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Biomass Carbonization

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Abstract

Carbonization is the art of reinventing the waste biomass into a carbon-/energy-rich charcoal. It redefines the principles of renewable energy and power generation. Char is produced by a pyrolysis process in which the biomass is heated in an inert atmosphere to high temperatures until absorbed volatiles are expelled thus enriching its heating value and energy content. Carbonization itself is an old process that is being used till now, but the renewed interest in it especially with biomass is because it opens new doors for commercial and scientific applications. The carbon can be extracted from the produced char to form the precious graphite and graphene. This chapter provides a general overview about slow pyrolysis processes including carbonization and the torrefaction process which is a mild carbonization process. The characterization of different biomass species and their effect on the carbonization process and the final product will be also discussed. Different carbonization processes and methodologies which vary in the process parameters will be addressed, and the most promising ones will be highlighted. An important addition to this chapter is the general design parameters, methodologies, and factors that must be taken into consideration when designing carbonization reactors for lab and industrial designs.

Keywords: biomass, carbonization, torrefaction, slow pyrolysis, biochar, charcoal

1. Introduction

The depletion and rising cost of the fossil fuels along with the rising greenhouse effect created energy and environmental concerns. This urged researches to look for a proper alternative for fossil fuels thus appeared the increasing interest in renewable energy sources. Renewable energy is defined as the energy obtained from naturally repetitive and persistent flows of energy occurring in the local environment [1]. This can be achieved without demolishing the current infrastructure for power generation by finding alternative fuels that can work on the fossil fuels burners currently in place. These alternatives can be produced from biomass because they are the only alternative renewable source of carbon. Biomass is a term for organic waste that stems from plants and produced by photosynthesis making them all green energy sources. During their formation, biomasses already used the exact same amount of carbon dioxide they will later emit as exhaust, so they are usually referred to as a carbon neutral fuel when it is burnt [2–4].

Waste biomass encompasses a wide range of materials, and their availability is advantageous. The wastes usually have a trivial value and could be considered as a pollutant to the environment due to their wrongful disposal methods. There exist many sources of waste biomass either from agriculture or industrial sectors as waste from agricultural processes or frozen vegetables/fruits factories, respectively.

The usage of these different kinds of biomasses has positive economic and environmental impacts and can be called a truly renewable source, because it is a by-product of a different primary production which adds a real additional income. There exist numerous pathways to upgrade the biomass into biofuel either by thermochemical or biochemical methods [5, 6]. In this chapter we are concerned with the thermochemical conversion.

Biomass thermochemical conversion is performed by heat application to start the decomposition of organic materials by cracking the hydrocarbonaceous bonds to transform it into a richer form of energy. Thermochemical conversion processes include combustion, pyrolysis, carbonization, co-firing, gasification, and liquefaction [7]. Pyrolysis is considered as the starting point of all thermochemical conversion technologies because it involves all chemical reactions to form solid “char,” liquid “bio-oil,” and gas “biogas” carried out under oxygen-free or oxygen-limiting conditions. The gases and the bio-oil are from the volatile fraction of biomass, while the char is mostly the fixed carbon component [8].

The proportions of these pyrolysis products depend on the pyrolysis method (fast, slow, or conventional) and reaction parameters. In pyrolysis, biomass is heated in the absence of air.

Pyrolysis can be classified according to the applied heating rate during the process into fast and slow pyrolysis. In fast pyrolysis, the heating rate is very high, and the residence time is lower; these parameters increase the bio-oil yield fraction. On the other hand, slow pyrolysis has lower heating rates that result in higher solid yields or char; hence, our focus will be on it. Slow pyrolysis is even further classified into carbonization as well as torrefaction. This classification depends on the operating temperature of the process and the residence time. Carbonization process utilizes higher operating temperatures and longer residence times than torrefaction. Carbonization aims to produce a highly carbonaceous product, while torrefaction could be a pretreatment process for further processing [9]. The product from any of the two slow pyrolysis processes is called “char,” while charcoal is reserved for the carbonization products. Charcoal refers to the highly carbonaceous product that is intended to be used as a fuel. Furthermore, charcoal can be used in the smelting and sintering processes as a reductant in the metallurgical industry [10]. Char can also be further processed to get activated carbon which is used as an adsorbent [11]. Furthermore, char has a good potential to be used as a soil fertilizer, hence termed “biochar” [12].

Carbonization is the oldest known thermochemical process that allowed humans to convert wood into charcoal, which is the first biofuel that has been used by humans to step out of the Stone Age by refining ores into metals. Carbonization was performed in the early ages by gathering the wood into a cone-shaped pile, covering it with earth, slowly combusting the wood, and allowing for the water content and volatile substances to exit from a central chimney, turning the wood into coal.

This chapter will focus on the slow pyrolysis especially carbonization process for biomass conversion. A brief discussion will be provided for the carbonization products and their characterization techniques. Finally, an overview of carbonization reactor design along with their production techniques concludes the chapter.

2. Carbonization vs. torrefaction

Sometimes carbonization process is confused with other thermochemical processes like torrefaction. Both carbonization and torrefaction are two branches from the pyrolysis process. They both include heating the biomass at specified temperature for a specific residence time until its properties are upgraded for better use either for fuel, fertilizing, or adsorption applications. And even they have the same general

	Torrefaction	Carbonization
Temperature (°C)	200-300	>300
Residence time	< 2 hours	>2 hours and could reach days
Operating pressure	Atmospheric	Up to 10 atmospheres
Environment	Inert or oxygen limited	Inert or oxygen limited
Heating rate	Low	Low
Main outcome	High energy density	High fixed carbon
Moisture content (%)	<5	<5
Fixed carbon (%)	30	85
Volatiles (%)	65	10
Bio-oil yield (%)	5	30
Biogas yield (%)	15	35
Solid yield (%)	80	35
Hydrophobicity	Hydrophobic	Hydrophobic

Table 1.
 Comparison between torrefaction and carbonization [4, 9, 13].

definition which is given for pyrolysis. The main objective of the carbonization process is to obtain the maximum attainable fixed carbon, but this comes on the account of the product which will suffer low energy yield, energy density and hydrocarbon content. On the other hand, torrefaction aims at maximizing the energy density and energy yield, but this will not provide high carbon content. So, based on the product motivation of both processes, they differ in their process parameter settings in terms of temperature range and residence time which produce either torrefied or carbonized products. Carbonization temperature and time are much higher than of torrefaction. **Table 1** shows the main differences between the carbonization and torrefaction processes. It can be seen in **Table 1** that the environment for both torrefaction and carbonization can be either inert or oxygen limited. Sometimes even small traces of oxygen could provide better results especially with carbonization more than torrefaction. This limited amount partially combusts small fraction of the biomass which delivers enough internal heat to successfully complete either the carbonization process. This also provides more homogeneous product due to better heat distribution across the biomass [9, 13]. Carbonization removes almost all the volatiles in the biomass. Torrefaction retains most of the volatiles except for the very light ones that get easily cracked at low temperatures.

3. Biomass carbonization process

The production of solid biomass fuel has been practiced for thousands of years through carbonization providing early people with charcoal for heat purposes and iron ore extraction. The carbonization process occurs slowly heating the biomass to high temperatures exceeding 400°C and for several hours. The products from this process are charcoal when it is used as fuel, biochar when used as fertilizer or soil amendments, biocoke for metal extraction, and finally activated carbon when regular charcoal is upgraded for adsorption and purification purposes. These products are further explained later in Section 5.

Figure 1 shows the complete carbonization process with all its stages until its intended products are reached. It also shows how the biomass should look in each

stage. A brief explanation of each process is provided indicating key features of each stage. The heat source for this complete process should be by a means of renewable energy like initially the burning part of the raw biomass or by solar heating. Electrical heating is only viable in research but inapplicable and not cost-effective for industrial scale.

The different process regions and heating stages indicated in both **Figures 1** and **2** are further explained as follows.

3.1 Predrying

This is the first step of the carbonization process where the biomass is heated from the room temperature to the drying temperature which is approximately

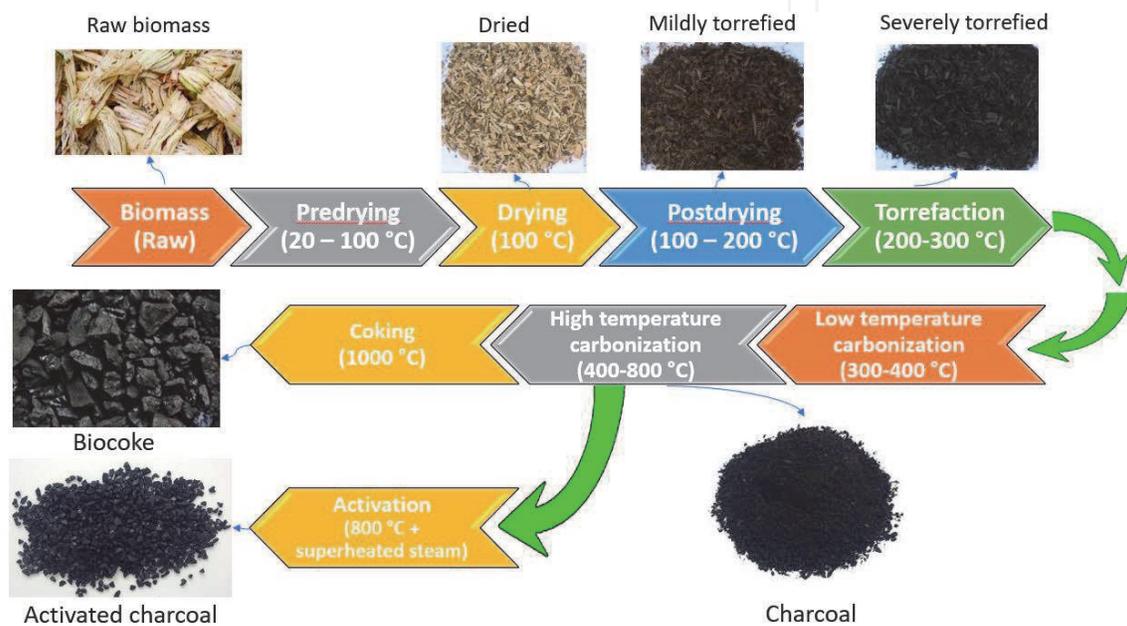


Figure 1.
Complete carbonization process including its products.

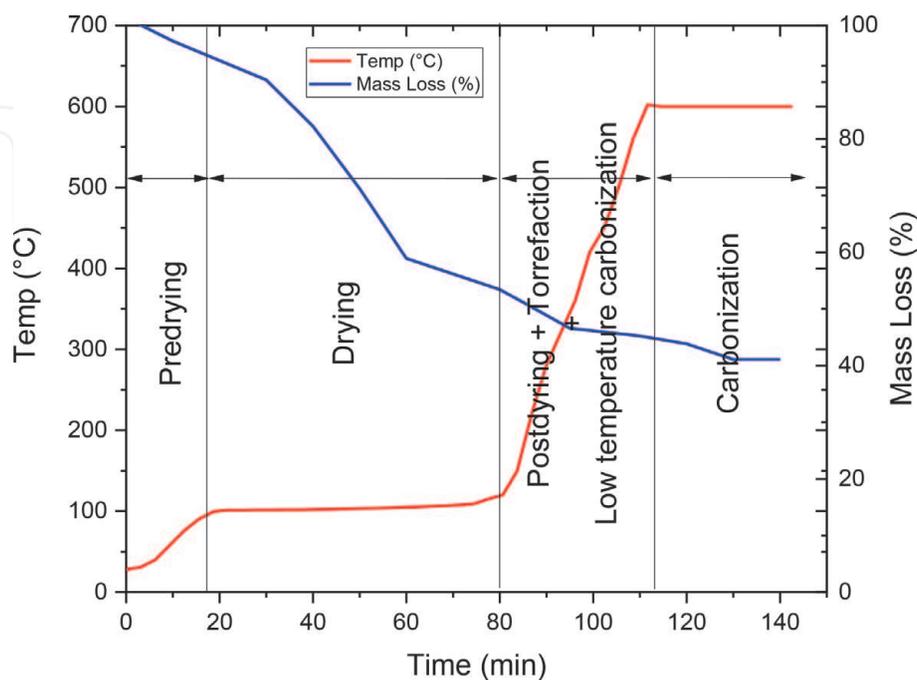


Figure 2.
Temperature and mass loss profiles for carbonization process.

100°C. During this stage, the heat is mostly transferred by conduction from the reactor's walls to the biomass. This stage usually has a steep temperature rise. The heat supplied to the biomass accounts mainly for increasing the moisture temperature to the evaporation temperature.

3.2 Drying

This step is the highest step in energy consumption because of the high latent heat of water especially for biomasses with high initial moisture content like water hyacinth and sewage sludge. All heat supplied during this stage is just to convert the moisture content in the biomass from the liquid to the vapor phase. The biomass's temperature is almost constant during this stage regardless of the reactor's outer temperature because evaporation occurs at constant temperature. In order to reduce the heat loss during this stage, sun drying should be employed for the raw biomass before its introduction to the reactor.

3.3 Postdrying

After drying is complete, the heat energy added to the biomass starts to increase its temperature. This stage ranges between 100 and 200°C. During this stage no significant decomposition starts within the biomass. Only the water molecules bound inside the fibers and very light volatiles are expelled during this stage. This stage does not require high heat and is usually quick.

3.4 Torrefaction

Torrefaction occurs between 200 and 300°C. During this stage the decomposition starts. The first constituent of the biomass to start decomposing is the hemicellulose. By the end of this stage, almost all hemicellulose is decomposed, and small fractions of the cellulose start decomposing. If the heating process is stopped at this stage to keep the temperature constant, a torrefied product with high energy density and low fixed carbon content is obtained.

3.5 Low-temperature carbonization

This stage occurs between 300 and 400°C. During this stage, both hemicellulose and cellulose completely decompose, and the lignin starts to degrade. The biomass' structure keeps breaking and decomposing to produce slightly richer fixed carbon content compared to torrefaction. However, this results in lower energy density.

3.6 High-temperature carbonization

If heating continues over 400°C, a very-high-carbon-rich charcoal is obtained. The degree of lignin degradation depends on the final temperature. During this stage, very high fixed carbon contents are obtained.

3.7 Coking

If the purpose of the carbonization is to use the product in metal ore extraction, then the heating is increased until the temperature exceeds 1000°C. This produces biocoke which is extremely carbon rich.

3.8 Activation

If the purpose is to produce activated carbon for adsorption, the heating continues until 800°C in superheated steam to remove the tar. The product of this stage has a very large pore volume making it most suited for adsorption and purification applications. This is done by heating the already made charcoal to 800°C in a superheated steam atmosphere. This superheated steam performs two major functions during the activation process. The first is to isolate the charcoal from the oxidative environment ensuring that it does not burn. The second is to remove the tarry residue which is blocking the finely structured pores inside the charcoal. After this steam heating, the product must be cooled in a non-oxidative environment then stored in an airtight container. This activation process makes the inner pores in the charcoal more accessible for adsorption. It also increases the pore surface area which gives the activated charcoal excellent adsorption capacity.

3.9 Cooling

This is the final step in the process line. If the product is removed from the reactor exactly after the carbonization ends, it will ignite, because the reactor's final temperature is much higher than the ignition temperature of the produced charcoal. So, it must be cooled first before it is exposed to the oxidative atmosphere. Usually the extracted heat during the cooling stage is recovered in the form of hot air to be used for biomass predrying before it enters the reactor. This could drastically reduce the very high input heat during the drying stage and increase the overall efficiency of the system.

Figure 2 shows the typical temperature and mass loss profiles for the biomass during the stages of the carbonization process. The mass loss during the heating process depends on the temperature and the biomass's constituents. At temperatures less than 100°C, the mass loss is for surface moisture and light volatiles, 100–120°C for loss of water, 120–200°C for volatile compounds, 200–300°C for hemicellulose, 275–350°C for cellulose, and 160–900°C for lignin [9, 14, 15].

Before discussing the specifics of the different products from the carbonization process, we need first to understand how to characterize these products in the next section.

4. Characterization of the biomass and the carbonized solids

The use of any biomass for conversion to energy will be affected by its characteristics. These initial characteristics will change after being carbonized. This information influences and determines the overall efficiency of the conversion process as well as the overall economics. These characteristics need to be understood in detail before any judgment is made on the carbonized products.

These following mentioned properties are of the greatest importance for characterization.

4.1 Proximate analysis

Proximate analysis gives the general composition of the biomass in terms of gross components such as moisture content (MC), volatile matter (VM), ash (ASH), and fixed carbon (FC). This proximate analysis is performed by thermogravimetric analysis (TGA). The TGA is performed in an inert atmosphere, usually nitrogen, with an initial temperature heating rate of 12°C/min from the

room temperature to 105°C with a holding time of 15 min to remove the moisture content. Then the sample is heated to 900°C with a heating rate of 20°C/min to perform the pyrolysis; then a holding time of 15 min is established at 900°C to ensure all volatiles are removed. After that the temperature is reduced to 850°C then pure oxygen or air fills the test chamber instead of the nitrogen to burn the remaining sample. The remaining amount after the burning is the ash content. The fixed carbon is obtained by subtracting the ash content from the already existing amount before oxygen introduction [4, 16]. The abovementioned temperature profile is shown in **Figure 3** [4].

Figure 4 shows a sample for a TGA analysis and how the proximate analysis can be obtained from it. Each one of the four results is briefly explained below. **Table 2** presents some proximate and ultimate analyses results for selected raw biomasses.

4.1.1 Moisture content (MC)

Biomasses are always characterized with high moisture content as all plants depend heavily on water to grow. The total moisture content of some biomass can reach over 90% such as water hyacinth [17]. MC is undesirable during biomass carbonization because water drains very-high-energy amounts to evaporate and this energy is non-recoverable. Thus, sun drying is very important as it does not consume any power and it makes it easier to finish the drying at the carbonization plant. MC is also an important factor to assess the cost of transportation for the raw biomass. The MC for pyrolyzed or carbonized biomasses should be negligible.

4.1.2 Volatile matter (VM)

VM emerges from the biomass devolatilization which is the cracking of the heavy hydrocarbons in the biomass into lighter volatiles. These volatiles are in the gaseous phase during the pyrolysis process. If these volatiles are captured and cooled, part of them will condensate to become bio-oil, and the remaining will stay as no condensable gases which are called biogas. VM percentage varies according to the TGA process itself as VM depends highly on the heating rate [9]. As the heating rate increases, VM decreases as the time for devolatilization is reduced.

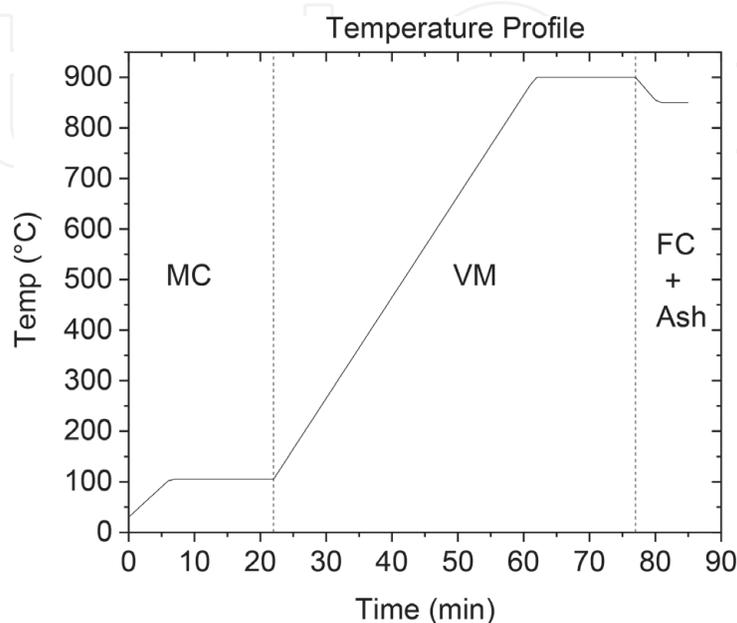


Figure 3.

The temperature profile of TGA test to obtain the proximate analysis [4].

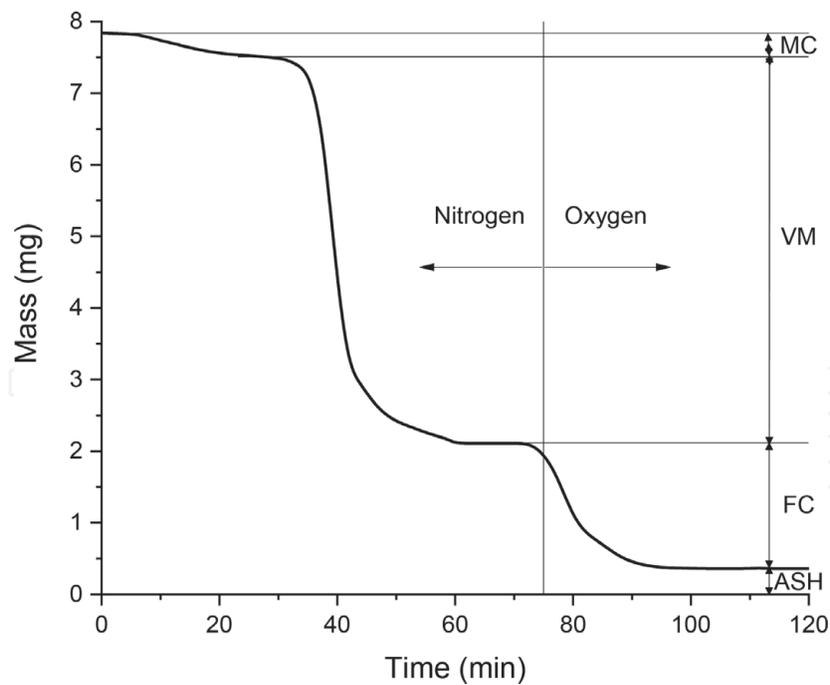


Figure 4.
TGA analysis sample for cotton stalks raw sample [4].

Biomass	Wood	Wheat straw	Rice husk	Rice straw	Lignite coal	Bituminous coal
MC (%)	20	16	8.2	8.5	34	11
VM (%)	82	59	69.5	64.7	29	35
FC (%)	17	21	12.5	8.9	31	45
Ash (%)	1	4	9.8	17.7	6	9
C (%)	51.6	48.5	50.7	52.8	56.4	73.1
H (%)	6.3	5.5	6.9	7.3	4.2	5.5
O (%)	41.5	45.6	41.4	39.1	18.4	8.7
N (%)	0	0.3	1	0.65	1.6	1.4
S (%)	0.1	0.1	—	0.11	—	1.7
Heating value (Mj/kg)	18.6	17.3	21.9	22	26.8	34

Table 2.
Proximate and ultimate analyses results for some raw biomasses [2, 4].

4.1.3 ASH content (ASH)

The ash obtained from biomass conversion does not necessarily come entirely from the biomass itself. During biomass collection and handling, some dirt, rock residue, other impurities, or small pieces of trash are often collected and mixed with the original biomass. All these impurities constitute the major inorganic component of the biomass feedstock which finally remain as ash. So, it is highly recommended that the samples used for characterization and analysis should be washed first and screened to ensure that the collected samples represent the studied biomass. These screening or cleaning processes will not be applicable in large-scale industries as they will cost time and money to swift through the huge biomass bulk. So, these

Biomass		Proximate analysis (%wt)						
		Wet basis			Dry basis			
		MC	VM	Ash	FC	VM	Ash	FC
Rice husk	Raw	8.2	69.5	9.8	12.4	75.4	10.6	14
	Dried	2.7	73.3	10.4	13.5	75.3	10.6	14.1

Table 3.
 Comparison between the wet and dry basis proximate analysis results.

impurities have to be accepted as a drawback in large-scale industrial plants as they will slightly reduce the quality of the carbonized product.

4.1.4 Fixed carbon (FC)

The fixed carbon (FC) is determined from Eq. (1).

$$\%FC = 100 - (\%Ash + \%VM + \%MC) \quad (1)$$

FC represents the solid carbon in the biomass that remains in the char after devolatilization.

4.1.5 Proximate analysis calculation criteria

The proximate analysis can either be calculated based on dry basis (db) which excludes the moisture content or wet basis (wb) which includes the moisture content. Usually the results obtained from the TGA analysis are based on wet basis as they show the moisture content. However, it is not fair to consider the moisture content in judging in which biomass is better than the other because the drying efficiency can relatively affect all proximate analysis parameters. **Table 3** shows that wet analysis cannot be a good judge on the biomass' quality due to different moisture contents of the original sample and after converting to dry basis, both results are the same.

In order to calculate the proximate analysis based on the wet or dry basis, Eqs. (2, 3) are used, respectively.

$$\%property = property / (MC + VM + FC + Ash) * 100\% \quad (2)$$

$$\%property = property / (VM + FC + Ash) * 100\% \quad (3)$$

where property refers to MC, VM, FC, and Ash for wet basis and refers only to VM, FC, and Ash for dry basis.

4.2 Elemental composition

The elemental composition is obtained by performing elemental or ultimate analysis which is sometimes called CHNSO analysis. This analysis results in the composition of the hydrocarbon fuel in terms of its basic elements. The results are based on dry ash-free (DAF) analysis. This means that the moisture content (MC) and the inorganic materials (ASH) are disregarded from the results. The MC and ASH are obtained from the abovementioned proximate analysis in Section 4.1. Some sample elemental analysis results for some raw biomasses are presented in **Table 2**. A typical ultimate analysis result is given in the following form shown in Eq. (4).

$$C + H + N + S + O + MC + ASH = 100\%, \quad (4)$$

where C , H , N , S , and O are the mass percentages of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively, in the fuel.

Generally, in any biomass you will find major percentages of C , H , and O and minor percentages of N . However, S is not usually found in most of the biomasses which is a plus when their carbonized products are combusted, as they will not generate the corrosive sulfuric acid (H_2SO_4) or produce harmful SO_2 emissions. The moisture content is basically water which has the chemical form of H_2O ; the hydrogen and oxygen in this water aren't included in the H and O in Eq. (4). However, this water is expressed as a general term in MC . Thus, the hydrogen and oxygen in the elemental analysis represent only the amounts in the organic components of the fuel itself.

From the ultimate analysis results, we can get the atomic ratios (H/C) and (O/C). H/C and O/C are often represented as Y - X plot which is called "van Krevelen" diagram as shown in **Figure 5** for some general classifications of different hydrocarbon fuels. This figure shows that biomass has very high relative amounts of oxygen and hydrogen, which results in relatively low heating values. The idea from pyrolysis is to move on the van Krevelen diagram from the biomass area to the coal area. The higher the pyrolysis temperature, the closer the produced charcoal approaches coal in the lower left corner of the van Krevelen diagram. To reach anthracite, pyrolysis temperature and residence time should be greatly increased which is done during carbonization.

4.3 Heating value (HV)

The heating value is defined as the amount of released heat by unit mass or unit volume for a fuel initially at 25°C when it is combusted, and the products have been cooled to 25°C again. If this heat includes the latent heat of water vaporization (i.e., the water vapor in the products is condensed), then it is called higher heating value (HHV), else, it is called lower heating value (LHV) [9]. HV could be obtained either experimentally using a calorimeter or numerically using empirical equations. These empirical equations can either depend on the results from proximate analysis, elemental analysis, or both combined in a single Equation [18]. One of the most

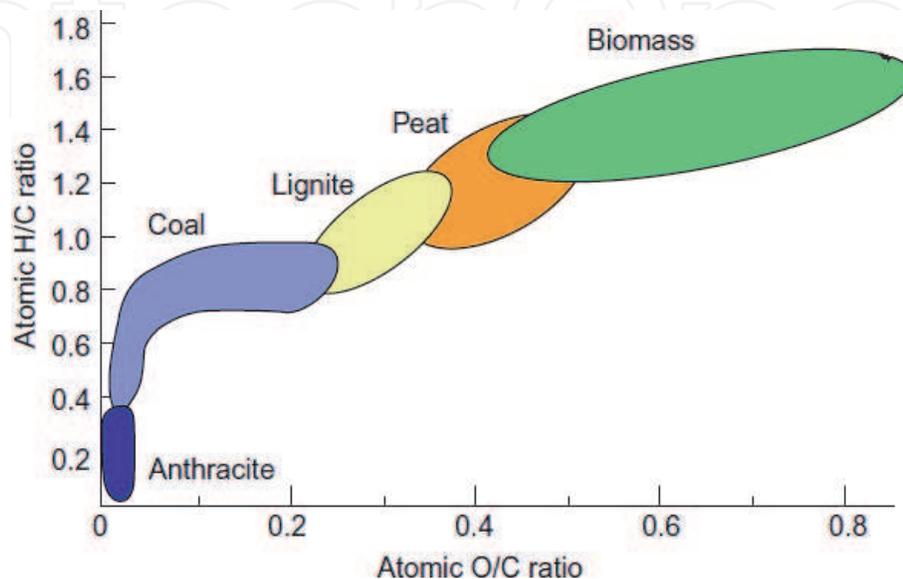


Figure 5.
Van Krevelen diagram, adapted from Basu [9].

used correlations to empirically calculate the HHV from the elemental analysis is provided by Ozyuguran et al. [19] which is shown in Eq. (5). This equation is mostly used because it has the highest value of regression coefficient (R^2) of 0.9441 when compared to experimental results, takes all five parameters (C, H, N, S, O) into consideration, can be used with all biomasses, and has a mean absolute error of 0.3178%, an average absolute error of 1.6978%, an average bias error of 0.0549%, and a root mean square deviation of 0.4230 [19]. The correlation is as follows:

$$HHV \left(\frac{MJ}{kg} \right) = -4.9140 + 0.2611 [\%N] + 0.4114 [\%C] + 0.6114 [\%H] - 0.02097 [\%O] + 0.3888 [\%S] \quad (5)$$

where %N, %C, %H, %O, and %S are the mass percentages of the elemental nitrogen, carbon, hydrogen, oxygen, and sulfur based on dry ash-free ultimate analysis.

For more information about the numerical equations to calculate either the higher or the lower heating value, refer to the article of Ozyuguran et al. [19] and Vargas-Moreno et al. [18].

4.4 Solid and energy yields and enhancement factor

The solid yield (SY) defines the percentage remaining mass fraction of the original biomass after carbonization as shown in Eq. (6). The solid yield could either be defined based on dry basis (db) or wet basis (wb) if the original biomass mass is taken after or before drying, respectively. As biomass contains high water levels, it would be unjust to use the SY on wb because it will give very low numbers, so it is usually taken based on dry basis. Sometimes even when the raw biomass might contain a large amount of impurities and ashes, the SY is taken based on dry ash-free (DAF) basis. The enhancement factor (EF) represents the percentage increase in the heating value due to the carbonization process which is shown in Eq. (7); it is usually calculated based on the higher heating value.

Neither solid yield nor enhancement factor can singularly define the effectiveness of the carbonization or pyrolysis process. The reason is that when the pyrolysis conditions are more severe (i.e., higher temperature and residence time), the remaining mass will become lower. However, the product's higher heating value will be higher. So, in order to correctly judge the performance of the pyrolysis process, both factors should be taken into consideration. The result of this is the energy yield (EY) which is the multiplication of both solid yield and the enhancement factor as shown in Eq. (8).

The solid yield (SY), enhancement factor (EF) of HHV, and energy yield (EY) should be always calculated for all pyrolyzed biomasses to monitor the overall effectiveness and efficiency of the conversion process [20, 21].

$$SY(\%) = \frac{M_{carbonized}}{M_{raw}} * 100 \quad (6)$$

$$EF = \frac{HHV_{carbonized}}{HHV_{raw}} \quad (7)$$

$$EY(\%) = \frac{M_{carbonized}}{M_{raw}} * \frac{HHV_{carbonized}}{HHV_{raw}} * 100 = SY * EF \quad (8)$$

where M_{raw} and $M_{carbonized}$ represent the masses of the raw and torrefied samples, respectively.

4.5 Grindability

The fibrous and plastic nature of raw biomass makes it very hard to handle and transport especially if pneumatic transport is used. They could clog the system and will need large pneumatic channels to pass through them. This creates a process difficulty. Also, if biomass is required to replace coal or be used with coal in co-combustion systems, it must be finely ground and pulverized into very small and fine particles which is very hard for raw biomass and will cost a lot. The grindability is evaluated by calculating the Hardgrove Grindability Index (HGI) [22]. The HGI is measured by a small ball milling machine where a standard mass of 50 g is ground for a given time subject to a known ball force. The resulting product is sieved to measure amounts dropping below 75 μm which is compared against some standards to find the HGI value. The higher the HGI index, the lower the power required to grind the sample [9]. Esteban and Carrasco performed a study to compare the power required to grind one ton of raw wood biomass and coal to a fineness of d_{50} of approximately 500 μm . They found that biomass would require from 130 to 170 kWh where coal would need less than 20% of that power which is in the range of 7 to 36 kWh [23]. Pyrolysis, either torrefaction or carbonization, completely breaks down the biomass' cell structure due to the high heat applied. The treatment temperature is the most influential parameter for grinding. This makes the carbonized products the most brittle and least fibrous which can be even ground by hand. Generally speaking, carbonization highly increases the HGI and thus the grindability of the treated biomass making it fit to be used with regular coal pulverizers, pneumatic systems, and burners allowing for carbonized biomass to replace the fossil coal.

4.6 Hydrophobicity

Raw biomass is hygroscopic due to their fibrous nature which means that it can easily absorb moisture even after drying. This means that if raw biomass is required to be used as a source of energy, it must be dried exactly prior to its burning as it cannot be kept dry during storage. As mentioned above in Section 4.1.1, moisture is a bad thing when using and handling biomass. Biomass consists of three main components, hemicellulose, cellulose, and lignin; their moisture uptake is in the same order from higher to lower [24, 25]. As hemicellulose decomposes in the range of 220–300°C, 275–350°C for cellulose, and 160–900°C for lignin [9, 14, 15]. This means that all pyrolysis treatments which start from 200°C result in almost complete breakdown of the hemicellulose, converting the treated biomass from hygroscopic into hydrophobic nature. This means that carbonized biomass is the most hydrophobic. This eases their handling, storage, and transportation. The hydrophobicity can be determined by the immersion test. In this test, a small sample weight of approximately 0.5 g with particle size less than 1 mm is immersed in deionized water at room temperature in a sintered glass filter for 2 hours. The sample is then air-dried for 1 hour. After that its moisture content is estimated, and the moisture uptake can be identified [22].

5. Carbonization products

5.1 Charcoal (fuel)

Charcoal is the name given to the carbonization product when the main intent of its use is fuel. It is the oldest carbonized fuel ever used by humans. Nowadays

charcoal is produced and used as smokeless fuel source or for barbeques. Charcoal is produced at relatively low carbonization temperatures up to 500°C but at a very slow heating rate which takes a very long time. According to Antal and Mochidzuki [26], the fixed carbon content of charcoal should have less than 30% volatile matter and less than 5% ash content. These values correspond to charcoal calorific values between 28 and 33 MJ/kg.

5.2 Activated charcoal

Activated charcoal is an updated version of the regular charcoal with very high pore number and surface area. This means that it cannot be obtained directly from the carbonization process and it needs further processing to obtain it. The activation process is a two-step process. First the charcoal is produced from regular carbonization. The second step is performed by removing the tar from the inner pores of the charcoal by means of a superheated steam. The activation process is further explained in Section 3.8. The activated charcoal is a valuable product used in the chemical and environmental industries in adsorption. It is also used to remove pollutants from fluids. The pore surface area required for the activated charcoal is specified by the physical structures using the Brunauer–Emmett–Teller (BET) surface area technique. The commercial grades of activated carbons require a specific surface area between 500 and 1500 m²/g. This is a much better upgrade from the carbonized biochar which has a maximum BET surface area of 500 m²/g [27].

5.3 Biochar (fertilizer)

Biochar is the name given to charcoal when its intention is to be used as a fertilizer. To produce biochar, carbonization occurs at high temperatures more than 500°C. Biochar is known for its carbon sequestration potential and soil amendment properties. Biochar is considered as a greenhouse gas reduction route because it increases the carbon content stably retained in the soil. Due to the high thermal stresses applied on the biochar during its formation, it becomes very tough to degrade with time. It can remain in its form for hundreds of years and retaining this carbon in the soil ensuring its fertility for this time [28]. The International Biochar Initiative (IBI) provides a standardized definition for the biochar's characteristics that is most suitable for soil amendment [29].

Sometimes when there is a need for new cultivation area, the first place to look for is the forest remains. These remains are burnt which results in forming biochar which has high carbon content and enhances the soil and improves its fertility. However, if these forest remains are large, this burning could contribute to the overall greenhouse effect because the burning is not controlled and is performed in open air so most of the carbon is burnt and only small parts of the total carbon in biomass is retained as stable solid char in the soil. The higher the degree of carbonization, the higher the fixed carbon amount and the better is the property of biochar [30].

5.4 Biocoke

For metal ore extraction, even regular fossil coal is not enough. The coal is carbonized or coked at very high temperatures to produce the coke. So, biomass can be severely carbonized to produce the biocoke which is a substitute for conventional coke. This severe carbonization process is called coking. Coking temperature can exceed 1000°C. Biocoke should have a volatile matter content less than 15% and ash content between 0.5 and 5% [26]. During metal extraction process, biocoke is

heated with metallic ores with oxides or sulfides. The carbon in the biocoke combines with oxygen and sulfur which facilitates metal extraction. Biocoke has been used for extraction of iron from iron ore during the dawn of metallurgical industries. Steel industry is one of the highest contributors in CO₂ emissions due to their heavy carbon and coke usage. This motivated the use of biocoke in blast furnace to reduce heavy carbon dioxide emissions from the iron and steel industries. Sometimes, the biocoke is pulverized and injected into the blast furnaces.

5.5 Advantages of the carbonization products

Carbonization products have a large number of benefits which can be obtained through the recycling of the biomass waste as follows:

- Renewable solid fuel source
- Carbon-negative process
- Reduces dependability on carbon positive fossil fuels
- Improves the fertility of the soil and subsequently the crop production yield
- Less chemical fertilizers required
- Soil remediation
- Improves water quality
- Counteracts land desertification by increasing its fertility
- Improves water and nutrition retention in the soil

6. Carbonization reactors

There exist hundreds of simple and complicated carbonization reactors with different technologies such as kilns, retorts, and converters. Kiln describes the simplest traditional char-making equipment from wooden logs. Retorts and converters are the industrial reactors that can produce char as well as capture some volatiles and bio-oil. The difference between retorts and converters is the size of the biomass used. Retorts are used for long and thick wood logs, while converters are used with small particles of biomass [31]. These reactors can be characterized according to many classifications as follows [32]:

- The required final product
- Mode of operation (batch or continuous)
- Heat transfer method (direct, indirect, or microwave)
- Input heat source (electric, gas, or biomass combustion)
- Biomass loading method

- Operating pressure
- Construction material (soil, brick, concrete, or steel)
- Mobility (stationary, portable)

In this section, the used characterization method is the feeding system of the biomass into the reactor which includes batch and continuous systems.

6.1 Batch reactors

These reactors are the simplest and easiest ones to build and operate. However, they have some influential drawbacks. The most important disadvantage is the inhomogeneous quality of charcoal due to varying temperature gradients inside the reactor, uneven gas circulation, partial combustion, and uneven particle sizes. Thus, to have a homogeneous product, a good temperature control must be employed to improve the quality of the final product.

6.1.1 Kilns

Kiln is one of the simplest and primitive designs in biomass slow pyrolysis carbonization reactors that usually use wood. Kilns do not need external heat source to heat up; they are built in a way that supplies the required heat internally from partially burning the wood. **Figure 6** shows a primitive construction for the mound kiln where the wood logs are stacked on the ground and an earth covering is built over it, leaving small openings at the bottom for air supply. The stacking and the small openings limit the oxygen supply to the wood just enough to burn some wood to provide heat for carbonization. Since the kiln is well insulated, all the generated heat is retained inside it, and that helps slow down the thermal degradation of the wood into charcoal [9]. The central stack is added to the kiln to remove vapors and volatiles from the pile during the carbonization process and to provide access to the pile for the initial ignition of the wood. Once a small fire is established inside the kiln, the carbonization process begins. The color and density of the flue gases are used to judge the process maturity. White smoke indicates the moisture removal, and it is observed early in the beginning of the process. Yellow smoke indicates the initiation of the pyrolysis, and the kiln's temperature reached 250°C at least. Blue smoke indicates the near completion of the carbonization process. The

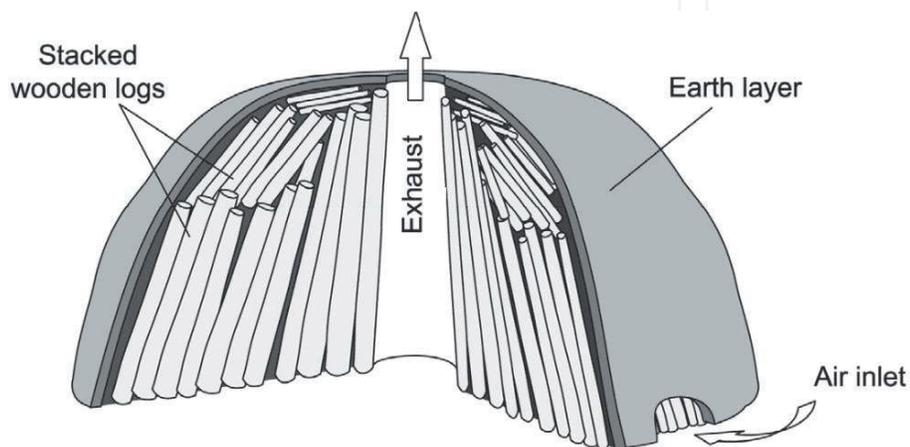


Figure 6.

Cross-sectional view of the mound kiln, adapted from Ronsse et al. [13].

carbonization time depends on the batch size and can reach a maximum of 1 month for very large kilns exceeding 28 tons per batch.

A modification to earth kilns has been made using steel and brick kilns where instead of covering the stack with earth material, the kiln is made from steel or bricks. This provides much better temperature distribution and production homogeneity. Using bricks improves the thermal insulation and the distributed air infiltration inside the kiln [33].

6.1.2 Retorts

The major difference between kilns and retorts is how the pyrolysis heat is generated which is shown in **Figure 7**. As mentioned in the previous section, heat is generated internally in the kilns. In retorts, heat is generated from an external heat source then transferred to the biomass by different means which are:

- Direct heating (the hot gases pass through the reactor and come in contact with the biomass)
- Indirect heating (the heat from the hot gases are transferred to the biomass through the retort's wall)

In both direct and indirect heating, the heat can be generated through different routes which are:

- Burning some raw biomass to generate the main heat which is aided with and after burner to burn the volatiles released from the carbonization process as shown in **Figure 7(b)**.

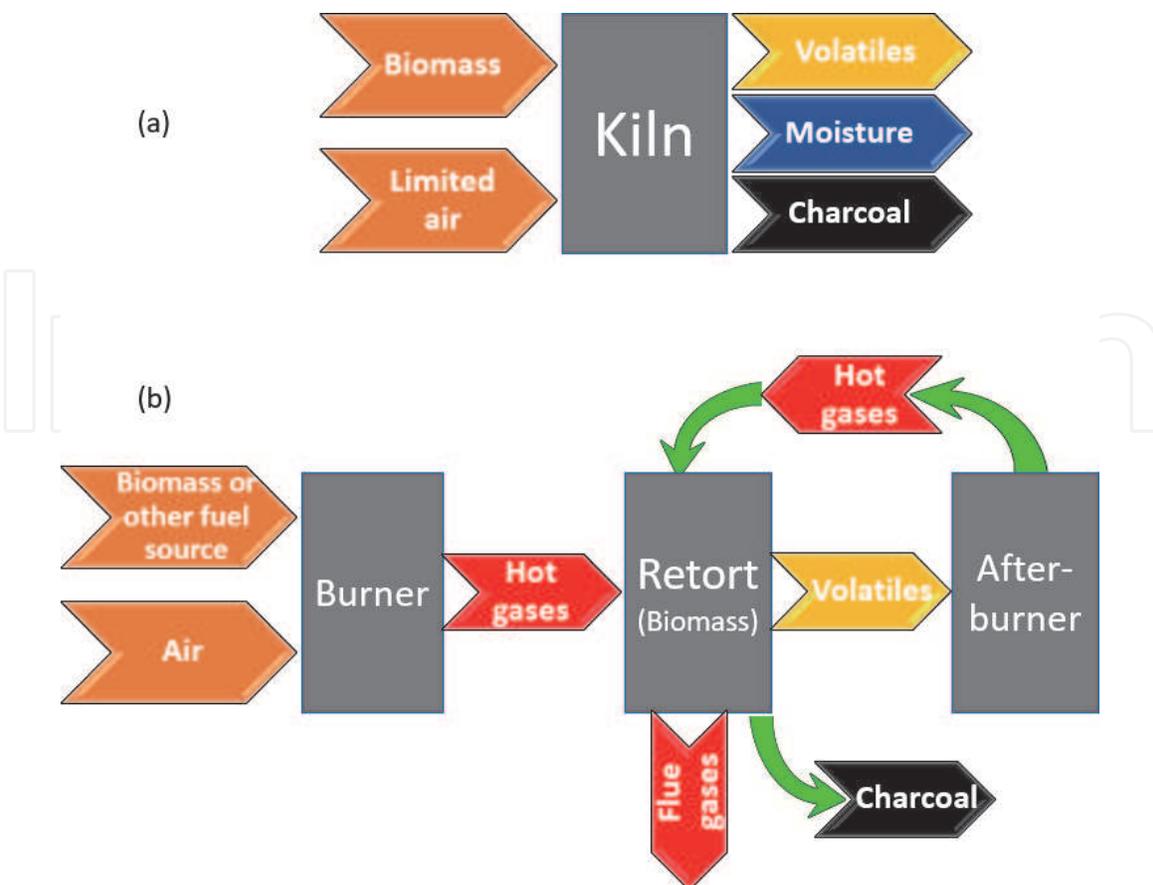


Figure 7.
Comparison between the process sequence of (a) kilns and (b) retorts.

- Burning some external fuel like gas for the main heating aided with burning the volatiles.
- Burning biomass or another external fuel only for the main burner without utilizing the volatiles. But this is the least efficient way and will not be cost-effective.

The advantage of retorts over kilns is that there is no partial combustion for the biomass inside the reactor which increases the output char yield. However, in the case of direct retort heating, partial combustion could still occur. This could occur if the combustion in the burner or the after burner is lean. This will result in excess air in the hot gases which will come into contact with the biomass leading to partial combustion. However, this partial combustion is much less than what happens in the kilns because in kilns it is how heat is generated, while in retorts it's a by-product of direct heating. Also, in the direct heating, sample size must be controlled because small sizes would increase the pressure drop of the hot gases across the retort.

6.2 Continuous reactors

Industrial applications require continuous supply of the carbonization product required so they cannot always have the privilege of working with batch reactors. So continuous reactors had to be developed. Almost all continuous reactors incorporate a sort of mixing mechanism. This greatly increases the product homogeneity and char yield and reduces the carbonization residence time. These are all advantages from the industrial need's point of view. However, continuous systems are more complicated than batch systems as they incorporate many moving heated parts, conveyors, and motors. The speed of these reactors must be optimized according to the required outcome to control the residence time and ensure that the biomass does not exit prematurely. There exist numerous designs for the continuous systems, but we will only consider two of the most used ones: the rotary drum and rotary screw carbonizers. In order for the process to be continuous, the combustion source should be continuous as well. That's why all these reactors utilize the volatiles during the carbonization process to heat the reactor. At the beginning of the process or if the volatiles cannot produce the required heat, there will be an extra biomass screw feeder directly to the burner [34]. All these continuous systems will require an external source for electricity to drive the electrical motors controlling the biomass feeder, rotating drum, afterburner's air blower, and the cooler.

6.2.1 Rotary drum

Rotary drums are basically cylindrical retorts mounted on geared electrical motor as shown in **Figure 8**. It is obvious from the figure that the drum is inclined with the direction of the flow. This is to ensure the flow continuity by gravity as well as good mixing. The degree of inclination and the drum's rotating speed control the flow speed as well as the residence time. The flow control here is not exact as it will differ according to the biomass' shape and physical structure.

6.2.2 Rotary screw

Figure 9 shows the basic construction of the screw carbonizer. It is similar to the rotary drum type except that it does not require being inclined like the drum type,

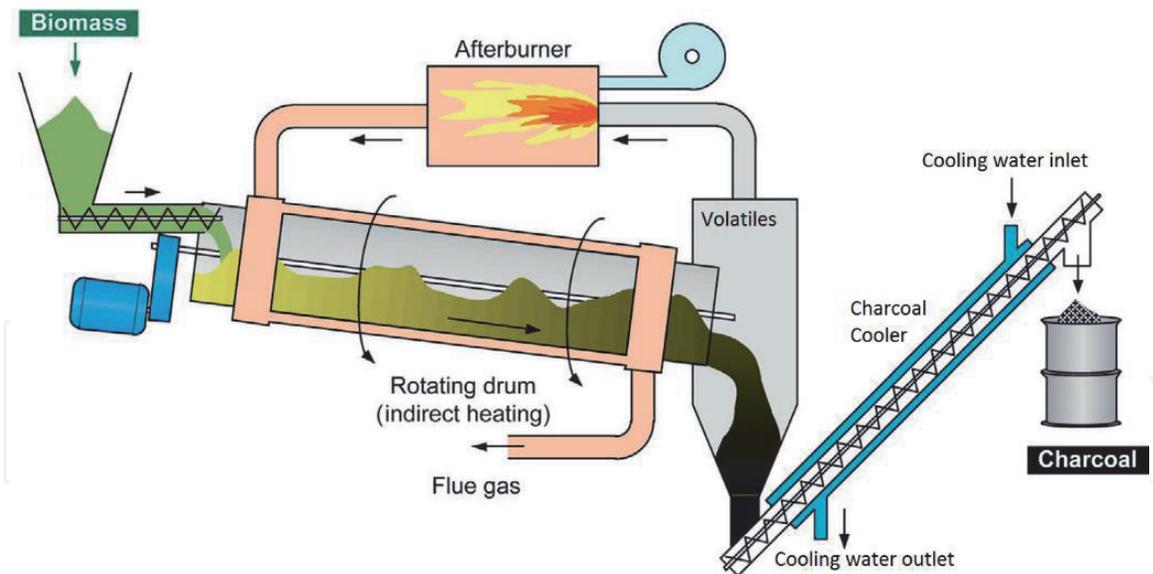


Figure 8.
Rotary indirectly heated drum adapted from Ronsse [13].

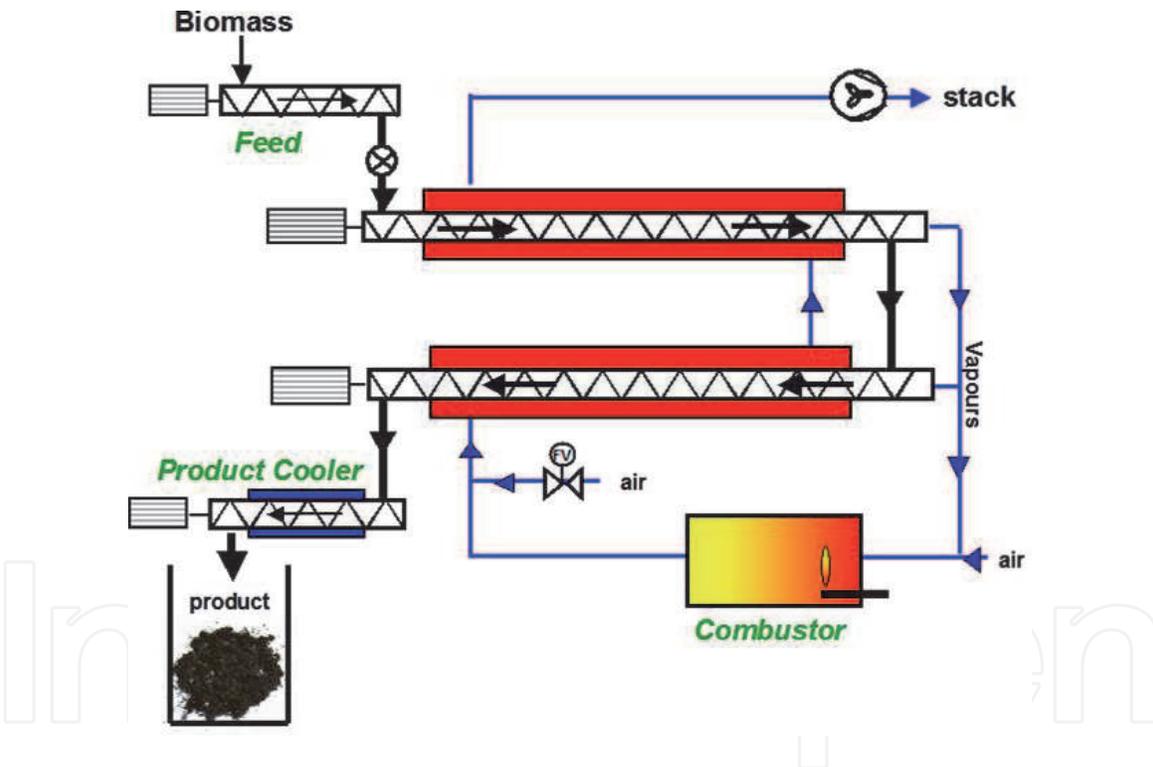


Figure 9.
Rotary indirectly heated screw carbonizer.

and the biomass is transported through the carbonization zone via the rotating helical screw. The screw movement controls the exact flow speed and the residence time. As the volume between two screw teeth is constant, an exact correlation between volumetric charcoal flow rate and the rotating speed can be obtained. So, simply by manipulating the screw's rotational speed, the flow can be adjusted. This reactor can accommodate variable sized biomasses because of the high mechanical power of the driving screw. This system is prone to clogging problems which might interrupt the operation if the biomass is too lumpy. The use of mechanical screw force to move the biomass is advantageous as this mechanical force aids in breaking large biomass lumps into fine powder.

7. Conclusion

Biomass is a renewable, sustainable, and carbon neutral source of solid fuel, soil fertilizer, water and air purifier, and metal ore extractor. Carbonization, which is a slow pyrolysis process, can produce these varied products. Carbonization process is a thermochemical process that has been performed for hundreds of years to upgrade the raw biomass into useful solid product. The process conditions depend on the required product. Both charcoal and biochar are produced by the same process with heating up to 500°C; however they differ in their usage which is either as fuel or soil amendment and fertilizer, respectively. Biocoke production process is the same as for charcoal and biochar except that the heating continues up to and might be exceeding 1000°C. Activated carbon is made from charcoal which is post treated with superheated steam to remove the tarry residue and improving its surface area and pore volume making it suitable for adsorption applications. Several characterization techniques should be performed on both the raw biomass and its carbonized products to judge the carbonization system's effectiveness.

Kilns are mostly used when the manual labor is experienced and just needs basic knowledge of performing this carbonization process. Retorts, although they are still simple, are more complicated than kilns and harder to manufacture. Both kilns and retorts are batch systems. Continuous reactors are gaining raised interest from the industry due to their time effectiveness, automated process, homogeneous product, and continuous product supply. Two of the most common continuous systems are the rotary drum and rotary screw systems. They are almost the same except in the biomass transportation mechanism. Rotary screw is more controllable than rotary drum. As the process parameters depend on the raw biomass characteristics, the reactors must be adjusted and optimized with different operating conditions for each biomass used. These continuous systems enabled the overall system size to be reduced opening new pathways to making them portable and easily transported according to the biomass availability.

Conflict of interest

The authors declare no conflict of interest.

Abbreviation

TGA	Thermogravimetric analysis
MC	Moisture content
VM	Volatile matter
FC	Fixed carbon
HV	Heating value
HHV	Higher heating value
LHV	Lower heating value
SY	Solid yield
EY	Energy yield
EF	Enhancement factor
DAF	Dry ash-free basis
db	Dry basis
wb	Wet basis
BET	Brunauer–Emmett–Teller
HGI	Hardgrove Grindability Index

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