

Chapter 2
Thermal Conversion of Biomass

Abstract

Biomass can be converted into cleaner fuels using bio-chemical and thermo-chemical conversion routes. Biochemical conversion routes are time consuming and less efficient. The thermal conversion routes are faster and efficient in conversion. The conversion of biomass to energy through ‘combustion’ is in practice since man learnt how to make fire. Subsequently thermal-conversion processes like torrefaction and slow, intermediate, fast and flash pyrolysis were developed. The torrefaction is used to obtain densified bio-mass as a cleaner solid fuel. The pyrolytic processes are capable of yielding gaseous, liquid (bio-oil) and solid (bio-char) in varying amounts depending upon the rate of heating. Gasification is used to convert biomass into synthesis gas (syngas) that can be used as a gaseous fuel or for producing other liquid products. Thermal liquefaction of biomass is used for extracting soluble components from the biomass as value added products. Pyrolysis can be carried out at relatively lower temperatures and ambient pressures. The pyrolysis of biomass is a complex process that involves a series of parallel and sequential physiochemical changes like drying, decomposition, de-polymerization, and scores of secondary reactions. Efforts have also been made to propose thermal degradation pathways through which cellulose, hemicellulose and lignin degrade into smaller molecules.

2. Biomass conversion processes

Conversion of lignocellulosic biomass to energy and value added products can be carried out by using thermo-chemical routes (combustion, pyrolysis, gasification, and liquefaction) as depicted in Fig. 2.1 or biochemical routes (anaerobic digestion to methane, ethanol fermentation, hydrogen production for fuel cells, etc.) as show in Fig. 2.2. The thermo-chemical process is more appropriate than the biochemical process because the later

process needs long time for conversion into value added products and is less efficient (Ahmad et al., 2017). The thermal- conversion of biomass is a relatively simpler and cleaner conversion processes to produce energy from biomass in the form of solid, liquid and gaseous fuels. Out of this pyrolysis is the most potential process to convert biomass into solid, liquid and gaseous form among other thermo-chemical processes due to its simplicity and capability of yielding gaseous, liquid and solid products in relatively larger amounts. Pyrolysis has received more attention in recent years due to its simplicity, low operating cost and high inherent safety (Dai et al., 2017; Ganesapillai et al., 2016). It also yields liquid bio-fuel (bio-oil) and solid residue (bio-char) as valuable by-products in relatively larger amounts compared to other thermal conversion processes.

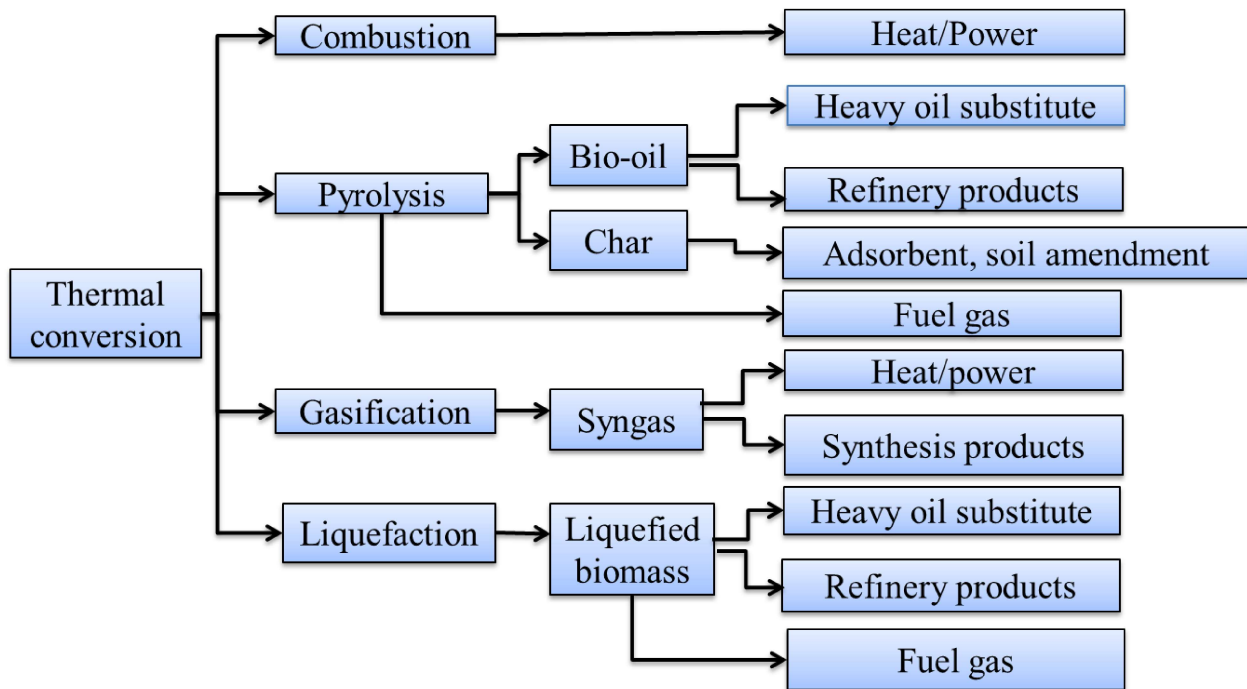


Fig. 2.1 Thermal conversion routes (modified form (Cai et al., 2017))

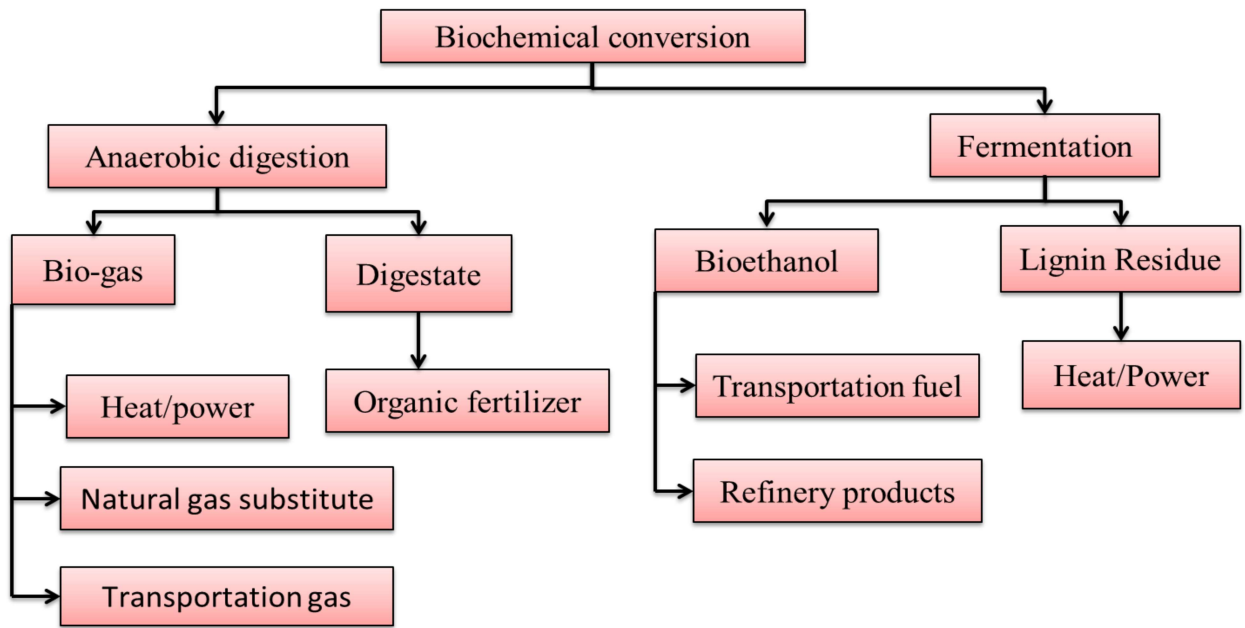


Fig. 2.2 Biochemical conversion routes (modified form (Cai et al., 2017))

Lignocellulosic biomass can be converted into several valuable end-products that can be used as substitute for the conventional fossil fuels are showing in Fig. 2.3.

	General Processes	Specific Processes	Main Products	Fossil Fuel Substitution	
Biomass	Bio-conversion	Alcoholic fermentation	Ethanol	Gasoline, Diesel Additives	
		Anaerobic fermentation	Biogas	Gasoline, Diesel, LPG, Kerosene, Natural Gas	
	Thermal conversion	Pyrolysis	Charcoal	Coal, Lignite, Fuel Oil, Natural Gas	
		Gasification	Synthesis gas, Methanol	Fuel oil, Gasoline	
		Liquefaction	Fuel	Gasoline, Diesel, etc.	
		Esterification	Bio-diesel	Diesel	
		Thermal catalytic cracking		Bio gasoline	Gasoline, Diesel, Kerosene
				Bio-diesel	
				Kerosene and other products	

Fig. 2.3 Thermo-chemical and biochemical conversion process products as substitutes to conventional fossil fuels

2.1 Thermo-chemical conversion processes

Because of the low cost of fossil fuels, biomass thermo-chemical conversion processes for electricity generation have been overlooked in the past. Nonetheless, owing to the energy demands and environmental issues over fossil fuel energy generation, these developments have been revisited. The thermo-chemical conversion of biomass is an achievable pathway to overcome the aforementioned obstacle of other conversion technology utilizing biomass as bio-fuels. The essential purpose of the thermo-chemical conversion processes is to diminish undesirable by-products through the optimization of the process parameters (Mardhiah et al., 2017). Thermo-chemical conversion depends on the process parameters such as temperature range, heating rate, residence time, types of feedstock, flow rate of inert gas, ratio of steam to air, etc. Heat and chemical processes are applied during the thermo-chemical conversion to deliver biofuel of high quality and densified energy content (Goyal et al., 2008). On the basis of process parameters and their condition the thermo-chemical conversion processes are mainly classified as torrefaction, combustion, gasification, pyrolysis and hydrothermal liquefaction (Ong et al., 2020). Torrefaction is a thermal treatment method used to improve the energy content of lignocellulosic fuels or to prepare it for combustion, pyrolysis, gasification, and liquefaction under in inert conditions (Chew et al., 2011). The temperature and reaction time for torrefaction are usually 200–300°C and 15–60 minutes, respectively (Gan et al., 2018). Bio-char, bio-oil, and syngas are the end products of pyrolysis of biomass at temperatures ranging from 300 to 700°C. The hydrothermal liquefaction (HTL) produces bio-oil or crude oil at temperatures ranging from 250 to 374°C and pressures ranging from 4 to 22 MPa. The HTL, unlike pyrolysis, does not necessitate pre-drying. The gasification is the process of transforming biomass

into synthesis gas or syngas, such as carbon monoxide (CO) and hydrogen (H₂) at temperatures above 700°C (Ong et al., 2019). Figure 2.4 depicts various thermal conversion processes together with their corresponding primary and end-products.

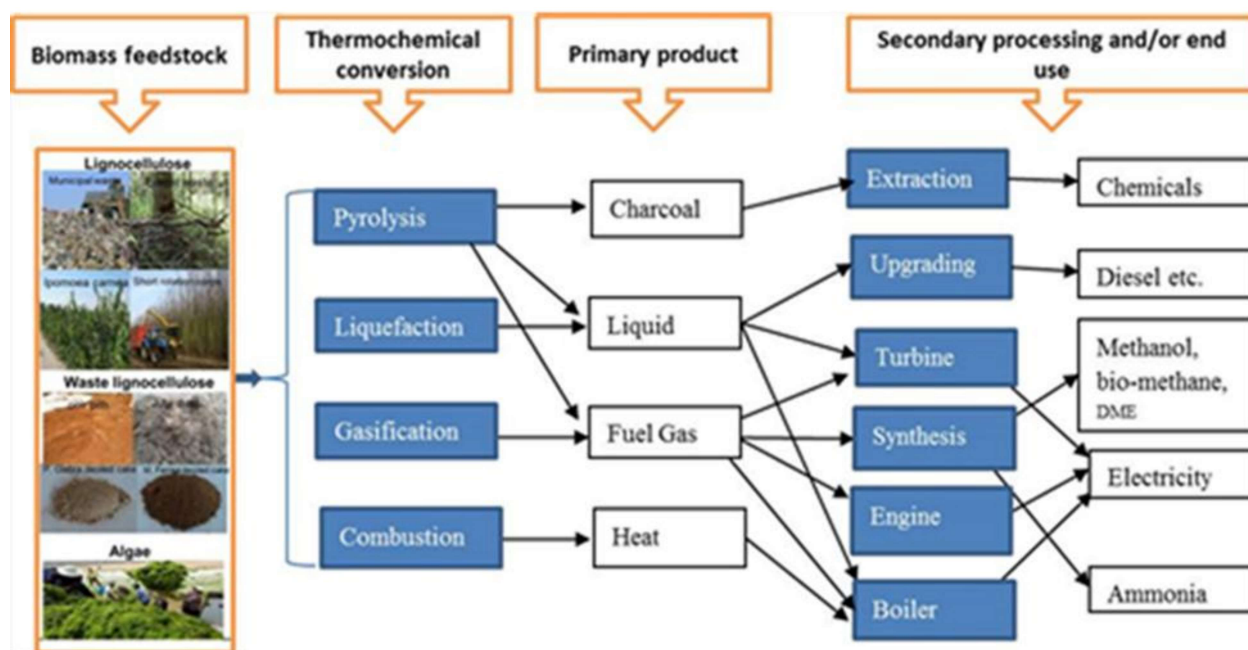


Fig.2.4 Thermal conversion processes with their corresponding primary and end products

2.1.1 Torrefaction

Torrefaction is a thermochemical process that produces a solid fuel with improved combustion properties. This process entails heating biomass at 200–300°C for a set amount of time in an inert or oxygen-depleted environment, typically between 15 and 60 minutes. Biochar (torrefied solid biomass), condensable liquids, and non-condensable gases are all generated. Carboxylation and dehydration reactions break the biomass's tenacity and fibrous structure in order to eliminate oxygen-bearing organic compounds and water from the feedstock. As a result, the energy density of torrefied solid biomass increases as the torrefaction process proceeds, and it has been used as a feedstock to produce heat and

power through the gasification and co-firing processes. Increased residence time during torrefaction lowers the hydrogen and oxygen compositions of biomass, as well as the carbon content, lowering the volatile matter content. Torrefaction, which converts low-quality biomass into a high-energy density, low-moisture feedstock, has also been widely recognized as a promising thermal pretreatment tool for bio-char production (Ong et al., 2020). Figure 2.5 depicts the fundamental concept of torrefaction of raw biomass.

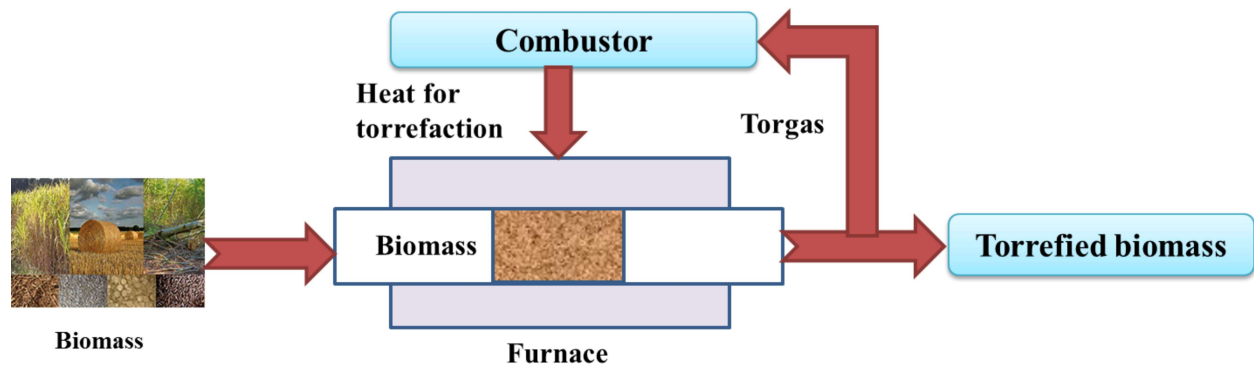
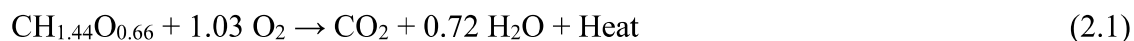


Fig. 2.5 General process of torrefaction (Ong et al., 2020)

2.1.2 Combustion

Combustion is one of the oldest thermo-chemical conversion processes that include homogeneous and heterogeneous reactions. In combustion, the reaction is carried out in the presence of biomass and oxygen at high temperature condition to produce water vapors, heat and carbon dioxide. A general representation of combustion process of a typical biomass is given as (Tursi et al., 2019).



The biomass combustion process is exothermic in nature. Combustion is done inside combustion chambers at temperatures going between 800 to 1000°C. A basic prerequisite of the dry biomass utilized is its moisture content, which ought to be lower than 50%.

2.1.3 Pyrolysis

The process of pyrolysis has been taking place since the development of vegetation on this planet. Flame jumping from forest fires is the case of "flame pyrolysis" (Basu et al., 2010). The first use of pyrolysis of wood into charcoal started around 4000 BC was for iron metal reduction.

Pyrolysis is the thermo-chemical conversion process of various biomass feedstocks into liquid (bio-oil), solid (charcoal), and gaseous (combustible gas also known as syngas) products within the temperature range of 300 to 700°C and in the absence of oxygen or in the presence of an inert gas (Lebaka et al., 2013). High temperatures permit the vaporization of the unstable components of the biomass delivering gases and decomposition of larger molecules into vapors that can be condensed into a liquid fuels. The liquid fuel utilized for different heating and energy applications. The pyrolysis process additionally generates other combustible products, for example, charcoal and gas.

The yields of products mainly depend on pyrolysis conditions. For example, bio-char is the main product when the reaction temperature is under 450°C, whereas bio-oil is the primary product in the range of 350–700°C. High temperatures beyond 700°C lead to the formation of gases. Pyrolysis processes are classified into three types, namely, slow, fast, and flash pyrolysis processes, based on the experimental conditions (temperature, residence time, heating rate, and particle size).

The three major components in the lignocellulosic biomass are unevenly distributed in the cell bio-mass wall. Hemicellulose, cellulose, and lignin contents of the different types of lignocellulosic biomass can range from 15–30%, 40–60%, and 10–25%, respectively. The interaction among the major components in the biomass makes the biomass pyrolysis quite complex. The thermal degradation characteristic of a biomass can be analyzed through the thermal behavior of individual components. However, hemicellulose is an amorphous structure with a low degree of polymerization. Hemicellulose degrades in two stages, which are the cracking of side unit within 100°C and the center wall decomposition at temperatures of 240–290°C. Lignin is a complex aromatic polymer structure that requires more than 500°C to produce abundant hydrocarbon compounds. Figure 2.6 shows the basic process of pyrolysis of biomass feedstock into useful pyrolytic products for various applications as indicated.

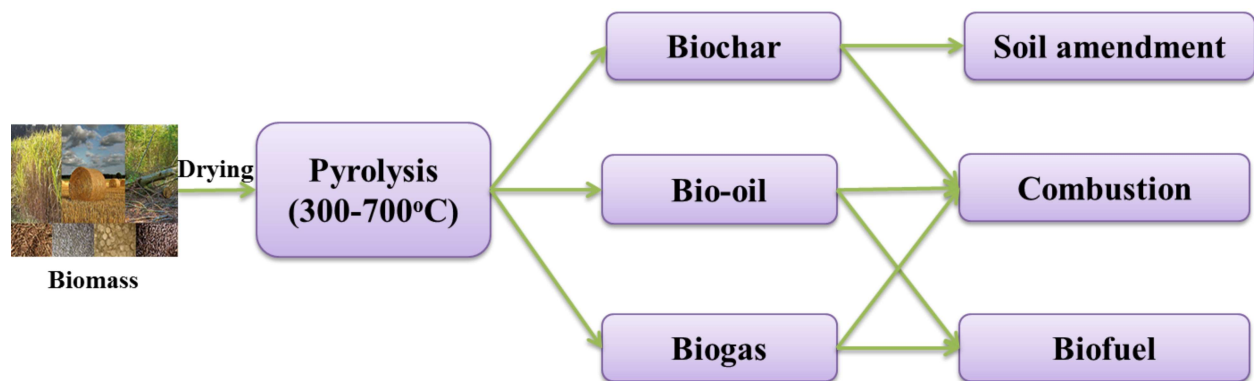


Fig. 2.6 Biomass pyrolysis and its products and their applications (Ong et al., 2020)

2.1.3.1 Mechanism of Pyrolysis

Pyrolysis of biomass feedstock is a very complex phenomenon due to many reactions in occurring in series or parallel i.e. moisture removal, de-polymerization, isomerization,

decarboxylation and char formation. The major stages of thermal degradation of biomass during pyrolysis are (i) moisture removal (ii) primary decomposition (formation of char, depolymerization, and fragmentation) and (iii) secondary reaction (cracking of vapors and depolymerization) (Collard et al., 2014). It can be seen from Fig. 2.7 that the pyrolysis reaction start from an undetermined solid phase that is very complex in nature and before producing gaseous or liquid product it undergoes several intermediate reactions.

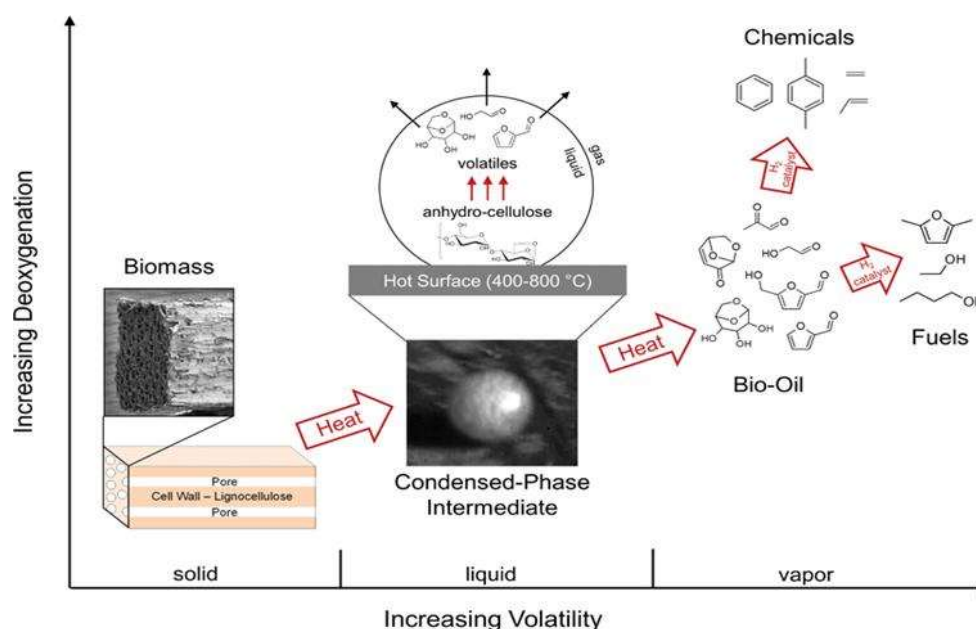


Fig. 2.7 Mechanism of pyrolysis adopted from (Mettler et al., 2011)

2.1.3.1.1 Moisture removal

Moisture removal is the first fundamental step of biomass pyrolysis since it generally utilizes the dry biomass for conversion. Removal of moisture is over up to around 150°C, the actual temperature, however, will depend upon the nature of biomass. Presence of moisture in biomass during pyrolysis can prompt a lower liquid yield, decreased heating value, and higher amount of bio-char (Akhtar et al., 2012).

2.1.3.1.2 Primary decomposition

Biomass is solidly complex and is a cluster of hemicellulose, cellulose, lignin, extractive, and a limited quantity of inorganic substances. At the starting of the pyrolysis, the chemical bonds present in the biomass are broken down into smaller bonds leading to the formation of hot volatiles. These fundamental reactions include char formation, depolymerization, and fragmentation.

2.1.3.1.3 Biochar formation

Char formation includes the transformation of biomass components into solid residues which results because of the development and conversion of benzene rings into stable polycyclic structures. The formation of non-condensable gases takes place during thermal conversion.

2.1.3.1.4 Depolymerization

Depolymerization includes fracture of polymer chains into their respective monomers diminishing the level of polymerization in the chain and release of volatiles. These hot volatile molecules react and/or condense as liquids. The depolymerization reactions in the temperature range of 250°C – 500°C (Mohan et al., 2006)

2.1.3.1.5 Fragmentation

Fragmentation reaction of biomass represents the destruction of chemical bonds within the monomers unit of the polymer into stable gases. The fragmentation reactions take place above 600°C.

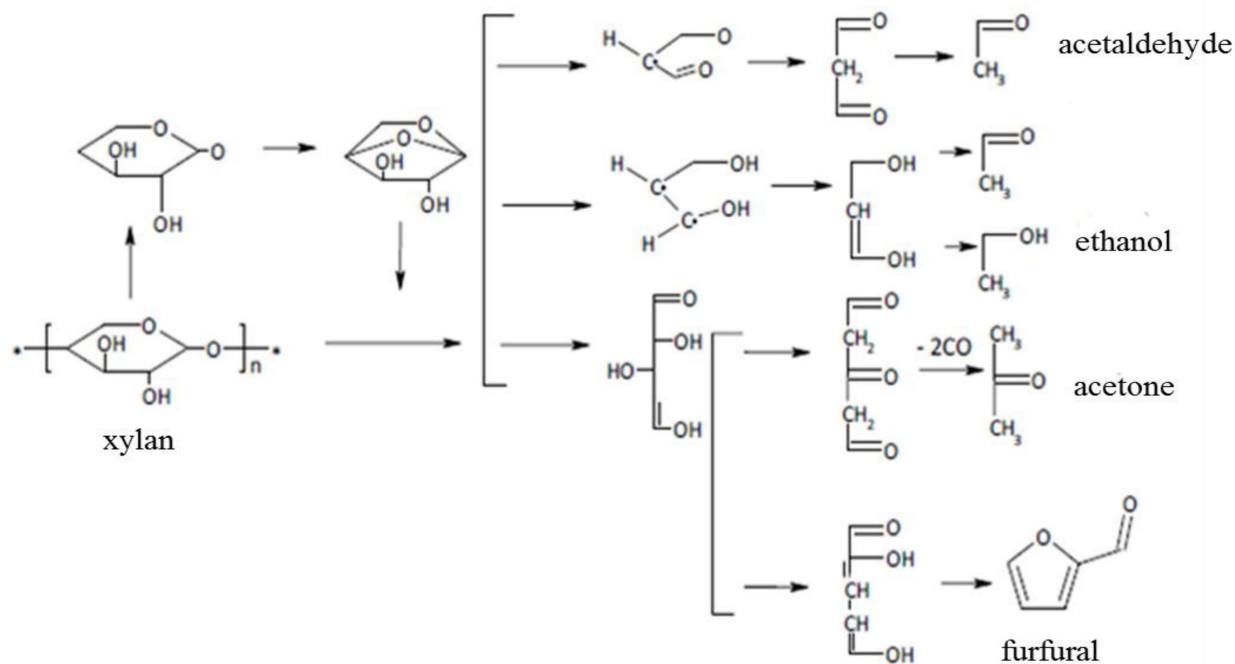


Fig. 2.9 Mechanism of hemicellulose pyrolysis (Antal et al., 1995)

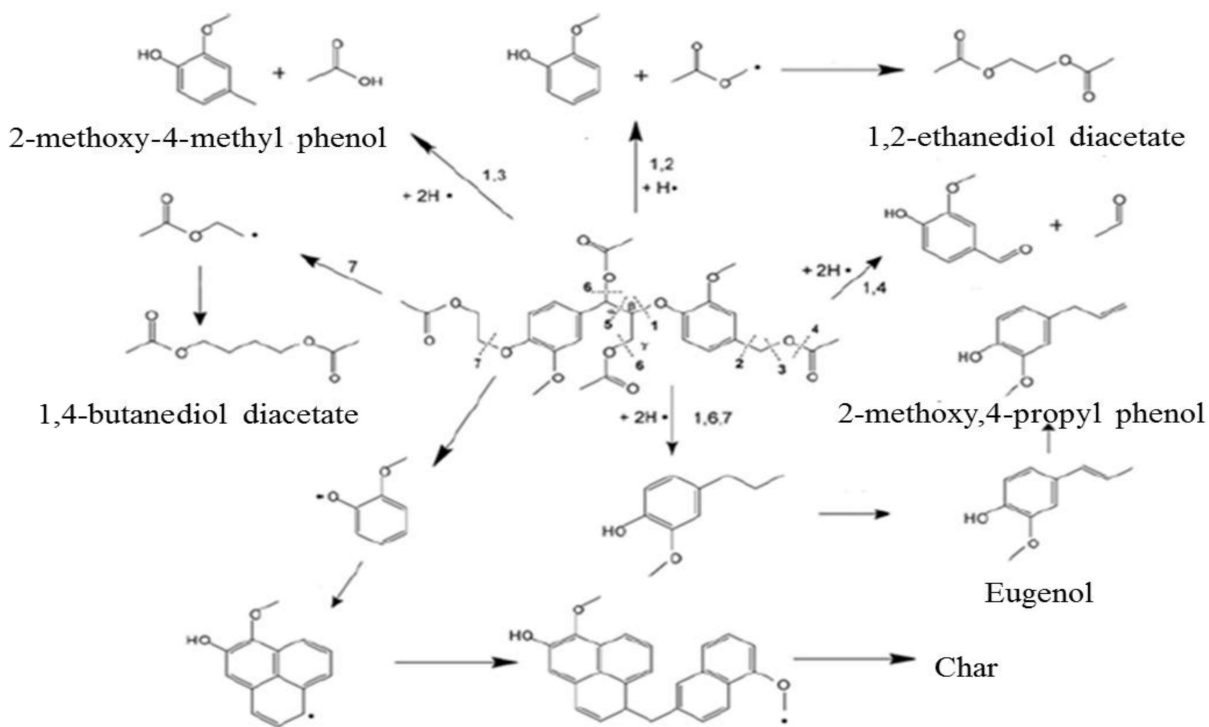


Fig. 2.10 Mechanism of lignin pyrolysis (Antal et al., 1995)

2.1.3.2 Types of pyrolysis

In general pyrolysis process can be classified in to three types as per the process conditions (reaction temperature and heating rate) as: slow pyrolysis, medium pyrolysis and fast pyrolysis.

2.1.3.2.1 Slow pyrolysis

In slow pyrolysis, bio-char is the main product and occurs at a lower heating rate and temperature with a longer residence time (see Table 2.1). Higher residence time inside the reactor leads to the secondary reaction and which produces char due to the combustion of biomass using hot vapor. Therefore it produces lower amount of liquid and gaseous products. For this reason, the emissions of CO, CO₂, nitrogen oxides, and dust are lower in comparison to the intermediate and fast pyrolysis processes. This process has the advantage of upgrading the quality of feedstock.

2.1.3.2.2 Intermediate pyrolysis

Intermediate pyrolysis is more appropriate than slow pyrolysis for the generation of liquid fuel since it is utilized at lower temperature (450°C - 550°C) with higher residence time of vapors (10s - 20s). In this process the quality of finished products improve in the light of the fact that in this process the chemical reaction happens in a controlled way which offers sufficient scope of variation in the process parameters. The various operation condition of intermediate pyrolysis is presented in Table 2.1.

2.1.3.2.3 Fast pyrolysis

In contrast to the slow and intermediate pyrolysis, fast pyrolysis produces bio-oil as the primary product at a high heating rate and short residence time. Fast pyrolysis produces approximately 60-75wt% bio-oil, 13-20wt% gas and 12-20% biochar. The detailed process conditions of fast pyrolysis are summarized in Table 2.1.

Table 2.1 Summary of fast, intermediate, and slow pyrolysis processes (Toro et al., 2021)

Item	Unit	Slow pyrolysis	Intermediate pyrolysis	Fast pyrolysis	Flash pyrolysis
Heating rate	°C/s	≤1.5	3-5	10-200	Very high >1000
Biomass moisture content	%wt	≤50	≤40	≤10	≤10
Biomass particle size	N.A	Large particle size	Coarsely/shredded	Fine particulates	105–250 μm
Biomass residence time	s	600–7200	≤600	≤2	Very short <0.5s
Vapor residence time	s	600–7200	2–30	1-2	<0.5s
Vapor yield	%wt	25-35	25	13-20	13
Bio-oil yield	%wt	25-35	40-50	60-75	75
Bio-char yield	%wt	30-40	25-30	12-20	12

2.1.4 Gasification

Biomass gasification process is carried out in the presence of air, steam, or oxygen at higher temperature ($>1000\text{ }^{\circ}\text{C}$) to obtain a syngas. The products of gasification are also known as producer or product gas. Syngas is mainly composed of mixture of CO and H₂, certain amount of CO₂ and CH₄ and small amount of aliphatic hydrocarbons, benzene, toluene, and tars (besides CO₂ and H₂O). Approximately 50% of syngas is meet from H₂ and CO, where the remaining from CH₄ and aromatic hydrocarbons. The general processes of fix-bed gasification for syngas production are shown in Fig. 2.11.

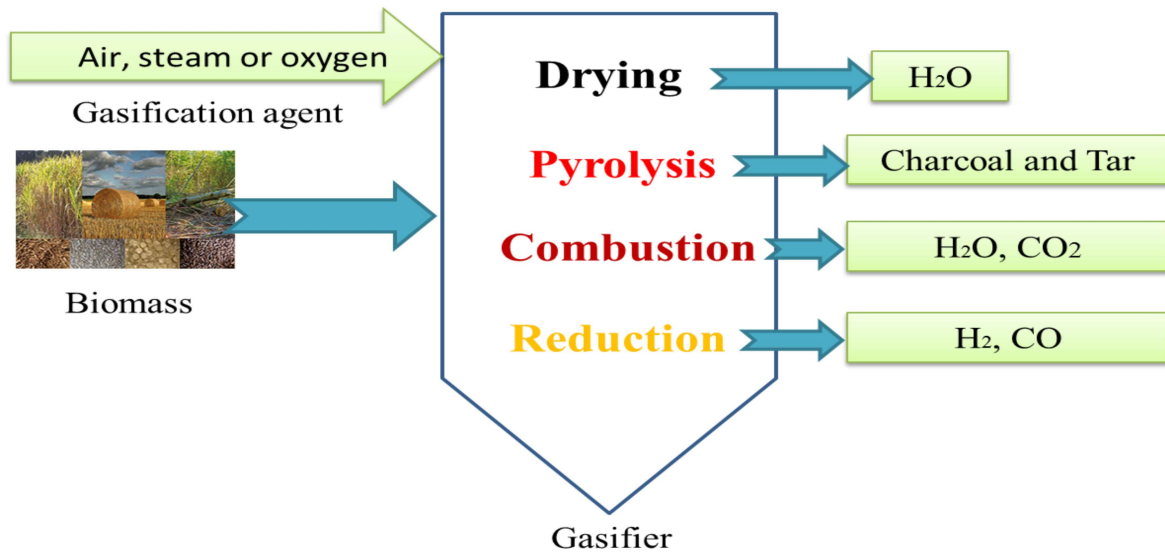


Fig. 2.11 The general process of traditional downdraft fix-bed gasification for syngas production (Ong et al., 2020)

The major reactions occurring in the gasifier are given as:

Partial oxidation:



Complete oxidation:



Water gas reaction:



Water gas shift reaction:



Methane formation:



Types of gasifiers:

The fixed bed gasifier has been the traditionally used for gasification, and are operated at temperatures around 1000°C. Depending on the direction of air flow, the gasifier is classified as updraft gasifier (Fig. 2.12) and downdraft gasifier (Fig. 2.13).

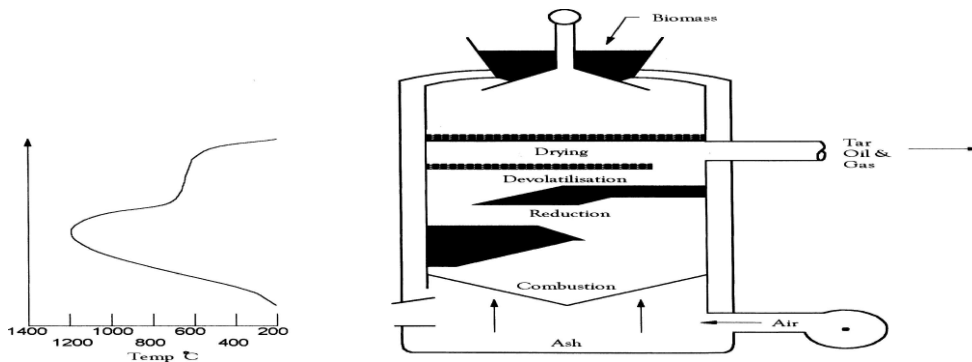


Fig. 2.12 Block diagram of updraft gasifier (McKendry et al., 2002)

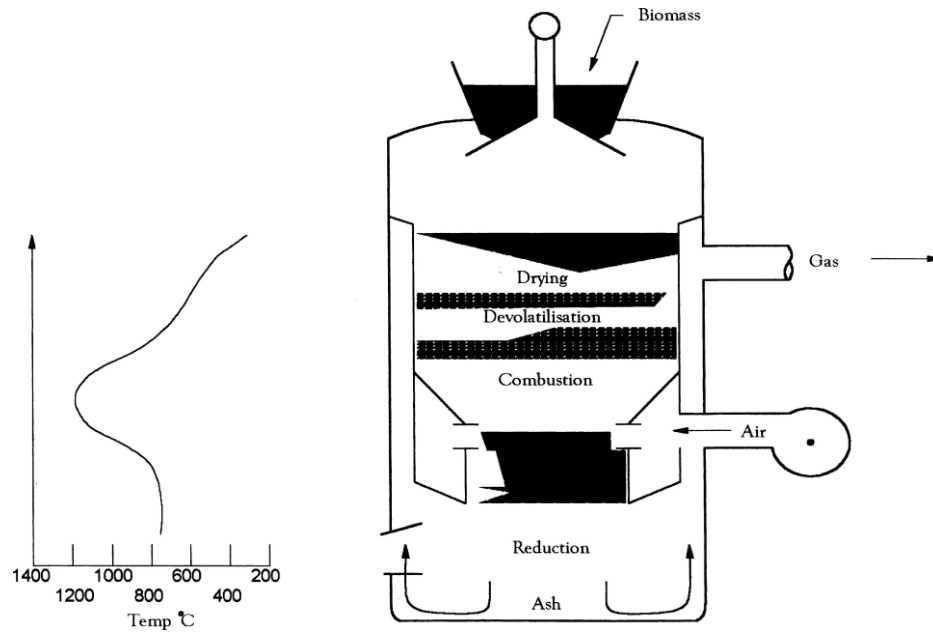


Fig. 2.13 Block diagram of downdraft gasifier (McKendry et al., 2002)

2.1.5 Hydrothermal liquefaction

Tursi et al (2019) define liquefaction is a thermo-chemical conversion method that breaks down polymeric compounds and transforms them to liquid using supercritical water at temperatures ranging from 280 to 370°C and high pressures (10-25 MPa) to turn biomass into value-added chemicals and electricity. Because of its high heating value and low oxygen content, the manufactured commodity is a chemically stable fuel. The primary reason for liquefaction is to manufacture bio-oil with a high H/C ratio. It also does not need dry biomass as a feedstock. Liquefaction increases bio-oil production by reducing HHV, increasing bio-oil yield, and increasing oxygen and nitrogen content. This technology is ideal for transforming high-moisture biomass, such as microalgae, without the need for drying. Compared to pyrolysis, liquefaction has a range of advantages, including lower

energy consumption, lower operating temperature, and higher tar yield (Ong et al., 2019). The basic reaction steps of liquefaction are shown in Fig. 2.14.

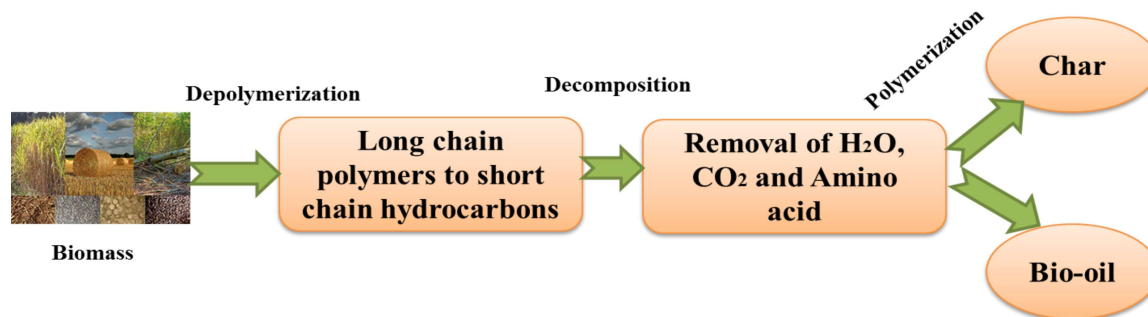


Fig. 2.14 General process of hydrothermal liquefaction (HTL) (Ong et al., 2020)

Table 2.2 summarizes the advantages and disadvantages of various thermal conversion processes. From this table and the preceding discussion it is clear that pyrolysis has several operational advantages over other thermal conversion processes besides being simple in nature. Further, it yields more bio-oil, biochar and gas. In view of this it has received renewed attention during past few years. In this work the thermal degradation of some agricultural and industrial biomasses abundantly available in India has been investigated using thermo-gravimetric and differential thermo-gravimetric (TG/DTG) analytical technique. A laboratory scale fixed-bed tubular reactor has been used to obtain pyrolysis products under controlled conditions. The TG/DTG data have been analyzed the kinetic behavior and elucidate the reaction mechanism. The pyrolysis products have been characterized to know their composition and fuel characteristics. The results are presented and discussed in this thesis.

Table 2.2 Brief summary of advantages and disadvantages of various thermal conversion processes

Processes	Advantages	Disadvantages
Combustion	<ul style="list-style-type: none"> ❖ Produced heat can be used directly for heating and steam generation ❖ Industrially mature and a commercial technology 	<ul style="list-style-type: none"> ❖ Emission problems ❖ Heat cannot be stored ❖ Need for larger flue gas cleaning system ❖ Ash disposal problem
Gasification	<ul style="list-style-type: none"> ❖ Lower air emissions ❖ Less gas cleaning equipment is required due to the comparatively smaller volume of gaseous products ❖ Produced char can be used as activated carbon and/or for soil amendment 	<ul style="list-style-type: none"> ❖ Higher capital cost ❖ Very complex operation due to need for oxygen separation ❖ Higher ash content results in agglomeration
Pyrolysis	<ul style="list-style-type: none"> ❖ Little or no emission ❖ Lower operating temperature than gasification and combustion ❖ Yields different types of end products (solid, liquid, and gaseous) ❖ Liquid fuel can be used for boiler operation or obtaining various types of chemicals ❖ Bio-oil has higher energy density than syngas ❖ Produced bio-char can be used for different application ❖ Potential integration into bio-refineries 	<ul style="list-style-type: none"> ❖ Not yet fully commercialized ❖ The heating value of bio-oil is lower than diesel and petrol ❖ Need separate equipment for engine and boiler applications ❖ Immiscible with hydrocarbons ❖ Difficulty in storage due to viscous and corrosive nature
Hydrothermal Liquefaction	<ul style="list-style-type: none"> ❖ Lower oxygen content than pyrolytic liquid ❖ Requires lower processing of biomass 	<ul style="list-style-type: none"> ❖ More expensive and complex than pyrolysis ❖ Requires long residence time and high pressure