

Biochar Production Technology

Robert Brown

Introduction

Biochar production cannot be properly discussed without first distinguishing it from char and charcoal. All three forms of carbonaceous material are produced from pyrolysis, the process of heating carbon (C)-bearing solid material under oxygen (O_2)-starved conditions. Char is defined here as any carbonaceous residue from pyrolysis, including natural fires. Thus, char is the most general term to employ in scientific descriptions of the products of pyrolysis and fires, whether from biomass or other materials. Charcoal is char produced from pyrolysis of animal or vegetable matter in kilns for use in cooking or heating. Biochar is carbonaceous material produced specifically for application to soil as part of agronomic or environmental management (see Chapters 1 and 7). No standard currently prescribes the composition or preparation of biochar to distinguish it from charcoal produced as fuel. However, advances in our understanding of what makes for 'good' charcoal in agronomic and environmental management applications will

inevitably encourage separate designations for charcoal and biochar.

Since most information on the preparation of carbonaceous material stems from charcoal production, this chapter will draw significantly from our understanding of charcoal. Although C is the major constituent of charcoal, its exact composition and physical properties depend upon the starting material and the conditions under which it is produced. Charcoal contains 65 to 90 per cent C with the balance being volatile matter and mineral matter (ash) (Antal and Grønli, 2003). Superficially, charcoal resembles coal, which is also derived from vegetable matter; indeed, the word charcoal may have originally meant 'the making of coal' (*Encyclopedia Britannica*, 1911). However, the geological processes from which coal is derived are quite different from charcoal-making, resulting in important differences in chemical composition, porosity and reactivity.

Charcoal is readily generated in open fires, whether forest fires or camp fires. Thus,

it was available to early humankind whose first apparent use of it was in the creation of spectacular cave paintings during the last Ice Age (Bard, 2002). Charcoal eventually found application in other fields, including agronomy, medicine, metallurgy, pyrotechnics and chemical manufacture. However, its largest application has always been in the preparation of smokeless fuel for cooking, residential heating, smelting and steel-making. The process of charcoal-making removes most of the volatile matter responsible for smoke during burning. Charcoal is a relatively clean-burning fuel that represented an important

innovation in the controlled use of fire. Charcoal or, rather, biochar as a C sequestration agent and soil amendment, on the other hand, is still poorly understood.

This chapter is divided into three sections: historical production of charcoal in traditional kilns; mechanisms of char production from plant materials; and modern methods of pyrolysis appropriate to sustainable production of biochar. The carbonaceous residue of pyrolysis will be referred to variously as char, charcoal or biochar, depending upon the context of the discussion.

History of charcoal-making

The earliest charcoal kilns consisted of temporary pits or mounds, which have the virtue of simplicity and low cost. While these simple kilns are still widely employed in the developing world, various kinds of brick, metal and concrete kilns have been introduced to improve the yield of charcoal-making. All of these operate in batch mode, requiring the periodic charging and discharging of the kiln. A recent innovation in charcoal-making is the multiple hearth kiln, which operates continuously, offering energy efficiency and environmental performance advantages compared to batch kilns. Virtually all charcoal kilns employ wood as feedstock, although in principle any biomass could be used to produce charcoal. Traditional charcoal-making goes through three successive stages that can be characterized by the colour of smoke emitted: drying (white smoke), pyrolysis (yellow smoke) and process complete (blue smoke). Among the best sources of information on the construction and operation of charcoal kilns is the report by the United Nations Food and Agriculture Organization (FAO, 1983).

Pit kilns employ the simplest strategy for controlling access of air and reducing heat

loss during carbonization: burying a stack of smouldering wood in the ground (FAO, 1983). Small pit kilns may be only 1 cubic metre in volume. A small fire is started in the pit and additional wood is added to make a strong fire. At this point a canopy of branches and leaves is added to support a layer of earth of about 0.2m in depth. Carbonization may proceed for up to two days before the pit is uncovered and the charcoal is allowed to cool before unloading. Large pit kilns can be 30m³ or larger and produce 6t or more of charcoal per load. As illustrated in Figure 8.1, burning in large pit kilns takes place progressively from one end to the other. Large pit kilns do not necessarily have higher yields than small pits, but they are more efficient in the use of labour. Pit kilns must be continuously tended, opening and closing vent holes in the soil layer, to ensure the correct balance between combustion and pyrolysis in the pile. The pit kiln is ideal where the soil is well drained, deep and loamy. Charcoal yields are generally very low and the charcoal is not uniform in quality. The venting of particulate matter and volatile organic compounds to the atmosphere are obvious disadvantages.

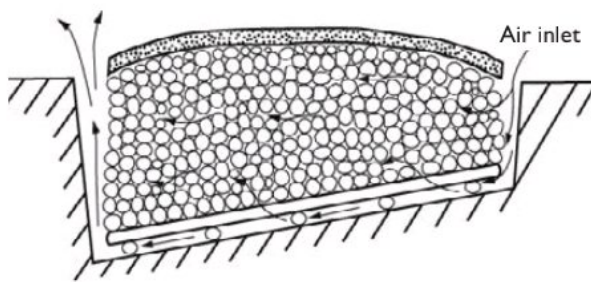


Figure 8.1 Large pit kiln

Source: adapted from FAO (1983)

The mound kiln is essentially an above-ground version of the pit kiln, with earth mounded up over a stack of wood for the purpose of controlling air filtration and heat loss during carbonization (FAO, 1983). The mound is preferred to a pit when the water table is close to the surface or the soil is hard to work. It is also employed when a permanent site near an agricultural village (which has more scattered wood resources) is preferred to a temporary site located within a timber resource. A typical mound kiln is about 4m in diameter at the base and 1m to 1.5m high in the shape of a flattened hemisphere (see Figure 8.2). Long pieces of fuel wood are stacked vertically against a central post, while shorter logs are placed vertically towards the periphery. Gaps between logs are filled with small wood to make a dense pile. It is covered with straw or dry leaves and then a layer of loamy or sandy earth to seal the mound. The centre post is removed before lighting, the space serving as both the place to ignite the pile as well as the flue for the smoke to exhaust from the pile. About six to ten vents at the base of the mound allow for control of air filtration during carbonization. Similar to the pit kiln, the mound kiln has a relatively low charcoal yield and, as illustrated in Figure 8.3, is a source of significant atmospheric pollution.

The brick kiln is an important improvement over traditional pit and mound kilns, producing good-quality charcoal at relatively high yields (FAO, 1983). Capital cost is rela-

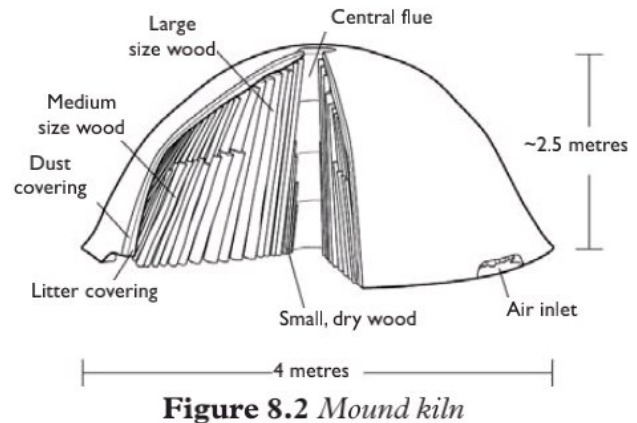


Figure 8.2 Mound kiln

Source: adapted from FAO (1983)

tively low and labour costs are moderate. The kiln is constructed completely out of bricks, which provide good heat insulation, in a hemispherical or beehive shape of 5m to 7m in diameter, set into a brick foundation (see Figure 8.4). The kiln has two openings diametrically opposite one another and perpendicular to prevailing winds. One opening is used to charge the kiln, while the other is used to discharge the charcoal. These openings can either be closed with steel doors or simply bricked over and sealed with mud. Air infiltration is controlled by vents around the base of the kiln, while smoke is exhausted from an 'eye' hole at the top of the kiln. Carbonization may occur over the course of



Figure 8.3 Operation of a mound kiln showing the heavy smoke emitted during the carbonization process

Source: Weald and Downland Open Air Museum

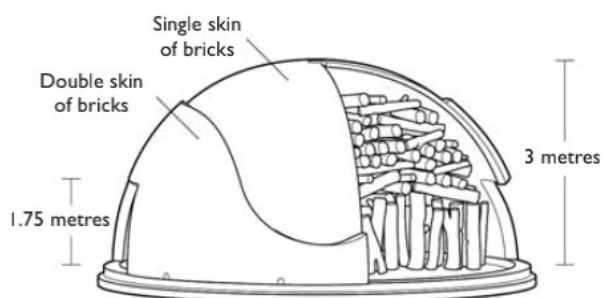


Figure 8.4 *Brick kiln*

Source: adapted from FAO (1983)

six to seven days, followed by a ‘purging’ stage of one to two days, during which the perimeter vents are sealed, and, finally, a cooling stage of three days in which the eye hole is also sealed.

Metal kilns originated in Europe during the 1930s and spread to the developing world in the 1960s. Although a number of variations exist, the transportable metal kiln developed by the Tropical Products Institute (TPI) (Whitehead, 1980) is illustrative of the main features of this type of kiln. As shown in Figure 8.5, the TPI kiln consists of two interlocking cylindrical sections and a conical cover with four steam release ports. The kiln is supported on eight channels projecting radially from the perimeter of the base section. These are designed to serve as air inlets or, when fitted with smoke stacks, to vent smoke out of the kiln. During carbonization, four of the channels are fitted with smoke stacks. The metal kiln has several advantages over traditional or brick kilns. The flow of air into, and smoke out of, the kiln is readily controlled, which improves charcoal yield and quality. Unskilled personnel can be quickly trained to operate the kiln and it does not require the constant attention of traditional kilns. Carbonization is complete in three days and all of the charcoal can be recovered from the kiln. The kiln can be operated in areas of high rainfall. The metal kiln does not, however, mitigate the air pollution associated with charcoal-making.



Figure 8.5 *Transportable metal kiln, Tropical Products Institute (TPI)*

Source: adapted from Whitehead (1980)

The concrete kiln, also known as the Missouri kiln, is a rectangular structure constructed of reinforced concrete or concrete block with steel doors (see Figure 8.6). The kiln is designed for mechanized loading and unloading of wood and charcoal. A typical kiln is about 7m wide and 11m long with a vault height of 4m. This gives it a capacity of about 180m³ of wood, which is about three times greater than brick kilns. Concrete kilns typically produce 16t of charcoal during a three-week cycle. Yields are higher than for metal kilns because of better thermal insulation and larger volume-to-surface area ratios. Thermocouples within the kiln also contribute to better yields by allowing hot and cold spots to be identified and corrected by controlling airflow into the kiln. The Missouri kiln is fitted with eight 0.15m diameter pipes to serve as chimneys. These can be connected to a central flue and afterburner to mitigate atmospheric emissions of carbon monoxide (CO), volatile organic compounds (VOCs) and particulate matter (PM) (Yronwode, 2000). However, control of emissions from batch-type kilns is difficult because the emissions never reach a steady-state condition.

A multiple hearth kiln is a refractory-lined vertical steel shell containing a series of

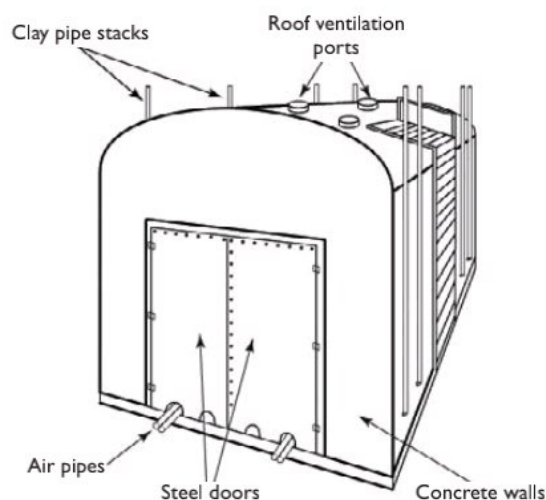


Figure 8.6 *The Missouri-type charcoal kiln*

Source: adapted from Maxwell (1976)

shelves or hearths supported by the walls of the kiln (see Figure 8.7) (Radian Corporation, 1988). A rotating shaft fitted with rabble arms penetrates the centre of the shell. As the shaft rotates, the rabble arms sweep slowly across the hearths, moving carbonizing wood either radially inward or outward toward penetrations in the hearths where the material drops to the next lower hearth. Air flowing upward through the hollow shaft is admitted to the hearths. Gases and vapours released from the carbonizing wood travel counter-currently to the flow of biomass in the kiln. Continuous multiple hearth kilns produce an average of 2.5 t hr^{-1} of charcoal. As a continuous flow reactor, the multiple hearth kiln offers superior control of carbonization time and gas flow, which is expected to improve charcoal yields and quality. Continuous processes are also more amenable to pollution control compared to batch processes. After-burning is estimated to reduce emissions of PM, CO and VOCs by at least 80 per cent (Rolke et al, 1972).

In addition to CO_2 and water (H_2O), smoke emitted from a charcoal kiln contains CO, methane (CH_4), VOCs and PM, which contribute to air pollution. Some of the VOCs are commercially valuable compounds,

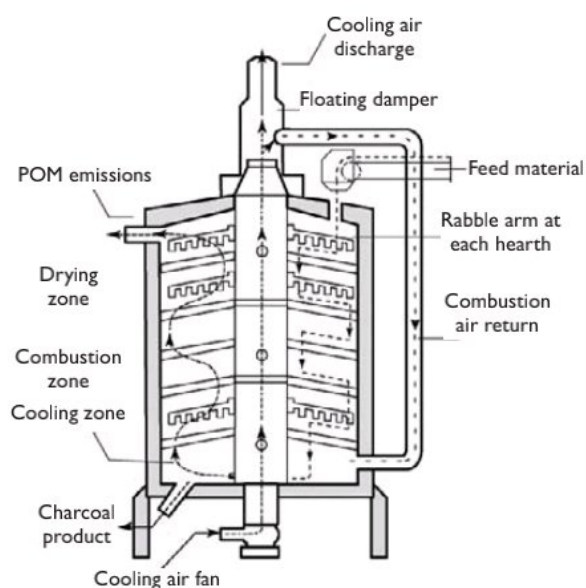


Figure 8.7 *The continuous multiple hearth kiln for charcoal production*

Note: POM = polycyclic organic matter

Source: adapted from Radian Corporation (1988)

which can be recovered by distillation. In fact, 'wood tar' and 'pyroligneous acid' were often the main reason to operate kilns before the development of petroleum-based chemicals. Destructive distillation of wood produced commercially significant quantities of acetic acid and methanol (wood alcohol) (Sjostrom, 1993). Emissions are usually characterized as CO, CH_4 , non-methane hydrocarbons (NMHC), and total suspended particulates (TSP), although NMHC is a misnomer because it usually includes methanol, acetic acid and other oxygenated organic compounds. Table 8.1 lists ranges of emission levels for these pollutants from different kinds of charcoal kilns (Moscowitz, 1978). Clearly, dramatic improvements can be achieved using controlled continuous kilns compared to batch kilns.

The charcoal yield η_{char} from a kiln is given by:

$$\eta_{\text{char}} = (m_{\text{char}}/m_{\text{bio}}) \times 100 \quad [1]$$

Table 8.1 Air emissions per kilogram biomass from different kinds of charcoal kilns

	CO (g kg ⁻¹)	CH ₄ (g kg ⁻¹)	NMHC ¹ (g kg ⁻¹)	TSP ² (g kg ⁻¹)
Uncontrolled batch	160–179	44–57	7–60	197–598
Low-control batch	24–27	6.6–8.6	1–9	27–89
Controlled continuous	8.0–8.9	2.2–2.9	0.4–3.0	9.1–30

Notes: 1 NMHC = non-methane hydrocarbons (includes recoverable methanol and acetic acid).

2 TSP = total suspended particulates.

Source: Moscovitz (1978)

Table 8.2 Charcoal yields (dry weight basis) for different kinds of batch kilns

Kiln type	Charcoal yield (%)
Pit	12.5–30
Mound	2–42
Brick	12.5–33
Portable steel (TPI)	18.9–31.4
Concrete (Missouri)	33

Source: Kammen and Lew (2005)

where m_{char} is the dry mass of charcoal from the kiln and m_{bio} is the dry mass of biomass loaded into the kiln. Table 8.2 shows the range of charcoal yields from different kinds of batch kilns, which all employ wood of unspecified species. Although reported yields range widely for a given type of kiln, in general, brick and steel kilns yield more charcoal than pit and mound kilns, and concrete kilns are expected to have highest yields

among batch kilns. The effect of biomass composition and kiln operating conditions on charcoal yield and properties is virtually unexplored in the published literature.

Biochar is the product of pyrolysis, which is the decomposition of C-bearing compounds at elevated temperatures in the absence of O₂. This decomposition process is not perfectly understood, especially for complicated polymeric materials such as biomass from which charcoal is traditionally derived. In addition to biochar, other products of pyrolysis include condensable vapours (that yield insoluble tars and pyrolygineous acid) and gas. The quantity of these products depends upon the composition of the biomass and the conditions under which pyrolysis occurs (Shafizadeh, 1982). An idea of the different yields of liquid, biochar and gas for various operating modes of pyrolysis is given in Table 8.3.

Table 8.3 Typical product yields (dry basis) for different modes of pyrolysis

Mode	Conditions	Liquid (%)	Char (%)	Gas (%)
Fast	Moderate temperature ~ 500°C	75	12	13
	short vapour residence time ~ 1sec			
Moderate	Moderate temperature ~ 500°C	50	20	30
	Moderate vapour residence time ~ 10–20sec			
Slow	Moderate temperature ~ 500°C	30	35	35
	Very long vapour residence time ~ 5–30min			
Gasification	High temperature >750°C	5	10	85
	Moderate vapour residence time ~ 10–20sec			

Source: Bridgwater (2007)

Mechanisms of biochar production from biomass substrates

The major constituents of fibrous biomass are cellulose, hemicellulose and lignin, with smaller quantities of organic extractives and inorganic minerals. These constituents can vary considerably among different kinds of biomass or even within a species depending upon soil type, climatic conditions and time of harvest. Examples of the variation in composition of different kinds of biomass are given in Table 8.4.

Cellulose is a linear condensation polymer of β -(1-4)-D-glucopyranose (O'Sullivan, 1997; see Figure 8.8). The repeating unit of the cellulose polymer is cellobiose, which consists of two anhydroglucose units. The number of glucose units in a cellulose chain is known as the degree of polymerization (DP). The average DP for native cellulose is on the order of 10,000. The coupling of adjacent cellulose molecules by hydrogen (H) bonds and van der Waal's forces results in a parallel alignment giving cellulose a crystalline structure. Cellulose exist as sheets of glucopyranose rings lying in a plane with successive sheets stacked on top

of each other to form three-dimensional particles that aggregate into elementary fibrils with a crystalline width of 4nm to 5nm. This crystalline micro-fibril arrangement makes cellulose more resistant to thermal decomposition than hemicellulose.

Hemicellulose is a large number of heteropolysaccharides built from hexoses (D-glucose, D-mannose and D-galactose), pentoses (D-xylose, L-arabinose and D-arabinose) and deoxyhexoses (L-rhamnose or 6-deoxy-L-mannose and rare L-fucose or 6-deoxy-L-galactose) (Sjostrom, 1993). Small amounts of uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid) are also present. Hardwoods are rich in xylans such as O-acetyl-(4-O-methylglucurono) xylan and contain small amounts of gluco-mannan. Softwoods are rich in glucomannans such as O-acetyl-galactoglucomannan and smaller amounts of xylans such as arabino-(4-O-glucurono) xylan. Softwood hemicelluloses have more mannose and galactose units and less xylose units and acetylated hydroxyl

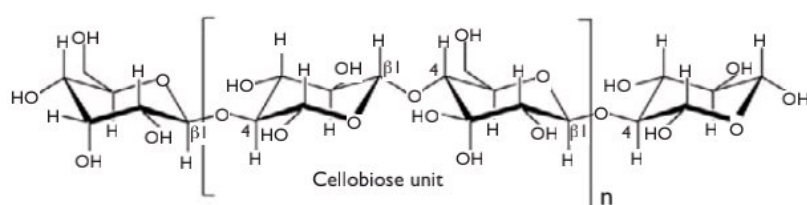


Figure 8.8 Chemical structure of cellulose

Source: adapted from Mohan et al (2006)

Table 8.4 Typical content of several examples of biomass (dry basis)

Feedstock	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)	Extractives (wt %)	Ash (wt %)	Reference
Hybrid poplar	45	19	26	7	1.7	Hamelinck et al (2005)
Willow	43	21	26	–	1	Sassner et al (2006)
Switchgrass	32	25	18	17	6	Hamelinck et al (2005)
Miscanthus	38	24	25	5	2	de Vrije et al (2002)
Maize stover	39	19	15	–	4.6	Chandrakant and Bisaria (1998)
Wheat straw	38	25	14	–	10	Chandrakant and Bisaria (1998)

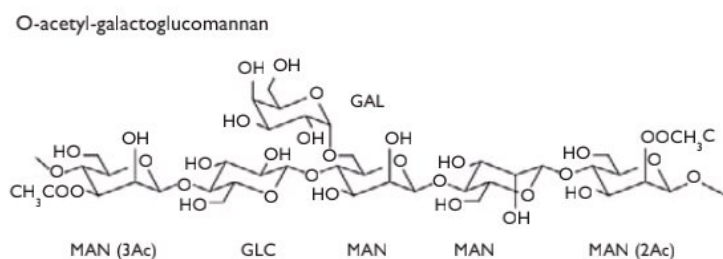


Figure 8.9 Structural formula for a common hemicellulose found in softwoods

Notes: Ac = acetyl group;
GAL = galactose; GLC = glucose;
MAN = mannose.

Source: adapted from Hartman (2006)

groups than do hardwood hemicelluloses.

Figure 8.9 gives the structural formula for a typical hemicellulose, illustrating the short side-chains that distinguish hemicellulose from cellulose. The chemical and thermal stability of hemicelluloses is lower than for cellulose due to its lack of crystallinity and lower degree of polymerization, which is only 100 to 200 (Sjostrom, 1993).

Lignin, a phenylpropane-based polymer, is the largest non-carbohydrate fraction of lignocellulose (Sjostrom, 1993). It is constructed of three monomers: coniferyl alcohol, sinapyl alcohol and coumaryl alcohol, each of which has an aromatic ring with different substituents (see Figure 8.10). Softwood lignin contains a higher fraction of coniferyl phenylpropane units (guaiacyl lignin), while hardwood lignin is a co-polymer of both coniferyl and sinapyl phenylpropane units (guaiacyl-syringyl lignin). Lignin has an amorphous structure, which leads to a large number of possible inter-linkages between individual units.

Ether bonds predominate between lignin units and covalent bonds exist between lignin and polysaccharides. Unlike cellulose, lignin cannot be depolymerized to its original monomers.

Bundles of elementary cellulose fibrils are embedded in a matrix of hemicellulose with a thickness of 7nm to 30nm. Lignin is located primarily on the exterior of microfibrils where it covalently bonds to hemicellulose (Klein and Snodgrass, 1993). Lignin impregnates the cell wall, reduces the pore sizes, shields the polysaccharides and contributes to the recalcitrance of lignocellu-

lose (Saxena and Brown, 2005).

Plant materials also contain other organic compounds collectively known as 'extractives'. These include resins, fats and fatty acids, phenolics and phytosterols, among other chemical compounds. Extractives are classified as either hydrophilic or lipophilic, depending upon whether they are soluble in water or organic solvents, respectively. Resin is often used to describe the lipophilic extractives with the exception of phenolic substances. Extractives can influence gaseous emission profiles during pyrolysis, but they are not thought to substantially influence charcoal yield because of their low concentrations.

The inorganic content of biomass includes the major elemental nutrients nitrogen (N), phosphorus (P), and potassium (K), as well as smaller amounts of sulphur (S), chlorine (Cl), silicon (Si), alkaline earth metals, transition metals and various trace elements. That part of the inorganic content remaining after oxidation of the biomass at high temperature is known as ash.

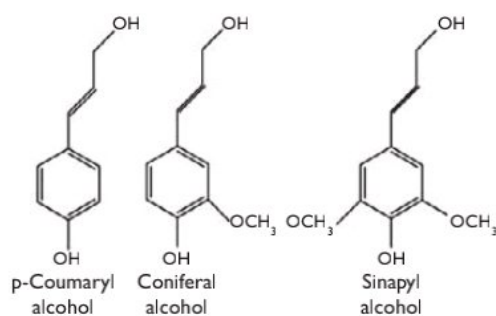


Figure 8.10 Monomers from which lignin is assembled

Source: adapted from Mohan et al (2006)

Table 8.5 Influence of heating rate on pyrolysis of cellulose in a thermogravimetric analyser with nitrogen as sweep gas (flow rate unspecified)

Heating rate (°C min ⁻¹)	Enthalpy of pyrolysis (J kg ⁻¹)	Onset temperature of pyrolysis (°C)	Temperature of maximum decomposition rate (°C)
5	+780	314	345
10	+498	337	360
30	+455	350	383
50	+440	362	396

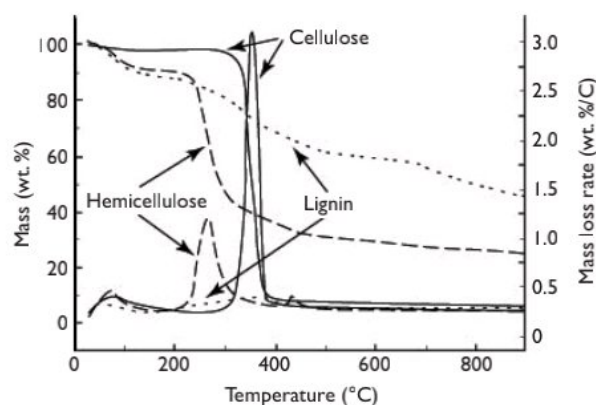
Source: Gupta and Lilley (2003)

Cellulose, hemicellulose, and lignin have distinctive thermal decomposition behaviours that depend upon heating rates. As illustrated in Table 8.5, pyrolysis is initiated at higher temperatures as the heating rate is increased (Gupta and Lilley, 2003). At very low heating rates typical of muffle furnaces or traditional charcoal kilns, cellulose decomposition begins at temperatures as low as 250°C (William and Besler, 1996).

The temperature dependence of the decomposition of cellulose, hemicellulose (xylan) and lignin is illustrated in Figure 8.11 using data obtained by Yang et al (2007) from a thermogravimetric analyser (TGA) operated at a constant heating rate of 10°C min⁻¹ and swept with 120 mL min⁻¹ of N₂. Hemicellulose is the first to decompose, beginning at 220°C and substantially completed by 315°C (see also Chapter 17). Cellulose does not start to decompose until about 315°C. In the swept gas environment of a TGA, essentially all of the cellulose is

converted to non-condensable gas and condensable organic vapours and aerosols once 400°C is attained. As subsequently explained, cellulose can be the source of considerable biochar under different operating conditions. Although lignin begins to decompose at 160°C, it is a slow, steady process extending to 900°C and yielding a solid residue approaching 40 per cent by weight of the original sample.

Pyrolysis products of hemicellulose include non-condensable gases (primarily CO, CO₂, H₂ and CH₄), low molecular weight organic compounds (carboxylic acids, aldehydes, alkanes and ethers), and some water (Rutherford et al, 2004). Some of these compounds can be recovered in commercially significant quantities. For example, both acetic acid and furfural have been manufactured by thermal processing of hemicellulose-rich biomass. On the other hand, heavy molecular weight (tarry) compounds are produced in relatively small

**Figure 8.11** Thermogravimetric analysis of the pyrolysis of cellulose, hemicellulose (xylan) and lignin at constant heating rate (10°C min⁻¹) with N₂ (99.9995 per cent) sweep gas at 120 mL min⁻¹

Source: adapted from Yang et al (2007)

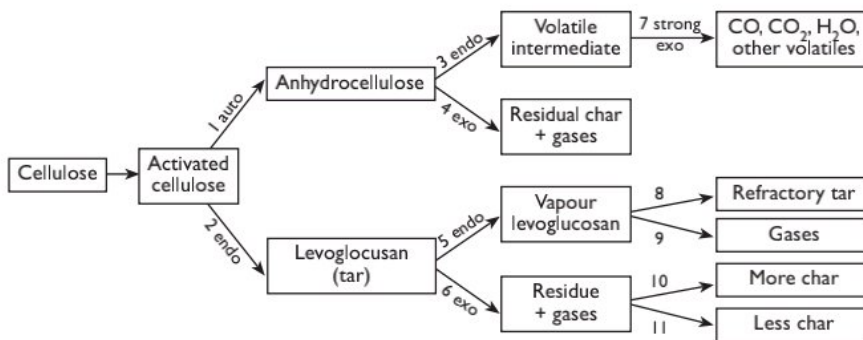


Figure 8.12 Reaction pathways for cellulose decomposition

Source: numbers refer to specific reactions described in Mok and Antal (1983)

amounts compared to pyrolysis of cellulose and lignin (Rutherford et al, 2004).

The products of cellulose decomposition can vary markedly depending upon reaction conditions. Figure 8.12 illustrates the detailed reaction mechanism proposed by Mok and Antal (1983). Cellulose decomposition includes both an exothermic pathway via anhydrocellulose and an endothermic pathway via levoglucosan. The anhydrocellulose pathway yields char and non-condensable gases in a process that is overall exothermic, but it occurs at extremely slow heating rates making this pathway of little practical importance. The levoglucosan (anhydroglucose) pathway is an endothermic devolatilization process that can lead to either predominately tarry vapours or char as the final product. A combination of

temperature, residence time and naturally occurring catalysts in biomass determine the extent of secondary reactions, which yield a wide variety of organic compounds, including aldehydes, ketones, carboxylic acids, alcohols, and anhydrosugars from cellulose pyrolysis (Mohan et al, 2006).

Given sufficient time, the chemical equilibrium products of cellulose pyrolysis are mostly solid C (biochar), CO₂ and H₂O, and smaller quantities of CO and CH₄ (Antal and Grønli, 2003). As illustrated in Figure 8.13, pressure has little effect on equilibrium composition especially above 0.1MPa (atmospheric pressure), while increasing temperature slightly reduces biochar yield, which approaches an asymptotic limit of about 25 per cent by weight of the starting mass of cellulose.

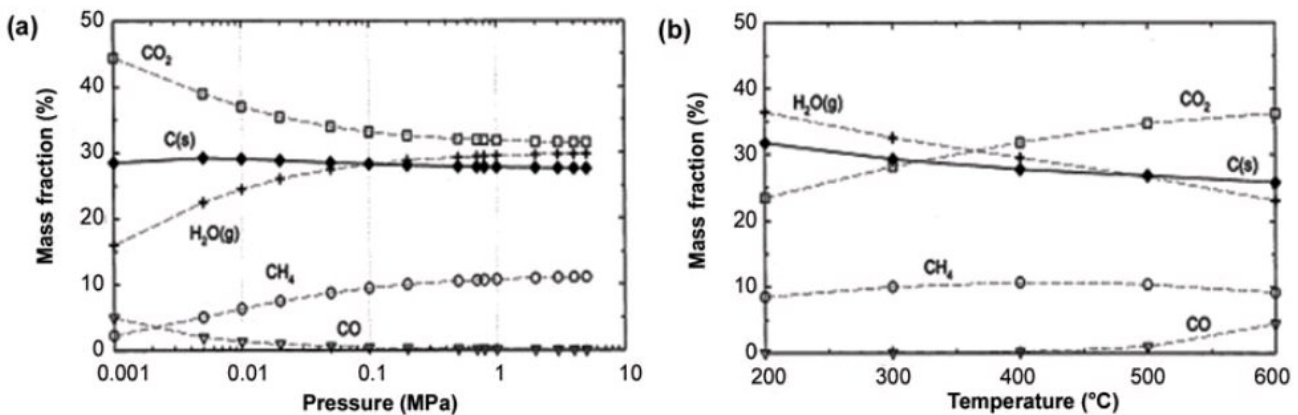


Figure 8.13 Chemical equilibrium products of cellulose pyrolysis: (a) effect of pressure at 400°C; (b) effects of temperature at 1MPa

Source: Robert Brown

Pyrolysis of lignin yields non-condensable gases, condensable vapours and liquid aerosols, and biochar (Mohan et al, 2006). The non-condensable gases, representing about 10 per cent by weight of the original lignin, consist of CO, CH₄ and ethane (C₂H₄). The condensable vapours and liquid aerosols are recovered as pyroligneous acid and insoluble tar. The pyroligneous acid is an aqueous phase of methanol, acetic acid, acetone and soluble tar. The insoluble tar contains homologous phenolic compounds derived from cleavage of ether and C–C bonds. Lignin is more difficult to dehydrate than cellulose or hemicelluloses and produces more residual biochar. For comparable temperatures and times, lignin weight loss is typically less than half that of cellulose.

From the previous discussions, carbonization efficiency is expected to be a function of both the composition of the biomass and the conditions under which biochar is produced. Although the biochar yield described by Equation 1 is of some practical application, it is not an exact measure of the amount of C produced from biomass since it does not account for the ash contents of the biomass feedstock and biochar product. A more meaningful measure of carbonization efficiency is the fixed C yield:

$$\eta_{fc} = \frac{m_{char} c_{fc}}{m_{bio} (1 - b_a)} \quad [2]$$

where c_{fc} is the fixed C content of biochar as measured by ASTM Standard 5142 (ASTM, 2004) and b_a is the ash content of the dry biomass. This represents the conversion of ash-free organic mass in the feedstock into ash-free C (Antal et al, 2000). A perfect kiln would have fixed C yield equal to the solid C yield predicted by thermodynamic equilibrium. For example, the pyrolysis of cellulose at 400°C and 1MPa should have a fixed C yield of 27.7 per cent, as illustrated in Figure 8.14 (calculated using the chemical equilibrium software package STANJAN; Bishnu et al, 1996).

In fact, biochar yields from biomass are considerably less than theoretical expectations. Traditional kilns can have efficiencies as low as 8 per cent (FAO, 1985). This can arise from the infiltration of O₂ with air into the kiln, which gasifies biochar to CO and CO₂ and greatly reduces equilibrium yields of C, as illustrated in Figure 8.14.

Even in the absence of O, however, low biochar yields can result if vapours and gases are removed from the reaction zone before thermodynamic equilibrium can be attained. Although it is often assumed that biochar is the result of solid-phase reactions in which devolatilized biomass leaves behind a carbonaceous residue (primary biochar), in fact, biochar is also formed by decomposition of organic vapours (tars) to form coke (secondary biochar). This secondary biochar is as chemically reactive as the primary

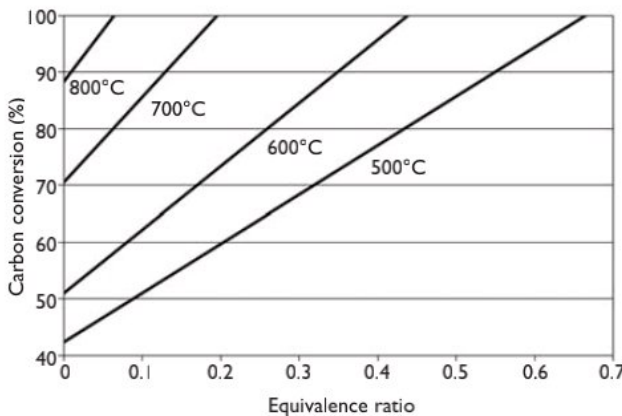


Figure 8.14 Carbon conversion for gasification of cellulose as a function of equivalence ratio (fraction of stoichiometric O requirement for theoretical complete combustion) calculated with STANJAN chemical equilibrium software

Source: Robert Brown

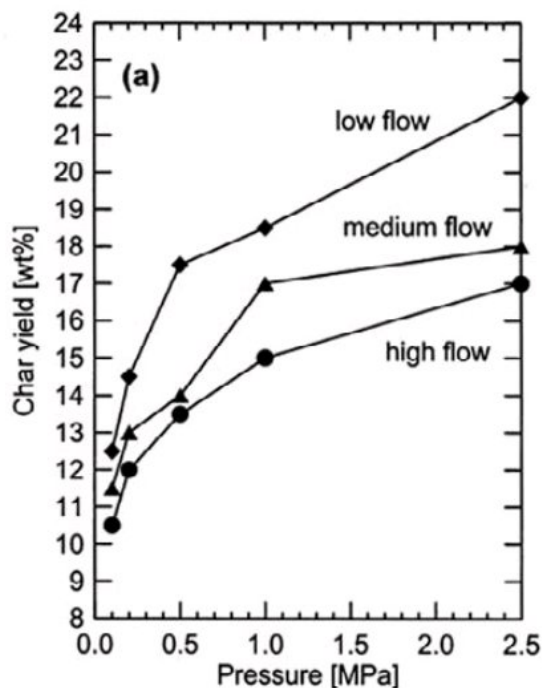


Figure 8.15 Effect of pressure and purge gas flow rate on carbonization of cellulose

Source: Mok and Antal (1983)

biochar despite differences in its formation (Chen et al, 1997). It is likely that decomposition of these vapours is catalysed by the primary biochar (Radovic and Sudhakar, 1997). At the very least, escape of pyrolytic vapours prevents the attainment of thermodynamic equilibrium by the original reactants, which favours high biochar yields. Varhegyi et al (1988) and later Suuberg et al (1996) were able to vary the biochar yield of pyrolysing cellulose from a few per cent to almost 20 per cent simply by controlling the venting of vapours during TGA experiments. Klason (1914) recognized the importance of primary and secondary reactions in biochar production almost 100 hundred years ago but this fact has yet to be fully exploited in biochar manufacture.

The existence of primary and secondary reactions in biochar-making helps to explain two phenomena that are otherwise difficult to

understand. These are the effect of pressure on biochar yields and the report of both endotherms and exotherms during wood pyrolysis.

According to thermodynamic calculations, the pyrolysis of cellulose or wood should not be strongly influenced by pressure (see Figure 8.13). In fact, studies dating back as far as the pioneering research by Klason (1914) have claimed significant effects of pressure on biochar yields, although others have reported otherwise (Frolich et al, 1928). The question was taken up by Mok and Antal (1983) who demonstrated that, in tubular flow reactors, biochar yields increased from around 10 per cent by weight to over 20 per cent by weight as the pressure was increased from 0.1MPa to 2.5MPa. They also discovered that the effect was dependent upon the rate at which the reactor was purged with inert gas (see Figure 8.15). This later observation led them to suggest that pressure is a kinetic rather than a thermodynamic effect: high pressures prolong the intra-particle residence time of pyrolysing vapours, as well as increase the rate of decomposition reactions that allow a closer approach to the expectations of thermodynamic equilibrium. Sweep gas removes vapours before they have a chance to decompose and deposit secondary biochar.

Researchers have variously suggested enthalpies of pyrolysis that have ranged from endothermic (Kung and Kalelkar, 1973) to exothermic (Roberts, 1970) Mok and Antal (1983) used tubular flow reactors imbedded in a differential scanning calorimeter to measure the heat of pyrolysis as a function of pressure and purge gas flow (see Figure 8.16). They found the heat of pyrolysis was endothermic at low pressures and exothermic at high pressures. Furthermore, the pressure at which the process transitioned from endotherm to exotherm was dependent upon purge gas flow, with low flow rates moving the transition to lower pressures. They attrib-

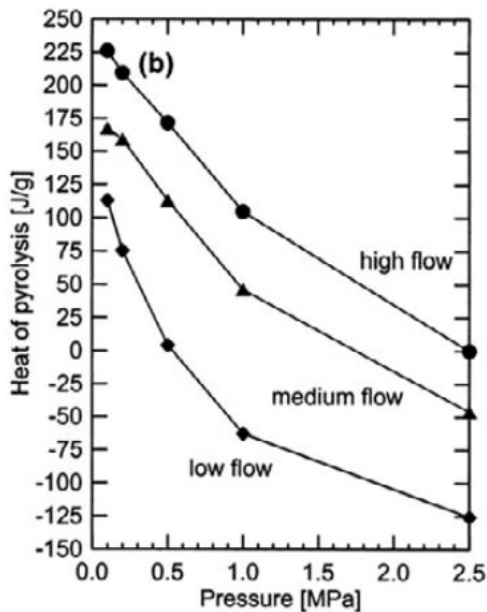


Figure 8.16 Effect of pressure and purge gas flow rate on heat of pyrolysis for cellulose

Source: Mok and Antal (1983)

uted the endotherm to the devolatilization of levoglucosan (reaction 5 in Figure 8.12) and the exotherm to *in-situ* carbonization of levoglucosan (reaction 6 in Figure 8.12). Taken together, Figure 8.15 and Figure 8.16 suggest the ability to control pyrolysis not only to improve biochar yields, but to improve the energy performance of biochar reactors.

Porosity is an important property of biochar. Although the vascular structure of plant materials contribute to large pores in biochar, most of biochar's high surface area derives from nanopores created during the

heating process. Porosity is a complex function of heating temperatures, heating rates and heating times (see Chapter 2).

Under conditions of slow pyrolysis, Rutherford et al (2004) found evidence that aliphatic C in pyrolysing biomass must first be converted into fused-ring aromatic C before porosity can develop. For cellulose, this transformation of aliphatic C does not occur below 250°C, while for lignin, which already contains significant amounts of aromatic C, temperatures closer to 300°C are required to convert its aliphatic C. At higher temperatures, aromatic C was gradually lost and porosity began to develop. Thus, it would appear that the fused-ring structures of aromatic C provide a matrix in which micropores can be created.

Porous carbons are categorized as either graphitizable carbon or non-graphitizable carbon (Byrne and Marsh, 1995). In both cases, C atoms are arranged in fused hexagonal rings stacked as small crystallites. However, upon heating to high temperatures, the crystallites of graphitizable C reorient themselves into parallel sheets of C atoms, known as graphite, which destroys the porosity of the material. In non-graphitizable C, the crystallites are randomly oriented and strongly cross-linked to one another, which resists reorientation upon heating and preserves porosity. Carbon derived from pyrolysing biomass is non-graphitizable and is thought to be associated with the high oxygen content of the starting material (Franklin, 1951).

Opportunities for advanced biochar production

Traditional charcoal-making technologies are both energy inefficient and highly polluting. An examination of the physical and chemical processes associated with pyrolysis and carbonization of wood suggests that signifi-

cant improvements can be made in both of these respects. It might also be possible to control the properties of biochar for agronomic and C sequestration applications. Finally, better utilization of the co-products

of pyrolysis might improve the economic prospects of biochar production.

Some specific goals for advanced biochar manufacture include:

- continuous feed pyrolysers to improve energy efficiency and reduce pollution emissions associated with batch kilns;
- exothermic operation without air infiltration to improve energy efficiency and biochar yields;
- recovery of co-products to reduce pollution emissions and improve process economics;
- control of operating conditions to improve biochar properties and allow changes in co-product yields; and
- feedstock flexibility allowing both woody and herbaceous biomass (such as crop residues or grasses) to be converted to biochar.

Some technologies that hold promise for helping to achieve these goals include drum pyrolysers, rotary kilns, screw pyrolysers, the Flash Carbonizer, fast pyrolysis reactors, gasifiers, hydrothermal processing reactors, and wood-gas stoves, all of which produce varying quantities of gas and liquids along with biochar.

The drum pyrolyser moves biomass through an externally heated, horizontal cylindrical shell by the action of paddles. No air is intentionally admitted to the drum, although some air enters in the voids between feedstock particles. The process is characterized as 'slow pyrolysis', taking several minutes for the biomass to transit the drum, although the time is short compared to traditional batch carbonization. The residence time of vapours is long enough that most of it is cracked to non-condensable gases, even though some tar remains with the gas. Some of the gas is burned in a firebox below the drum to heat the biomass to pyrolysis temperatures. Biomass is first dried before entering the drum pyrolyser to ensure good

biochar and gas quality. The drum pyrolyser of BEST Energies (undated) is one of the few continuous pyrolysers that has been employed in production of biochar.

Rotary kilns should also be suitable as continuous pyrolysers (Arsenault et al, 1980; Bayer and Kutubuddin, 1988). They are similar to drum pyrolysers in the employment of an externally heated cylindrical shell except that the shell is oriented at an angle to the horizontal and rotated to allow gravity to move the biomass down the length of the kiln. They are expected to have similar solids residence times (5 to 30 minutes). The advantage over the drum pyrolyser is the absence of moving parts in the interior. Rotary kilns for biomass pyrolysis have been investigated at low temperatures (350°C) and moderately high temperatures (600°C to 900°C). Klose and Wiest (1999) showed that variations in biomass feed rate and operating temperatures for a rotary kiln pyrolyser allowed wide control on the relative yields of condensable vapours and non-condensable vapours, while biochar yield remained relatively constant in the range of 20 to 24 per cent. This lack of control over biochar yields suggests that the relatively large volume of a rotary (or drum) kiln does not encourage re-condensation of tarry vapours to produce secondary biochar.

Screw pyrolysers move biomass through a tubular reactor by the action of a rotating screw (see Figure 8.17). Some screw pyrolysers are externally heated while others use a heat carrier such as sand to heat the biomass as it is transported through the tube. The screw pyrolyser is attractive for its potential to operate at relatively small scales. One of the first such pyrolysers was the twin-screw Lurgi-Ruhrgas mixer reactor originally developed for producing town gas or olefins from coal using sand as a heat carrier. During recent years it has been successfully employed to convert biomass into bio-oil and biochar (Henrich, 2004). The Haloclean Pyrolysis Reactor is another screw reactor

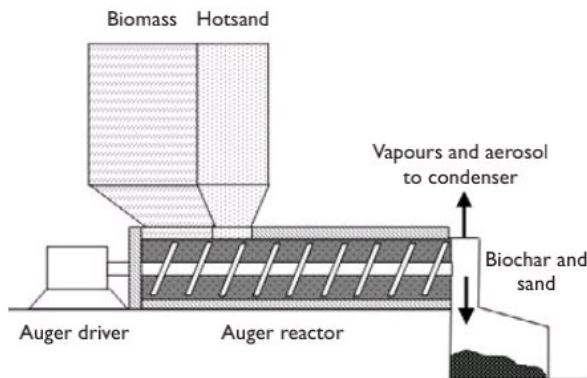


Figure 8.17 *Screw pyrolyser with heat carrier*

Source: Robert Brown

originally developed to treat electronic wastes, but finding applications in biomass pyrolysis (Haloclean, undated). It uses iron spheres as heat carrier. An example of an externally heated screw pyrolyser is the system developed by Advanced Biorefinery, Inc (ABRI, undated).

The Flash Carbonizer was developed by Antal et al (2003) at the University of Hawaii as a way of producing biochar through the ignition of a flash fire at elevated pressure in a packed bed of biomass. They report fixed C yields of up to 100 per cent of the theoretical limit in as little as 20 or 30 minutes, and observed a significant improvement in yields at elevated pressure and the preferential oxidation of combustible gases released during pyrolysis compared to biochar product.

Fast pyrolysis quickly heats biomass and extracts vapours for the preferential production of bio-oil compared to gas and biochar (Mohan et al, 2006). Although several kinds of reactors have been designed for fast pyrolysis, the high heat- and mass-transfer rates obtainable in fluidized beds make them ideal reactors for bio-oil production (see Figure 8.18). Typical yields are 60 to 70 per cent by weight bio-oil, 12 to 15 per cent by weight biochar, and 13 to 25 per cent by weight non-condensable gases for reactors operated at around 450°C to 500°C and for particles

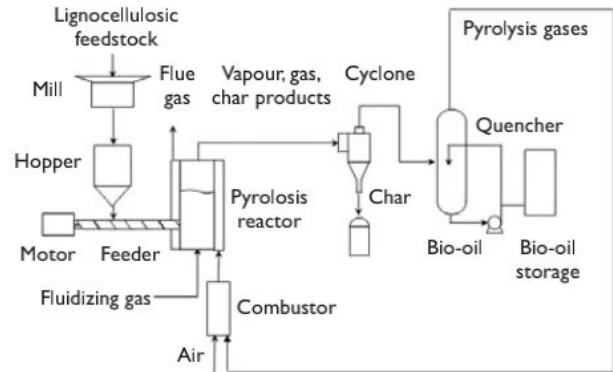


Figure 8.18 *Fluidized-bed fast pyrolysis reactor*

Source: Robert Brown

comminuted to about 1mm to 2mm in diameter (for an extensive review of the subject, see Mohan et al, 2006). The distribution of products can be dramatically altered by changing particle size, reaction temperature and gas flow rate through the fluidized bed. The relatively high flow rates of gas and relatively low residence time of biochar in the bed might be expected to produce biochars with properties distinct from biochar produced by slow pyrolysis. However, whether this biochar has properties that are inferior or superior to biochar from more traditional charcoal kilns is not known.

Gasifiers would seem to be a poor choice for biochar production since they are designed to produce gaseous products (mostly CO, CO₂, H₂, and N₂) at the expense of oils and biochar (McKendry, 2002). In fact, the operation of traditional charcoal kilns more closely resembles the operation of gasifiers than pyrolysers and the amount of biochar produced can be as high as 10 per cent by weight of the biomass gasified (Reed, 1981). By definition, pyrolysis occurs in the complete absence of O₂, which requires an external heat source to reach operating temperatures. In contrast, a gasifier admits O₂ (or air) to burn part of the biomass in order to supply the heat needed to drive the endothermic biomass devolatilization

processes that yield condensable vapours, flammable gases and biochar. Most traditional kilns are not externally heated but allow air infiltration to burn part of the kiln charge. Typical gasifiers operate at equivalence ratios close to 0.25 to provide sufficient heat to drive the gasification process. As Figure 8.14 illustrates, C conversion is a strong function of gasification temperature. Biochar yields could exceed 30 per cent in a gasifier operated at 500°C and an equivalence ratio of 0.25. Thus, modern gasifiers offer prospects for advanced biochar production with possible advantages in process control and reduction of pollution emissions.

Figure 8.19 illustrates three kinds of gasifiers suitable for co-production of producer gas and biochar: updraught, downdraught and fluidized bed (Brown, 2003). Updraught gasifiers are very similar to charcoal kilns except that more air is admitted in an effort to maximize gas production. Chipped fuel is admitted from above and insufficient air for complete combustion enters from below. The producer gas contains large quantities of tars, making them undesirable for many applications, but they have the virtue of relatively low cost. In contrast, downdraught gasifiers move fuel and gas in the same direction, which has the advantage of forcing tarry vapours released from the pyrolysing biomass through a zone of hot charcoal where it decomposes. Modern designs usually include tuyeres that admit air or O₂ directly into a region known as the throat where combustion forms a bed of hot biochar. The producer gas is relatively free of tar. Disadvantages include the need for tightly controlled fuel properties and a tendency for sintering of ash in the concentrated oxidation zone. In a fluidized-bed gasifier, the gas stream passes vertically upward through a bed of inert particulate material to form a turbulent mixture of gas and solid. Biomass injected into the bed is rapidly heated and pyrolysed. Fluidized beds can be scaled to a large size and are able to

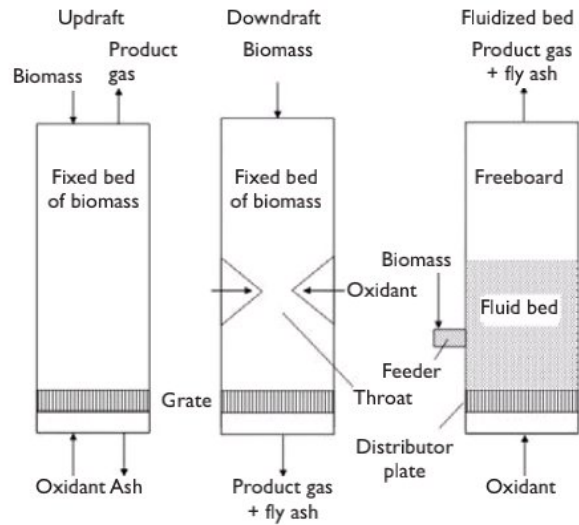


Figure 8.19 *Different kinds of gasifiers suitable for co-production of producer gas and biochar*

Source: Robert Brown

process a wide variety of fuels. Disadvantages include relatively high power for gas blowers and high particulate loadings in the gas exiting the fluidized bed.

Hydrothermal processing (HTP) describes the thermal treatment of wet biomass to produce primarily carbohydrate, liquid hydrocarbons or gaseous products, depending upon the reaction conditions, with biochar as a co-product (Elliot et al, 1991, 2004; Allen et al, 1996). As the reaction temperature increases, higher pressures are required to prevent boiling of the water in the wet biomass. Thus, processing conditions range from hot compressed water at 200°C to supercritical water above 374°C. Although systematic studies of biochar yields have not been performed for HTP, chemical equilibrium considerations would suggest that biochar yield decreases with increasing temperature.

Wood-gas stoves are designed for efficient domestic cooking with wood in the developing world (Kammen, 1996). As illustrated in Figure 8.20, they are essentially miniature batch-operated gasifiers with close-coupled combustion of the volatile

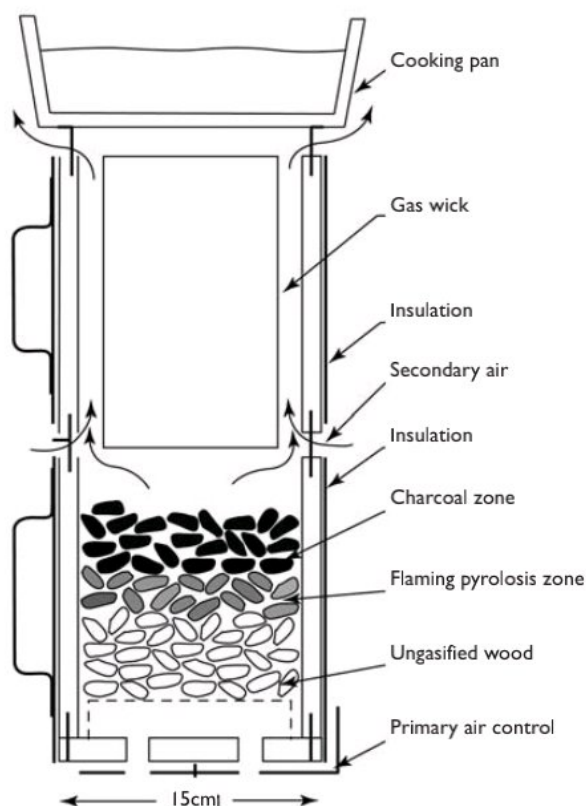


Figure 8.20 Wood-gas stove

Source: Robert Brown

gases to provide heat for cooking. The charcoal remaining at the end of devolatilization

of the biomass can be burned in the stove to supply additional heat, but it can also be recovered as biochar with yield of 20 to 25 per cent by weight (La Fontaine and Reed, 1993). Although the amount produced per batch is only about 150g, daily use by hundreds of thousands of households in a developing country might produce significant quantities of biochar for agronomic and environmental management (see Chapter 9).

Despite these several possibilities for producing biochar, very little work has been reported in the literature on the yields and properties of biochar relevant to agronomic or environmental management applications. As the discussion earlier in this chapter indicates, these yields and properties will be influenced by the composition of the biomass feedstock, but quantitative prediction is currently not possible. The possibility of controlling operating conditions to improve process efficiency and optimize co-product distribution has not been explored despite the theoretical possibilities. Advances in biochar production will require both basic research to understand the mechanisms of biochar formation and demonstration projects to prove the technical and economic feasibility of large-scale biochar production.

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