

Chapter 5

Pyrolysis

5.1 INTRODUCTION

Pyrolysis is a thermochemical decomposition or cracking of biomass or similar feedstock into a range of useful products, either in the total absence of oxidizing agents or with a limited supply that does not permit gasification to an appreciable extent. Its product includes gases, biochar, and biooil, but primary motivation of pyrolysis is production of liquids for fuel or chemical production. During pyrolysis, large complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules of gas, liquid, and char (Fig. 5.1).

Pyrolysis is precursor of both combustion and gasification processes but does require external agents like oxygen and steam like the latter do. It has similarity to or overlaps with processes like cracking, devolatilization, carbonization, torrefaction, dry distillation, destructive distillation, and thermolysis, but it has no similarity with gasification (Chapter 7), which involves chemical reactions with an external agent known as *gasification medium*. Pyrolysis of biomass is typically carried out in a temperature range of 300–650°C compared to 800–1000°C for gasification and 200–300°C for torrefaction (Chapter 4). A discussion on the difference between these processes is given in Section 4.2.1 and Table 5.1.

Production of noncondensable gases like CH₄, CO is of secondary importance in pyrolysis. Biooil is the liquid product of pyrolysis, and is of primary importance in this process. So, more details of its production is discussed in Section 5.7. Biochar is the solid product of biomass pyrolysis. Owing to its growing importance for carbon sequestration, biochar is elaborated later in Section 5.8.

This chapter explains the basics of pyrolysis and effects of different parameters on product yield. A brief discussion of different types of pyrolyzer and the design implications of a typical pyrolysis plant is also included here.

5.1.1 Historical Background

Charcoal from wood via pyrolysis was essential for extraction of iron from iron ore in the preindustrial era. Fig. 5.2 shows a typical beehive oven used in early times to produce charcoal from biomass using a slow pyrolysis process. This

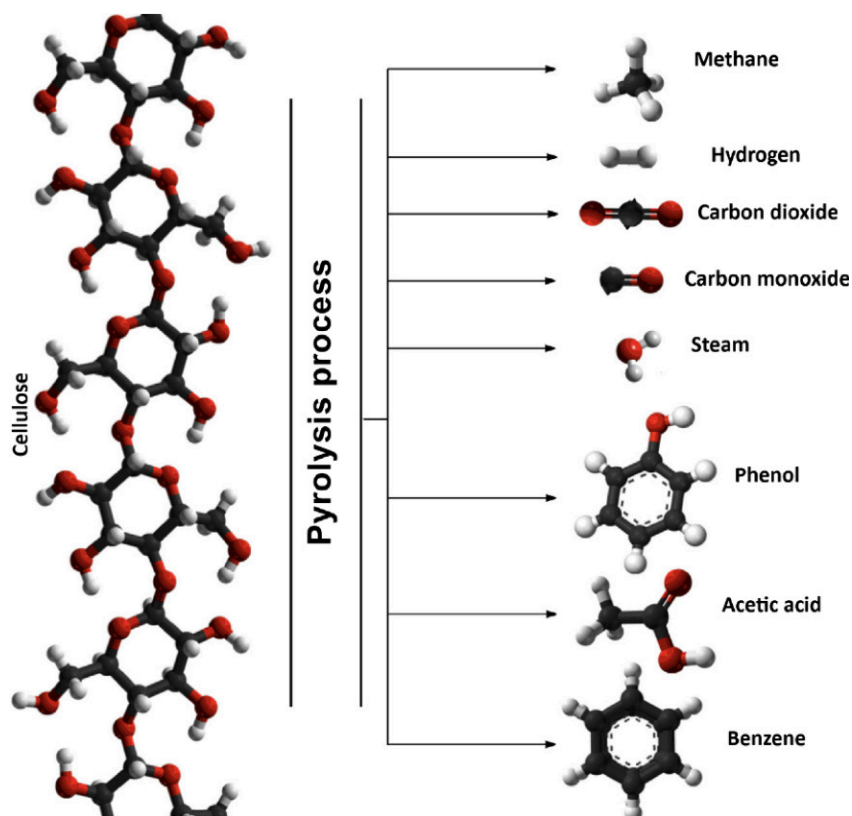


FIGURE 5.1 Decomposition of large hydrocarbon molecules into smaller ones during pyrolysis.

practice continued until the wood supply nearly ran out and coal, produced inexpensively from underground mines, replaced charcoal for iron production.

The modern petrochemical industry owes a great deal to the invention of a process for production of kerosene using pyrolysis. In the mid-1840s, Abraham Gesner, a physician practicing in Halifax, Canada (Fig. 5.3), began searching for a cleaner-burning mineral oil to replace the sooty oil from whales, the primary fuel used during those times on the eastern seaboard of the United States and in Atlantic Canada. By carefully distilling a few lumps of coal at 427°C, purifying the product through treatment with sulfuric acid and lime, and then redistilling it, Gesner obtained several ounces of a clear liquid (Gesner, 1861). When this liquid was burned in an oil lamp similar to the one shown in Fig. 5.3, it produced a clear bright light that was much superior to the smoky light produced by the burning of whale oil. Dr. Gesner called his fuel *kerosene*—from the Greek words for wax and oil. Later, in the 1850s, when crude oil began to flow in Pennsylvania and Ontario, Gesner extracted petro-based kerosene from that.

TABLE 5.1 Characteristics of Some Thermal Decomposition Processes

Pyrolysis Process	Residence Time	Heating Rate	Final Temperature (°C)	Products
Torrefaction	10–60 min	Very small	280	Torrefied biomass
Carbonization	Days	Very low	>400	Charcoal
Fast	<2 s	Very high	~500	Bio-oil
Flash	<1 s	High	<650	Bio-oil, chemicals, gas
Ultrarapid	<0.5 s	Very high	~1000	Chemicals, gas
Vacuum	2–30 s	Medium	400	Bio-oil
Hydropyrolysis	<10 s	High	<500	Bio-oil
Methanopyrolysis	<10 s	High	>700	Chemicals

Source: Following: Mohan, D., Pittman Jr., C.U., Steele, P.H., 2003. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* 20, 848–889.

The invention of kerosene, the first transportable liquid fuel, brought about a revolution in lighting that touched and is still the case in even the remotest parts of the world. It also had a major positive impact on the ecology. For example, in 1846, more than 730 ships hunted whales to meet the huge demand for whale oil. In just a few years after the invention of kerosene, the hunt was reduced to only a few ships, saving whales from possible extinction.

5.2 PYROLYSIS

The process of pyrolysis involves rapid heating of biomass or other feedstock in the absence of air or oxygen at a certain temperature, known as the *pyrolysis temperature*, and holding it there for a specified time to produce noncondensable gases, solid char, and liquid product. The liquid product is of primary interest in pyrolysis. The nature of its product depends on several factors, including pyrolysis temperature and heating rate.

When exposed to rapid heating the large molecules of biomass undergoes primary decomposition. The product of cracking reaction comprises of condensable gases and solid char. The condensable gas may undergo secondary cracking breaking down further into noncondensable gases (CO, CO₂, H₂, and

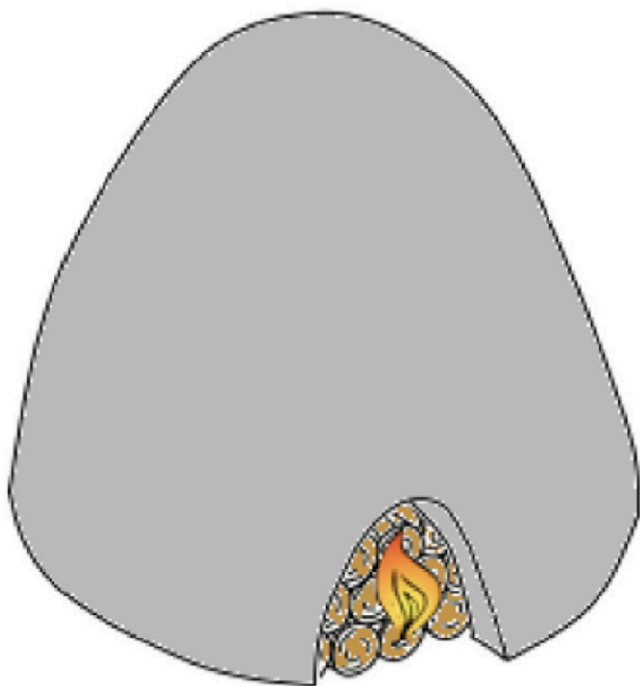
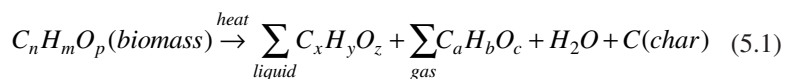


FIGURE 5.2 Beehive oven for charcoal production through slow pyrolysis of wood.

CH_4), liquid, and char (Fig. 5.4). This decomposition occurs partly through gas-phase reactions and partly through gas–solid-phase thermal reactions. In gas-phase reactions, the condensable vapor is cracked into smaller molecules of noncondensable permanent gases such as CO and CO_2 , but these are of less interest in pyrolysis.

The pyrolysis process may be represented by a generic reaction such as:



Pyrolysis is an essential pre-step in a gasifier, and this step is relatively fast, especially in reactors with rapid mixing. This process produces a solid product that is more energy dense than the parent biomass, but its liquid product or gaseous product is less energy dense. While the parent biomass has a lower heating value (LHV) in the range of 19.5–21 MJ/kg dry basis, its liquid yield has a lower LHV in the range of 13–18 MJ/kg wet basis (Diebold et al., 1997; Table 5.2).

Fig. 5.5 shows the pyrolysis process by means of a schematic of a fluidized bed pyrolysis plant. Biomass is fed into a pyrolysis chamber containing hot solids (fluidized bed) that heat the biomass to the pyrolysis temperature, at which its decomposition starts. The condensable and noncondensable vapors

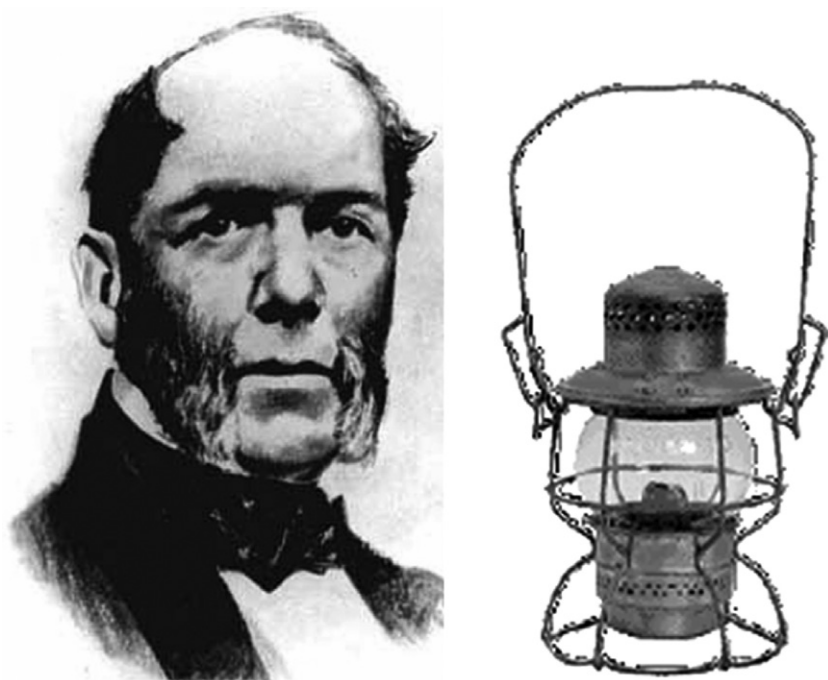


FIGURE 5.3 Abraham Gesner, inventor of kerosene and his kerosene lamp.

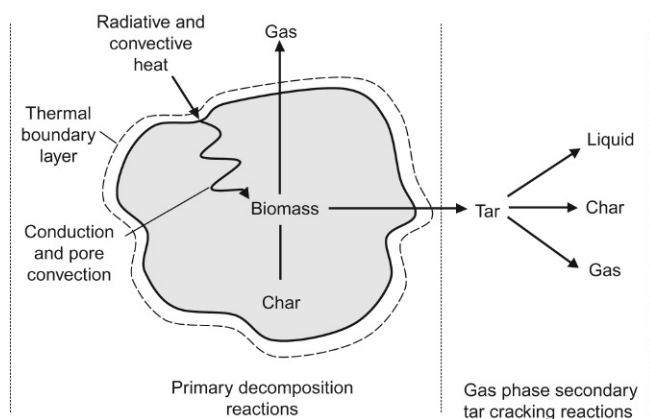


FIGURE 5.4 Pyrolysis process in a biomass particle.

released from the biomass leave the chamber, while the solid char produced remains partly in the chamber and partly in the gas. The gas is separated from the char and cooled downstream of the reactor. The condensable vapor condenses as biooil or pyrolysis oil. The noncondensable gases leave the chamber as product gas, which is the product of interest. Similarly, the solid char

TABLE 5.2 Comparison of Heating Values of Some Fuels

Fuel	Pet-coke	Bitu-minous Coal	Saw-dust	Bio-oil	Pyroly-sis Gas	Biochar
Units	MJ/kg	MJ/kg	MJ/kg dry	MJ/kg	MJ/Nm ³	MJ/kg
Heating value	~29.8	~26.4	~20.5	13–18	11–20	20–25

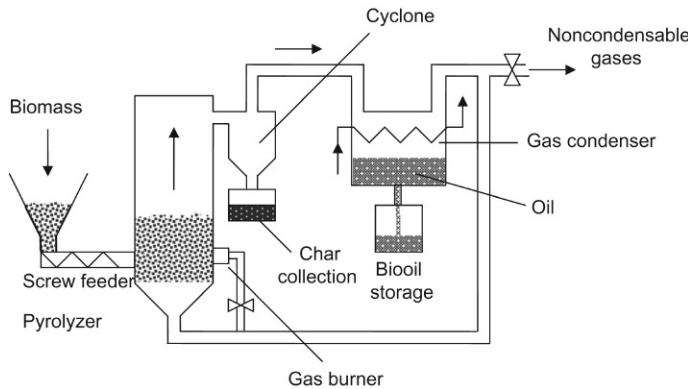


FIGURE 5.5 Simplified layout of a pyrolysis plant with bubbling fluidized bed.

may be collected as a commercial product or burned in a separate chamber to produce heat that is necessary for pyrolysis. As this gas is free from oxygen, part of it may be recycled into the pyrolysis chamber as a heat carrier or fluidizing medium. There are, of course, variations of the process, which will be discussed later.

5.2.1 Pyrolysis Products

As mentioned earlier, pyrolysis involves a breakdown of large complex molecules into several smaller molecules. Its product is classified into three principal types:

1. Liquid (tars, heavier hydrocarbons, and water)
2. Solid (mostly char or carbon)
3. Gas (e.g., CO_2 , H_2O , CO , C_2H_2 , C_2H_4 , C_2H_6 , C_6H_6)

The relative amounts of these products depend on several factors including the heating rate and the final temperature reached by the feedstock.

The pyrolysis product should not be confused with the “volatile matter” constituent of a fuel as discussed in [Section 3.6.2](#). Proximate analysis, discussed in this section, lump together the liquid and gas yields of pyrolysis as “volatile matter,” and the char yield as “fixed carbon.” Since the relative fraction of pyrolysis yields depends on many operating factors, determination of the volatile matter of a fuel requires the use of standard conditions of heating rate and final temperature as specified in the test codes ([Section 14.1.2.1](#)).

5.2.1.1 Liquid

The liquid product of pyrolysis, known as biooil, tar or biocrude, is a black tarry fluid containing up to 20% water, that consists mainly of homologous phenolic compounds. Biooil is a mixture of complex hydrocarbons with large amounts of oxygen and water. Compounds found in biooil fall into the following five broad categories ([Piskorz et al., 1988](#)):

- Hydroxyaldehydes
- Hydroxyketones
- Sugars and dehydrosugars
- Carboxylic acids
- Phenolic compounds

Rapid and simultaneous depolymerization and fragmentation of the cellulose, hemicellulose, and lignin components of biomass produce biooil. In a typical operation, the biomass is subjected to a rapid increase in temperature followed by an immediate quenching to “freeze” the intermediate pyrolysis products. Rapid quenching is important, as it prevents further degradation, cleavage, or reaction with other molecules (see [Section 5.4.2](#) for more details).

5.2.1.2 Solid

Biochar is the solid yield of pyrolysis. It should not be confused with the *fixed carbon* measured by proximate analysis. Biochar is primarily carbon (~85%), but it can also contain some oxygen and hydrogen and some inorganic ash if that is present in the parent biomass. The heating value of biochar is in the range 25–32 MJ/kg dry basis, which is substantially higher than that of the parent biomass or its liquid product. As biomass is carbon neutral, the combustion of biochar is considered more environment friendly than coal.

Biochar is characterized by large pore surface area. Hence it has a large number on nonfuel use such as adsorption of chemicals and carbon storage in ground.

5.2.1.3 Gas

Primary decomposition of biomass produces both condensable gases (vapor) and noncondensable gases (*primary gas*). The vapors, which are made of heavier molecules, condense upon cooling, adding to the liquid yield of pyrolysis. The

noncondensable gas mixture contains lower-molecular-weight gases like carbon dioxide, carbon monoxide, methane, ethane, and ethylene. These do not condense on cooling. Additional noncondensable gases, produced through secondary cracking of the vapor (see Section 5.4.2) at higher temperature (Fig. 5.6), are called *secondary gases*. The final noncondensable gas product is thus a mixture of both primary and secondary gases. The LHV of primary gases is typically 11 MJ/Nm^3 , but the LHV of gases formed after severe secondary cracking of the vapor is much higher: 20 MJ/Nm^3 (Diebold and Bridgwater, 1997). Table 5.2 gives the range of LHV of the pyrolysis gases comparing it with the heating values of biooil, raw biomass, and fossil fuels.

5.2.2 Types of Pyrolysis

Based on the heating rate, pyrolysis may be broadly classified as slow and fast. It is considered slow if the time, t_{heating} , required to heat the fuel to the pyrolysis temperature, T_{pyr} is much longer than the characteristic pyrolysis reaction time, t_r , and vice versa. That is:

- Slow pyrolysis: $t_{\text{heating}} \gg t_r$
- Fast pyrolysis: $t_{\text{heating}} \ll t_r$

By assuming a simple linear heating rate ($T_{\text{pyr}}/t_{\text{heating}}$, K/s), these criteria may be expressed in terms of heating rate as well.

Pyrolysis may also be conducted under nonoxidizing environment like hydrogen, steam, or water. For example hydrolyrolysis is carried out in H_2 , while hydrous pyrolysis is conducted in H_2O . These types are used mainly for the production of chemicals. Depending on the medium and pressure at which the pyrolysis is carried out, there could be different pyrolysis types with its characteristic products and applications.

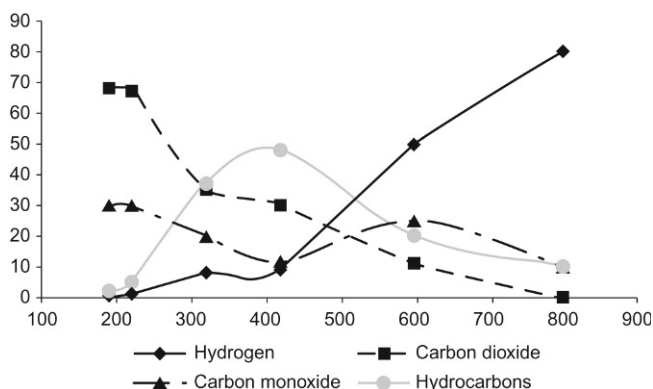


FIGURE 5.6 Release of gases during dry distillation of wood. (Drawn based on the data of Nikitin, 1966. Chemistry of Cellulose and Wood. Academy of Sciences of the USSR, Institute of High Molecular Compounds, Moscow, Leningrad (translated in 1966 from Russian).).

Slow and fast pyrolysis are carried out generally in the absence of a medium. In slow pyrolysis, the residence time of vapor in the pyrolysis zone (vapor residence time) is of the order of minutes or longer. This process is not used for traditional pyrolysis, where production of liquid is the main goal. Slow pyrolysis is used primarily for char production and is broken down into two types: carbonization and torrefaction (Chapter 4). Torrefaction takes place at a very low and narrow temperature (200–300°C), while carbonization takes place at much higher and broad temperature.

In fast pyrolysis, the vapor residence time is in the order of seconds or milliseconds. This type of pyrolysis, used primarily for the production of biooil and gas, is of two main types: flash and ultrarapid.

Table 5.1 compares the characteristics of different thermal decomposition processes and shows carbonization as the slowest and ultrarapid as the fastest. Carbonization produces mainly charcoal; fast pyrolysis processes target production of liquid or gas. Following sections present brief discussion of several types of pyrolysis classified by the thermal condition of operation and the medium.

5.2.2.1 *Slow Pyrolysis*

Carbonization is a slow pyrolysis process, in which the production of charcoal or char is the primary goal. It is the oldest form of pyrolysis, which is in use for thousands of years. Here, the biomass is heated slowly in the absence of oxygen to a relatively low temperature (~400°C). The process is conducted over an extended period of time, which in ancient times ran for several days to maximize the char formation. Carbonization thus allows adequate time for the condensable vapor to be converted into char and noncondensable gases. Fig. 5.2 is a sketch of a typical beehive oven in which large logs were stacked and covered by a clay wall. It allows a certain amount of oxygen for partial combustion of wood. A small fire at the bottom provides the required heat for carbonization. The fire essentially stays inside the well-insulated closed chamber.

5.2.2.2 *Conventional Pyrolysis*

Conventional pyrolysis heats the biomass at a moderate rate to a moderate temperature (~600°C). The product residence time is of the order of minutes. It yields all three types of pyrolysis product (gas, liquid, and char).

5.2.2.3 *Fast Pyrolysis*

The primary goal of fast pyrolysis is to maximize the production of liquid or biooil. The biomass is heated so rapidly that it reaches the peak (pyrolysis) temperature before it decomposes. The heating rate can be as high as 1000–10,000°C/s, but the peak temperature should be below 650°C if biooil is the product of interest. However, the peak temperature can be up to 1000°C if the production of gas is of primary interest. Fluidized beds similar to the one shown in Fig. 5.5 may be used for fast pyrolysis.

Four important features of the fast pyrolysis process that help to increase the liquid yield are (i) very high heating rate, (ii) reaction temperature within the range of 425–600°C, (iii) short residence time (<3 s) of vapor in the reactor, and (iv) rapid quenching of the product gas.

5.2.2.4 Flash Pyrolysis

In flash pyrolysis, biomass is heated rapidly, but not as high as fast pyrolysis, to a relatively modest temperature range of 450–600°C. The product, containing condensable and noncondensable gas, leaves the pyrolyzer within a short residence time of 30–1500 ms (Bridgwater, 1999). Upon cooling, the condensable vapor is then condensed into a liquid fuel known as “bio-oil.” Such an operation increases the liquid yield while reducing the char production. The yield of biooil in flash pyrolysis could be as high as 70%–75% of the total pyrolysis product (www.btgworld.com) while with a lower heating rate (~50 °C/min), it is in the range of 40%–60% (Debdoubi et al., 2006).

5.2.2.5 Ultrarapid Pyrolysis

Ultrarapid pyrolysis involves extremely fast rate of heating of biomass to a temperature higher than that of fast pyrolysis. Because the reactor temperature is also low (~650°C), one can achieve a liquid yield as high as 90% (Hulet et al., 2005). In one method, heat-carrier solids impact on biomass stream, resulting in a very high heating rate. A rapid quenching of the primary product follows the pyrolysis in the reactor. A gas–solid separator separates the hot heat-carrier solids from the noncondensable gases and primary product vapors and returns them to the mixer. They are then heated in a separate combustor. Then a non-oxidizing gas transports the hot solids to the mixer. A precisely controlled short uniform residence time is an important feature of ultrarapid pyrolysis. To maximize the product yield of gas, the pyrolysis temperature is around 1000°C for gas and around 650°C for liquid.

It may be noted that difference between fast, flash, and ultrarapid pyrolysis is often blurred.

5.2.2.6 Pyrolysis in the Presence of a Medium

Conventional pyrolysis is carried out in the absence of an oxidizing medium such as air, but a special type is conducted in a medium such as water or hydrogen. Hydropyrolysis is one such type where this thermal decomposition of biomass takes place in an atmosphere of high-pressure hydrogen. One shortcoming of conventional pyrolysis is that the biooil produced is rich in oxygen. Hydropyrolysis can produce biooil with reduced oxygen. It can also increase the volatile yield and the proportion of lower-molar-mass hydrocarbons (Rocha et al., 1997) in the pyrolysis product. Its higher volatile yield is attributed to hydrogenation of free-radical fragments sufficient to stabilize them before they recombine and form char (Probstein and Hicks, 2006, p. 99).

Hydrous pyrolysis is another example of pyrolysis in a nonoxidizing medium where the medium is high-temperature water. This process could convert biomass like turkey offal into light hydrocarbon for production of fuel, fertilizer, or chemicals. In a two-stage process, the first stage takes place in water at 200–300°C under pressure; in the second stage, the produced hydrocarbon is cracked into lighter hydrocarbon at a temperature of around 500°C (Appel et al., 2004).

5.3 PYROLYSIS PRODUCT YIELD

The product of pyrolysis depends on the design of the pyrolyzer, the physical and chemical characteristics of the biomass, and important operating parameters such as:

- Heating rate
- Final temperature (pyrolysis temperature)
- Residence time in the reaction zone

Besides these, other factors such as pressure, composition of pyrolysis medium, and presence of catalysts (Shafizadeh, 1984) also affect the pyrolysis product. Mahinpey et al. (2009) for example noted increase in liquid yield and decrease in gas yields when pressure was increased.

By changing the final temperature and the heating rate, it is possible to change the relative yields of the solid, liquid, and gaseous products of pyrolysis. For example, rapid heating gives higher volatiles and more reactive char than those produced by a slower heating process; slower heating rate and longer residence time result in secondary char produced from a reaction between the primary char and the volatiles.

5.3.1 Effect of Biomass Composition

The composition of the biomass, especially its hydrogen-to-carbon (H/C) ratio, has an important bearing on the pyrolysis yield. Each of the three major constituents of a lignocellulosic biomass has its preferred temperature range of decomposition. Analysis of data from thermogravimetry on some selected biomass suggests the following temperature ranges for initiation of pyrolysis (Kumar and Pratt, 1996):

- Hemicellulose: 150–350°C
- Cellulose: 275–350°C
- Lignin: 250–500°C.

The individual constituents undergo pyrolysis differently, making varying contributions to yields. For example, cellulose and hemicellulose are the main sources of volatiles in lignocellulose biomass. Of these, cellulose is a primary source of condensable vapor. Hemicellulose, on the other hand, yields more noncondensable gases and less tar than that released by cellulose (Reed, 2002,

p. II-109). Owing to its aromatic content, lignin degrades slowly, making a major contribution to the char yield.

Cellulose decomposes over a narrow temperature range of 300–400°C (Fig. 4.5A). In the absence of any catalyst, pure cellulose pyrolyzes predominantly to a monomer, levoglucosan (Diebold and Bridgwater, 1997). Above 500°C, the levoglucosan vaporizes, with negligible char formation, thus contributing mainly to gas and oil yields.

Hemicelluloses are the least-stable components of wood, perhaps because of their lack of crystallinity (Reed, 2002, p. II-102). It decomposes within 200–300°C (Fig. 4.5A).

Unlike cellulose, lignin decomposes over a broader temperature range of 280–500°C, with the maximum release rate occurring at 350–450°C (Kudo and Yoshida, 1957). Lignin pyrolysis produces more aromatics and char than that produced by cellulose (Soltes and Elder, 1981). It yields about 40% of its weight as char under a slow heating rate at 400°C (Klass, 1998). Lignin makes a modest contribution to the liquid yield (~35%), which contains aqueous components and tar. It yields phenols via cleavage of ether and carbon–carbon linkages (Mohan et al., 2006). The gaseous product of lignin pyrolysis is only about 10% of its original weight.

5.3.2 Effect of Pyrolysis Temperature

During pyrolysis, a fuel particle is heated at a defined rate from the ambient to a maximum temperature, known as the *pyrolysis temperature*. The fuel is held there until completion of the process. The pyrolysis temperature affects both composition and yield of the product. Fig. 5.6 is an example of how, during the pyrolysis of a biomass, the release of some product gases changes with different temperatures. We can see that the release rates vary widely for different gaseous constituents.

The amount of char produced also depends on the pyrolysis temperature. Low temperatures result in greater amount of char; high temperatures result in less. Fig. 5.7 shows how the amount of solid char produced from the pyrolysis of a biomass decreases with increasing temperature, but the heating value of the char increases with temperature. This happens because the fixed carbon, which has a higher heating value, in the char increases while the volatile content of the char decreases. The amount of noncondensable gas (CO_2 , CO , H_2 , CH_4) increases with temperature.

5.3.3 Effect of Heating Rate

The rate of heating of biomass particles has an important influence on the yield and composition of the pyrolysis product. Rapid heating to a moderate temperature (400–600°C) yields higher condensable volatiles and hence more liquid, while slower heating to that temperature produces more char. For example,

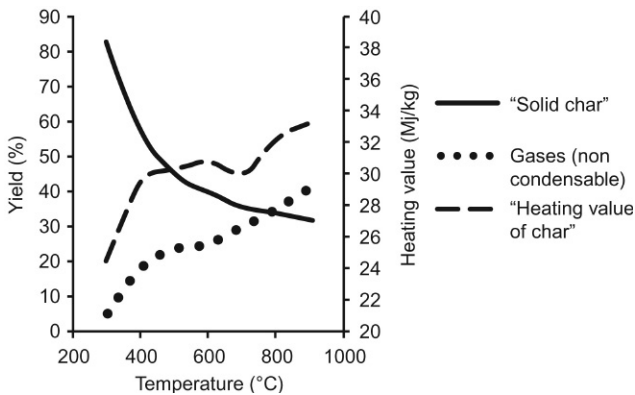


FIGURE 5.7 Char yield from pyrolysis decreases with temperature while gas yield increases. Heating value of the solid char produced increases with temperature. ((Data for grape bagasse (0.63–1.0 mm and HHV–17.2 MJ/kg dry) replotted from Encinar, J.M., Beltran, F.J., Bernalte, A., Ramiro, A., Gonzalez, J.F., 1996. Pyrolysis of two agricultural residues: olive and grape bagasse: influence of particle size and temperature. *Biomass Bioenergy* 11(5), 397–409.).)

Debdoubi et al. (2006) observed that during pyrolysis of Esparto, when the heating rate increased from 50°C/min to 250°C/min, the liquid yield increased from 45% to 68.5% at a pyrolysis temperature of 550°C.

The heating rate alone, however, does not define the pyrolysis product. The residence time of the product in the reactor is also important. During slow heating, a slow or gradual removal of volatiles from the reactor permits a secondary reaction to occur between char particles and volatiles, leading to a secondary char formation.

The operating parameters of a pyrolyzer are adjusted to meet the requirement of the final product of interest. Tentative design norms for heating in a pyrolyzer include the following (Table 5.1):

1. To maximize char production, use a slow heating rate (<0.01–2.0°C/s), a low final temperature, and a long gas residence time.
2. To maximize liquid yield, use a high heating rate, a moderate final temperature (450–600°C), and a short gas residence time.
3. To maximize gas production, use a moderate to slow heating rate, a high final temperature (700–900°C), and a long gas residence time.

Production of charcoal through carbonization uses step (1). Fast pyrolysis uses step (2) to maximize liquid yield. Step (3) is used when gas production is to be maximized.

5.3.4 Effect of Particle Size

The composition, size, shape, and physical structure of the biomass could exert some influence on the pyrolysis product through their effect on heating rate.

Finer biomass particles offer less resistance to the escape of condensable gases, which therefore escape relatively easily to the surroundings before undergoing secondary cracking. This results in a higher liquid yield. Larger particles, on the other hand, facilitate secondary cracking due to the higher resistance they offer to the escape of the primary pyrolysis product. For this reason, older methods of charcoal production used stacks of large-size wood pieces in a sealed chamber (Fig. 5.2).

5.3.5 Effect of Catalyst

Catalysts could exert important influence on pyrolysis especially in increasing the liquid yield. Waste treatment like plastics recycling could be done effectively through catalytic pyrolysis (Jorn, 2015). Catalyst like clay materials, molecular sieves, such as HZSM-5, ZSM-5, MCM-41, SBA-15, HUSV, REV and their modified catalysts are most widely used in catalytic pyrolysis of biomass.

5.4 PYROLYSIS KINETICS

A study of pyrolysis kinetics provides important information for the engineering design of a pyrolyzer or a gasifier. It also helps explain how different processes in a pyrolyzer affect product yields and composition. Three major processes that influence the pyrolysis rate are chemical kinetics, heat transfer, and mass transfer. This section describes the physical and chemical aspects that govern the process.

5.4.1 Physical Aspects

From a thermal standpoint, we may divide the pyrolysis process into following four stages though the boundaries between these steps are not sharp:

1. *Drying* ($\sim 100^{\circ}\text{C}$). During the initial phase of heating at low temperature, the free moisture and some loosely bound water in biomass is released. The free moisture evaporates, and then the heat is conducted into the biomass interior (Fig. 5.4). If the humidity is high, the bound water aids the melting of the lignitic fraction, which solidifies on subsequent cooling. This phenomenon is used in *steam bending* of wood, which is a popular practice for shaping it for furniture (Diebold and Bridgwater, 1997).
2. *Initial stage* ($100\text{--}300^{\circ}\text{C}$). In this stage, exothermic dehydration of the biomass takes place with the release of water and low-molecular-weight gases like CO and CO₂. Torrefaction takes place in this stage.
3. *Intermediate stage* ($> 200^{\circ}\text{C}$). This is *primary pyrolysis*, and it takes place in the temperature range of $200\text{--}600^{\circ}\text{C}$. Most of the vapor or precursor to bio-oil is produced at this stage. Large molecules of biomass particles decompose into char (*primary char*), condensable gases (vapors and precursors of the liquid yield), and noncondensable gases.

4. *Final stage* ($\sim 300\text{--}900^\circ\text{C}$). The final stage of pyrolysis involves secondary cracking of the vapor released into char and noncondensable gases. If they reside in the biomass long enough, relatively large-molecular-weight condensable gases can crack, yielding additional char (called *secondary char*) and gases. This stage typically occurs above 300°C (Reed, 2002, p. III-6). The condensable gases, if removed quickly from the reaction site, condense outside in the downstream reactor as tar or biooil.

Temperature has a major influence on the product of pyrolysis. A higher pyrolysis temperature favors production of hydrogen, and that increases quickly above 500°C (Fig. 5.6). Above 900°C the shift reaction (Eq. (7.16)) makes additional contribution to the hydrogen yield. The carbon dioxide yield on the other hand is high at lower temperatures and decreases at higher temperatures. The release of hydrocarbon gases peaks at around 450°C and then starts decreasing above 500°C , boosting the generation of hydrogen.

Hot char particles can catalyze the primary cracking of the vapor released within the biomass particle and the secondary cracking occurring outside the particle but inside the reactor. To avoid cracking of condensable gases and thereby increasing the liquid yield, rapid removal of the condensable vapor is very important. The shorter the residence time of the condensable gas in the reactor, the less the secondary cracking and hence the higher the liquid yield.

As mentioned earlier, some overlap of the above stages in the pyrolysis process is natural. For example, owing to its low thermal conductivity ($0.1\text{--}0.05\text{ W/m K}$), a large log of wood may be burning outside while its interior may still be in the drying stage, and water may be squeezed out from the ends. During a forest fire, this phenomenon is often observed. The observed intense flame comes primarily from the combustion of the pyrolysis products released from the wood interior rather than from the burning of the exterior surface.

5.4.2 Chemical Aspects

As mentioned earlier in Section 3.3.2, a typical biomass has three main polymeric components: cellulose, hemicellulose, and lignin. Each of them has its characteristic mode of decomposition, rate of degradation, and preferred temperature range of decomposition. These are explained below.

5.4.2.1 Cellulose

Decomposition of cellulose is a complex multistage process. The Broido–Shafizadeh model (Bradbury et al., 1979) is the best-known description of this process and can be applied, at least qualitatively, to most biomass (Bridgwater et al., 2001). According to this model (Fig. 5.8) the pyrolysis process involves an intermediate prereaction (I) followed by two competing first-order reactions:

- *Reaction I*: Intermediate prereaction (I)
- *Reaction II*: dehydration (dominates at low temperature and slow heating rates)

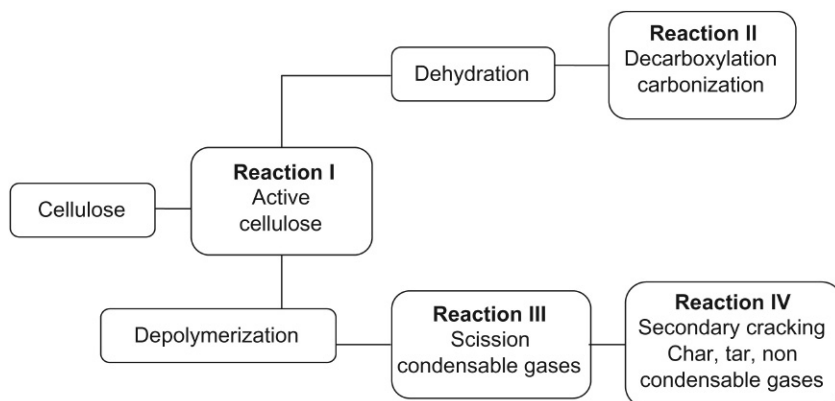


FIGURE 5.8 Modified “Broido–Shafizadeh” model of cellulose, which can be reasonably applied to the whole biomass.

- *Reaction III*: depolymerization (dominates at fast heating rates)

Reaction II involves dehydration, decarboxylation, and carbonization through a sequence of steps to produce char and noncondensable gases like water vapor, carbon dioxide, and carbon monoxide. It is favored at low temperatures ($<300^{\circ}\text{C}$) (Soltes and Elder, 1981, p. 82) and slow heating rates (Reed, 2002, p. II-113).

Reaction III involves depolymerization and scission, forming vapors that include both tar and condensable gases. The condensable vapor, if permitted to escape the reactor quickly, can condense as biooil or tar. Levoglucosan is an important intermediate product in this step (Klass, 1998, p. 228), which is favored under faster heating rates (Reed, 2002, p. II-113) and higher temperatures ($>300^{\circ}\text{C}$) (Soltes and Elder, 1981, p. 82).

If the condensable vapor is allowed to reside longer inside the biomass within the reactor, it can undergo secondary reactions (reaction IV), cracking the vapor into secondary char, tar, and gases (Fig. 5.8).

Reaction I precedes reactions II and III and forms a very short-lived intermediate product called *active cellulose*, which is liquid at reaction temperature but solid at room temperature (Boutin and L    , 2001; Bradbury et al., 1979; Bridgwater et al., 2001).

Unstable species produced from reaction I are not detected in the final production in most pyrolysis processes. Reaction I is, however, apparent in most pyrolysis processes. It is, however, apparent in ablative pyrolysis, where wood is dragged over a hot metal surface to produce the feeling of smooth lubrications due to the process of intermediate liquid product, “active cellulose.”

The Broido–Shafizadeh model, though developed for one biomass component (cellulose), can be applied to the pyrolysis of an entire biomass such as wood. Depolymerization (reaction III) (Fig. 5.8) has activation energies higher

than those of dehydration (reaction II) (Bridgwater et al., 2001). Thus, a lower temperature and a longer residence time favor this reaction, producing primarily char, water, and carbon dioxide. On the other hand, owing to its higher activation energy, reaction III is favored at higher temperatures, fast heating rate, and longer residence times, yielding mainly gas. Moderate temperature and short vapor residence time avoid secondary cracking, producing mainly condensable vapor—the precursor of biooil, which is of great commercial importance. For cellulose pyrolysis, Table 5.3 gives some suggested reaction rate constants for reactions I, II, III, and IV.

If a log of wood is heated very slowly, it shows glowing ignition, because reaction II predominates under this condition, producing mostly char, which ignites in contact with air without a yellow flame. If the wood is heated faster, it burns with a yellow flame, because at a higher heating rate, reaction III predominates, producing more vapors or tar, both of which burn in air with a bright yellow flame.

5.4.2.2 Hemicellulose

Hemicellulose produces more gas and less tar. Additionally, it also produces less char than that by cellulose. However, hemicellulose produces the same amount of aqueous product of pyroligneous acid (Soltes and Elder, 1981, p. 84). Hemicellulose undergoes rapid thermal decomposition (Demirbas, 2000), which starts at a temperature lower than that for cellulose or lignin. It contains more combined moisture than lignin, and its softening point is lower as well. The exothermic peak of hemicellulose appears at a temperature lower than that for lignin (Demirbas, 2000). In slow pyrolysis of wood, hemicellulose pyrolysis

TABLE 5.3 Rate Constants (Eq. 5.5) for Pyrolysis of Cellulose According to Broido–Shafizadeh Model

Reaction ($dm/dt = A_i(V_i^3 - V_i)e^{-E_i/RT}$)	A_i (s^{-1})	E_i (kJ/mol)
I—First degradation (active cellulose), Bradbury et al. (1979)	2.8×10^{19}	243
II—Dehydration (char + gas), Bradbury et al. (1979)	1.31×10^{10}	153
III—Depolymerization (tars), Bradbury et al. (1979)	3.16×10^{14}	198
IV—Secondary cracking (gas, char), Uden et al. (1988)	4.28×10^6	107.5

begins at 130–194°C, with most of the decomposition occurring above 180°C (Mohan et al., 2006, p. 126).

5.4.2.3 Lignin

Pyrolysis of lignin typically produces about 55% char (Soltes and Elder, 1981), 15% tar, 20% aqueous components (pyroligneous acid), and about 12% gases. It is more difficult to dehydrate lignin than cellulose or hemicellulose (Mohan et al., 2006, p. 127). The tar produced from it contains a mixture of phenolic compounds, one of which, phenol, is an important raw material of green resin (a resin produced from biomass). The aqueous portion comprises methanol, acetic acid, acetone, and water. The decomposition of lignin in wood can begin at 280°C, continuing to 450–500°C and can reach a peak rate at 350–450°C (Kudo and Yoshida, 1957).

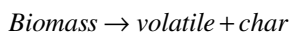
5.4.3 Kinetic Models of Pyrolysis

To optimize the process parameters and maximize desired yields, knowledge of the kinetics of pyrolysis is important. However, it is very difficult to obtain reliable data of kinetic rate constants that can be used for a wide range of biomass and for different heating rates. This is even more difficult for fast pyrolysis as it is a nonequilibrium and non-steady-state process. For engineering design purposes, a “black-box” approach can be useful, at least for the first approximation. The following discussion presents a qualitative understanding of the process based on data from relatively slow heating rates.

Kinetic models of the pyrolysis of lignocellulosic fuels like biomass may be broadly classified into three types (Blasi, 1993):

1. *One-stage global single reactions.* The pyrolysis is modeled by a one-step reaction using experimentally measured weight-loss rates.
2. *One-stage, multiple reactions.* Several parallel reactions are used to describe the degradation of biomass into char and several gases. A one-stage simplified kinetic model is used for these parallel reactions. It is useful for determination of product distribution.
3. *Two-stage semiglobal reactions.* This model includes both primary and secondary reactions, occurring in series.

One-stage or overall single-reaction model is the basic and simplest one. This model is based on a single overall reaction, which neglects the presence of ash and assumes moisture to remain in the volatile:



The rate of pyrolysis depends on the unpyrolyzed mass of the biomass. Thus, the decomposition rate of mass, m_b , in the primary pyrolysis process may be written as:

$$\frac{dm_b}{dt} = -k(m_b - m_c) \quad (5.2)$$

Here, m_c is the mass of char remaining after complete conversion (kg), k is the first-order reaction rate constant (s^{-1}), and t is the time (s).

The fractional change, X , in the mass of the biomass may be written in non-dimensional form as:

$$X = \frac{(m_0 - m_b)}{(m_0 - m_c)} \quad (5.3)$$

where m_0 is the initial mass of the biomass (kg).

Substituting fractional conversion for the mass of biomass in Eq. (5.2),

$$\frac{dX}{dt} = -k(1 - X) \quad (5.4)$$

Solving this equation, we get:

$$X = 1 - A \exp(-kt) \quad (5.5)$$

where A is the preexponential coefficient, $k = E/RT$. E is the activation energy (J/mol), R is the gas constant (J/mol K), and T is the temperature (K).

Owing to the difficulties in extracting data from dynamic thermogravimetric analysis, reliable data on the preexponential factor, A , and the activation energy, E , are not easily available for fast pyrolysis (Reed, 2002, p. II-103). However, for slow heating, we can obtain some reasonable values. If the effect of secondary cracking and the heat-transfer limitation can be restricted, the weight-loss rate of pure cellulose during pyrolysis can be represented by an irreversible, one-stage global first-order equation.

For the one-step global reaction model, Table 5.4 lists values of the activation energy E and the preexponential factor A , for the pyrolysis of various biomass types at a relatively slow heating rate. Other models are not discussed here, but details are available in several publications, including Blasi (1993).

5.5 HEAT TRANSFER IN A PYROLYZER

The preceding discussions assume that the heat or mass transport rate is too high to offer any resistance to the overall rate of pyrolysis. This is true at a temperature of 300–400°C (Turner and Mann, 1981), but at higher temperatures, heat and mass transport influence the overall rate and so they cannot be neglected. This section deals with heat transport during pyrolysis.

During pyrolysis, heat is transported to the particle's outer surface by radiation and convection. Thereafter, it is transferred to the interior of the particle by conduction and pore convection (Fig. 5.4). The following modes of heat transfer are involved in this process (Babu and Chaurasia, 2004b).

TABLE 5.4 Kinetic Rate Constants for One-Step Single-Reaction Global Model

Fuel	Temperature (K)	E (kJ/mol)	A (s ⁻¹)	References
Cellulose	520–1270	166.4	3.9×10^{11}	Lewellen et al. (1977)
Hemicellulose	520–1270	123.7	1.45×10^9	Min (1977)
Lignin	520–1270	141.3	1.2×10^8	Min (1977)
Wood	321–720	125.4	1.0×10^8	Nolan et al. (1973)
Almond shell	730–880	95–121	1.8×10^6	Font et al. (1990)
Beech saw-dust	450–700	84 ($T > 600\text{K}$)	2.3×10^4	Barooah and Long (1976)

- Conduction inside the particle
- Convection inside the particle pores
- Convection and radiation from the particle surface

In a commercial pyrolyzer or gasifier, the system heats up a heat-transfer medium first; that, in turn, transfers the heat to the biomass. The heat-transfer medium can be one or a combination of the following:

- Reactor wall (for vacuum reactor)
- Gas (for entrained-bed or entrained-flow reactor)
- Heat-carrier solids (for fluidized bed)

Bubbling fluidized beds use mostly solid–solid heat transfer. Expression for gas to particle heat transfer in bubbling fluidized bed is given in Kunii and Levenspiel (1991, pp. 268–272). Circulating fluidized beds (CFB) and transport reactors make use of their excellent gas–solid heat transfer, good solid–solid heat transfer and superior mixing in expanded bed. Basu (2015) gives expression for estimation of heat transfer to coarse particle in CFB of fine particles.

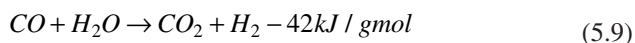
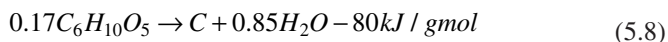
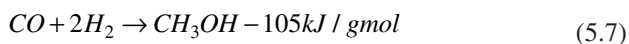
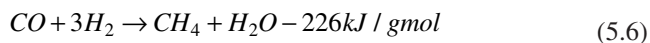
Since heat transfer to the interior of the biomass particle is mostly by thermal conduction, the low thermal conductivity of biomass (~ 0.1 W/m K) is a major deterrent to the rapid heating of its interior. For this reason, even when the heating rate of the particle's exterior is as fast as $10,000^\circ\text{C/s}$, the interior can be heated at a considerably slower rate for a coarse particle. Because of such slower heating of the interior, the secondary reactions within the particles become increasingly important for larger particle sizes, and as a

result the liquid yield reduces (Scott and Piskorz, 1984). Experimental results (Seebauer et al., 1997), however, do not show much effect of particle size of the biomass.

5.5.1 Is Pyrolysis Autothermal?

An important question for designers is whether a pyrolyzer can meet its own energy needs or is dependent on external energy. The short and tentative answer is that a pyrolyzer as a whole is not energy self-sufficient. The reaction heat is inadequate to meet all energy demands, which include heat required to raise the feed and any inert heat-transfer media to the reaction temperature, heat consumed by endothermic reactions, and heat losses from the reactor. In most cases, it is necessary to burn at least a part of the noncondensable gases and the char produced to provide the heat required. If that is not adequate, external heat sources are necessary to supply the energy required for pyrolysis. Next section discusses the heat requirement of reactions taking place in a pyrolyzer.

The dehydration (reaction II) process is exothermic, while depolymerization (reaction III) and secondary cracking (reaction IV) are endothermic (Bridgwater et al., 2001). Among reactions between intermediate products of pyrolysis, some are exothermic and some are endothermic. In general, pyrolysis of hemi-cellulose and lignin is exothermic. Cellulose pyrolysis is endothermic at lower temperatures ($<400\text{--}450^\circ\text{C}$), and it becomes exothermic at higher temperatures owing to the following exothermic reactions (Klass, 1998):



(All equations refer to a temperature of 1000K, and $C_6H_{10}O_5$ represents the cellulose monomer.)

For this reason, a properly designed system initially requires external heat only until the required temperature is reached.

The char production process from cellulose (Eq. (5.8)) is slightly exothermic. However, at a higher temperature, when sufficient hydrogen is produced by reaction (Eq. (5.9)), other exothermic reactions (Eqs. (5.6 and 5.7)) can proceed. At low temperatures and short residence times of volatiles, only endothermic primary reactions are active (heat of reaction -225 kJ/kg), while at high temperatures exothermic secondary reactions (heat of reaction 20 kJ/kg) are active (Blasi, 1993).

In conclusion, for design purposes, one may neglect the heat of reaction for the pyrolysis process, but it is necessary to calculate the energy required for vaporization of products and for heating feedstock gases to the pyrolysis temperature (Boukiss et al., 2007).

Design of pyrolysis reactor could allow for partial combustion of the char into CO through the reaction, $[C + \frac{1}{2} O_2 = CO - 111 \text{ kJ/gmol}]$ to provide the heat required in the system. The air supply should be controlled to avoid excess oxygen in the system. Complete combustion of char to CO₂ may be allowed only if the combustion reaction could take place outside the pyrolysis zone.

For highest liquid yield the reactor should be designed to operate at 500°C and very short residence time of gas in the reaction zone (Boukiss et al., 2007).

5.5.2 Mass Transfer Effect

Mass transfer can also influence the pyrolysis product. For example, a sweep of gas over the fuel quickly removes the products from the pyrolysis environment. Thus, when mass transfer rate is high the secondary reactions such as thermal cracking, repolymerization, and recondensation are minimized (Sensoz and Angin, 2008).

5.6 PYROLYZER TYPES

Pyrolyzers have been used since ancient times to produce charcoal (Fig. 5.2). Early pyrolyzers operated in batch mode using a very slow rate of heating for long periods to maximize the production of char. If the objective of pyrolysis is to produce the maximum amount of liquid or gas, then the rate of heating, the peak pyrolysis temperature, and the duration of pyrolysis has to be chosen differently. Table 5.5 lists the choice of heating rate, temperature, and gas residence time for maximization of the yield.

The choice of these operating parameters could influence the choice of reactor type. Several types of reactors have been developed for pyrolysis. Based on the gas–solid contacting mode in the reactor, they can be broadly classified as fixed bed, fluidized bed, and entrained bed, and then further subdivided depending on design configuration. The following are some of the major pyrolyzer designs in use:

1. Fixed or moving bed (Fig. 5.2)
2. Bubbling fluidized bed (Fig. 5.5)
3. Circulating fluidized bed (CFB) (Fig. 5.9)
4. Ultrarapid reactor (Fig. 5.10)
5. Ablative reactor (Fig. 5.11)
6. Rotating cone (Fig. 5.12)
7. Vacuum reactor (Fig. 5.13)
8. Solar pyrolysis (Fig. 5.14)

TABLE 5.5 Effect of Operating Variables on the Pyrolysis Yield

To Maximize Yield of	Maximum Temperature	Heating Rate	Gas Residence Time
Char	Low	Slow	Long
Liquid	Low (~500 °C) ^a	High	Short
Gas	High	Low	Long

^aBridgwater (1999).
Source: Table compiled from Demirbas, A., 2001. Biomass resources facilities and biomass conversion processing for fuels and chemicals. *Energ. Convers. Manage.* 42 (11), 1357–1378.

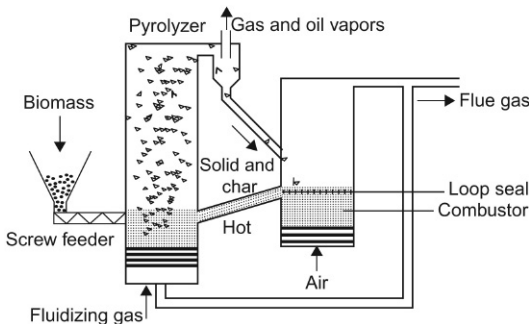


FIGURE 5.9 Circulating fluidized bed pyrolyzer.

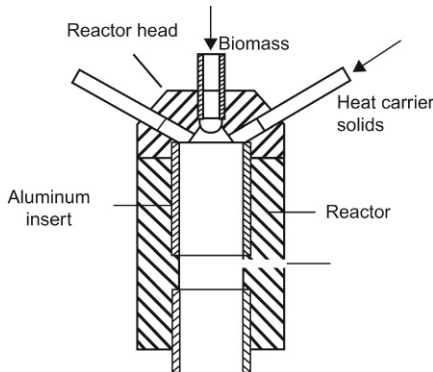


FIGURE 5.10 Ultrarapid pyrolyzer.

5.6.1 Fixed-Bed Pyrolyzer

Fixed-bed pyrolysis, operating in batch mode, is the oldest pyrolyzer type. Heat for the thermal decomposition of biomass is supplied either from an external source or by allowing limited combustion as in a beehive oven (Fig. 5.2). The

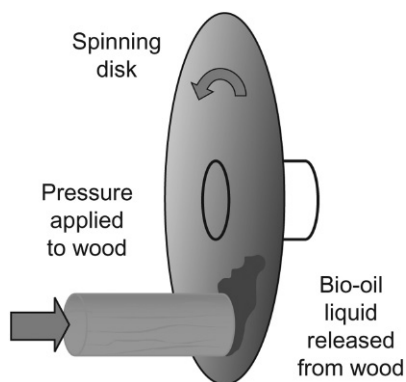


FIGURE 5.11 Ablative pyrolyzer.

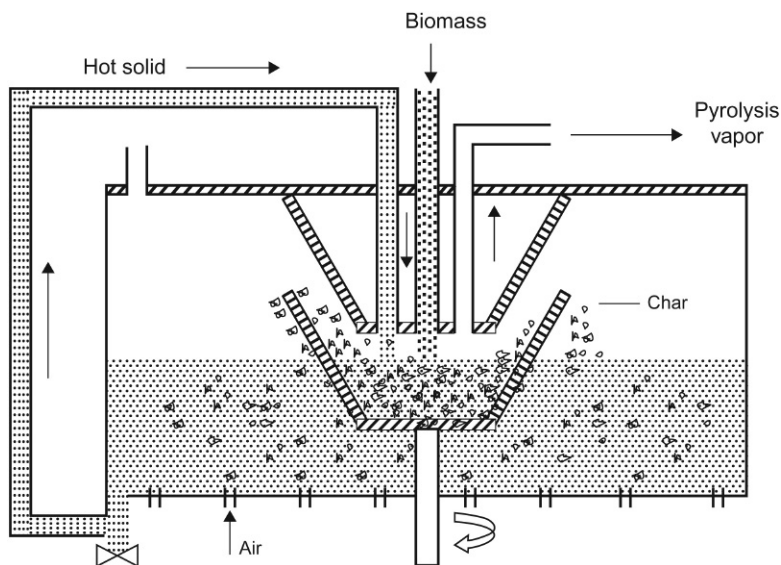


FIGURE 5.12 Rotating pyrolyzer.

product may flow out of the pyrolyzer because of volume expansion of the gaseous product while the solid char remains in the reactor. In some designs, a sweep gas is used for effective removal of the product gas from the reactor. This gas is necessarily inert and oxygen free. The main product of this type of pyrolysis is char owing to the relatively slow heating rate and the long residence time of the product in the pyrolysis zone.

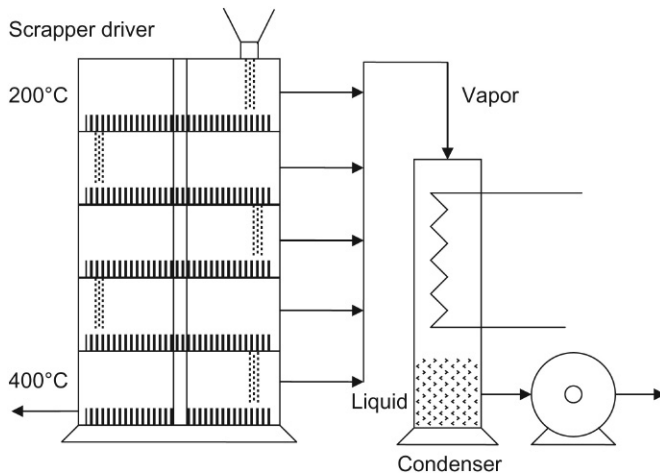


FIGURE 5.13 Vacuum pyrolyzer.

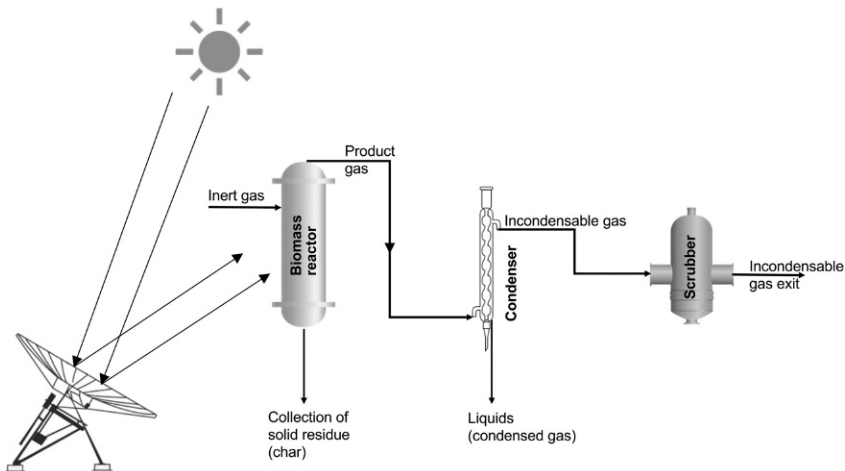


FIGURE 5.14 Solar pyrolyzer draw new.

5.6.2 Bubbling-Bed Pyrolyzer

Fig. 5.5 show bubbling fluidized-bed pyrolyzers. Crushed biomass (2–6 mm) is fed into a bubbling bed of hot sand or other solids. The bed is fluidized by an inert gas such as recycled flue gas. Intense mixing of inert bed solids (sand is commonly used) offers good and uniform temperature control. It also provides high heat transfer to biomass solids. The residence time of the solids is considerably higher than that of the gas in the pyrolyzer.

The required heat for pyrolysis may be provided either by burning a part of the product gas in the bed, as shown in Fig. 5.5, or by burning the solid char in a separate chamber and transferring that heat to the bed solids. The pyrolysis product would typically contain about 70%–75% liquid on dry wood feed. As shown in the figure, the char in the bed solids acts as a vapor-cracking catalyst, so its separation through elutriation or otherwise is important if the secondary cracking is to be avoided to maximize the liquid product. The entrained char particles are separated from the product gas using single- or multistage cyclones. A positive feature of a bubbling fluidized-bed pyrolyzer is that it is relatively easy to scale up.

5.6.3 CFB Pyrolyzer

Fig. 5.9 shows schematic of a circulating fluidized bed (CFB) type of pyrolyzer. This type works on the same principle as the bubbling fluidized bed except that the bed is highly expanded and solids continuously recycle around an external loop comprising a cyclone and loop seal (Basu, 2006, p. 35). The riser of the CFB operates in a special hydrodynamic regime known as *fast bed*. It provides good temperature control and uniform mixing around the entire height of the unit. The superficial gas velocity in a CFB is considerably higher than that in a bubbling bed. High velocity combined with excellent mixing allows a CFB to have large throughputs of biomass. Here, gas and solids move up the reactor with some degree of internal refluxing. As a result, the residence time of average biomass particles is longer than that of the gas, but the difference is not as high as it is in a bubbling bed. A major advantage of this system is that char entrained from the reactor is easily separated and burnt in an external fluidized bed. The combustion heat is transferred to the inert bed solids that are recycled to the reactor by means of a loop seal.

5.6.4 Ultrarapid Pyrolyzer

High heating rate and short residence time in the pyrolysis zone are two key requirements of high liquid yield. The ultrarapid pyrolyzer, shown in Fig. 5.10, developed by the University of Western Ontario provides extremely short mixing (10–20 ms), reactor residence (70–200 ms), and quench (~20 ms) times. The inert gas nitrogen is heated at 100°C above the reactor temperature and injected at very high velocity into the reactor to bombard a stream of biomass injected in the reactor. The reactor can also use a heat-carrier solid like sand that is heated externally and bombarded on a biomass stream through multiple jets. Such a high-velocity impact in the reactor results in an exceptionally high heating rate. The biomass is thus heated to the pyrolysis temperature in a few milliseconds. The pyrolysis product leaves the reactor from the bottom and is immediately cooled to suppress a secondary reaction or cracking of the oil vapor. This process is therefore able to maximize the liquid yield during pyrolysis.

Ensyn of Canada developed a commercial process where biomass is introduced into a vessel and rapidly heated to 500°C by a tornado of upflowing hot sand; it is then cooled within seconds. The heating rate is of the order of 1000°C/s, and the reactor residence time is from a few hundredths of a millisecond to a maximum of 5 s, which gives a liquid yield as high as 83% for wood (Hulet et al., 2005).

5.6.5 Ablative Pyrolyzer

This process, shown in Fig. 5.11, involves development of high pressure between biomass particles and hot reactor wall. This allows uninhibited heat transfer from the wall to the biomass, causing the liquid product to melt out of the biomass the way frozen butter melts when pressed against a hot pan. The biomass sliding against the wall leaves behind a liquid film that evaporates and immediately leaves the pyrolysis zone, which is the interface between biomass and wall. As a result of high heat transfer and short gas residence time, a liquid yield as high as 80% is reported (Diebold and Power, 1988). The pressure between biomass and wall is created either by mechanical means or by centrifugal force. In a mechanical system, a large piece of biomass is pressed against a rotating hot plate.

5.6.6 Rotating-Cone Pyrolyzer

In this process, biomass particles are fed into the bottom of a rotating cone (360–960 rev/min) together with an excess of heat-carrier solid particles (Fig. 5.12). Centrifugal force pushes the particles against the hot wall; the particles are transported spirally upward along the wall. Owing to its excellent mixing, the biomass undergoes rapid heating (5000 K/s) and is pyrolyzed within the small annular volume of the cone. The product gas containing biooil vapor leaves through another tube, while the solid char and sand spill over the upper rim of the rotating cone into a fluidized bed surrounding it, as shown in Fig. 5.12. The liquid product is subsequently condensed out of the vapor. The char burns in the fluidized bed, and this combustion helps heat the cone as well as the solids that are recycled to it to supply heat for pyrolysis. Special features of this reactor include very short solids residence time (0.5 s) and a small gas-phase residence time (0.3 s). These typically provide a high (60%–70% on dry feed) liquid yield (Hulet et al., 2005). The absence of a carrier gas is another advantage of this process. Its complex geometry of the system may raise some scale-up issues.

5.6.7 Vacuum Pyrolyzer

A vacuum pyrolyzer, as shown in Fig. 5.13, comprises a number of stacked heated circular plates. A vacuum pump maintains vacuum that decrease the boiling point of gas products and avoids adverse chemical reactions. The top plate is at about 200°C while the bottom one is at about 400°C. Biomass fed to the

top plate drops into successive lower plates by means of scrapers. The biomass undergoes drying and pyrolysis while moving over the plates. No carrier gas is required in this pyrolyzer. Only char is left when the biomass reaches the lowest plate. Though the heating rate of the biomass is relatively slow, the residence time of the vapor in the pyrolysis zone is short. As a result, the liquid yield in this process is relatively modest, about 35%–50% on dry feed, with a high char yield.

5.6.8 Solar Pyrolyzer

Photosynthesis process stores solar energy in biomass in chemical form. Pyrolysis is an attractive option for unlocking major part of the stored energy in liquid form. Production of biofuels could be potential means of storage of solar energy in chemical form. But pyrolysis being endothermic process it requires an external energy input to reach 400–650 °C (Table 5.2), which is the preferred operating temperature of pyrolysis. Fossil fuels often provide this energy, but a more sustainable approach would be to use concentrated solar energy instead. Concentrated solar radiation focused on biomass (Fig. 5.14) could rapidly heat it to the required high pyrolysis temperature while the reactor remains at lower temperature reducing the rate of secondary decomposition. Amongst the different types of solar concentrators parabolic trough type is best for tubular reactors. Some experiments (Morales et al., 2014) shows high liquid yield and conversion rate to increase with decreasing biomass particle size.

5.7 PYROLYZER DESIGN CONSIDERATIONS

This section discusses considerations in the design of pyrolyzer for production of liquid fuel and charcoal.

5.7.1 Production of Liquid Through Pyrolysis

Pyrolysis is one of several means of production of liquid fuel from biomass. The maximum yield of organic liquid (pyrolytic oil or biooil) from thermal decomposition may be increased to as high as 80% (dry weight) through proper choice of heating rate and pyrolysis temperature, and evacuation of product from the reaction zone. Table 5.1 gives the effect of heating rate, pyrolysis temperature, and residence time on the pyrolysis product. These findings may be summarized as follows:

- A slower heating rate, a lower pyrolysis temperature, and a longer residence time maximize the yield of solid char.
- A higher heating rate, a higher pyrolysis temperature, and a shorter residence time maximize the gas yield.
- A higher heating rate, an intermediate pyrolysis temperature, and a shorter residence time maximize the liquid yield.

Heat transfer is a major consideration in the design of a pyrolyzer. The heat balance for a typical pyrolyzer may be written as:

[Heat released by char conversion] + [Heat in incoming stream] = [Heat required for pyrolysis] + [Surface heat loss] + [Heat in exiting products]

$$\frac{[\text{Heat released by char combustion}] + [\text{Heat in incoming stream}]}{[\text{Heat required for pyrolysis}] + [\text{Heat loss}]} \quad (5.10)$$

Estimation of surface heat loss accurately is difficult before the unit is designed. So, for preliminary assessment, experience dictates it to be 10% of the heat in the incoming stream (Boukis et al., 2007, p. 1377). For an integrated system, air supply needs to be controlled to avoid reduction in pyrolysis yield.

Fast or flash pyrolysis is especially suitable for pyrolytic liquefaction of biomass. The liquid yield is highest at 500°C and drops sharply above and below this temperature (Boukis et al., 2007). The residence time is generally in the range of 0.1–2.0 s. These values depend on several factors, including the type of biomass (Klass, 1998). We can use a kinetic model [Liden et al. (1988) for example] for a reasonable assessment of liquid yields over a wide range of conditions.

The product of pyrolysis is a mixture of several hydrocarbons, which allows production of fuel and chemicals through appropriate refining methods. The heating value of the liquid produced is a little lower or in the same range (13–18 MJ/kg) as that of the parent biomass. The liquid contains several water-soluble sugars and polysaccharide-derivative compounds and water-insoluble pyrolytic lignin. It contains a much higher amount of oxygen (~50%) than does most fuel oil. It is also heavier (specific gravity ~1.3) and more viscous. Unlike fuel oil, pyrolytic oil increases in viscosity with time because of polymerization. This oil is not self-igniting like fuel oil, and as such it cannot be blended with diesel for operating a diesel engine.

Pyrolytic oil, the liquid product of pyrolysis, is a good source of some useful chemicals, like natural food flavoring, that can be extracted, leaving the remaining product for burning. It may be subjected to hydrocracking to produce gasoline and diesel.

5.7.2 Effect of catalyst on liquid production

Catalysts can help increase liquid yield as well as produce superior grade of chemicals and transport fuels from biooil. Most biomass process begins with pyrolysis followed by catalytic upgrading, which is a post-pyrolysis upgrading. Integrated catalytic cracking where catalysts are used during pyrolysis is highly promising, but is yet to be explored and utilized fully.

Alkali metals like Na and K naturally occur in many biomass but they increase the secondary reaction, reducing liquid yield and quality (Brown, 2011). Zeolite catalysts can increase the liquid yield of biomass pyrolysis to some ex-

tent. Direct production of pyrolysis product into gasoline in presence of ZSM-5 has been attempted (Carlson et al., 2008). Catalysts like K_2CO_3 , Na_2CO_3 also improve liquid yield but right choice of temperature has greater effect on liquid yield (Gullu, 2003).

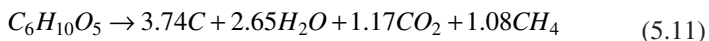
Catalytic upgrading of pyrolysis product is more established. Brown (2011) lists a large number of catalysts used by different groups. A major part of this upgrade involves reduction of oxygen content of the biooil through deoxygenation, a process much enhanced by catalysts.

5.8 BIOCHAR

Biochar is a solid product of the slow pyrolysis process discussed in Section 5.2.2.1. It is an excellent fuel and at the same time, a great soil amendment agent. It provides an alternative to complete burning of agricultural products or forest residues that release the entire carbon to the atmosphere. Biochar production on the other hand retains a part of that carbon in stable solid form in soil for hundreds of years. Owing to its growing importance for carbon sequestration, many institutions are taking a closer look at this.

Some researcher (Lal, 2008) describes biochar as a more effective means of reduction of atmospheric carbon inventory than other conventional means such as amine scrubbing with underground sequestration. Such biotic sequestration removes atmospheric CO_2 through photosynthesis. Another approach involves combining pyrolysis for energy production with biochar production for soil remediation and carbon sequestration (Lehman, 2007). It takes advantage of biochar's proven stability against decay and ability to retain nutrients.

Biochar typically contains 50%–90% fixed carbon, 0%–40% volatiles, 1%–15% moisture and 0.5%–5% ash. These values depend on the type of parent biomass, pyrolysis temperature, environment, and a host of other factors. Biochar, is a preferred product of slow pyrolysis at a moderate temperature of about 400°C. Thermodynamic equilibrium calculation shows that the char yield of most biomass may not exceed 35%. Table 5.6 gives the theoretical equilibrium yield of different products of biomass at different temperatures. Actual yield, however, could be much different. Assuming that cellulose represents biomass, the stoichiometric equation for production of charcoal (Antal and Gronli, 2003) may be written as:



Pyrolysis temperature is the most important parameter influencing the properties of biochar. For example, the Brunauer-Emmett-Teller (BET) surface area of coconut shell char increased continuously from 130 to 702 m^2/g between 400°C and 1000°C (Li et al., 2008). The cation exchange capacity of biochar also increased and the pH increases steadily, but the carbon yield or carbon recovery decreased with temperature within the temperature range of 200–800°C (Lehman, 2007).

TABLE 5.6 Thermodynamic Equilibrium Concentration of Pyrolysis of Cellulose at Different Temperatures

Products	Temperature (°C)				
200	300	400	500	600	
C	32	28	27	27	25.2
H ₂ O	36.5	32.5	9.5	27	22.5
CH ₄	8.5	10	10.5	10	9
CO ₂	23.9	28	32	35	36
CO	0	0	0.1	1.2	4.5

Source: Derived from Antal, M.J., Allen, S.G., Schulman, D., Xu, X., Divilio, R.J., 2000. Biomass gasification in super-critical water. Ind. Eng. Chem. Res. 39, 4040–4053.

Biochar has a special appeal in greenhouse gas reduction as its production can greatly increase the amount of carbon retained in the ground in stable form, similar to what is done for carbon sequestration. The carbon in agricultural residues and forest residues when left on the ground is released over the time to the atmosphere as CO₂ or CH₄, and thus return to the atmosphere. On the other hand, if biomass is converted into biochar, as much as 50% or more of the carbon contained in the biomass could stay in the soil as a stable biochar residue.

In most shifting cultivation systems around the world, the natural vegetation is burned after slashing. Between 38% and 84% of the biomass carbon is released to the atmosphere during such burn (Lehman et al., 2006). This is a very inefficient way of producing biochar. Pyrolysis provides the best means of production of biochar as it does not release harmful volatiles and smoke to the atmosphere while a making a good use of it for production of chemical and energy feedstock. Additionally, it allows recovery of good amount of fixed carbon of the biomass.

As mentioned earlier, biochar is produced through pyrolysis as the solid by-product. The quality of biochar is defined by its following characteristics:

- The BET or internal surface area
- pH of the char
- Cation exchange capacity (CEC) of biochar
- Carbon recovery in char

Above characteristics of biochar depend on how biochar is produced. It is thus influenced by the following three processes and feed parameters:

1. Temperature
2. Type of biomass
3. Reaction time

5.8.1 Potential Benefits of Biochar

Biochar has a number of benefits as listed below (<http://www.biochar.ca/>, <http://www.biocharfarms.org/>):

1. Sequesters carbon and thereby minimizes climate change
2. Carbon negative emission
3. Displaces carbon positive fossil fuels
4. Reduces nutrient losses in soils
5. Reduces fertilizer use
6. Enhances marginal soil productivity
7. Increases sustainable food production
8. Improves water retention, aeration, and tilth
9. Higher CEC

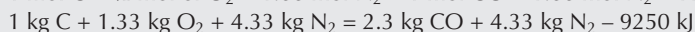
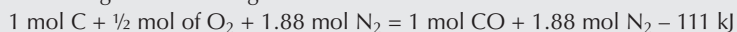
Example 5.1

A fluidized bed pyrolyzer operates at 400°C to pyrolyze biomass. For each kg of biomass the product of pyrolysis comprises 0.27 kg solid carbon in char, 0.095 kg H₂O, 0.105 kg CH₄, 0.32 kg CO₂ and 0.427 of condensable organics. The airflow into the pyrolyzer is controlled such that it does not leave any excess oxygen but provides the required heat for the system. Find the amount of air required per kg of biomass pyrolyzed. Ambient temperature is 25°C.

Neglect any heat requirement for the overall pyrolysis reactions. Take specific heat of condensable organics at 1.4 kJ/kg.C. The specific heat of CO, CO₂, N₂, CH₄ at 400°C is calculated as 1.035, 1.11, 0.98 and 3.42 kJ/kg.C respectively. Take the enthalpy of steam at 400°C is 3193 kJ/kg.

Solution

Energy demand of the pyrolyzer is met by partial combustion of carbon in char into CO through the following reaction:



Now, we calculate the heat in product gas of partial combustion leaving the system at 400°C as:

$$= 2.3 \times 1.03 \times (400 - 25) + 4.33 \times 0.98 \times (400 - 25) = 2486 \text{ kJ/kg of carbon}$$

Enthalpy of pyrolysis product leaving at 400°C per kg of biomass pyrolyzed is as below.

$$\text{CO}_2 = 0.32 \text{ kg} \sim 0.32 \times 1.11 \times (400 - 25) = 133.7 \text{ kJ/kg biomass}$$

$$\text{CH}_4 = 0.105 \text{ kg} \sim 0.105 \times 3.41 \times (400 - 25) = 134.5 \text{ kJ/kg biomass}$$

$$\text{H}_2\text{O} = 0.095 \text{ kg} \sim 0.095 \times 3193 = 303 \text{ kJ/kg biomass}$$

$$\text{Organics} = 0.427 \sim 0.427 \times 525 = 525 \text{ kJ/kg biomass}$$

$$\text{Solid carbon} = 0.27 \text{ kg} \sim 0.27 \times 0.7 \times (400 - 25) = 70.8 \text{ kJ/kg biomass}$$

$$\text{Total enthalpy} = 133.7 + 123.5 + 303 + 224 + 70.8 = 865 \text{ kJ/kg biomass}$$

Taking into account heat loss amount of char to be converted = $(865 \times 1.1)/6762 = 0.14 \text{ kJ/kg biomass}$.

Air (23% oxygen) required to burn 0.14 kg carbon = $1.33 \times 0.14 / 0.23 = 0.81 \text{ kJ/kg biomass}$

10. Improves water quality by reducing contaminated runoff and nutrient loss
11. Soil remediation
12. Reversal of desertification on massive scales and can work in tandem with reforestation
13. A better alternative to slash-and-burn of agricultural residues
14. Decreases nitrous oxide and methane emissions from solids
15. Net primary production
16. Generates carbon offsets and increased on-farm profitability for the company.

SYMBOLS AND NOMENCLATURE

A	preexponential factor (s^{-1})
E	activation energy (J/mol)
k	reaction rate (s^{-1})
m_b	mass of biomass at time t (kg)
m_c	mass of char residue (kg)
m_0	initial mass of biomass (kg)
R	universal gas constant (J/mol K)
T	temperature (K)
T_{pyr}	pyrolysis temperature (K)
t	time (s)
t_{heating}	heating time (s)
t_r	reaction time (s)
X	fractional change in mass of biomass