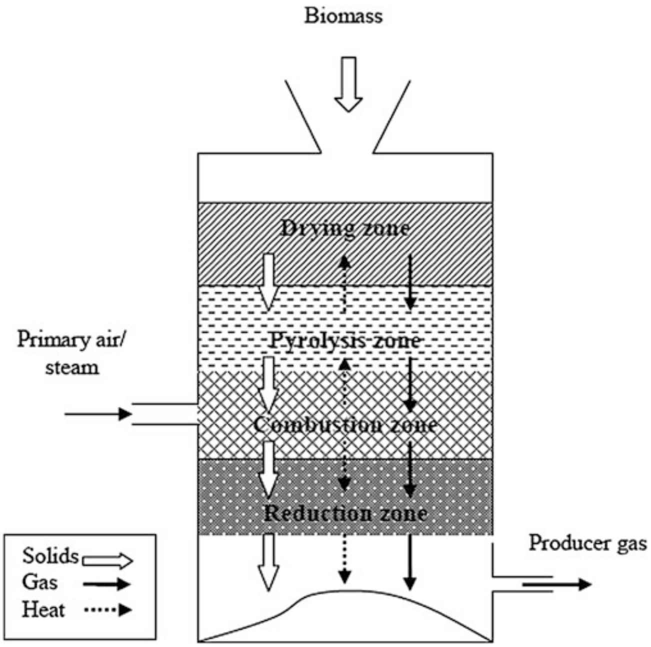


Fig. 1.12 Schematic of a downdraft gasifier

Oxidation reactions:

$$\begin{array}{ll} C + O_2 \rightarrow CO_2 & \Delta H_r^o = -394\,\mathrm{kJ/mol} \\ CO + \frac{1}{2}O_2 \rightarrow CO_2 & \Delta H_r^o = -284\,\mathrm{kJ/mol} \\ CH_4 + 2O_2 \leftrightarrow\ CO_2 + 2H_2O & \Delta H_r^o = -803\,\mathrm{kJ/mol} \\ H_2 + \frac{1}{2}O_2 \rightarrow H_2O & \Delta H_r^o = -242\,\mathrm{kJ/mol} \end{array}$$

Water–gas shift reaction:

$$CO + H_2O\ \leftrightarrow CO_2 + H_2 \quad \Delta H_r^o = -41.2\,\mathrm{kJ/mol}$$

Methanation reactions:

$$\begin{array}{ll} 2CO + 2H_2 \rightarrow CH_4 + CO_2 & \Delta H_r^o = -247\,\mathrm{kJ/mol} \\ CO + 3H_2 \leftrightarrow CH_4 + H_2O & \Delta H_r^o = -206\,\mathrm{kJ/mol} \\ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O & \Delta H_r^o = -165\,\mathrm{kJ/mol} \end{array}$$

Steam reforming reaction:

$$\begin{array}{ll} CH_4 + H_2O \leftrightarrow CO + 3H_2 & \Delta H_r^o = +206\,\mathrm{kJ/mol} \\ CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 & \Delta H_r^o = -36\,\mathrm{kJ/mol} \end{array}$$

The kinetics of the above reactions is discussed at length by Basu [11]. The above reactions occur in different zones in the reactor or in different regions of the biomass

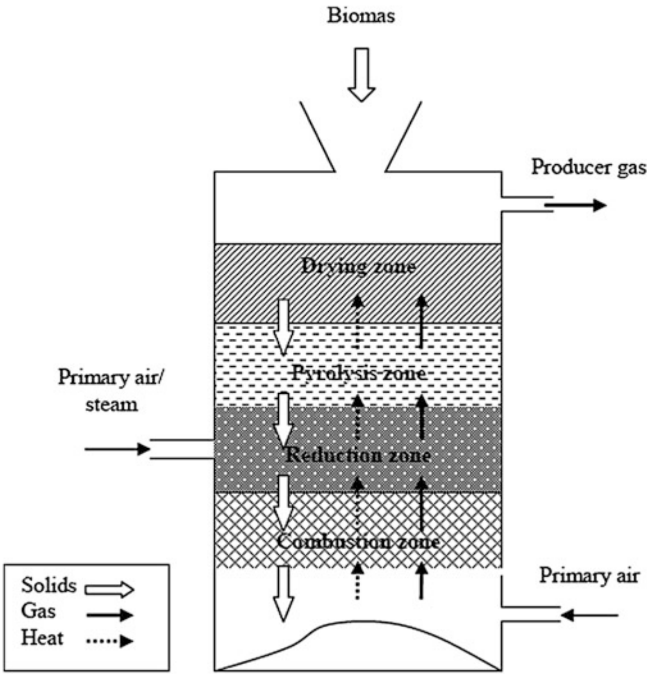


Fig. 1.13 Schematic of an updraft gasifier

particle depending on the surrounding temperature and the presence or absence of air/oxygen.

To summarize, gasification produces volatile gases and carbon char. The volatile gases are converted to CO, H_2 and CH_4, whereas the carbon char is combusted to produce CO. In case of low temperatures and short residence times in the hot zone, medium-sized molecules may escape and condense as undesirable tars and oils. This tar, being viscous, creates problems of fouling in the gasifier, and needs to be removed. This can be done by catalytic cracking of the tar, which gives CO, H_2, and H_2O. The role of catalysis in cracking is discussed in detail by Bridgwater [13].

The performance efficiency of a gasifier process or a gasifier unit is described in terms of "% cold gas efficiency" which is defined as follows:

$$\%\ \text{cold gas efficiency} = \left[\frac{\text{HHV}_{\text{gas}} \times v_{\text{gas}}}{\text{HHV}_{\text{fuel}} \times m_{\text{fuel}}}\right] \times 100$$

The extent of carbon conversion or fuel utilization can also be determined and related to the production efficiency of the gasifier process.

$$\%\ \text{carbon conversion} = \left[1 - \frac{m_{\text{ash}} \times \frac{\%\,\text{C}_{\text{ash}}}{100}}{m_{\text{fuel}} \times \frac{\%\,\text{C}_{\text{fuel}}}{100}}\right] \times 100$$

where

HHV_{gas} = higher heating value of the producer gas, kJ/m^3
HHV_{fuel} = higher heating value of the biomass feedstock, kJ/m^3
v_{gas} = volumetric rate of producer gas, m^3/h
m_{fuel} = input mass rate of biomass fuel, kg/h
m_{ash} = mass rate of gas residue exiting the gasifier, kg/h
$\% \ C_{ash}$ = weight percent of carbon in the ash residue, %
$\% \ C_{fuel}$ = weight percent of carbon in the biomass fuel, %

In general, operating the gasifier with 100% carbon utilization, with simultaneous maximization of cold gas efficiency, is not possible. The carbon efficiency has to be always sacrificed in order to achieve producer gas of the desired specifications [17].

Gasifier Designs

A variety of gasifier designs have been developed depending upon the nature of the gasification process involved, nature of feedstock used, scale of operation, and the product specifications required. These designs can be classified either on the basis of the manner in which the feedstock is handled in the gasifier or, on the basis of the manner in which heat is supplied to the gasifier. The first category of gasifiers are the fixed-bed gasifiers, fluidized-bed gasifiers, and the entrained flow gasifiers. The salient features of each of these are summarized in Table 1.6. The oxidation reactions taking place in the gasifier are generally exothermic reactions.

In most gasifiers the energy released as a result of these reactions is used to serve a dual purpose: first, to fuel the endothermic reactions taking place in the gasifier, and second, to maintain the high temperatures required in the gasifier. Such a gasification process, in which the heat released in one portion of the gasifier is partly or fully utilized to propel other endothermic gasification reactions taking place in the equipment, is a called direct gasification process. If no oxidizing agent is added, there will be no exothermic reactions taking place in the gasifier, and the heat required for the gasification processes will have to be supplied from some external source of heat. Such systems where the heat requirements for the gasification process are supplied externally are called indirect gasification systems or allothermal gasification. Figure 1.14 shows a schematic diagram of the direct and indirect gasification systems. As the direct gasifiers use a part of their input stream to drive other reactions taking place in the system, the overall efficiency of such systems is reduced.

On the other hand, as the indirect gasifiers use an external source of energy for the purpose, such gasifiers are expected to be more energy efficient, especially if solar energy is used as the source. Use of sunlight to drive an endothermic gasification reaction increases the calorific value of the initial biomass, with an added advantage of being a renewable source. An optimized design of such an indirect gasification system may even increase the energy content of the product stream beyond that of the feedstock. The gasification systems in which the heat producing processes or reactions are separated from the processes which consume heat are

Table 1.6 Types of gasifier systems

Based on handling of feedstock	*Fixed bed gasifier* • Can handle large and coarse particles • Distinct gasifier zones are present at a macroscopic level • Release lower temperature gas product • High particulate content in gas product stream • High gasifying agent consumption • Ash is removed as slag or dry	Updraft gasifier • Can tolerate more moisture in feedstock • Producer gas exits from top and at lower temperature (130–150°C) • Product contaminated with tars, oils and particulate matter from incoming fuel • Suitable for direct heating applications only Downdraft gasifier • Radiant and conductive heat transfer from lower pyrolysis and combustion zones provide heat for drying of biomass • Properly designed and positioned "throat" increase velocity of gas and promote heat and mass transfer • Gives least amount of tar • Widely used for small-scale applications Cross-flow gasifier • High temperature (>1,500°C) reached in the combustion zone • Reaction zone is small with low thermal capacity • Short start-up time and response time • Tar production is low • Generally used for gasification of charcoal (with very low ash content) • Suitable for small-scale biomass gasification units
	Fluidized bed gasifier • Uses inert material such as sand to mix solid fuel with gas phase • High operating temperatures (1,000–1,200°C) • Gasifier zones at microscopic levels in individual particle • Uniform temperature distribution • Better solid–gas contact and heat transfer rates • Equipped with cyclone separators at the top for removal of particulates from product • Suitable for feedstocks with low ash fusion temperature • Ash removed as slag or dry	Bubbling fluidized bed gasifier • Exit gas temperatures usually 700–800°C • Residence time is short • Suitable for medium-sized units (<25MWth) • Suitable for treated MSW biomass Circulating fluidized bed gasifier • Provides long residence time • Suitable for fuels with high volatiles • Capacity of 60 MWth achieved

(continued)

Table 1.6 (continued)

	Entrained flow gasifier • Operate at higher temperatures (1,200–1,600°C) and higher pressures (2–8 MPa) • High oxygen demand • Require small and uniform particle size distribution (<0.4 mm) in feedstock (not suitable for fibrous materials) • High reactivities and high capacities • Low higher hydrocarbons and low tar formation • Product low in methane content hence, better suited for synthesis gas production • High operating temperatures causes ash to get converted into slag which may be corrosive • Not suitable for high ash content feedstocks • Preferred for IGCC plants	Top-feed entrained flow gasifier • Vertically cylindrical reactor vessel • Pulverized biomass fed along with oxygen through a centrally mounted jet burner at the top of reactor • Flow of all reactants occurs from single burner • Product, gas, and slag flow in the same direction Side-feed entrained flow gasifier • Fuel injected through horizontal nozzles set opposite to each other at the lower part of gasifier • Opposing jets of fuel and gasifying agent improve degree of mixing • High oxygen availability in mixing zone accelerates exothermic reactions • Product gas moves upwards and exits from top • High temperatures (above ash-melting points) prevent ash entrainment with product
Based on method of heat supply	*Direct gasifiers* • Use portion of product or input stream to drive gasification reactions	• Reduced overall efficiency • Using pure oxygen makes the process comparable to indirect gasification however, cost efficiency reduces
	Indirect gasifiers • The combustion process is separated from the gasification process • Energy efficiency greater than direct gasifiers • Produces medium calorific value product and flue gases • Complete conversion of biomass is possible • High investment and maintenance cost	Char indirect gasifier • Residual char is combusted to provide energy for gasification • Gives very high throughputs and yields of gas Gas indirect gasifier • Fraction of combustible process gas burned to provide heat for gasification • Versatile and can use a wide variety of feedstock Gasifier using solar energy • Uses concentrated solar energy as external energy source which is renewable • Calorific value of biomass feedstock increases • Energy content of exit stream can exceed that of feedstock • Reactor design is a major challenge

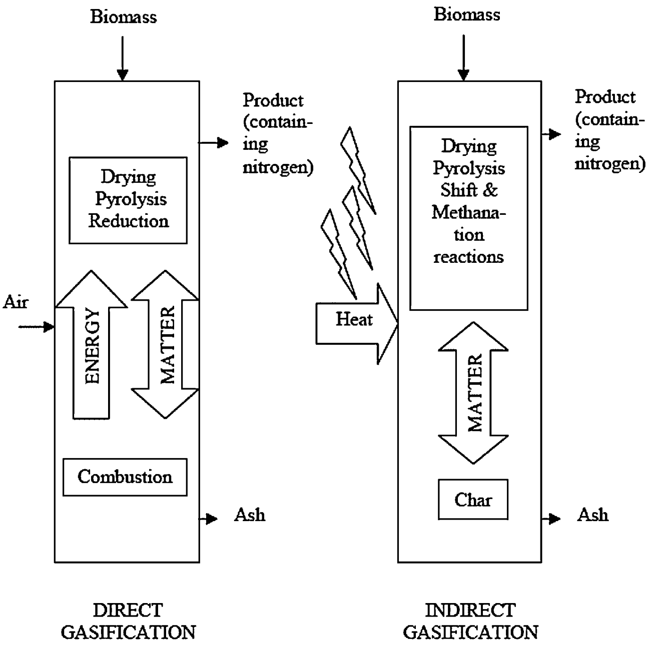


Fig. 1.14 Schematic of direct and indirect gasification process

also categorized under indirect gasification systems. Such systems therefore consist of two reactors connected by an energy flow. Typically, the oxidation or combustion reactions which are exothermic in nature are separated from the pyrolysis and gasification reactions which require heat. The heat from the combustion reactor is provided to the gasification reactor by means of hot sand which is circulated between the two reactors. The different designs of gasifiers, along with their salient features, advantages and disadvantages, have been reviewed by a number of authors [10, 11, 17–19]. A summary of these is given in Table 1.6.

In addition to the gasifier designs summarized in Table 1.6, there are other gasifiers which are modifications of the existing designs. Transport gasifier, twin reactor system, and chemical looping gasifier designs are modifications of the circulating fluidized-bed gasifier. The transport gasifier is a hybrid of entrained flow and fluidized-bed gasifier systems. Its construction and process design attributes to it, a higher throughput, better mixing and consequently, higher heat and mass transfer rates. However, it is more suitable for gasification of coal; its suitability for gasification of biomass is yet to be proven [11]. The twin reactor system is a dual fluidized-bed gasifier where the combustion process in the gasification of biomass is separated from the gasification process using separate fluidized-bed reactors. Such a design prevents the dilution of the product mix by nitrogen which is released subsequent to air combustion in normal fluidized-bed gasification process. These are used for gasification of coal as well as biomass. Different industrial-scale units are described by Basu [11]. The chemical looping gasifier process is a relatively recent development in which a bubbling fluidized-bed gasifier is coupled with a circulating fluid bed regenerator to obtain a continuous stream of hydrogen from agricultural feedstock. In- situ sequestration of carbon dioxide, formed during the gasification process, is done by using calcium oxide which reacts with carbon dioxide to form calcium carbonate, which is then reconverted into calcium oxide in the circulating bed regenerator [20].

Plasma gasification technology is a newly developed self-sustaining technology which is used especially for conversion of municipal solid waste into electric power. It is relatively insensitive to the quality of feedstock which is the most desired feature for MSW processing. The garbage is converted into a finely shredded mass and is then fed into a plasma chamber which consists of a sealed stainless steel vessel which is filled with either ordinary air or nitrogen. A 650 V electric current is passed between two electrodes which tears off electrons from air to create plasma. The energy generated in the process is sufficient to disintegrate the garbage into its constituent elements, forming syngas along with other by-products depending on the nature of MSW used as feedstock. The syngas, which leaves the plasma chamber at a temperature of $\sim$ 1,200°C is fed to a cooling system, where the heat transferred from the syngas to the cooling water generates steam, which can be used in a steam turbine to generate electricity. The gas, after appropriate clean-up, can be used either for the usual applications of syngas, or in a gas generator to generate electricity. Part of the electricity generated is used to generate plasma in the plasma chamber. Figure 1.15 shows a schematic of the process.

Hydrothermal gasification involves gasification of biomass in an aqueous medium using supercritical water, i.e., water at a temperature and pressure beyond the critical point of water (374.29°C and 22.089 MPa). The conventional thermal methods of biomass conversion are cost-effective only when the moisture content of biomass feedstock is low. However, certain biomass such as aquatic biomass and MSW may contain moisture even up to 90% weight basis. In such cases, either the biomass has to be dried separately or, process heat is used to dry the excess moisture, both of which reduce the efficiency of the process. Another alternative in such cases is the use of biochemical methods for biomass conversion. However, these methods suffer from a major disadvantage of being very slow, having a low efficiency and producing only methane and no hydrogen. In order to get hydrogen, steam reforming process is required to be carried out. In contrast, the hydrothermal gasification process is relatively rapid and can tolerate very high moisture contents without compromising on the efficiency of the process [21]. Supercritical water has some unique properties which make it suitable for biomass gasification:

- it causes rapid hydrolysis of biomass
- the intermediate reaction products, including gases have a high solubility
- single-phase reactions are possible, thus eliminating interphase barriers for mass transfer
- being non-polar, supercritical water is a good solvent for substances like lignin which show low solubility in ordinary water.

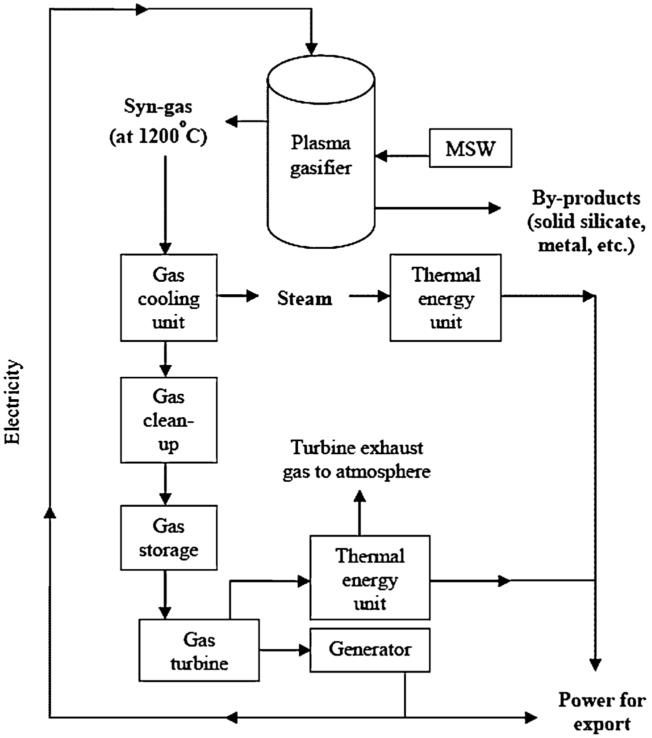


Fig. 1.15 Schematic of plasma gasification unit

Hydrothermal gasification causes splitting of the organic molecules present in the biomass by hydrolysis and oxidation reactions. The biomass gets broken down to methane, hydrogen, carbon monoxide, and carbon dioxide. The major advantages of hydrothermal gasification are that it is suitable for biomass with high moisture contents; the product formed is rich in hydrogen; char and tar formation is low; the tar that is formed gets cracked and dissolves in the supercritical water. In addition, automatic separation of the product gas from the liquid containing char and tar takes place which obviates the need for a separate gas cleaning process which is usually required for all the conventional gasification or, for that matter for all thermochemical conversion processes. Elements such as sulfur, nitrogen, halogens, etc. leave the process along with the aqueous effluents. However, due to this, corrosion of the reactor is a major problem as the presence of water causes the elemental by-products to get converted into acids which can corrode the reactor. Products such as bio-oil, methanol, hydrogen and a range of chemicals including phenol can be obtained from hydrothermal gasification of biomass. Hydrothermal gasification is most suitable for processing of MSW, and other biomass having very high moisture content as the efficiency of this process is independent of moisture content.

Downstream processing in gasification

An ideal gasification process converts biomass completely into carbon monoxide and hydrogen, i.e., syngas. This syngas can be used directly for the generation of electricity via internal or external combustion engines or for synthesis of liquid biofuel and other chemicals. However, the hot syngas from the gasifier may be contaminated to a varying degree, depending on the design of the gasifier used, process controls exerted, medium of gasification (oxygen, air, steam, etc.), and nature of biomass feedstock used. The product, instead of pure syngas may consist of a mixture of syn-gas and carbon dioxide, methane, water, and smaller hydrocarbons—condensable and non-condensable. This gaseous product may be further contaminated by contaminants comprising particulate matter, alkali compounds, nitrogen compounds, sulfur compounds, and condensable tars. Hence, syngas cleaning is an important component of downstream processing in the gasification process. Cold cleaning (at temperatures <30°C), warm cleaning (at temperatures between 30 and 300°C) and hot cleaning (at temperatures >300°C) may be done depending on the final application of the syngas. The particulate matter in the syngas is removed through physical means by using ceramic or metal based filters. Particle agglomeration techniques may precede the physical filtration process in order to facilitate the filtration process and prevent the clogging of the filter surface by fine ash deposits. High porosity nanoparticle membrane filters are also being developed for removal of sticky materials from the gaseous product. The alkali and elemental contaminants may be removed by passing the gas through a bed of suitable high capacity sorbents. Tar formation is one of the major issues in the gasification process. The tar present in the syngas can condense into a thick viscous liquid which can stick on the various surfaces of the process equipment such as turbines and engines. Primary tar formation, i.e., the tar formation in the gasifier can be controlled by using optimum operating conditions as well as by use of appropriate catalysts which cause cracking of the tar. Secondary tar removal, i.e., removal of tar present in the syn-gas already collected from the gasifier can be done by filtering, gas scrubbing, passing through cyclone separators, catalytic cracking, steam reforming, or by thermal cracking methods. Kumar et al. [22] have reviewed the various aspects of downstream processing in gasification. The main methods for tar removal are steam reforming and catalyst cracking. In steam reforming, the tar is reacted with at temperatures of around 650–700°C where the tar gets converted to syngas:

$$C_xH_y + xH_2O \leftrightarrow xCO + \left(x + \frac{y}{2}\right)H_2$$

For obtaining hydrogen as the major product, the above reaction is followed by water–gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Steam reforming may be a part of the gasification process or may be performed separately after the gasification. Tar cracking involves thermal cracking of the long chain hydrocarbons in the tar into smaller molecules, finally forming CO and H_2. This can also be performed in situ, in the gasifier or separately. Bridgwater [13] describes the use of catalysts such as dolomite, fluid catalytic cracking catalysts, and metal catalysts for removal of tar from the gasification product.

Biomass gasification is the latest generation of thermochemical biomass-to-energy conversion processes. A number of commercial gasifiers, based on the various types described previously in this section, are operational, and some of them have successfully completed several years of operation. The Atlanta-based Future Energy Resources Corporation (FERCO) has commercialized the Silva-Gas TM gasification technology in partnership with the US Department of Energy and the Burlington Electric Department at Vermont, USA. This facility, which was operational in 2001, is a low inlet gas velocity, high throughput biomass gasification process, which can convert more than 285 tons of biomass such as forest residue, MSW, agricultural waste, and energy crops into SilvaGas, a medium Btu gas. This gas is piped directly to Burlington Electric Department's McNeil generating plant, where it produces more than 140 MWh of electric power. Another circulating fluidized-bed gasifier developed by Foster Wheeler at Lahiti Kymijarvi, Finland, has completed several years of operation and can produce 60 MWth energy. It uses paper, textiles, wood, and peat fuels with an average moisture content of about 50%. It provides hot but low calorific value gas around 2 MJ/Nm^3 which can be used for heating purposes only. A demonstration plant with a bubbling fluidized-bed gasifier design has been developed as a part of the Carbona Project, at Skive, Denmark, and commissioned in late 2007. It uses wood-based biomass and has an efficiency of 90%. The product generated is a mixture of carbon monoxide, hydrogen, and methane, having a heating value of 5 MJ/kg, which is used for CHP application and generates 6,000 kW of power. Plasma gasification plants, mainly for the processing of MSW have also been developed, one of them being the Hitachi demonstration plant set up at Yoshii, Japan, commissioned in 1999. This plant was developed as a solution to dioxin, ash, and energy recovery problems from incineration-to-waste energy plants in Japan. It processes 20 tons/day of MSW and produces steam for industrial use. The plant emissions are much reduced, and the slag produced is a glassy product which can be used as a construction material. Another plasma gasification plant—the Hitachi combined MSW and Sewage Sludge gasification plant, is a commercial scale plant, Mihama and Mikdata, Japan, and commissioned in 2002. This plant treats 24 tons/day MSW and 4 tons/day sewage sludge to generate energy which is used in the municipal wastewater treatment facility. The same company has a 200 tons/day plasma gasification plant which has been fully operational since 2003, at Utashinai, Japan which uses automobile shredder residue as feed. The syngas produced is used to generate power and process steam. The hydrothermal gasification process is still at the development stage, but considering the numerous advantages it offers over other conventional gasification processes, it will not be long before commercial-scale plants see the light of the day.

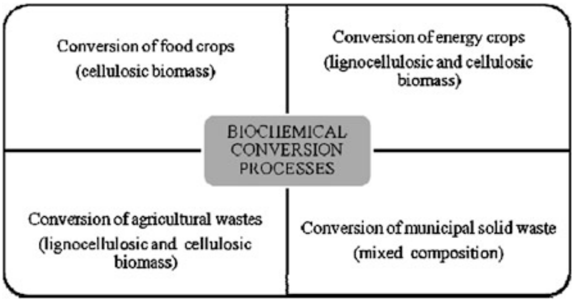


Fig. 1.16 Feedstock for biochemical conversion processes

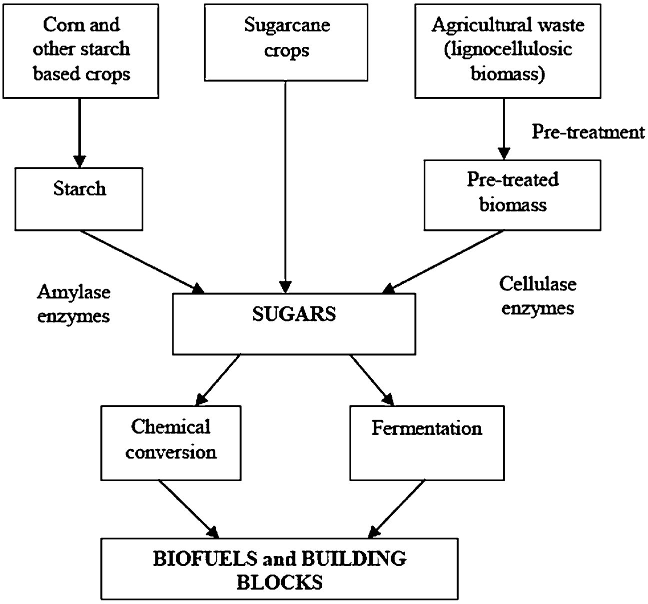


Fig. 1.17 Biochemical conversion of cellulosic and lignocellulosic feedstock

1.2.1.2 Biochemical Conversion Processes

The biochemical methods of conversion of biomass are more environment friendly than the thermochemical processes described above. These processes are mainly used for conversion of organic wastes, both agricultural and municipal solid waste (Fig. 1.16), which are relatively difficult to process due to their very low energy density and, difficulty in handling. The schemes for processing the two types of wastes are outlined in Figs. 1.17 and 1.18.

In principle, these methods can be considered to be the reverse of photosynthesis. The products of biochemical conversion methods comprise biogas and

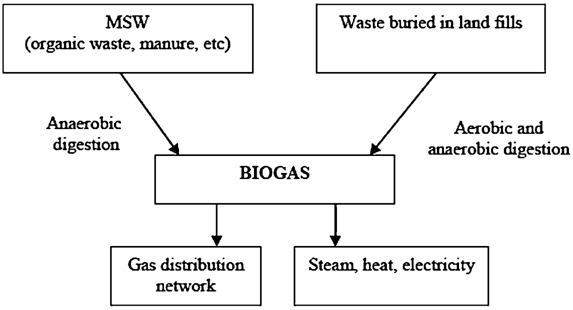


Fig. 1.18 Biochemical conversion of municipal solid waste and landfill waste

landfill gas; liquid biofuels such as biodiesels, bioethanol, biomethanol, and pyrolysis oils; and hydrogen. Biogas is a mixture of methane and carbon dioxide, generated as a result of the decay of sewage or animal waste. A similar product generated at landfill sites is called landfill gas. The landfill gas generated from landfill sites, if it is not collected, escapes into the atmosphere. Pipelines laid at the landfill sites before the construction of the site makes it possible to collect the landfill gas which can be used to generate electricity with the help of large internal combustion engines. The output of the landfill gas can be as high as 1,000 m^3/h [16]. Processing lignocellulosic feedstock, including lignocellulosic waste gives liquid biofuels such as ethanol which can be used as a transport fuel by mixing with gasoline. A host of other products such as methane, producer gas, esters, and other chemicals having a cellulosic origin can also be obtained. Hydrogen is going to be an important energy carrier of the future. The biochemical processes can be classified into three categories:

- *Aerobic fermentation* (which can also be considered as biogasification of biomass), which produces compost, carbon dioxide, and water.
- *Anaerobic digestion* which produces fertilizer gas and biogas.
- *Alcoholic fermentation* which produces ethanol, carbon dioxide, and waste.

The main disadvantage of biochemical processes is that they are slow, involving very long time periods.

Aerobic Fermentation

The production of landfill gas from landfill sites is carried out by a complex process involving a succession of microbial population. The initial fermentation is aerobic fermentation which is carried out by bacteria already present in waste. This stage is followed by an anaerobic digestion stage. During the aerobic fermentation stage, the carbon in the biomass is converted into carbon dioxide and water. These reactions are strongly exothermic and increase the temperature of the landfill waste, consequently increasing the activity of the other microorganisms. If this stage continues for long, the amount of methane, which is the product of the anaerobic digestion stage, decreases. In order to shorten the aerobic fermentation stage, and consequently prevent the reduction in methane yield, the landfill waste is made to pass through compactors, which serves a dual purpose of increasing the density of the landfill waste and simultaneously removing a substantial amount of oxygen from the waste. After an initial phase of aerobic fermentation, the waste gradually becomes anaerobic as oxygen is depleted from it. The subsequent fermentation causes the breakdown of complex polymeric components in the biomass into simpler compounds, followed by volatile fatty acids, followed by carbon dioxide, hydrogen, and acetic acid.

Anaerobic Digestion

Anaerobic digestion involves the microbial fermentation of cellulosic/lignocellulosic biomass in the absence of oxygen for about 2–8 weeks. A similar process involving municipal solid waste, which may, in addition to cellulosic components, contain polymeric substances, fats, proteins, etc. is termed as anaerobic digestion. This is the most commonly used, commercially viable process under the biochemical methods of biomass conversion. The product of anaerobic fermentation comprises 65–70% methane, 30–35% carbon dioxide, and traces of other gases such as H_2S and hydrogen. This product has a heating value of 26 MJ/m^3 [23].

Lignocellulose is very refractory in nature and requires harsh pretreatment procedures before it can be used for fermentation. The pretreatment procedures usually used are described in “Forest Biorefinery”. Following the pretreatment procedure, lignocellulose breaks down to cellulose, hemicellulose, and lignin. The cellulose and hemicellulose subsequently undergo anaerobic, or alcoholic fermentation to give biogas or ethanol. Alcoholic fermentation is discussed in the following section.

Anaerobic fermentation/digestion is also called biomethanation as methane is the major end product of the process. It can be carried out according to a two-stage scheme or a four-stage scheme. The two-stage scheme originated in the 1930s and involves two major metabolic groups of bacteria- the acid forming and the methane forming bacteria. The acid forming bacteria are a complex species of bacteria which hydrolyze the primary substrate polymers such as polysaccharides, proteins, and lipids, and ferment these to mainly fatty acids and other organic acids, alcohols, ammonia, sulfide, carbon dioxide, and methane. The methane forming bacteria involve a group of bacteria which degrade the products of the first stage to methane and carbon dioxide.

The current processes used (Fig. 1.19), involve four stages which are executed by four different groups of organisms, and end up with different end products [24].

The *first phase* involves facultative, or strictly anaerobic bacteria such as *Streptococcus*, *Peptococcus*, *Micrococcus*, and *Clostridium* (a thermophilic species). These convert the polymers/polysaccharides into the biomass to small monomers or oligomers such as glucose, cellobiose, amino acids, short chain fatty acids, and glycerol. Carbon dioxide and hydrogen are released in the process. In

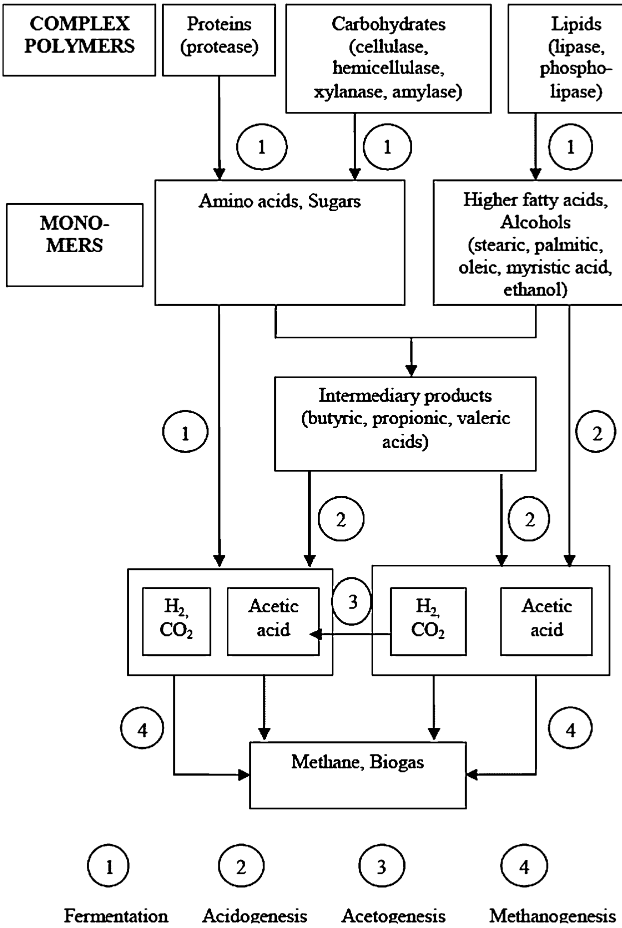


Fig. 1.19 Anaerobic digestion process

other words, in this phase, the biomass is hydrolyzed to give smaller fragments, which are then processed further by other groups of microbes. This process is catalyzed by extracellular hydrolases such as cellulase, xylanase, protease, and lipase. This stage is relatively slow and may often be the rate limiting stage in the process.

The *second phase* is the acidogenesis phase which again involves facultative and strictly anaerobic microbes such as *Bacteriodes, Clostridium, Butyribacterium, Propionibacterium, Pseudomonas, and Ruminococcus*. Some of these are hydrolytic and others, non-hydrolytic. The products of this phase are short chain fatty acids such as formate, acetate, butyrate, isobutyrate, and succinate. Among these, acetate is the major short chain fatty acid. Small quantities of alcohols (methanol, ethanol, glycerol, and butanol) and acetone may also be produced depending on the nature of the initial feedstock and the anaerobic digestion process used. This stage of fermentative acidogenesis is rapid and often leads to accumulation of the short chain fatty acids. If this happens, it usually leads to reduced methane formation, followed by methanation failure in the subsequent methanation stage. This usually happens when the feedstock contains large amounts of readily fermentable carbohydrates, and when the loading rate is high.

The *third phase* involves strictly anaerobic bacteria, which are syntrophic acetogens—*Syntrophomonas wolfei and Syntrophobacteri wolinii*. They are called syntrophs because they are in close proximity to methanogens, the group of microbes that are responsible for methanogenesis, which is the fourth phase of anaerobic digestion (the syntrophy occurs through interspecies hydrogen transfer). The syntrophic acetogens convert substances such as ethanol, and esters such as propionate, butyrate, valerate, and other short chain fatty acids containing three or more than three carbons to acetate, hydrogen, and carbon dioxide. The hydrogen produced is rapidly consumed by the methanogens, which reduces the partial pressure of hydrogen and takes the processes forward toward generation of methane in the next phase. Syntrophic acetogens grow very slowly (require more than one week to grow to sufficient numbers), making this stage another possible rate limiting step (in addition to the first hydrolytic stage).

In case of inefficiency of this acetogenesis phase, accumulation of the non-acetic acid small chain fatty acids, i.e., the products of the second phase occurs, which reduces the pH of the fermentation reactor. This inhibits the methanogens, thus reducing the formation of methane, which eventually ceases completely.

The *fourth phase* involves a group of microbes called the methanogens that are completely different from bacteria and belong to a class called Archaea. These are strict anaerobes, which require a very narrow range of environmental conditions of pH and temperature and a reduction potential of <300 mV. These are present naturally in anaerobic environments such as swamps and wetlands and grow slowly. Hence, this is a third possible rate limiting step in the process of anaerobic digestion. These microbes use acetate, hydrogen, carbon dioxide (the products of the third phase), in addition to methanol, formate, methylamines, and methyl sulfides as their substrate. Depending on the substrate specificity and methanogenesis pathway, these microorganisms are classified into two categories—the Hydrogenotrophic methanogens and the Acetoclastic or acetotrophic methanogens. The Hydrogenotrophic methanogens use hydrogen produced by both the acidogens, as well as the syntrophic acetogens to reduce carbon dioxide to methane or to convert methanol, methylamines and methyl sulfides to methane. A wide diversity of species is found in this category. Acetoclastic or acetotrophic methanogens convert acetate to methane. As acetate is the major product of the preceding stage of anaerobic digestion, two-thirds of the methane produced is by this class of microorganisms. Only two genera in this category have been identified—*Methanosaeta* (formerly called methanothrix) and *Methanosarcina*. The latter is both acetotrophic as well as hydrogenotrophic. All these processes are endothermic processes. The yield of the anaerobic digestion processes depend on the nature of feedstock used. Yu Zhongtang et al. [24] have listed the Biochemical methane potential (BMP) of a variety of feedstock such as livestock manure, food-processing wastes, municipal solid wastes, crop residues, and energy crops. From among the livestock manure evaluated, poultry manure had the highest BMP of 460 m^3/dry ton, whereas beef and dairy cattle manure had a BMP of 148–250 m^3/dry ton. Among the food-producing wastes, fresh fruit and vegetable waste had a BMP of 228–495 m^3/dry ton and municipal solid (organic fraction) waste had a BMP of 300–550 m^3/dry ton. Agricultural residue such as corn stover and wheat straw had a BMP of 250 and 161–241 m^3/dry ton, respectively. Energy crops such as sugar beet and grass silage had a BMP of 380 and 390 m^3/dry ton respectively. The technologies currently used for anaerobic fermentation/ digestion, along with their salient features are shown in Table 1.7.

Alcoholic Fermentation

Alcoholic fermentation involves the production of alcohols such as ethanol and butanol from biomass. Fermentation has been used since ages to produce alcohol from carbohydrate substrates. The feedstock for this fermentation has been agricultural commodities such as sugarcane, beet sugar and corn starch—the more common one being starch. The microorganism used for this fermentation has been mainly, yeast. The technology for such fermentations is very well established and has been commercially used for production of ethanol, with state-of-the art fermentation plants, the world over. However, the food versus fuel controversy has prompted the search for other feedstocks such as cellulosic/lignocellulosic biomass for use as substrate for fermentation to ethanol. The bioethanol so produced can be used as a fuel as such or, more appropriately, as an admixture in diesel, as gasohol. The use of such substrates, especially lignocellulosic substrates, for successful commercial fermentation, is still a challenging task mainly due to the highly refractory nature of lignocellulose. In addition to physicochemical methods for efficient hydrolysis of lignocellulose, enzymatic hydrolysis methods are also being researched the latter having an advantage of being carried out in situ in the fermenter. Persistent research efforts in this area have resulted in the development of efficient and economic fermentation processes and technologies even for such a refractory material. The world's first cellulosic ethanol demonstration plant has been set up at Yonroe-Tennesee and has begun operations since January 2010.

The biochemistry of lignocellulose/cellulose conversion into easily fermentable sugars has been studied exhaustively and a multitude of reviews and treatises on the subject is available in the literature. This section will discuss the recent advances that have taken place in the area. Lignocellulose consists of cellulose which is a glucose polymer; hemicellulose, which consists of mixed hexoses and pentoses; and xylan which is a xylose polymer. All these substances need to be essentially converted into monosaccharides before they can be fermented by the usual fermentation process. This process of breaking down the complex polysaccharides into simple soluble sugars is called saccharification. *Saccharomyces cerevisiae* was the predominantly used species for this conversion. However, this microorganism, which is conventionally used for conversion of starch into ethanol,

Table 1.7 Anaerobic digestion systems and technologies

Type of reactor/technology	Salient features	Applications
Continuous Stirred Tank Reactor (CSTR)	– First type of anaerobic digestion reactor developed; still in use – Good mass transfer – Cannot be operated at high hydraulic loading rates – Not suitable for biomass with low concentration of readily biodegradable substances	Batch CSTR produces 4,000 m^3 of biogas per day in biomethanation plant at Karlsruhe, Germany Centralized biogas plant operating three thermophilic CSTRs with a total volume of 7,000 m^3 in Lemvig, Denmark
• Completely Mixed Contact Reactor (CMCR) or Anaerobic Contact Reactor (ACR)	– Can handle high-strength feedstocks with large amounts of suspended solids – High loading rates possible – Active microbial mass retained in reactor	
• Sand Filter bed reactor	– Can handle high-strength feedstocks – Active microbial mass retained in reactor – High loading rates possible – Less susceptible to upsets – Capable of digesting high-fat feedstocks – High conversion capacity – Vulnerable to clogging	Pilot scale reactor developed, large scale reactor not yet developed
Mixed Plug Flow Loop Reactor (MPFLR)	– Tank reactor with U-shape design – Biomass enters at one end, flows forward, and loops back and exits from the same end through a separate outlet Contents mixed by means of gas or water jets in direction perpendicular to the plug flow of the reactor Solids separated from the effluent may be recycled	Suitable for medium to high solid content feedstock Industrial-scale MPFLR plant at Herrema Dairy Farm, Indiana digests more than 400 m^3 of manure slurry with about 8% solids

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
Anaerobic Filter Reactor (AFR)	Comprises a tank filled with rocks, gravel, or plastic granules which act as a filter medium as well as a substrate on which most microbes adhere and grow as a biofilm – Some microbes grow as clusters/granules within the void spaces – Hydraulic residence time(HRT) and solids retention time (SRT) are separated – Suitable for feedstocks where phases 3 and 4 are prolonged, requiring long ($\geq$20 days) SRT – High possibility of clogging of filter	Suitable for feedstocks rich in carbohydrates Not suitable for feedstock with high separated solids(SS) such as manure slurry unless SS is removed
• Anaerobic expanded bed reactor(AEBR)	– Design is a variant of AFR, similar in all aspects except that the filter medium is fluidized instead of immobilized	
• Anaerobic fluidized bed reactor (AFBR)	– Large surface area is provided for digestion reaction – Friction between fluidized particles promotes transfer of substrates, nutrients, and metabolic products across biofilms, simultaneously preventing excessive build-up of bio-film – Effluent is re-circulated – High organic loading rates possible – Reduced reactor clogging – High SS (up to 10%) can be treated – Energy consumption is higher compared to AFR – Scale-up is more difficult – Requires longer start-up time and uniform distribution of influent	

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
Upflow Anaerobic Sludge Blanket Reactor (UASB)	– Microbial biomass is kept as suspension and forms a blanket of sludge at the bottom of the reactor – Mixing between the sludge and the influent is achieved by high up-flow velocity of influent and rising biogas – Solid–liquid–gas separator at the upper part of the reactor separates the biogas from the sludge granules – No recirculation of solids separated from the effluent is required – Operational costs are low – High loading rates possible – Not suitable for influents containing large amounts of SS – Requires long start-up time	Most common anaerobic digestion reactors used worldwide, suitable for medium strength waste streams such as waste from brewery, food processing, beverage, bioethanol, pulp and paper, fermentation, chemical, and pharmaceutical industries
Anaerobic Baffled Reactor (ABR)	– Consists of several baffled USAB reactors connected in series – A settler is provided at the inlet where the SS in the influent settles – Influent passes over and under the baffles as it flows toward the outlet – Compartmentalized configuration facilitates spatial separation of acidogenic and methanogenic processes – Reduced risk of microbial biomass washout, hence, effluent has a low COD – Shallow reactors necessary so that sufficient liquid and gas up-flow velocities can be maintained – Even distribution of influent difficult to maintain	Suitable for treating waste waters of any organic strength

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
Expanded Granular Sludge Blanket Reactor (EGSB)	– Latest development in anaerobic digesters – It is a USAB reactor with a greater height to diameter ratio, enabling greater up-flow velocity (>4 m/h) – Part of effluent is re-circulated – Increase in up-flow velocity expands the sludge bed and eliminates dead zones, thus improving mass transfer and digestion rates – High loading rates possible (HRT < 2 h)	Suitable for high strength feedstocks
Internal Circulation Reactor (IC)	– It is a combination of USAB and EGSB reactors—design similar to two USAB reactors stacked one on top on the other – Lower portion has an expanded granular sludge bed – Influent enters at the bottom through a distribution system and is mixed with the effluent which is recirculated from the top to the bottom through a down pipe – Due to the presence of the sludge bed at the bottom, most of the microbiological reactions of anaerobic digestion processes occur in this lower compartment – The reactor has a down pipe (from bottom to top of the reactor) and a rise pipe (in the upper compartment of the reactor), which cause internal circulation of the water and sludge in the reactor- the rising gas causes a gas-lift, carrying water and sludge upward to the gas–liquid separator, through the rise pipe, consequently causing some water and sludge to drain downward through the down pipe	Suitable for treatment of a variety of industrial waste waters, including food processing and manure waste waters

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
	– The undigested portion from the lower compartment is continued in the upper portion and the biogas is collected by the upper phase separator – The effluent leaves the reactor through an overflow weir in the upper portion of the reactor – Improved efficiency – No energy required for recirculation – Biogas has an increased methane content	
Anaerobic Hybrid Reactor (AHR)	– It is a combination of EGSB and AFR reactors – Upper portion contains a packed zone of microbial biomass carrier and the lower portion contains a sludge blanket – Hydrolysis and acidogenesis occurs in the sludge blanket, whereas methanogenesis takes place in the packed zones – Packed zone reduces microbial washout even at high up-flow velocities that are essential to increase mixing and mass transfer – Start-up period required to reach stable operation is very long (several months)	Laboratory-scale demonstrates suitability and efficiency of AFR to treat high strength industrial waste waters including cheese whey, molasses waste water, dairy manure slurry, wood fiber waste water, and palm mill oil waste water. Very few industrial-scale reactors exist, one of which is an AHR installed at a cheese factory in Turkey to treat cheese wheys
Anaerobic Sequencing Batch Reactor (ASBR)	– A fill-and-draw cycle employed – ASBR filled with influent and mixed with sludge already present in the reactor – Anaerobic digestion takes place during mixing – Mixing stopped after completion of biogas production – Sludge allowed to settle at bottom – Liquid supernant removed by floating pump until liquid level drops to a pre-set level – Reactor re-filled with influent and cycle re-starts	Used to produce methane from winery waste water and swine slurry manure

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
Covered Lagoon Digester	– Comprises a large waste lagoon covered with a flexible or floating gas-impermeable cover – Long retention time and high dilution rate – Suitable for low solids feedstock (0.5–2%) – Operates at ambient temperature – Suitable for tropical regions where temperature is high throughout the year – Simple and cheap to construct, operate and maintain – Low biogas output	Can be used to generate sufficient power to fulfill in-house power requirements
'Dry' Anaerobic Digestion Technologies (DRANCO technology)	– Comprises of a large tank with a separate mixing compartment at the bottom – Shredded organic solid waste (<40 mm diameter) added and mixed (ratio 6:1 to 8:1) with digested sludge in the mixing compartment – Steam added to the mixture to raise temperature to required temperature – Pre-heated mixture pumped to the top portion of the digester – Counter current movement of feed stock and biogas – Biogas collected from top – Average retention time of 20 days – Offers advantages of high loading rates, construction simplicity, smaller digester volumes with no accumulation in digester	Suitable for low moisture, high solid content (>15%) organic waste, energy crops and crop residues DRANCO digester in Victoria, Spain, with a volume of 1,770 m^3 has a capacity of 120,750 tons per year, producing 5,962 tons of biogas, 6,000 MWh electricity, and 12,580 tons of compost per year
Two-Stage Digester	– Hydrolysis and acidogenesis stages separated from syntrophic acetogenesis and methanogenesis stages by carrying them out in two different reactors – Both reactors optimized respectively with respect to feeding rate, HRT, SRT, pH, and mixing	An industrial-scale mesophilic two-stage CSTR digester, operating at 39°C installed in a farm in Lower Austria has a capacity of 2,000 m^3 each, capable of digesting a variety of feedstock including pig manure, energy crops, and residue from vegetable and sugar processing

(continued)

Table 1.7 (continued)

Type of reactor/technology	Salient features	Applications
	– Enhanced stability, reduced reactor volumes, increased loading rates and improved yield – Construction and operation costs higher than the single stage reactors – Any of the above reactors can be used, CSTR and CMCR are the most commonly used ones	industry. It produces a total of 1MWh of electricity and 1.2 MWh of heat.
Temperature-Phased Anaerobic Digester (TPAD)	– It is a two-stage digester system, the – First one is thermophilic and the second is mesophilic – Enhanced hydrolysis and acidogenesis in first reactor – Efficient and stable syntrophic acetogenesis and methanogenesis in the second reactor – Due to the thermophilic digestion in the first stage, sanitation of waste streams occurs	Co-digestion of primary sludge and organic fraction of MSW successfully done in TPAD Suitable for dairy cattle manure and food processing wastes

Source Ref. [24]

is not suitable for lignocellulosic-based ethanol production because *Saccharomyces* is capable of fermenting glucose alone to ethanol, whereas lignocellulosic biomass hydrolysate usually consists of a mixture of oligosaccharides. A number of novel enzymes and improved microbial strains, which have been specifically engineered to convert such a recalcitrant substance like lignocellulose into easily fermentable sugars, have been successfully developed. Some of the microbial strains developed are *Scheffersomyces stiptis, Candida shehatae, Kluyveromyces marxianus, Escherichia coli* and *Zymonas mobilis* [25]. The enzymes responsible for breaking down cellulose from lignocellulosic biomass comprise a multitude of enzymes which fall into the category of glycosyl hydrolases which exist in the form of a complex assembly of enzymes called "cellulosome". These glycosyl hydrolases include both cellulases and non-cellulosic structural polysaccharidases. The details of the different modules of enzymes comprising the cellulosome are discussed in detail by Berg Miller et al. [26]. The true cellulases, present in the glycosyl hydrolases, cleave the β-1,4-glucosidic bonds of cellulose, resulting in the production of cellobiose. A number of other enzymes, having varying degrees of specificities, are responsible for hydrolyzing different forms of cellulose present in the cellulosic plant material. Non-cellulosic structural polysaccharidases are a diverse group of enzymes that are capable of cleaving the different types of bonds present in the main chain backbone (xylanases and mannanases) and the side chain constituents (arabinofuranosidases, glucuronidases, acetyl esterases, xylosidases, and mannosidases) of the substrate. Ladisch et al. [27] provide an elaborate description of the cellulose enzyme system and the mode of action of fungal cellulases. Current research efforts in the field of enzymatic hydrolysis of cellulosic plant material are going increasingly toward identifying newer glycosyl hydrolases. The currently followed approach for accomplishing this is by attempting to genetically modify the most efficient existing microbial systems such as those found in the grass eating ruminant animals, e.g., *Fibronobacter succinogenes, Ruminococcus albus,* and *Ruminococcus flavefaciens* into making newer and more efficient glycosyl hydrolases by using molecular engineering concepts. The research progress in the field is comprehensively outlined by Berg Miller et al. [26].

An alternative to the above-mentioned enzymatic hydrolysis of lignocellulosic biomass is acid hydrolysis, which has a few advantages over enzymatic hydrolysis in that, it is quick, no dedicated support of enzyme production system is required, and high temperatures can be used, allowing lower acid concentrations. However, the major drawback of acid hydrolysis process is the degradation of the hexoses and pentoses to acids such as hydroxymethyl furfural (HMF) from glucose and furfural from xylose, in addition to some other acids produced. These acids reduce the activity of the ethanol producing microorganisms. HMF further breaks down to formic acid which may lead to a total inhibition of ethanol formation. Figure 1.20 shows a schematic of the various acids produced during pretreatment/acid hydrolysis of lignocellulosic biomass.

In addition to these acids, metals leached out from the hydrolysis equipments and other SO_2 inhibitors released from additives also retard microbial growth and other metabolic activity. More than a 100 such inhibitors have been detected. Liu

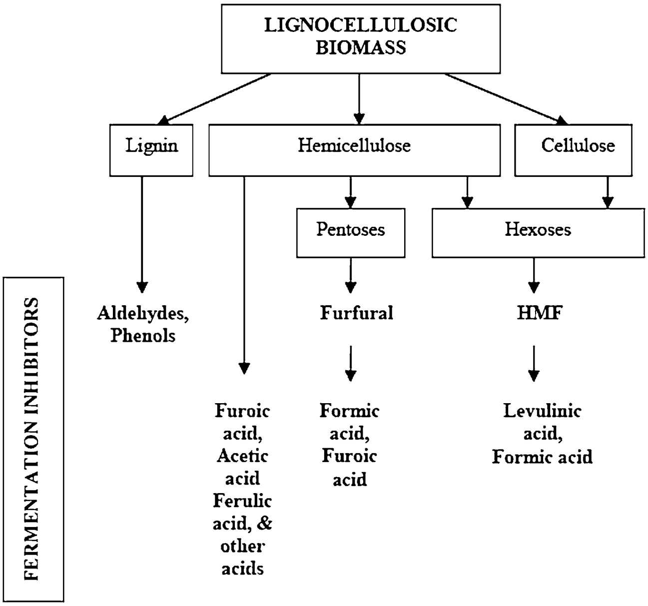


Fig. 1.20 Fermentation inhibitors produced during degradation of lignocellulosic biomass (Adapted from [28])

et al. [28] have classified such inhibitory compounds on the basis of the functional group present on the inhibitor agent. These degradation products have an inhibitory effect on the ethanol producing organisms, reducing the yield of ethanol from the process. An obvious solution to this problem lies in the removal of the aldehyde and/or other inhibitory agents at regular intervals. This can be carried out by physicochemical processes such as vacuum evaporation to reduce the volatile inhibitors; alkali treatment, using $Ca(OH)_2$ or NaOH to precipitate out substances having aldehyde and ketone functional groups; and adding activated charcoal or diatomaceous earth to physically adsorb the inhibitory agents, thus improving the yield of ethanol. Use of anion- and cation- exchange resins has also been investigated with results more favorable than all the other methods mentioned above. A combination of two or more methods is preferred depending on the nature of inhibitors present. Enzymatic treatment using peroxidases and laccases obtained from the lignolytic fungus *Trametes versicolor* has been found to improve the yield of ethanol by removing the phenolic inhibitors from the substrate. Alternatively, in situ ‘detoxification’ solutions to this problem are being explored. One such solution comprises development of inhibitor-tolerant strains of yeast or bacteria that can withstand the presence of the inhibitors. The inhibitor conversion pathways and mechanisms of in situ detoxification have been reviewed by Liu et al. [28].

Using recombinant yeast for improved ethanol production is yet another area in which ongoing research efforts are likely give good returns. The improvement of cellulase expression in *S. cerevisiae* has also been exploited. The contribution of a number of researchers in developing strains with improved cellulose expression has been compiled by Liu et al. [28]. Similarly, hemicellulase expression in *S. cerevisiae* has also been studied.

The above developments, along with simultaneous advances in fermentation technologies, are certainly expected to take ethanol production from the more economical lignocellulosic biomass to new heights.

The fermentation technologies used for fermentations have also advanced rapidly, with many progressive modifications in the conventional batch and continuous fermentation processes. Combination of both, the batch and continuous process, called the fed-batch processes have also been developed. Fermentations using novel immobilized cell systems have been used to enhance the efficiency and productivity of the fermentation processes. Methods such as "growth arrested process" have been developed, where a high productivity of intermediate metabolic products such as lactate and succinate, as well as other organic acids, has been achieved by arresting the growth of the microorganisms at the particular stage at which the target products are produced, by maintaining the conditions in the reactor which stop further growth of the organisms [29].

1.2.1.3 Processes Based on Algal Biomass

Life on earth is believed to have started with algae. Algae are photosynthetic organisms capable of converting solar energy into chemical energy and in the process, consume CO_2 and release O_2. With the advent of fossil fuels, the focus shifted from tapping solar energy via photosynthesis toward burning the fossil fuel to generate energy. The predominant use of fossil fuels over several years has made us realize the dangers that the GHGs released from burning these fuels, pose to the environment. The rapid depletion of these fuels and the millennia required for their renewal have now forced us to look for safer and renewable alternatives to the fossil fuels. Thus, we have now come a full circle toward again reverting to biomass, the unlimited solar energy and photosynthesis, to meet our ever increasing energy demands. Algae are considered to be the most photosynthetically efficient plants on the earth. There is a large variety of algae ranging from small unicellular organisms to fairly complex and differentiated forms of multicellular organisms. They thrive on land as well as in water, using sunlight, CO_2, and water for growth. Like other plants, algae use photosynthesis to convert solar energy into chemical energy and store it in the form of high energy substances such as oils, carbohydrates, and proteins. In other plants, the predominant storehouse of this chemical energy is carbohydrates, whereas in algae, this energy is stored in the form of oils. A one-hectare algae farm on wasteland can produce over 10–100 times the oil produced by any other oil crop known till date [30]. The lipid content in different species of microalgae was found to vary from as low as 12–14% of dry weight in *Scenedesmus obliquus*, to as high as 80% of dry weight in *Botyococcus braunii* [31]. Algal energy is becoming increasingly popular because algae can be grown on wastelands and unarable lands, thus enabling all agricultural land completely available for growing food crops. Thus, third-generation biofuels, free from the food versus fuel controversy, can be obtained in abundance by efficient cultivation and harvesting of algae.

Algae can be classified on the basis of their fundamental cellular structure, life cycle, and pigmentation. According to the cellular structure, algae may be either unicellular or multicellular. The multicellular algae growing mainly in saltwater or freshwater are called macroalgae or “seaweeds”. There are three different types of pigmentations seen in macroalgae: (1) green seaweed (*Chlorophyceae*), (2) red seaweed (*Rhodophyceae*), and (3) brown seaweed (*Phaeophyceae*). Microalgae which are microscopic photosynthetic organisms growing in both marine and freshwater environments are called microalgae (*Cyanophyceae* or blue-green algae).

Cultivation and harvesting of algae

Algae can be cultivated in open ponds, photobioreactors, or in closed and hybrid systems. Open pond systems for cultivation of algae are cheap and economical, but suffer from the obvious disadvantages. In that, they require a large expanse of land and water and are susceptible to contamination by other microorganisms, and to climatic changes.

Photobioreactors are closed tank systems, where most of the disadvantages stated under open pond systems can be obviated. These systems, though they involve higher infrastructure costs, are more efficient and offer higher biomass concentrations, high surface-to-volume ratios, and shorter harvest times. A major advantage with these reactors is that along with cultivation of algae, they can be used for simultaneous scrubbing of power plant flue gases and removing nutrients from wastewater. A variety of designs is available to give higher productivity and reproducibility as better control of cultivation conditions is possible. Demirbas et al. [30] have described the different types of systems available for cultivation of algae and the comparative costs involved for each system.

Harvesting of algae can be done by a number of different methods such as centrifugation, foam fractionation, flocculation, membrane filtration, and ultrasonic separation. The harvesting costs may contribute to about 20–30% of the total cost of cultivation.

Products obtained from algal biomass

The products obtained from algal biomass include bio-oil, biodiesel, bioethanol, biomethane, biohydrogen, and other value-added products. Table 1.8 lists the different products obtained from algal biomass and the conversion technologies used for their production.

Algal biomass is very rich in oil content. This oil can be extracted from the algal biomass by solvent extraction methods. It can be used as such as fuel, or it can be converted to biodiesel, by the process of transesterification, for use as a

Table 1.8 Conversion technologies used and products obtained from algal biomass

Conversion technology		Product
Biochemical conversion methods	Dark fermentation	Ethanol, hydrogen
	Anaerobic digestion	Methane, hydrogen
	Photo-fermentation	Ethanol, hydrogen
	Biophotolysis	Hydrogen
Thermochemical conversion methods	Gasification	Hydrocarbon gas
	Pyrolysis	Oil, gas, charcoal
	Liquifaction	Oil
Chemical separation methods	Solvent extraction	Oil
Direct combustion	Power generation	Electricity or power

Source Ref. [32]

transportation fuel. Biodiesel, used as a transportation fuel, has a distinct advantage where it can be used directly in any diesel engine, without modification. Bioalcohol is the most widely used liquid fuel. It can be generated from microalgae by two methods: (1) the conventional yeast-mediated fermentation of carbohydrate rich algal biomass such as starch containing green algae, glycogen containing cyanobacteria, and glycerol-rich *Dunaliella*, and (2) "self-fermentation" of carbohydrates contained in algae by endogenous algal enzymes induced under anaerobic conditions. This has been reported for *Chlamydomonas* [28]. Both these processes give a product yield that is uneconomical. However, there are many companies which are attempting to devise economically viable methods for ethanol production from algal biomass. One such company Algenol Biofuels Inc. has successfully developed the Direct to Ethanol® algae technology. In this technology, overexpression of the genes responsible for converting carbohydrates to ethanol is achieved by genetic modification techniques, resulting in metabolically hybrid algae which have an increased photosynthetic ability. These hybrid algae use CO_2 from the surroundings (collected from industrial emissions), and produce ethanol within the algal cells. This ethanol diffuses through the cell wall into the culture medium and evaporates along with water into the head space provided for it in an enclosed, sealed photobioreactor. The ethanol–water vapor mixture condenses on the inner surface of the photobioreactor and is collected as liquid, which is further concentrated and distilled into fuel ethanol. Optimization of cultivation and productivity of the hybrid algae is being evaluated. This technology is expected to provide an 80% reduction in GHGs compared to gasoline. Biomethane is produced by the usual anaerobic fermentation methods described in "Anaerobic Digestion". The yield of methane is again lower with algal biomass due to the natural tendency of most species of algal biomass to resist biodegradation. In addition to this, the ammonia which is released from the algal biomass acts as an inhibitor in the microbiological conversion process. The problem of resistance of the algal biomass toward biodegradation has been addressed by using thermochemical and mechanical pretreatment techniques which solubilize the biomass by breaking down the recalcitrant cell walls. This has been found to increase the methane production rates by about 30% for microalgal biomass harvested from sewage ponds [28].

The second problem posed by the inhibitory effect of ammonia has been circumvented by adding carbon-rich wastes to the microalgal biomass. The additional bacterial biomass added by way of this carbon-rich waste reduces ammonia levels through nitrogen sequestration, thus improving the methane yields. Biotechnology-based approaches such as developing bacterial cultures that are more resistant to ammonia inhibition are also being explored. Hydrogen can be generated from algal biomass by mainly three ways; (1) Dark fermentation, where anaerobic fermentation of carbohydrate products such as starch, glycogen, and glycerol is carried out by anaerobic bacteria, in absence of light. This process yields hydrogen, solvents, and mixed acids, (2) Light-driven fermentations, also called photo-fermentations, where the organic acids formed during dark fermentation are converted into hydrogen by nitrogen-fixing photosynthetic bacteria, and (3) Bio-photolysis, which involves the splitting of water into hydrogen and oxygen by microalgae.

The other value-added products obtained from algae include, small molecules such as iodine, algin, mannitol, and lignin-related fractions; polymers such as alginates, carrageenans, agars, and sulfated polysaccharides; high value oils such as long-chain polyunsaturated fatty acids (PUFA) which include substances having a high nutraceutical value, e.g., arachidonic acid, docosahexanoic acid, eicosapentanoic acid, etc. Research in algal methods of conversion merits special attention because it provides third-generation biofuels which do not compete with food crops nor with the arable land required for their cultivation and hence remains excluded from the food versus fuel controversy. Algal biorefineries are now being set up which are expected to give multiple products in a cost-effective manner using the different biomass conversion technologies mentioned above (Table 1.8). These are discussed in "Aquaculture-Based Biorefinery (Algae and Seaweed Based Biorefinery)".

1.2.2 Conversion of Biomass to Biofuels: The Biorefinery Concept

A biorefinery is a facility that integrates biomass conversion process and equipments to produce fuel, power, heat, and value-added chemicals from all types of feedstock comprising of biowaste and/or renewable biomass in a manner that it is zero waste producing. Thus, the bioconversion methods discussed in the previous sections are integrated to give multiple products. Biorefineries, since 1990s have evolved through a number of stages: The first stage of development can be considered to be the Phase I biorefinery which used a single feedstock and was processed to give a single product. The Phase II biorefinery uses again a single feedstock but has flexible processing capabilities which finally result in a range of products. A conventional sugar plant, which produces sugar, ethanol, and biodegradable plastics is an example of this type of a biorefinery. Thus, a phase II biorefinery incorporates a flexibility in terms of processing methods as well as products. A phase III biorefinery is the present “integrated biorefinery”, where a variety of feedstocks can be handled via different conversion processes simultaneously to produce a range of products. A Phase III biorefinery offers complete flexibility in terms of type of feedstock that can be used, conversion processes as well as product mix. Feedstock flexibility has, however, the first priority [33]. A present biorefinery can be considered to be analogous to a petroleum refinery which produces multiple fuels and products from petroleum. An excellent analogy with respect to the flow chart for both types of biorefineries is given in a report by the U.S. Department of Energy [34].

In the interest of mankind, it is absolutely essential that dependence on fossil fuels be reduced.

Integration of green chemistry into biorefineries and use of low environmental impact technology is the focus of all research efforts in the area of biorefinery. This, in concurrence with economically viable processes, will successfully replace petroleum refinery and products resulting from it, by biorefinery products.

1.2.2.1 Products of Biorefinery

Bio-based products can be classified into three categories: Biofuels (biodiesel, bioethanol, biogas), bioenergy (heat and power), and bio-based chemicals and materials (fine chemicals, cosmetics, polymers, plastics, composites). In a biorefinery, the biomass conversion processes are integrated in such a manner that almost all types of feedstocks can be converted to the above-mentioned products. Biofuels are produced in higher volumes and are responsible for increasing the carbon credits of the industry, whereas other products such as fine chemicals, pharmaceuticals, and polymers are produced in comparatively lower quantities, but, being high value products, increase the profitability of the biorefinery.

Biomass processing in a biorefinery involves two major transformations [3] the first transformation involves a bulk separation or extraction of the biomass using processes such as grinding, followed by fractionation or cracking by biological or physicochemical techniques. This step leads to release of such molecules from the biomass which are capable of undergoing second transformation involving processes such as fictionalization to yield a variety of molecules. These transformations give rise to a large number of bio-based products in which the most important one can be considered to be biofuels/energy (Fig. 1.21).

Integrated biorefineries employ various combinations of feedstocks and conversion technologies to produce a variety of products, with the main focus on producing biofuels. Side products can include chemicals (or other materials) and heat and power.

This section focuses only on the energy aspects of biorefinery, though, other valuable products are also available from biorefinery [36, 37].

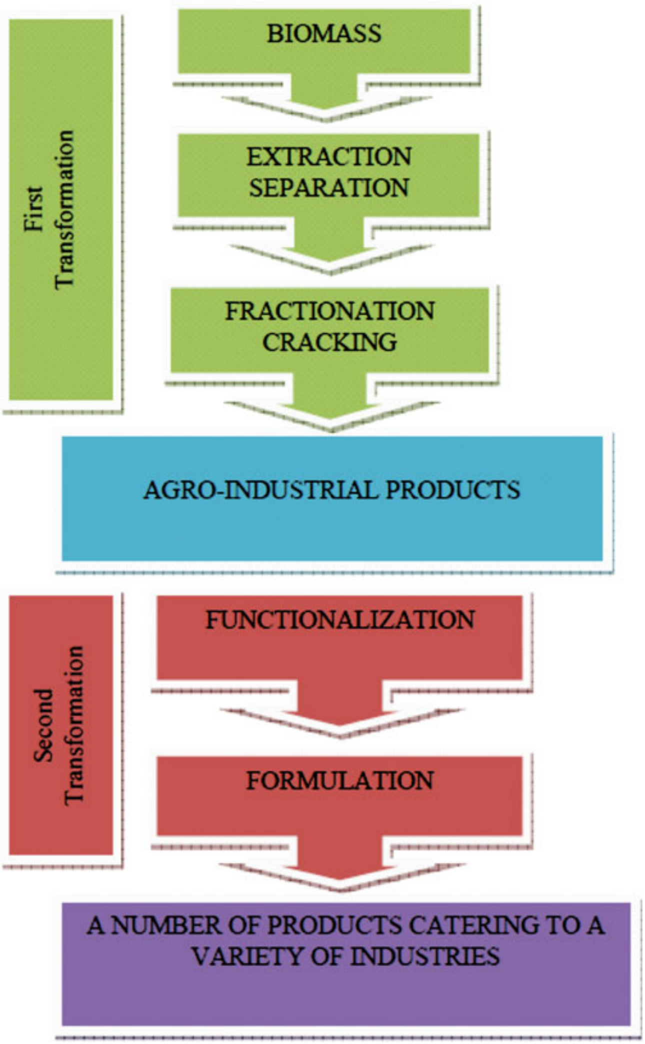


Fig. 1.21 General scheme for biomass conversion in a Biorefinery (Adapted from [35])

1.2.2.2 Feedstock for Biorefinery/Types of Biorefinery

Biorefineries can be classified into a number of categories depending on the feedstock used.

1. Biorefinery based on agriculture sector feedstock (dedicated crops and residue) including oilseed biorefinery
2. Forest biorefinery (forest residue mainly lignocellulosic feedstock)

Table 1.9 Classification of biorefinery based on feedstock

Type of biorefinery	Characteristic features	Resultant Products
Biorefinery based on agriculture and non-agriculture sector feedstock (dedicated crops and residue) including oilseed biorefinery		
• Cereal biorefinery	Uses dedicated starch crops, sugar crops, and grains	Bioethanol
• Oilseed biorefinery	Uses oil seed crops and oil plants	Vegetable oils and biodiesel
• Green biorefinery	Uses grasses and green plants	Bioethanol
• Lignocellulosic biorefinery	Uses agriculture wastes and crop residues	Bioethanol (lignocellulosic)
Forest biorefinery (forest residue mainly lignocellulosic feedstock)	Uses forest residues, barks, saw dust, pulping liquors ,and fibers	Fuels, energy, chemicals, and materials
Biorefinery based on industry (process residues and leftovers) and municipal solid waste and waste water (domestic waste)	Uses all types of wastes including forest generated waste, industrial waste, and municipal solid waste	Methane, hydrogen, biofuels, energy, chemicals, and materials
Aquaculture-based biorefinery (algae- and seaweed-based biorefinery)	Uses different types of aquatic biomass capable of tapping the unlimited energy from sun	Third-generation bioethanol, energy, pharmaceutical products

3. Biorefinery based on industry (process residues and leftovers), and municipal solid waste and waste water (domestic waste)
4. Aquaculture-based biorefinery (algae- and seaweed-based biorefinery).

The salient features of all these types of biorefineries are given in Table 1.9.

Biorefinery Based on Agriculture Sector Feedstock (Including Dedicated Crops and Residue, and Oilseed Feedstock)

These biorefineries use as their feedstock, dedicated crops (food or non-food crops), such as cereal crops, oilseed crops, grasses, and other non-food green plants, or residues generated from the agricultural crops. The first- and second-generation biofuels can be produced from this type of biorefinery. Presently, biodiesel, bioethanol, and biogas are the main types of biofuels which are produced by commercially viable technologies. An overview of the conversion processes for these biorefineries is shown in Fig. 1.22.

These biofuels are presently produced from agriculture sector feedstock. The agriculture sector feedstock mainly contains sugar, starch, and cellulosic biomass which can be converted to biofuel (bioethanol) mainly by fermentation processes.

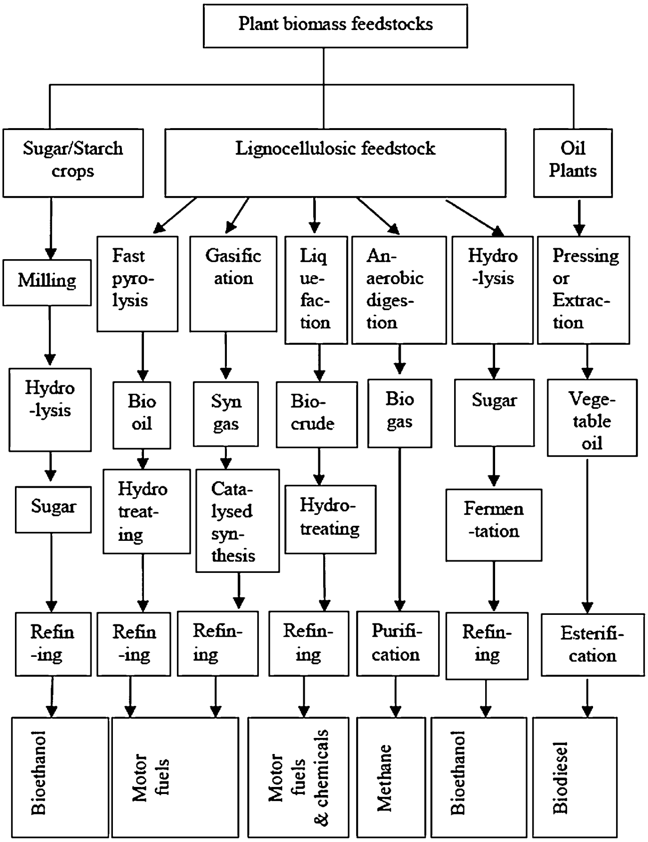


Fig. 1.22 Overview of conversion processes for agriculture sector feedstocks to biofuels (*Source* Ref. [38])

For this purpose, the macromolecular starch and cellulose is first hydrolyzed by enzymatic hydrolysis into smaller molecules like glucose. Fermentation of these sugars by either aerobic or anaerobic fermentation processes converts them to ethanol. The process details are already discussed in Sect. 1.2.1.2. The alcohol produced from food crops is called grain alcohol and that produced from lignocellulosic feedstock such as agricultural residues (wheat straw, rice straw, etc.), grasses (switch grass) is called biomass ethanol or bioethanol or lignocellulosic ethanol. The agriculture-based feedstock, which was, until recent times used as the major source for biofuel generation, is gradually being replaced by agriculture sector residue such as wheat straw.

Agricultural residue-based biorefinery
Prasad Kaparaju et al. [39] investigated the production of biofuels—bioethanol (from cellulose), biohydrogen (from hemicelluloses), and biogas (from effluents from bioethanol and biohydrogen production) from wheat straw in an effort to

establish an energy-efficient and economical process within a biorefinery network. Part of the wheat straw was used as such without pretreatment and part of it was pretreated using hydrothermal pretreatment techniques. The pretreated wheat straw resulted in a liquid fraction hydrolysate which contained mainly hemicelluloses and a solid fraction which was rich in cellulose. Six different scenarios were studied: (1) untreated wheat straw was incinerated as such and energy was generated, (2) untreated wheat straw was anaerobically digested to generate biogas, (3) pre-treated wheat straw was used for conversion into biogas, (4) pretreated wheat straw was converted to bioethanol alone, via fermentation, (5) pretreated wheat straw was converted to bioethanol and biogas, and lastly, (6) pretreated wheat straw was converted to bioethanol, biohydrogen, and biogas. From among all six cases, they showed that the use of wheat straw for production of biogas alone, or for production of multiple biofuels, were the most energy-efficient processes as compared to production of monofuel such as bioethanol by fermenting hexose sugars alone. Thus, in other words, the biorefinery concept was more energy efficient rather than using biomass conversion technologies for generation of any one fuel.

Whole crop biorefinery

Parallel to the use of agriculture residues instead of whole food crops as feedstock for biofuel generation, the use of whole non-food crops is also gaining popularity as feedstock for biomass conversion. Dedicated non-food crops which can be grown on unproductive lands are being considered as a more practical and economical option to even agricultural residues, as feedstock for biorefineries (whole crop biorefineries), as these would not use agricultural land for their generation as also, the entire plant could be used as feedstock. Such a whole crop biorefinery using the Jatropha plant for sustainable production of biodiesel has been described by Naik et al. [40]. Such a biorefinery can produce biodiesel as the main product, along with the production of other valuable chemicals as by-products from the solid residue obtained from the production of biodiesel. The oil cake remaining after removal of oil can be used to generate second-generation biofuelsand other important chemicals. The scheme for such a whole crop biorefinery using dedicated oil crops is shown in Fig. 1.23.

Takara et al. [41] investigated the suitability of banagrass for production of biofuel in a biorefinery concept. Banagrass (*Pennisetum purpureum*) is a perennial grass which is a good source of lignocellulosic biomass. Banagrass resembles sugarcane but shows a yield double to that of sugarcane and switchgrass in terms of biomass. A new concept of wet or green processing has been proposed. The biomass is taken as such without drying and subjected to dilute acid hydrolysis. It was found that the yield of fermentable sugars after the wet, juice processing was the maximum compared to dry, juice processing. This hydrolysate can be processed further for serving as a substrate for fermentation to ethanol. The process has a particular advantage in regions where banagrass can be grown throughout the year in that, it will reduce the time and cost of drying the biomass prior to pretreatment for extraction of cellulose. Co-products can also be obtained from the

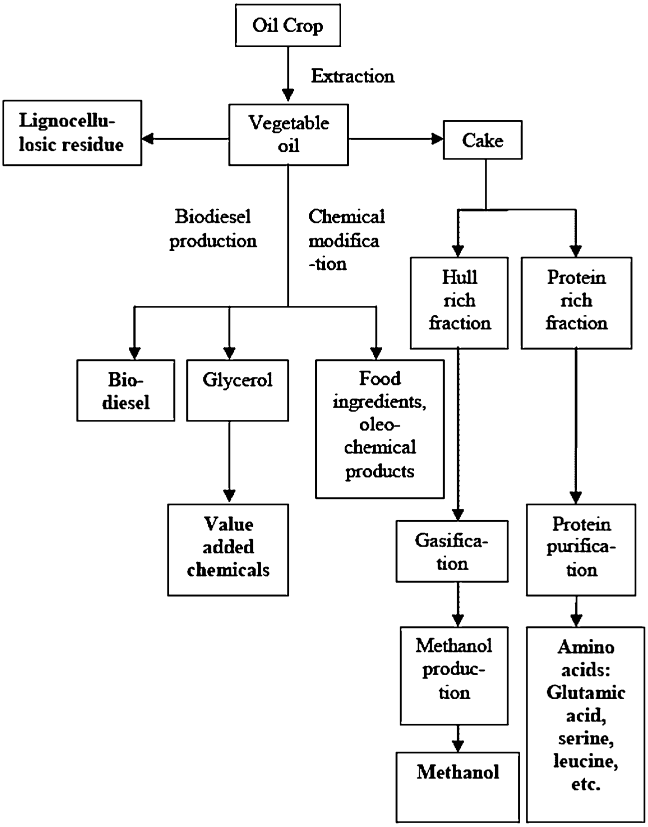


Fig. 1.23 Whole crop biorefinery (Adapted from Ref. [40])

nutrient-rich liquid substrates generated out of wet processing, which would be otherwise destroyed during downstream processing of the biomass. The biorefinery concept in this case offers a unique flexibility such that in times when the commodity value of ethanol is less, the process can be adapted such that the nitrogen-rich juice is utilized for the production of fungal biomass and aquaculture feed. The nitrogen-free clean fiber can be used for heat/steam electricity generation via gasification, whereas in times of high demand for ethanol, the process is used for the generation of ethanol.

Oilseed biorefinery

The conversion of oil crops to biofuels—Fatty Acid Methyl Esters (FAME), more commonly known as biodiesel involves processes like transesterification, where the vegetable oil is chemically reacted with an alcohol, in presence of a homogenous or a heterogenous catalyst. In the catalytic conversion process, in turn the catalyst plays an important role in an oil seed biorefinery. Catalysts that selectively convert a particular substrate to the desired product and the catalytic reactor

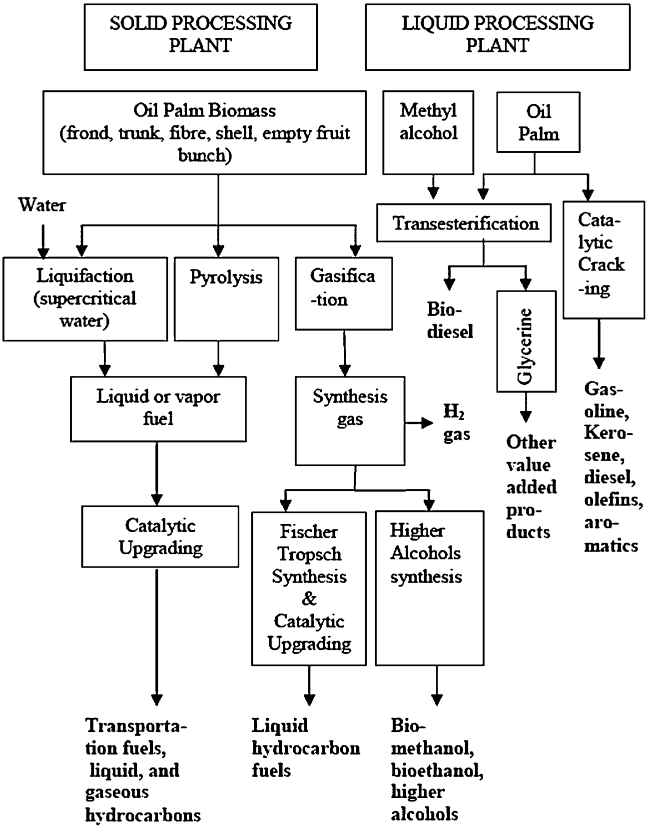


Fig. 1.24 Conceptual palm oil-based biorefinery (Adapted from Ref. [42])

parameters related to the design, operation, and control of the catalytic reactor are the key factors responsible for the development of an economically viable process. Chew et al. [42] have proposed a biorefinery based on palm oil and palm biomass for the production of biofuels. The conceptual biorefinery would consist of two plants. One plant would treat the solid portions of the Palm tree biomass whereas the other plant would treat the expressed oil portion. The solids processing plant will carry out liquefaction using supercritical water, pyrolysis, and gasification of the biomass, and the liquid/oil processing plant will carry out transesterification and catalytic cracking of the expressed oil portion of the palm biomass. The products of the biorefinery would comprise of different biofuels, gaseous hydrocarbons, hydrogen, glycerine, olefinic, and aromatic compounds. Figure 1.24 shows the scheme for such a biorefinery along with the various products obtained therein.

The catalytic processes proposed by them for the purpose include (a) catalytic cracking of palm oil for production of biodiesel, (b) production of hydrogen and

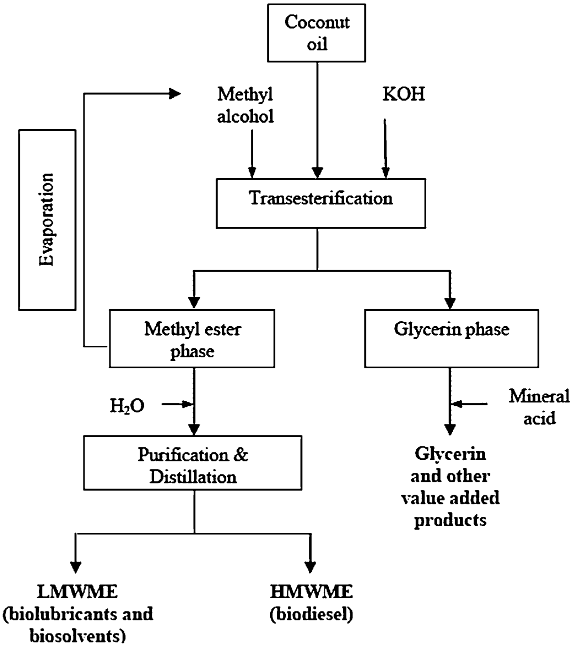


Fig. 1.25 Conceptual biorefinery for valorization of coconut oil (Reproduced with permission from [43])

syngas from biomass gasification, (c) Fischer-Tropsh synthesis for conversion of syngas into liquid fuels, and (d) upgrading of liquid fuels obtained from liquefaction/pyrolysis of biomass. Catalyst plays a key role in all the above processes in terms of economy and product distribution. They have reviewed a number of catalysts which can be used for the palm oil-based biorefinery.

The biorefinery approach has been used for the valorization of coconut oil by Abderrahim Bouaid et al. [43]. Coconut oil, the main substrate for obtaining biodiesel by a process of transesterification, is a very costly raw material. The high cost of this substrate makes the process of obtaining biodiesel from coconut oil economically unviable. Hence, a process outlined in Fig. 1.25 has been proposed to get multiple products from coconut oil which would then make the process of conversion of coconut oil to biodiesel economically effective. Coconut oil contains 42–49% lauric acid. This lauric acid can be converted to methyl laurate, by a transesterification process. Methyl laurate forms the basis for the production of a number of products like lauryl sulfate (biodegradable surfactants), coconut estolide esters (LMWME's) which serve as a base for biodegradable lubricants, and recently, biodiesel (methyl ester) a HMWME, which is emerging as a promising substitute for conventional fuels. The proposed biorefinery approach uses an integrated process for generation of HMWME (biodiesel) and LMWME (laurate and myristate methyl esters which can used as biolubricants and biosolvents). The lauric fraction has importance in the detergent industry as it is the preferred material for the manufacture of soaps and detergents due to its exceptional

Table 1.10 Feedstock obtained from forest biomass

Forest product	Example
Forest residue or forestry waste generated in forests	Dead trees, forest-fire remains ,and waste generated while culling and logging
Industrial or manufacturing waste (waste generated during manufacture of wood products)	Residue from pulp and paper manufacture, bark or outer layer of pulpwood which is removed at the pulp mill, spent cooking liquor (called black liquor), or liquid waste generated in the pulping process and is characterized by a heavy concentration of dissolved organic chemicals

cleansing properties. Under optimum conditions, a yield of 77.54% for HMWME's and 20.63% for LMWME's was obtained.

Gary Luo et al. [44] proposed a novel biorefinery concept for the production of biofuels (biodiesel and bioethanol) from rapeseed and straw. The process effluents from this process were further used for additional production of biofuels (biohydrogen and biomethane). The overall bioenergy recovery was found to increase to 60% compared to an energy recovery of 20% in case of a conventional biodiesel conversion process.

Forest Biorefinery

A biorefinery using forest residues as its feedstock is called a forest biorefinery. The enormous scope of using biomass generated from forests for energy generation has been excellently highlighted by Klass [45] by way of the statistics presented in his book titled "Biomass for renewable energy, fuels and chemicals". According to this statistics, forests cover only about 9.5% of the earth's surface or about 32% of the total land area but account for 89.3% of the total standing biomass and 42.9% of total annual biomass production. In terms of energy, forests alone could produce 1,030 quadrillion BTU/year which is equivalent to more than double the world's total primary consumption of about 460 quadrillion BTU in 2005. Thus, forest biomass can be considered to be a very important source for feedstock of a biorefinery. Forest biomass can be categorized into two categories as shown in Table 1.10.

The use of forest biomass for energy generation had taken a back seat until a few years ago due to the depletion of forests as a result of felling trees for producing forest products like lumber, paper, and other items. However, this excellent source of fuel has again gained importance since the development of biorefinery concept as it is now being recognized as an attractive alternative for pulp and paper mills which see in it, the incentive of increasing their revenue by producing biofuels and other chemicals in addition to their core products, as also the forest waste can be processed in a typical forest biorefinery to yield a number of valuable products including biofuels, without jeopardizing the forest vegetation.

Table 1.11 Lignocellulosic pretreatment techniques

Type of pretreatment	Process involved		Comments
Methods involving conversion of lingocellulosic feedstock into a form which can be effectively hydrolyzed	Physical methods	• Mechanical comminution • Ultrasonic comminution • Irradiation using gamma, electron beam,microwave radiation	Lower performance and higher costs involved
	Chemical methods	• Acid solubilization of hemicellulose • Alkali treatment for delignification and removal of hemicellulose • Oxidative H_2O_2 delignification • Organosolv processes (using organic or aqueous/organic solvent mixed with an inorganic acid catalyst	Show high degree of selectivity but involve harsh reaction conditions which may not be suitable for biorefinery scheme due to adverse effects on later downstream biological processing
	Physicochemical/ or thermo-chemical methods	• Hydrothermolysis • Aqueous or steam/aqueous uncatalyzed solvolysis • Ammonia fiber explosion • CO_2 explosion • Steam explosion	Milder chemical conditions but extreme operational conditions (elevated pressure and temperature) Increased cost of biorefinery
Methods involving conversion of lignocellulosic feedstock into a form which can be effectively hydrolyzed	Biological methods		Low energy inputs Low equipment requirements Resultant cost saving No environmentally damaging waste products generated Hazardous chemicals and conditions avoided Lengthy pretreatment times and degradation of polysaccharides, reducing total fermentable substrate

(continued)

Table 1.11 (continued)

Type of pretreatment	Process involved	Comments
Methods involving fractionation of Lignocellulosic feedstock into its core components viz. lignin, cellulose and hemicellulose	Acid-based fractionation	Process can be carried out at relatively low temperature (50°C) and atmospheric pressure Process is independent of biomass type It is a capital intensive technology
	Ionic liquid-based fractionation	Better downstream processing possible More environmentally benign technique Better than most physical and chemical pretreatment methods

Forest biomass is mainly lignocellulosic in nature. Lignocellulose consists of cellulose (40–47%), hemicellulose (25–35%), lignin (16–31%), and other extractives (2–8%), where the polysaccharides cellulose and hemicellulose are tightly cross-linked with lignin via ester and ether linkages with the purpose of providing structural rigidity to higher plants and trees and protecting the cell walls of plants from various external physical and chemical hazards. Therefore lignocellulose, in its native form, is highly refractory in nature and resistant to most hydrolytic processes which aim at extracting cellulose for further hydrolyzing it to fermentable sugars which can be converted to biofuels. Hence, pretreatment of lignocellulose is essential before it can be used for other conversion processes in a biorefinery. Table 1.11 gives a list of the types of pretreatment that can be done on lignocellulose before it can be used in a biorefinery [46, 47].

The pretreatment of lignocellulosic feed stock serves the basic purpose of converting the native lignocellulosic biomass into a form where hydrolysis can be effectively achieved. Among these, the biological methods of pretreatment have a number of advantages in that, the equipment requirement is modest, no environmentally damaging waste products are generated, and hazardous chemicals and conditions are avoided. All this results in a significant amount of cost saving. However, the total pretreatment time required is very lengthy and there are chances of degradation of polysaccharide which may reduce the total fermentable substrate. Newer methods of pretreatment aim at not only improving hydrolysis but also carrying out fractionation, where the lignocellulosic biomass is converted to its core components—cellulose, hemicelluloses, and lignin. A lot of work still needs to be done, however, to carry out fractionation of lignocelluloses in a manner that is technically feasible and at the same time, economically viable. The conceptual ideas for the purpose have been proposed by a number of researchers. FitzPatrick et al. [47] have reviewed these techniques at length.

A majority of lignocellulosic biomass including forest biomass is used in a kraft mill where the lignocellulosic feedstock is processed to paper pulp, which serves as an important intermediate material for the generation of a variety of paper products. Figure 1.26a and b shows a schematic of a typical Kraft mill and how the biorefinery concept can be integrated into such a kraft mill to get multiple products including energy products and other value-added products [48].

The key requirement of integrating the biorefinery concept into a kraft mill is the recovery of hemicellulose which will enable its conversion into ethanol and/or other products. Mao et al. [49] introduced a “near neutral” process prior to pulping, for extraction of hemicellulose which otherwise ends up in the black liquor. However, this “near neutral” process modifies the energy balance of the kraft pulp mill. During the pretreatment process, approximately 10% of hemicellulose and lignin is extracted. This reduces the calorific value of the black liquor which is used for production of steam. Thus, less steam is produced whereas the steam consumed in the extraction process is greater. Marinova et al. [48] studied the effect of introducing a hemicellulose extraction and conversion stage into a Canadian hardwood Kraft pulp mill on the energy supply and demand of the mill. On the basis of their studies, they have proposed process optimization methods

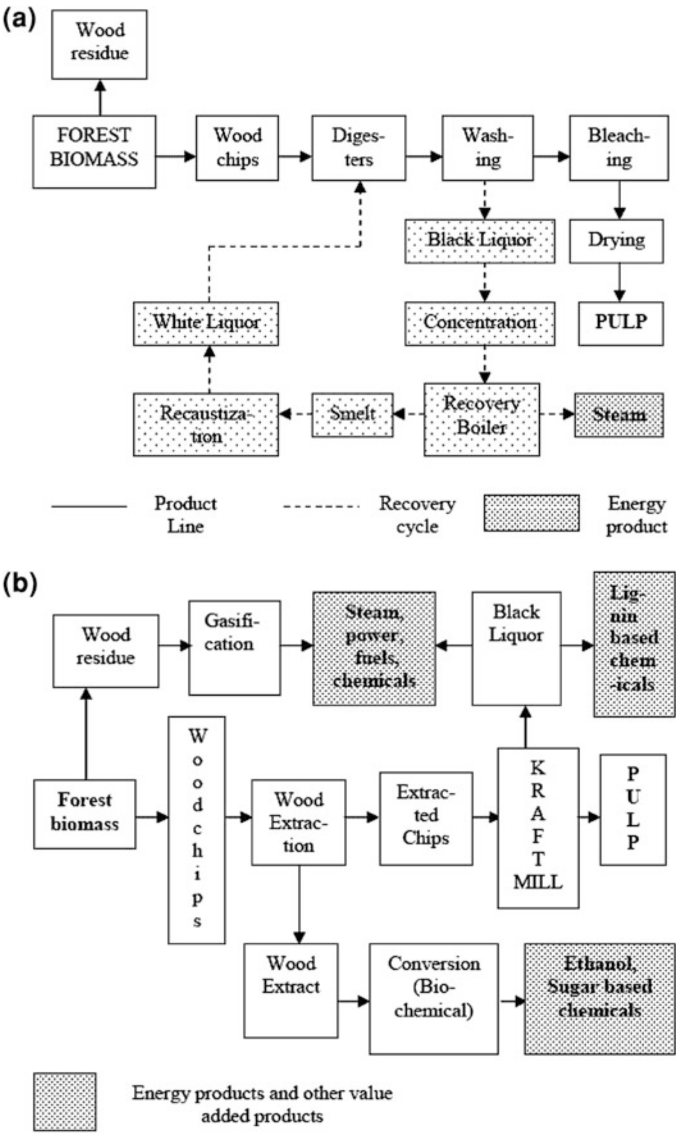


Fig. 1.26 **a** Schematic diagram of a conventional Kraft mill (Adapted from [48]) **b** Integration of the biorefinery concept with the conventional Kraft mill (Adapted from [48])

such as internal heat recovery; optimization of water reutilization within a process so that treated water consumption is reduced; replacement of steam injection systems by heat exchangers which increases condensate recovery rate and decreases steam consumption, and integration of absorption heat pumps which are expected to reduce the cooling and heating utilities requirements. These measures have been shown to reduce the steam consumption in a Kraft mill by 5.04 GJ/Adt, thus making the process more cost-effective and economical.

The lignin, which remains after processing has the potential to serve as an important precursor for a wide variety of products. The US DOE gives a comprehensive data regarding the possible products that can be obtained out of processing of this residual lignin [37]. Presently, very few Kraft mills separate and use lignin for producing other products.

Biorefinery Based on Industry (Process Residues and Leftovers), and Municipal Solid Waste

Residues and wastes comprise of the following:

- Municipal solid waste
- Municipal sewage sludge
- Animal waste
- Crop residues
- Industrial waste
- Forest waste.

Use of crop residues and forest waste for biomass conversion has already been discussed in the earlier sections. This section will focus specifically on the major source of biorefinery feedstock viz. municipal solid waste and industrial waste. Municipal soild waste also includes municipal green waste such as tree trimmings and gardening wastes, waste wood, and paper component of domestic rubbish.

Municipal solid waste can be defined as a combination of domestic, light industrial, and demolition solid waste generated within a community [6]. There are established priorities so far as disposal of municipal solid waste is concerned. Recycling, if it is economical to do so, enjoys the first priority. The green component of MSW can be separated out and used for compost or as mulch. The use of municipal green waste for energy production has the advantage that it reduces the waste load to municipal landfills which consequently reduces GHG methane arising from its decomposition. The anaerobic conversion process used for such conversions has already been discussed in "Anaerobic Digestion" The biorefinery integration into the waste conversion process is described in Fig. 1.27 which shows a current waste biorefinery and how an advanced future biorefinery could be developed to maximally tap the potential of waste-to-energy technology.

Aquaculture-Based Biorefinery (Algae and Seaweed Based Biorefinery)

Though the second-generation biofuels overcome the disadvantages of using edible food crops as feedstock, the cultivation of non-edible crops—which serves as the feedstock for the second-generation biofuels—still require land and other resources which could otherwise be used for cultivation of food crops. Hence, the

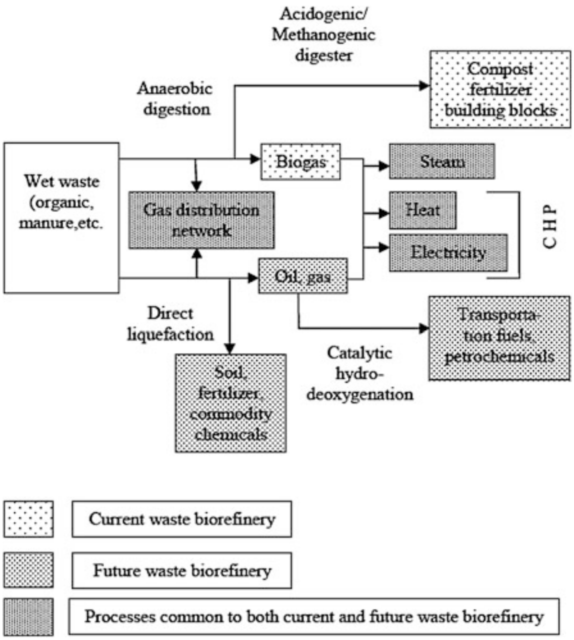


Fig. 1.27 Current and future "Waste" biorefinery (*Source* Ref. [50])

third- generation of biofuels offers an excellent alternative to the first- and second-generation biofuels in that they do not use arable land for their generation but use algae and seaweeds, which can be cultivated on completely nonproductive land and use significantly less water than terrestrial crops. Sea weeds/algae thrive on sea water using merely sunlight and some simple nutrients present in the sea water. About 75% of the earth's surface is covered by water, and seawater comprises about 97% of total water present on the earth. Hence, there is an immense potential for cultivation of algae/seaweeds. Algae as feedstock for production of biofuels include all unicellular and simple multicellular organisms such as prokaryotic microalgae (e.g. cyanobacteria), eukaryotic microalgae (e.g., green and red algae), and diatoms. Millions of years of evolution have enabled algae to develop an efficient system which is capable of capturing unlimited amounts of solar energy continuously via photosynthesis and converting simple inorganic molecules to complex organic compounds such as carbohydrates, fats, and proteins. The photosynthetic efficiencies of algae are much higher than most terrestrial plants, hence algae can absorb higher amounts of CO_2 from atmosphere and as a result, provide higher amounts of these complex molecules, which can be converted to biofuels (bioethanol) and other molecules. Figure 1.28 shows the variety of compounds that can be obtained from algae.

Singh et al. [51] have comprehensively reviewed all the aspects of using algae as a potential feedstock for the generation of third- generation biofuels. Other than the advantages of higher photosynthetic efficiencies and nonrequirement of arable land, use of algae as feedstock for biorefineries offer many other advantages

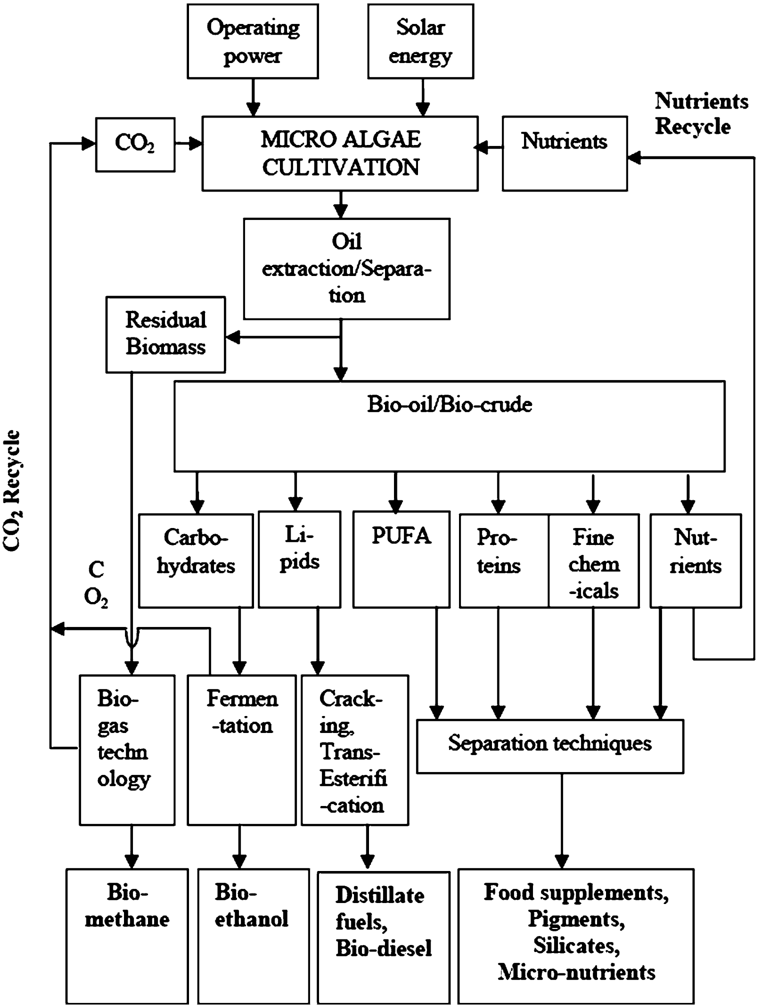


Fig. 1.28 Products obtained from an algal biorefinery (Adapted from Ref. [51])

compared to plant biomass feedstock. Algae have an almost exponential growth potential-doubling of biomass in as short a time as 3.5 h can be possible. In addition, more than five harvests can be obtained in a year [52]. Another major advantage of algae is that they thrive on nutrients such as nitrogen and phosphorous, which can be obtained from wastewater, and on organic effluent from agro-food industry, thus serving a dual advantage of utilization of waste water and enhanced cultivation of algal feedstock. Algae also do not require fertilizers, herbicides, and pesticides like their plant counterparts for their sustained cultivation.

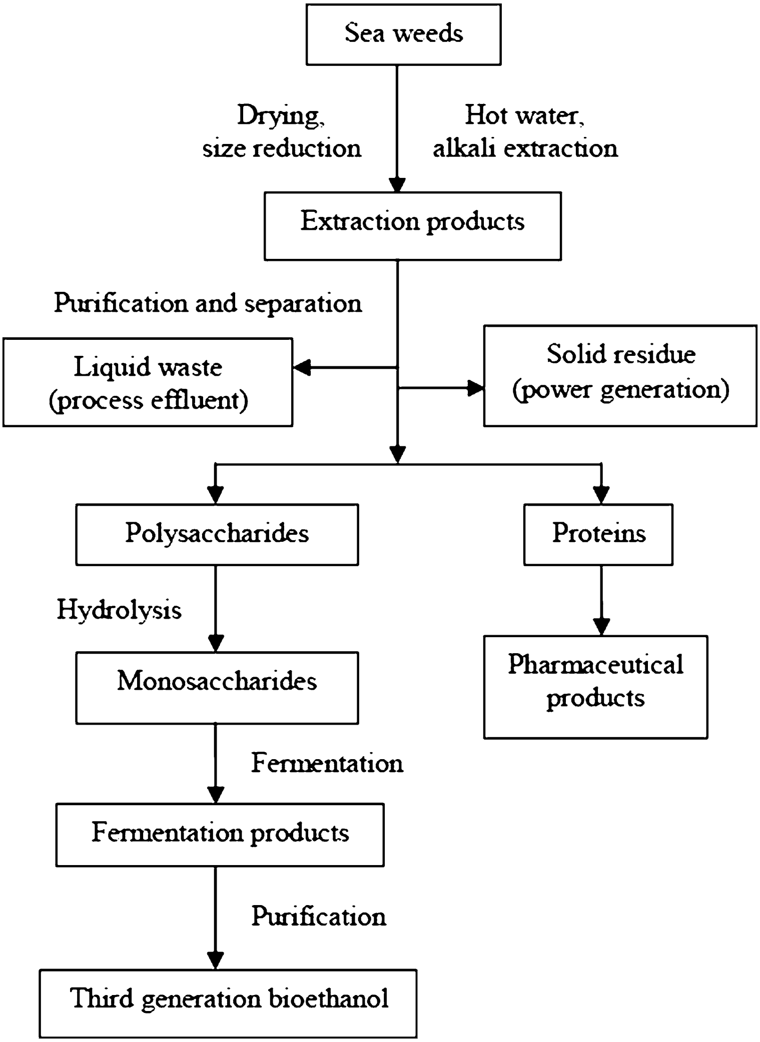


Fig. 1.29 Flow chart for conversion of seaweeds into third-generation biofuels using the algal biorefinery concept. (Adapted from [52])

Microalgae are rich in carbohydrates. These can be fermented to produce bioethanol. Chung Sheng et al. [52] have reviewed the potential of such a biorefinery in playing the role of a sustainable energy provider for efficient production of bioethanol. A number of flow charts have been proposed for efficient production of biofuel from algae.

The common steps in all processes involve collection of algae, extraction, purification, and separation of polysaccharides, hydrolysis, fermentation, and final purification (Fig. 1.29).

In order to successfully compete with a petroleum refinery, the efficiency of biofuel production of an algal biorefinery can be enhanced significantly by developing good strains of algae with increased carbohydrate content which will give a high yield on fermentation. Simultaneous production of biogas using methane fermentation technique is also possible. The residual biomass can be reprocessed to make fertilizers.

Algae also contain a lipid fraction which can be used for production of biodiesel. Microalgal lipids are neutral lipids having a lower degree of unsaturation (similar to fossil fuels). By integrating processes such as transesterification, cracking, etc., into an algal biorefinery, a range of products other than bioethanol, which is normally obtained by hydrolysis and fermentation of carbohydrates, can be obtained [51]. Such an integrated algal biorefinery is shown in Fig. 1.28.

In addition to the biofuels viz. bioethanol, biodiesel, and biogas, other products such as food supplements, pigments, etc. can also be obtained from an algal biorefinery. There are a number of algae-based biorefineries in different regions of the world, producing the products stated above. Mussgnug et al. [53] have investigated six species of freshwater and saltwater algae and cyanobacteria for their suitability as substrates for production of biogas. They showed that the methane content of biogas from microalgae was 7–13% higher compared to that obtained out of maize fermentation. They also reported that drying as pretreatment step decreased the amount of biogas production to approximately 80%. *Chlamydomonas reinhardtii* has the ability to produce hydrogen via hydrolysis of water during illumination. The hydrogen production cycle induces an increase in the amount of starch and lipids within the cells which increase the fermentative potential of the algal biomass. Thus, a two-step biorefinery process where hydrogen is produced in the first step by sulfur deprivation method, and subsequently, the remaining biomass, after production of hydrogen is used as substrate for anaerobic fermentation was found to increase the biogas production to 123%, compared to the use of fresh algal biomass. This synergistic effect gives a dual advantage of providing an environment friendly gaseous fuel hydrogen, and an increased amount of biogas.

1.2.2.3 Integrated Biorefinery

Most biorefineries have the capability to produce biofuels as well as high value chemicals. An important question that is obviously expected to arise in this context is, whether a biorefinery should be energy oriented or product oriented. A hybrid biorefinery or, as it is more commonly called, an integrated biorefinery, which can produce both category products efficiently, and has the capability of switching over to alternative feedstocks as and when required, is the answer to this question. An integrated biorefinery employs various combinations of feedstocks and conversion technologies to produce a variety of products with a main focus on producing biofuels. Thus an integrated biorefinery would involve the integration of all the above-mentioned biorefineries with respect to feedstock used and biomass conversion processes employed, in order to get maximum benefits from the biorefinery concept. The World's first integrated biorefinery project was launched in October 2003 as a joint effort between the U.S. Department of Energy's National Renewable Energy Laboratory (NREL) and Du Pont. Since then, a large number of such integrated biorefineries, at various stages of development, and operating with a variety of feedstock, yielding a range of products, have been successfully set up globally. Table 1.12 gives a list of integrated biorefineries operating in the US [54]. There are other such biorefineries being set up in the UK [55] and other parts of the world, which progressively incorporate state-of-the-art biomass conversion technologies and produce biofuels and other products in an effort to reduce GHG emissions and provide for a viable alternative to the fossil fuels.

For an integrated biorefinery to become a reality, it should be cost-effective. The logistics of feedstock availability, its generation and utilization will need to be very carefully planned for the purpose. Simultaneously, the bioconversion processes will also have to be integrated in a manner that is technically and economically feasible. The U.S. Department of Energy—Energy Efficiency and Renewable Energy has proposed a comprehensive outline for such a project (Fig. 1.30).

1.2.2.4 Comparison of Biorefinery with Petroleum Refinery

The chemical industry today is coming a full circle on its raw material resources. Till the early twentieth century, most industrial products were made from vegetable plants and crops. This situation changed after the 1970s when most of these natural products started being replaced by petroleum-based organic chemicals, and petroleum refineries acquired unprecedented importance. However, with rapid depletion of fossil fuels and the imminent danger of running out of fossil fuels completely, the biomass resources are once again gaining importance globally. Biorefineries, the counterpart of petroleum refineries, for generation of transportation fuels and other chemicals are being set up and technologies for their improvement are being developed. However, there are some fundamental differences between the two (Table 1.13), which need to be clearly defined and understood, if the future biorefineries are to completely replace the petroleum refineries.

The first and foremost difference is in the nature of the raw material used as feedstock. Raw material for an oil refinery, i.e., crude oil is usually rich in hydrocarbons and consists of mixture of different organic hydrocarbons, but has essentially no oxygen. Biomass, the raw material for biorefinery, on the other hand, consists of too little hydrogen, too much oxygen, and lower fraction of carbon compared to the crude oil. The presence of oxygen reduces the heat content of molecules and gives them high polarity, which makes blending with fossil fuel difficult. This becomes important while considering the power requirement and the cost efficiency of the processes used. Also, the composition of biomass varies with the source of feedstock. This has an advantage in that, this variety in composition

Table 1.12 Integrated biorefineries in USA

Name of company	Feedstock used	Conversion technology	Primary product	Scale of operation	Location
Lignol	Woody biomass, forest resources	Biochemical	Ethanol	Demonstration plant (2,500,000 ga/year)	Washington
Pacific Biogasol	Hybrid Poplar, stover, wheat straw	Biochemical	Ethanol	Demonstration plant (2,700,000 ga/year)	Oregon
Zeachem Inc.	Hybrid poplar, stover, and corn cobbs	Hybrid	Ethanol	Pilot plant (250,000 ga/year)	Oregon
Amyris Biotechnologies Inc.	Sweet sorghum (energy crop)	Biochemical	Biodiesel	Pilot plant (1,370 ga/year)	California
Logos technologies	Corn stover, wood grass and wood chips	Biochemical	Ethanol	Pilot plant (50,000 ga/year)	California
Sapphire Energy Inc.	Algae	Algae	Algal lipids	Demonstration plant (1,000,000 ga/year)	New Mexico
UOP LLC	Forest residue, corn stover, bagasse, switch grass, algae	Thermochemical, pyrolysis	Biodiesel, gasoline	Pilot plant (60,000 ga/year)	Hawaii
Clear Fuels Technology	Woody waste, and bagasse	Thermochemical, gasification	Biodiesel jet fuel	Pilot plant (151,000 ga/year)	Colorado
Abengoa	Stover, switch-grass, woody biomass	Biochemical	Ethanol	Commercial (15,000,000 ga/year)	Kansas
POET	Corn cobbs	Biochemical	Ethanol	Commercial plant (25,000,000 ga/year)	Iowa
ICM Inc.	Corn fiber, switch-grass, energy sorghum	Biochemical	Ethanol	Pilot plant (345,000 ga/year)	Missouri
Flambeau River Biofuels	Mill residues, forest residues, other woody biomass	Thermochemical, gasification	Biodiesel, Fischer–Tropsch waxes	Commercial plant (9,000,000 ga/year)	Wisconsin
New page	Mill residues, forest residues, other woody biomass	Thermochemical, gasification	Renewable Fischer–Tropsch liquids	Demonstration plant (8,200,000 ga/year)	Wisconsin

(continued)

Table 1.12 (continued)

Name of company	Feedstock used	Conversion technology	Primary product	Scale of operation	Location
Haldor Topsoe Inc.	Wood waste, forest residue	Thermochemical, gasification	Renewable gasoline	Pilot plant (345,000 ga/year)	Illinois
Gas technology institute	Wood waste, corn stover, algae	Thermochemical, Pyrolysis	Renewable gasoline, biodiesel	R & D scale	Illinois
Elevance Renewable Sciences	Algae oils, plant and animal oils	Chemical	Renewable diesel, jet fuel	R & D scale	Illinois
Archer Daniel Midland	Corn stover	Biochemical	Ethanol	Pilot plant (25,800 ga/year)	Illinois
Blue fire LLC	Wood waste, sorted MSW	Biochemical	Ethanol	Commercial plant (19,000,000 ga/year)	Mississippi
EverKem	MSW, forest residues	Thermochemical Gasification	Ethanol	Demonstration plant (10,000,000 ga/year)	Mississippi
Myriant	Sorghum	Biochemical	Bioproducts	Demonstration plant	Louisiana
Verenium	Sugarcane bagasse, sorghum	Biochemical	Ethanol	Demonstration plant (1,400,000 ga/year)	Louisiana
Mascoma	Aspen	Biochemical	Ethanol	Commercial plant (20,000,000 ga/year)	Michigan
American Process Inc.	Hardwood derived hydrolyzate	Biochemical	Ethanol	Pilot plant (894,000 ga/year)	Michigan
Range Fuels	Woody biomass, forest residues, thinnings	Thermochemical gasification	Ethanol, methanol	Commercial plant (20,000,000 ga/year)	Georgia
Renewable Energy Institute	Rice hulls and forest residues	Thermochemical gasification	Renewable diesel	Pilot plant (625,000 ga/year)	Ohio
INEOS New Planet Bioenergy LLC	MSW	Hybrid	Ethanol	Demonstration (8,000,000 ga/year)	Florida
Algenol Biofuels	Algae	Algae	Ethanol	Pilot plant (100,000 ga/year)	Florida
Solazyme Inc	Algae	Algae	Algal lipids	Pilot plant (300,000 ga/year)	Pennsylvania
RSA	Forest resources	Bio–chemical	Biobutanol	Demonstration plant (1,500,000 ga/year)	Maine

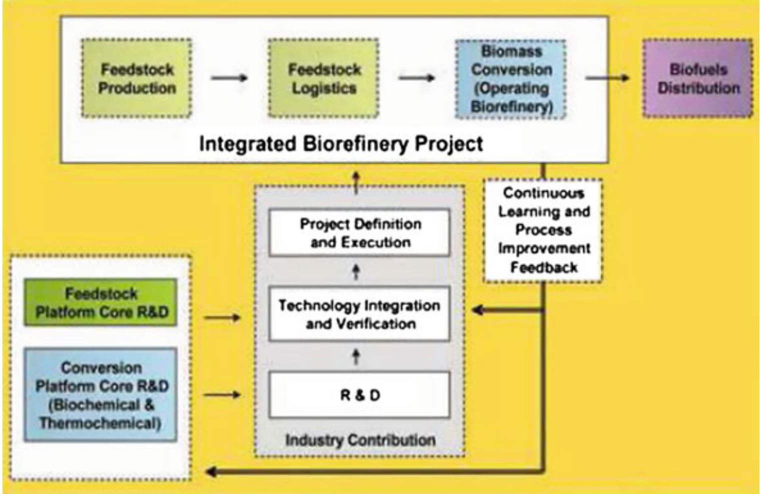


Fig. 1.30 Integrated biorefinery project (*Source* http://www1.eere.energy.gov/biomass/biorefineries_development.html)

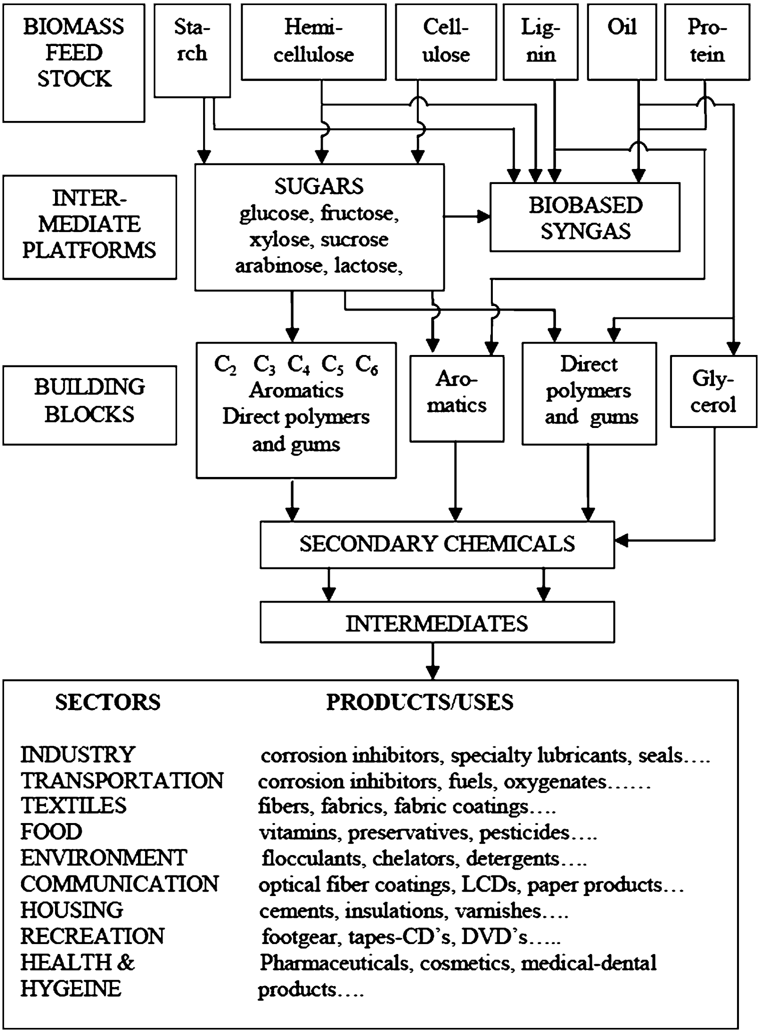
can be exploited to facilitate formation of more classes of products compared to those that can be obtained from an oil refinery. However, an associated disadvantage is that a larger range of processing technology is needed for a biorefinery. Thus it is essential that a biorefinery be equipped to cope up with such drastic changes in the feedstock composition. The integrated biorefineries already discussed above are a step toward this objective. The second fundamental difference lies in the availability of the feedstock. Feedstock for a petroleum refinery is available throughout the year whereas the biorefinery feedstock, especially that required for the first- and second-generation biofuels, is seasonal. Thus, a petroleum refinery can be operated throughout the year, whereas a biorefinery has to essentially operate in a seasonal time frame. Again, the integrated biorefineries are a remedy to this limitation. Biorefineries which can switch over from one feedstock to another, depending on its availability, without compromising on the efficiency and cost-effectiveness need to be developed. A third aspect, which goes in favor of biorefineries, is the fact that it is possible to set up these biorefineries in rural areas, and as dispersed industrial complexes, so that the feedstock is locally available, thus avoiding the complex logistics of feedstock transportation and associated costs. Petroleum refineries, on the other hand, are essentially large industrial complexes set up at locations distant from the oil resources, making the transportation costs of its raw material to the refinery location, indispensable. Lastly, though the products of both the refineries are almost comparable, the intermediate products, or the chemical and biorefinery platforms, which enable further processing of the intermediate products to other value-added chemicals differ [56]. Figures 1.31 and 1.32 give an overview of the chemical and biorefinery platforms and the products obtained from them.

Table 1.13 Comparison between a biorefinery and a petroleum refinery

Biorefinery	Petroleum refinery
Lower carbon content than petroleum feedstock, lesser amounts of hydrogen, and higher amounts of oxygen	Mixture of different hydrocarbons—rich in hydrocarbons content than biorefinery feedstock
Presence of oxygen reduces the heat content of molecules and gives them high polarity	Amount of oxygen being less, higher heat content of molecules, and lower polarity
Higher polarity makes blending with fossil fuel difficult	Different products of oil refinery can be easily blended with each other
Biorefinery can be set up in close vicinity of feedstock required for it hence possibility of local availability of feedstock reduces transportation costs	Oil resources located at specific locations not necessarily near the oil refinery thus increasing transportation costs
Composition of feedstock is variable	Lower variations in composition of raw material compared to biomass feedstock
Capable of processing a varied composition of raw material	Not designed for wide variation in raw material composition
Facilitates formation of more classes of products	Product range is limited compared to biorefinery
Larger range of processing technology is required	Comparatively narrower range of processing technology required
Can be developed as dispersed industrial complexes of various sizes	Essentially consists of a single large industrial complex
Usually set up in rural areas, thus contributing in the economic development of these areas	Essentially set up in urban areas
Earns carbon credits	Depletes carbon resources
Possibility of developing carbon negative fuels	No such possibility exists
Feedstock composition and availability is dependent on seasonal changes thus bringing in variability in nature and yield of products	No such variability exists, hence can be run throughout the year with a fixed product spectrum
Long-term storage facility for feedstock required	No such requirement
Biorefinery platform is different from an oil refinery platform in terms of product range	Oil refinery platform is different from a biorefinery platform in terms of product range

1.2.3 Biomass Conversion into Electricity

Biomass can be used to generate various forms of energy. Biomass conversion into biofuels (which serve as a source of energy when burnt) has already been discussed in the earlier sections. This section focuses on the use of biomass for electricity generation. The conventional sources of electricity generation include the nonrenewable sources such as coal, natural gas, nuclear energy, hydroelectric power, petroleum and other fossil fuels, and the renewable sources such as biomass, wind energy, solar energy, and geothermal source of energy. Currently, the world over, nuclear energy, fossil fuel, and natural gas are the major sources of commercial generation of electricity. The prospective shortage of fossil fuel and



SECTORS	PRODUCTS/USES
INDUSTRY	corrosion inhibitors, specialty lubricants, seals....
TRANSPORTATION	corrosion inhibitors, fuels, oxygenates......
TEXTILES	fibers, fabrics, fabric coatings....
FOOD	vitamins, preservatives, pesticides....
ENVIRONMENT	flocculants, chelators, detergents....
COMMUNICATION	optical fiber coatings, LCDs, paper products...
HOUSING	cements, insulations, varnishes....
RECREATION	footgear, tapes-CD's, DVD's.....
HEALTH & HYGEINE	Pharmaceuticals, cosmetics, medical-dental products....

Fig. 1.31 Biorefinery platform

the adverse health and environmental effects of these sources (e.g., emission of GHGs and adverse effects related to the electricity generation from nuclear sources) have made it imperative that a transition be made from these to more safe and environment friendly sources such as renewable sources for the generation of electricity. Presently, a very small proportion of electricity generation is from renewable sources. Biomass is a very significant source of energy which can be tapped for the generation of electricity. The most common types of biomass used for electricity generation are agricultural residues, forest residues, and dedicated energy crops. The use of biomass for electricity generation has been increasing

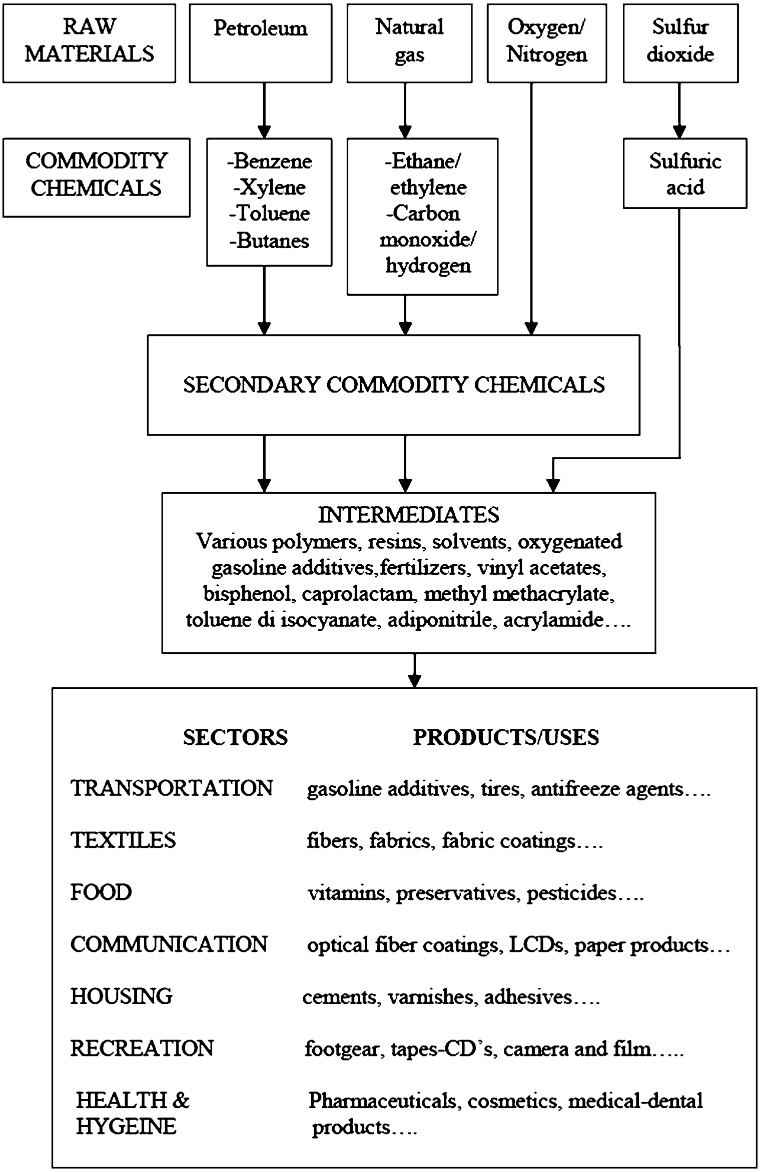


Fig. 1.32 Petroleum refinery platform

gradually by an average of about 13 TWh per year between 2000 and 2008, and constitutes about 2% of the total global generation of electricity over the last 20 years [57]. Figure 1.33 shows the contribution of biomass toward electricity generation at the global level.

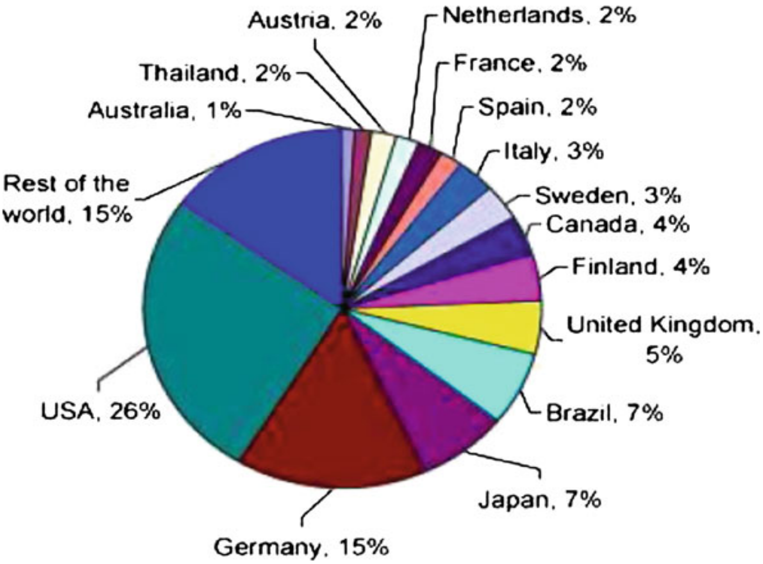


Fig. 1.33 Global contribution of biomass toward generation of electricity (Reproduced with permission from [57])

The US is the major producer of electricity from biomass (producing 26% of the global electricity production from biomass), followed by Germany (15%), Brazil (7%),and Japan (7%).

Projects are being undertaken where combined heat and power generation (CHP) systems are developed which have the capacity to fulfill the energy and power requirements of large populations using biomass energy. In this context, it is worthwhile to mention an experimental model bioenergy village—Jühunde (Fig. 1.34) which has been developed by the International Centre for Sustainable Development in Göttingen, Germany under the leadership of Professor Hans Ruppert of the University of Göttingen. A large biomass fermenter converts the waste biomass collected from the surroundings into methane. A combined heat and power station burns this gas to either provide heating through a combined village heating grid or provides electricity through a public grid. The energy produced by this plant is sufficient to satisfy all the energy needs of the Jühunde village which has about 770 inhabitants. The post-fermentation residue is used as a fertilizer for growing further biomass. Delegations from Japan and China have since visited this bioenergy village to study the technology involved therein and the possibility of scaling up the project to suit larger requirements [58]. The economics and scalability of such projects need to be studied critically so that more such self-sustaining localities can be developed.

Evans et al. [57] have enlisted the cost of power production from biomass cited in the literature. There is a considerable variation in the cost of power which depends mainly on the feedstock factors such as cost of generating/procuring the

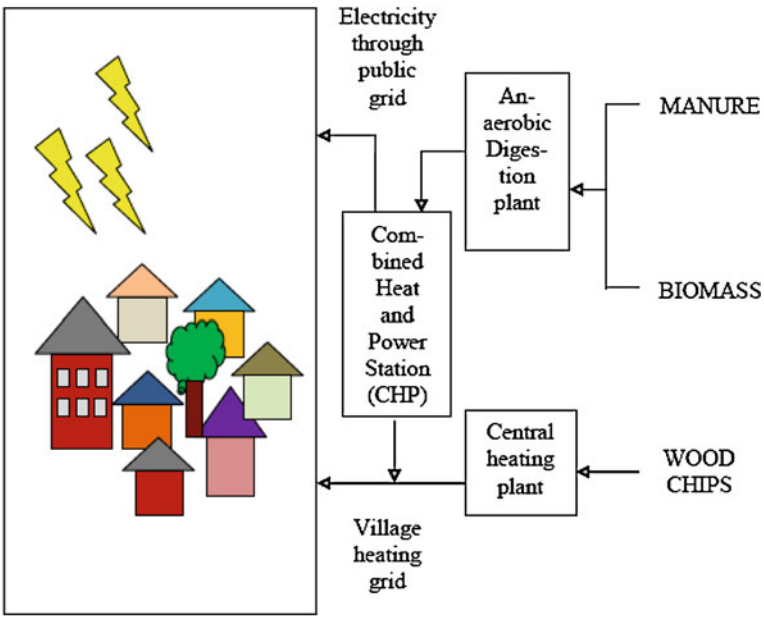


Fig. 1.34 Model Bioenergy Village—Jühunde. (Adapted from [58])

feedstock and energy density of the feedstock, transportation factors such as cost of transportation of the biomass, other factors such as conversion technology used.

1.2.3.1 Current Technologies for Electricity Generation from Biomass

There are currently three established technologies for the production of electricity from biomass—pyrolysis, gasification, and direct combustion. These are already discussed at length in Sect. 1.2.1.1 Direct combustion is the oldest method for electricity generation from biomass where complete oxidation of biomass in presence of excess air is done to produce carbon dioxide and water. Hot flue gases are used to heat the process water to steam, which can be used to drive a turbine resulting in production of electricity. This is not a very efficient method of electricity generation when compared to pyrolysis and gasification. Pyrolysis involves the thermal destruction of biomass under anaerobic conditions without the addition of steam or air resulting in the production of gases and condensable vapors. Combustion of these gases is done in a gas turbine resulting in generation of electricity. This method is more efficient than direct combustion but requires more process control and investment. The gasification method comprises controlled addition of steam to the biomass resulting in partial oxidation of the biomass to produce combustible gases which have a high calorific value. These gases are fed to a combined gas turbine to produce electricity. This method, like pyrolysis is more efficient than direct combustion but requires more process control and investment. The carbon emissions produced as a result of electricity generation from biomass are much lower than the other energy counterparts. The highest carbon emissions during electricity generation from biomass is reported to be 60 g CO_2 equivalent/kWh, which is less than one-third of the lowest CO_2 emission during electricity produced from natural gas and one-fifth of the lowest CO_2 emissions produced from a coal- fired power station [57].

1.3 Economics and Modeling of Biomass Conversion Processes to Energy

The technology for conversion of biomass to first generation biofuels is well established and also commercialized. The technologies for second-, third- and fourth- generation biofuels are still at research stage. Hence, the production of second-, third-, and fourth-generation biofuels is presently costlier than the first-generation biofuels. In general, the overall cost of production decreases as the scale of the production unit increases. As the newer biomass conversion technologies reach the stage of maturity required for large-scale production, the costs of production of these second-, third-, and fourth-generation biofuels is likely to become comparable to the first-generation biofuels. The current focus of research is therefore aimed at economizing the production technologies by way of reducing various costs, integrating various technologies on the basis of pinch analysis, increasing the scale of production and diversifying the product range to include value-added products wherever possible. Techno-economic analysis of the different individual biomass conversion processes has been carried out. Comparative studies of the different biomass conversion technologies have also been done. Points of cost reduction can be identified and the scope of process integration can studied for the production of biofuels. As there are no commercial-scale production units for second-generation onwards biofuels, in most cases, the production costs are estimated on the basis of models developed using different production technologies. The entire life cycle right from generation of the biomass to its collection and transportation to the biorefinery/power plant to waste disposal subsequent to the generation of energy is considered for the economic assessment of the biomass conversion process.

Dwivedi et al. [59] have reviewed the economics of ethanol production from cellulose using different conversion technologies. The conversion technology used has a greater impact on the cost of production compared to the type of feedstock used hence, such a study is expected to bring the cost of ethanol production from cellulose feedstock comparable to that from starch-based feedstock. In other words, proper selection and integration of conversion technology is likely to bring the production of second-generation bioethanol comparable in cost to the first-generation bioethanol. The economics of several hydrolysis-based conversion

Table 1.14 Cost comparison of hydrolysis-based conversion technologies for ethanol production from cellulose

Process	Cost of biomass used			
	$ 50/dry ton		$ 108/dry ton	
	Cost of ethanol ($/gal) for 25 Mgal/year	Cost of ethanol ($/gal) for 5 Mgal/year	Cost of ethanol ($/gal) for 25 Mgal/year	Cost of ethanol ($/gal) for 5 Mgal/year
Simultaneous saccharification and fermentation	1.48	1.88	2.11	2.51
Concentrated acid hydrolysis, neutralization, and fermentation	2.28	2.76	3.01	3.49
Ammonia disruption, hydrolysis and fermentation	1.81	2.4	2.48	3.06
Steam disruption, hydrolysis and fermentation	1.63	2.15	2.25	2.77
Acid disruption and transgenic microorganism fermentation	1.86	2.45	2.5	3.1
Concentrated acid hydrolysis, acid recycle, and fermentation	1.86	2.19	2.5	2.83
Acidified acetone extraction, hydrolysis, and fermentation	1.7	2.13	2.3	2.72

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technologies show that the cost is highest for concentrated acid hydrolysis, neutralization, and fermentation technology and lowest for simultaneous saccharification and fermentation technology (Table 1.14).

Thermoeconomic modeling is carried out to evaluate the various available technologies for a process and select the most suitable one from among them, and to establish optimum operating conditions for the process after identifying critical parameters which will affect the economy of the selected process. This will enable one to assess the competitiveness of different processes and select that or those processes which are likely to offer the greatest economic advantage, energy production and are at the same time environment friendly and sustainable. Tock et al. [60] have carried out thermo-economic modeling for thermochemical production of liquid fuels (FT fuels, methanol, and dimethyl ether) from biomass with respect to process description and process integration. A thermodynamic model has been developed and used to calculate liquid–vapor and chemical equilibrium; an energy model has been developed to minimize the energy consumption taking place in a process, by carrying out thermodynamic calculations to get feasible energy targets which can be achieved by optimizing the process operating conditions, heat recovery, and energy conversion. This is based on identification and definition of hot and cold streams, temperature-enthalpy profiles, and their minimum approach temperature. Economic model is developed considering the size of all such equipments required and type of construction material required for fabricating them that are responsible for the productivity of the overall process. The cost of equipment is estimated from capacity-based correlations. For evaluating the production costs, the total annual costs for the system, which include the annual investment cost, cost of operation and maintenance, cost of raw material, and electricity supply and demand are divided by the amount of fuel produced. The electricity and fuel sale price is calculated using the biomass break-even cost (expressed in terms of the expenditure per MWh of biomass) that defines the maximum resource price for which the process is profitable.

Caputo Antonio et al. [61] studied the economics of biomass to energy conversion in combustion and gasification plants with specific reference to the effect of logistics variables with the aim of assessing the feasibility/profitability of direct production of electric energy from biomass. The study was carried out on combustion and gasification plants in the capacity range of 5–50 MW. The scale effects were found to be very significant in that profitability of both combustion and gasification systems increased with scale-up of plant size. Also, the influence of logistics on economic performance reduced with increasing plant size. The logistics included purchase and transport cost of biomass, operating labor, maintenance, and ash transport/disposal costs. The effects of these on the total capital investment and total operating cost were evaluated. In terms of capital and operating costs, combustion-based process showed a lower total capital investment but a higher total operating cost compared to the gasification system. The gasification system has a lower biomass consumption compared to combustion system and thus, has a lower operating cost. However, in spite of the lower operating cost, the high capital investment, especially in absence of fiscal incentives and adequate financial support, makes the gasification system less profitable than the combustion system. The biomass purchase cost and biomass transportation cost for a gasification process is much more significant compared to the operational labor, maintenance, and ash transport/disposal costs. It is therefore possible to improve the performance and profitability of a gasification-based approach to the extent that it is comparable to the combustion-based approach by taking advantage of the technological advances and by improving the logistics of biomass procurement and transportation.

With advances in technology and ever increasing fossil fuel and electricity costs, the profits incurred by biorefineries and other biomass conversion technologies is likely to increase enormously due to an added advantage of value-added products generated during the conversion plus the carbon credits earned due the environment friendly processes used, which would give additional monetary and non-monetary benefits to the company. However, the advanced efficient conversion technologies would require a concurrent improvement in the biomass generation collection and transportation efficiencies and improved fuel/energy transport efficiencies. We are gradually moving from carbon neutrality toward carbon negativity, where the amount of carbon generated as a result of consumption of the fuel/energy would be significantly less than that used up by the biomass during its generation.

1.4 Future of Biomass Conversion into Energy

Biomass is the only renewable organic resource available in great abundance. If exploited to its fullest extent, it has the capacity to completely replace fossil fuels for energy generation, simultaneously maintaining a clean environment, free from the greenhouse gases. Technologies for the production of the third- and fourth-generation biofuels are likely to have a very great impact on reducing the problem of global warming caused by the GHGs and in taking us from an era of carbon neutral environment to a carbon-negative environment. These include biofuels produced by upgraded pyrolysis and gasification technologies and solar-to-fuel technologies. The concept of biorefineries has already made the biomass conversion technology a great attraction among industry investors because biorefineries have the potential of reaping great profits by generating costly fuels as the main product, and in addition to this, costlier value-added products such as chemicals, as by-products, the original cost of the initial raw material being almost negligible. The future biorefineries would use efficient feedstock upgrading processes, where the raw materials are continuously upgraded and refined. Fractionating the biomass into its core constituents before using it as feedstock will give the much lacking uniformity in the biomass, making the processing in a biorefinery all the more efficient. Only the residue remaining after all the useful components are converted, should be used for generation of heat and electricity. This will ensure complete usage of the biomass. The catalytic cracking/upgrading technologies used in the thermochemical conversion methods are likely to improve with the use of nanoparticle-based catalysts. Simultaneously, the development of biocatalysts will enable biomass conversions under milder conditions, and with greater efficiencies, leading to more environment friendly “green” processes. Bioethanol and biodiesel are the two biofuels that have the potential of replacing gasoline. The rapid advances and the unlimited scope of the biochemical conversion technologies and the algal conversion processes are likely to make this a reality in the near future. Genetic manipulation of microorganisms to improve production of efficient cellulases and hemicellulases will go a long way in improving yields and reducing conversion times in the biochemical conversion of lignocellulosic biomass. Recombinant DNA technology is being applied to bacteria and fungi in order to achieve this. Strains of microorganisms which have the ability to co-ferment different types of substrates simultaneously, will improve the economy and efficiency of the biochemical conversion processes. On the other hand, transgenically modified plants can be grown which will have a reduced lignin content and an upregulated cellulose biosynthesis. "Plant factories" can be set up, where such genetically modified plants can be grown which have the capacity to capture and store more carbon so that the overall energy density of the biomass increases. The bright future of biomass conversion into energy is clearly evident from the large number of integrated biorefineries which have already come up in different parts of the world.

References

1. Demirbas A (2004) Combustion characteristics of different biomass fuels. Progress in energy and combustion science 30:219–230
2. www.ieabcc.nl
3. www.vt.tuwien.ac.at/biobib/biobib/html
4. www.ecn.nl/Phyllis
5. Iyer PVR, Rao TR, Grover PD (2002) Biomass: thermo-chemical characterization. Indian Institute of Technology, New Delhi
6. Sofer SS, Zaborsky OR (1981) Biomass conversion processes for energy and fuels. Plenum Press, New York
7. Sims R (2002) The brilliance of bioenergy: in business and in practice. James & James, London
8. Yokoyama S (2008) The Asian biomass handbook. Japan Institute of Energy, Japan
9. Loo S, Koppejan J (2008) The handbook of biomass combustion and co-firing. Earthscan, UK, USA
10. Overend RP (2004) Thermochemical conversion of biomass, in renewable energy sources charged with energy from the sun and originated from earth-moon interaction. In: Shpilrain EE (ed) Encyclopedia of Life Support Systems (EOLSS), Eolss Publishers, UK (http://www.eolss.net)
11. Basu P (2010) Biomass gasification and pyrolysis: practical design and theory. Academic Press, USA
12. Bridgewater AV (2010) Fast pyrolysis of biomass for energy and fuels. In: Crocker M (ed) Thermochemical conversion of biomass to liquid fuels and chemicals, RSC energy and environment series no. 1, Royal Society of Chemistry, UK
13. Bridgewater AV (1994) Catalysis in thermal biomass conversion. Appl Catal A Gen 116:5–47
14. Balat M et al (2009) Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems. Energy Convers Manag 50:3147–3157
15. Roy C, Yang J, et al (1997) Development of a novel vacuum pyrolysis reactor with improved heat transfer potential. In: Bridgewater AV (ed) Developments in thermochemical biomass conversion, vol. 1, Chapman & Hall, UK
16. Demirbas A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers Manag 42:1357–1378
17. Neathery JK (2010) Biomass gasification. In: Crocker M (ed) Thermochemical conversion of biomass to liquid fuels and chemicals, RSC energy and environment series no. 1, Royal Society of Chemistry, UK
18. Damartzis T, Zabaniotou A (2011) Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review. Renew Sustain Energy Rev 15:366–378

19. Belgiorno V, De Feo G, Della Rocca C, Napoli RMA (2003) Energy from gasification of solid wastes. Waste Manag 23:1–15
20. Acharya B, Dutta A, Basu P (2009) Chemical-looping gasification of biomass for hydrogen-enriched gas production with in-process carbon dioxide capture. Energy Fuels 23(10):5077–5083
21. Yoshidaa Y et al (2003) Comprehensive comparison of efficiency and CO2 emissions between biomass energy conversion technologies—position of supercritical water gasification in biomass technologies. Biomass Bioenergy 25:257–272
22. Kumar A, Jones DD, Hanna MA (2009) Thermochemical biomass gasification: a review of the current status of the technology. Energies 2:556–581
23. Küçük MM, Demirbas A (1997) Biomass conversion processes. Energy Convers Mgmt 38(2):151–165
24. Yu Z, Morrison M, Schanbacher FL (2010) Production and utilization of methane biogas as renewable fuel. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels: strategies for global industries. Wiley, UK
25. Hughes SR, Qureshi N (2010) Biofuel demand realization. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels : strategies for global industries. Wiley, UK
26. Berg Miller ME, Brulc JM, Bayer EA et al (2010) Advanced technologies for biomass hydrolysis and saccharafication using novel enzymes. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels: strategies for global industries. Wiley, UK
27. Ladisch MR, Lin KW, Voloch M, Tsao GT (1983) Process considerations in the enzymatic hydrolysis of biomass. Enzyme Microb Technol 5:82–102
28. Liu ZL, Blaschek HP (2010) Biomass conversion inhibitors and in situ detoxification. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels: strategies for global industries. Wiley, UK
29. Inui M, Vertès AA, Yukawa H (2010) Advanced fermentation technologies. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels: strategies for global industries. Wiley, UK
30. Demirbas A, Demirbas MF (2010) Algae energy: algae as a new source of biodiesel. Springer, London
31. Packer M (2009) Algal capture of carbon dioxide; biomass generation as a tool for greenhouse gas mitigation with reference to New Zealand energy strategy and policy. Energy Policy 37(9):3428–3437
32. Huesemann M, Roesjadi G, Benemann J, Metting FB (2010) Biofuels from microalgae and seaweeds. In: Vertis AA, Qureshi N, Blaschek HP, Yukawa H (eds) Biomass to biofuels: strategies for global industries. Wiley, UK
33. Kamm B, Kamm M (2004) Principles of biorefineries. Appl Microbiol Biotechnol 64:137–145
34. http://www1.eere.energy.gov/biomass/pdfs/35523.pdf
35. Octave S, Thomas D (2009) Biorefinery: toward an industrial metabolism. Biochimie 91:659–664
36. http://www1.eere.energy.gov/biomass/pdfs/35523.pdf
37. http://www1.eere.energy.gov/biomass/pdfs/pnnl-16983.pdf
38. Demirbas A (2010) Biorefineries: for biomass upgrading facilities. Springer, London
39. Kaparaju P, Serrano M, Thomsen AB, Kongjan P, Angelidaki I (2009) Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. Bioresour Technol 100:2562–2568
40. Naik SN, Goud VV, Rout PK, Dalai AK (2010) Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev 14:578–597
41. Takara D, Khanal SK (2011) Green processing of tropical banagrass into biofuel and biobased products: an innovative biorefinery approach. Bioresour Technol 102(2):1587–1592
42. Chew TL, Bhatia S (2008) Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. Bioresour Technol 99:7911–7922

43. Bouaid A, Martínez M, Aracil J (2010) Biorefinery approach for coconut oil valorisation: A statistical study. Bioresour Technol 101:4006–4012
44. Luo G, Talebnia F, Karakashev D, Xie L, Zhou Q, Angelidaki I (2011) Enhanced bioenergy recovery from rapeseed plant in a biorefinery concept. Bioresour Technol 102(2):1433–1439
45. Klass DL (1998) Biomass for renewable energy, fuels and chemicals. Academic Press, San Diego
46. Mousdale DM (2008) Biofuels: biotechnology, chemistry and sustainable development. CRC Press, Boca Raton
47. FitzPatrick M, Champagne P, Cunningham MF, Whitney RA (2010) A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. Bioresour Technol 101:8915–8922
48. Marinova M, Mateos-Espejel E, Jemaaa N, Paris J (2009) Addressing the increased energy demand of a Kraft mill biorefinery: the hemicellulose extraction case. Chem Eng Res Des 87:1269–1275
49. Mao H, Genco JM, Yoon S-H, Van Heiningen A, Pendse H (2008) Technical economic evaluation of a hardwood biorefinery using the "near-neutral" hemicellulose pre-extraction process. J Biobased Mater Bioenergy 2(2):177–185
50. www.biorefinery.euroview.eu
51. Singh J, Gu S (2010) Commercialization potential of microalgae for biofuels production. Renew Sustain Energy Rev 14:2596–2610
52. Goh CS, Lee KT (2010) A visionary and conceptual macroalgae-based third-generation bioethanol (TGB) biorefinery in Sabah, Malaysia as an underlay for renewable and sustainable development. Renew Sustain Energy Rev 14:842–848
53. Mussgnug JH, Klassen V, Schlüter A, Kruse O (2010) Microalgae as substrates for fermentative biogas production in a combined biorefinery concept. J Biotechnol 150:51–56
54. http://www1.eere.energy.gov/biomass/integrated_biorefineries.html
55. www.nnfcc.co.uk/publications/NNFCC-position-paper-biorefineries-definitions-examples-of-current-activities-and-suggestions-for-UK-development/at_download/file
56. Cherubini F (2010) The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Convers Manag 51:1412–1421
57. Evans A, Strezov V, Evans TJ (2010) Sustainability considerations for electricity generation from biomass. Renew Sustain Energy Rev 14:1419–1427
58. Moore A (2005) Short-circuiting our fossil fuel habits. EMBO Reports 6(3):205–206
59. Dwivedi P, Alavalapati JRR, Lal P (2009) Cellulosic ethanol production in the United States: conversion technologies, current production status, economics, and emerging developments. Energy Sustain Dev 13:174–182
60. Tock L, Gassner M, Maréchal F (2010) Thermochemical production of liquid fuels from biomass: thermo-economic modeling, process design and process integration analysis. Biomass Bioenergy 34:1838–1854
61. Caputo AC, Palumbo M, Pelagagge PM, Scacchia F (2005) Economics of biomass energy utilization in combustion and gasification plants: effects of logistic variables. Biomass Bioenergy 28:35–51