

### 4.3. THERMAL GASIFICATION OR THERMOCHEMICAL CONVERSION OF BIOMASS

#### 4.3.1. Biomass Direct combustion

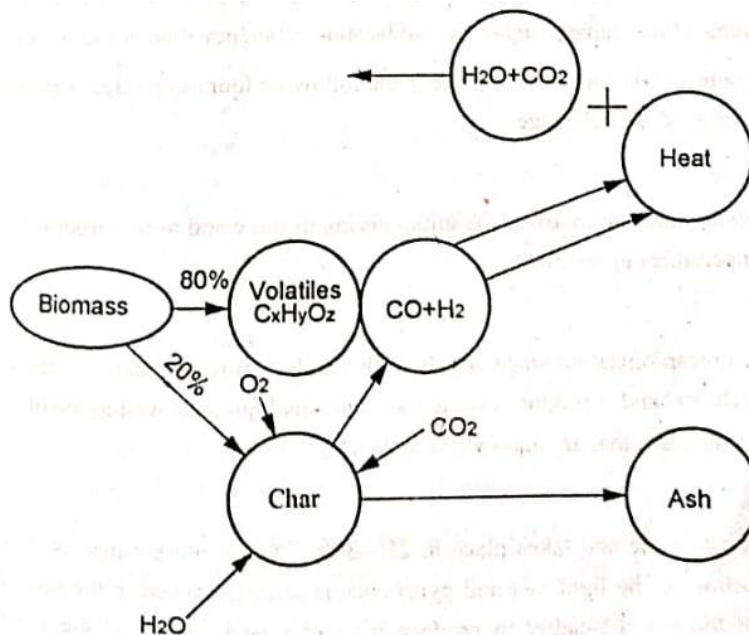


Figure 4.5 Biomass direct combustion

Biomass direct combustion is not only the oldest form of combustion used by humanity but it is also one of the most complex combustion systems to manage. The main biomass for combustion is wood which has been used over the years. It is burnt to provide heat for cooking, comfort heat (space heat), crop drying, factory processes and forming steam for electricity production and transport. As direct combustion involves the use of solid fuels in a multi-phase reaction system with extensive interaction between thermal and mass fluxes, these have only recently been properly analyzed to design efficient combustion systems.

#### processes

The key to understanding solid fuel combustion processes is to recognize that only flue gases burn and release heat, liquids and solids do not burn themselves but actually consume heat in the drying and volatilization processes needed for them to be chemically converted into flue gases. The main fuel intermediates are the volatile hydrocarbons and energy rich organic molecules, carbon monoxide (CO) and hydrogen (H<sub>2</sub>).

#### Carbonisation

Wood is heated with a restricted air flow to form a high carbon product by removing volatile materials from it. This process is termed as carbonisation. The final product is known as charcoal. It is extensively used as a domestic fuel. Charcoal contains 20-

25% volatiles and 75-80% fixed carbon on a dry basis. It burns smokeless and it can be preserved for longer period. Charcoal stoves have a higher overall burning efficiency than wood stoves.

The carbonisation process takes place in the following four main stages determined by the temperature attained in each stage.

Stage 1:

It is endothermic and involves the initial drying of the wood to be carbonised. This stage occurs at temperatures up to 200°C.

Stage 2:

It is the precarbonisation stage which is also endothermic. It occurs in the temperature range of 170-300°C and it produces some pyroligneous liquids as well as small quantities of non-condensable gases that are mainly CO and CO<sub>2</sub>.

Stage 3:

This is exothermic and takes place in 250-300°C temperature range. At this stage, the greater proportion of the light tars and pyroligneous acids produced in the second stage are released from the wood steadily to produce the carbonised residue of the wood which is charcoal.

Stage 4:

It follows at temperatures above 300°C during which the bulk of the remaining volatile components of the charcoal are driven off. Thus, it increases the carbon content of the charcoal.

#### 4.3.2. Pyrolysis

Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen or with restricted air or oxygen supply. It involves the simultaneous change of chemical composition and physical phase and it is irreversible. Biomass is heated either in the absence of oxygen or by partial combustion biomass with restricted air or oxygen supply. In a pyrolysis process, all forms of organic materials including rubber and plastics are processed

The basic process steps for biomass pyrolysis include:

- (a) heat transfer from a heat source that heats the biomass
- (b) initiation of the pyrolysis reaction in the biomass due to the increased temperature
- (c) product formation in the vapor phase resulting in heat transfer between the hot vapor products and the unreacted biomass
- (d) condensation of products from the vapor phase and

(e) autocatalytic reactions between products.

The pyrolysis process consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. Thermal decomposition of organic components in biomass starts at 350°C-550 °C and goes up to 700°C-800°C in the absence of air/oxygen. The long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the form of gases, condensable vapours (tars and oils) and solid charcoal under pyrolysis conditions. Rate and extent of decomposition of each of these components depend on the process parameters of the reactor temperature, biomass heating rate, pressure, reactor configuration, feedstock etc.

The products of pyrolysis are three types of fuels. They are as follows:

1. Bio-oil: It comes from the combustible gases of the process which are condensed into a liquid. Bio-oil can be used as a low grade diesel oil.
2. Bio-char: It is the solid material that is created in the process. It is being promoted for its potential to improve soil properties and fertility as well as sequester carbon.
3. Syngas: These are the permanent gases (CO<sub>2</sub>, CO, H<sub>2</sub> and light hydrocarbons) that remain after the pyrolysis process is over. Syngas can be used in place of natural gas or converted with catalysts to ethanol.

For example, the products of pyrolysis of wood are mainly charcoal (25%), wood gas (20%), pyrolyginous acid (40%), and tar or wood oil (15% ), excluding the moisture content. The last two liquid products are obtained by the condensation of volatiles from wood. Both liquid and gaseous products of pyrolysis are combustible and they are potential fuel feedstocks.

There are two types of pyrolysis systems. Fast pyrolysis optimizes bio-oil production by increasing the rate of pyrolysis temperature greater than 800°C. This process yields approximately 60-70% bio-oil, 15-25% bio-char and 10-15% syngas. In contrast, slow pyrolysis uses slower heating rates at less than 450°C and bio-char is the major end product.

#### 4.3.3. Gasification

Abundant quantities of agricultural wastes such as rice husk, bagasse (sugarcane waste), coconut husk, cereal straw, etc., are produced worldwide every year. They are now under utilised. The major portion of these wastes undergoes natural decomposition resulting in the production of various greenhouse gases which create environmental problems. As mentioned earlier, solid biomass fuels are usually inconvenient, have low energy density and can only be used for certain limited

applications. Conversion of the same biomass to a combustible mixture such as producer gas solves most of these problems with use of solid biomass fuels.

Gasification of biomass is thermal decomposition in the presence of controlled air. It is the conversion process of solid and carbonaceous fuels into combustible gas mixtures known as producer gas. It is also referred to as wood gas, water gas and synthesis gas. This gas can be burned directly in a furnace to generate the process heat for electricity generation. Alternative fuel from biomass is prepared through a gasification process in gaseous form which substitutes for fuel in internal combustion engine.

Biomass contains carbon, hydrogen and oxygen molecules for complete combustion to produce carbon dioxide (CO<sub>2</sub>) and water vapour (H<sub>2</sub>O). Partial combustion produces carbon monoxide (CO) as well as hydrogen (H) which are both combustible gases. By weight, wood gas or producer gas obtained from the charring wood contains approximately 10-20% hydrogen (H<sub>2</sub>), 15-30% carbon monoxide (CO) and small amount of methane. All are combustible. It also contains 45-60% noncombustible nitrogen (N<sub>2</sub>).

### **Steam gasification:**

Methane is directly produced from woody matter by treating at high temperature and pressure with hydrogen gas. The hydrogen can be added or more commonly generated in the reactor vessel from carbon monoxide and steam.

#### 4.3.4. Liquefaction

Liquefaction is a promising technology among the thermochemical processes to convert biomass to liquid valuable products. Bio-oils, bio-crudes or polyols obtained via liquefaction of biomass can be upgraded to gasoline and diesel like fuels and various polymeric materials. In the liquefaction process, biomass is converted to liquefied products through complex physical and chemical reactions. Biomass is broken into small molecules in the presence of various factors such as heat, pressure, catalyst and solvents. These small molecules are unsteady and reactive, and can polymerize into oil like substances with a broad range of molecular weight distribution.

Liquefaction can be divided in two categories such as direct liquefaction and indirect liquefaction. Direct liquefaction refers to pyrolysis or solvolysis liquefaction to produce liquid as and oils or condensable organic vapors.

On the other hand, indirect liquefaction is a type of condensing procedure of a gas mixture (CO-H) to produce liquid products in the present of catalysts. In the indirect liquefaction process firstly, biomass is gasified to syngas in the presence of partial O<sub>2</sub>/air at very high temperature more than 1000°C and then this gas mixture undergoes a catalytic reaction. In this reaction, Fe, Co, Ru- and Ni-based catalysts are

mostly used at high temperature around 340°C or low temperature around 230 °C to produce olefins and gasoline or diesel and linear Les respectively.

Two important processes of liquefaction of biomass are discussed here.

#### (4) Liquefaction through pyrolysis:

As mentioned earlier, pyrolysis is the thermal decomposition of organic compounds in the absence of air. The resulting product streams depend on the rate and duration of heating. Liquid yields exceeding 70% are produced under fast pyrolysis conditions. It is characterised as having fort residence time ( $< 0.5$  s) at moderate temperatures of 450 to 600°C and rapid quenching the end of the process. Rapid quenching is essential if high molecular weight liquids are to be condensed rather than further decomposed to low molecular weight gases.

Pyrolysis liquid from fast pyrolysis is a low viscosity, dark brown fluid up to 15 to 20% water. It contrasts with the black, tarry liquid resulting from slow pyrolysis. Fast pyrolysis liquid is a complicated mixture of hydrocarbons arising from the uncontrolled degradation of highly lignin in lignocelluloses biomass. The liquid is highly oxygenated which makes it unstable. It contains many different compounds, namely phenols, sugars and both aliphatic and aromatic hydrocarbons. The low pH of pyrolysis liquids makes the liquids highly corrosive. The liquid also contains particulate char. The higher heating values of pyrolysis liquids are ranging from 17 MJ/kg to 20 MJ/kg with liquid densities of about 1280 kg/m<sup>3</sup>.

Pyrolysis liquids can be used directly as a substitute for heating oil. In some cases, they are also suitable as fuel for combustion turbines or modified diesel engines. However, there are several problems with pyrolysis liquids. The storage of these liquids becomes difficult due to phase separation and polymerisation of liquids and corrosion of containers. The high oxygen and moisture content of pyrolysis liquids makes them incompatible with conventional hydrocarbon fuels.

#### (b) Liquefaction through methanol synthesis:

Methanol is a liquid fuel that can be burned in a modified internal combustion engines. It is also known as methyl alcohol.

Methanol (CH<sub>3</sub>OH) produced by the reaction of CO and H<sub>2</sub> at 330°C and 150 atm pressure is given by



NI-90.77 kJ/mol

The CO<sub>2</sub> and H<sub>2</sub> are required for this process. It can be produced by gasifying biomass fuels. Gasification often produces less hydrogen than 2:1 ratio of H<sub>2</sub> to CO for methanol synthesis. Thus, the gas mixture (producer gas /synthesis gas) is often

reacted with steam in the presence of a catalyst to promote a shift to high hydrogen content as



$$\Delta H -40.57 \text{ kJ/mol}$$

$\text{CO}_2$  and  $\text{H}_2\text{S}$  in the synthesis gas are removed prior to the methanol reactor. The gas reacts with a catalyst at elevated temperature and pressure to produce methanol in a highly exothermic reaction.

The yields of methanol from woody biomass are expected to be in the range of 480 - 568 litres/tons. Methanol can be used as a liquid fuel in petroleum engines. It has an energy density of 23 MJ/kg.

#### 4.3.2 BIOCHEMICAL CONVERSION OF BIOMASS AND ITS CLASSIFICATION

It makes use of metabolic action of microbial organism on biomass to produce liquid and gous fuel. There are two major biochemical processes. They are given below.

- Anaerobic digestion
- Alcoholic or Ethanol fermentation.

##### **Anaerobic Digestion**

In anaerobic digestion, biogas is produced by the bacterial decomposition of wet sewage sludge, animal dung or green plants in the absence of oxygen. Biogas is also known as swamp ga, sewer gas, fuel gas, marsh gas, wet gas and in India more commonly as "gobar" .The aerobic digestion process breaks down the organic matter into simpler organic compounds. The final product is a mixture of methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ) and some trace gases known as biogas. The process is called anaerobic fermentation. The main fuel component of biogas is methane gas. Carbon present in biomass may be ultimately divided between fully oxidized  $\text{CO}_2$  and fully reduced  $\text{CH}_4$ . It is given by the following equation.

Decaying wet biomass 20-55°C Anaerobic fermentation Biogas(largely  $\text{CH}_4$ , and  $\text{CO}_2$ )

The natural decay process, 'anaerobic decomposition' can be speeded up by using at thermally insulated air-tight tank with a stirrer unit and heating system. The reactions are sightly exothermic and small amount of heat is also generated which helps to maintain the favourable temperature. The most useful biomass materials appear to be animal manure, algae, kelp, hyacinth, plant residues and other organic waste materials with high moisture content.

Anaerobic digestion basically involves the following three phases.

- (i) hydrolysis
- (ii) an acid phase and (iii) methane phase.

The hydrolysis phase covers the breakdown of large molecules into smaller ones by enzymes that are decomposable by bacteria. During the acid phase, complicated molecules

such as proteins, fats and carbohydrates are decomposed by acid-forming bacteria into organic acids, carbon dioxide, hydrogen, ammonia and some impurities. Organic acids are mainly short-chain fatty acids. During methane phase, the methane-forming bacteria converts fatty

acids into methane.

Anaerobic digestion is a simple and low-cost process that can be economically carried out in rural areas where organic wastes are generated in plenty. Biogas is a renewable and not a fossil fuel that is created as a byproduct of plant and animal materials. The complete decomposition of animal or human wastes takes around 10 days. Each kilogram of organic material can be expected to yield 450-500 litres of biogas at atmospheric pressure. The residue left after digestion is valuable fertilizer.

### **Alcoholic Fermentation:**

Ethyl alcohol or ethanol known as alcohol and technically termed ethanol is a colourless and flammable liquid with a chemical formula  $C_2H_5OH$ . It is the alcoholic product of fermenting the sugars in natural raw materials with yeast. The natural raw materials include vegetable matter, growing crops, farm waste, waste organic products (straw and saw dust), molasses, wastes of paper and pulp industries etc.

Alcoholic fermentation or ethanol fermentation is the decomposition of biomass in the absence of air and simple hexose sugars ( $C_6H_{12}O_6$ ) in aqueous solution by action of enzyme present in yeast in acidic conditions. The chemical process involved in ethanol fermentation is given by the following equation.



Ethanol can be produced by the fermentation of any feedstock that contains sugar or starches. It can be produced from cellulose materials that can be converted into fermentable sugar. These three groups of biomass are as follows:

- (i) sugars (sugar beets, sugarcane, sweet sorghum, fruits)
- (ii) starches (small grains such as corn and wheat, potatoes, cassava) and
- (iii) cellulose (wood, solid waste, agricultural residues).

Sugar crops contain monosaccharide forms of sugar such as glucose. It can readily be fermented into alcohol by yeast with no intermediate processing. In fermentation, ethanol is produced by the fermentation of sugar solution. After about 30 hrs of fermentation, the brew contains 6-10% alcohol removed by distillation. One tonne of sugar will produce up to 520 litres of alcohol in which a tonne of grain 350 litres and a tonne of wood are estimated 260 to 540 litres

Starch crops contain sugar units that are tied together in long chains. Yeast cannot use these disaccharide forms of sugar until the starch chains are converted into individual six- carbon groups such as glucose or fructose. This conversion process can be done fairly by the use of cooking in a dilute acid solution or reacting the starch with thermophilic (heat tolerant) enzymes. Cellulose crops contain chemicals called polysaccharides. These chains must be broken down to release the sugar. Breaking the chemical bonds of cellulose is more complicated than breaking down starch to simple sugar. The conversion is typically done physically (milling or heat treatment) or chemically (basic or acid reactions).