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UNIVERSITY, BHOPAL (M.P.)

Post Graduate Diploma in Energy Management



MADHYA PRADESH BHOJ OPEN UNIVERSITY: BHOPAL

SELF-LEARNING MATERIAL

BIOMASS ENERGY

PGDRE 103

SELF-LEARNING MATERIAL

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DRE 103: BIOMASS ENERGY

UNIT -1: INTRODUCTION

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1.2.1 PRODUCTION OF BIOMASS

1.2.2 PHOTOSYNTHETIC EFFICIENCY

1.3 CLASSIFICATION OF BIOMASS

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OBJECTIVES

This unit will give you an overview of the use of biomass as energy sources. The unit also discusses the characteristics of biomass and different biomass conversion systems for using as fuel.

1.1 OVERVIEW OF BIOMASS AS ENERGY SOURCE

The word biomass consists of “bio” + “mass”, and was originally used in the field of ecology simply referring to the totality of animal and plant. After the oil shocks, the meaning of the word was widened beyond ecological field and came to include the meaning “biological resources as energy source”, since it was vigorously proposed that alternative (new) energy sources should be promoted. There is still no strict definition of biomass, and the definition differs from one field to another. From the perspective of energy resources, a common definition is “a general term for animal and plant resources and the wastes arising from them, which have accumulated in a certain amount (excluding fossil resources)”.

Biomass is a term for all organic material that stems from plants (including algae, trees and crops). Biomass is produced by green plants converting sunlight into plant material through photosynthesis and includes all land- and water-based vegetation, as well as all organic wastes. The biomass resource can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. When the bonds between adjacent carbon, hydrogen and oxygen molecules are broken by digestion, combustion, or decomposition, these substances release their stored, chemical energy. Biomass has always been a major source of energy for mankind and is presently estimated to contribute of the order 10– 14% of the world's energy supply (Mckendry, 2002).

Plants produce biomass by a process called photosynthesis in which the energy from the sun converts carbon dioxide and water to carbohydrates and oxygen. Various types of biomass can be burned to produce energy. Examples include wood (from trees), straw, poultry litter, food wastes and a special grass called Miscanthus. When plant biomass is burned, carbon dioxide (a greenhouse gas partly responsible for climate change) is released into the atmosphere. However, the amount of carbon dioxide released is not more than the amount absorbed by the plant when it is growing. This is known as the carbon cycle and a simple illustration of how it works is shown below.

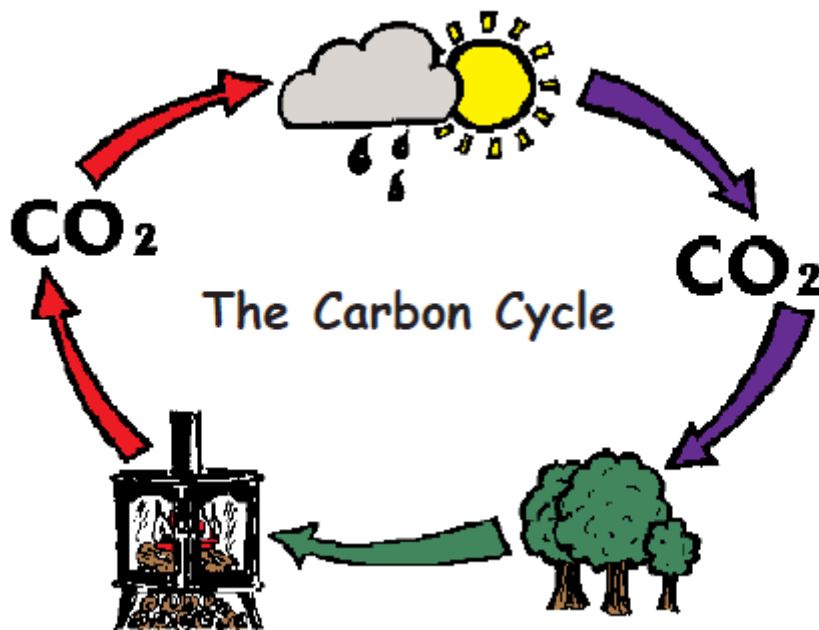


Fig 1: Simple illustration of carbon cycle

1.1.1. TRANSITION IN ENERGY USE

Until the 18th century almost all energy used by man was supplied locally from traditional energy sources. Before man had started using petroleum, coal was the major source of energy. At present, petroleum and natural gas provide more than 55% of the total world energy demand. The world's petroleum resources are expected to last only for next 30 - 40 years

while coal is likely to last for about 200 years. There is a need to save energy, our largest potential, and to replace fossil fuels soon. As the substitute of the fossil fuels, the uses of various new and renewable sources of energy are getting more and more importance all over the world. The most obvious renewable source of energy is the sun itself and the best solar energy-converting machine available is the green plant.

Biomass is a renewable energy source not only because the energy it contains comes from the sun, but also because biomass can re-grow over a relatively short period of time. Through the process of photosynthesis, chlorophyll in plants captures the sun's energy by converting carbon dioxide from the air and water from the ground into carbohydrates—complex compounds composed of carbon, hydrogen, and oxygen. When these carbohydrates are burned, they turn back into carbon dioxide and water and release the energy they captured from the sun. In this way, biomass functions as a sort of natural battery for storing solar energy. As long as biomass is produced sustainably—meeting current needs without diminishing resources or the land's capacity to re-grow biomass and recapture carbon—the battery will last indefinitely and provide sources of low-carbon energy.

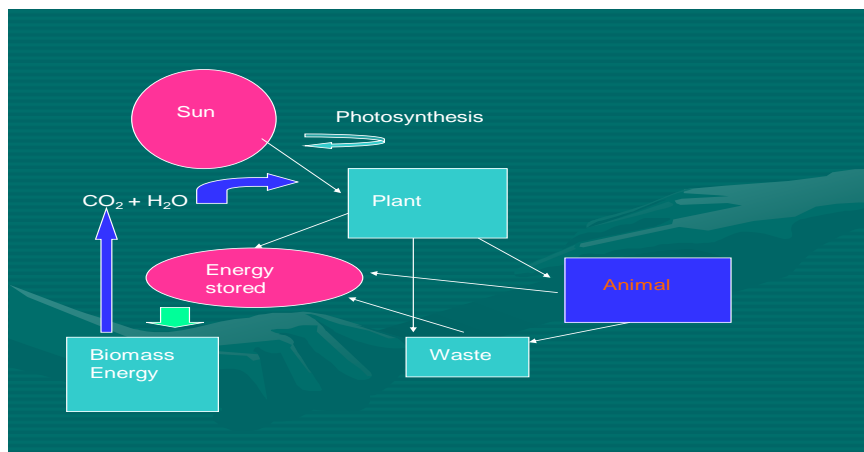


Fig 2: Renewable nature of biomass as energy source

1.1.2. BIOMASS AS A SOURCE OF ENERGY:

Biomass energy's share in developing countries is estimated at 35% of the total energy consumed, but in rural areas this may be up to 75% used mainly for cooking & heating.

Developed Countries	Developing Countries
Industrial countries (av.) -- < 3%	Nepal—95%
Finland – 15%	Malawi-94%
Sweden—25%	Kenya-75%
USA-4%	China-33%
	Brazil-25%

In India, biofuels (fuelwood, crop residues and cowdung) meet 85–90% of the domestic energy demand and 75% of all rural energy demand. Inadequate access and poor quality of energy services continue to be a very critical dimension of rural poverty in India. India has 17% of the world's population and just 0.8% of the world's known oil and natural gas resources. India produces only about 25 % of the total annual requirement of oil. Huge amount of money is spent for importing oil and natural gas. Therefore, we need energy security to supply lifeline energy to all its citizens, at affordable costs at all times.

1.1.3. WHY DO WE CARE ABOUT BIO-FUELS?

Why do we care about bio-fuels?

Answer #1: Energy Security



We need energy security to supply lifeline energy to all its citizens, at affordable costs at all times

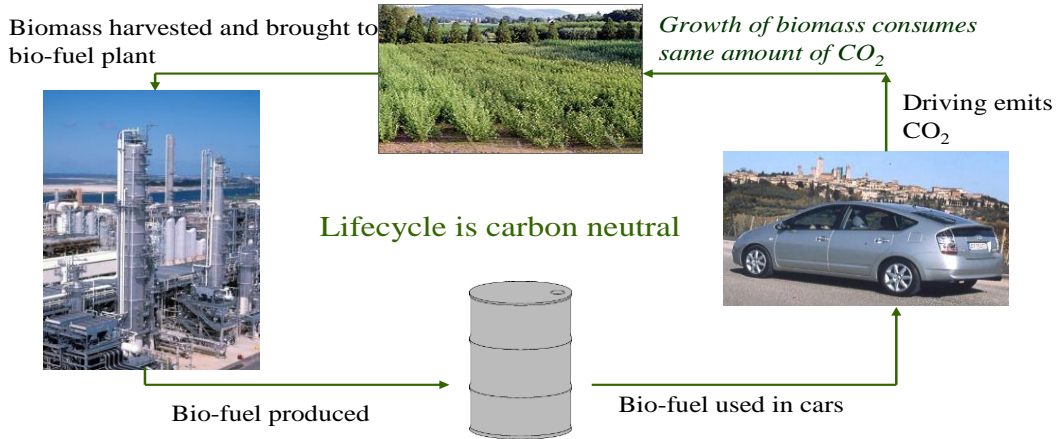
Energy Senario- India's perspective

Ranks World's fifth in terms of energy demand accounting 3.6% of total global energy demand and expected to grow at 4.8% in the future and produces only 25% of its total requirements of oil.

Why do we care about bio-fuels?

Answer #2: Climate Change

Production and use of bio-fuels does not generate greenhouse gases



Why do we care about bio-fuels?

Answer #3: Local Resources



❖ Different tree species are available in the forest

❖ Jatropha as biodiesel feedstock

Why do we care about bio-fuels?

Answer #4: Price

Price of gasoline and diesel continues to rise due to tightness in global oil supplies. Bio-fuels could relieve some market pressure.



1.1.4. HOW IMPORTANT IS BIOMASS ?

- Renewable Source of Energy
- Only Renewable Carbon after petroleum
- Widely available
- Income generating source in Rural areas
- More volatile matter than coal. Burning easy

Biomass chemical (empirical) formula--- $C H_{1.45} O_{0.7}$

Coal chemical (empirical) formula----- $C H_{0.8} O_{0.08}$

Biomass has twice hydrogen and more oxygen per carbon atom than coal.

- can be converted to solid, liquid and gaseous fuel

Drawback

- High moisture than coal
 - Wheat straw- 8 to 15%
 - Wood- 30-60%
 - Bituminous coal 5 to 10%
- Low calorific value than coal

Dry wood- 17-20 MJ/kg

Coal - 23-33 MJ/kg (Bituminous coal)

- Energy density at the point of production is lower for biomass than coal.
- Small biomass energy conversion unit as well as dispersed installation is favourable because of low density and the dispersed nature of biomass production.

While the mass density of biomass makes it less attractive as a fuel than coal, its chemical attributes makes it superior in many ways. The ash content of biomass is typically much lower than for coals and the ash is generally free of toxic metals and other trace contaminants that make difficult the disposal of coal ash in environmentally accepted ways. Furthermore, the ash recovered at biomass conversion facilities has fertilizer value and can be dispersed over the biomass growing areas to help replenish the nutrients removed from the site during harvesting. Also, sulfur (S), which is converted to sulfur dioxide (SO₂) during combustion and contributes to acid deposition, is a major environmental problem associated with combustion of coal, which contains typically 0.5 to 5 percent S by weight; for comparison, the S content of typical biomass feedstocks ranges from 0.01 to 0.1 percent (Johansson *et al.*,1993).

1.1.5. INDUSTRIAL AND HOME USE OF BIOMASS

Wood related industries and home owners consume the most biomass energy. Paper and pulp industries burn their own wood wastes in large furnaces and boilers to supply 60% of the energy needed to run the factories. In our homes, we burn wood in stoves and fireplaces to cook meal and warm our residence. Biomass is also used for water heating in the households.

Biomass can be used as source of industrial energy production with the following routes:

1. Dendrothermal (Dendro— Greek word meaning tree) power generation:

Biomass → direct combustion → steam → turbine → generator → Electricity

2. Biogasification

(i) Gasifier (digester) → anaerobic digester → Biogas (60% CH₄ + 40% CO₂)

(ii) Thermal biomass gasification → producer gas

Heat is used to convert biomass chemically into a pyrolysis oil. Pyrolysis also can convert biomass into phenol oil, a chemical used to make wood adhesives, molded plastics, and foam insulator. Wood adhesives are used to glue together plywood and other composite wood products.

1.1.6. THE FUTURE OF BIOMASS

Biomass has the potential to provide a cost effective and sustainable supply of energy, while at the same time the countries are more interested with the reduction of green house gases. In

case of developing countries the future of biomass will lie on more efficient biomass production and conversion along with modernization of biomass technologies. In case of developed countries the possible direction may be direct combustion of residue and wastes for electricity generation, bioethanol and biodiesel utilization as transport fuel, combined heat and power generation from energy crops etc. In the short to medium term, biomass waste and residues are expected to dominate biomass supply, to be substituted by energy crop in the longer term. The future of biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high energy conversion efficiencies. Key intermediates for petroleum industries such as cellulose, lactic acid and levulinic acid may be provided from biomass stock only. Levulinic acid salts have been proposed to replace ethylene glycol as engine coolant.

1.1.7. DRIVERS FOR BIOMASS

In the past 10 years, there has been renewed interest, world-wide, in biomass as an energy source. There are several reasons for this situation: • Firstly, technological developments relating to the conversion, crop production, etc. promise the application of biomass at lower cost and with higher conversion efficiency than was possible previously. For example, when low cost biomass residues are used for fuel, the cost of electricity produced is more competitive in comparison with fossil fuel-based power generation. More advanced options to produce electricity look promising and allow a cost-effective use of energy crops e.g. production of methanol and hydrogen by means of gasification processes. • The second main stimulus is the agricultural sector in Western Europe and in the US, which is producing food surpluses. This situation has led to a policy in which land is set aside in order to reduce surpluses. Related problems, such as the de-population of rural areas and payment of significant subsidies to keep land fallow, make the introduction of alternative, non-food crops desirable. Demand for energy will provide an almost infinite market for energy crops grown on such (potentially) surplus land. • Thirdly, the potential threat posed by climate change, due to high emission levels of greenhouse gases (CO₂ being the most important one), has become a major stimulus for renewable energy sources in general. When produced by sustainable means, biomass emits roughly the same amount of carbon during conversion as is taken up during plant growth. The use of biomass therefore does not contribute to a build up of CO₂ in the atmosphere. But these three main issues are not the only stimuli: biomass is also an indigenous energy source, available in most countries and its application may diversify the fuel-supply in many situations, which in turn may lead to a more secure energy supply. Biomass production can generate employment and if intensive agriculture is replaced by less intensively managed energy crops, there are likely to be environmental benefits, such as reduced leaching of fertilisers and reduced use of pesticides. Moreover, if appropriate crops are selected, restoration of degraded lands may be possible. Depending on the crops used and the way the biomass is cultivated, increased biodiversity can be obtained, compared to current agricultural practice. Biomass is available on a renewable basis, either through natural

processes, or it can be made available as a by-product of human activities i.e. organic wastes. The potential of biomass energy derived from forest and agricultural residues world-wide, is estimated at about 30 EJ/yr, compared to an annual world-wide energy demand of over 400 EJ. If biomass is to contribute to a larger extent to the world's energy supply, then energy farming, the cultivation of dedicated crops for energy purposes, will be required, using fallow land and marginal lands, the latter being largely unsuited for food crops. When energy crops are considered as a source of biomass, the total energy potential of biomass for energy production may be considerably larger than the energy potential of biomass residues. In 1992 at the Rio United Nations Conference on environment and development, the renewable intensive global energy scenario (RIGES) suggested that, by 2050, approximately half the world's current primary energy consumption of about 400 EJ/yr, could be met by biomass and that 60% of the world's electricity market could be supplied by renewables, of which biomass is a significant component (Price, 1998).

Biomass can be converted into three main types of product:

- electrical/heat energy,
- transport fuel,
- chemical feedstock.

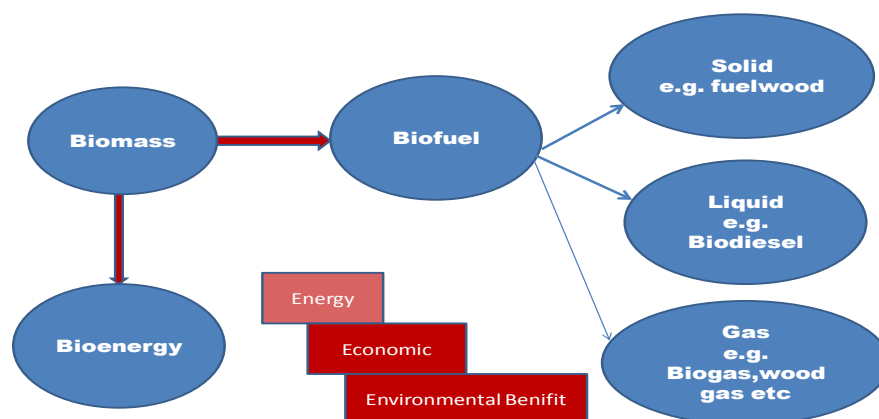


Fig 3: Schematic representation of biomass-biofuel implication

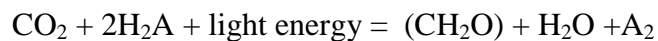
1.2 PRODUCTION OF BIOMASS, PHOTOSYNTHESIS EFFICIENCY OF C₃ & C₄ PLANTS ON BIOMASS PRODUCTION

1.2.1 PRODUCTION OF BIOMASS

While it is recognized that photosynthesis is the ultimate source of biomass production in plants, little attempt has been made to exploit the considerable knowledge of the light and dark reactions of the process to increase the production of biomass.

Photosynthesis is the process by which chlorophyll containing organisms – green plants, algae, and some bacteria – capture energy in the form of light and convert it to chemical energy. Virtually all the energy available for life in the Earth's biosphere, the zone in which life can exist, is made available through photosynthesis.

A generalised, unbalanced, chemical equation for photosynthesis is



The formula H_2A represents a compound that can be oxidised, i.e. from which electrons can be removed and CH_2O is a general formula for the carbohydrates incorporated by the growing organism. In the vast majority of photosynthetic organisms – that is, algae and green plants – H_2A is water (H_2O) and A_2 is oxygen (O_2); in some photosynthetic bacteria however, H_2A is hydrogen sulphide (H_2S). Photosynthesis involving water is the most important and best understood and therefore will be discussed in more detail.

Photosynthesis consists of two stages: a series of light-dependent reactions that are temperature-independent and a series of temperature-dependent reactions that are light independent. The rate of the first series, called the light reaction, can be increased by increasing light intensity (within certain limits) but not by increasing temperature. In the second series, called the dark reaction, the rate can be increased by increasing temperature (within certain limits) but not by increasing light intensity.

Another differentiator amongst plant species is the type of photosynthetic pathway utilised by the plant. Most plants utilize the C_3 photosynthesis route, the C_3 determining the mass of carbon contained in the plant material. Another photosynthesis pathway is represented by C_4 plants, which accumulate a significantly greater dry mass of carbon than do C_3 plants, giving a biomass with increased potential for energy conversion. Examples of C_3 species are poplar, willow, wheat and most other cereal crops, while the perennial grass, Miscanthus, sweet sorghum, maize and artichoke, all use the C_4 route.

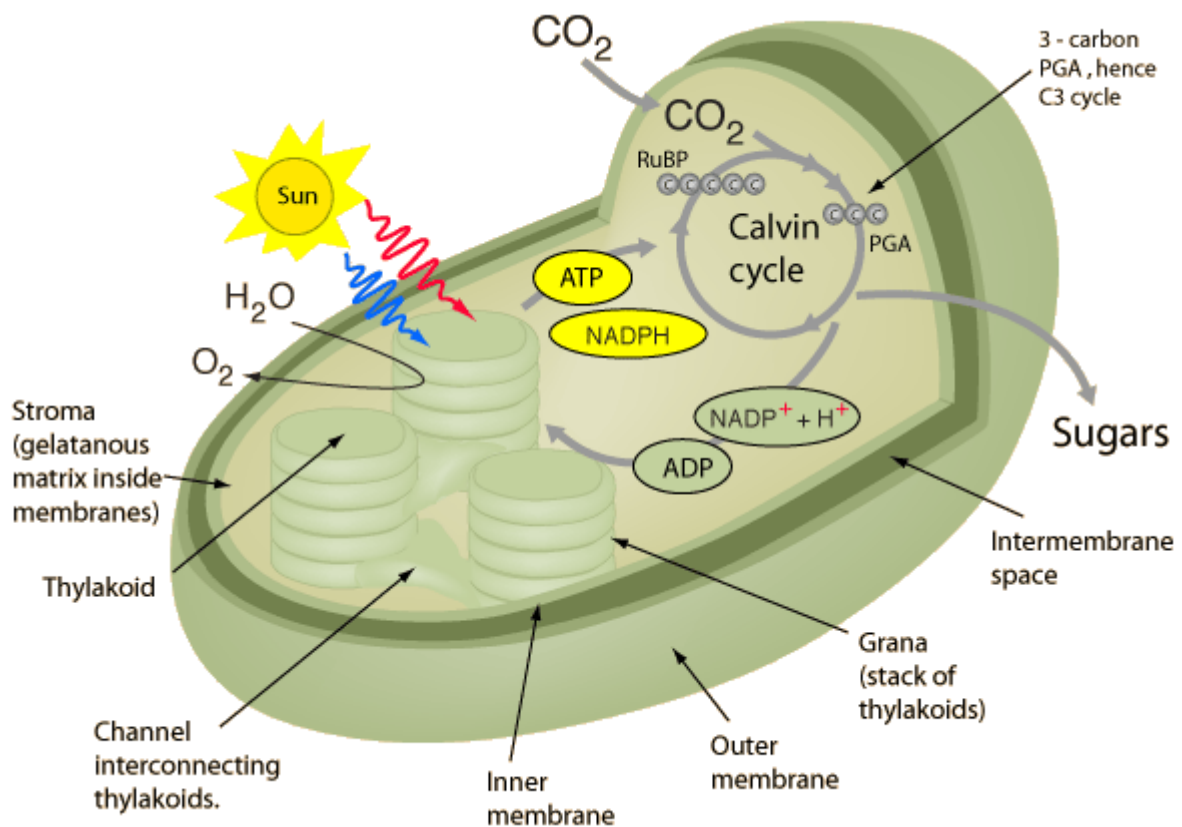
C_3 Photosynthesis : C_3 plants.



- Called C₃ because the CO₂ is first incorporated into a 3-carbon compound.
- Stomata are open during the day.
- RUBISCO, the enzyme involved in photosynthesis, is also the enzyme involved in the uptake of CO₂.
- Photosynthesis takes place throughout the leaf.
- **Adaptive Value:** more efficient than C₄ and CAM plants under cool and moist conditions and under normal light because requires less machinery (fewer enzymes and no specialized anatomy)..
- Most plants are C₃.

C₃ Photosynthesis

Plants which use only the Calvin cycle for fixing the carbon dioxide from the air are known as C₃ plants. In the first step of the cycle CO₂ reacts with RuBP to produce two 3-carbon molecules of 3-phosphoglyceric acid (3-PGA). This is the origin of the designation C₃ or C₃ in the literature for the cycle and for the plants that use this cycle.



The entire process, from light energy capture to sugar production occurs within the chloroplast. The light energy is captured by the non-cyclic electron transport process which uses the thylakoid membranes for the required electron transport.

About 85% of plant species are C₃ plants. They include the cereal grains: wheat, rice, barley, oats. Peanuts, cotton, sugar beets, tobacco, spinach, soybeans, and most trees are C₃ plants. Most lawn grasses such as rye and fescue are C₃ plants.

C₃ plants have the disadvantage that in hot dry conditions their photosynthetic efficiency suffers because of a process called photorespiration. When the CO₂ concentration in the chloroplasts drops below about 50 ppm, the catalyst rubisco that helps to fix carbon begins to fix oxygen instead. This is highly wasteful of the energy that has been collected from the light, and causes the rubisco to operate at perhaps a quarter of its maximal rate.

The problem of photorespiration is overcome in C₄ plants by a two-stage strategy that keeps CO₂ high and oxygen low in the chloroplast where the Calvin cycle operates. The class of plants called C₃-C₄ intermediates and the CAM plants also have better strategies than C₃ plants for the avoidance of photorespiration.

C₄ Photosynthesis : C₄ plants.



(**Phosphoenolpyruvate carboxylase (also known as PEP carboxylase, PEPCase, or PEPC; EC 4.1.1.31) is an enzyme in the family of carboxy-lyases that catalyzes the addition of bicarbonate to phosphoenolpyruvate (PEP) to form the four-carbon compound oxaloacetate)**

- Called C₄ because the CO₂ is first incorporated into a 4-carbon compound.
- Stomata are open during the day.
- Uses PEP Carboxylase for the enzyme involved in the uptake of CO₂. This enzyme allows CO₂ to be taken into the plant very quickly, and then it "delivers" the CO₂ directly to RUBISCO for photosynthesis.
- Photosynthesis takes place in inner cells (requires special anatomy called Kranz Anatomy)
- **Adaptive Value:**

- Photosynthesizes faster than C3 plants under high light intensity and high temperatures because the CO₂ is delivered directly to RUBISCO, not allowing it to grab oxygen and undergo photorespiration.
- Has better Water Use Efficiency because PEP Carboxylase brings in CO₂ faster and so does not need to keep stomata open as much (less water lost by transpiration) for the same amount of CO₂ gain for photosynthesis.
- C4 plants include several thousand species in at least 19 plant families. Example: four wing saltbush pictured here, corn, and many of our summer annual plants.

C4 Photosynthesis

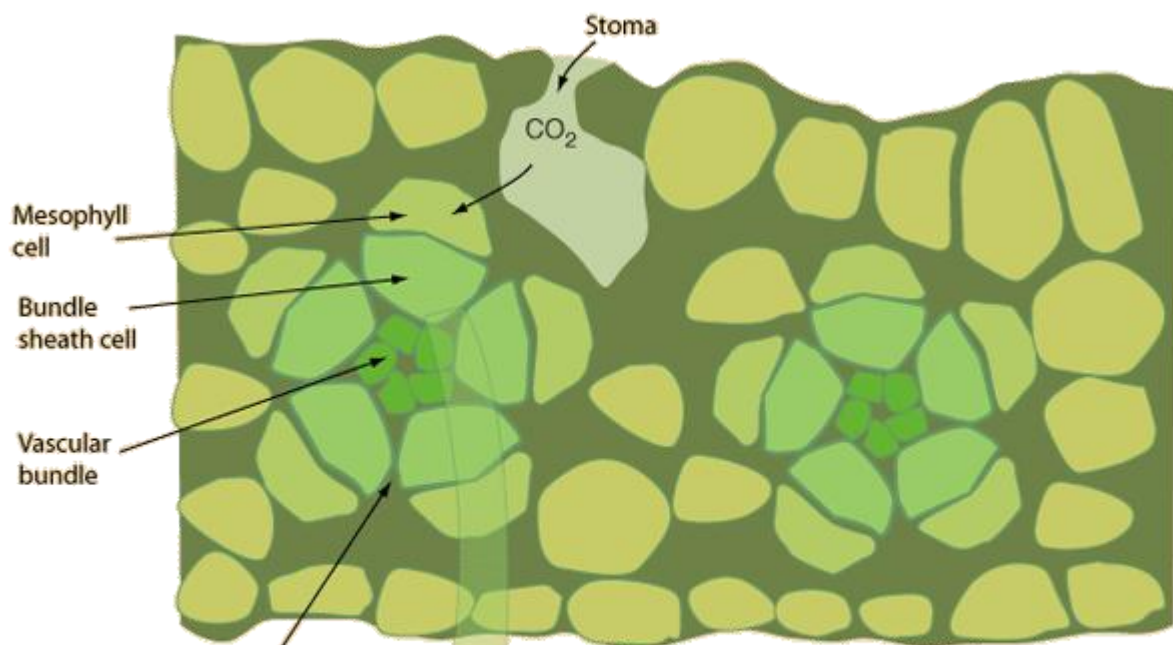
Sugarcane is a champion at photosynthesis under the right conditions and is a prime example of a C4 plant, one which uses C4 photosynthesis.

Sugarcane has been recorded at 7% photosynthetic efficiency.



C4 plants almost never saturate with light and under hot, dry conditions much outperform C3 plants. They use a two-stage process where CO₂ is fixed in thin-walled mesophyll cells to form a 4-carbon intermediate, typically malate (malic acid). The reaction involves phosphoenolpyruvate (PEP) which fixes CO₂ in a reaction catalyzed by PEP-carboxylase. It forms oxaloacetic acid (OAA) which is quickly converted to malic acid. The 4-carbon acid is actively pumped across the cell membrane into a thick-walled bundle sheath cell where it is split to CO₂ and a 3-carbon compound.

This CO₂ then enters the Calvin cycle in a chloroplast of the bundle sheath cell and produces G3P and subsequently sucrose, starch and other carbohydrates that enter the cell's energy transport system.



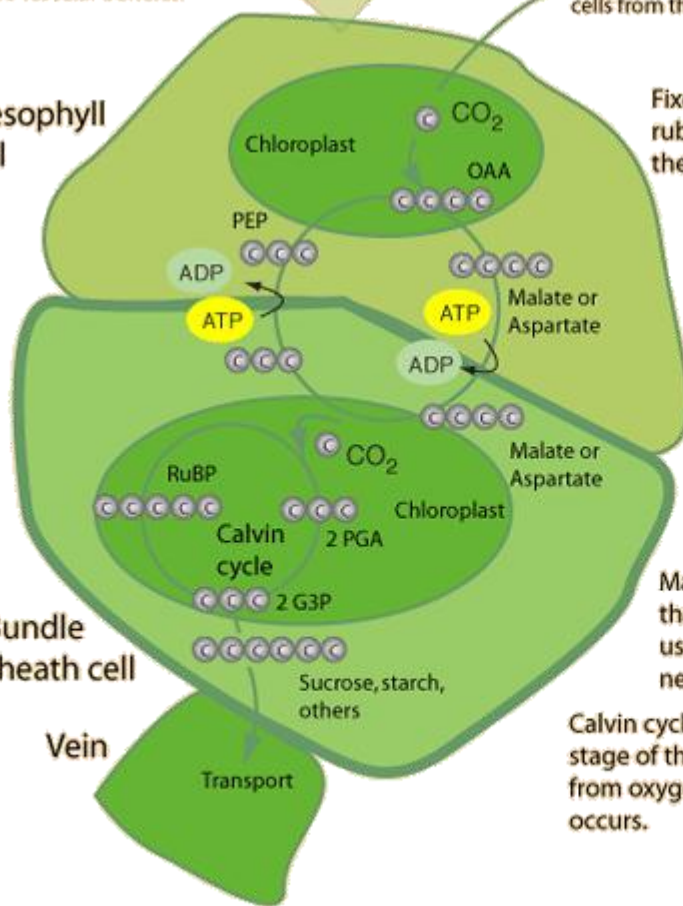
Kranz or "halo" anatomy of cells clustered around the vascular bundles.

Section of a leaf of a C4 plant.

CO₂ diffuses into the mesophyll cells from the nearby stoma.

Mesophyll cell

Fixes carbon, but has no rubisco and does not employ the Calvin cycle.



Pumps the 4-carbon compounds through the membrane at the expense of ATP.

Maintains CO₂ level 10-120x higher than normal. This optimizes the use of the rubisco and less of it needs to be made.

Calvin cycle used to fix CO₂ in this second stage of the process. Rubisco protected from oxygen, so no photorespiration occurs.

The advantage that comes from this two-stage process is that the active pumping of carbon into the bundle sheath cell and the blocking of oxygen produce an environment with 10-120x as much CO₂ available to the Calvin cycle and the rubisco tends to be optimally utilized. The

high CO₂ concentration and the absence of oxygen implies that the system never experiences the detractive effects of photorespiration.

The drawback to C₄ photosynthesis is the extra energy in the form of ATP that is used to pump the 4-carbon acids to the bundle sheath cell and the pumping of the 3-carbon compound back to the mesophyll cell for conversion to PEP. This loss to the system is why C₃ plants will outperform C₄ plants if there is a lot of water and sun. The C₄ plants make some of that energy back in the fact that the rubisco is optimally used and the plant has to spend less energy synthesizing rubisco.

Moore, *et al.* say that only about 0.4% of the 260,000 known species of plants are C₄ plants. But that small percentage includes the important food crops corn, sorghum, sugarcane and millet. Also included are crabgrass and Bermuda. Many tropical grasses and sedges are C₄ plants.

CAM Photosynthesis : CAM plants. CAM stands for Crassulacean Acid Metabolism



- Called CAM after the plant family in which it was first found (Crassulaceae) and because the CO₂ is stored in the form of an acid before use in photosynthesis.
- Stomata open at night (when evaporation rates are usually lower) and are usually closed during the day. The CO₂ is converted to an acid and stored during the night. During the day, the acid is broken down and the CO₂ is released to RUBISCO for photosynthesis
- **Adaptive Value:**
 - Better Water Use Efficiency than C₃ plants under arid conditions due to opening stomata at night when transpiration rates are lower (no sunlight, lower temperatures, lower wind speeds, etc.).
 - May CAM-idle. When conditions are extremely arid, CAM plants can just leave their stomata closed night and day. Oxygen given off in photosynthesis is

used for respiration and CO_2 given off in respiration is used for photosynthesis. This is a little like a perpetual energy machine, but there are costs associated with running the machinery for respiration and photosynthesis so the plant cannot CAM-idle forever. But CAM-idling does allow the plant to survive dry spells, and it allows the plant to recover very quickly when water is available again (unlike plants that drop their leaves and twigs and go dormant during dry spells).

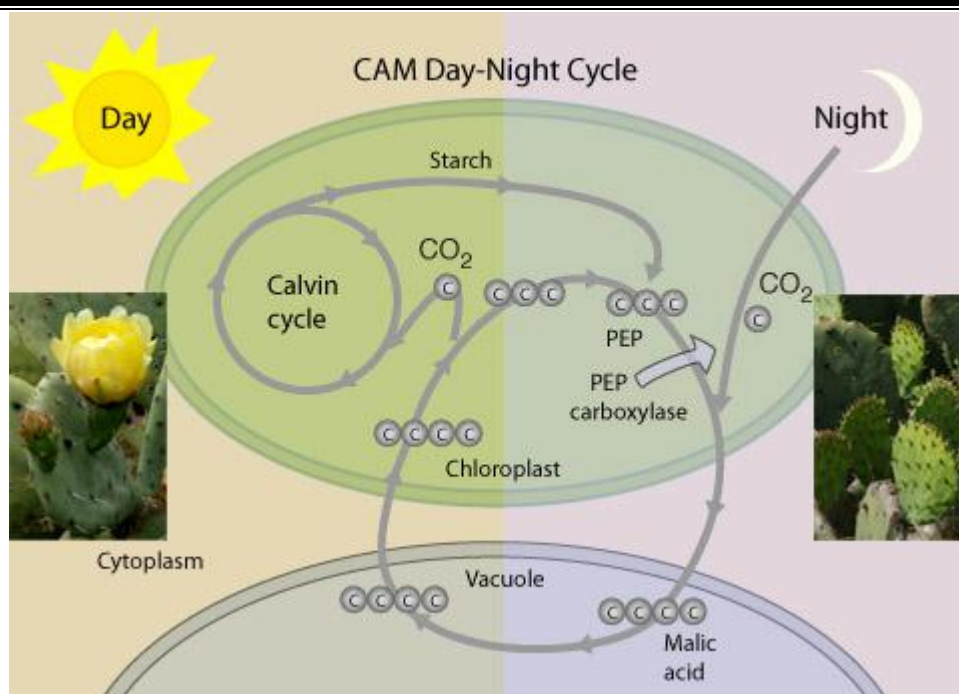
- CAM plants include many succulents such as cactuses and agaves and also some orchids and bromeliads

Crassulacean Acid Metabolism (CAM)

The CAM plants represent a metabolic strategy adapted to extremely hot and dry environments. They represent about 10% of the plant species and include cacti, orchids, maternity plant, wax plant, pineapple, Spanish moss, and some ferns. The only agriculturally significant CAM plants are the pineapple and an Agave species used to make tequila and as a source of fiber.



The sketch below of the day-night cycle of the CAM plants is patterned after Moore, et al. The name Crassulacean Acid Metabolism came from the fact that this strategy was discovered in a member of the Crassulaceae which was observed to become very acidic at night and progressively more basic during the day.



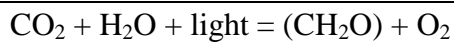
The acidity was found to arise from the opening of their stomata at night to take in CO_2 and fix it into malic acid for storage in the large vacuoles of their photosynthetic cells. It could drop the pH to 4 with a malic acid concentration up to 0.3M . Then in the heat of the day, the stomata close tightly to conserve water and the malic acid is decarboxylated to release the CO_2 for fixing by the Calvin cycle. PEP is used for the initial short-term carbon fixation as in the C4 plants, but the entire chain of reactions occurs in the same cell rather than handing off to a separate cell as with the C4 plants. In the CAM strategy, the processes are separated temporally, the initial CO_2 fixation at night, and the malic acid to Calvin cycle part taking place during the day.



With stomata open only at night when the temperature is lower and the relative humidity higher, the CAM plants use much less water than either C3 plants or C4 plants. Some varieties convert to C3 plants at the end of the day when their acid stores are depleted if they have adequate water, and even at other times when water is abundant

1.2.2 PHOTOSYNTHETIC EFFICIENCY

Photosynthesis can be simply represented by the equation:



Approximately 114 kilocalories of free energy are stored in plant biomass for every mole of CO_2 fixed during photosynthesis. Solar radiation striking the earth on an annual basis is equivalent to 178,000 terawatts, i.e. 15,000 times that of current global energy consumption. Although photosynthetic energy capture is estimated to be ten times that of global annual energy consumption, only a small part of this solar radiation is used for photosynthesis. Approximately two thirds of the net global photosynthetic productivity worldwide is of terrestrial origin, while the remainder is produced mainly by phytoplankton (microalgae) in the oceans which cover approximately 70% of the total surface area of the earth. Since biomass originates from plant and algal photosynthesis, both terrestrial plants and microalgae are appropriate targets for scientific studies relevant to biomass energy production.

Any analysis of biomass energy production must consider the potential efficiency of the processes involved. Although photosynthesis is fundamental to the conversion of solar radiation into stored biomass energy, its theoretically achievable efficiency is limited both by the limited wavelength range applicable to photosynthesis, and the quantum requirements of the photosynthetic process. Only light within the wavelength range of 400 to 700 nm (photosynthetically active radiation, PAR) can be utilized by plants, effectively allowing only 45 % of total solar energy to be utilized for photosynthesis. Furthermore, fixation of one CO_2 molecule during photosynthesis, necessitates a quantum requirement of ten (or more), which results in a maximum utilization of only 25% of the PAR absorbed by the photosynthetic system. On the basis of these limitations, the theoretical maximum efficiency of solar energy conversion is approximately 11%. In practice, however, the magnitude of photosynthetic efficiency observed in the field, is further decreased by factors such as poor absorption of sunlight due to its reflection, respiration requirements of photosynthesis and the need for optimal solar radiation levels. The net result is an overall photosynthetic efficiency of between 3 and 6% of total solar radiation. Upper bound on efficiency can be estimated from theoretical consideration as follows:

- 1) Percentage of Photosynthetically Active Radiation (PAR) in white light, the light that can actually be absorbed i.e. 50% of the total Sun radiation to the earth surface.
- 2) The fraction of the incident light absorbed is a function of many factors, such as leaf size, canopy shape, and reflectiveness of the plant. It is estimated to have an upper limit of 80%. This effectively corresponds to the utilization of eight photons out of every 10 in the active incident radiation.

3) The theoretical maximum energy efficiency of converting the effectively absorbed PAR to glucose is determined by the facts that a minimum of eight photons of PAR are required to produce glucose for each CO₂ molecule converted, the corresponding energy stored in the produced glucose is 28 percent of the light energy of the photons. Similarly 40% is utilized for dark reaction.

Therefore, Photosynthetic efficiency is

$$100 \times 0.50 \times 0.80 \times 0.28 \times 0.60 = 6.7 \text{ percent}$$

This photosynthetic efficiency is further lower for C₃ plant.

1) Additional losses occur because C₃ plants lose about 30 percent of the already fixed CO₂ during photorespiration (which competes with photosynthesis in the presence of light and does not occur in C₄ plant).

2) C₃ plant becomes light-saturated at lower light intensities than for C₄ plant. So, that C₃ plant are unable to utilize perhaps 30 percent of light absorbed by photosynthetically active Compound. Thus the maximum efficiency of energy consumption of C₃ is about

$$0.7 \times 0.7 \times 6.7 = 3.283$$

So, C₄ plants show higher photosynthetic efficiency than C₃ plant.

1.3 CLASSIFICATION OF BIOMASS

The general classification of biomass varieties as fuel resources can be divided preliminarily and roughly into several groups and sub-groups according to their distinct biological diversity and similar source and origin as follows:

1. Wood and woody biomass Coniferous or deciduous; angiospermous or gymnospermous; soft or hard; stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species
2. Herbaceous and agricultural biomass annual or perennial and field-based or processed-based such as:
 - 2.1. Grasses and flowers (alfalfa, arundo, bamboo, bana, brassica, cane, cynara, miscanthus, switchgrass, timothy, others)
 - 2.2. Straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat, others)
 - 2.3. Other residues (fruits, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, cakes, others)
3. Aquatic biomass Marine or freshwater algae; macroalgae (blue, green, blue-green, brown, red) or microalgae; seaweed, kelp, lake weed, water hyacinth, others.

4. Animal and human biomass wastes Bones, meat-bone meal, chicken litter, various manures, others.
5. Contaminated biomass and industrial biomass wastes (semi-biomass) such as municipal solid waste, demolition wood, refuse-derived fuel, sewage sludge, hospital waste, paper-pulp sludge, waste papers, paperboard waste, chipboard, fibreboard, plywood, wood pallets and boxes, railway sleepers, tannery waste, others.
6. Biomass mixture blends from the above varieties.

Researchers characterize the various types of biomass in different ways but four main types are:

1. Wastes: agricultural production wastes / agricultural processing wastes / crop residues / mill wood wastes / urban wood wastes / urban organic wastes
2. Forest Product: Wood / logging residues/ trees, shrubs and wood residues / saw dust, bark etc.
3. Energy crops: Short rotation woody crops / herbaceous woody crops / grasses /starch crops (corn, wheat and barley) / sugar crop (cane and beet) / forage crop (grass, alfalfa etc.), oilseed crops (soybean, sunflower etc.)
4. Aquatic plants: Algae/ Water weed/ Water hyacinth / reed etc.

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DRE 103: BIOMASS ENERGY

UNIT-2: BIOMASS AS FUEL

UNIT STRUCTURE

OBJECTIVES

- 2.1. PHYSICOCHEMICAL CHARACTERISTICS OF BIOMASS AS FUEL. BIOMASS CONVERSION ROUTES: BIOCHEMICAL, CHEMICAL
- 2.2. AND THERMO-CHEMICAL
 - 2.2.1. DENSIFICATION OF BIOMASS
 - 2.2.2. BIOMASS LIQUEFACTION
 - 2.2.3. GREEN DIESEL FUEL FROM BIO-SYNGAS VIA FISHER-TROPSCH SYNTHESIS
 - 2.2.4. BIO-ALCOHOLS FROM BIOMASS
 - 2.2.5. BIODIESEL FROM VEGETABLE OILS

SUGGESTED READINGS

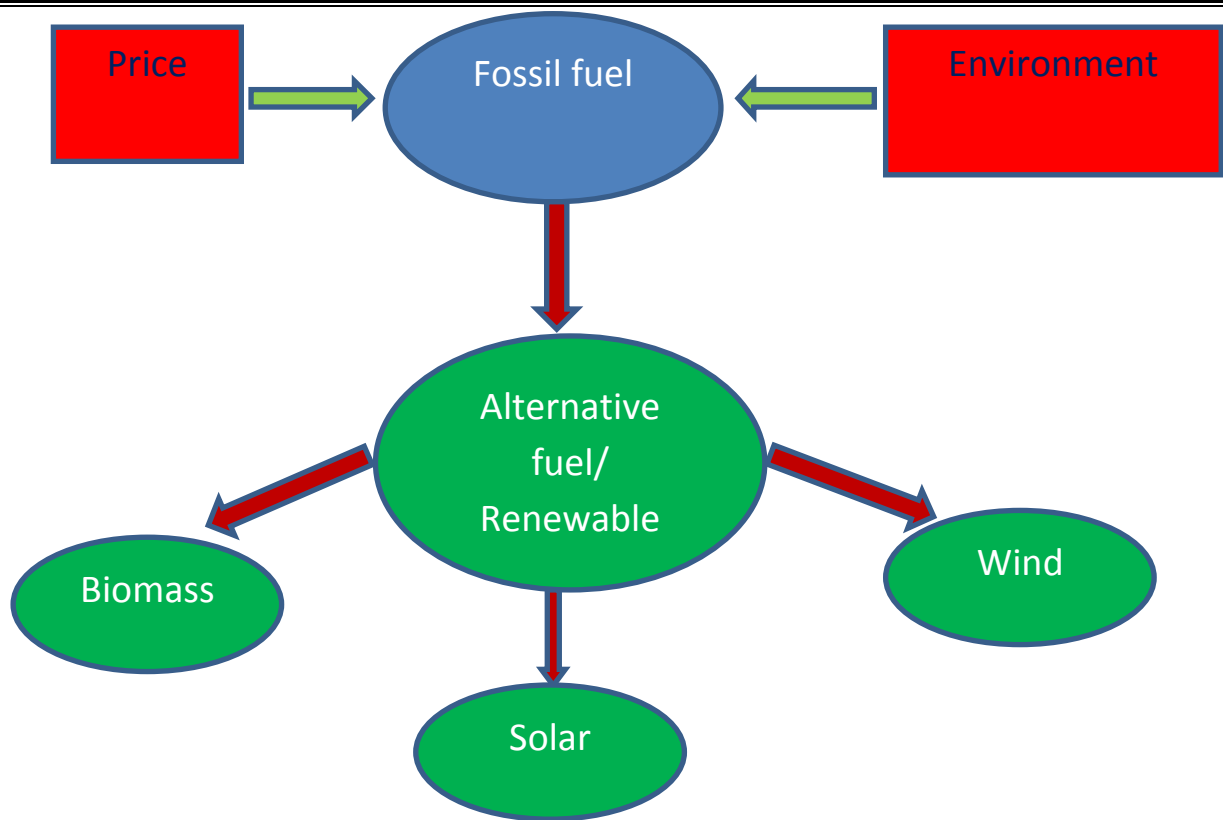
REFERENCES

OBJECTIVES

This unit will give you the idea about the fuel characteristics of biomass and different biomass conversion systems.

2.1. PHYSICOCHEMICAL CHARACTERISTICS OF BIOMASS AS FUEL.

Increasing crude oil prices and environmental concerns have resulted in the search for alternative fuels



The use of biomass to produce bio energy in order to provide a wide range of energy services (heat, light, comfort, entertainment, information, mobility etc.) and to produce biomaterials as substitutes for those presently manufactured from petro-chemicals, is an integrating response to a number of global problem. The energy in biomass from plant matter originally comes from solar energy through the process known as photosynthesis. The energy, which is stored in plants and animals (that eat plants or other animals), or in the wastes that they produce, is called biomass energy. Stored plant energy may be released by burning it directly or various processes such as thermochemical gasification, pyrolysis, hydrolysis, fermentation to ethanol, esterification to biodiesel, biomethanation etc. The net energy available from biomass when it is combusted ranges from about 8 MJ/kg for green wood, to 20 MJ/kg for dry plant matter (Demirbas, 1998a; 1998b), to 55 MJ/kg for methane, as compared with about 27 MJ/kg for coal (Twidell, 1998).

Biomass can also provide a renewable source of hydrogen and a wide range of biomaterials and chemical feedstock (Chisholm, 1994). It is chemically similar in origin to fossil fuels, which originated from biomass millions of years ago and can therefore provide direct substitution for virtually all products currently derived from the processing of petrochemicals. These include lubricants, polymers, high matrix composites, textiles, biodegradable plastics, paints, adhesive, thickeners, stabilizers, synthetic fabrics and a range of celluloses. Biomass can be converted into this wide variety of biomaterials as well as into energy carriers using

existing and novel conversion technologies and thus it has the potential to be a significant new source of energy and materials for the twenty-first centuries.

Biomass represents the total cellular substances of plants, animals and microorganisms. It represents the total cellular substances of plants, animals and microorganisms. For bioenergy purposes, plant roots are normally excluded from the definition. As they grow plants photosynthesis and store the captured solar energy as chemical energy in their leaves, stems, bark, fruits, seeds and roots. Annual and perennial species that are cultivated specifically to produce solid, liquid or gaseous energy feedstock tend to be particularly efficient in this conversion process and are termed “energy crops”. Organic residues and wastes originating from plant materials, or from animals that feed on those plants, are also used as source of biomass. The biomass sources can be classified into woody biomass, agricultural biomass and municipal waste products (Fig1).

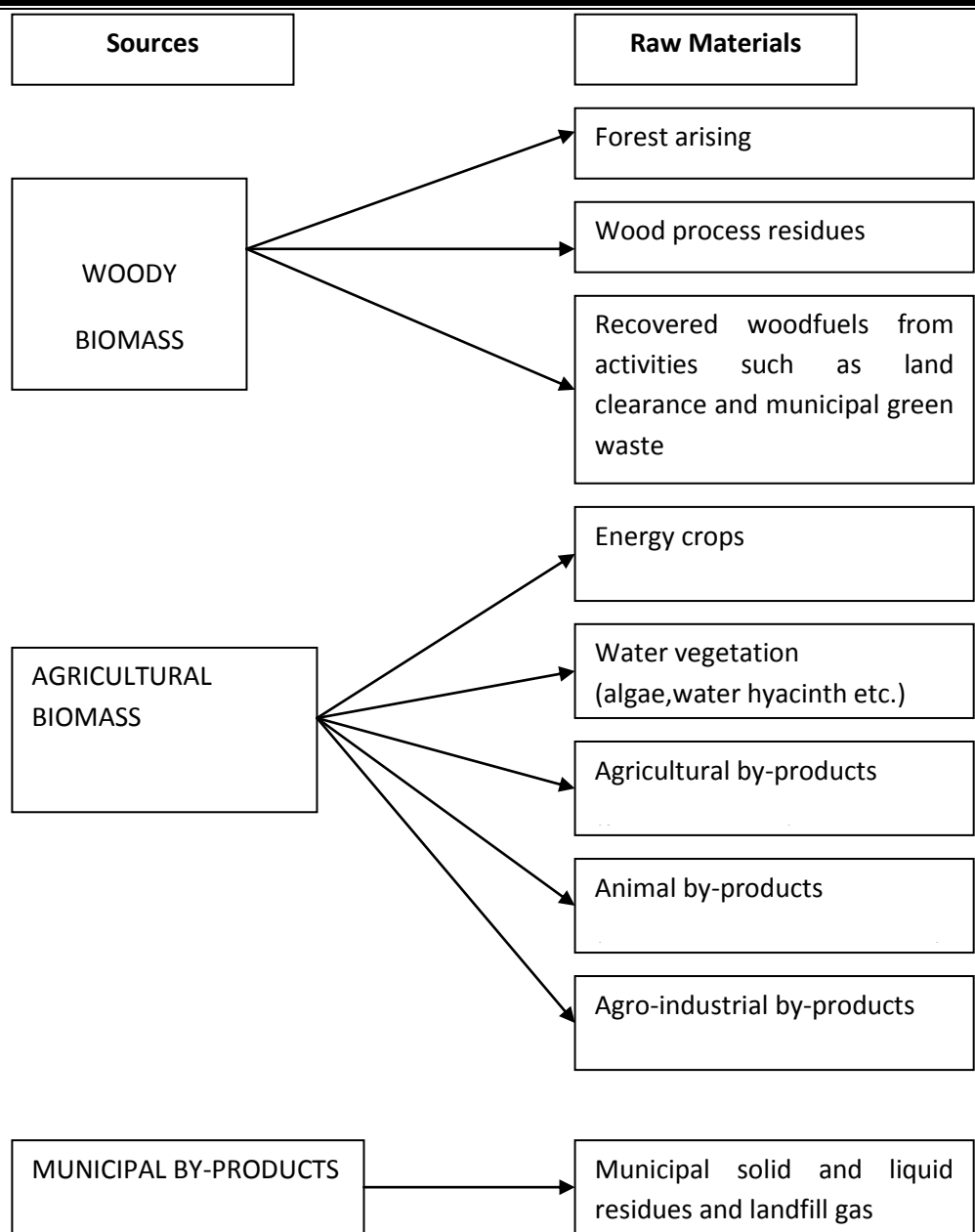


Fig1: Major sources of biomass

It is the inherent properties of the biomass source that determines both the choice of conversion process and any subsequent processing difficulties that may arise. Equally, the choice of biomass source is influenced by the form in which the energy is required and it is the interplay between these two aspects that enables flexibility to be introduced into the use of biomass as an energy source.

As indicated above, the categories of biomass considered in this study are woody and herbaceous species; the two types examined by most biomass researchers and technology providers. Dependent on the energy conversion process selected, particular material properties become important during subsequent processing.

The main material properties of interest, during subsequent processing as an energy source, relate to:

- moisture content (intrinsic and extrinsic),
- calorific value,
- proportions of fixed carbon and volatiles,
- ash/residue content,
- alkali metal content,
- cellulose/lignin ratio.

For dry biomass conversion processes, the first five properties are of interest, while for wet biomass conversion processes, the first and last properties are of prime concern. The quantification of these materials properties for the various categories of biomass is discussed in the following section (McKendry, 2002).

Moisture content

Two forms of moisture content are of interest in biomass:

- intrinsic moisture: the moisture content of the material without the influence of weather effects,
- extrinsic moisture: the influence of prevailing weather conditions during harvesting on the overall biomass moisture content.

In practical terms, it is the extrinsic moisture content that is of concern, as the intrinsic moisture content is usually only achieved, or applicable, under laboratory conditions. Table 1 lists the typical (intrinsic) moisture contents of a range of biomass materials. Also of importance in respect of the prevailing weather conditions at the time of harvesting, is the potential contamination of the harvested biomass by soil and other detritus, which can in turn have a significant deleterious impact on other 'material' properties during subsequent treatment or processing. The parameters of interest that are affected by such contamination are the ash and alkali metal content of the material.

Other factors aside, such as conversion to alcohol or gas/oil, the relationship between biomass moisture content and appropriate bio-conversion technology is essentially straight forward, in that thermal conversion requires low moisture content feedstock (typically <50%), while bio-conversion can utilize high moisture content feedstock. Thermal conversion technologies can also use feedstock with high moisture content but the overall energy balance for the conversion process is adversely impacted.

On this basis, woody and low moisture content herbaceous plant species are the most efficient biomass sources for thermal conversion to liquid fuels, such as methanol. For the production of ethanol by biochemical (fermentation) conversion, high moisture herbaceous plant species,

such as sugarcane, are more suited: such species can also be fermented via another biochemical process, anaerobic digestion (AD), to produce methane.

Calorific value

The calorific value (CV) of a material is an expression of the energy content, or heat value, released when burnt in air. The CV is usually measured in terms of the energy content per unit mass, or volume; hence MJ/kg for solids, MJ/l for liquids, or MJ/Nm³ for gases. The CV of a fuel can be expressed in two forms, the gross CV (GCV), or higher heating value (HHV) and the nett CV (NCV), or lower heating value (LHV). The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapour and therefore represents the maximum amount of energy potentially recoverable from a given biomass source. The actual amount of energy recovered will vary with the conversion technology, as will the form of that energy i.e. combustible gas, oil, steam, etc. In practical terms, the latent heat contained in the water vapour cannot be used effectively and therefore, the LHV is the appropriate value to use for the energy available for subsequent use. Table 1 lists the CV of a range of biomass materials. When quoting a CV, the moisture content needs to be stated, as this reduces the available energy from the biomass. It appears normal practice to quote both the CV and crop yield on the basis of dry matter tones (dmt), which assumes zero percent moisture content. If any moisture is present, this reduces the CV proportional to the moisture content.

Table 1
Proximate analysis of some biomass feedstocks (wt%)

Biomass	Moisture ^a (%)	VM (%)	FC (%)	Ash (%)	LHV (MJ/kg)
Wood	20	82	17	1	18.6
Wheat straw	16	59	21	4	17.3
Barley straw	30	46	18	6	16.1
Lignite	34	29	31	6	26.8
Bituminous coal	11	35	45	9	34

^a Intrinsic.

Proportions of fixed carbon and volatile matter

Fuel analysis has been developed based on solid fuels, such as coal, which consists of chemical energy stored in two forms, fixed carbon and volatiles:

- the volatiles content, or volatile matter (VM) of a solid fuel, is that portion driven-off as a gas (including moisture) by heating (to 950 °C for 7 min)

- the fixed carbon content (FC), is the mass remaining after the releases of volatiles, excluding the ash and moisture contents.

Laboratory tests are used to determine the VM and FC contents of the biomass fuel. Fuel analysis based upon the VM content, ash and moisture, with the FC determined by difference, is termed the proximate analysis of a fuel. Table 1 gives the proximate analyses of some typical biomass sources: values for lignite and coal are given for reference.

Elemental analysis of a fuel, presented as C, N, H, O and S together with the ash content, is termed the ultimate analysis of a fuel. Table 2 gives the ultimate analyses for some biomass.

The significance of the VM and FC contents is that they provide a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidised, depending on how the biomass is to be utilized as an energy source. This type of fuel analysis is of value for biological conversion processes only once the fuel is produced, enabling a comparison of different fuels to be undertaken.

Table 2
Ultimate analyses for typical biomass materials (wt%)

Material	C	H	O	N	S	Ash
Cypress	55.0	6.5	38.1	–	–	0.4
Ash	49.7	6.9	43.0	–	–	0.3
Beech	51.6	6.3	41.4	–	–	–
Wood (average)	51.6	6.3	41.5	0	0.1	1
Miscanthus	48.1	5.4	42.2	0.5	<0.1	2.8
Wheat straw	48.5	5.5	3.9	0.3	0.1	4
Barley straw	45.7	6.1	38.3	0.4	0.1	6
Rice straw	41.4	5	39.9	0.7	0.1	
Bituminous coal	73.1	5.5	8.7	1.4	1.7	9
Lignite	56.4	4.2	18.4	1.6 ^a	–	5

^a Combined N and S.

Table 3 summaries the fuel properties of selected biomass materials.

Table 3
Properties of selected biomass materials (wt%)

Material	Moisture content (%H ₂ O)	HHV ^a (MJ/kg)	FC content (%)	VM content (%)	Ash content (%)	Alkali metal content (as Na and K oxides) (%)
Fir	6.5	21	17.2	82.0	0.8	–
Danish pine	8.0	21.2	19.0	71.6	1.6	4.8
Willow	60	20.0	–	–	1.6	15.8
Poplar	45	18.5	–	–	2.1	16
Cereal straw	6	17.3	10.7	79.0	4.3	11.8
Miscanthus	11.5	18.5	15.9	66.8	2.8	–
Bagasse	45–50	19.4	–	–	3.5	4.4
Switchgrass	13–15	17.4	–	–	4.5	14
Bituminous coal	8–12	26–2	57	35	8	–

^a Dry basis, unless stated otherwise.

Comparison of biofuels with fossil fuels, such as coal, shows clearly that the higher proportion of oxygen and hydrogen, compared with carbon, reduces the energy value of a fuel, due to the lower energy contained in carbon–oxygen and carbon–hydrogen bonds, than in carbon–carbon bonds

Ash/residue content

The chemical breakdown of a biomass fuel, by either thermo-chemical or bio-chemical processes, produces a solid residue. When produced by combustion in air, this solid residue is called ‘ash’ and forms a standard measurement parameter for solid and liquid fuels. The ash content of biomass affects both the handling and processing costs of the overall, biomass energy conversion cost. During biochemical conversion, the percentage of solid residue will be greater than the ash content formed during combustion of the same material. For a biochemical conversion process, the solid residue represents the quantity of non-biodegradable carbon present in the biomass. This residue will be greater than the ash content because it represents the recalcitrant carbon which cannot be degraded further biologically but which could be burnt during thermo-chemical conversion.

Dependent on the magnitude of the ash content, the available energy of the fuel is reduced proportionately. In a thermo-chemical conversion process, the chemical composition of the ash can present significant operational problems. This is especially true for combustion processes, where the ash can react to form a ‘slag’, a liquid phase formed at elevated temperatures, which can reduce plant throughput and result in increased operating costs.

Alkali metal content

The alkali metal content of biomass i.e. Na, K, Mg, P and Ca, is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockages of airways in the furnace and boiler plant. It should be noted that while the intrinsic silica content of a biomass source may be low, contamination with soil introduced during harvesting can increase the total silica content significantly, such that while the content of intrinsic silica in the material may not be a cause for concern, the increased total silica content may lead to operational difficulties.

Cellulose/lignin ratio

The proportions of cellulose and lignin in biomass are important only in biochemical conversion processes. The biodegradability of cellulose is greater than that of lignin, hence the overall conversion of the carbon-containing plant material present as cellulose is greater than for plants with a higher proportion of lignin, a determining factor when selecting biomass plant species for

biochemical processing. Table 4 gives the proportions of cellulose/hemicellulose/lignin for softwoods and hardwoods and for comparison, wheat straw and switchgrass.

Table 4
Cellulose/lignin content of selected biomass (wt%)

Biomass	Lignin (%)	Cellulose (%)	Hemi-cellulose (%)
Softwood	27–30	35–40	25–30
Hardwood	20–25	45–50	20–25
Wheat straw	15–20	33–40	20–25
Switchgrass	5–20	30–50	10–40

For the production of ethanol, a biomass feedstock with a high, cellulose/hemi-cellulose content is needed to provide a high, l/t, yield. While the lignin content represents a potentially large energy source, current techniques involving hydrolysis/enzymatic systems cannot convert the lignin to syngas. To illustrate the effect of cellulose content on yield, up to 280l/t of ethanol can be produced from switchgrass, compared with 205l/t from wood, an effect largely due to the increased proportion of lignin in wood.

Bulk density

An important characteristic of biomass materials is their bulk density, or volume, both as-produced and as-subsequently processed (Table 5). The importance of the as-produced, bulk density is in relation to transport and storage costs. The density of the processed product impacts on fuel storage requirements, the sizing of the materials handling system and how the

material is likely to behave during subsequent thermo-chemical/biological processing as a fuel/feedstock (McKendry, 2002).

2.2. BIOMASS CONVERSION ROUTES: BIOCHEMICAL, CHEMICAL AND THERMO-CHEMICAL

Biomass is composed of organic carbonaceous materials such as woody or lignocellulosic materials, various types of herbage, especially grasses and legumes, and crop residues. Biomass can be converted to various forms of energy by numerous technical processes, depending upon the raw material characteristics and the type of energy desired. Biomass energy is one of humanity's earliest sources of energy.

Biomass is used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles, and providing process heat for industrial facilities. Biomass is the most important renewable energy source in the world and its importance will increase as national energy policies and strategies focus more heavily on renewable sources and conservation. Biomass power plants have advantages over fossil-fuel plants, because their pollution emissions are less. Energy from biomass fuels is used in the electric utility, lumber and wood products, and pulp and paper industries. Biomass can be used directly or indirectly by converting it into a liquid or gaseous fuel (Pandey, 2009).

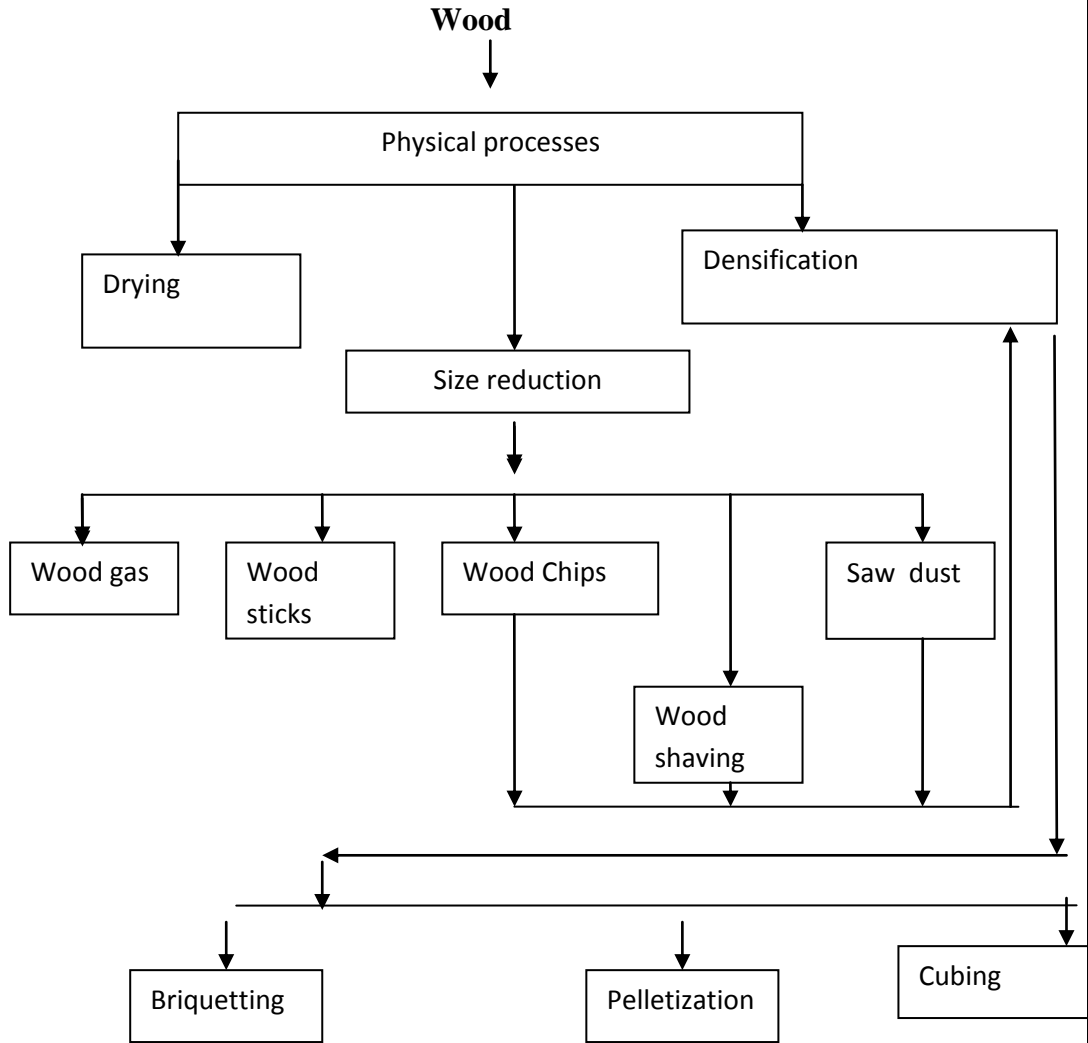
Some of the basic wood energy conversion processes can be described as follows:

<u>Process</u>	<u>Description</u>
1. Drying	Decreasing the moisture content by mechanical means.
2. Briquetting	Densification (binding the particles to about one fifth the loose bulk) by compression under heat & pressure.
3. Pettelization	Densification (compression to one third of the loose bulk) and cutting into standard pellet size under pressure.
4. Combustion	Burning with liberation of heat
5. Pyrolysis	Thermal Decomposition of organic matter in absence of air
6. Carbonization	Burning with the liberation of heat.

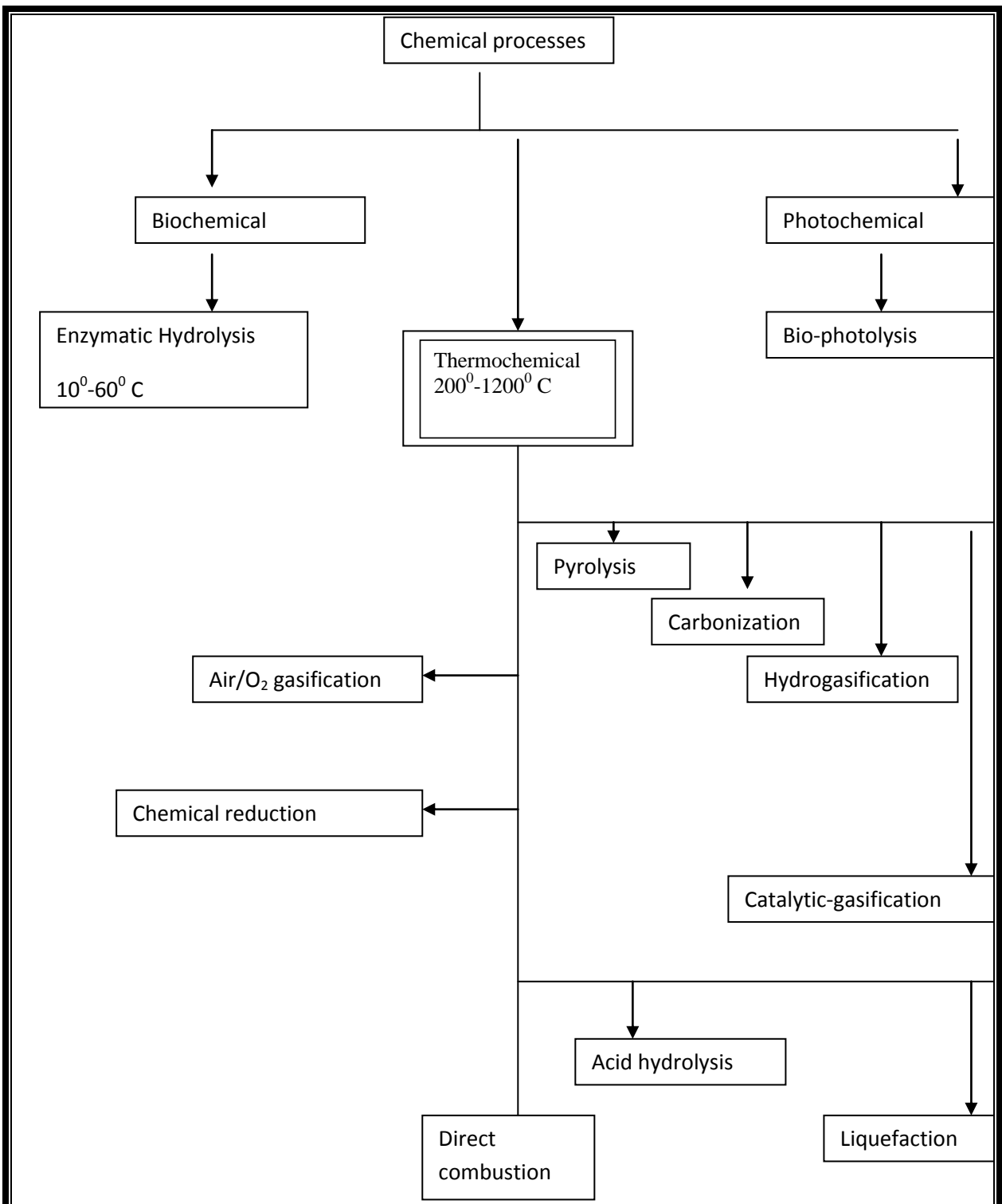
7. Liquefaction	Conversion to an oil by reaction with synthesis gas and an alkaline catalyst under high temperature and pressure
8. Hydrolysis	Chemical decomposition through addition of water.
9. Biophotolysis	Production of hydrogen in a chemical form through solar energy
10. Hydro-gasification	Conversion to a gaseous state in the presence of hydrogen.
11. Catalytic gasification	Conversion to a gaseous state by using a catalyst in an inert gas atmosphere.
12. Chemical reduction	Change in chemical composition through heat and pressure

Schematic representation of the wood energy conversion processes can be summerised as follows:

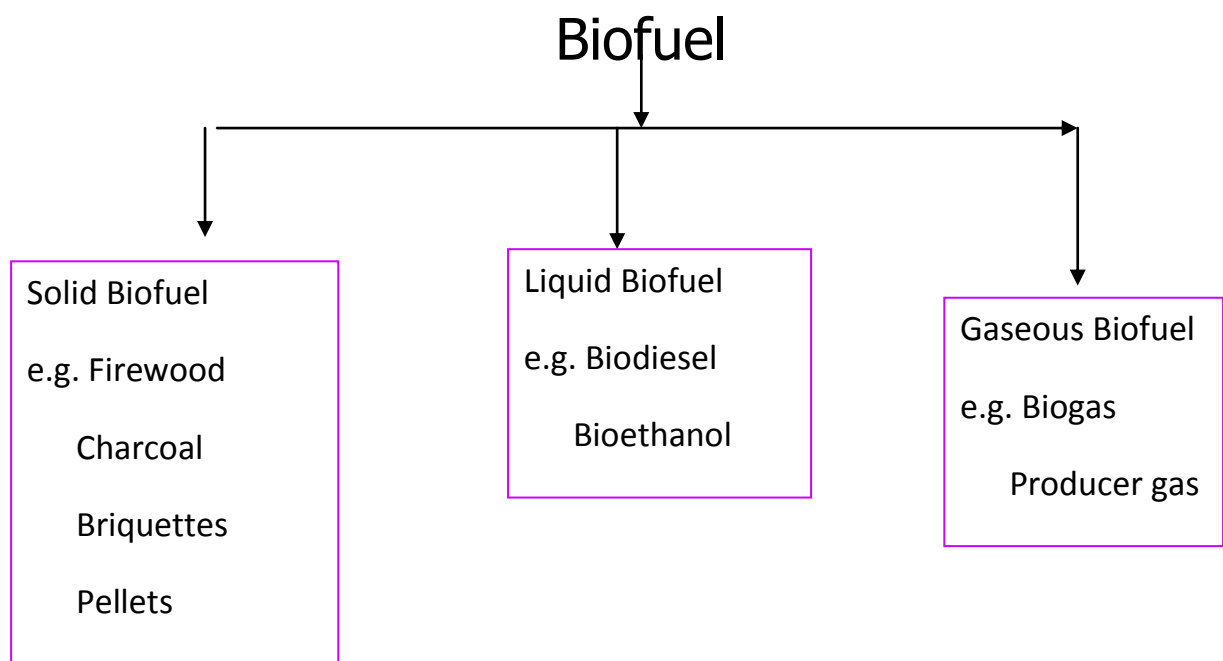
Wood Energy Conversion Processes



After the physical processes, chemical conversion of biomass materials (wood) may be done as follows:



Besides the above classification, the conversion of biomass to biofuel may be discussed on the following route.

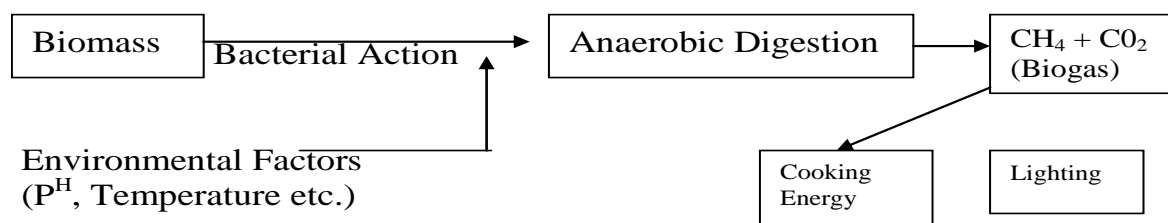


Biomass to energy conversion processes are:

1. Biochemical Conversion
2. Chemical conversion
3. Thermochemical conversion

1. Biochemical conversion:

Biochemical conversion:



In biochemical conversion, biomass is digested in wet condition with the help of microorganism (e.g. different groups of bacteria) in limited oxygen or oxygen free atmosphere. The overall process is called anaerobic digestion of biomass where the water content of the process may be up to 90-92%. Bacteria can breakdown the biomass with the help of enzymes release by them and final product of the process is called biogas (60% CH₄ + 40% CO₂). The undigested portion of the process (called sludge) is richer in manure value which can be used as fertilizer in crop field.

2. Chemical conversion:

Chemical conversion refers mainly to acid degradation which leads to hexoses, pentoses and lignin-processing. The intermediates can be converted to alcohols, aldehydes and some other chemicals. Seeds of the crops, which contain a high proportion of fatty acid rich oil, can be converted to biodiesel by transesterification reactions with low molecular weight alcohol.

3. Thermochemical conversion:

Thermo means heat. In this process, biomass is converted to form of useful energy by treating the biomass (dry biomass i.e. moisture content 13-15%) in a thermal environment. Chemicals contained in biomass are converted to solid, liquid and gaseous fuels. This conversion enables the versatile use of biomass for energy purposes. Some of the thermal conversion processes are

- i) **Direct conversion:** Biomass is burned directly in open air atmosphere which liberates heat along with CO_2 and H_2O . Heat thus liberated is used for cooking food, room and space heating and generating electricity by dendrothermal processes.
- ii) **Pyrolysis:** Pyrolysis is the thermal process where biomass is burned under limited or oxygen free atmosphere in high temperature (approx. 250°C - 600°C). The products of the pyrolysis are solid, liquid and gas. Pyrolysis process can be divided into different processes according to the desired products.
 - a) **Slow pyrolysis:** Major product is solid fuel. In this process, dry biomass is heated in a limited oxygen or oxygen free atmosphere and rate of reaction is proceeded in a slow rate (say $1^\circ\text{C}/\text{min}$) to reach a temperature less than 500°C . In this process, 80% solid will produce with vapours. Vapours can be eliminated, combusted and remaining product is solid carbon rich fuel called charcoal. (CV of charcoal is appr. 30 MJ/Kg, but CV of wood is appro. 20MJ/Kg). As carbon rich compound can be produced by this process, the overall process is called carbonization.
 - b) **Fast pyrolysis:** In this process, the high temperature pyrolysis is done in high rate (say $100^\circ\text{C}/\text{min}$) combustion. Biomass is combusted at high temperature around 1100°C . This process is called fast pyrolysis and major product is gaseous fuel i.e. producer gas. As major product is gas, the process is also called gasification.

- c) **Flash pyrolysis:** In this process, biomass is burned in oxygen free atmosphere and the high rate of the reaction is achieved at one time burning in a pyrolysis reactor. The major product of this process is liquid along with other pyrolysis products.
- d) **Gasification:** This process is similar to fast pyrolysis. Dry Biomass is burned in oxygen deficient process at high temperature (1100⁰C) in a gasifier or reactor and producer gas is the final product of this process.

Biomass Gasifier

- **Niche & Decentralized Applications**
- **MW Size Equipments**
- **Technology R&D and Manufacturing in India**
- **Economics and supply-chain not yet favorable**

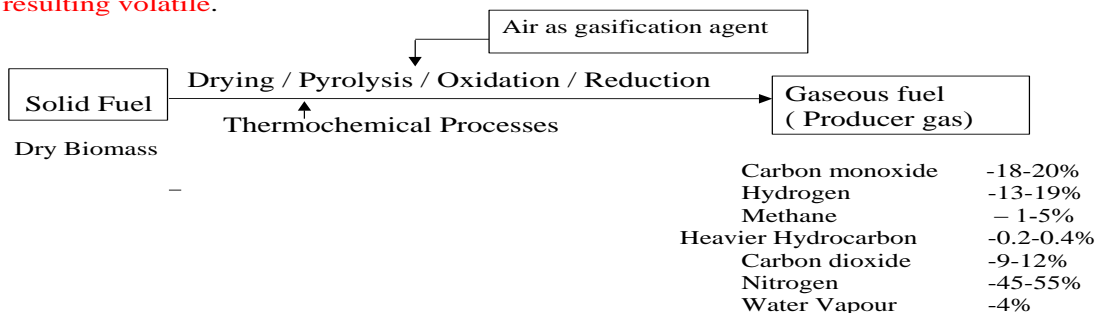
- ▶ Gosaba Island, Sunderbans
- ▶ 500 kW, 5 x 100 kW AG series Gasifiers
- ▶ No Disruption till date
- ▶ Supplying 800 households
- ▶ Managed by Rural Energy Co-operative

Source: MoP, 2004



Gasification of Biomass

Gasification is the process by which organic matter is converted to gas through thermal decomposition in an oxygen deficient environment, followed by secondary reaction of the resulting volatile.



The Calorific Value of the gas is about 900-1200 Kcal/Nm³

Fig: Schematic representation of biomass gasification

Schematic Representation of the Biomass gasification with end uses:

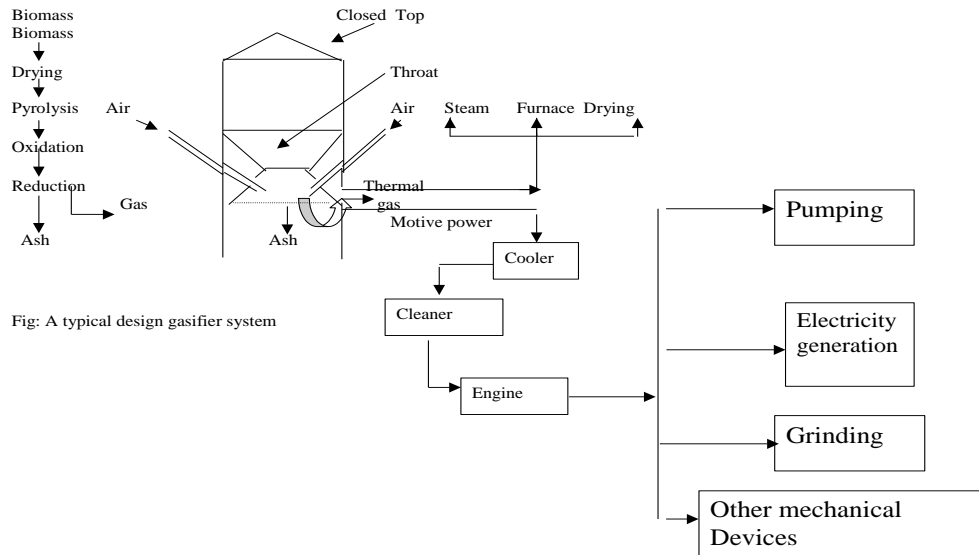


Fig: A typical design gasifier system

Fig: Schematic representation of biomass gasification with end uses



5 kw Biomass Gasifier Unit

Energy plant species

The plant species selected for the fuelwood purpose should have

- (a) multiple uses,
- (b) wide adaptability to difficult sites,
- (c) capacity to establish with little after care,
- (d) ability to fix atmospheric nitrogen,
- (e) fast growth,
- (f) tolerance to wide range of environments, soil types, rainfall regimes, terrain and
- (g) ability to produce wood of high calorific value
- (h) High fuel value Index,

2.2.1. DENSIFICATION OF BIOMASS

Definition of Densification: Biomass densification means the use of force in the form of mechanical pressure to reduce the volume of vegetable matter and its conversion to a solid form which is easier to handle and store than the original material.

There are number of densification techniques which are collectively called “briquetting”.

Densification has the following advantages:

- (a) The bulk density is increased by a factor of 2-3 and the actual density to a still higher level. This enables major saving in transportation and handling.
- (b) The physical dimensions and the combustion characteristics of the fuel become homogenous and uniform because of the required particle size, pile porosity and density.

The major uses of densified fuel are

- i) Domestic fuel for cooking and water heating in conventional stoves.
- ii) Fuel for small sized natural draft system like kilns, ovens, furnaces and hearths.
- iii) Grate burning fuel in pile or stoker burning for steam raising.
- iv) Fuel for fluidized bed reactors where high energy densities are needed.
- v) Fuel for wood gasifier to generate producer gas or low energy gases.

Before going for densification, the following considerations are essentials:

- i) Densification is an energy consuming process and necessitates the use of electrical energy inputs for size reduction, transportation, moisture agglomeration and for moisture removal (20-150 kwh/tones of fuel).
- ii) Densification involves investment into the system (Rs. 1-1.5 lakh per tones/day capacity depending on the accessories).

Densification processes are three types:

- i) binderless technique
 - ii) with binder where tar, molasses, sodium bentonite, resins or wax, lignin from paper & pulp industries.
 - iii) Pyrolysis technology
1. In the binderless techniques, the cellulose bonding collapses due to the high temperature (200⁰C) and very high pressure (21000 psi) prevailing and the lignin is fluidized, flowing evenly through the granular mass.
 2. With binder technology, binders are used as a mixture with the granulated biomass and under low pressure bonding into solid fuel takes place. The cost of conversion is higher due to the expenses that have to be incurred on the purchase of binders, the preparation steps and the special feed system needed.

Densification consists of the following steps:

- i) Preprocessing : This applies to char densification. Wood is converted into charcoal or byproduct char at 275-300⁰C before being densified. Charcoal is formed by any standard carbonization technique.
- ii) Size reduction: The surface area to volume ratio of the wood/char is increased by shredding it in hammer mills and passing it through a screen mechanism which has a mesh size of about 8mm.
- iii) Moisture removal: The moisture content of the particles is controlled by heating the materials in an atmosphere free of air. Moisture plays a controlling role in the densification process and must be between 10 to 25%. If it is less than 10%, the

total pressure required for densification becomes too high and the dies wear out fast. If it is more than 25%, the quality of the final product is poor.

- iv) Mixing and conditioning: The dry fuel particles are mixed with binders wherever applicable. In biomass processes, the feed is heated to improve its flow behaviour.
- v) Agglomeration: This is the main sub process in densification. The main type of agglomeration are
 - a) Compaction: The feed is compacted into units of definite size.
 - b) Extrusion: Densified feed is taken out as rods of infinite length and cut at regular intervals after it emerges from the densifier.
 - c) Fusion: Fusion is an unconventional process of bringing together the liquid binder and feed particles.

2.2.2. BOMASS LIQUEFACTION

Liquefaction is a thermochemical conversion process of biomass or other organic matters into primarily liquid oil products in the presence of a reducing reagent, for example, carbon monoxide or hydrogen. Liquefaction is usually conducted in an environment of moderate temperatures (from 550 to 675 K) and high pressures. Aqueous liquefaction of lignocellulosic materials involves disaggregation of the wood ultrastructure followed by partial depolymerization of the constitutive families (hemicelluloses, cellulose, and lignin). Solubilization of the depolymerized material is then possible (Chornet and Overend 1985). During liquefaction, hydrolysis and repolymerization reactions occur. At the initial stage of liquefaction, biomass is thermochemically degraded and depolymerized to small compounds, and then these compounds may rearrange through condensation, cyclization, and polymerization to form new compounds in the presence of a suitable catalyst. With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase (Demirbas, 2000). The alkali (NaOH, Na₂CO₃, or KOH) catalytic aqueous liquefaction of wood to oils may be a promising process to make good use of them. Liquid products obtained from the wood samples could eventually be employed as fuels or other useful chemicals after suitable refining processes.

Liquefaction was linked to hydrogenation and other high-pressure thermal decomposition processes that employed reactive hydrogen or carbon monoxide carrier gases to produce a liquid fuel from organic matter at moderate temperatures, typically between 550 and 675 K.

Direct liquefaction involves rapid pyrolysis to produce liquid tars and oils and/or condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert noncondensable, gaseous products of pyrolysis or gasification into liquid products. In the liquefaction process, the carbonaceous materials are converted to liquefied products through a complex sequence of physical structure and chemical changes. The changes involve all kinds of processes such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis results in micellar-like substructures of the biomass. The depolymerization of biomass leads to smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups, and keto groups also occur (Chornet and Overend 1985). The micellar-like broken down fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation (Demirbas 2000). The heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling. For this reason, organic solvents are added to the reaction system. Among the organic solvents tested, propanol, butanol,

acetone, methyl ethyl ketone, and ethyl acetate were found to be effective for the formation of heavy oil having low viscosity.

Alkaline degradation of whole biomass or of its separate constituent components (cellulose and lignin) leads to a very complex mixture of chemical products. In turn, these compounds, due to their greater variance in structure, must involve extensive and complex mechanistic pathways for their production. Clarification of these mechanisms should lead to a better understanding of the conversion process. Several distinctly different classes of compounds, including mono- and dinuclear phenols, cycloalkanones and cycloalkanols, and polycyclic and long chain alkanes and alkenes, were identified by Eager, Pepper, and Roy (1983).

2.2.3. GREEN DIESEL FUEL FROM BI O-SYNGAS VIA FI SHER-TROPSCH SYNTHESIS

Gasification processes provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly hydrogen and carbon monoxide ($H_2 + CO$) which is also called bio-syngas. To produce bio-syngas from a biomass fuel, the following procedures are necessary: (1) gasification of the fuel, (2) cleaning of the product gas, (3) use of the synthesis gas to produce chemicals, and (4) use of the synthesis gas as energy carrier in fuel cells.

Bio-syngas is a gas rich in CO and H_2 obtained by gasification of biomass. In the steam-reforming reaction of a biomass material, steam reacts with hydrocarbons in the feed to

predominantly produce bio-syngas. Figure 2.1 shows the production of diesel fuel from bio-syngas by Fisher-Tropsch synthesis (FTS). The Fischer–Tropsch synthesis was established in 1923 by German scientists Franz Fischer and Hans Tropsch. The main aim of FTS is the synthesis of longchain hydrocarbons from CO and H₂ gas mixture. The use of iron-based catalysts is attractive due to their high FTS activity as well as their water-gas shift reactivity, which helps make up the deficit of H₂ in the syngas from modern energy-efficient coal gasifiers (Rao et al. 1992). The interest in using iron-based catalysts stems from its relatively low cost and excellent water-gas shift reaction activity, which helps to make up the deficit of H₂ in the syngas from coal gasification (Jothimurugesan et al. 2000).

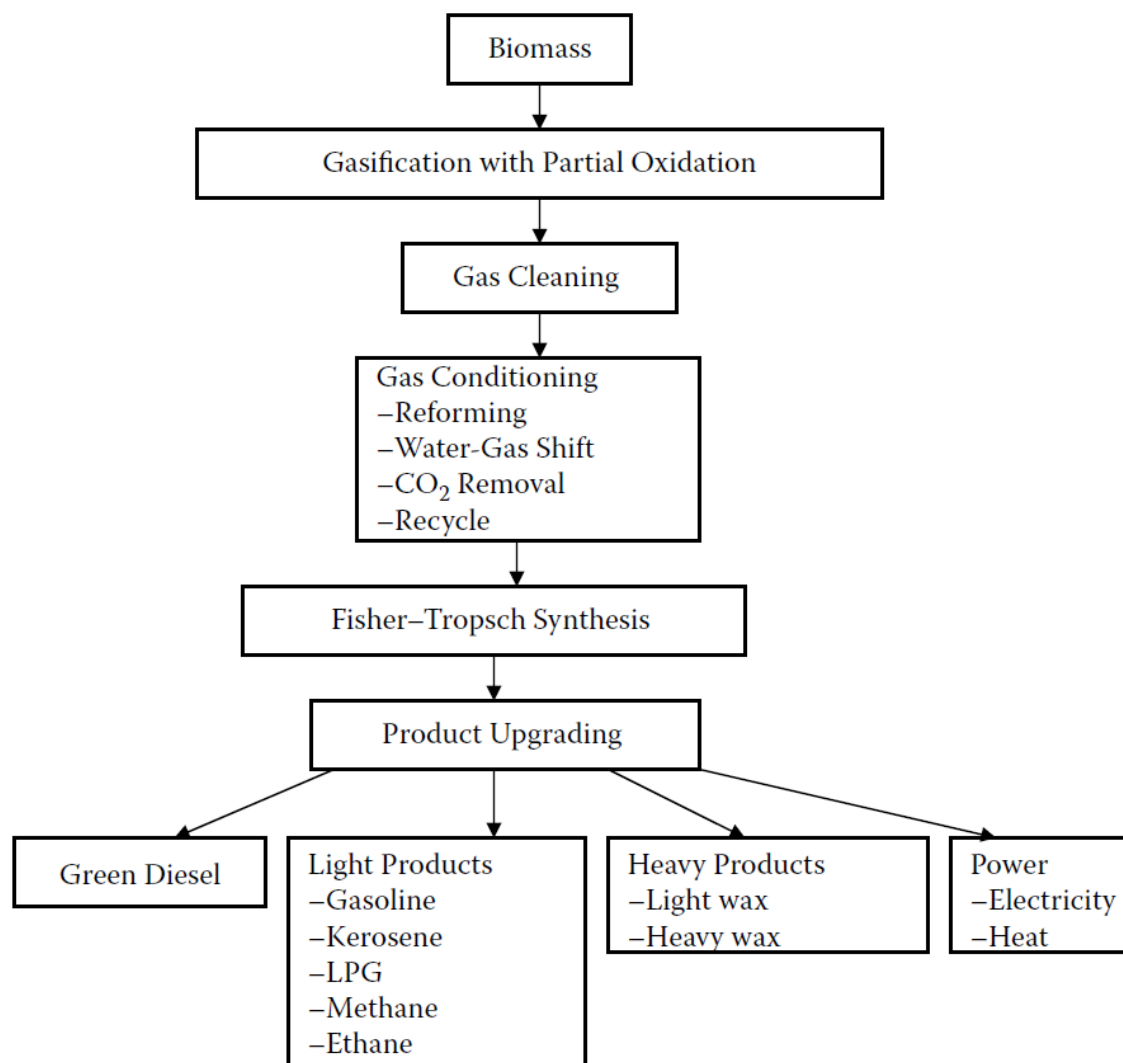


Fig 2.1 Green diesel and other products from biomass via Fisher-Tropsch synthesis.

The FTS-based gas to liquids technology includes three processing steps, namely syngas generation, syngas conversion, and hydroprocessing. It has been estimated that the FTS should be viable at crude oil prices of about \$20 per barrel (Dry 2004). The current commercial applications of the FT process are geared to the production of the valuable linear

alpha olefins and of fuels such as liquefied petroleum gas (LPG), gasoline, kerosene, and diesel. Since the FT process produces predominantly linear hydrocarbons the production of high quality diesel fuel is currently of considerable interest (Dry 2004). The most expensive section of an FT complex is the production of purified syngas and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity.

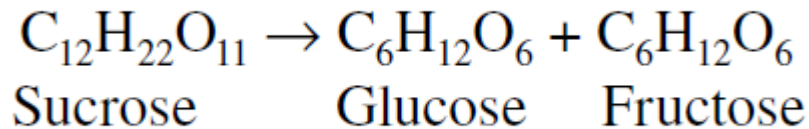
2.2.4. BIO-ALCOHOLS FROM BIOMASS

The alcohols are oxygenates, fuels in which the molecules have one or more oxygen, which decreases the combustion heat. Practically, any of the organic molecules of the alcohol family can be used as a fuel. The alcohols that can be used for motor fuels are methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$), and butanol ($\text{C}_4\text{H}_9\text{OH}$). However, only methanol and ethanol fuels are technically and economically suitable for internal combustion engines (ICEs). Ethanol (ethyl alcohol, grain alcohol, $\text{CH}_3\text{-CH}_2\text{-OH}$ or ETOH) is a clear, colorless liquid with a characteristic, agreeable odor. Ethanol can be blended with gasoline to create E85, a blend of 85% ethanol and 15% gasoline. E85 and blends with even higher concentrations of ethanol, such

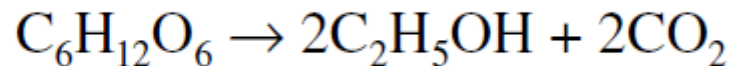
as E95, are being explored as alternative fuels in demonstration programs. Ethanol has a higher octane number (108), broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time, and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an ICE. Disadvantages of ethanol include its lower energy density than gasoline, its corrosiveness, low flame luminosity, lower vapor pressure, miscibility with water, and toxicity to ecosystems.

Bioethanol is derived from alcoholic fermentation of sucrose or simple sugars, which are produced from biomass. Bioethanol is a fuel derived from renewable sources of feedstock, typically plants such as wheat, sugar beet, corn, straw, and wood. By contrast, petrol, diesel, and the road fuel gases LPG and compressed natural gas (CNG) are fossil fuels in finite supply. Bioethanol is a petrol additive/substitute. It is possible that wood, straw, and even household wastes may be economically converted to bioethanol. Bioethanol can be used as a 5% blend with petrol under the EU quality standard EN 228. This blend requires no engine modification and is covered by vehicle warranties. With engine modification, bioethanol can be used at higher levels, for example, E85 (85% bioethanol). Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(\text{CH}_2\text{O})_n$. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple

sugars (Gnansounou, Dauriat , and Wyman 2005). First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.



Second, zymase, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol.



2.2.5. BIODIESEL FROM VEGETABLE OILS

Biodiesel is a fuel consisting of long chain fatty acid alkyl esters made from renewable vegetable oils, recycled cooking greases, or animal fats (ASTM D6751). Vegetable oil (m)ethyl esters, commonly referred to as “biodiesel,” are prominent candidates as alternative diesel fuels. Biodiesel is technically competitive with or offer technical advantages compared to conventional petroleum diesel fuel. Methyl esters of vegetable oils have several outstanding advantages among other new-renewable and clean engine fuel alternatives, as the physical characteristics of fatty acid (m)ethyl esters are very close to those of diesel fuel and the production process is relatively simple. Furthermore, the methyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation. There are more than 350 oil bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines. Dilution, micro-emulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. The purpose of the transesterification process is to lower the viscosity of the oil. Ethanol is a preferred alcohol in the transesterification process

compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment (Demirbas 2003). The properties of biodiesel are close to those of diesel fuels. The biodiesel was characterized by determining its viscosity, density, cetane number, cloud and pour points, characteristics of distillation, flash and combustion points and higher heating value (HHV) according to ISO norms.

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SUGGESTED READINGS

1. **Handbook of Plant-based biofuel by Ashok Pandey (eds.), CRC press.**

DRE 103: BIOMASS ENERGY

UNIT-3: BIOCHEMICAL CONVERSION OF BIOMASS FOR ENERGY PRODUCTION

UNIT STRUCTURE

OBJECTIVES

3.1 ANAEROBIC DIGESTION, BIOGAS PRODUCTION MECHANISM

3.1.1. WHAT IS BIOGAS?

3.1.2. ANAEROBIC DIGESTION

3.1.3. BIOGAS PRODUCTION MECHANISM

3.2. TYPES OF DIGESTERS

3.2.1. INSTALLATION, OPERATION AND MAINTENANCE OF BIOGAS PLANT

3.2.2. OPERATION AND MAINTENANCE

3.3. BIOGAS PLANTS MANURE-UTILIZATION AND MANURE VALUES

3.4 BIOGAS UTILIZATION AND STORAGE

3.4.1. BIOGAS STORAGE

3.5 BIOGAS FOR MOTIVE POWER GENERATION ETC

OBJECTIVES

This unit is prepared to give you the basic knowledge of biomass energy production by biochemical conversion processes. You will be enlightened on the microorganism assisted anaerobic digestion of biomass which leads to produce biogas.

3.1 ANAEROBIC DIGESTION, BIOGAS PRODUCTION MECHANISM

3.1.1. WHAT IS BIOGAS?

Biogas is a mixture of gases contained methane and CO₂ with trace amount of H₂S and some other gases produced by anaerobic digestion (in absence of air) of organic wastes. Different group of bacteria are responsible to convert organic wastes to biogas.

60% methane,

40% Carbon di-oxide

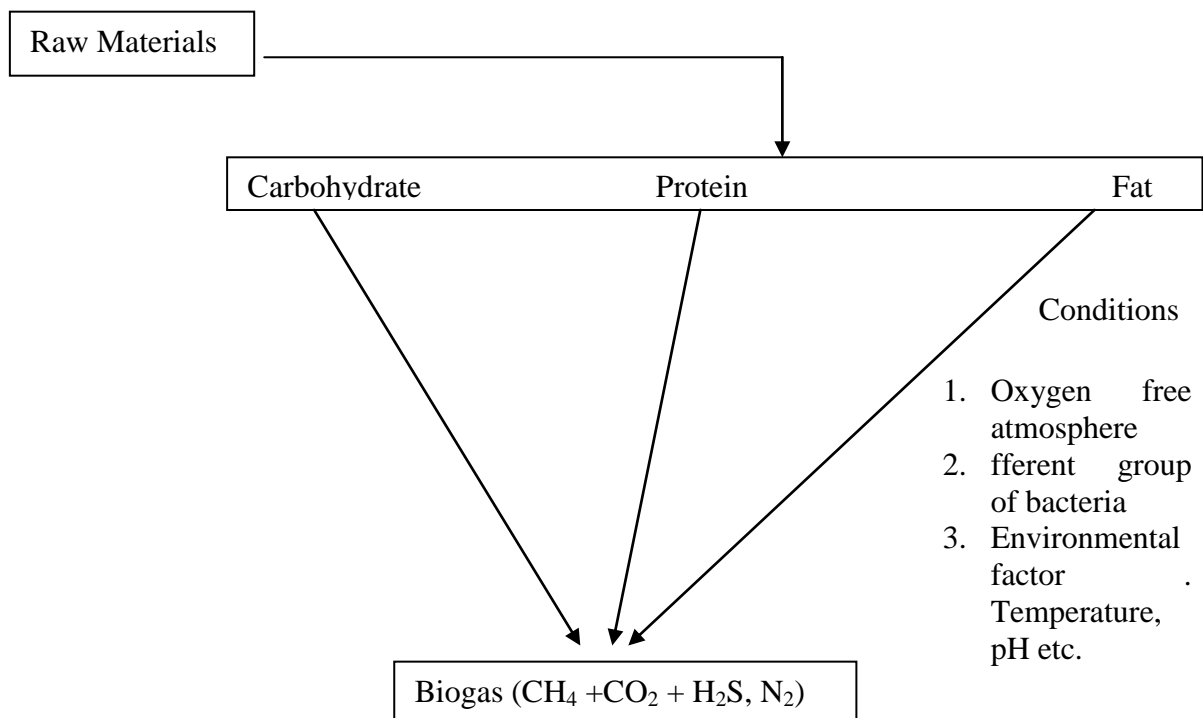
Trace amount—H₂, H₂S, Ammonia

Carbon di-oxide and other impurities are removed to enrich methane for burning to produce heat.

3.1.2. ANAEROBIC DIGESTION

Anaerobic digestion is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen. It is used for industrial or domestic purposes to manage waste and/or to release energy.

Anaerobic digestion is widely used as a source of renewable energy. The process produces a biogas, consisting of methane, carbon dioxide and traces of other 'contaminant' gases. This biogas can be used directly as cooking fuel, in combined heat and power gas engines or upgraded to natural gas-quality biomethane. The use of biogas as a fuel helps to replace fossil fuels. The nutrient-rich digestate also produced can be used as fertilizer.



Benefit of Anaerobic digestion:

- i) Odor Control
- ii) Energy production'
- iii) Conversion of organic N to inorganic N
- iv) Homogeneous effluent
- v) Other crop benefit?
- vi) Pathogen reproduction?
- vii) Weed seed sterilization?

Other key facts:

- i) There is no reduction in manure volume.
- ii) There is no reduction in manure nutrients (Some organic nitrogen is converted to ammonia nitrogen and could be volatilized in the manure storage.
- iii) There is no increase in manure nutrient

Terms to know:

Volatile solid: A measure of the weight of solid that is combustible “volatize” at a temperature of 600⁰C. It is reported as a percent of the total weight of the manure sample. Methane production is often based on the volatile solid portion of the manure.

Volatile solid production

Dairy =10 lbs VS per day

Swine= 8.5 lbs VS per day.

Layer = 12 lbs VS per day

(per 1000 lbs live weight).

Approximately 50-70 % of the VS can be converted. This depends on species and digester design.

Total Solid (TS) and dry matter: An aliquot of wastewater is dried at 105⁰C to constant weight.

Suspended solid (SS): The amount of particulate matter in a sample is determined by either filtration or centrifugation. It is expressed as dry weight.

Volatile Suspended Solids (VSS): The suspended solids, separated from a sample, are dried and subsequently ashed at 600-650⁰C. The amount of ash is subtracted from the total amount of SS: $VSS = SS - \text{ash}$.

Mixed liquor (ML): The mixture of sludge and water in the aeration basin is called mixed liquor.

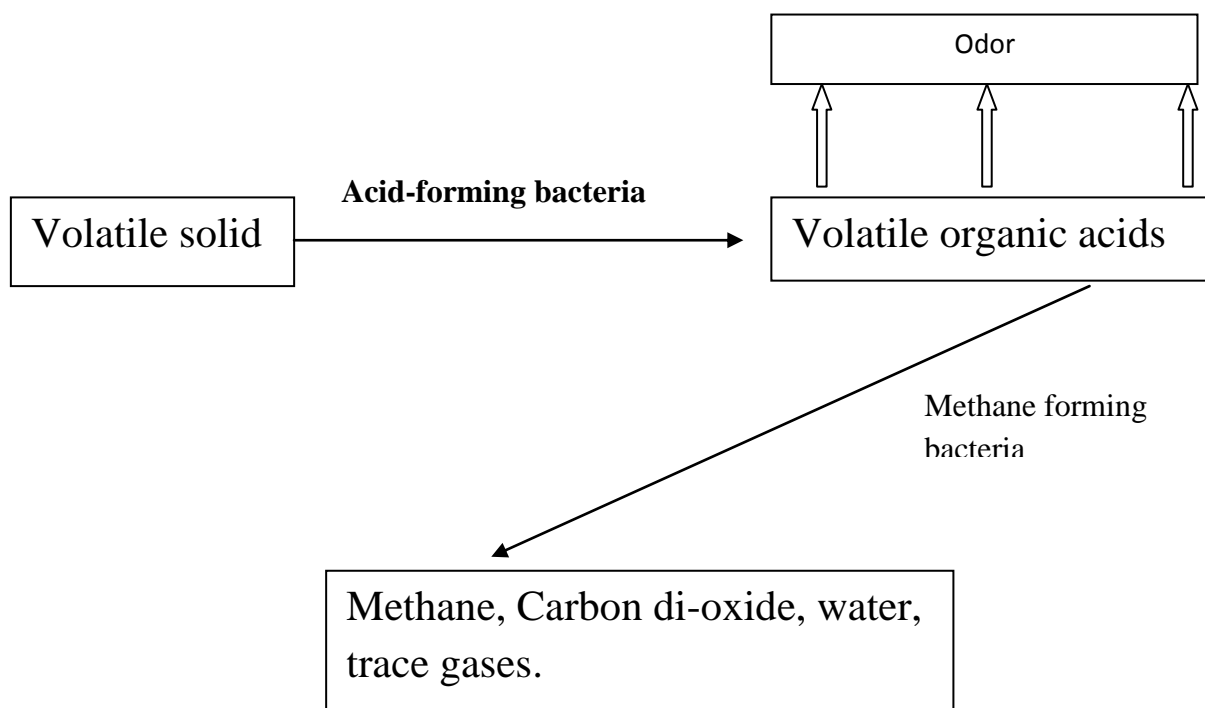
Microbial biomass in the reactor (MLSS): The mixed liquor suspended solid (MLSS) represent the total amount of sludge present in the mixed liquor. The term which more closely reflects the active biomass is the mixed liquor volatile suspended solid (MLVSS).

Hydraulic Retention time (HRT): The amount of time the manure spends in the digester. Reported as the ratio of digester volume to the amount of manure added per day. HRT affects the amount of methane produced.

10 gallons per day to a 100 gallons tank has a 10 day HRT.

Loading rate: Amount of volatile solids per unit of time per volume of digester. A standard digester will have loading rates of between 0.1 to 0.5 lbs VS/day/ft³ digester (30 days HRT).

More details on digestion process



System Classifications

A wide variety of systems have been developed to anaerobically treat biomass like Municipality Solid Waste (MSW) .

They can be split into a variety of categories such as :-

1) Wet or Dry:

Wet – The msw feedstock is slurried with a large amount of water to provide a dilute feedstock of 10-15% dry solids.

Dry – The feedstock used has a dry solids content of 20 – 40%.

2) Batch or Continuous:

Batch – The reactor vessel is loaded with raw feedstock and inoculated with digestate from another reactor. It is then sealed and left until thorough degradation has occurred. The digester is then emptied and a new batch of organic mixture is added.

Continuous – The reactor vessel is fed continuously with digestate material, fully degraded material is continuously removed from the bottom of the reactor.

3) Single Step/Multi-Step

Single Step – All digestion occurs in one reactor vessel.

Multi-Step – Process consists of several reactors, often the organic acid forming stage of the anaerobic digestion process (acetogenesis) is separated from the methane forming stage (methanogenesis). This results in increased efficiency as the two microorganisms are separate

in terms of nutrient needs, growth capacity and ability to cope with environmental stress. Some multistage systems also use a preliminary aerobic stage to raise the temperature and increase the degradation of the organic material. In other systems the reactors are separated into a mesophilic stage and a thermophilic stage.

3.1.3. BIOGAS PRODUCTION MECHANISM

Biomethanation or methanogenesis: is a microbiological anaerobic process in which organic matter is progressively degraded through a well-organized community of several microbial population, which will be referred to as active biomass, ultimately to methane, CH_4 and bicarbonate, or Carbon dioxide, HCO_3^- or CO_2 .

The three steps of biogas production

Biogas microbes consist of a large group of complex and differently acting microbe species, notable the methane-producing bacteria. The whole biogas-process can be divided into three steps: hydrolysis, acidification, and methane formation. Three types of bacteria are involved as shown in the figure-1.

Hydrolysis

In the first step (hydrolysis), the organic matter is enzymolyzed externally by extracellular enzymes (cellulase, amylase, protease and lipase) of microorganisms. Bacteria decompose the long chains of the complex carbohydrates, proteins and lipids into shorter parts. For example, polysaccharides are converted into monosaccharides. Proteins are split into peptides and amino acids.

Acidification

Acid-producing bacteria, involved in the second step, convert the intermediates of fermenting bacteria into acetic acid (CH_3COOH), hydrogen (H_2) and carbon dioxide (CO_2). These bacteria are facultatively anaerobic and can grow under acid conditions. To produce acetic acid, they need oxygen and carbon. For this, they use the oxygen solved in the solution or bounded-oxygen. Hereby, the acid-producing bacteria create an anaerobic condition which is essential for the methane producing microorganisms. Moreover, they reduce the compounds with a low molecular weight into alcohols, organic acids, amino acids, carbon dioxide, hydrogen sulphide and traces of methane. From a chemical standpoint, this process is partially endergonic (i.e. only possible with energy input), since bacteria alone are not capable of sustaining that type of reaction.

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Methane formation

Methane-producing bacteria (Table-1), involved in the third step, decompose compounds with a low molecular weight. For example, they utilize hydrogen, carbon dioxide and acetic acid to form methane and carbon dioxide. Under natural conditions, methane producing microorganisms occur to the extent that anaerobic conditions are provided, e.g. under water (for example in marine sediments), in ruminant stomachs and in marshes. They are obligatory anaerobic and very sensitive to environmental changes. In contrast to the acidogenic and acetogenic bacteria, the methanogenic bacteria belong to the archaeobacter genus, i.e. to a group of bacteria with a very heterogeneous morphology and a number of common biochemical and molecular-biological properties that distinguish them from all other bacterial general. The main difference lies in the makeup of the bacteria's cell walls.

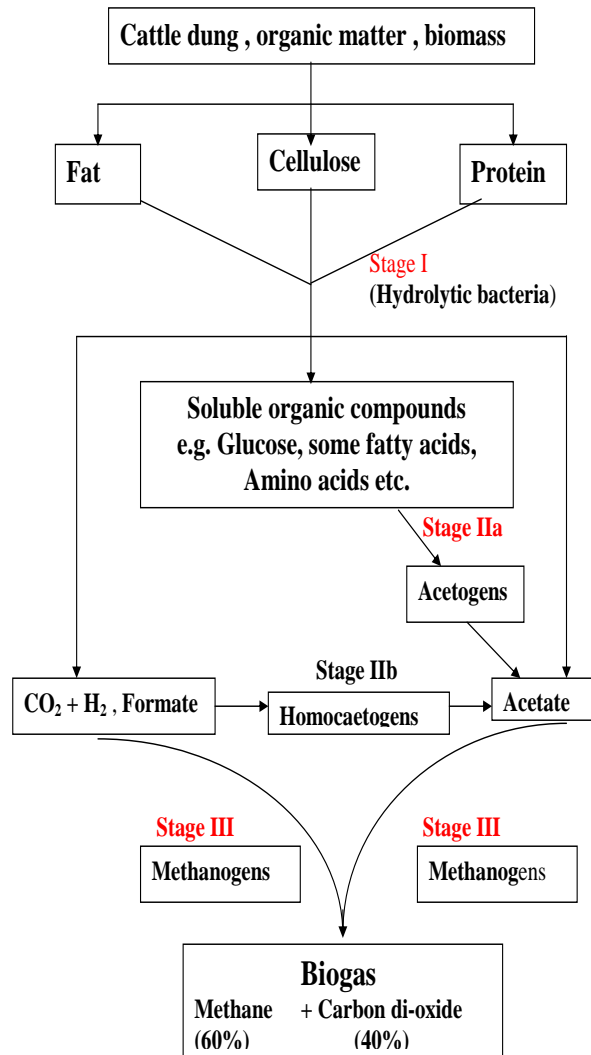


Fig. 1: Three stages of methane production from organic residue

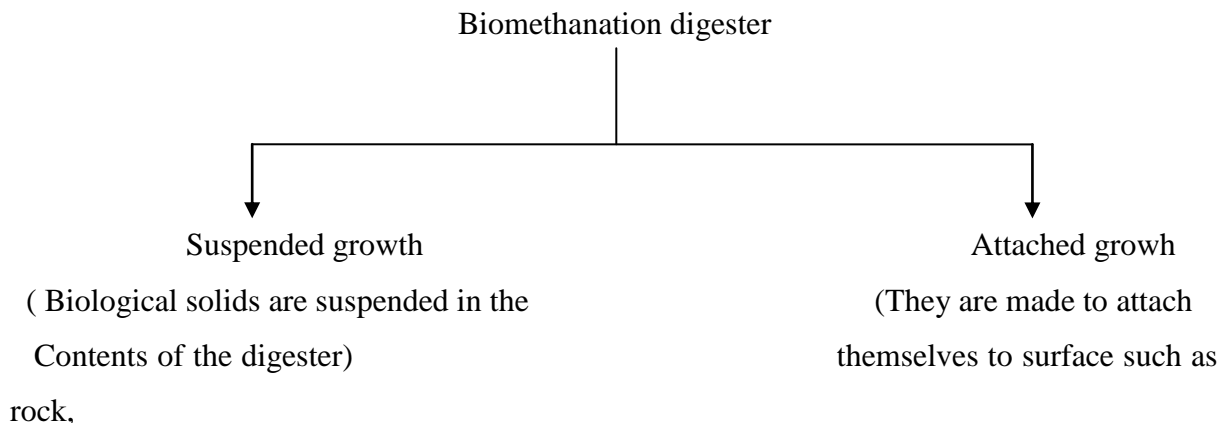
Table-1: Types of Methane bacteria helpful in biomethanation

Microorganism	Substrates-Sole Electron Donor for Methanogenesis
<i>Methanobacterium arbophilicum</i>	Hydrogen
<i>Methanobacterium formicicum</i>	Hydrogen or formate
<i>Methanobacterium ruminantium</i>	Hydrogen or formate
<i>Methanobacterium mobile</i>	Hydrogen or formate
<i>Methanobacterium thermoautotrophicum</i>	Hydrogen
<i>Methanococcus vannieli</i>	Hydrogen or formate
<i>Methanobacillus</i>	Hydrogen or formate

Factor influencing the biogas production:

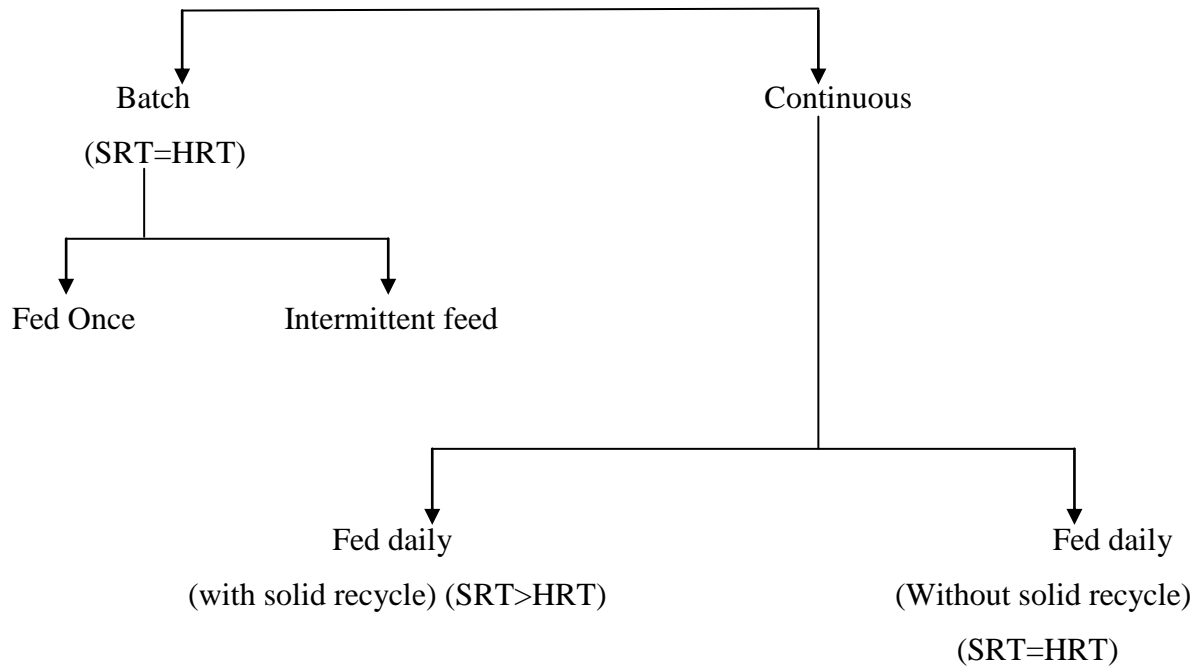
Factors	Optimum Conditions (Bhattacharyya <i>et al.</i>,1993)
Carbon/ Nitrogen ratio	30:1 is the ideal ratio. But it may be vary from 20:1 to 40:1 depending on the substrate.
Solid concentration	10-20% Total Solid Concentration of the Substrate for Semi-Continuous types of digester.
Temperature	35⁰C (less than 15⁰C is not favorable for gas generation)
Retention Period	30 to 55 days.(it varies from place to place depending on temperature in winter season)
p^H	6.6 –8.2 (7.2 p^H is the optimum for gas generation)
Toxic substances	Fungicide, Insecticide, Pesticide, heavy metals, Detergents, Phenyl, etc are harmful for gas generating bacteria.
Mixing	1: 1 ratio should be maintained for mixing fresh cow-dung with water to get TS 10% and to prevent the digester from scum formation.

3.2. TYPES OF DIGESTERS



e.g. Most of the digesters of developing countries.

Plastic or ceramics media)



SRT= Solids retention time

HRT= Hydraulic retention time

MRT= Microorganism retention time.

1. Batch and Fed batch system

The simplest technology for biomethanation is its batch system. A biomass substrate, either alone or as a mixture with some active biomass as inoculums introduce at once at a time $t=0$, into the closed vessel. Water is added in the case of solid biomass to submerged it. The reactor may be heated or not, mixed or not.

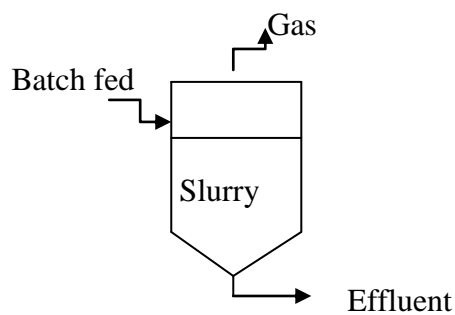
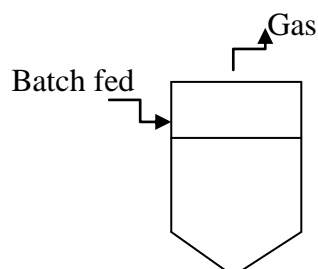


Fig: Single Batch



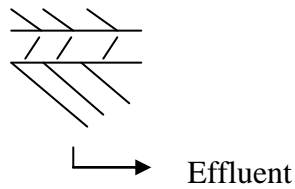
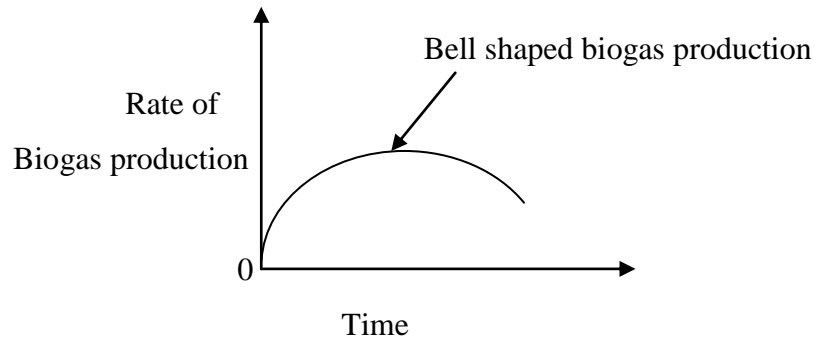


Fig: Fed Batch

If one plot rate of biogas formation against time---



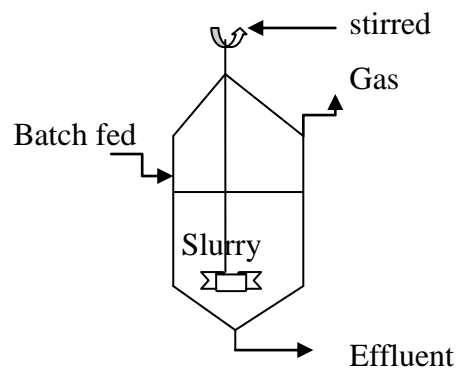
Two ways may be considered to equalize the biogas production. In the first way, the biomass substrate is not introduced into the methane digester at once but added to it in proportions with time. The technology is then called “fed-batch”. The methane reactor reactor design is same for batch and fed-batch systems.

The second way in a batch system is to introduce the biomass at once into the methane digester but to add water progressively with time. This way is particularly applicable where water sources are scarce.

The dry fermentation process has been used in batch digesters. In this process, biomass can be fed to the batch digester at a solid concentration as high as about 30 pc., which is much higher than the 6-9 percent generally used in batch systems.

Sanitary landfills can also be considered as batch reactors. Although landfills are not customarily designed for optimizing gas production, studies have demonstrated the feasibility of tapping biogas from landfills.

2. Continuous, completely mixed without recycle:



Salient feature

- 1) SRT=HRT (although practically there is likely to be incomplete mixing of the digester content)
- 2) Though complete mixing, certain portion of the materials fed to the system on a given day will leave the system of the same day. This portion is inversely proportionate to the SRT of the digester.
- 3) It is the most widely used biomethanation digester with 10% TS. All Indian biogas digester installed in rural areas are semi-continuous without recycle types.

Mixing of Methane digesting liquor occurs either by:

1. Liquid recirculation (internal or external)
2. Gas recirculation
3. Mechanical agitator with a propeller
4. With a paddle.

Energy requirement in gas recirculation is less than mechanical mixing. But, efficiency is less when thick material with large particle size is to be handled.

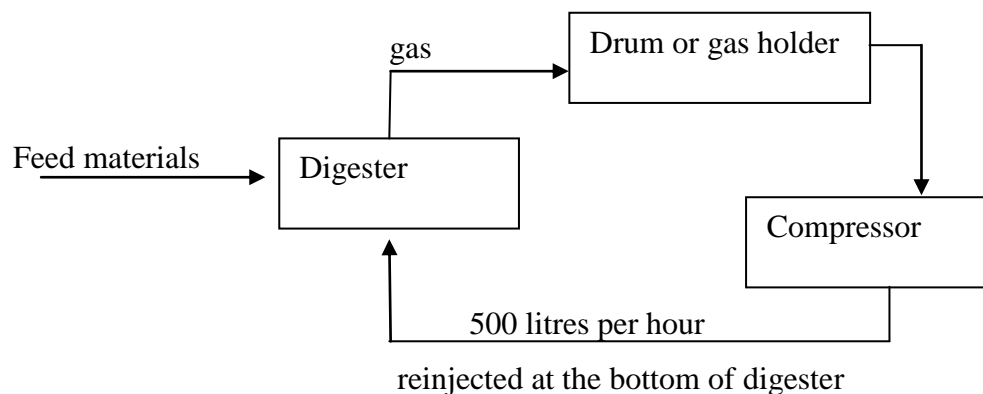


Fig: Gas-recirculation model for biogas digestion

Indian type digesters:

Fixed-dome plants

A fixed-dome plant consists of a digester with a fixed, non-movable gas holder, which sits on top of the digester. When gas production starts, the slurry is displaced into the compensation tank. Gas pressure increases with the volume of gas stored and the height difference between the slurry level in the digester and the slurry level in the compensation tank.

The costs of a fixed-dome biogas plant are relatively low. It is simple as no moving parts exist. There are also no rusting steel parts and hence a long life of the plant (20 years or more)

can be expected. The plant is constructed underground, protecting it from physical damage and saving space. While the underground digester is protected from low temperatures at night and during cold seasons, sunshine and warm seasons take longer to heat up the digester. No day/night fluctuations of temperature in the digester positively influence the bacteriological processes.

Examples of Indian fixed dome type digester are Deenbandhu, Janata models etc.

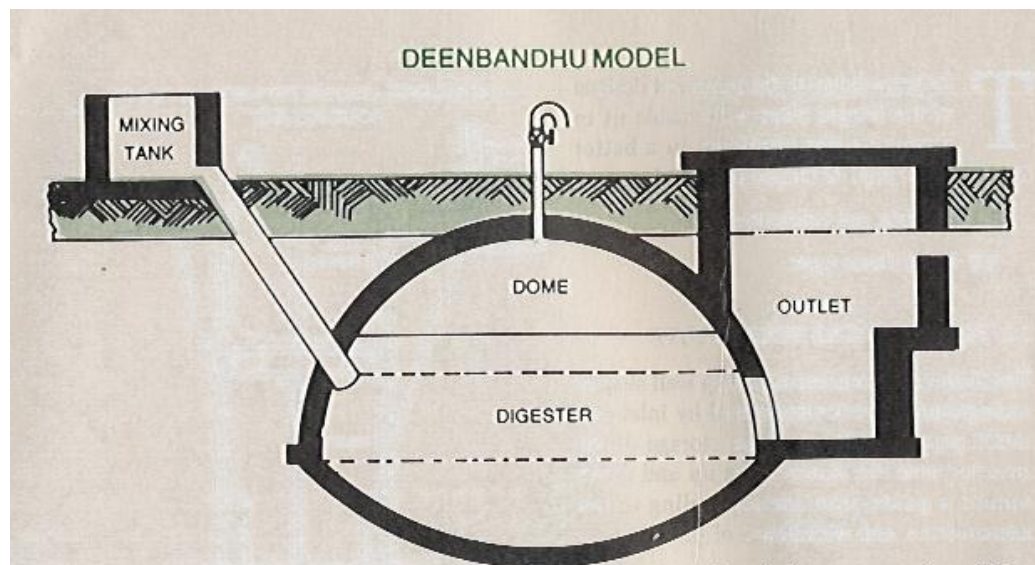


Fig: Indian fixed dome type digester (Deenbandhu model)

Function

A fixed-dome plant comprises of a closed, dome-shaped digester with an immovable, rigid gas-holder and a displacement pit, also named 'compensation tank'. The gas is stored in the upper part of the digester. When gas production commences, the slurry is displaced into the compensating tank. Gas pressure increases with the volume of gas stored, i.e. with the height difference between the two slurry levels. If there is little gas in the gas-holder, the gas pressure is low.

Digester

The digesters of fixed-dome plants are usually masonry structures, structures of cement and ferro-cement exist. Main parameters for the choice of material are:

Technical suitability (stability, gas- and liquid tightness);

cost-effectiveness;

availability in the region and transport costs;

availability of local skills for working with the particular building material.

Fixed dome plants produce just as much gas as floating-drum plants, if they are gas-tight.

However, utilization of the gas is less effective as the gas pressure fluctuates substantially.

Burners and other simple appliances cannot be set in an optimal way. If the gas is required at

constant pressure (e.g., for engines), a gas pressure regulator or a floating gas-holder is necessary.

Gas-Holder

The top part of a fixed-dome plant (the gas space) must be gas-tight. Concrete, masonry and cement rendering are not gas-tight. The gas space must therefore be painted with a gas-tight layer (e.g. 'Water-proofer', Latex or synthetic paints). A possibility to reduce the risk of cracking of the gas-holder consists in the construction of a weak-ring in the masonry of the digester. This "ring" is a flexible joint between the lower (water-proof) and the upper (gas-proof) part of the hemispherical structure. It prevents cracks that develop due to the hydrostatic pressure in the lower parts to move into the upper parts of the gas-holder.

Floating-drum plants

Floating-drum plants consist of an underground digester and a moving gas-holder. The gas-holder floats either directly on the fermentation slurry or in a water jacket of its own. The gas is collected in the gas drum, which rises or moves down, according to the amount of gas stored. The gas drum is prevented from tilting by a guiding frame. If the drum floats in a water jacket, it cannot get stuck, even in substrate with high solid content.

Material of digester and drum

The digester is usually made of brick, concrete or quarry-stone masonry with plaster. The gas drum normally consists of 2.5 mm steel sheets for the sides and 2 mm sheets for the top. It has welded-in braces which break up surface scum when the drum rotates. The drum must be protected against corrosion. Suitable coating products are oil paints, synthetic paints and bitumen paints. Correct priming is important. There must be at least two preliminary coats and one topcoat. Coatings of used oil are cheap. They must be renewed monthly. Plastic sheeting stuck to bitumen sealant has not given good results. In coastal regions, repainting is necessary at least once a year, and in dry uplands at least every other year. Gas production will be higher if the drum is painted black or red rather than blue or white, because the digester temperature is increased by solar radiation. Gas drums made of 2 cm wire-mesh-reinforced concrete or fiber-cement must receive a gas-tight internal coating. The gas drum should have a slightly sloping roof, otherwise rainwater will be trapped on it, leading to rust damage. An excessively steep-pitched roof is unnecessarily expensive and the gas in the tip cannot be used because when the drum is resting on the bottom, the gas is no longer under pressure.

Floating-drums made of glass-fiber reinforced plastic and high-density polyethylene have been used successfully, but the construction costs are higher compared to using steel.

Floating-drums made of wire-mesh-reinforced concrete are liable to hairline cracking and are intrinsically porous. They require a gas-tight, elastic internal coating. PVC drums are unsuitable because they are not resistant to UV.

Guide frame

The side wall of the gas drum should be just as high as the wall above the support ledge. The floating-drum must not touch the outer walls. It must not tilt, otherwise the coating will be damaged or it will get stuck. For this reason, a floating-drum always requires a guide. This guide frame must be designed in a way that allows the gas drum to be removed for repair. The drum can only be removed if air can flow into it, either by opening the gas outlet or by emptying the water jacket.

KVIC model:



Fig: Indian floating drum gas holder

Types of floating-drum plants

There are different types of floating-drum plants:

KVIC model with a cylindrical digester, the oldest and most widespread floating drum biogas plant from India.

Pragati model with a hemisphere digester.

Ganesh model made of angular steel and plastic foil.

Floating-drum plant made of pre-fabricated reinforced concrete compound units.

Floating-drum plant made of fibre-glass reinforced polyester.

3.2.1. INSTALLATION, OPERATION AND MAINTENANCE OF BIOGAS PLANT

Prerequisites

Basic inputs for family size biogas plants are animal dung and water. It should therefore be ascertained as to where there is an adequate supply of these inputs. Also, there should be sufficient free space available to build the gas plant and manure pits for storing outlet slurry (Bhattacharyya *et al*, 1993).

Technical feasibility

Family size biogas plant is intended to meet the domestic fuel needs mainly for cooking and also for lighting. In the first place it is necessary to make an assessment of the fuel needs. To decide about the feasibility of a proposal, it is necessary to have broad idea about (i) requirements of biogas for various uses (ii) quantity of biogas that could be obtained from various animal wastes and biomass.

(i) Requirement of biogas

Requirement of gas for different activities:

- ◆ **Cooking:** The requirement of gas for cooking ranges from 8 to 10 cft (0.23M^3 to 0.29M^3)/ person/day.
- ◆ **Lighting:** Gas required for lighting a single mantle lamp of 100 candle power is 4.5 to 5 cft per hour. (0.13M^3 to 0.14M^3)
 - **Duel fuel engine:** Requirement of biogas for running duel fuel engine is 15 cft (0.45M^3) per hour per H.P.

(ii) **Quantity of bioag that could be obtained from various wastes:** Biogas obtained per kg of feed material is expressed in m^3 .

Feed Material

Name of the animals basis)	m^3/Kg	Kg/day (Wet
Buffalo	0.04	15
Horse	0.06	10
Cow	0.04	10
Calf	0.04	5
Sheep/Goat	0.05	2
Pig	0.08	2
Human	0.10	0.4
Poultry bird	0.18	0.06

Deciding the capacity (size) of a family size biogas plant: (Ref: Bhattacharchay *et al*, 2003)

It is better to illustrate this with an example instead of a long description: We, therefore, consider the following case for deciding the size.

No. of cattle available

Buffalo----- 3 Medium size, stable bound

Bullocks----- 4 Taken for agricultural operation during the day

Calf ----- 1 stable bound

Requirement of gas

Cooking – 6 family members +2 others on average i.e. 8 persons daily (adults)

Lighting—1 lamp of 100 candle power for 4 hours daily.

Calculation

Buffalo are of medium size and stable bound. Hence dung production could be

$$3 \times 15 \text{ Kg.} = 45 \text{ Kg/day} \text{----- (A)}$$

Bullocks are away for work during the day. Hence collection of dung during the night only should be taken into account, which would be fixed at 60 percent of the daily production. If we put the dung production at 10 Kg/bullock/day then the daily production of dung would be 6 Kg/day/bullock.

Therefore,

$$\text{Dung production from bullocks, } 4 \times 6 \text{ Kg} = 24 \text{ Kg/day} \text{----- (B)}$$

$$\text{Dung production from 1 calf, } 1 \times 5 \text{ Kg} = 5 \text{ kg/day} \text{----- (C)}$$

$$\text{Total availability of dung} = A + B + C = 45 + 24 + 5 = 74 \text{ Kg/day}$$

$$\text{Gas generation} \quad 74 \text{ kg} \times 0.04 \text{ m}^3 = 2.96 \text{ m}^3/\text{day} \text{----- (X)}$$

Actual requirement :

$$\text{Coking for 8 persons daily} \quad : 8 \times 0.28 \text{ m}^3 = 2.24 \text{ m}^3/\text{day}$$

$$\text{Lighting - 1 lamp single mantle for 4 hrs daily} \quad : 4 \text{ hrs} \times 0.14 \text{ m}^3 = 0.56 \text{ m}^3/\text{day}$$

$$\text{Hence, total requirement is} \quad = 2.80 \text{ m}^3/\text{day} \text{----- (Y)}$$

$$X > Y$$

The proposal is sound and 3 m³/day biogas plant is recommended.

Selection of site for biogas plant

1. As nearer as possible to the source of animal waste.

2. As nearer as possible to the point of utilization
3. A place with enough open space
4. A place fully exposed to sunlight
5. Away from drinking water source. Safe distance is 15 meters.
6. Site should be slightly in higher elevation.
7. The edge of biogas plant should be about 2 meters away from the foundation of the house or any other building.

3.2.2. OPERATION AND MAINTENANCE

- 1. Daily Routine**
- 2. Weekly Routine**
- 3. Monthly Routine**
- 4. Half yearly/yearly routine**

Daily Routine

- (a) About 25 Kg cowdung / m³ is necessary to feed the biogas plant . So digester capacity x 25 = daily requirement of cowdung for each biogas plant
- (b) In case of KVIC model, gas holder should be done half rotation clockwise and 2-3 times anticlockwise, immediately after feeding.
- (c) As far as possible, the main gate valve is opened only when gas is required. In any case, it should be made as a practice to close the gate valve at night, when no more gas is required. Next day the valve is opened when gas is to start.

Weekly Routine

- (a) The burners and lamps are cleaned
- (b) The water remover/water trap may be checked
- (c) Stirring is to be done inside the digester to break scum
- (d) In case of KVIC, the dry mat that must have been collected in the gap between the digester wall and gas holder may be removed manually.

Monthly Routine

- (a) Gate valve and gas pipe line be tested for leakage
- (b) If the manure pit by the side of the gas plant is full, the outlet slurry may be diverted to the next pit

Half yearly/yearly routine

- (a) Gas holder, dome and pipe line are checked for leakage and corrective steps are taken where necessary.
- (b) Wornout accessories are repaired or replaced.

(c) The manure from the pits which are full is removed for manuring purpose and the pits are kept ready for further use.

3.3. BIOGAS PLANTS MANURE-UTILIZATION AND MANURE VALUES

Organic manures (farmyard, compost or green) are transformed to humus in the soil by soil microflora. This humus play pivotal role in maintaining soil fertility. The following is the most important role of humus in soil fertility;

1. Due to dark colouration, it warms up the soil absorbing sunlight.
2. Helps in soil aggregation.
3. Make soils porous, hence facilitates aeration and crop root penetration.
4. Increases water holding capacity.
5. Prevents leaching of nutrients.
6. Buffer pH change.
7. Forms complexes with harmful lements like copper, alluminium and minimizes plant toxicity.
8. Adsorbs herbicides, pesticides, and prevents their washing.
9. Supply N,P and S during degradation.
10. Supplies nutrients to beneficial soil microbes.
11. Change membrane permeability of root hairs and enhances nutrient uptakes.

None of the synthetic fertilizer plays such multifarious role in soil fertility. The average nutrient content of some commonly available organic manures are as follows:

Manure	% Content N ₂	% content P ₂ O ₅	% content K ₂ O
1. Fresh cow dung	0.3—0.4	0.1—0.2	0.1—0.3
2. Farmyard manure	0.4—1.5	0.3—0.9	0.3—1.9
3. Compost	0.5—1.5	0.3—0.9	0.8—1.2
4. Residue of biogas plant	1.5—2.5	1.0—1.5	0.8—1.2
5. Poultry manure	1.0—1.8	1.4—1.8	0.8—0.9

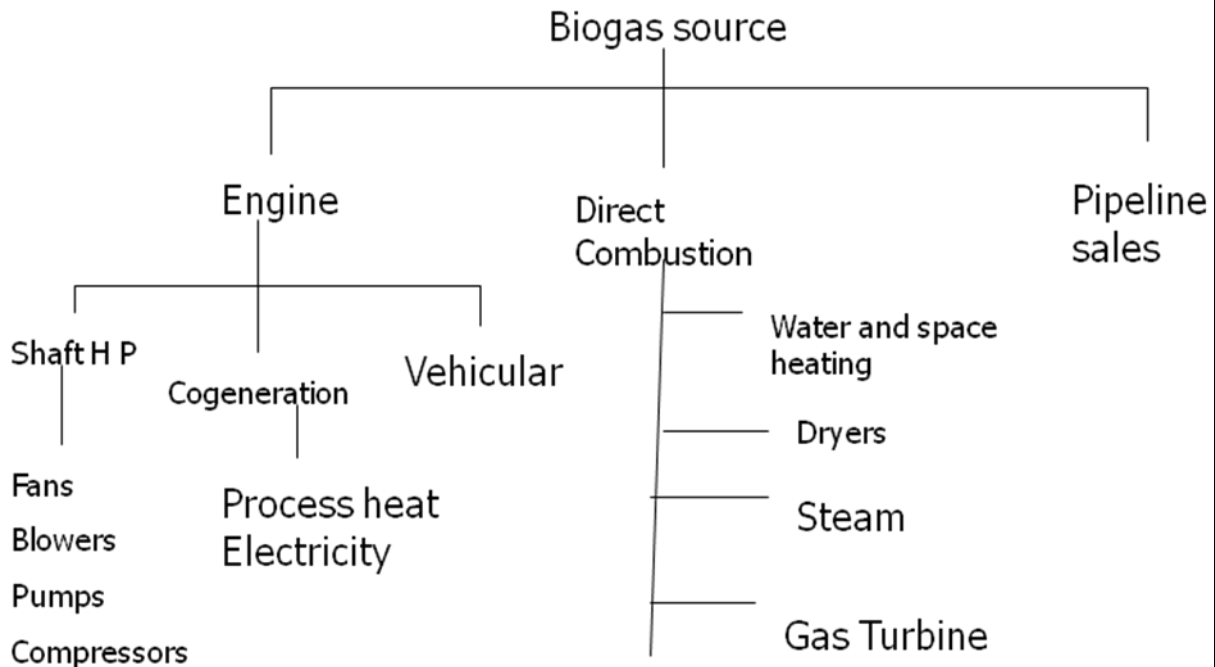
Different methods of applying residual biogas plant slurry as manure

- (a) Air dried biogas plant slurry can be applied by spreading on the agricultural land, at least one week before sowing the seeds/transplanting the seedlings.
- (b) The liquid slurry can be mixed directly with the running water in irrigation canal which will spread in the cultivation land.
- (c) Biogas palnt slurry can also be coated on the seeds prior to sowing. This acts as insecticide and prevents seeds/plants from insect attack. It also helps in early germination and healty growth of seedlings

(d) Biogas plant slurry is also being used for fish culture, which mainly acts as a supplementary feed. On an average 15-25 lit wet slurry can be applied per day in a 1200 m³ to 2400 m³ pond. Slurry mixed with oil cake or rice bran in 2:1 ratio increases the fish production remarkably.

3.4 BIOGAS UTILIZATION AND STORAGE

Options for Utilization of Biogas- schematic representation



Direct Combustion

- Simplest method of biogas utilization
- Conversion of combustion system to biogas system basically– fuel burner modification
 - a) Orifice enlargement
 - b) Intake air restriction
 - c) fuel delivery and
 - d) control system

Conversion of natural as or propane burners to biogas principally involves maintaining an appropriate exit velocity and corresponding biogas pressure drop for proper fuel and air mixture.

The Pressure drop across a burner orifice will increase with decrease in hating value of biogas. To compensate this 40% o 60% orifice diameter to be increased.

Internal Combustion Engine

Since biogas has a lower volumetric energy content than natural gas or diesel fuel, an engine may be derated. This derating for natural gas engine may be upto 20%. Hydrogen sulfide limit is 10ppm and exhaust temperature should be 88°C to prevent condensation. Spark ignition engine are the easiest engines to convert to biogas due to the wide availability of natural gas fired unit. Fueling of diesel engine with biogas requires supplement with up to 20% diesel fuel for ignition, due to lack of an ignition spark and low cetane rating of biogas. Vehicular engine requires gas clean-up, compression and filling station as well as storage and carburetion system. A standard 10.5m³, 20 x 10⁶ Pa cylinder of pure CH₄, has an energy equivalent to 14 litres of gasoline.

3.4.1. BIOGAS STORAGE

Both biogas and biomethane can be stored for on-farm uses. In practice, however, most biogas is used as it is produced. Thus, the need for biogas storage is usually of a temporary nature, at times when production exceeds consumption or during maintenance of digester equipment. Important considerations for on-farm storage of biogas include (1) the needed volume (typically, only small amounts of biogas need to be stored at any one time), (2) possible corrosion from H₂S or water vapor that may be present, even if the gas has been partially cleaned, and (3) cost (since biogas is a relatively low-value fuel).

Low-Pressure Storage of Biogas

Floating gas holders on the digester form a low-pressure storage option for biogas systems. These systems typically operate at pressures up to 10-inch water column (less than 2 psi). Floating gas holders can be made of steel, fiberglass, or a flexible fabric. A separate tank may be used with a floating gas holder for the storage of the digestate and also storage of the raw biogas. One advantage of a digester with an integral gas storage component is the reduced capital cost of the system. The least expensive and most trouble-free gas holder is the flexible inflatable fabric top, as it does not react with the H₂S in the biogas and is integral to the digester.

Table: On farm storage options for biogas and biomethane

Purpose of Storage	Pressure (psi)	Storage Device	Material	Size (ft) ³
Short and intermediate storage for on-farm use (currently used on farms for	< 0.1	Floating Cover	Reinforced and non-reinforced plastics, rubbers	Variable volume usually less than one day's production
	<2	Gas bag	Reinforced and non-reinforced plastics, rubbers	150 – 11,000
		Water sealed gas holder	Steel	3,500

biogas storage)	2 – 6	Weighted gas bag	Reinforced and non-reinforced plastics, rubbers	880 – 28,000
		Floating roof	Plastic, reinforced plastic	Variable volume, usually less than one day's production
		Possible means of storage for later on- or off-farm use (could be used for biomethane)	10 – 2,900	Propane or butane tanks
	>2,900	Commercial gas cylinders	Alloy steel	350

Source: Source: Ross *et al.*, 1996

3.5 BIOGAS FOR MOTIVE POWER GENERATION ETC

Biogas can be used for generation of mechanical power (motive power) through heat engine. There are two options of using purified biogas in engine. Fueling spark ignition engine using 100% purified biogas is one of the options. Moreover, biogas can also be used in compression ignition engine (diesel engine) in dual-fuel mode with partial replacement of diesel. Whatever the mode of use, purification of biogas to remove impurities, CO₂ and hydrogen sulphide is desirable before using it in engine.

Working principles of internal combustion (IC) engine are briefly highlighted below to understand the working of engine with biogas.

Working principles of internal combustion engine

Spark ignition (SI) engine is run on Otto Cycle and compression ignition (CI) is run on Diesel cycle. On the basis of construction and working features, IC engines are classified into two-stroke cycle and four-stroke cycle engine. Four stroke cycle engine is commonly used for power generation and therefore, is described below.

The engine consists of a cylinder (to provide space for combustion), reciprocating piston (to compress gas and receive power), connecting rod (connecting reciprocating piston with crank shaft) and rotating crank shaft (main power outlet). There are other auxiliary components to assist related functions of engine operation. The four reciprocating motions *i.e.* strokes *viz.*, intake, compression, power and exhaust complete a cycle of operation, and these are described below.

Intake stroke: The air-fuel mixture is sucked in to the cylinder by the piston sliding downward in case of SI engine. In case of diesel engine (CI), only air is sucked during intake stroke.

Compression stroke: The piston sliding upward compresses the mixture (or air in case of CI engine) using work of the crankshaft. Top of the piston can move up to upper dead centre

leaving some space above it. During process pressure increases and volume decreases. Changes of pressure and volume during the processes for SI and CI engine are shown in Fig. 1 as 1-2.

Power stroke: While the piston is in the upper dead-center, the mixture is ignited using a spark plug in case of SI engine. In case of CI engine, pressurized atomized fuel, pumped by fuel injection pump, is injected into the compressed air to initiate combustion (process 2-3 in Fig.1). The pressure of the gas generated by burning fuel pushes the piston back into the bottom dead centre and hence work is performed i.e. power is generated (process 3-4 in Fig.1.)

Exhaust stroke: The burnt exhaust gas is ejected by the rising piston through an exhaust valve during exhaust stroke.

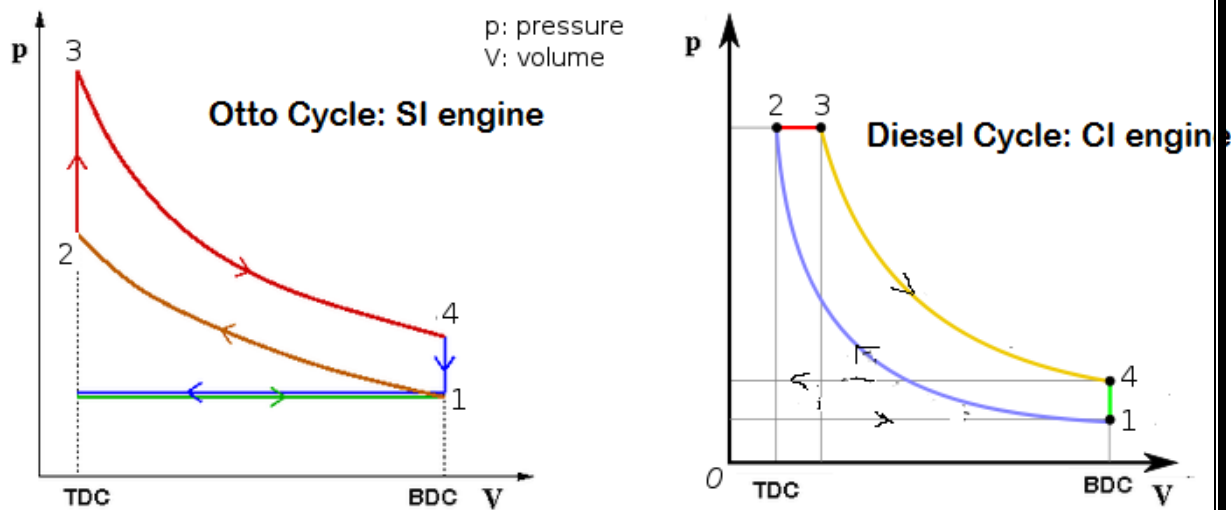


Fig. 1 The Pressure-Volume diagram of SI and CI engine

The general descriptions of working of SI and CI engine are highlighted above. More descriptions are available in related Text Books.

Uses of biogas in SI engine

While using biogas in spark ignition engine, a mixing chamber or carburetor is used to mix air and purified biogas at desired ratio. The mixture is sucked during suction stroke and at the end of compression stroke it is ignited through spark plug similar to the normal SI engine (petrol engine). However, adjustment of ignition timing is necessary for proper combustion and hence smooth functioning of the engine. Due the relatively lower calorific value of biogas fuel, decrease in power could be noticed.

Uses of biogas in CI engine

In compression ignition *i.e.* diesel engine biogas is used to partially replace diesel fuel and operation is known as dual-fuel mode of operation. Initially, engine is run on 100% diesel and intake manifold used for suction of air is connected with purified stored biogas source. This facilitates suction of a mixture of biogas and air during intake stroke. The engine is run normally without disconnecting diesel fuel. However, diesel requirement is reduced as air is reached with gaseous biogas fuel. Reduction of diesel requirements up to 80% is reported. If the biogas supply is interrupted, normal operation can proceed with 100% diesel fuel.

Fuel replacement with the use of biogas as a fuel

As discussed above, biogas can be used as a fuel in stationary and mobile engines, to generate motive power for irrigation pumping, drive farm machinery or generate electricity. Calorific value pure methane is about 38 MJ/m³ at 15.5°C and 1 atmosphere. However, the calorific value of biogas varies from 20-25 MJ/m³. In terms of energy equivalents 1.33 - 1.87 m³ of biogas is required to replace one litre of petrol fuel. For replacement of one litre of diesel fuel about 1.5 - 2.1 m³ of biogas is required. With 25-30% thermal efficiency of engine, approximately 0.60 m³ of biogas per kWh of mechanical power would be required. Converting this to electricity, approximately 0.75 m³ of biogas is required per kWh.

Care while planning to use biogas for generation of motive power

It is utmost important to take appropriate care while planning to use biogas for motive power generation and/or electricity generation. First, availability of sufficient quantity of gas as per requirement is to be ensured. Second, gas should be free from H₂S, excessive CO₂, moisture etc. Hydrogen sulphide (H₂S) is particularly harmful in internal combustion engines. Its chemical reactions and its combustion product - sulphur dioxide - lead to corrosion and wear on engines. Similarly, moisture also causes improper combustion. Third, the selections of appropriate engine size and type are also important consideration for successful engine operation using biogas as fuel.

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UNIT STRUCTURE

OBJECTIVES

4.1 BIODIESEL

4.2. BIODIESEL: INTRODUCTION

4.3. TRANSESTERIFICATION

4.3.1. FACTORS EFFECTING TRANSESTERIFICATION PROCESS

4.4. FUEL QUALITY OF BIODIESEL

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4.4.3. CALORIFIC VALUE

4.4.4. FLASH POINT

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4.4.6. ASH CONTENT

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4.5.1. COPPER STRIP CORROSION

4.5.2. LUBRICITY

4.5.3. SULPHUR CONTENT

4.5.4. CARBON RESIDUE

4.5.5. WATER CONTENT

4.6 PERFORMANCE OF ENGINE FUELLED WITH BIODIESEL

4.7. THE MAJOR OBSTACLE TO WIDESPREAD USE OF BIODIESEL

4.8 ALCOHOL PRODUCTION FROM BIOMASS- TYPES OF MATERIALS OF ALCOHOL PRODUCTION-PROCESS DESCRIPTION, UTILIZATION

4.8.1. ALCOHOL AS A BIOFUEL: INTRODUCTION

4.8.2. MERITS OF BIO-ETHANOL

4.8.3. FEEDSTOCKS FOR BIO-ETHANOL

4.8.4. BIO-ETHANOL PRODUCTION PROCESS

4.8.4.1. BIO-CHEMICAL PRODUCTION OF ETHANOL

4.8.4.2. THERMO-CHEMICAL PRODUCTION OF ETHANOL

4.8.5. USES OF BIO-ETHANOL

OBJECTIVES

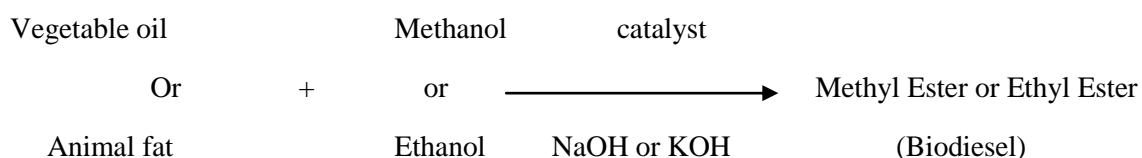
This unit is prepared to give you the basic understanding on the liquid biofuels that can be used as transportation fuel replacing fossil based petroleum oil. Main emphasis is given on biodiesel and bioethanol.

4.1 BIODIESEL – the mechanism of transesterification, fuel characteristics of biodiesel, technical aspects of biodiesel engine utilization

With the depletion of oil resources as well as negative environmental impact associated with the use of fossil fuels, there is a renewed interest in alternate energy sources. As the world reserves of fossil fuels and raw materials are limited, active research interest has been stimulated in nonpetroleum, renewable, and nonpolluting fuels. Biofuels are the only alternate energy source for the foreseeable future and can still form the basis of sustainable development in terms of socioeconomic and environmental concerns. Biodiesel and bioethanol, derived from plant sources, appear to be promising future energy sources.

4.2. BIODIESEL: INTRODUCTION

Liquid biofuels, primarily biodiesel and bioethanol, are processed from agricultural crops and other renewable feedstocks. Biomethanol can also be produced from lingo-cellulosic materials and pyrolytic oil is the result of advanced conversion of biomass feedstocks. From renewable sources such as vegetable oils, animal fats and recycled cooking oils, biodiesel can be produced. Chemically, it is defined as the monoalkyl esters of long chain fatty acids derived from renewable lipid sources.



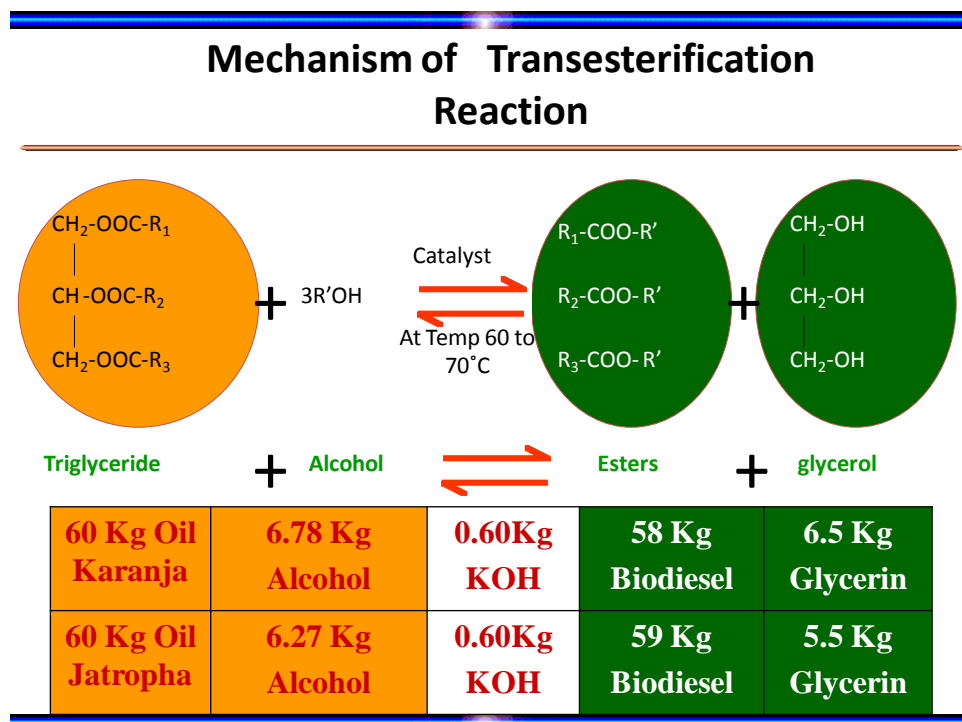
Biodiesel can be used in neat form or blended with petroleum diesel for use in diesel engines. Physical and chemical properties are similar to petroleum based diesel fuel and the operating performance of the diesel does not change. Blending biodiesel with diesel fuel accelerate its biodegradability. Biodiesel samples degraded more rapidly than dextrose and were 95 p.c. degraded at the end of 28 days. On the other hand, diesel fuel was approximately 40 p.c. degraded after 28 days.

All naturally occurring oil and fats are triglycerides or triacylglycerides. Studies have shown that triglycerides hold promise as alternative fuel for diesel engine. However, direct use of oil/fat is unsatisfactory for diesel engine due to its higher viscosity and free fatty acid content. Moreover, formation of gum due to oxidation and polymerization, combustion carbon deposit, lubricating oil thickening are some of the obvious problems. Several processes have been evolved to convert viscous and thick oil into biodiesel. Pyrolysis, micro-emulsification and transesterification are some of the commonly cited conversion process. However, transesterification has been the most commonly used conversion process amongst the three.

There have been at least four alternative feedstock paths for biodiesel production i.e. plantation of broad-acre oil seed crops, utilization of used cooking oils and animal fats, promotion of plantation of oil bearing trees and lastly, to develop and investigate other untapped feedstock. Vegetable oils for biodiesel production vary considerably with location according to climate and feedstock availability. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe; palm oil predominates in tropical countries, and soybean oil and animal fats in the USA. However, biodiesel production from conventional sources (soybean, rapeseed, palm, etc.) increasingly has placed strain on food production, price and availability.

4.3. TRANSESTERIFICATION

Transesterification, commonly known as alcoholysis, is the reaction of an oil or fat with an alcohol to form esters (Biodiesel) and glycerol. The overall transesterification reaction is composed of three consecutive reactions where di-glycerides and mono-glycerides are formed as intermediates.



Theoretically, the transesterification reaction is an equilibrium reaction in which excess alcohol is required to shift the reaction equilibrium to the right side and produce more methyl esters as product. A catalyst is usually used to improve the reaction rate and hence yield. The overall chemical reaction of the transesterification process is summarized in Fig 1.

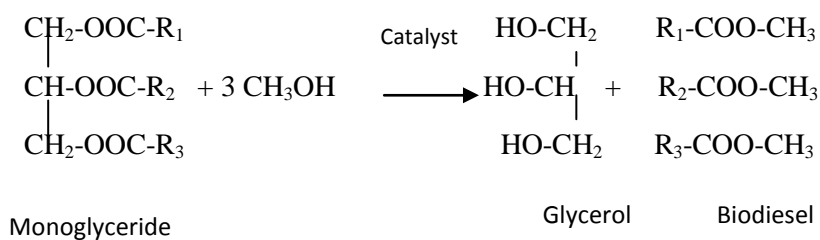


Fig 1 Transesterification reaction

A number of catalysts have been reported as successful for transesterification process. Primarily the catalysts can be classified as either alkaline or acidic type. Now-a-days heterogeneous types of catalyst are gaining attention because of their superiority over homogeneous catalysts. Heterogeneous catalysts are less corrosive which can be separated from the reaction mixtures and can be reused. Free fatty acid (FFA) content of the feedstock governs the selection of appropriate type of catalyst. The reaction mechanisms of alkaline and acidic transesterification are shown in Fig 2 and Fig 3, respectively.

It is reported that high quality feedstock (refined vegetable oil) can be easily converted into biodiesel by alkaline catalytic transesterification, because of the low level of FFA content. NaOH, KOH, Na-metal are the alkali catalysts generally used in this type of reaction. Alkali catalyst (either NaOH or KOH or Na-metal) when mixed with alcohol, the actual catalyst, alkoxide group is formed. As shown in the Fig 2, the reaction is completed in three different steps. The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate which reacts with an alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). Finally, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a di-glyceride. A small amount of water is also generated in the reaction, which may produce soap during transesterification reaction.

Some low quality feedstocks *viz.*, used frying oils, animal fats, soapstocks and greases, are available for the production of biodiesel which reduces the feedstock cost. But these types of feedstocks contain more amount of FFA and therefore, cannot be converted to biodiesel using alkaline catalytic transesterification. Because FFAs react with an alkaline catalyst, forms soap and water, which decrease the ester yield and also create problems in ester separation. For such feedstocks, acid catalysis is preferred.

The acid catalyzed transesterification process is catalyzed by acids, preferably by hydrochloric and sulfuric acids (Fig 3). The protonation of the carbonyl group of the ester leads to the carbocation which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate, which eliminates glycerol to form the new ester.

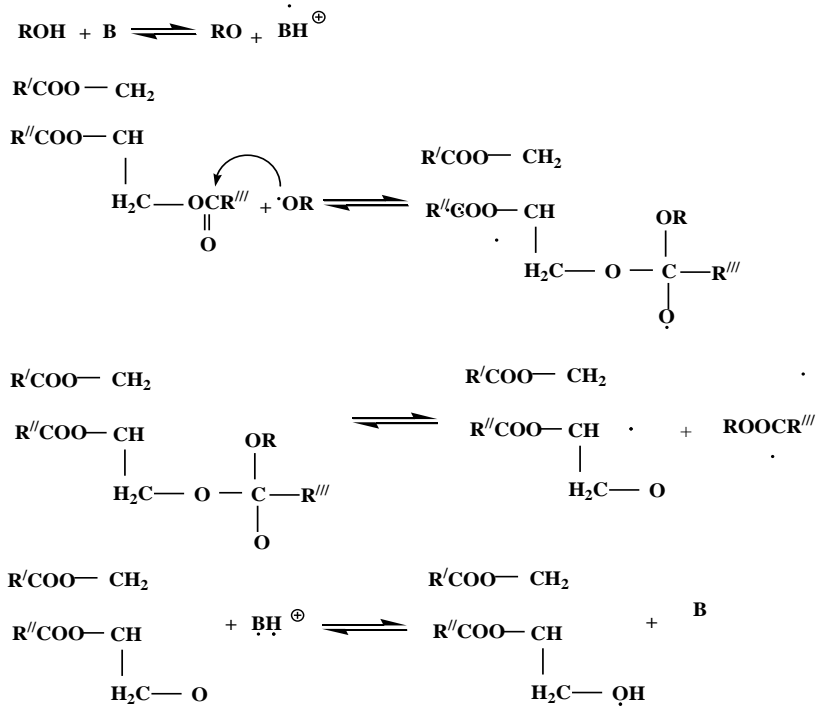
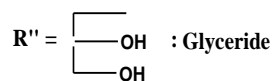
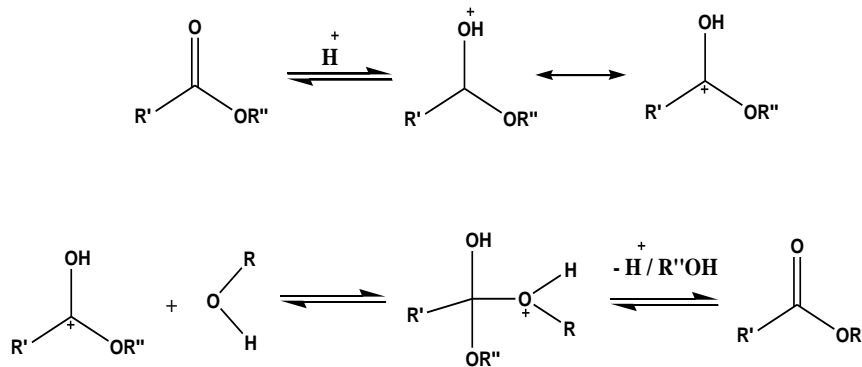


Fig 2 Mechanism of alkaline catalytic transesterification



R' = Carbon chain of fatty acid

R = alkyl group of alcohol

Fig 3 Mechanism of acid catalytic transesterification

4.3.1. FACTORS EFFECTING TRANSESTERIFICATION PROCESS

There are several parameters such as, (i) type of catalyst, (ii) concentration of catalyst, (iii) type of alcohol, (iv) alcohol to oil molar ratio (v) reaction time, (vi) reaction temperature and (vii) reaction pressure by which transesterification process is affected. A wide range of variations of these transesterification parameters are possible. Selection of optimum parameters is mostly governed by the nature and composition of feedstocks.

Methanol to oil molar ratio is important parameter affecting transesterification reaction. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glycerides

to yield three moles of biodiesel and one mole of glycerol. However, practically the alcohol to oil molar ratio requirement differs from the stoichiometric molar ratio. The type of catalyst, the type of alcohol, the characteristics of feedstock and reaction environment (temperature and pressure) govern the requirement of optimum molar ratio.

Time of transesterification is another important factor affecting the transesterification reaction. In general, acid catalytic process requires more time as compared to alkaline catalytic process for conversion of triglycerides to biodiesel. Reaction completion time is also dependent on the alcohol to oil molar ratio. The reaction is found faster with high molar ratio, whereas longer time is required for lower molar ratio to get the same conversion.

Reaction temperature and pressure are important considerations as these are related to economy of biodiesel production. It is desired to produce biodiesel at ambient pressure and temperature to reduce the cost of production.

4.4. FUEL QUALITY OF BIODIESEL

It is desired to produce good quality biodiesel in terms of some well defined and standard parameters. Viscosity, density, cetane number, oxidation stability, acid value, cold flow properties, flash point, are the quality parameters which have standard definition as well as assessment procedures. Assessments of these quality parameters are imperative while reporting a new variety of biodiesel. There are also well established standards *viz.*, ASTM 6751-07 and EN 14214-07 available for assessment of these quality parameters. With an ideal production procedure, the quality of biodiesel depends upon the characteristics of feedstock.

Biodiesel properties are greatly influenced by the fatty acid composition that is present in the parent oil. Viscosity, cetane number, oxidation stability, low temperature flow ability are influenced by fatty acid profile. Chain length and number of double bonds of the fatty acids are the key factors influencing those properties.

4.4.1. VISCOSITY

Viscosity is a measure of internal fluid friction which opposes any dynamic change in the fluid motion. Higher viscosity of fuel has severe implication on engine operation due to poor atomization of the fuel spray and improper fuel injection. It is reported that viscosity of any fuel is reflection of the chemical structure. Viscosity increases with increase in chain length and decreases with the increase in number of double bonds. It is also reported that viscosity and heat content of biodiesel fuel increases together. Ideally biodiesels should have viscosity closer to diesel fuel. Viscosity of biodiesel is determined according to ASTM D445 specification using kinematic viscosity apparatus. Allowable limit of biodiesel viscosity as per this standard is 1.9 cSt to 6.0 cSt.

4.4.2. DENSITY

Density is an important property which influences the fuel injection system of engine. It is reported that fuel amount, injection timing, injected spray pattern are directly affected by viscosity as well as density. A fuel having lower viscosity and density is preferred for improved atomization and better formation of air to fuel mixture. Molecular structure of fuel has some influence on the density of fuel. It has been seen that as the chain length and saturation level increases, the fuel density also increases. There are certain correlations with the density of fuel with exhaust emissions, particularly particulate matter (PM) and nitrous oxide (NO_x). Greater increases in PM and NO_x emission are noticed in fuels having higher fuel density. Density of biodiesel sample is measured according to ASTM D287 using hydrometer. The variation of biodiesel densities are reported in the range of 850-890 kg/m³.

4.4.3. CALORIFIC VALUE

Calorific value is the net heat content of fuel and it affects brake thermal efficiency and specific fuel consumption of diesel engine. Calorific value or heat content of a fuel is a function of its viscosity and density. Calorific values are measured by ASTM D5865, using auto bomb calorimeter. Calorific values of biodiesel are found to vary between 35 MJ/m³ to 40 MJ/m³

4.4.4. FLASH POINT

The flash point is the temperature at which the sample starts burning when it comes into contact with fire. This temperature can be directly correlated with its volatility; an important fuel feature for engine's starting and warming. Fuel having high viscosity and low volatility could lead bad start up in cold condition and also cause misfiring and ignition delay. It is reported that fuels having high flash point cause carbon deposit in the combustion chamber. Flash point is determined using ASTM D93. ASTM limit for Flash point is 130 °C.

4.4.5. ACID VALUE

Acid value of oil is an important determining parameter for transesterification reaction. Acid values are usually determined using ASTM D664 standard. About 2 g of ethanolic sample is titrated against 0.1 N ethanolic KOH, using indicator phenolphthalein to determine the titration end point. Acid value is then calculated using the standard formula.

4.4.6. ASH CONTENT

Ash content is a measuring parameter for suitability of the fuel in long term engine application. Ash contents of biodiesel samples are determined by ASTM D874 standard. A furnace having provision for temperature control is used for this measurement. Reduction in sample weight after keeping the sample in furnace at 750 °C for 5 minutes is measured with a

sensitive balance. The difference in weight is expressed as the ash content of the sample. Minimum ash content is preferred.

4.4.7. CETANE NUMBER

The cetane number is an indicator which reflects the ignition quality of a fuel for diesel engine. It is reported that cetane number influences ignition delay time that is the time between the start of injection and start of combustion. CN of fuel should be within the optimum limit for better ignition properties. Both low and high cetane numbers of diesel fuel are not desirable for better ignition properties. Cetane number of fuel is also the reflection of the chemical composition of parent material. As mentioned earlier with increasing chain length, decreasing branching and unsaturation, cetane number increases. Minimum Cetane number is specified as 47 by ASTM standard.

4.4.8. LOW TEMPERATURE FLOW PROPERTIES

Low temperature flow properties are determined through measurement of cloud point and pour point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid when cooled. The pour point is the lowest temperature after which the fuel ceases to flow. Fatty acid profile of the parent material has major implication on cold flow properties of biodiesel. It is reported that the cold flow properties of biodiesel fuel increases with increasing carbon atoms in the carbon chain and decreases with increasing double bonds. Cloud and pour points of biodiesel fuel are determined by ASTM D2500 and ASTM D97 standard, respectively, using cloud and pour point bath. Cloud point range of -1 °C to 16 °C and pour point range between -6 °C and 12 °C are reported for different biodiesel.

4.5. DISTILLATION CHARACTERISTICS

It is reported that the distillation (volatility) characteristic of fuel affects engine performance and also this is important from safety point of view. Distillation is also an indication of Cetane Index. In compression ignition (CI) engine, when atomized fuel comes in contact with the high temperature air, it vaporizes, and undergoes a series of spontaneous chemical reactions. Volatility of fuel determines the readiness to produce potentially explosive vapor. Sim-dis method is used using ASTM D287 and D86 correlation. As per ASTM recommendation, 90% distillation at 360 °C is desired.

4.5.1. COPPER STRIP CORROSION

The corrosion behavior of the fuel is tested through a standard test called ASTM D130 by using a copper strip. It is believed that free moisture, sulphur compound and similar impurities present in fuel could cause corrosion of the engine components, when it is acted upon on such fuel. Maximum corrosion index of 3 is recommended.

4.5.2. LUBRICITY

Lubricity is an index of lubricating behavior of the fuel that ideal fuel should possess certain level of lubricity. There are several procedures to determine the lubricity index of fuel. In this study, high frequency reciprocating rig (HFRR) is used to determine the lubricity index (ASTM D6079) of both

the biodiesel samples. Wear scar on a spherical metal ball undergoing high frequency reciprocating load is measured as an index of the lubricity.

4.5.3. SULPHUR CONTENT

Sulphur is an undesirable constituent of the fuel as the combustion of sulphur causes environmental problem. Sulphur may originate either from the feedstock or the chemical used in conversion process. The sulphur analyzer using ASTM D5453 standard is used to determine the sulphur content of biodiesel. Maximum allowable sulphur mass in biodiesel fuel is .005% (ASTM D5453).

4.5.4. CARBON RESIDUE

The carbon residue value is an indication of the deposit forming tendency of a fuel. It is the tendency of the fuel to form carbon deposits under high temperature conditions in an inert atmosphere, and is expressed as Conradson Carbon Residue (CCR). Carbon residue of fuel is measured by ASTM D4530 standard, using Conradson Carbon Residue apparatus and allowable limit is .05% (mass).

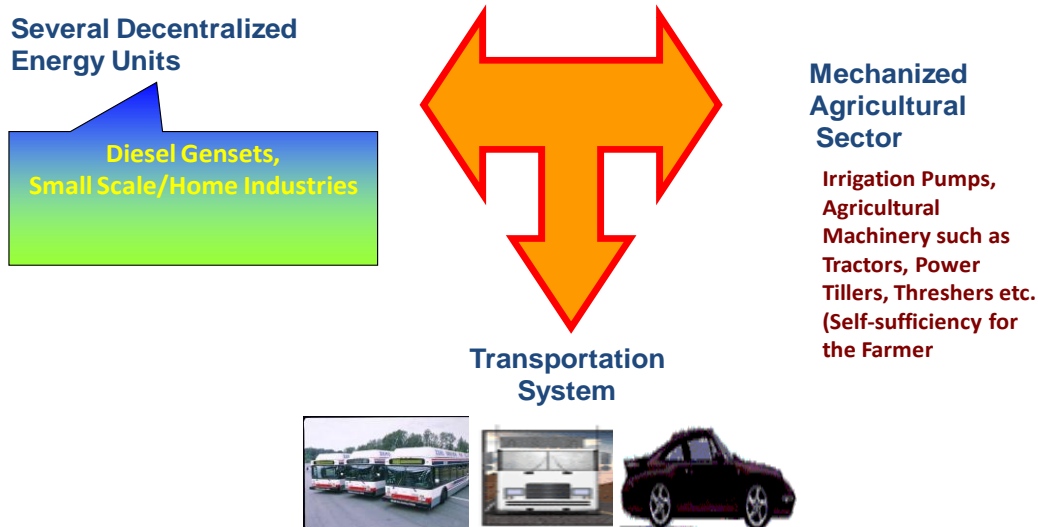
4.5.5. WATER CONTENT

The amount of water content of any fuel is primarily required for determining its economic value. Various methods are used for determination of water content such as evaporation, distillation, xylene and the Karl-Fisher titration method. Water content is generally determined by direct measurement of mass of water evaporated during distillation, using ASTM D287 and 0.05% is allowable limit of water content.

4.6 PERFORMANCE OF ENGINE FUELLED WITH BIODIESEL

Conventional diesel engines are operated by using biodiesel or blends of biodiesel and petro-diesel. Three distinct aspects *viz.*, (i) combustion efficiency, (ii) emission characteristics and (iii) engine health require attention while investigating engine performance using biodiesel fuel either neat or blended with petro-diesel. Differences in engine performance behaviour are reported while comparing diesel fuel with biodiesel with respect to above aspects. In most of the cases, the fuel characteristics of biodiesel are linked with the varying engine performance. In general higher viscosity and lower calorific value of biodiesel are considered as attributing factors of poor atomization *vis-à-vis* improper combustion and lower rate of heat release. In contrast, compared to conventional diesel fuel, higher cetane number of biodiesel result in shorter ignition delay, and longer combustion duration, and hence, low particulate emission. If engine is operated on biodiesel for longer time, adjustment of injection timing is recommended for better thermal efficiency. Studies have shown that diesel-biodiesel blends reduce smoke opacity, particulates, unburnt hydrocarbons, carbon dioxide and carbon monoxide emission. Limitation of using biodiesel is also reported as it has tendency to form crystal at low temperature. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operations. However, uses of appropriate additive are shown to decrease the crystallization temperature and hence overcome the problem.

Application Areas of Biodiesel



4.7. THE MAJOR OBSTACLE TO WIDESPREAD USE OF BIODIESEL

- a) Cost involvement of feedstock ---- about 80% of the total operating cost
- b) The high price of biodiesel -----large part due to the high price of the feedstock.

These developments necessitate an urgent need to identify most potent low cost feedstock for biodiesel production and their characterization for cataloguing them for immediate use and also for future crop improvement.

Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Rapeseed and sunflower oil are predominantly used in Europe. Palm oil predominates in tropical countries, and soybean oil and animal fats in the USA.

There are a large number of seed bearing plants available in the forest of North East India. Vegetable oil can be extracted from the seeds or kernels of these plant species for producing biodiesel. But very little is known about their oil content, seed bearing capacities, growth etc. Names of some such tree species are given below:

Species Name	Local Name (Assamese)	Parts
1. <i>Artocarpus chaplasha</i> Roxb.	Cham Kothal	Kernels
2. <i>Bischofia javanica</i> Blume	Uriam	Seeds
3. <i>Croton tiglium</i> Linn.	Koni bih	Kernels
4. <i>Cinnamomum glaucescens</i>	Cinnamon	Kernels

5. <i>Hevea brasiliensis</i> Willd	Rubber	Kernels
6. <i>Michelia champaca</i> Linn.	Titalsopa	Seeds
7. <i>Mangium chinensis</i>	Bogamarulia	Seeds
8. <i>Sterculia villosa</i>	Udal	Kernels
9. <i>Mesua ferra</i> Linn.	Nahar	Kernels
10. <i>Pongamia glabra</i>	Koroch	Kernels

Properties of Jatropha / Karanja oil Methyl Ester Vs diesel

Characteristics	Jatropha Oil Methyl Ester	Karanja Oil Methyl Ester	Diesel
Density (g/cc at 15° C)	0.88	0.88	0.81
Viscosity at 30oC (cSt)	3.5	4.77	2.6 - 4.1
Flash Point (°C)	162	174	74
Cloud point (°C)	6	19	-1
Pour point (°C)	1	6	-6

4.8 ALCOHOL PRODUCTION FROM BIOMASS- TYPES OF MATERIALS OF ALCOHOL PRODUCTION-PROCESS DESCRIPTION, UTILIZATION

4.8.1. ALCOHOL AS A BIOFUEL: INTRODUCTION

Bio-ethanol is ethyl alcohol, chemically known as EtOH (C₂H₅OH). Bio-ethanol and bio-ethanol/gasoline blends have a long history as alternative transportation fuels. Use of alcohol in internal combustion (IC) engines in Germany and France is dated back as early as 1894. It is also found that Brazil has been using bio-ethanol as a transportation fuel since 1925. The use of bio-ethanol as fuel was also noticed in Europe and the United States. However, after World War II, bio-ethanol's potential was largely ignored until the oil crisis of the 1970s.

It is seen that global production of bio-ethanol increased from 17.25 billion liters in 2000 to over 46 billion liters in 2007. The United States, Brazil, and several EU countries have the largest programs

promoting bio-ethanol in the world. With initiatives in America, Asia, and Europe, total global fuel bio-ethanol demand could further increase up to 125 billion liters by 2020. The United States is the world's largest producer of bio-ethanol fuel, accounting for nearly 47% of global bio-ethanol production. Brazil is the world's largest exporter of bio-ethanol and second largest producer after the United States. In Brazil bio-ethanol is produced from sugar cane, 80% of it being used in domestic purpose and approximately 20% is exported.

4.8.2. MERITS OF BIO-ETHANOL

Ethanol has higher oxygen content. The increased proportion of oxygen allows better oxidation of the gasoline hydrocarbons resulting reduction in the emission of CO and aromatic compounds. Moreover, bio-ethanol has a higher octane number (108), broader flammability limits, higher flame speeds and higher heats of vaporization. These properties allow for a higher compression ratio and shorter burn time, which lead to theoretical efficiency advantages over gasoline in an IC engine. As we know that Octane number is a measure of the gasoline quality for prevention of early ignition, which leads to cylinder knocking. The fuels with higher Octane numbers are preferred in spark-ignition internal combustion engines.

4.8.3. FEEDSTOCKS FOR BIO-ETHANOL

Bio-ethanol feedstocks can be classified into three major groups *viz*, (1) sucrose-containing feedstocks (e.g. sugar cane, sugar beet, sweet sorghum and fruits), (2) starchy materials (e.g. corn, milo, wheat, rice, potatoes, cassava, sweet potatoes and barley), and (3) lignocellulosic biomass (e.g. wood, straw, and grasses). There is a growing interest to find out cheaper carbohydrate sources for production of bio-ethanol. Ethanol is currently produced from crops, such as corn, sugar cane, and soybeans. However, the use of food and feed materials for bio-fuels raises many concerns including food shortages. In India edible resources are not encouraged for bio-ethanol production. Some of the major sources used worldwide are discussed below.

(a) Sugar as source for bio-ethanol production

Globally about 60% of bio-ethanol is produced from sugarcane and 40% from other sources. In Brazil, about 79% of ethanol is produced from fresh sugar cane juice and the remaining percentage from cane molasses. Sugar cane molasses is the main feedstock for ethanol production in India. In European countries, sugar beet molasses is used as sucrose containing feedstock. Sugar beet has been shown to possess some advantages over sugarcane. Sugar beet is a lower cycle of crop, has higher yield, and high tolerance of a wide range of climatic variations, and also has low water and fertilizer requirement.

(b) Starch as source for bio-ethanol production

Starch is also a prospective feedstock for bio ethanol production. It is a high yield feedstock for bio-ethanol production. Hydrolysis of starch is required to produce bio-ethanol by fermentation. Starch is a biopolymer, (homopolymer) consisting only one monomer, D-

glucose. To produce bio-ethanol from starch it is necessary first to break down the chains of carbohydrate for obtaining glucose syrup. The syrup can be converted into bio-ethanol by the action of yeasts. Starch (from corn and wheat) is most utilized feedstock for bio-ethanol production in America and Europe.

Corn is first milled for extracting starch, which is then enzymatically treated for obtaining glucose syrup. Then, this syrup is fermented into ethanol. Milling is performed either by wet or dry condition. Corn grain is separated into its components during wet-milling process. Starch is converted into ethanol and the remaining components are used as co-products. Besides corn wheat, ethanol can be produced from rye, barley, and sorghum. Cassava is a tuber crop and has gained interest due to its availability in tropical countries. Ethanol production from cassava can be accomplished using either the whole cassava tuber or the starch extracted from it.

(c) Lignocellulosic biomass for bio-ethanol production

Lignocellulosic biomasses are also identified as feedstock for ethanol production, primarily due to its abundant availability. Lignocellulosic complex is the most abundant biopolymer in the Earth as these biomasses comprise about 50% of world total biomass.

Prospective lignocellulosic materials identified for bio-ethanol production are crop residues (cane bagasse, corn stover, wheat straw, rice straw, rice hulls, barley straw, sweet sorghum bagasse, olive stones and pulp), hardwood (aspen, poplar), softwood (pine, spruce), cellulose wastes (newsprint, waste office paper, recycled paper sludge), herbaceous biomass (alfalfa hay, switchgrass, reed canary grass, coastal Bermudagrass, thimothy grass), and municipal solid wastes (MSW).

4.8.4. BIO-ETHANOL PRODUCTION PROCESS

Production process can be classified as (i) Bio-chemical production and (ii) Thermo-chemical production process. Bio-chemical production is more common than thermo-chemical production process.

4.8.4.1. BIO-CHEMICAL PRODUCTION OF ETHANOL

In Bio-chemical production process, two main reactions are involved *viz.*, hydrolysis and fermentation. Complex polysaccharides of the raw feedstock are converted to simple sugars in Hydrolysis. Acids and enzymes are used to catalyze this reaction while biomass is used to convert into bio-ethanol. Fermentation is a series of chemical reactions that convert sugars to ethanol. The fermentation reaction is caused by yeast or bacteria, which feed on the sugars. Ethanol and carbon dioxide are produced as the sugar is consumed by yeast.

As discussed earlier, some plants, like sugar cane and sugar beets, store the energy as simple sugars. Other plants store the energy as more complex sugars, called starches (Corn, wheat etc). Unlike, sugar and starch rich biomass, lignocellulosic biomass is made up of very complex sugar polymers.

The digestibility of cellulose present in biomass is hindered by many physicochemical, structural, and compositional factors. In the conversion of lignocellulosic biomass to fuel, the biomass needs to be treated so that the cellulose in the plant fibers is exposed. Pretreatment uses various techniques, including ammonia fiber explosion, chemical treatment, biological treatment, and steam explosion, to change the structure of cellulosic biomass and to make cellulose more accessible. Further, acids or enzymes can be used to break down the cellulose into its constituent sugars. Enzyme hydrolysis is widely used to break down cellulose into its constituent sugars. A typical scheme of pretreatment of lignocellulosic biomass is shown in Fig 1.

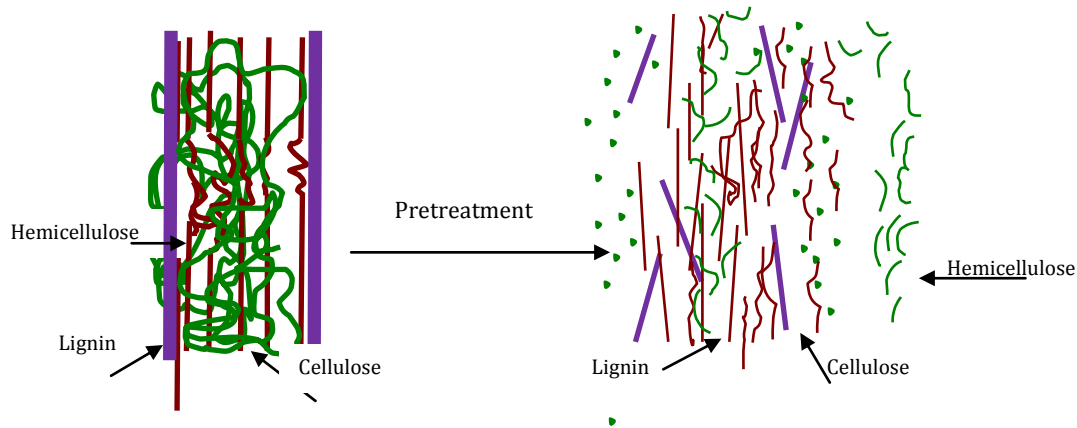


Fig 1 Changes of physical structure during pretreatment of biomass

Processing of lignocelluloses to bio-ethanol consists of four major unit operations: (1) pretreatment, (2) hydrolysis, (3) fermentation, and (4) product separation/distillation. The flowchart for conversion of lignocellulosic biomass and starch to ethanol is shown in Fig 2.

Hydrolysis of lignocelluloses followed by fermentation is complicated than fermentation of sugar. In hydrolysis the cellulosic part of the biomass is converted to sugars, and fermentation converts these sugars to bio-ethanol. As stated earlier, to increase the yield of hydrolysis, a pretreatment step is needed that softens the biomass and breaks down cell structures to a large extent. Acid hydrolysis and enzymatic hydrolysis are the common hydrolysis process.

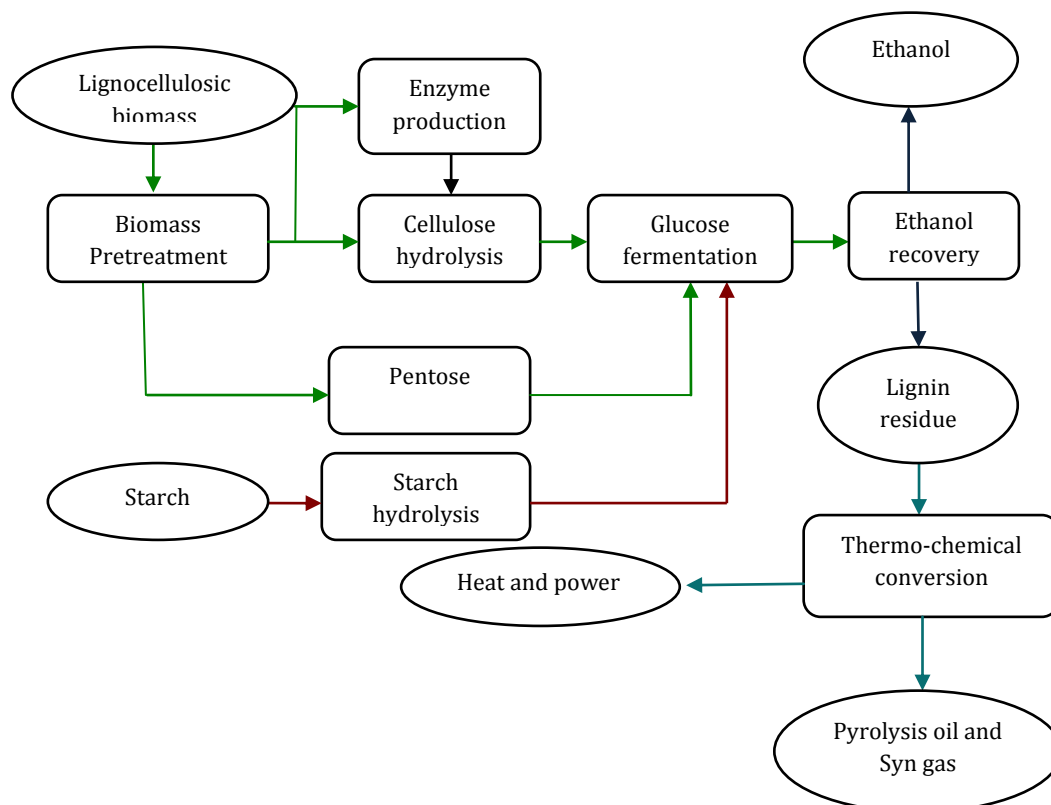


Fig 2 Conversion of lignocellulosic biomass and starch to Bio-ethanol

Acid hydrolysis is one of the oldest and most applied technologies for converting lignocelluloses into fermentable sugars. The hydrolysate obtained is used for bio-ethanol fermentation by microorganisms such as yeast. Lignocelluloses hydrolysate contains glucose, and also various monosaccharides, such as xylose, mannose, galactose, and arabinose, and oligosaccharides. Microorganisms should be required to efficiently ferment these sugars for the successful industrial production of bio-ethanol. The overall chemistry of fermentation is to convert glucose sugar ($C_6H_{12}O_6$) to alcohol (C_2H_5OH) and carbon dioxide gas (CO_2).

4.8.4.2. THERMO-CHEMICAL PRODUCTION OF ETHANOL

Two ethanol production processes employ thermo-chemical reactions. Lignocellulosic biomass materials are first thermo-chemically gasified and the synthesis gas (a mixture of hydrogen and carbon monoxide) bubbled through specially designed fermenters in a hybrid thermo-chemical and biological system. A micro-organism that is capable of converting the synthesis gas is introduced into the fermenters under specific process conditions to cause fermentation to bio-ethanol. There is another thermo-chemical ethanol production process, which does not use any microorganisms. In this process, biomass materials are first thermo-chemically gasified and the synthesis gas passed through a reactor containing catalysts, which cause the gas to be converted into ethanol.

4.8.5. USES OF BIO-ETHANOL

Bio-ethanol could be used as a pure fuel or as a mixture of fuel with fossil fuels without affecting the performance of the engine. Blended fuel could be used in conventional engine without modifications. The most common blend of bio-ethanol with petrol is gasohol (E10).

Gasohol is prepared by blending bio-ethanol (10%) and gasoline i.e. petrol (90%). E10 is burnt in internal combustion engines (ICEs). In Brazil, ethanol is used as clean or as gasohol. In the European Union, according to EN 228 standard, bio-ethanol could be used as 5% blend with petrol. It is found that bio-ethanol is an oxygenated fuel that contains about 35% of oxygen and thereby reduces particulate and nitrogen oxides (NO_x) emissions from combustion. The reduction in fossil fuel consumption and hence greenhouse gas (GHG) emissions are achieved using bio-ethanol as a fuel.

PROBABLE QUESTIONS

1. What are the major reasons of going for alternative fuels like bio-diesel and bio-ethanol?
2. Discuss the common feedstock used for production of (a) biodiesel and (b) bio-ethanol. Do you see any regional variations of suitability of feedstock for production of these alternative fuels?
3. With the help of neat sketch discuss the transesterification process used for biodiesel production.
4. What are major factors which influence the conversion process of oil into biodiesel?
5. Listing the major fuel properties, discuss the quality aspects of biodiesel. What is the significance of fatty acid profile of parent oil used for biodiesel production?
6. Explain the major consideration of using biodiesel in IC engine.
7. How do the bio-ethanol production processes from (a) sugar, (b) starch and (c) lingo-cellulose differ?
8. What is thermo-chemical conversion process of bio-ethanol?
9. Do you think India has any bio-fuel policy? Discuss.
10. What is the current status of the use of bio-fuel (bio-ethanol and bio-diesel) in national and international context?

DRE 103: BIOMASS ENERGY

UNIT-5: CHEMICAL CONVERSION OF BIOMASS FOR ENERGY PRODUCTION

UNIT STRUCTURE

5.1. CHEMICAL CONVERSION PROCESSES

5.1.1. BASIC PROCESSES FOR WOOD ENERGY CONVERSION

5.2 HYDROLYSIS AND HYDROGENATION

5.2.1. PRETREATMENT OF LIGNOCELLULOSIC BIOMASS FOR EFFICIENT

HYDROLYSIS AND BIOFUEL PRODUCTION

5.2.1.1 ACID HYDROLYSIS OF LIGNOCELLULOSIC BIOMASS

5.2.1.2. ALKALINE HYDROLYSIS.

5.2.2. HYDROGENATION

5.2.2.1 CATALYSTS

5.2.2.2. HYDROGENATION-DERIVED RENEWABLE DIESEL

5.2.2.3. HYDROGENATION ON BIOMASS TO LIQUID FUEL PRODUCTION

SUGGESTED READINGS

Objectives: This unit will give you an idea of the technological aspects and their present or developing applications of fuel produced by chemical conversion of biomass.

5.1. CHEMICAL CONVERSION PROCESSES

There are a number of technological options available to make use of a wide variety of biomass types as a renewable energy source. Conversion technologies may release the energy directly, in the form of heat or electricity, or may convert it to another form, such as liquid biofuel or combustible biogas. While for some classes of biomass resource there may be a number of usage options, for others there may only one appropriate technology. A range of chemical processes may be used to convert biomass into other forms, such as to produce a fuel that is more conveniently used, transported or stored, or to exploit some property of the process itself. Other chemical processes are converting straight and waste vegetable oils into biodiesel by transesterification.

5.1.1. BASIC PROCESSES FOR WOOD ENERGY CONVERSION

The available energy in wood energy resources is always presented in the form of chemical energy imposing reactions for its release and, consequently, the performance of some actions of interest such as cooking or steam generation. Besides, there are a lot of situations where biomass conversion is required. Biomass, which is basically a solid fuel, must be converted into another more homogeneous or more suitable fuel for its end use form of energy such as, a gaseous or liquid fuel for the generation of mechanical energy in internal combustion engines. In general, it can be said that biomass energy use is the inverse photosynthesis, for it tries to recovery the solar energy stored by the vegetable by consuming atmospheric oxygen and restoring carbon dioxide into the air.

This way, the employment of several technologies based on some conversion processes is justified. The processes of biomass energy conversion can be classified in three groups: physical, thermo-chemical and biological processes. Figure 5.1 shows a scheme of these processes indicating the main reagents and products that may be intermediate fuels or energy for end use. Densification, size reduction and the attainment of vegetable oils through pressing, typically when the original chemical composition of the raw material is not affected, are considered as physical processes. The thermo-chemical processes are characterized by high temperatures and include direct combustion, gasification, pyrolysis, and liquefaction, which are considered to be the most common for wood energy systems, above all, because of the wood low content of moisture. Among biological conversion processes, alcoholic fermentation and anaerobic digestion are the most used ones and they usually take place whenever there is high-moistured biomass, such as animal manure, and temperatures close to the ambient ones. They are not of much interest for the conversion of wood energy resources.

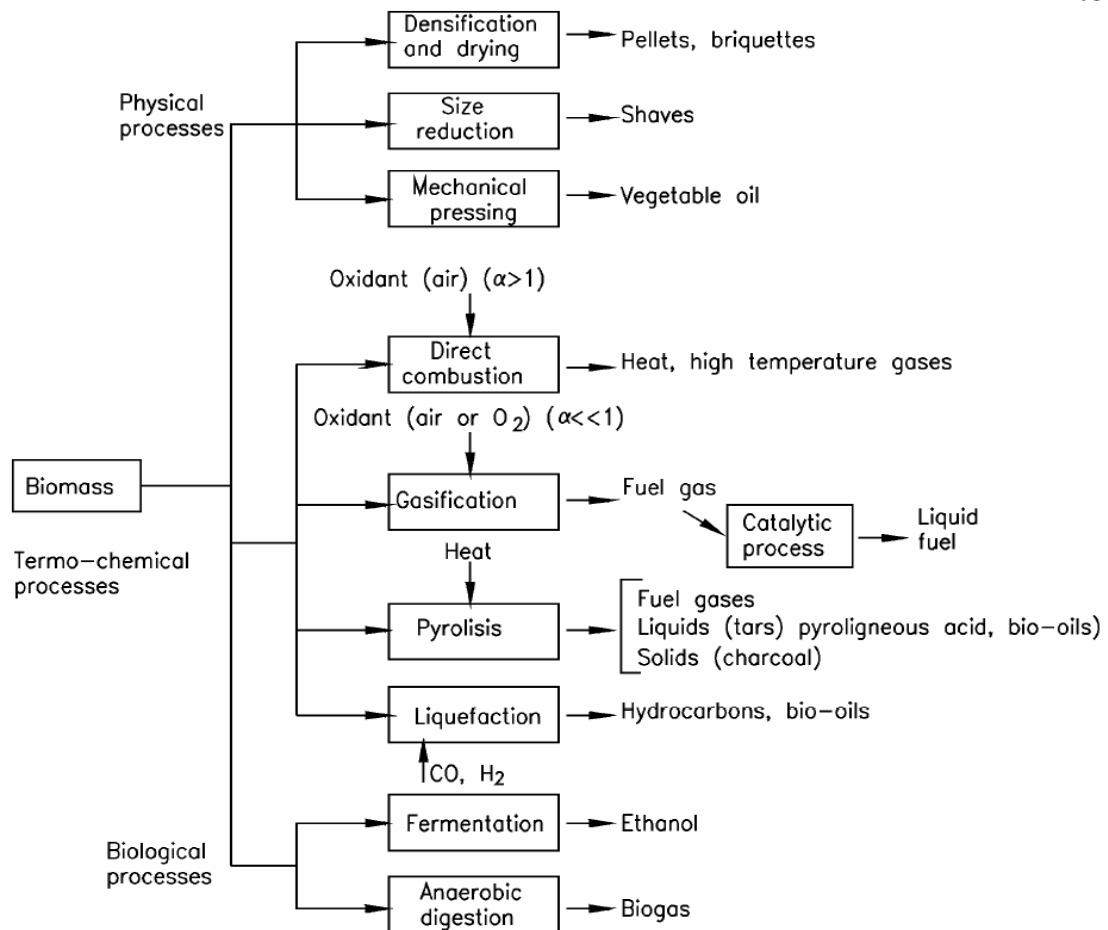


Figure 5.1: Biomass energy conversion processes

Converting Wood into Liquid Oil

Wood can also be made into a type of liquid oil, also called bio-oil, by heating it quickly to a high temperature in the absence of oxygen. This process is called fast pyrolysis. In addition to producing liquid oil, this process produces char and a combustible syngas.

Bio-oil can be burned in boilers to heat buildings or in generators to produce electricity. Since the bio-oil contains a much higher amount of energy per unit volume than wood, it is easier and cheaper to transport than wood. The pyrolysis syngas, as mentioned earlier, can be used much like natural gas. The char can be processed into briquettes for grilling and can also be used to purify metals and as an additive to fertilizer.

Converting Wood into Transportation Fuels

Wood can also be used to produce transportation fuels, such as ethanol, methanol, or biodiesel. Ethanol is produced through a process called fermentation in which wood is exposed to microorganisms. As these microorganisms decompose the wood, enzymes are

produced. These enzymes trigger a chemical reaction that exposes and breaks down the sugars in the wood. Certain microbes can then be added to the sugar solutions to convert them into ethanol, a colorless alcohol, and other byproducts. Once processed, ethanol can be used in combination with gasoline to make E-10 or E-85 to power vehicles equipped to burn it. E-10 contains 90 percent gasoline and 10 percent ethanol and can be used in most modern vehicles; E-85 contains 15 percent gasoline and 85 percent ethanol and can be used in engines modified to run on higher concentrations of ethanol, such as flexible-fuel vehicles. Research is progressing quickly to make this process feasible on a large scale.

Another liquid, methanol, can be produced from woody biomass. When woody biomass is gasified, the resulting gas can be converted to a liquid. This is one method of producing methanol. Methanol can be used to fuel vehicles or to produce other chemical products. Currently, most methanol is produced using natural gas.

Additionally, biodiesel is a liquid fuel that can be used to power machinery and vehicles. In a process called alcoholysis, oils extracted from wood are combined with alcohol and a catalyst to produce a renewable diesel fuel. Thanks to relatively new technological breakthroughs, woody biomass can provide the substances needed to manufacture renewable diesel fuels on a larger scale.

Converting waste biomass to chemicals

Waste biomass includes municipal solid waste (MSW), municipal sewage sludge (SS), industrial

biosludge, manure, and agricultural residues. When treated with lime, biomass is highly digestible by a mixed culture of acid-forming microorganisms. Lime treatment doubles the ruminant digestibility of agricultural residues; thus, it may be used to upgrade their feed value. Alternatively, lime-treated biomass can be fed to an industrial-scale mixed-acid fermentor where acetic, propionic, and butyric acids are produced. To control the pH, these acids are neutralized with calcium carbonate. The resulting calcium salts may be thermally converted to ketones - such as acetone, methyl ethyl ketone, and diethyl ketone - which are useful industrial solvents. Further, these ketones may be hydrogenated to alcohols – such as propanol, butanol, and pentanol - which may be used as industrial solvents or motor fuel. Alternatively, the calcium salts may be acidified to recover the acid (Figure-2).

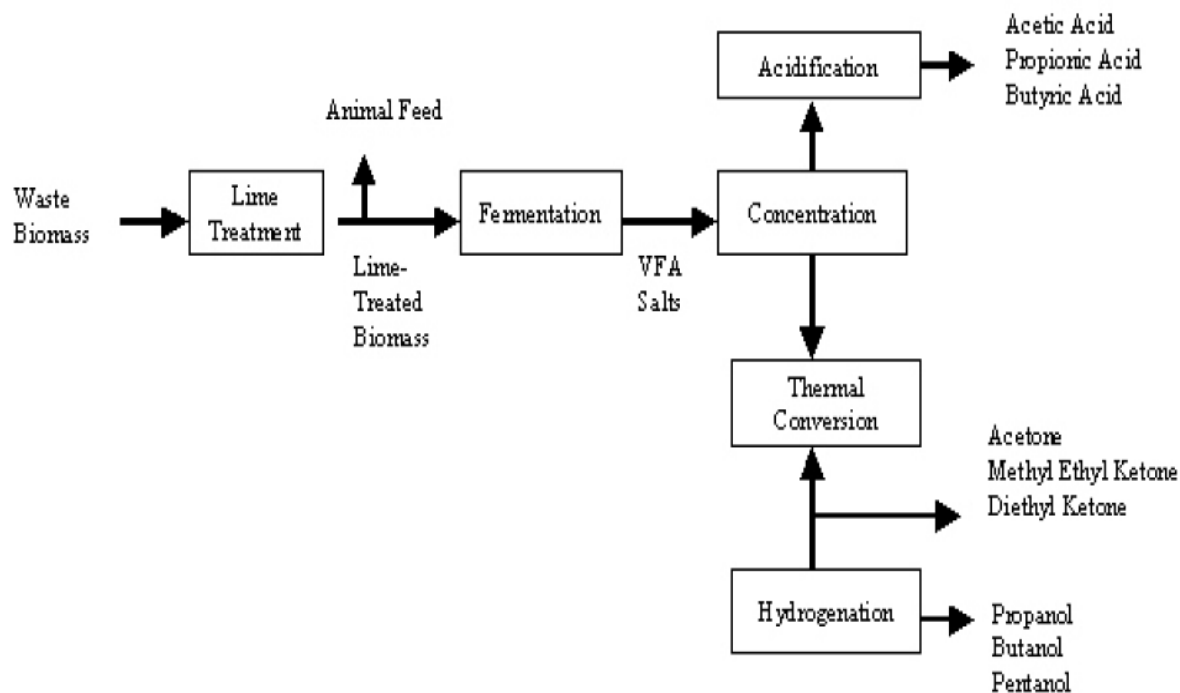


Figure 5.2: Process schematic for waste conversion to energy chemicals.

5.2 HYDROLYSIS AND HYDROGENATION

Hydrolysis is a chemical process in which a water molecule is added to a substance resulting in the split of that substance into two parts. One fragment of the target molecule (or parent molecule) gains a hydrogen ion (H^+) from the split water molecule. The other portion of the target molecule collects the hydroxyl group (OH^-) of the split water molecule. In effect an acid and a base are formed. The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water spontaneously ionizes into hydroxyl anions and hydrogen cations. The salt, too, dissociates into its constituent anions and cations. For example, sodium acetate dissociates in water into sodium and acetate ions. Sodium ions react very little with the hydroxyl ions whereas the acetate ions combine with hydrogen ions to produce acetic acid. In this case the net result is a relative excess of hydroxyl ions, causing a basic solution. However, under normal conditions, only a few reactions between water and organic compounds occur. In general, strong acids or strong bases must be added to catalyse hydrolysis.

Acid–base-catalysed hydrolyses are very common; one example is the hydrolysis of amides or esters. Their hydrolysis occurs when the nucleophile (a nucleus-seeking agent, e.g., water or hydroxyl ion) attacks the carbon of the carbonyl group of the ester or amide. In an aqueous

base, hydroxyl ions are better nucleophiles than polar molecules such as water. In acids, the carbonyl group becomes protonated, and this leads to a much easier nucleophilic attack. The products for both hydrolyses are compounds with carboxylic acid groups.

Hydrolysis of polysaccharides

Sucrose. The glycoside bond is represented by the central oxygen atom, which holds the two monosaccharide units together. Monosaccharides can be linked together by glycosidic bonds, which can be cleaved by hydrolysis. Two, three, several or many monosaccharides thus linked form disaccharides, trisaccharides, oligosaccharides or polysaccharides, respectively. Enzymes that hydrolyse glycosidic bonds are called "glycoside hydrolases" or "glycosidases". The best-known disaccharide is sucrose (table sugar). Hydrolysis of sucrose yields glucose and fructose. Invertase is a sucrase used industrially for the hydrolysis of sucrose to so-called invert sugar. Lactase is essential for digestive hydrolysis of lactose in milk. Deficiency of lactase in humans causes lactose intolerance. The hydrolysis of polysaccharides to soluble sugars is called "saccharification". Malt made from barley is used as a source of β -amylase to break down starch into the disaccharide maltose, which can be used by yeast to produce beer. Other amylase enzymes may convert starch to glucose or to oligosaccharides. Cellulose is converted to glucose or the disaccharide cellobiose by cellulases. Animals such as cows (ruminants) are able to digest cellulose because of symbiotic bacteria that produce cellulases.

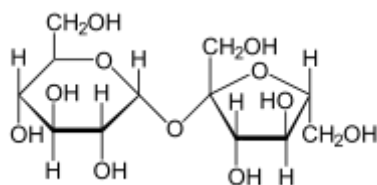


Figure 5.3: Sucrose structure

Sucrose-the glycoside bond is represented by the central oxygen atom, which holds the two monosaccharide units together.

5.2.1. PRETREATMENT OF LIGNOCELLULOSIC BIOMASS FOR EFFICIENT HYDROLYSIS AND BIOFUEL PRODUCTION

Biofuels produced from various lignocellulosic materials, such as wood, agricultural, or forest residues, have the potential to be a valuable substitute for, or complement to, gasoline. Many physicochemical structural and compositional factors hinder the hydrolysis of cellulose present in biomass to sugars and other organic compounds that can later be converted to fuels. It has been reported that cellulosic ethanol and ethanol produced from other biomass resources have the potential to cut greenhouse gas emissions by 86%. The presence of lignin

in lignocelluloses leads to a protective barrier that prevents plant cell destruction by fungi and bacteria for conversion to fuel. For the conversion of biomass to fuel, the cellulose and hemicellulose must be broken down into their corresponding monomers (sugars), so that microorganisms can utilize them. Three major hydrolysis processes are typically used to produce a variety of sugars suitable for ethanol production: dilute acid, concentrated acid, and enzymatic hydrolysis. Hemicellulose can be readily hydrolyzed by dilute acids under moderate conditions, but much more extreme conditions are needed for cellulose hydrolysis. In the dilute-acid process, the reaction is carried out at high temperature and pressure, and because of low yields of glucose from cellulose in the hydrolysis step, the ethanol yield is low. The use of concentrated acid in the hydrolysis process can yield higher quantities of ethanol because of the approximately 100% conversion to glucose from cellulose. The dilute-acid hydrolysis process uses high temperatures (160-230 °C) and pressures (10 atm). The acid concentration in the dilute-acid hydrolysis process is in the range of 2-5%. The acid concentration used in the concentrated-acid hydrolysis process is in the range of 10-30%. Lower operating temperatures (<50 °C) and atmospheric pressures are required during the concentrated-acid hydrolysis process. The concentrated-acid hydrolysis involves longer retention times and results in higher ethanol yields than the dilute-acid hydrolysis process. Enzymes produced by a variety of microorganisms are also capable of breaking down lignocellulosic materials to sugars but require longer retention times. Enzymatic hydrolysis is the most common method of producing ethanol from lignocellulosic biomasses.

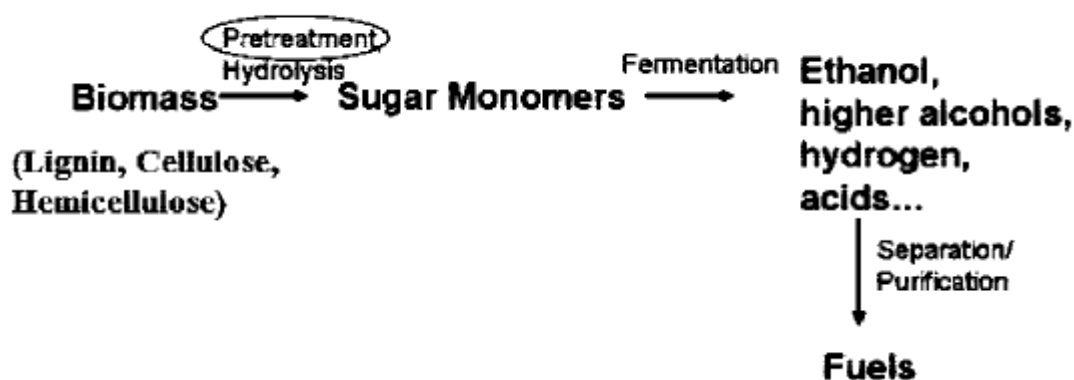


Figure 5.4: Schematic of conversion lignocellulosic biomass to fuel

The digestibility of cellulose present in lignocellulosic biomass is hindered by many physicochemical, structural, and compositional factors. In the conversion of lignocellulosic biomass to fuel, the biomass needs to be treated so that the cellulose in the plant fibers is exposed. Pretreatment uses various techniques, including ammonia fiber explosion, chemical

treatment, biological treatment, and steam explosion, to alter the structure of cellulosic biomass to make cellulose more accessible. Then, acids or enzymes can be used to break down the cellulose into its constituent sugars. Enzyme hydrolysis is widely used to break down cellulose into its constituent sugars. A schematic for the conversion of biomass to fuel is shown in Figure 4. The conversion includes the hydrolysis of various components in the lignocellulosic materials to fermentable reducing sugars and the fermentation of the sugars to fuels such as ethanol and butanol. The pretreatment step is mainly required for efficient hydrolysis of cellulose to its constituent sugars. The hydrolysis is usually catalyzed by acids or cellulase enzymes, and the fermentation is carried out by yeasts or bacteria. The factors affecting the hydrolysis of cellulose include porosity (accessible surface area) of the biomass materials, cellulose fiber crystallinity, and content of both lignin and hemicellulose. The presence of lignin and hemicellulose makes the accessibility of cellulase enzymes and acids to cellulose more difficult, thus reducing the efficiency of the hydrolysis process. Pretreatment is required to alter the size and structure of the biomass, as well as its chemical composition, so that the hydrolysis of the carbohydrate fraction to monomeric sugars can be achieved rapidly and with greater yields. The hydrolysis process can be significantly improved by removal of lignin and hemicellulose, reduction of cellulose crystallinity, and increase of porosity through pretreatment processes.

5.2.1.1 ACID HYDROLYSIS OF LIGNOCELLULOSIC BIOMASS

Dilute Acid Hydrolysis

The dilute acid process is conducted under high temperature and pressure, and has a reaction time in the range of seconds or minutes, which facilitates continuous processing. As an example, using a dilute acid process with 1% sulfuric acid in a continuous flow reactor at a residence time of 0.22 minutes and a temperature of 510 K with pure cellulose provided a yield over 50% sugars. In this case, 1000 kg of dry wood would yield about 164 kg of pure ethanol. The combination of acid and high temperature and pressure dictate special reactor materials, which can make the reactor expensive. The first reaction converts the cellulosic materials to sugar and the second reaction converts the sugars to other chemicals. Unfortunately, the conditions that cause the first reaction to occur also are the right conditions for the second to occur. The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

Concentrated Acid Hydrolysis

Hydrolysis of cellulosic materials by concentrated sulfuric or hydrochloric acids is a relatively old process (table 5.1). The concentrated acid process uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This method generally uses concentrated sulfuric acid followed by a dilution with water to dissolve and hydrolyze or convert the substrate into sugar. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recovers the acid for recycling. The solid residue from the first stage is dewatered and soaked in a 30 to 40% concentration of sulfuric acid for 1 to 4 hours as a pre-cellulose hydrolysis step. The solution is again dewatered and dried, increasing the acid concentration to about 70%. After reacting in another vessel for 1 to 4 hours at low temperatures, the contents are separated to recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage hydrolysis. The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. Table 5 shows the yields of bioethanol by concentrated sulfuric acid hydrolysis from cornstalks. The acid and sugar are separated via ion exchange and then acid is re-concentrated via multiple effect evaporators. The low temperatures and pressures employed allow the use of relatively low cost materials such as fiberglass tanks and piping. The low temperatures and pressures also minimize the degradation of sugars. Unfortunately, it is a relatively slow process and cost effective acid recovery systems have been difficult to develop. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization forms large quantities of calcium sulfate, which requires disposal and creates additional expense.

Enzymatic Hydrolysis

Another basic method of hydrolysis is enzymatic hydrolysis. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. There are two technological developments: enzymatic and direct microbial conversion methods. The chemical pretreatment of the cellulosic biomass is necessary before enzymatic hydrolysis. The first application of enzymatic hydrolysis was used in separate hydrolysis and fermentation steps. Enzymatic hydrolysis is accomplished by cellulolytic enzymes. Different kinds of "cellulases" may be used to cleave the cellulose and hemicelluloses. A mixture of endoglucanases, exoglucanases, -glucosidases and cellobiohydrolases is commonly used (Ingram and Doran, 1995; Laymon et al., 1996).

Table 5.1: Yields of bioethanol by concentrated sulfuric acid hydrolysis from cornstalks (% dry weight)

<i>Amount of cornstalk (kg)</i>	1000
Cellulose content (kg)	430
Cellulose conversion and recovery efficiency	0.76
Ethanol stoichiometric yield	0.51
Glucose fermentation efficiency	0.75
Ethanol yield from glucose (kg)	130
<i>Amount of cornstalk (kg)</i>	1000
Hemicelluloses content (kg)	290
Hemicelluloses conversion and recovery efficiency	0.90
Ethanol stoichiometric yield	0.51
Xylose fermentation efficiency	0.50
Ethanol yield from xylose (kg)	66
Total ethanol yield from 1000 kg of cornstalks	196 kg (225.7 L = 59 gallons)

The endoglucanases randomly attack cellulose chains to produce polysaccharides of shorter length, whereas exoglucanases attach to the nonreducing ends of these shorter chains and remove cellobiose moieties, -glucosidases hydrolyze cellobiose and other oligosaccharides to glucose (Philippidis and Smith, 1995). For enzymes to work efficiently, they must obtain access to the molecules to be hydrolyzed. This requires some kind of pretreatment process to remove hemicelluloses and break down the crystalline structure of the cellulose or removal of the lignin to expose hemicelluloses and cellulose molecules.

5.2.1.2. ALKALINE HYDROLYSIS.

Some bases can be used for the pretreatment of lignocellulosic materials, and the effect of alkaline pretreatment depends on the lignin content of the materials. Alkali pretreatment processes utilize lower temperatures and pressures than other pretreatment technologies. Alkali pretreatment can be carried out at ambient conditions, but pretreatment times are on the order of hours or days rather than minutes or seconds. Compared with acid processes, alkaline processes cause less sugar degradation, and many of the caustic salts can be recovered and/or regenerated. Sodium, potassium, calcium, and ammonium hydroxides are suitable alkaline pretreatment agents. Of these four, sodium hydroxide has been studied the most. However, calcium hydroxide (slake lime) has been shown to be an effective pretreatment agent and is the least expensive per kilogram of hydroxide. It is possible to recover calcium from an aqueous reaction system as insoluble calcium carbonate by neutralizing it with inexpensive

carbon dioxide; the calcium hydroxide can subsequently be regenerated using established lime kiln technology.

The enzymatic hydrolysis of lime-treated biomass is affected by structural features resulting from the treatment. These are the extents of acetylation, lignification, and crystallization. Lime pretreatment removes amorphous substances (e.g., lignin and hemicellulose), which increases the crystallinity index. Alkaline pretreatment can play a significant role in exposing the cellulose to enzyme hydrolysis. Lignin removal increases enzyme effectiveness by eliminating nonproductive adsorption sites and by increasing access to cellulose and hemicellulose. Delignification highly depended on temperature and the presence of oxygen. Lignin and hemicellulose were selectively removed or solubilized, but cellulose was not affected by lime pretreatment at mild temperatures (25-55 °C).

Lime has been used to pretreat wheat straw (85 °C for 3 h), poplar wood (150 °C for 6 h with 14 atm of oxygen), switchgrass (100 °C for 2 h) and corn stover (100 °C for 13 h). Dilute NaOH treatment of lignocellulosic materials has been found to cause swelling, leading to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure. microwave-assisted alkali treatment is an efficient way to improve the enzymatic digestibility of switchgrass. Ammonia has also been used as a pretreatment to remove lignin.

The worldwide desire to reduce greenhouse gas emission will lead to an increased interest in renewable resources for energy production. Cellulosic biomass materials are among the candidates to be used as a renewable resource. Ethanol has very good characteristics to be used as a fuel either in a neat form or in a mixture with gasoline. Bioethanol is a domestically produced liquid fuel from cellulosic biomass resources. It is a high-octane fuel that can contribute substantially to the automotive fuel supply, Ethanol is a potentially clean-burning fuel that reduces smog and emissions of carbon monoxide. The use of gasohol (ethanol and gasoline mixture) as an alternative motor fuel has been steadily increasing around the world for a number of reasons. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide buildup. Ethanol, unlike gasoline, is an oxygenated fuel that contains 35% oxygen, which reduces particulate and NOx emissions from combustion.

5.2.2. HYDROGENATION

Hydrogenation is a chemical reaction between molecular hydrogen and an element or compound, ordinarily in the presence of a catalyst. The reaction may be one in which hydrogen simply adds to a double or triple bond connecting two atoms in the structure of the molecule or one in which the addition of hydrogen results in dissociation (breaking up) of the molecule (called hydrogenolysis, or destructive hydrogenation). Typical hydrogenation reactions include the reaction of hydrogen and nitrogen to form ammonia and the reaction of hydrogen and carbon monoxide to form methanol or hydrocarbons, depending on the choice of catalyst. Nearly all organic compounds containing multiple bonds connecting two atoms can react with hydrogen in the presence of a catalyst. The hydrogenation of organic compounds (through addition and hydrogenolysis) is a reaction of great industrial importance. The addition of hydrogen is used in the production of edible fats from liquid oils. In the petroleum industry, numerous processes involved in the manufacture of gasoline and petrochemical products are based on the destructive hydrogenation of hydrocarbons. In the late 20th century the production of liquid fuels by hydrogenation of coal has become an attractive alternative to the extraction of petroleum. The industrial importance of the hydrogenation process dates from 1897, when the French chemist Paul Sabatier discovered that the introduction of a trace of nickel as a catalyst facilitated the addition of hydrogen to molecules of carbon compounds.

The catalysts most commonly used for hydrogenation reactions are the metals nickel, platinum, and palladium and their oxides. For high-pressure hydrogenations, copper chromite and nickel supported on kieselguhr (loose or porous diatomite) are extensively used.

Hydrogenation is a chemical reaction of great importance to the petrochemical and fine chemical industries. In its most elementary sense, the term hydrogenation refers to the addition reaction of molecular hydrogen with an unsaturated carbon-carbon double bond as illustrated in figure 5.5.:

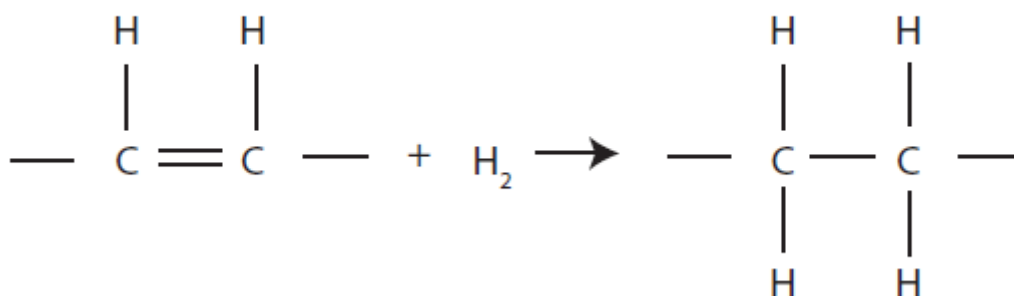


Figure 5.5: Typical hydrogen reaction

The first compound, called an alkene, is converted into the corresponding alkane. In addition to the example above, there are other ways in which molecular hydrogen can be reacted with other types of molecules. These include the incorporation of hydrogen accompanied by cleavage of the starting molecule as in hydrodesulfurization and reactions in which the starting molecule undergoes rearrangement such as isomerization.

Hydrogenation in Practical Use

For the petrochemical industry, many of the compounds found in crude oil are of little use since they contain multiple double bonds; they must be first converted to saturated compounds before use as commodities such as gasoline. In addition, countless other molecules are produced from petroleum; hydrogenation is most often the first step their production.

In the fine chemical and active pharmaceutical ingredient industries, the hydrogenation reaction is often an important step in producing the end product. The food industry uses hydrogenation to completely or partially saturate the unsaturated fatty acids in vegetable oils to convert them into solid or semi-solid fats (e.g. margarine). These latter compounds offer different cooking or taste characteristics that are more satisfactory for consumers. Hydrogenation will be a critical step in the upgrading of biocrude to usable, renewable biofuels. Biocrude has been hydrogenated to minimize its negative aspects. The instability of oil is reduced by reaction of the most unstable functional groups. Concurrently, the oxygenated component of the oil was also reduced, resulting in an improved energy density. Hydrotreated biocrude is also more miscible with refined petroleum products.

Vegetable oil Hydrogenation:

Hydrogenation is a process to add hydrogen atoms into double bonds of unsaturated fatty acids. As the result of hydrogenation, liquid oil becomes solid or semi-solid. A typical example of hydrogenation is in the process of margarine and shortening production. Vegetable oil is hydrogenated with gaseous H₂ in the presence of a metal catalyst (usually nickel catalyst). If the hydrogenation is completely performed, all the double bounds are converted to the saturated ones with the same carbon number. For example, complete hydrogenation of linoleic acid (18:2 !-6) generates stearic acid (18:0) (Figure 5.6).

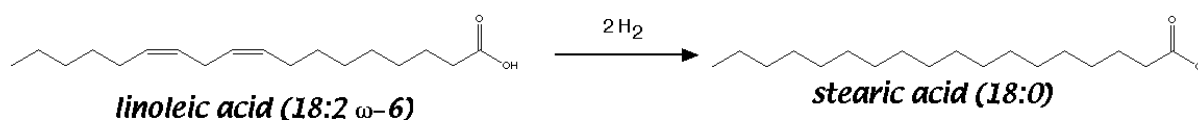
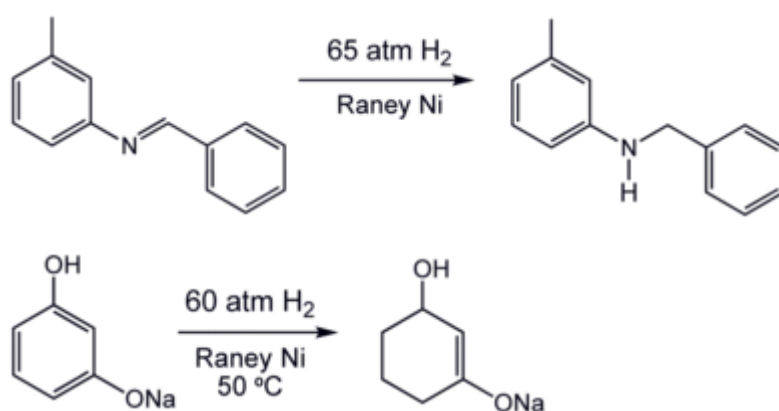


Figure: Complete hydrogenation of linoleic acid, giving stearic acid.

Vegetable oil is too soft for margarine or shortening because it is liquid. Saturated fat obtained by complete hydrogenation is too hard. Margarine requires something in the middle, i.e. not too hard but not too soft. Margarine and shortening makers “partially hydrogenate” their product. They only add hydrogen atoms until the oil is at the desired consistency. During the hydrogenation process, hydrogen atoms are inserted in no particular order. When they stop the incomplete hydrogenation process, unsaturated fatty acids are in varying stages of hydrogenation. Some molecules are mostly hydrogenated, while others are not. And the double bonds have often shifted to unnatural positions, resulting in the generation of trans fatty acids or trans fat, which is thought to increase risk of coronary heart disease.

5.2.2.1 CATALYSTS

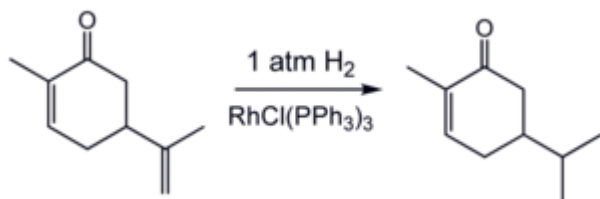
With rare exceptions, no reaction below 480 °C (750 K or 900 °F) occurs between H₂ and organic compounds in the absence of metal catalysts. The catalyst binds *both* the H₂ and the unsaturated substrate and facilitates their union. Platinum, palladium, rhodium, and ruthenium form highly active catalysts, which operate at lower temperatures and lower pressures of H₂. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and [Urushibara nickel](#)) have also been developed as economical alternatives, but they are often slower or require higher temperatures. The trade-off is activity (speed of reaction) vs. cost of the catalyst and cost of the apparatus required for use of high pressures. Notice that the Raney-nickel catalysed hydrogenations require high pressures:



Two broad families of catalysts are known - homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts dissolve in the solvent that contains the unsaturated substrate. Heterogeneous catalysts are solids that are suspended in the same solvent with the substrate or are treated with gaseous substrate.

Homogeneous catalysts

Illustrative homogeneous catalysts include the rhodium-based compound known as Wilkinson's catalyst and the iridium-based Crabtree's catalyst. An example is the hydrogenation of [carvone](#):^[6]



Hydrogenation is sensitive to steric hindrance explaining the selectivity for reaction with the [exocyclic](#) double bond but not the internal double bond.

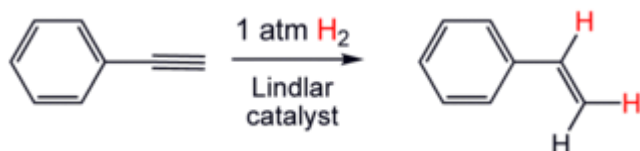
The activity and selectivity of homogeneous catalysts is adjusted by changing the ligands. For [prochiral](#) substrates, the selectivity of the catalyst can be adjusted such that one enantiomeric product is favored. Asymmetric hydrogenation is also possible via heterogeneous catalysis on a metal that is modified by a chiral ligand.

Heterogeneous catalysts

Heterogeneous catalysts for hydrogenation are more common industrially. As in homogeneous catalysts, the activity is adjusted through changes in the environment around the metal, i.e. the coordination sphere. Different faces of a crystalline heterogeneous catalyst display distinct activities, for example. Similarly, heterogeneous catalysts are affected by their supports, i.e. the material upon which the heterogeneous catalyst is bound.

In many cases, highly empirical modifications involve selective "poisons". Thus, a carefully chosen catalyst can be used to hydrogenate some functional groups without affecting others, such as the hydrogenation of alkenes without touching aromatic rings, or the selective hydrogenation of alkynes to alkenes using Lindlar's catalyst. For example, when the catalyst palladium is placed on barium sulfate and then treated with [quinoline](#), the resulting catalyst

reduces alkynes only as far as alkenes. The Lindlar catalyst has been applied to the conversion of [phenylacetylene](#) to styrene.^[8]



Asymmetric hydrogenation is also possible via heterogeneous catalysis on a metal that is modified by a chiral ligand.

5.2.2.2. HYDROGENATION-DERIVED RENEWABLE DIESEL

Hydrogenation-derived renewable diesel (HDRD), also known as green diesel or second-generation biodiesel, is the product of fats or vegetable oils—alone or blended with petroleum—refined by a hydrotreating process. HDRD meets the petroleum diesel ASTM specification. This allows it to be legally used in existing diesel infrastructure and vehicles. HDRD derived from domestic biological materials is an alternative fuel under the Energy Policy Act of 1992. HDRD can be produced from soybean, palm, canola, or rapeseed oil; animal tallow; vegetable oil waste or brown trap grease; and other fats and vegetable oils. Producing HDRD involves hydrogenating triglycerides to remove metals and compounds with oxygen and nitrogen using existing refinery infrastructure. Dedicated hydrotreating facilities that do not use conventional petroleum can also produce HDRD. Fuel producers are designing HDRD to substitute for or blend in any proportion with petroleum-based diesel without modifying vehicle engines or fueling infrastructure. To be used in diesel engines, HDRD must meet the same ASTM standards as conventional diesel. HDRD is compatible with existing fuel distribution systems. Blended HDRD can be distributed through modern infrastructure and transported through existing pipelines to dispense at fueling stations.

HDRD fuels can be an alternative to conventional transportation fuels. The benefits of HDRD fuels include:

- **Increased Energy Security**—HDRD can be produced domestically from a variety of feedstocks. **Fewer Emissions**—Carbon dioxide captured by growing feedstocks reduces overall greenhouse gas emissions by balancing carbon dioxide released from burning HDRD. Blends of HDRD can reduce carbon monoxide and hydrocarbons. In addition, HDRD's ultra-low sulfur content should enable using advanced emission control devices.

- More Flexibility—HDRD that meets quality standards can fuel modern diesel vehicles. This fuel is compatible with existing diesel distribution infrastructure (not requiring new pipelines, storage tanks, or retail station pumps), can be produced using existing oil refinery capacity, and does not require extensive new production facilities.
- Higher Performance—HDRD's high combustion quality results in similar or better vehicle performance compared to conventional diesel.

5.2.2.3. HYDROGENATION ON BIOMASS TO LIQUID FUEL PRODUCTION

Theoretically, it has been reported that the products of biomass conversion can be divided into five main groups i.e. biodiesel, alcohols (ethanol/methanol), biogas, biomass-to-liquid (BTL) and hydrogen [2]. Among these biomass conversion products, BTL is one of the promising alternative fuels to replace fossil fuels in transportation section. The advantage of BTL is its identical properties to conventional liquid fuels (e.g. gasoline); hence BTL can be entirely replaced the conventional liquid fuels without any engine modification required. Furthermore, this technology can convert any type of biomass to liquid fuel with almost the same properties.

Liquid fuels production based on biomass consists of four steps including hydrolysis, dehydration, aldol-condensation and hydrogenation. In the first reaction step, saccharides of biomass are converted to glucose and fructose molecules by using hydrolysis process. Then, glucose and fructose molecules are converted to hydroxyl-methyl furfural (HMF) and furfural over acid catalyst by dehydration process. Finally, these intermediates are converted to liquid alkanes (C₉-C₁₅) by aldol-condensation and hydrogenation over bifunctional catalyst. This liquid alkane is an efficient renewable fuel for transportation and industrial applications. The optimum temperatures for aldol-condensation of furfural with acetone and for condensation of HMF with acetone are 80 °C and 53 °C respectively. The product selectivity can be controlled by the molar ratio of reactants. When the molar ratio of furfural:acetone increases from 1:9 to 1:1, the selectivity for the formation of dimer species increases by 31% and this selectivity increases further by 12% when the ratio increases from 1:1 to 2:1. The production of liquid hydrocarbon with the number of carbon atoms ranging from C₇ to C₁₅ from biomass-derived carbohydrates by acid-catalyzed dehydration was followed by aldol condensation over solid base catalysts to form large organic compounds. These molecules were then converted into alkanes by dehydration/hydrogenation (APD/H) over bifunctional catalysts that contained acid and metal sites.

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DRE 103: BIOMASS ENERGY

UNIT-6: SYNTHESIS BIOFUEL

UNIT STRUCTURE

6.1 MODERN BIOFUEL SYNTHESIS

6.1.1. BIOFUELS TYPES AND GENERATIONS

6.1.2. PRODUCTION OF SYNTHESIS BIODIESEL VIA FISCHER-TROPSCH SYNTHESIS

6.1.3. DIESEL FUEL FROM VEGETABLE OIL BY DECARBOXYLATION

6.1.4. CATALYTIC HYDRODEOXYGENATION (HDO) OF VEGETABLE OILS TO

RENEWABLE ALKANE-TYPE BIOFUELS

6.1.5: PLATFORM BIOFUEL

6.2. BIO-REFINERY

REFERENCES

Objectives: This unit will give you an overview of bio-fuels of the first and second generation and their related feedstock with recently developed conversion processes. The unit is also prepared with the concept of bio-refineries and the valorization of different bio-based

6.1 MODERN BIOFUEL SYNTHESIS

Advanced technologies are now under development to convert biomass into various forms of secondary energy including electricity, gaseous and liquid biofuels, and even hydrogen. The purpose of biomass conversion is to provide fuels with clearly defined fuel characteristics that meet given fuel quality standards. To ensure that these fuel quality standards are met and these biomass based fuels can be used with a high efficiency in conversion devices (like engines, turbines) upgrading is needed. In general, there are various options to produce alternative transportation fuels based on biomass. Biogenous energy sources can be converted by means of highly different supply chains into gaseous and liquid biofuels that can be used for transportation purposes. This treatment leads to an upgrading of energy sources in terms of one or more properties named as follows:

- * Energy density,
- * Handling,

- * Storage and transport,
- * Environmental compatibility,
- * Utilizing of by-products and residues.

Depending on the conversion of biomass in principal three main pathways come into consideration (i) the thermo-chemical pathway, (ii) the physical-chemical conversion pathway, (iii) the bio-chemical conversion pathway. Those processes provide biofuels in the form of solids (mainly charcoal), liquids (mainly biodiesel and alcohols), or gases (mainly mixtures with methane or carbon monoxide), which can be used for a wide range of applications, including transport and high-temperature industrial processes.

6.1.1. BIOFUELS TYPES AND GENERATIONS

Biofuel is any fuel that is derived from biomass, recently living organisms or their metabolic byproducts, such as manure from cows. It is a renewable energy source, unlike other natural resources such as petroleum, coal and nuclear fuels. Biofuels can be grouped in 'generations', according to the type of technology they rely on and the biomass feedstocks they convert into fuel. The principal biofuels of the first and second generations, including respective feedstocks and production technologies are presented in Table 6.1.

Table 6.1. First and second generation biofuels and their related feedstock and conversion processes

	<i>Generic name</i>	<i>Chemical composition</i>	<i>Feedstocks</i>	<i>Technology</i>
<i>1st generation</i>	Biodiesel	Methyl or ethyl esters of fatty acids (FAME); Hydrocarbons (products of cracking)	Oil crops (e.g. rape, palm, soya, jatropha, canola, colza etc.), waste oil (e.g. frying oil), and animal fats	Cold/hot pressing, extraction & transesterification (Homogeneous, heterogeneous, and bio-catalysis); Hydrogenation (hydro-cracking)
	Bioethanol	Ethanol	Sugars (glycosides) and starch from bio-waste and woody biomass (sugarcane, sugar beet, cereals)	Hydrolysis & fermentation
	Vegetable oil	Straight Vegetable Oil (SVO) – triglycerides of fatty acids	Oil crops (e.g. rape, palm, soya, jatropha, canola, colza etc.)	Cold/hot pressing, extraction, and purification
	Biogas	Methan, hydrogen and light hydrocarbons	Biomass (humid)	Anaerobic digestion
<i>2nd generation</i>	Cellulosic bioethanol	Ethanol	Lignin, cellulose and hemicellulose from bio-waste	Hydrolysis & fermentation
	Bio-SNG	Synthetic (substitute) natural gas – methane	Lignocellulosic biomass	Pyrolysis, gasification, methanation
	Synthetic biofuels	Hydrocarbons (BTL/FT), methanol (biomethanol), mixed heavy alcohols, dimethyl ether (bio-DME)	Lignocellulosic biomass	Pyrolysis, gasification, synthesis
	Bio-hydrogen	Hydrogen	Lignocellulosic biomass	Pyrolysis, gasification, water gas shift reaction (WGSR)

First Generation Biofuels

First (1st)-generation biofuels are biofuels which are produced from food crops (sugar or oil crops) and other food based feedstock (e.g. food waste). These biofuels are on the market in considerable amounts today and their production technologies are well established. The most important biofuels of the 1st-generation are bioethanol, biodiesel, and biogas.

Bioethanol is produced by fermenting sugars from starch and sugar biomass (e.g. cereal crops such as corn or maize and sugarcane). It can be used in pure form in specially adapted vehicles or blended with gasoline in any proportion up to 10% (US), provided that fuel specifications are met.

Ethyl-tertiary-butyl-ether (ETBE) is synthesized from bioethanol and isobutylene. It can be blended with gasoline in any proportion up to 15%. It is currently the biggest biofuel contributor in Europe.

Biodiesel (FAME) is made from vegetable oils of rapeseed, soya, palm fruits or other oil crops via the reaction of triglycerides with methanol (transesterification process). It can be

used in pure form in specially adapted vehicles or be blended with automotive diesel in any proportion up to 5% (up to 30% for captive fleets).

Biogas is obtained by anaerobic treatment of manure and other humid biomass materials (e.g. in landfills), including food waste, and then upgraded to biomethane that can be feed-in into the natural gas grid and e.g. used in natural gas vehicles. There is a discussion whether to refer to biogas as to the first or the second generation, because it can be produced from a variety of biomass and not only from food crops. However, in view of the maturity and wide use of the technology of its production, in this paper biogas is considered within the first generation, which is also an opinion shared by many experts in the field. For these types of fuels, only easily extractible parts of plants are used, such as starch-rich corn kernels, grains or the sugar in canes or oilseeds are used. Remaining by-products, such as press cake from vegetable oil production, glycerine from biodiesel production or DDGS (Dried Distillers Grains with Solubles) from bioethanol based on starch, are typically used for fodder or chemical purposes. Integrated concepts that are in R&D stage include the energetic use of by-products (e.g. for process energy provision).

The production of 1st-generation biofuels is commercial today, with almost 50 billion litres (approx. 39.5 million t) of bioethanol and 5.4 million t of biodiesel produced worldwide in 2006. The production capacity of ETBE plants in Europe was approx. 2.3 million t in 2005.

Second Generation Biofuels

Different from the 1st generation the so called second (2nd) or 'next' generation of future biofuels can be produced from wider range of feedstocks, which are represented mainly by non-food crops. For example, the whole plant biomass can be used or waste streams that are rich in lignin and cellulose, such as wheat straw, grass, or wood. In order to breakdown this biomass, two main conversion pathways come into consideration: 1) hydrolysis (can be done via bio-chemical processes using special enzymes) of ligno-cellulose into sugars, which can then be fermented into alcohol - this technology is best known as 'cellulosic bioethanol' and is still in development; 2) thermo-chemical processes (use of high temperatures to pyrolyse and gasify biomass) of lignocelluloses to a raw gas which is then treated and conditioned into synthesis gas (syngas), consisting mainly of carbon monoxide and hydrogen. This gas can further be processed into different types of liquid and gaseous fuels via different fuel syntheses. Fuels from this route are then called 'synthetic biofuels'. Most promising liquid synthetic biofuels, also called BtL: biomass-to-liquids, are biomethanol and Fischer-Tropsch fuels. Gaseous synthetic biofuels are e.g. dimethylether (DME) and Bio-SNG, which is also a form of biomethane and can be similarly used as natural gas substitute like biogas. Alternatively, the cleaned and conditioned product gas can be converted into hydrogen.

Third Generation Biofuels

Third generation biofuels rely on biotechnological interventions in the feedstocks themselves. Plants are engineered in such a way that the structural building blocks of their cells (lignin, cellulose, hemicellulose), can be managed according to a specific task they are required to perform. For example, plant scientists are working on developing trees that grow normally, but that can be triggered to change the strength of the cell walls so that breaking them down to release sugars is easier. In third generation biofuels, a synergy between this kind of interventions and processing steps is then created: plants with special properties are broken down by functionally engineered enzymes. Notably, this latter generation of biofuels is only gradually being explored.

Ref; Background Paper on Biofuel Production Technologies WORKING DOCUMENT November 2007. prepared by Sergey Zinoviev, Sivasamy Arumugam, and Stanislav Miertus. International Centre for Science and High Technology United Nations Industrial Development Organization.

6.1.2. PRODUCTION OF SYNTHESIS BIODIESEL VIA FISCHER-TROPSCH SYNTHESIS

Over a catalyst of normally iron or cobalt, the synthesis gas consisting of H₂ and CO undergoes a chemical reaction where it is transformed into liquid hydrocarbons. The synthetic biodiesel is produced, in addition to naphtha, gasoline products and wax.

History

The history of the Fischer-Tropsch synthesis begins in the start of the 20th century, when in 1902 the French inventors Sabatier and Senderens discovered that CO could be hydrogenated over Co, Fe and Ni to methane. And in 1925 professor Franz Fischer, founding director of the Kaiser-Wilhelm Institute of Coal Research in Mülheim an der Ruhr, and his head of department, Dr. Hans Tropsch reported synthesis of hydrocarbon liquids and solid paraffins on Co-Fe catalyst under mild conditions of 250- 300 °C.

In 1932 the first small pilot plant was constructed in Mülheim by Prof. Franz Fischer and his coworkers. The development of synthetic fuel has always been closely connected to political issues. Germany became a natural promoter of the production due to its lack of oil reserves and its large coal reserves. During World War II, the British and Americans emplaced an oil embargo on Germany, further increasing Germanys interest in synthetic fuels. In the beginning of the 1940s about 600 000 tons of liquid hydrocarbons were produced in German facilities.

After World War II the American and British followed up their interest in the German synfuel industry by sending teams of scientist to Germany, to evaluate captured technical documents and interview scientists and engineers from the industry. The industry, nevertheless, had to close down due to competition from cheaper conventional fuels. In the 1950s new plants for synthetic fuels were built in Sasolburg, South Africa again sparked by political reasons. The two plants operated by Sason Synfuels fulfill about 28 percent of South Africa's diesel and petrol needs.

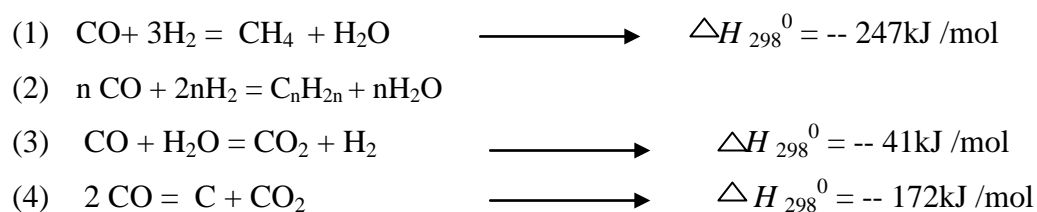
The oil crisis in the 1970s fueled new interest in synfuels, in the United States and the European Union financial support for research and development increased substantially. This resulted in extensive catalyst, kinetics, mechanisms and catalyst deactivation studies. In 1993 Shell and Petro AS opened Gas-to-liquid (GTL) plants in Malaysia (Bintulu) and in South Africa (Mossel Bay) respectively. The GTL plants utilize natural gas for synthesis gas production. Rapid growth in GTL-industry will bring production up to about 500 000 – 600 000 barrels per day by 2010.

In Germany a lot of research has been made on the developing of liquid fuels from biomass. Forschungszentrum Karlsruhe, the Claustahl University of Technology and Choren Industries GmbH are research institutions using the Fischer-Tropsch synthesis. The pilot plant built by Choren in Freiberg is currently the only BIG-FT plant in operation.

Rising oil prices and global warming are political issues potent to once again promote synthetic fuels. This time nonetheless, biomass may be considered a suitable feedstock.

Chemistry and Thermodynamics

The basic chemistry of the Fischer-Tropsch synthesis can be described by the following set of equations, adapted from Bartholomew (2006) :



Reaction (1) is methanation, reaction (2) is the production of hydrocarbons heavier than methane, reaction (3) is the water gas shift (WGS) reaction and reaction (4) is the Boudouard reaction. The methanation reaction (reaction 1) and the Boudouard reaction (reaction 4) are undesirable while reaction (2) is desired and is the most dominant reaction when applying cobalt-based FT catalyst. When using iron-based (Fe) catalyst the WGS reaction also readily occurs. Only Fe catalyzes the WGS (reaction 3) and therefore enabling the operation at a lower temperature. Furthermore, the equilibrium calculations indicate that methane formation is highly favored over formation of hydrocarbons of heavier molecular weight, thereby

implying a need for a catalyst designed for high selectivity for hydrocarbons other than methane. Co, Fe and Ru catalysts can be designed to meet this requirement. The reaction (2) is the chain building reaction. Figure 6.1 shows the biomass gasification and Fischer-Tropsch synthesis.

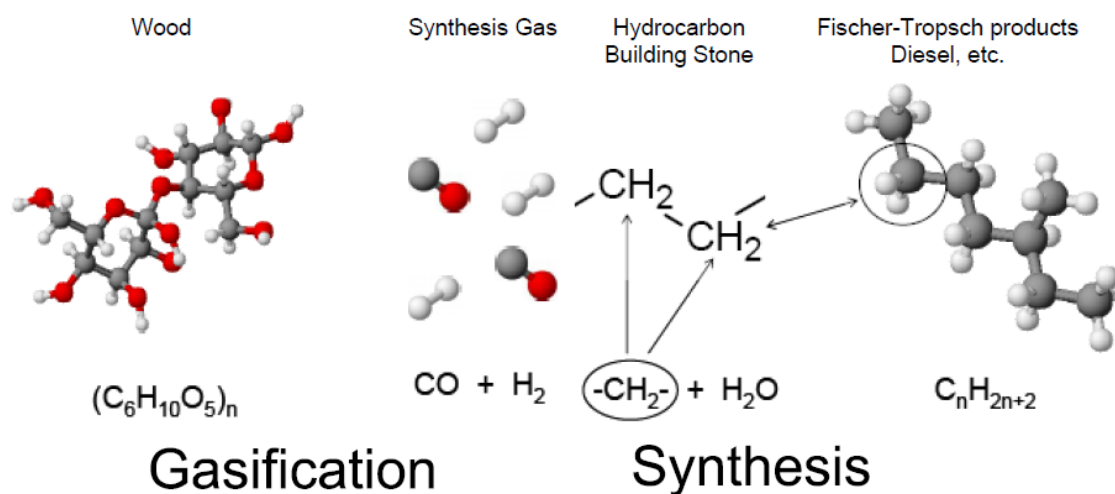


Figure 6.1: Biomass gasification and Fischer-Tropsch synthesis

Since the FT reaction is highly exothermic it is important to remove the heat of the reaction rapidly as the catalyst can be overheated and damaged. Also increased reaction temperature will increase methane production and reduce production of longer hydrocarbons chains.

Fischer-Tropsch reactors

Two classes of reactors are used, multi-tubular fixed bed and fluidized bed reactors (including slurry phase reactor). Multi-tubular fixed bed (Figure 6.2) consists of thousands of narrow tubes with surrounding water, where the temperature is controlled by releasing steam when pressure is increased.

The fluidized bed reactors contain immersed cooling coils and are excellent heat exchange systems. The fluidized bed reactors can be subdivided into three main types of reactors, the two-phase circulating fluidized bed reactor (Figure 6.3), the two-phase fixed fluidized bed reactor (Figure 6.4) and the three-phase slurry reactor (Figure 6.5). The slurry phase reactor was taken into use in beginning of the 1990s. The syngas is led into the bottom of the reactor, bubbles up through the slurry and builds carbon chains. In low temperature Fischer-Tropsch systems (LTFT, 200 – 240 °C) the most common reactors are the slurry phase reactor and the

multi-tubular fixed bed reactor. In the high temperature Fischer-Tropsch system (HTFT, 300 – 370 °C) the fluidized bed reactors are favored. LTFT creates longer carbon chains than HTFT and is hence more interesting when it comes to diesel production.

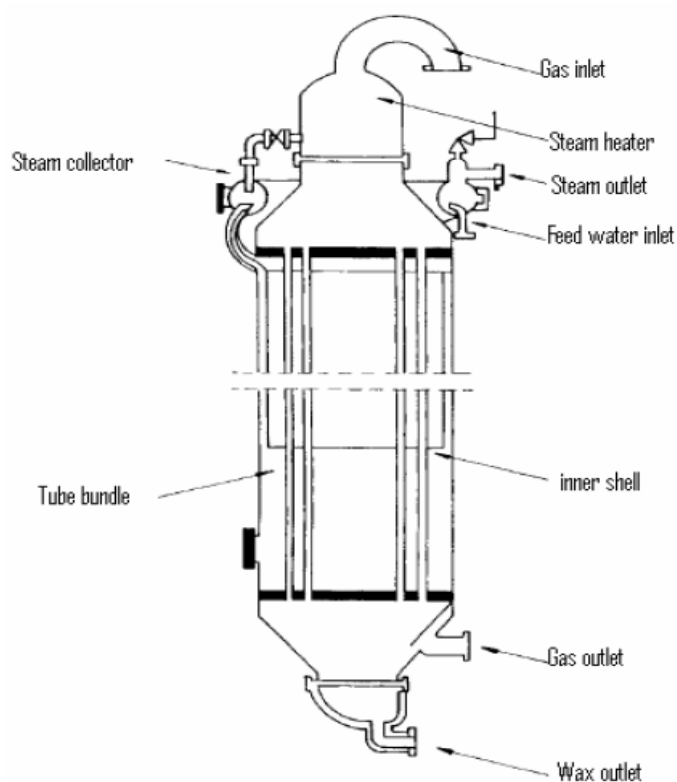


Figure 6.2 Multi-tubular fixed bed Fischer-Tropsch reactor

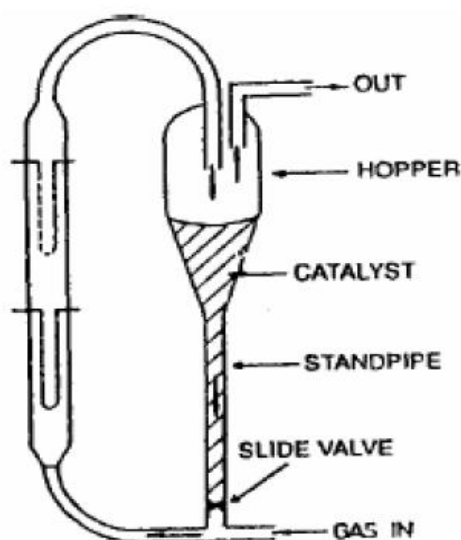


Figure 6.3: Circulating fluidized bed reactor

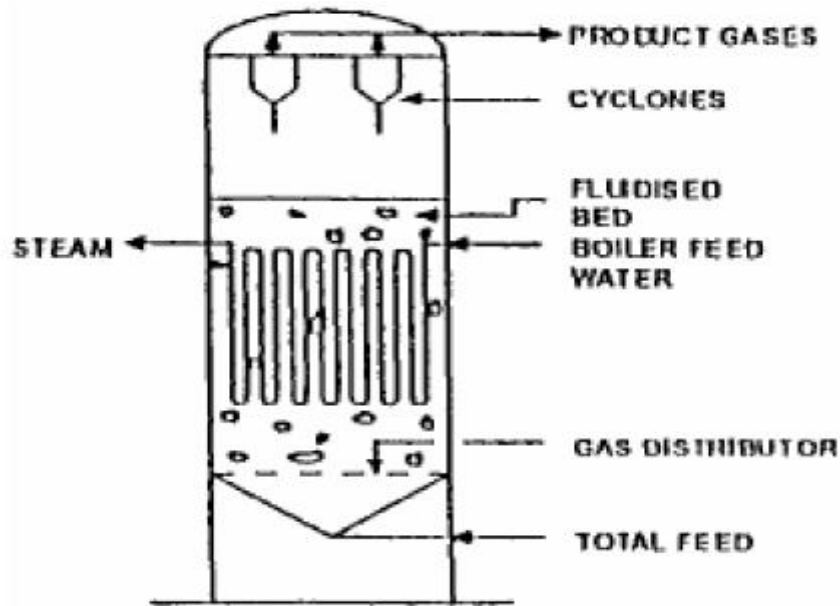


Figure 6.4 Fixed fluidized reactor

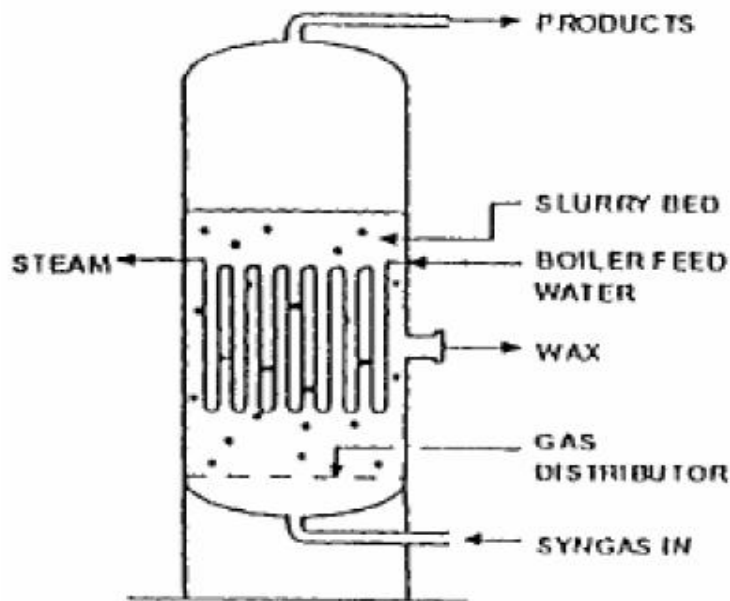


Figure 6.5. Slurry-phase bubbling bed reactor

When choosing reactor important attributes include size/throughput, capital and operating costs, thermal efficiency, heat removal, product selectivity, and flexibility in terms of operating conditions and product quality, maintenance of catalyst activity and/or ease of

regeneration and reactor stability. Given the various reactor attributes, a successful Fischer-Tropsch synthesis is heavily dependent on optimizing reactor design.

Fischer-Tropsch catalysts

Four different catalysts have sufficient activity to be considered for commercial application in the FT reaction, and those are; Fe-, Co-, Ni- and Ru-based catalyst. The ruthenium catalyst is the most active of the four but is very expensive due to limited availability. The nickel catalyst is also very active but has two major drawbacks, it produces much more methane than Co- and Fe-catalyst, and nickel forms volatile carbonyls resulting in continuous loss of metal at the operating conditions FT-plants operate. This leaves Co- and Fe-based catalyst as the only practical choices.

The Fe-catalyst is cheaper, but the Co-catalyst has longer life and higher activity. Use of iron catalyst will result in lower heavy hydrocarbon selectivity, and thus lowering the diesel output. Cobalt catalyst have higher heavy hydrocarbon selectivity, the heavy hydrocarbons can be cracked to the desired hydrocarbon length. For cobalt catalysts the WGS reaction has negligible activity, this means that the syngas has to have a H_2/CO usage ratio in the range 2.06 to 2.16. Due to the frequently occurring WGS reaction in iron catalysts systems, the H_2/CO usage ratio can be as low as 1.7.

Products

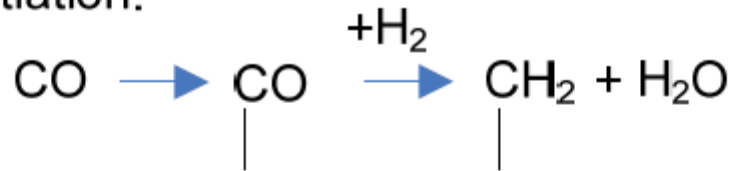
The products from the Fischer-Tropsch synthesis range from C1 compounds to high molecular mass waxes.

Product distribution

Depending on process conditions and catalysts used, the range of the products from the Fischer-

Tropsch varies (Table 6.2). The details on the elementary chemical steps occurring on the surface of the catalysts have always been a matter of controversy, but the general agreement is that a stepwise chain growth process is involved equivalent to the polymerization of monomers. The formation of higher hydrocarbons is believed to occur through the dissociation of carbon monoxide. Figure 6.6 shows the general accepted reaction pathway.

Initiation:



Chain Growth and termination:

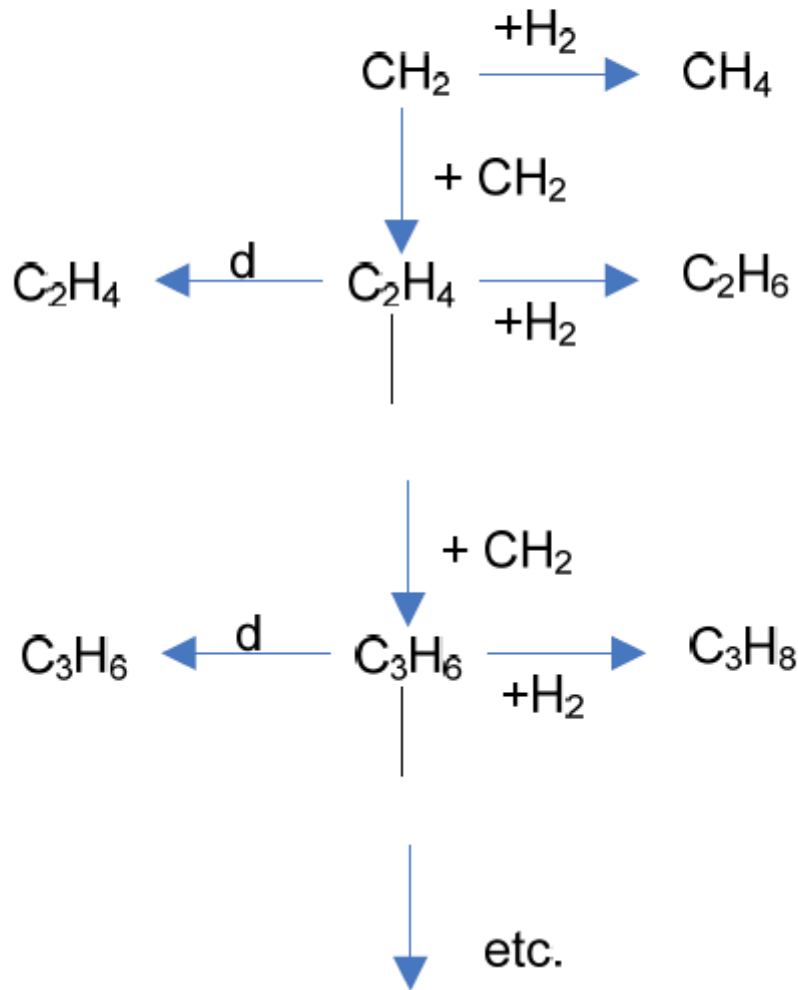


Figure 6.6: General accepted reaction pathway for the formation of higher hydrocarbons in Fischer-Tropsch synthesis

At each stage of growth process the surface species (at first, surface carbon) has the option of desorbing to produce an alkene, or to be hydrogenated to desorb as an alkane, or to continue the chain growth process by adding another CH_2 . The probability of chain growth can be denoted α .

The effect of temperature, partial pressures of H_2 and CO , feedgas composition, reactor used and

reduction of the catalyst are all important parameters which influence the product selectivity.

Increase of temperature results in a lowering of carbon number in the product selectivity.

According to Laan (1999) indicate most studies that increased pressure will shift product

selectivity towards heavier hydrocarbons and also he suggest that increasing H₂/CO ratio will result in lighter hydrocarbons and a lower olefin content. Deactivation of catalyst may also affect the selectivity to hydrocarbon products.

Table 6.2 Product from FT synthesis

Products from the Fischer-Tropsch synthesis	
C1-C2	SNG
C3-C4	LPG
C5-C10	Petroleum
C5-C7	<i>Lighth</i>
C8-C10	<i>Heavy</i>
C11-C20	Middle distillate
C11-C12	<i>Kerosene</i>
C13-C20	<i>Diesel</i>
C21-C30	Softwax
C31-C60	Hardwax

To maximize the yield of diesel production from the Fischer-Tropsch process, the heavy waxes should be cracked to shorter hydrocarbons and the light hydrocarbon liquids should be recycled to the synthesis gas. The remaining products will then typically be naphtha, LPG and/or kerosene. Nevertheless, other plant configurations could yield other products like jet fuel, solvents, illuminating paraffin, base oils and olefinic petrochemicals (Figure 6.7).

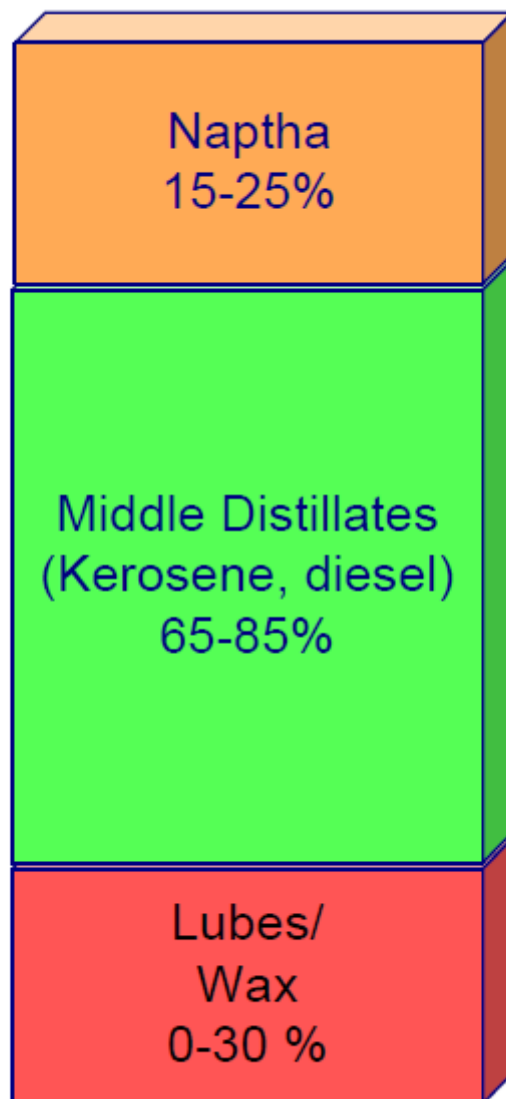


Figure 6.7: Typical breakdown of fractions from the Fischer-Tropsch synthesis

Though FT-diesel has lower lubricity than other conventional oil-derived fuels, it demonstrates several clear advantages over conventional diesel. Diesel ideally consists essentially of linear alkanes, and for a LTFT process with either iron or cobalt catalyst this is generally the case. The final product has according to Dry (2001) a high cetane number of about 75, the market requirement is about 45-50. Due to this high cetane number, FT-diesel can be blended with conventional diesel of lower quality which otherwise would not have been utilized as an automotive fuel. The emissions from the Fischer-Tropsch diesel are less than with conventional diesel.

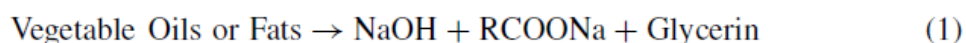
6.1.3. DIESEL FUEL FROM VEGETABLE OIL BY DECARBOXYLATION

A sustainable biofuel has two favorable properties, which are availability from renewable raw material and its lower negative environmental impact than that of fossil fuels. As an alternative fuel, vegetable oil is one of the renewable fuels. Vegetable oil is a potentially

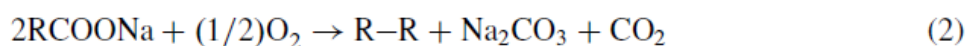
inexhaustible source of energy with an energetic content close to diesel fuel. There are four alternative fuels that can be relatively easily used in conventional CI engines: vegetable oil, biodiesel, Fischer-Tropsch (FT) diesel, and dimethyl ether (DME). The vegetable oils, such as palm, soybean, sunflower, peanut, and olive oils as alternative fuels, can be used for diesel engines. The vegetable oils as alternative engine fuels are all extremely viscous, with viscosities ranging from 10 to 20 times greater than petroleum diesel fuel. The major problem associated with the use of pure vegetable oils as fuels for diesel engines are caused by high fuel viscosity in compression ignition. The direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines.

Vegetable oils may be resources for fuels as petroleum alternatives (Figure 6.8). There are four different ways of modifying vegetable oils and fats to use them as diesel fuel, such as pyrolysis (cracking) and dilution with hydrocarbons (blending, emulsification, and transesterification). Figure 5 shows the use of vegetable oils as petroleum alternative fuels. The saponification and pyrolysis of sodium soap of vegetable oil proceeds as follows:

Saponification:



Pyrolysis of Na-soaps:



The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products, according to Eq. (2), with higher yields at lower temperatures (Demirbas, 2002).

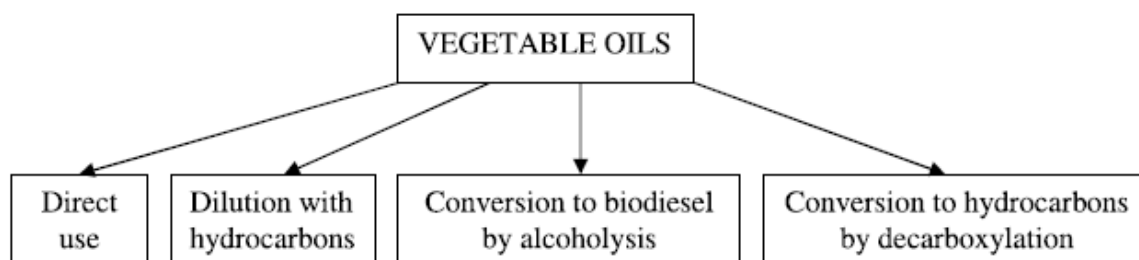


Figure 6.8: Use of vegetable oils as petroleum alternative fuels

The vegetable oils can be converted to petroleum compounds by effectively separating the carboxylic group without breaking the hydrocarbon chain. Hot compressed water is one of the candidates for treating the oils to produce petroleum (long chain hydrocarbon) because of its capability to hydrolyze triglyceride into free fatty acid and glycerol without catalyst. However, a free fatty acid is stable in subcritical water. Thus, to develop the petroleum recovery process from oils, decarboxylation of a free fatty acid is a key reaction.

6.1.4. CATALYTIC HYDRODEOXYGENATION (HDO) OF VEGETABLE OILS TO RENEWABLE ALKANE-TYPE BIOFUELS

Currently, biodiesel produced by transesterification of vegetable oils and methanol is widely used as a renewable fuel. However, biodiesel usually suffers from disadvantageous fuel properties such as relatively high freezing point due to the involved oxygen atoms, and limited

compatibility with gas engines, low chemical stability, and low caloric value due to the involved oxygen atoms and the unsaturated C–C bonds, as comparing with the present fossil fuels. In order to overcome these disadvantages of biodiesel, catalytic hydrodeoxygenation (HDO, the essential removal of oxygen atoms and saturation of unsaturated C–C bonds) of biomass derived fatty acids, aliphatic esters and/or vegetable oils for the production of diesel-like hydrocarbon fuels has been intensively investigated in recent years.

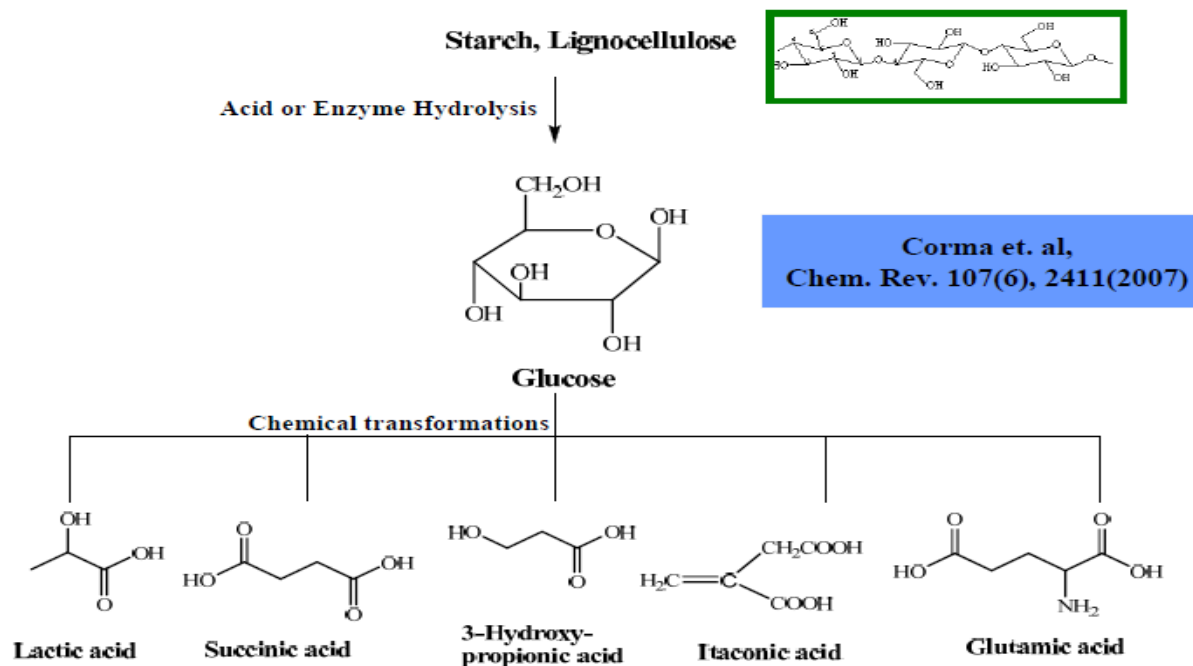
The primary HDO catalysts were mainly concentrated on dispersing noble metals Pt, Pd, and transition metals Ni–Mo, Co–Mo, and Ni–W on the supports of γ -Al₂O₃, activation carbon, SiO₂ and SBA-15, etc. Noble metals showed high activity and stability, but their extortionate cost limits their essential application on a large scale. On the other hand, the transition metals Ni and Co with promoters of Mo or W were comparable to the noble metals. NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts were widely used in HDO of vegetable oils for producing high yield of hydrocarbon fuels and the HDO mechanism investigation revealed that HDO of vegetable oils is a multistep reaction with oxygen-containing compounds including aliphatic alcohols and fatty acids as the intermediates. Aside from the above-mentioned HDO pathway, decarbonylation and/or decarboxylation also occurred parallel with obtaining the main products of aliphatic chain length hydrocarbons containing one less carbon than the corresponding feedstocks. It is noted that although these modified transition metals showed a highly catalytic performance in this kind of HDO reaction, the introduction of sulfur containing agents is necessary to keep the sulfided state of catalysts during catalyst pretreatment and HDO processing, which inevitably brings about sulfur pollution in the final products. For example, a previous report testified that the maximum molar concentration of heptanethiol in the liquid products was 0.4% with 400 ppm of H₂S addition, during HDO of methyl heptanoate over the sulfided NiMo/ γ -Al₂O₃ catalysts. Therefore, exploring nonsulfided metal catalyst for avoiding such drawbacks is of fundamental importance, but it still an open challenge.

6.1.5: PLATFORM BIOFUEL

An alternative biofuel, called furfural, is gaining new levels of attention because, like cellulosic ethanol, it is produced from waste biomass such as various agricultural residues,

corn fiber, corn stover, wheat straw, rice straw, and sugarcane bagasse, contain about 20–40% hemicellulose, the second most abundant polysaccharide in nature.

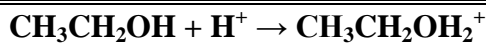
Glucose : Platform Chemical for Value-Added Chemicals



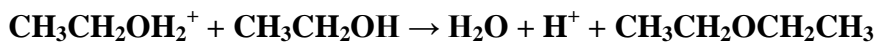
Furfural is a platform chemical and a feedstock that has the ability to substitute a variety of oil/coal/gas derived products. Furfural is used in agriculture as a fungicide and a nematicide, in the production of e.g. resins which can be applied for making fiberglass and aircraft components or as a platform chemical for fuels/chemicals. Furfural is also used as a flavour ingredient in 10 separate food categories and is found in different amounts of fruit juices, wine, coffee and tea. The interest for furfural has increased in the last few years due to its potential for competing with oil derivatives as a platform chemical. In addition, furfural, derived from C₅ sugars, can play a key role in the valorization of the hemicellulose contained in biomass when considering the development of a modern biorefinery concept.

As another line of research, diethyl ether (DEE) synthesized from bio-ethanol is a novel fuel which can be used in diesel engines as a mixture with bio-diesel or traditional diesel. Diethyl ether has a high cetane number of 85 - 96 and is used as a starting fluid for diesel and gasoline engines because of its high volatility and low auto ignition temperature. Diethyl ether can be prepared both in laboratories and on an industrial scale by the acid ether synthesis. Bioethers are produced by dehydration of bio-based alcohol.

Ethanol is mixed with a strong acid, typically sulfuric acid, H₂SO₄. The acid dissociates producing hydrogen ions, H⁺. A hydrogen ion protonates the electronegative oxygen atom of the ethanol, giving the ethanol molecule a positive charge:

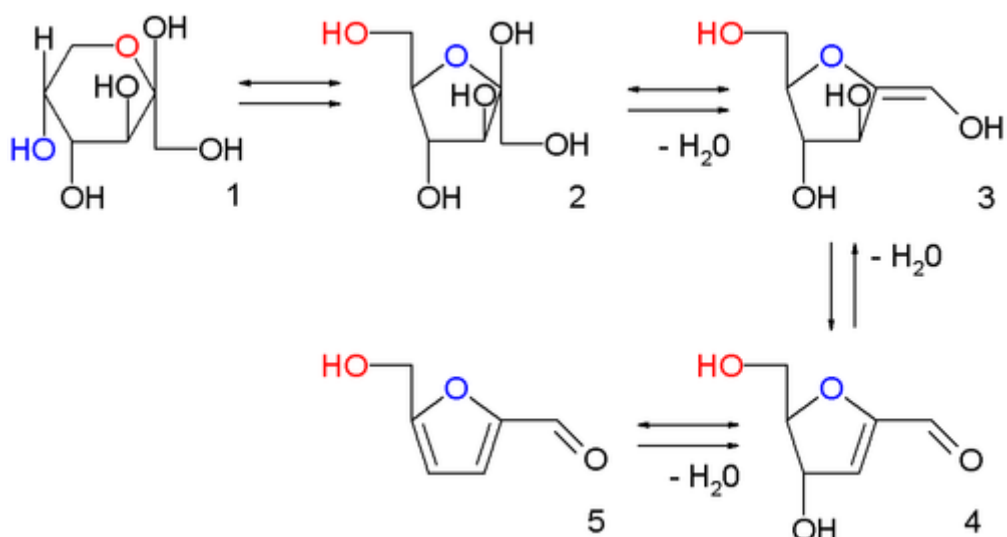


A nucleophilic oxygen atom of unprotonated ethanol displaces a water molecule from the protonated (electrophilic) ethanol molecule, producing water, a hydrogen ion and diethyl ether.



Scope of application

One of the best methods to produce biofuel would be to start from lignocellulosic material and to produce furanic biofuels, such as 5-hydroxymethylfurfural (HMF) via condensation and hydrogenation reactions.



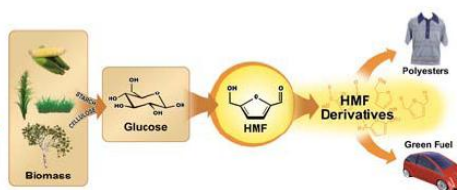
fructopyranose **1**, fructofuranose **2**, two intermediate stages of [dehydration](#) (not isolated) **3,4** and finally HMF **5**.

HMF can be converted to 2,5-dimethylfuran (DMF), which is a liquid biofuel that in certain ways is superior to ethanol. Oxidation of HMF also gives 2,5-furandicarboxylic acid, which has been proposed as a replacement terephthalic acid for the production of plastics. Furanic ester and ethers or 2,5-dimethylfuran are used as fuel additives. 2,5-dimethylfuran exhibits low water solubility and high research octane number (RON) and at the same time its energy density is high. 2,5-dimethylfuran was produced from dehydration of fructose using e.g. HCl as a catalyst. If glucose would be used instead of fructose as a starting material for synthesis of HMF, the challenge is to develop a catalyst, which enables in-situ isomerizing glucose to fructose, which in turn is thereafter easily transformed to HMF.

Direct cellulose conversion to 5(chloromethyl)furfural in the presence of LiCl in concentrated hydrochloric acid and its further transformation via hydrogenation using PdCl₂ yielded to 5-methyl-furfural was demonstrated.

Alternatively, 5-(chloromethyl)furfural can be converted to ethoxymethylfurfural in ethanol. This compound is a promising alternative fuel with the energy density of 8.7 kWh/L, whereas that for diesel is 9.7

State of the Art Furan derivatives (references)

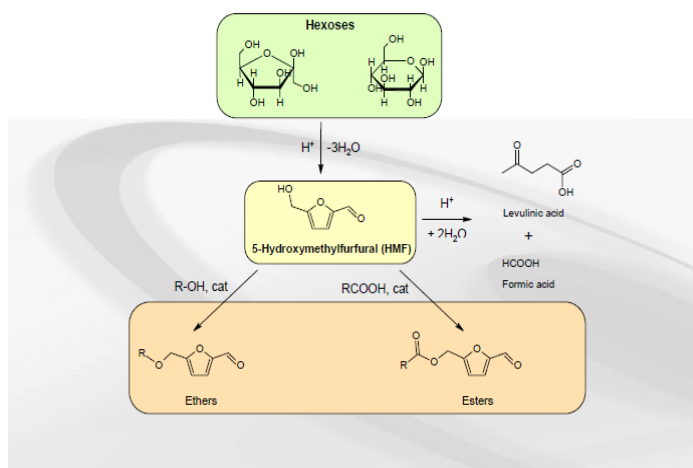


Picture from PNNL

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kWh/L.

Two new family of furan derivatives



6.2. BIO-REFINERY

Bio-refinery Definition:

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass.

“Biorefinery is the sustainable processing of biomass into a spectrum of marketable products”. Sustainable: maximising economics, and minimizing environmental aspects; fossil fuel and feedstock replacement.

Processing: upstream processing; transformation; fractionation; thermo-chemical and/or biochemical conversion; extraction; separation; downstream processing.

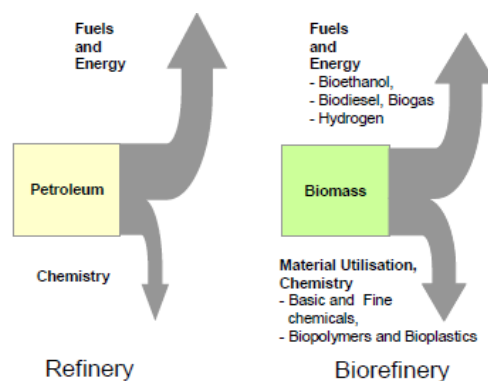
Biomass: crops; organic/forest residues; aquatic biomass.

Spectrum: more than one marketable product.

Marketable products: both intermediates and final products (i.e. fuels; power; heat; food; feed; chemicals; materials).

Bio-refinery concept:

The bio-refinery is not a single or fixed technology. Several different routes from feedstocks to products are being developed and demonstrated, and it is likely that multiple bio-refinery designs will emerge commercially in the future. The biorefinery concept is analogous to today's petroleum refinery, which produce multiple fuels and products from petroleum (figure- 6.9).



Biobased industrial products can only compete with petro-chemically based products if the raw materials are optimally exploited and a variety of value-creating chains are developed and established.
→ development of substance-converting basic product systems and multi product systems, especially biorefineries.

Figure 6.9: Bio-refinery concept.

By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-

value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use and perhaps enough for sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions.

Optimization and Efficiency.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, chemicals, feed, materials and energy from biomass. The objective of a biorefinery is to optimize the use of resources and minimize wastes, thereby maximizing benefits and profitability.

Biorefineries will encompass a variety of conversion processes and different sized installations due to the range of processes – biological, chemical and thermal – that can be employed. Optimization and high efficiency are the keys to making biorefineries sustainable and economically viable. Optimization can be achieved by future development in key areas and the efficient exploitation of chemical energy from biomass:

Technology. Developments in conversion technologies will lead to more of the plant being used to produce a wider, more flexible range of products – for example, chemicals and materials – in addition to fuels. Much of this development is technology dependent and will lead to improvements in environmental and economic performance of the production processes. The conversion processes and the end products that can be produced are dependent on the feedstocks available and how they are exploited.

Exploitation. The challenge is to find the optimum method of exploiting the chemical energy embedded in the biomass. Developing highly efficient conversion techniques – such as development of new microbial strains for the direct conversion of hemicelluloses (Figure 6.10) and advanced catalyst development to improve regeneration after transesterification – is a vital component of improving the conversion process. There are also existing technologies available for improving the crops that produce feedstocks for biorefineries.

Hemicellulose Biorefinery

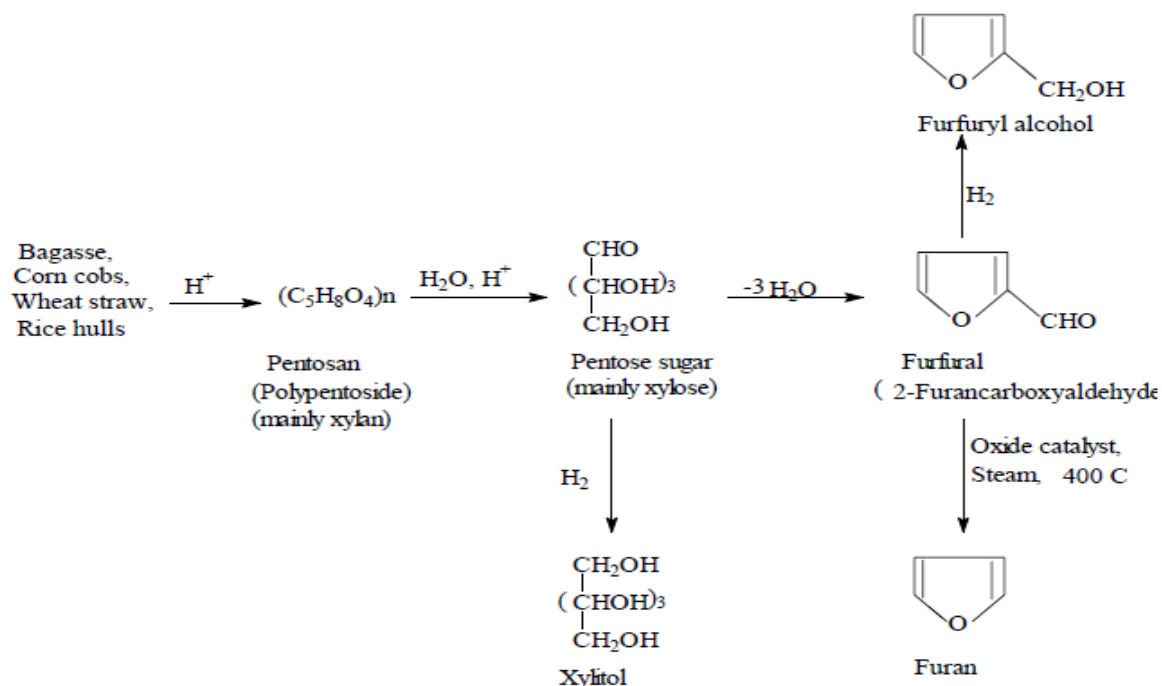


Figure 6.10: Hemicellulose Biorefinery

Logistics. Optimizing the efficiency of the supply chain will require feedstocks to be developed with characteristics that increase the efficiency of the conversion process and have the necessary characteristics to produce the end products. The logistics of biorefinery outputs must also be considered, including transportation and supply chain infrastructure (e.g. deep-water ports, roads, etc.), organization of storage facilities and identification of new trade routes. Biorefineries that are designed to be flexible and modular will be able to take a wider range of feedstock or adapt to changes in demand for specific chemicals without large capital costs. This flexibility will also mean that a biorefinery will be able to cope with a variety of feedstocks that mature at different times of the year. A modular installation will also be able to change its processing technologies as new feedstocks are developed.

From a research perspective, the emphasis must be on the development of a set of capabilities that are independent of particular fuels, chemicals and materials.

The economics and sustainability of biorefineries are dependent on their efficiency and can consequently be improved by optimization of the entity:

- **Economics.** The cost of production of bio-based products and, in particular, the investment needed for infrastructure and supply will have a direct bearing on their success as an alternative to fossil-based products. An efficient biorefinery will ensure cost minimization and a cost competitive end product. At present, efficiency is difficult to define since an efficient biorefinery

is still a concept. However, if one describes biorefinery efficiency in terms of utilizing local resources and the existing infrastructure, maximizing biomass-to-product conversion rates, ensuring flexibility in the products produced by the refinery and streamlining supply chains, then it is clear it will have a large impact on the economic viability of biorefineries.

- Sustainability. How the various processes in the conversion stage are combined will have significant impacts on the sustainability of biobased products. Throughout the biorefinery, there is the opportunity for improved recycling of heat/energy or the regeneration of catalysts in an integrated approach, which will have an impact on the carbon footprint of the overall process and resulting products. New biorefineries are often generating excess energy from waste products, which is then fed into the grid, often lowering the net CO₂ emissions from the overall process. Just as efficiency had an effect on the economics, the efficiency will also have an effect on the sustainability. The optimal biorefinery should be capable of utilizing biomass as a renewable energy source that can sustain our energy needs in the long term.

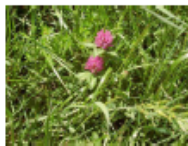
Some existing biorefineries:

Existing biorefineries, Phase I, (Selection)



Plants	Raw material	Country
Sugar and Ethanol production	Sugar cane	Brasilien 17 billion litre/a
Corn hydrolysis and Ethanol Production	Maize corn	U.S.A. 22 billion litre/a
Corn hydrolysis/ Sugar and Ethanol production	Cereal Corn Sugar beet	EU 1,5 billion litre/a In construction till mid 2008 3,4 billion litre/a

Existing biorefineries, Phase II, (Selection)



Plants	Raw material	Country
Corn hydrolysis & Lactic acid Fermentation & PLA production	Maize-Corn	U.S.A. 200 kt LA/a 140 kt PLA/a
Corn hydrolysis & 1,3-Propanediol Fermentation	Maize Corn	U.S. A. 45kt/a PDO

In construction biorefineries, Phase II, (Selection)

Plants	Raw material	Country
Ethanol-Fermentation & Dehydration & PE Production	Sugar cane Sugar cane	Brazil (1) 350 kt/a Start 2011 (2) 200kt/a

Europe: In construction biorefineries, Phase II, (Selection)



Plants/ Company Country	Raw material (Capacity)	Main-Products
LCF biorefinery Abengoa Bioenergy Spain	Corn stower Wheat straw Hay (70t/d)	Ethanol Lignin
LCF biorefinery Icelandic Biomass Iceland	Alaska Lupine Straw Barley Straw Hay (20kt/yr)	Ethanol Lignin
Green biorefinery Austria Industrial Consortium	Grass (5t/h)	Lactic acid, amino acid Fibres, biogas
Green biorefinery Germany Industrial Consortium	Alfalfa/ wild mix grass (30kt/a)	Proteins, Lactic acid Animal feeds,

<http://www.livemint.com/2008/09/01000457/CSIR-Godavari-Sugar-to-set-up.html>

Mint - Hindustan Times/ Wall Street Journal : September 03, 2008

INDIA -

The Council of Scientific and Industrial Research, or CSIR, has teamed up with Karnataka-based The Godavari Sugar Mills Ltd, or GSML, to set up the country's first biorefinery to convert crushed sugar cane into industrial raw materials such as **cellulose and lignin**



Current status of Industrialization

The biorefinery industry is gathering pace, with most second-generation plants expected to be ready for large-scale commercial production in a few years. Furthermore, the landscape of active players consists mainly of relatively small technology players, but also an increasing number of large multinational companies willing to invest in sustainable energy.

Nonetheless, a number of technology clusters, networks and partnerships are developing, often

composed of partners with complementary expertise along the biomass value chain, particularly with regard to second-generation technologies.

National mandates and policies are among the main industry drivers, which is why the status of

industrialization differs substantially between countries or regions. Before some of the inter-regional or international differences are explored below, some remarks about regulatory regimes in general are warranted. Generally speaking, all biofuel-producing countries have a mix of mandates and subsidies in place to support their national biofuel industries as a means to increase fuel supply security, CO₂ reduction or local farm revenues. Biomass-based power production is supported by similar measures.

United States	Brazil	European Union	China	India
Mandate of 36 billion gallons of biofuels by 2022.	30+ year commitment to 'alcohol program'.	5.75% blending target by 2010 and 10% by 2020.	Plan to substitute 20% of crude imports by 2020.	Blending targets in current drafts are 5% by 2012, 10% by 2017, 20% for long term.
Volumetric tax credit: USD 0.51/gal ethanol + USD 1.00/gal biodiesel.	Annual blending target for ethanol (25%).	Discussion on target waiver triggered by food crisis, but no change of policy so far.	Target of 1.7 billion gallons of ethanol by 2010.	Target of 20% biofuels by 2020.
Cellulosic biofuel producer tax credit: USD 1.01/gal. Small producer tax credit: USD 0.1/gal.	Biodiesel target of 5% by 2013.	Country-level subsidies average USD 1.90/gal for ethanol and USD 1.50/gal for biodiesel.	Investments in feedstock-rich countries.	Duty-free imports of jatropha to support biodiesel.
USD 1 billion in support for 2nd generation technology.	Lower taxes for ethanol (E100) than gasoline.	Penalty fee in 5 countries for noncompliance with biofuel target.	Commitment to develop non-food based biofuels - COFCO (Nat. Food Corp.) with PetroChina and Sinopec - 2nd generation multiple projects.	Individual states may set additional measures to promote biofuels or restrict transport of molasses over state boundaries.
*Corn/ Lignocellulose	*Sugarcane	*Rapeseed/ Lignocellulose	*Lignocellulose/ Various	*Various

Figure 6.11: Worldwide Mandates and Subsidies. Current policy status in five major world regions. (*) denotes key feedstock.

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DRE 103: BIOMASS ENERGY

UNIT-7: THERMO-CHEMICAL CONVERSION OF BIOMASS

- o Combustion in excess oxygen and oxygen deficient atmosphere
- o Carbonization, Charcoal production
- o Biomass gasification- different types-power generation from gasification
- o Biomass based power generation

UNIT STRUCTURE

7.1 OBJECTIVES

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7.3 COMBUSTION IN EXCESS OXYGEN AND OXYGEN DEFICIENT ATMOSPHERE

7.3.1 COMBUSTION FUNDAMENTAL

7.3.2 DOES AMOUNT OF OXYGEN IS CRITICAL PARAMETER FOR COMBUSTION?

7.4 CARBONISATION

7.4.1 CARBONISATION PROCESS

7.4.2 CHARCOAL PRODUCTION METHODS

7.5 BIOMASS GASIFICATION

7.5.1 GASIFICATION PROCESS

7.5.2 GASIFICATION TECHNOLOGY

7.6 THE UTILITIES OF PRODUCER GAS

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7.1 OBJECTIVES

There are several processes to convert biomass into useful heat or fuel. Thermo-chemical conversion is one of them. The objective of this unit is to introduce the learners about the different processes and products of thermo-chemical conversion of biomass into energy.

7.2 INTRODUCTION

First of all let us know what biomass is. A simple definition is “materials obtained from plant and animal origin are biomass”. Fuel wood that is used for cooking; cow dung which is used for cooking fuel or manure; straw and husk etc which are produced during crop production – are some of the examples of biomass. Biomass has historical importance. Early man used wood or dry plant materials to meet their basic requirements for heat. Even at later stage biomass has been primarily used to fulfill the industrial energy requirements. However, with the introduction of fossil based fuel (coal, oil and natural gas), the industrial uses of biomass have been reduced. But, traditionally biomass remains as dominant cooking fuel in major parts of the world till today. Conversion of biomass into useful energy through modern technology has been received renewed attention due to drawbacks of fossil based energy system.

What are the major processes of biomass to energy conversion?

Biomasses can produce energy through the following routes:

- Combustion (*domestic heat for cooking, lighting & space heating; industrial process heat, steam and electricity*);
- Gasification (*production of heat, fuel and electricity*)
- Pyrolysis (*production of charcoal and bio oil*)
- Fermentation (*production of ethanol*)
- Anaerobic digestion (*production of biogas*) and
- Extraction (*production of bio-diesel*)

These options are technologically matured and have wide ranges of applications. The first three of the above list are the thermo-chemical conversion options and will be discussed in this unit.

7.3 COMBUSTION IN EXCESS OXYGEN AND OXYGEN DEFICIENT ATMOSPHERE

7.3.1 COMBUSTION FUNDAMENTAL

What do we mean by combustion?

Combustion is a chemical reaction between substances, including oxygen and accompanied by the generation of heat and light in the form of flame. Combustion requires three elements viz., (a) fuel, (b) an oxidizer and (c) a source of heat. When these three elements are combined in the

appropriate environment, combustion will occur. If any of the elements is removed, combustion stops. Combustion of a given mass may be completed if all the required conditions are fulfilled or may be remain incomplete if any one of the required conditions is not met. The supply of adequate quantity of oxygen is one of the required conditions.

Combustion is basically an oxidation process:

Combustion refers to the rapid oxidation of fuel accompanied by the production of heat, or heat and light. Flue gas or gas of combustion is produced when any material is combusted. Complete combustion of a fuel is possible only in the presence of an adequate supply of oxygen or air

(Oxygen is one of the most common elements making up 20.9% of air). Rapid fuel oxidation results in large amounts of heat. Basically, solid or liquid fuel is converted into gas before it is burnt. Usually heat is required to change liquids or solids into gases. Fuel gases will burn in their normal state if enough air is present.

What is the role of nitrogen in combustion?

Most of the 79% of air (that is not oxygen) is nitrogen, with traces of other elements. Nitrogen is a temperature reducing dilutant which is unavoidable when air is used as oxidizer for combustion. Nitrogen reduces combustion efficiency by absorbing heat from the combustion of

fuels and diluting the flue gases. This reduces the heat available for transfer through the heat exchange surfaces. It also increases the volume of combustion by-products (*i.e.* flue gas). This nitrogen also can combine with oxygen (particularly at high flame temperatures) to produce oxides of nitrogen (NO_x), which are toxic pollutants.

Box 7.1

Example of combustion: Wood-burning in a stove

Wood is the fuel, air is the oxidizer and the initial source of heat is usually the flame from a match.

Once the oxidation is initiated, the heat generated by the exothermic reaction supports the combustion process. The entire combustion process could be seen to take place at the following stages

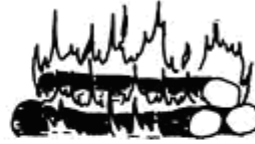
Temperature : up to 100 °C



Wood is heated to evaporate and drive off moisture.

Stage I

260-594 °C



Wood starts break down at around 260 C and volatile matter is released

Stage II

above 594



After release of volatile matter and starts burning

Stage III

What are the constituents of biomass fuel and what are the chemical reactions involved in combustion?

Ideally carbon and hydrogen are major constituents of biomass fuel. However, some other elements may also be the constituent of fuel as minor constituent. These constituents of the fuel combine with oxygen in the air to form carbon dioxide and water vapour. Reactions are exothermic and therefore, generate heat. Combustion reactions of C and H available in biomass fuel are provided in Box 2. Complete combustion of C produces CO₂ releasing more heat than the partial combustion (production of CO).

Box 7.1

Example of combustion: Wood-burning in a stove

Wood is the fuel, air is the oxidizer and the initial source of heat is usually the flame from a match.

Once the oxidation is initiated, the heat generated by the exothermic reaction supports the combustion

process. The entire combustion process could be seen to take place at the following stages
Box 7.2

Combustion reactions of C and H:

$C + O_2 \rightarrow CO_2$ (33.84 MJ/kg of carbon is generated in complete oxidation of C of fuel)

$2C + O_2 \rightarrow 2CO$ (10.17 MJ/kg of carbon is generated in partial oxidation of C of fuel*)

$2H + \frac{1}{2} O_2 \rightarrow H_2O$ (121.06 MJ/kg of Hydrogen in complete oxidation of H of fuel)

$S + O_2 \rightarrow SO_2$ (9.31 MJ/kg of Sulphur in complete oxidation of S of fuel)

*Each kilogram of CO formed means a reduction of 23.67MJ of heat.

$CO + \frac{1}{2} O_2 \rightarrow CO_2 + 23.67MJ/kg$ of CO

For any hydrocarbon C_nH_{2n+2} general form of combustion reaction:

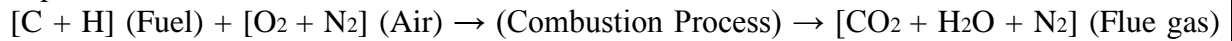
$C_nH_{2n+2} + ()O_2 \rightarrow nCO_2 + (n+1)H_2O + \text{heat}$

7.3.2 DOES AMOUNT OF OXYGEN IS CRITICAL PARAMETER FOR COMBUSTION?

From the forgoing discussion we have seen that combustion is an oxidation reaction involving oxygen. As we have seen the reaction equations (Box 7.2), oxygen plays an important role in combustion reaction. Ideally every atom of C and H of the fuel mass should get adequate opportunity to react with oxygen at required temperature. Thus, amount of oxygen required for each unit mass of fuel is critical for completion of combustion process. It is also mentioned earlier that in practical purpose air is used for combustion instead of pure oxygen. Therefore, amount of air required for completion of combustion process of unit mass of fuel need to be known. From the knowledge of the combustion reaction, the desirable ratio of air and fuel can be estimated which is discussed below.

What is Stoichiometric air fuel ratio?

A complete combustion is a process of burning all the carbon (C) to CO₂ and all the hydrogen (H) to H₂O (also all the sulphur to SO₂, if available). The combustion process can be expressed as:



Knowing the composition of the fuel (*e.g.* biomass) the exact amount of air required for complete combustion can be calculated. The ratio of **air to fuel** required to be maintained for complete combustion (or oxidation) of all the combustible compositions of the fuel is called stoichiometric air fuel ratio.

What is actual air fuel ratio?

The “complete combustion” is considered as a theoretical concept and it is used only to describe/compare the real or actual nature of combustion. The actual combustion takes place either in excess air (oxygen) environment or in deficient air environment. The air fuel ratio estimated based on the actual supply of air is called actual air fuel ratio.

What are the practical limitations of achieving complete combustion maintaining stoichiometric air fuel ratio?

Contact by every fuel molecule (atom) with oxygen at desired temperature is a chance phenomenon which is required for complete combustion. The chance depends upon the fuel type, method of air supply and combustion devices. This is true for all type of combustion devices (Box 7.3: Examples of some combustion devices). Density and moisture content are two important properties of fuel which effect the combustion reaction. Highly dense fuels resist the adequate mixing of fuel particle with air. On the other hand, presence of hygroscopic moisture (which is inevitable) adversely affect the combustion reaction. Excessive water vapour released, particularly during initial phase of combustion, adversely effect the ideal combustion. The supply of air also depends upon the design of combustion place *i.e.* device. Provision of a fan or chimney ensures force draft or positive supply of air (Box 7.3). On the other hand, fuel particle may be deprived of required air supply if design of combustion place is improper resulting inadequate supply of air. If combustion is incomplete the exhaust gas will contain unburnt C, H₂, CO etc. On the other hand, oxygen is supplied in excess quantity, it goes un-reacted with the exhaust gas.

Box 7.3

Examples of some common biomass combustion devices:

Biogas cooking stove similar to LPG stove

Domestic fuel wood stove – traditional or improved design

Furnace for bakery biscuit oven provided with chimney

Husk fired stove used in restaurant provided with chimney

If air content is higher than the stoichiometric ratio - the mixture is said to be **fuel-lean**. If air content is less than the stoichiometric ratio - the mixture is **fuel-rich**. Normally excess is provided to ensure complete combustion.

How can we calculate air requirement for combustion?

The detail procedure of estimation of air requirements has been demonstrated using a numerical problem (Problems 7.1).

Problem 7.1

Calculate stoichiometric air requirement for burning a biomass sample. Also determine the mass of air required if the biomass is supplied with 10% excess air for combustion. The composition of a biomass sample is given below,

Component Composition, mass %

Carbon 48.0 %
Hydrogen 5.0 %
Oxygen 40.0 %
Others, non combustable 7%

Solution:

Known: mass ratios of the elements

Need to find: (i) Stoichiometric air requirements, and (ii) mass of air for combustion, if 10% excess air is used.

Assumptions:

1. Air contains 23.2% oxygen and 76.8% nitrogen by mass.

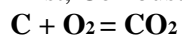
Solution:

As we know the carbon and hydrogen of the biomass sample are combustible components. The oxygen will be used from air. However, the sample is shown to have contains 40% oxygen which also will take part in reaction. Therefore, the net requirements from air will be reduced accordingly.

Stoichiometric air fuel ratio:

Considering 1 kg of fuel:

First, Combustion of C:

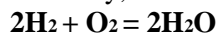


(12 kg + 32 kg = 44 kg) (Expressing in terms of molecular weight)

1 kg + 2.67 kg = 3.67 kg (Expressing for 1 kg of carbon)

0.48 kg + 1.28 kg = 1.76 kg (given, 1 kg of biomass will have 0.48 kg of C)

Similarly, combustion of H₂:



(4 kg + 32 kg = 36 kg)

1 kg + 8 kg = 9 kg

0.05 kg + 0.4 kg = 0.45 kg

Thus adding both the portion of estimated oxygen for complete combustion of 1 kg fuel, we can get mass of Oxygen = (1.28 kg for Carbon + 0.4 kg for Hydrogen) = 1.68 kg

However, the biomass sample has 0.400 kg of Oxygen per kg biomass. Therefore, the oxygen requirement from external source = 1.28 kg of O₂ per kg of biomass

The theoretical air required for complete combustion biomass i.e. stoichiometric air fuel ratio: Amount of fuel = 1 kg

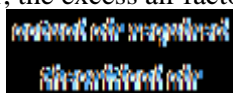
Amount of air to get 1.28 kg of oxygen = $1.28/0.232 = 5.52$ kg (considering oxygen content of air as 23.2%)

Stoichiometric air fuel ratio = 5.52

Calculation of mass of air if 10% excess air is supplied

For 10% excess air, the excess air factor is = 1.1

Excess air factor =



Actual air required = excess air factor × theoretical air

= 1.1×5.52 kg of air/kg of fuel

= 6.07 kg of air/kg of fuel

7.4 CARBONISATION

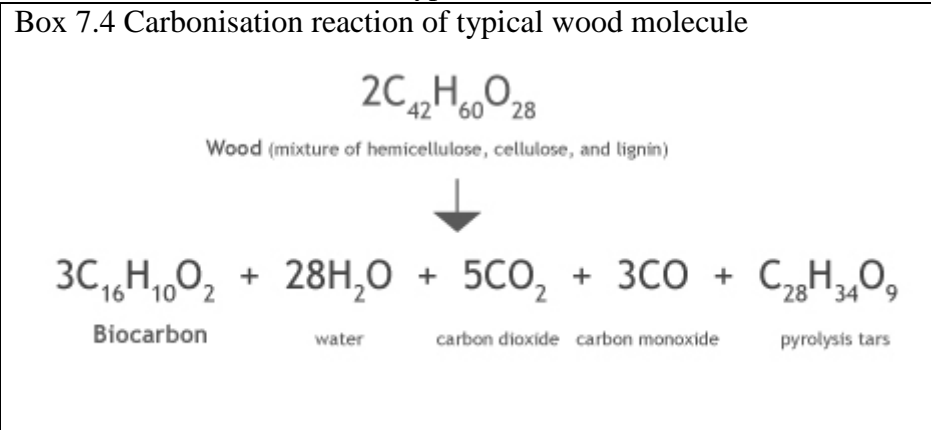
What do we mean by the carbonization?

Carbonisation is the term for the conversion of an organic substance into carbon or a carbon containing residue through a process called “pyrolysis” or destructive distillation. It is often used in organic chemistry with reference to the generation of coal gas and coal tar from raw coal. We can describe the fossil fuel production process as long term carbonization process under pressure and temperature provided by nature.

Is Carbonisation exothermic?

Overall, carbonisation is exothermic reaction and it could be made self-sustaining as a source of energy avoiding production of carbon dioxide. For example, heat release through carbonization of one gram of glucose is about 57 Joules. A carbonisation reaction of typical wood molecule is shown in Fig. 7.1

Box 7.4 Carbonisation reaction of typical wood molecule



7.4.1 CARBONISATION PROCESS

What is the process of Wood Carbonisation?

Wood is carbonized to produce charcoal. The conversion process involves certain stages. The carbonization stages are critical in charcoal production. However, the process is simple and not much expensive one.

Understanding of the composition of wood is required to understand the process:

Wood consists of three main components: cellulose, lignin and water. The cellulose and lignin and some other materials are tightly bound together in wood. The water is adsorbed or held as molecules of water on the cellulose/lignin structure. Air dry or "seasoned" wood still contains 12-18% of adsorbed water, where as growing, freshly cut or "unseasoned" wood contains about 40 to 100% adsorbed water expressed as a percentage of the oven dry weight of the wood.

Dry wood vs. moist wood for better carbonization:

To evaporate water requires a lot of energy so that using the sun to pre-dry the wood as much as possible before carbonization greatly improves conversion efficiency. The water remaining in the wood to be carbonised, must be evaporated in the kiln or pit and this energy must be provided by burning some of the wood itself which otherwise would be converted into useful charcoal.

What are steps of carbonization?

The first step in carbonization in the kiln is drying out of the wood at 100°C or below to remove moisture. The temperature of the oven dry wood is then raised to about 280°C. The energy for these steps comes from partial combustion of some of the wood charged to the kiln or pit and it

is an energy absorbing or endothermic reaction. When the wood is dry and heated to around 280°C, it begins to spontaneously break down to produce charcoal plus water vapour, methanol, acetic acid and more complex chemicals, chiefly in the form of tars and non-condensable gas consisting mainly of H₂, CO and CO₂. Air is admitted to the carbonising kiln or pit to allow some wood to be burned and the N₂ from this air will also be present in the gas. The O₂ of the air is used in burning part of the wood charged. The spontaneous breakdown or carbonization of the wood above a temperature of 280°C liberates energy and hence this

reaction is exothermic. This process of spontaneous breakdown or carbonization continues until only the carbonised residue called charcoal remains. Unless further external heat is provided, the process stops and the temperature reach a maximum of about 400°C.

What do we mean by the yield of carbonization process?

Yield is generally defined as the mass ratio of charcoal made and biomass fed i.e. Yield = mass of charcoal / mass of biomass feed.

Is information on yield sufficient to judge the process?

Both charcoal (product) and biomass (raw material) are varying in their characteristics. For example moisture contents vary with lot, climate and producer. Also the fixed carbon contents, volatile matter content, and ash content are parameters that are different with producer and production technology. Therefore these parameters are to be specified while yield is mentioned as an indicator of a technology. So, one should be aware that claims of high yields should be carefully evaluated in view of these quality aspects.

What are major products of a typical carbonization process?

Along with charcoal appreciable amounts of tarry residue and ash are produced. The ash content of the charcoal is about 3-5%; the tarry residue may amount to about 30% by weight and the balance is fixed carbon (65-70%). Further heating increases the fixed carbon content by driving off and decomposing more of the tars. A temperature of 500°C gives a typical fixed carbon content of about 85% and a volatile content of about 10%.

How does carbonization temperature affect yield and quality of charcoal?

The yield of charcoal at 500°C temperature is about 33% of the weight of the oven dry wood used for carbonisation. The yield of charcoal varies with temperature of carbonization due to the change in its content of volatile tarry material. Table 7.1 shows the effect of final carbonisation temperature on the yield and composition of the charcoal.

**Table 7.1
Effect of carbonisation temperature on yield and composition of charcoal**

Carbonisation dry wood Temperature °C	Chemical analysis of charcoal		Charcoal yield, % of oven
	Fixed carbon, %	Volatile material, %	
300	68	31	42
500	86	13	33
700	92	7	30

As can be seen from the Table 7.1, low carbonization temperatures give a higher yield of charcoal but this charcoal is low grade, is corrosive due to its content of acidic tars, and does not burn with a clean smoke-free flame. Good commercial charcoal should have a fixed carbon content of about 75%. The process of carbonisation can be categorized as (i) low

temperature carbonisation (LTC) at 600°C (ii) medium temperature carbonisation (MTC) at 800°C (iii) high temperature carbonisation (HTC) at 1000°C

How do raw wood characteristics affect yield and quality of charcoal?

The yield and quality of charcoal are also affected by the **characteristic** of wood. It is found that lignin content of the wood has a positive effect on charcoal yield. Higher is the lignin content higher is the yield of charcoal. Mature wood with characteristic denser structure is preferred for

charcoal production. It is reported that very dense woods sometimes produce a friable charcoal because the wood tends to shatter during carbonization. The friability of charcoal increases as carbonization temperature increases and the fixed carbon content increases as the volatile matter content falls. A temperature of 450 to 500°C gives an optimum balance between friability and the desire for high fixed carbon content.

7.4.2 CHARCOAL PRODUCTION METHODS

Brief descriptions of two commercial production processes are given below.

Kiln Methods (Fig. 7.2)

Traditionally, charcoal is made in mound or pit kilns. In kilning part of the feedstock is allowed to start and control the thermal process. There is a direct contact of the combusted pyrolysis vapours with the biomass feed resulting internal heating. Yield of kiln methods depends upon the

skills of the operators usually in the range of 5% to 20%. Also the quality of the charcoal is variable. Moreover, fixed carbon content differs, and there can be contamination with ash, sand and mud. The technology is widely used, both in developing countries and in industrialized countries.

However, the kilning technology has been improved with need based modification in the past to increase yield and quality. Missouri kilns, Argentine kilns, and Brazilian Beehive kilns are examples of improved kilning techniques. Beehive kilns can be found in large industrial complexes making charcoal for the steel industry in Brazil. In the USA this technique was also widely used for the manufacture of metallurgical charcoal, but it has been abandoned during the first half of the 20th century. In India, Missouri kilns were widespread till 1975 and later in the

state Missouri. Horner Charcoal Company (Tan eyville, Missouri) uses Missouri kilns for their charcoal production.



Fig. 7.1a Traditional plant

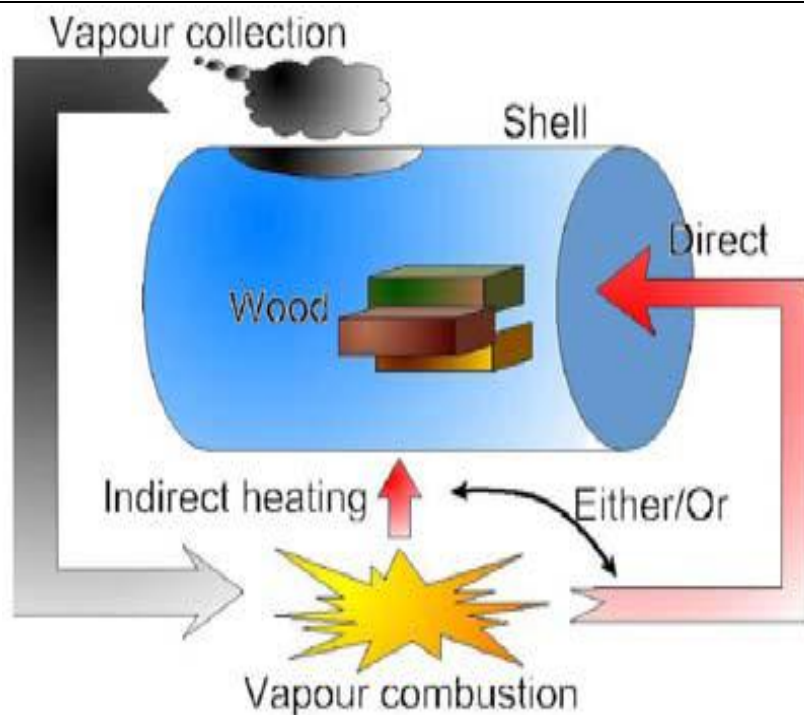


Fig.7.1b Modern plant

Modern Charcoal production process (Fig. 7.2b)

Most modern industrial charcoal makers use Retort method. In this method, the pyrolysis vapours are separated from the feed material, before being combusted. Only the vapours are used to provide the energy sustaining the process. Sometimes additional fuels are used, *e.g.* for startup

and in case of moist feed material. Direct contact of the biomass feed with oxygen (air) is prevented and thus, it is ensured that the entire biomass feed is available for conversion into charcoal. Charcoal yields from retort processes can be very high. Apart from higher yield separation of volatile enables the manufacturer to produce a variety of useful chemicals viz., acetic acid, wood vinegar, and methanol.

7.5 BIOMASS GASIFICATION

We have discussed and found that biomass is a solid fuel. There are different types of biomass (wood, plant leaves, agro-residues etc) which can be converted into gaseous fuel through a gasification process and gasifier technology. The details of the process and technology are discussed below.

7.5.1 GASIFICATION PROCESS

The gasification process is a thermochemical conversion process

Gasification is a thermochemical process. The word (thermochemical) means that (i) the chemical reactions are required for the desirable conversion and (ii) the reactions are possible in specific thermal environment. Gasification of carbonaceous materials (coal and materials of similar characteristics including biomass) is possible through such reactions providing required thermal environment. The gasification reactions produces are useful convenient gaseous fuel (producer gas) or chemical feedstock that can be burned to release energy or used for production of value-added chemicals.

How does gasification differ from combustion?

Gasification and combustion are closely related thermo-chemical processes. But there are important differences between them. Gasification reactions take place in oxygen deficient environment and therefore, complete oxidation of feedstock (*i.e.* biomass or similar solid fuel) does not take place. Subsequently, energy is embedded into chemical bonds in resultant gas (known as producer gas). On the other hand, in combustion process the constituents of feedstock are completely oxidized as full supply of oxygen is ensured, as a result, chemical bonds are broken down to release energy during the process itself. Now, we can summarize the gasification process as below:

The gasification process adds hydrogen to and strips carbon away from the feedstock to produce gases with higher hydrogen-to carbon (H/C) ratio, while combustion oxidizes the hydrogen and carbon into water and carbon dioxide, respectively.

What are the major constituents of gasification reaction?

Gasification of carbonaceous material (including biomass) results in production of combustible gases consisting of carbon monoxide (CO), hydrogen (H₂) and traces of Methane (CH₄). This mixture is called producer gas. Along with gaseous constituents tar, which is mixture of heavier hydrocarbon, is also generated in the gasification process.

What are the major applications of biomass gasification process?

Producer gas can be used to run internal combustion engines (both compression and spark ignition), can be used as substitute for furnace oil in direct heat applications and can be used to produce methanol.

What are the inputs required for biomass gasification?

Apart from biomass (*i.e.* feedstock) gasification requires a gasifying medium like steam or air or oxygen. Any one of them can be used as gasifying medium or agent. Gasifying medium or agent works to rearrange the molecular structure of the feedstock into gases or liquids. Further, it also adds hydrogen to the product. Chemically, gasifying agents react with solid carbon and heavier hydrocarbons to convert them into low-molecular-weight gases like CO and H₂.

Does the quality of product depend upon the gasifying medium?

The use of a medium is essential for gasification process. Oxygen is a commonly used gasifying medium. The oxygen initiates combustion reaction which is essential for gasification reaction. It may be supplied to a gasifier either in pure form or through air. The heating value and the

composition of the gas produced in a gasifier are strong functions of the nature and amount of the gasifying agent used. Heating value (expressed as MJ per normal cubic meter *i.e.* MJ/Nm³) is an important quality parameter of resultant gas. Some typical changes of heating value of producer gas with the change of gasifying medium are shown in Box 7.5.

Box 7.5	
Change of heating value of producer gas with change in gasifying medium	
Medium	Heating value (MJ/Nm ³)
Air	4 - 7
Steam	10 - 18
Oxygen	12 - 28

(Source: Biomass gasification and pyrolysis, Prabir Basu, page-119)

Gasification is accomplished through a series of reactions which are grouped into some steps.

What are the different steps involved in gasification process?

A typical biomass gasification process includes the following steps:

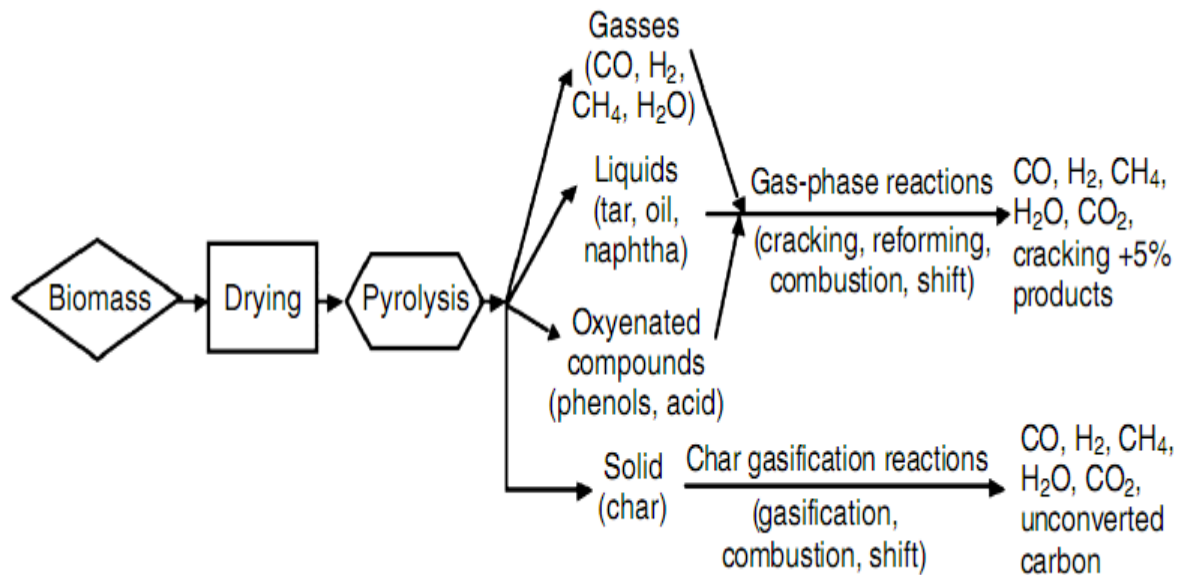
1. Drying
2. Thermal decomposition or pyrolysis

3. Partial combustion of some gases, vapors, and char

4. Gasification of decomposition products and char.

There is no sharp boundary between the steps and they often overlap. In a typical process, biomass is first heated (dried) and then it undergoes thermal degradation or pyrolysis. The products of pyrolysis (*i.e.*, gas, solid, and liquid) react among themselves as well as with the gasifying medium to form the final gasification product. In most commercial gasifiers, the thermal energy necessary for drying, pyrolysis, and endothermic reactions comes from a certain amount of exothermic combustion reactions allowed in the gasifier reactor (reactor is discussed

in the later part of this unit).



Box 7.6

Potential paths for gasification

The steps are shown in a layout in Box 7.6. The details of these steps are also discussed below.

Drying steps of gasification process:

The drying takes place within the reactor where feedstock (*i.e.* biomass fuel) receives heat from the hot zone of the reactor. This heat dries the feed, which releases water. Practically drying *i.e.* vaporization of moisture takes place at 100°C and nearby it. During drying within the reactor, the loosely bound water in the biomass is removed. As the temperature rises, the low-molecularweight compounds of the feedstock start volatilizing. This process continues until a temperature of approximately 200 °C is reached. (Some facts of feedstock drying is provided in Box 7.7)

Box 7.7

Moist feedstock vs. energy loss in the process If wood is used for gasification reaction in a reactor (details about the reactor will be discussed later in this unit), than moisture content of wood is very critical for the reaction. The typical moisture content of freshly cut wood ranges from 30 to 60% (for some biomass it may be more). It can be estimated from the simple thermodynamic calculation that every kilogram of moisture in the biomass robs away about 2.26 MJ of energy from the gasifier to vaporize water. This is loss as this part of energy is not recoverable. Therefore, for a high level of moisture this loss is a concern. Moisture of the feedstock can be classified into surface moisture and bonded moisture residing within the cell structure. Nothing much can be done to remove the inherent moisture residing within the cell structure, efforts may be made to drive away

the external or surface moisture. Importance of pre-drying – what should be the preferable moisture content of feedstock ? A certain amount of pre-drying is necessary to remove moisture from the biomass as much as possible before it is fed into the gasifier reactor. For the production of a fuel gas with a reasonably high heating value, most gasification systems use dry biomass with a moisture content of 10 to 20%.

(Source: Biomass gasification and pyrolysis, Prabir Basu, page-120)

Thermal decomposition or pyrolysis of gasification process:

Pyrolysis, which precedes gasification, involves the thermal breakdown of larger hydrocarbon molecules of biomass into smaller gas molecules (condensable and non-condensable) with no major chemical reaction with air, gas, or any other gasifying medium. In pyrolysis no external agent is added. One important product of pyrolysis is tar formed through condensation of the condensable vapor produced in the process. (Tar is a sticky liquid and it creates difficulty in industrial uses of the gasification product, we can describe tar as unavoidable and undesirable by-product of pyrolysis process).

Partial combustion of some gases, vapors, and char:

Most gasification reactions are endothermic i.e. heat is absorbed from the reaction environment. To provide the required heat of reaction as well as that required for heating, drying, and pyrolysis, a certain amount of exothermic combustion reaction (Box 7.8) is allowed in a gasifier Box 7.7

Moist feedstock vs. energy loss in the process If wood is used for gasification reaction in a reactor (details about the reactor will be discussed later in this unit), than moisture content of wood is very critical for the reaction. The typical moisture content of freshly cut wood ranges from 30 to 60% (for some biomass it may be more). It can be estimated from the simple thermodynamic calculation that every kilogram of moisture in the biomass robs away about 2.26 MJ of energy from the gasifier to vaporize water. This is loss as this part of energy is not recoverable. Therefore, for a high level of moisture this loss is a concern. Moisture of the feedstock can be classified into surface moisture and bonded moisture residing within the cell structure. Nothing much can be done to remove the inherent moisture residing within the cell structure, efforts may be made to drive away the external or surface moisture. Importance of pre-drying – what should be the preferable moisture content of feedstock ? A certain amount of pre-drying is necessary to remove moisture from the biomass as much as possible before it is fed into the gasifier reactor. For the production of a fuel gas with a reasonably high heating value, most gasification systems use dry biomass with a moisture content of 10 to 20%. (Source: Biomass gasification and pyrolysis, Prabir Basu, page-120) reactor. These reactions take place as partial combustion of some gases, vapors, and char available in the reactor.

Box 7.8

Heat of combustion reaction

Carbon combustion reaction ($C + O_2 \rightarrow CO_2$) is the best as it gives the highest amount of heat (394 kJ) per mole of carbon consumed. The next best is ($C + 0.5O_2 \rightarrow CO$), which also produces the fuel

gas CO, but produces only 111 kJ/mole of heat. The speed of later reaction is relatively slow. The chances of the above reaction depend upon the temperature of the reaction environment.

Gasification of decomposition products and char:

As mentioned above pyrolysis is must before gasification reaction. The gasification step follows pyrolysis and involves chemical reactions amongst

- (i) the hydrocarbons of the biomass fuel,
- (ii) steam (available from input or due to vaporization of feedstock moisture),
- (iii) carbon dioxide
- (iv) oxygen(input medium)
- (v) hydrogen (generated during reaction) and

– all of these are available in the reactor. Besides, various gases evolved during pyrolysis steps also take place in the gasification reaction.

How Char gasification is important?

Char gasification is the most important amongst all the gasification reaction. The char produced through pyrolysis of biomass is not necessarily pure carbon. It contains a certain amount of hydrocarbon comprising hydrogen and oxygen. Gasification of biomass char involves several

reactions between the char and the gasifying mediums. Gasifying agents like oxygen, carbon dioxide, and steam react with solid carbon to convert it into lower molecular-weight gases like carbon monoxide and hydrogen. As mentioned earlier, gasification reactions are generally endothermic, but some of them can be exothermic as well. For example, those of carbon with oxygen and hydrogen are exothermic, whereas those with carbon dioxide and steam are endothermic. A list of 14 different gasification reactions grouped into five types is provided in Box 7.9. The heat of reaction of the respective reactions is also provided along with the reaction equations.

Box 7.9

Typical gasification reactions at 25 °C.

(source: Biomass gasification and pyrolysis, Prabir Basu, page-121)

Reaction type	Reactions
Carbon Reactions	
R ₁ (Boudouard)	$C + CO_2 \leftrightarrow 2CO + 172 \text{ kJ/mol}$
R ₂ (water-gas or steam)	$C + H_2O \leftrightarrow CO + H_2 + 131 \text{ kJ/mol}$
R ₃ (hydrogasification)	$C + 2H_2 \leftrightarrow CH_4 - 74.8 \text{ kJ/mol}$
R ₄	$C + 0.5O_2 \rightarrow CO - 111 \text{ kJ/mol}$
Oxidation Reactions	
R ₅	$C + O_2 \rightarrow CO_2 - 394 \text{ kJ/mol}$
R ₆	$CO + 0.5O_2 \rightarrow CO_2 - 284 \text{ kJ/mol}$
R ₇	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O - 803 \text{ kJ/mol}$
R ₈	$H_2 + 0.5O_2 \leftrightarrow H_2O - 242 \text{ kJ/mol}$
Shift reaction	
R ₉	$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2 \text{ kJ/mol}$
Methanation reactions	
R ₁₀	$2CO + 2H_2 \rightarrow CH_4 + CO_2 - 247 \text{ kJ/mol}$
R ₁₁	$CO + 3H_2 \rightarrow CH_4 + H_2O - 206 \text{ kJ/mol}$
R ₁₂	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O - 165 \text{ kJ/mol}$
Steam-reforming reactions	
R ₁₃	$CH_4 + H_2O \leftrightarrow CO + 3H_2 + 206 \text{ kJ/mol}$
R ₁₄	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 - 36 \text{ kJ/mol}$

- sign of the heat refers generation of heat whereas + sign indicates the absorption of heat.

7.5.2 GASIFICATION TECHNOLOGY

The details about the reaction chemistry have been discussed in the previous section. The success of the completion of the above mentioned reactions will depend upon the soundness of the technology provided for reaction. A gasification reactor is required for providing the desired

space for reactions. There are different types of gasification reactor. Descriptions of the reactors are provided below:

Arrangement of feedstock bed and reactor classification:

Feedstock i.e. biomass fuel are kept in the reactor and gasification medium (mostly air) is circulated through the reaction zone. The output gas is taken out of the reaction zone. This is the general arrangement of working of a gasifier. The feedstock may be kept stationary or

kept fluidized. Moreover, the relative direction of air (medium) and resulted gas (producer gas) may also vary amongst the reactors. Broadly the reactors can be classified as (i) fixed bed updraft, (ii) fixed bed downdraft, (iii) cross draft and (iv) bubbling and circulating bed systems. These are described below.

Updraft gasifier reactor

The general arrangement of a typical Updraft gasifier is shown in Fig. 7.2. In this type of gasifier, fuel is fed from the top and the product gas leaves from the top. The gasifying agent (air, oxygen, steam, or their mixture) enters the gasifier through the bottom. The gas rises through a bed in the gasifier chamber. The air as it enters the bottom of the bed, meets first hot ash and unconverted chars descending from the top (Fig. 7.2). The temperature in the bottom layer exceeds the ignition temperature of carbon. Therefore the exothermic combustion reaction takes place in the presence of excess oxygen. The released heat of combustion provides thermal energy to the upward moving gas as well as the descending solids. The combustion reaction is very fast. Therefore, most of the available oxygen is consumed rapidly. As the available oxygen is reduced upward, the combustion reaction changes into partial combustion, releasing CO and a moderate amount of heat.

How the reaction equations can be described in terms of gas flow in an updraft gasifier?

The hot gas, a mixture of CO, CO₂, and steam (from the feed and the gasifying medium), moves further up into the gasification zone, where char from the upper bed is gasified by reaction R₁ and R₂ (Box 7.9). The carbon dioxide concentration increases rapidly in the first combustion

zone, but once the oxygen is nearly depleted, the CO₂ enters the gasification reaction (R₁ and R₂) with char, resulting in a decline in CO₂ concentration in the gasification zone.

How does the thermal energy (heat) is exchanged amongst the zones in an updraft gasifier?

Sensible heating of the hot gas provides the heat for the two endothermic gasification reactions R₁ and R₂. These are responsible for most of the gasification products like hydrogen and carbon monoxide. Because of their endothermic nature, the temperature of the gas reduces. The zone

above the gasification zone is pyrolysis zone for the pyrolysis of biomass. The residual heat of the rising hot gas assists drying of biomass in drying zone. Dried biomass then decomposes (pyrolyzed) into non-condensable gases, condensable gases, and char. Gases move up while the solid char descends. The topmost zone dries the fresh biomass fed into it using the balance heat of the hot gas coming from the bottom. This gas is a mixture of gasification and pyrolysis products. A part of the pyrolysis gas may burn above the gasification zone. Thus, the thermal energy

required for drying, pyrolysis, and gasification is supplied by the combustion of pyrolysis gas. The temperature profile and reactions are also shown in Fig. 7.2.

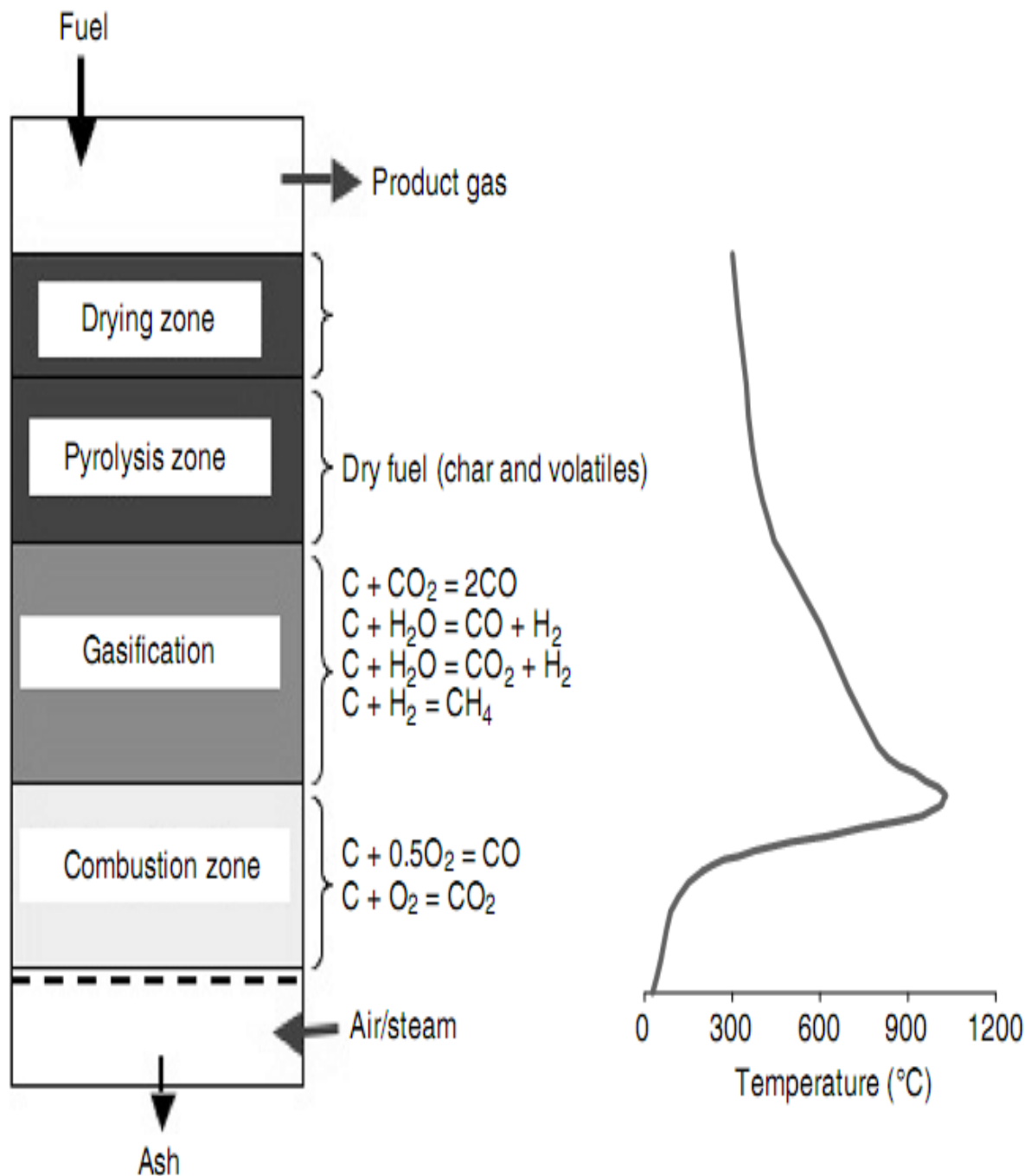


Figure 7.2 Arrangement of reaction zones in an updraft gasifier
 (Source: Biomass gasification and pyrolysis, Prabir Basu, page-131)

Downdraft gasifier reactor:

The reaction zones of downdraft gasifier are different than updraft gasifier. In downdraft gasifier, air (or steam and oxygen) is fed through lower section of the gasifier (Fig. 7.3). The pyrolysis and combustion products flow downward as shown in the Fig. 7.3. The hot gas moves downward

over the remaining hot char, where gasification takes place. The generation of heat and exchange amongst the zones also takes place in downdraft design similar way as discussed in the case of updraft design above. However, the sequence is different as the relative directions of flow of gas streams are different as shown in the Fig. 7.3. The temperature profile and reactions of the different zones are also shown in the Fig. 7.3.

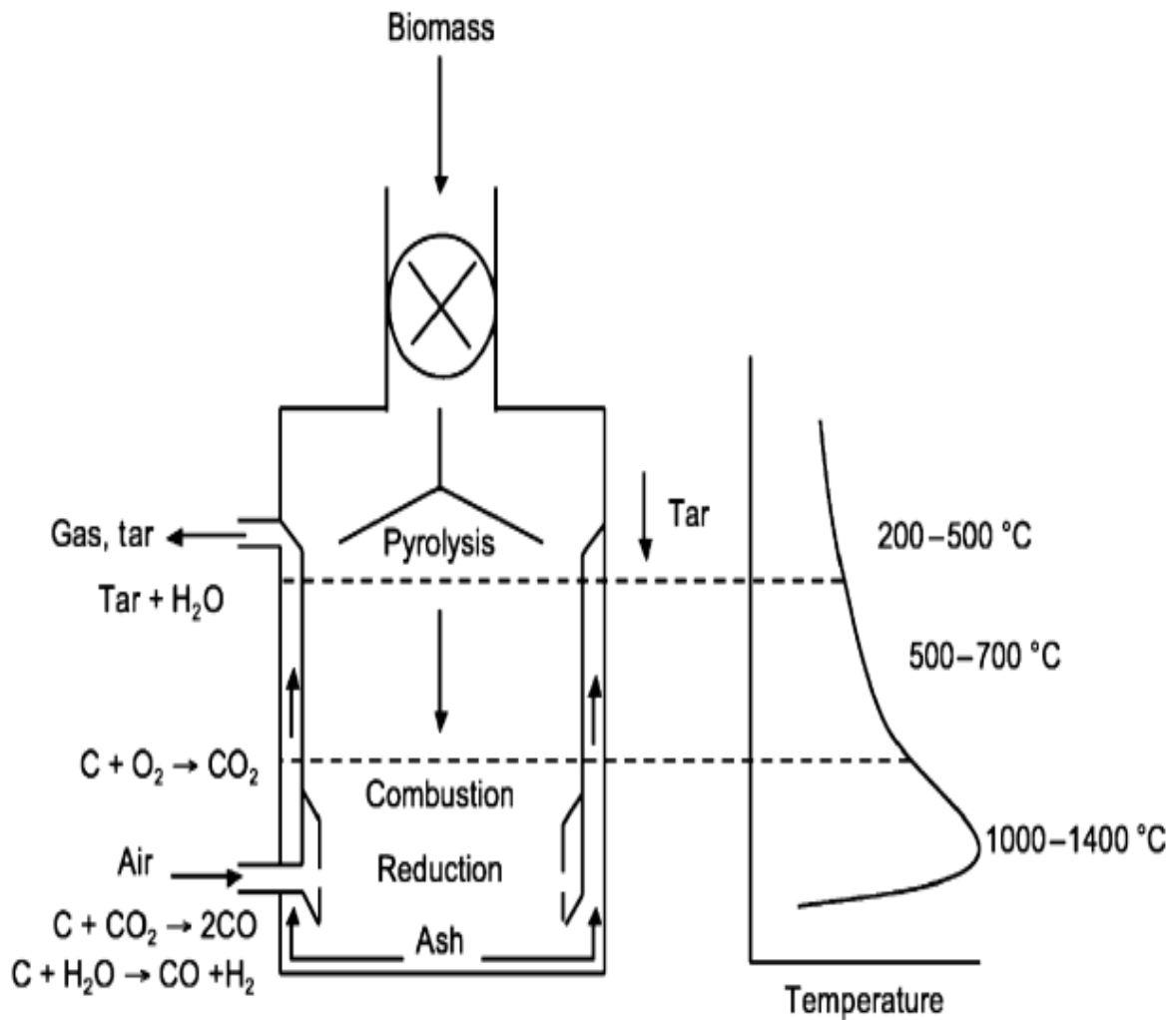


Fig. 7.3 Gasification reactions in a downdraft gasifier

(source: Adopted from book Biomass gasification and pyrolysis, Prabir Basu, page-132)

Some typical down draft gasifier reactors:

Downdraft reactors are advantageous because this type of reactor generates relatively less tar than the updraft gasifier. There are several configurations of downdraft gasifier reactors. Four typical classes are (i) open top configuration, (ii) closed top configuration without throat (iii) closed top configuration with throat and (iv) staged-air-entry open-top system. The arrangements of different zones of all of these types are presented in Figs. 7.4a-d.

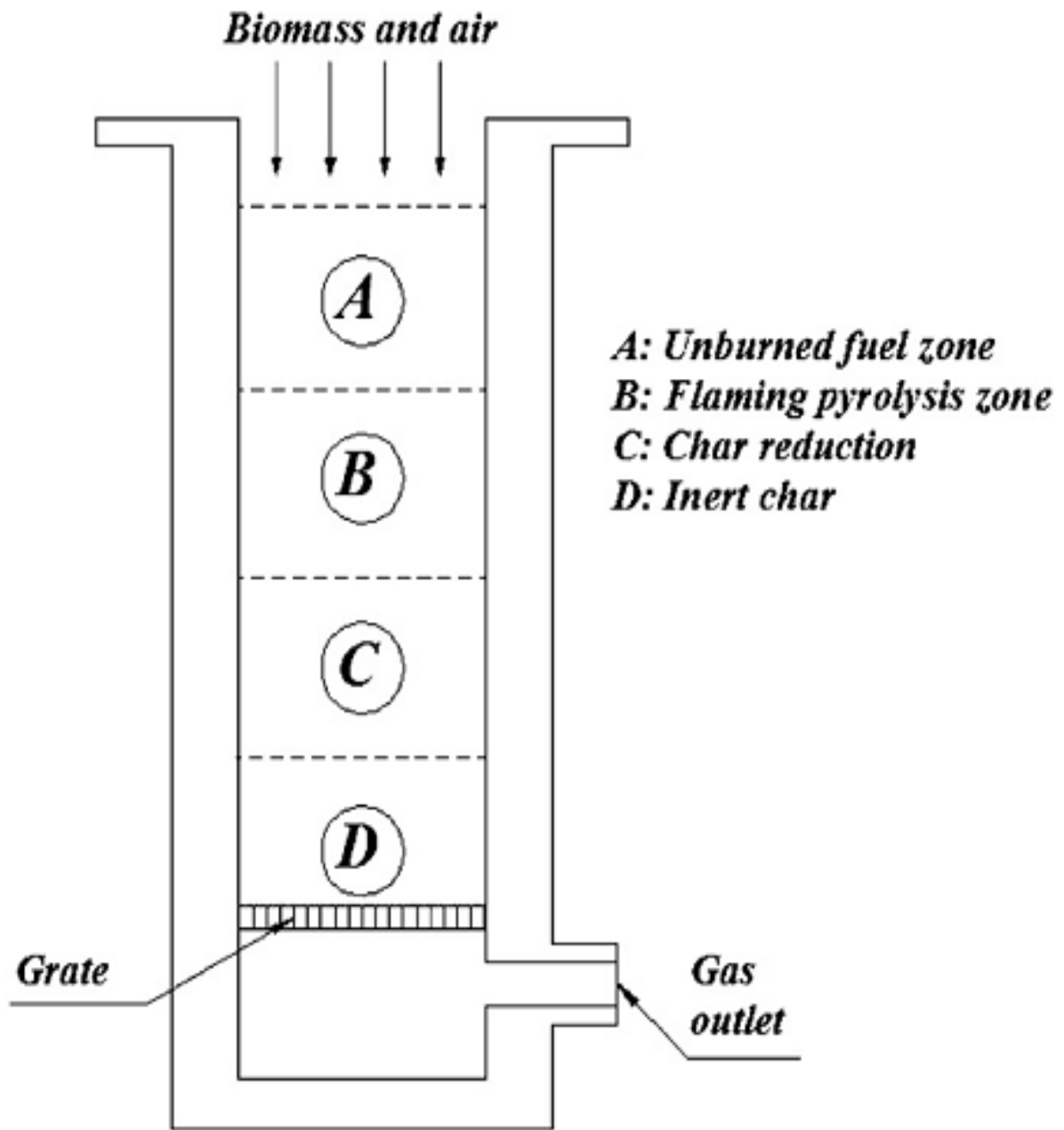


Fig. 7.4 a Downdraft gasifier with open top (source: Juan *et al*)

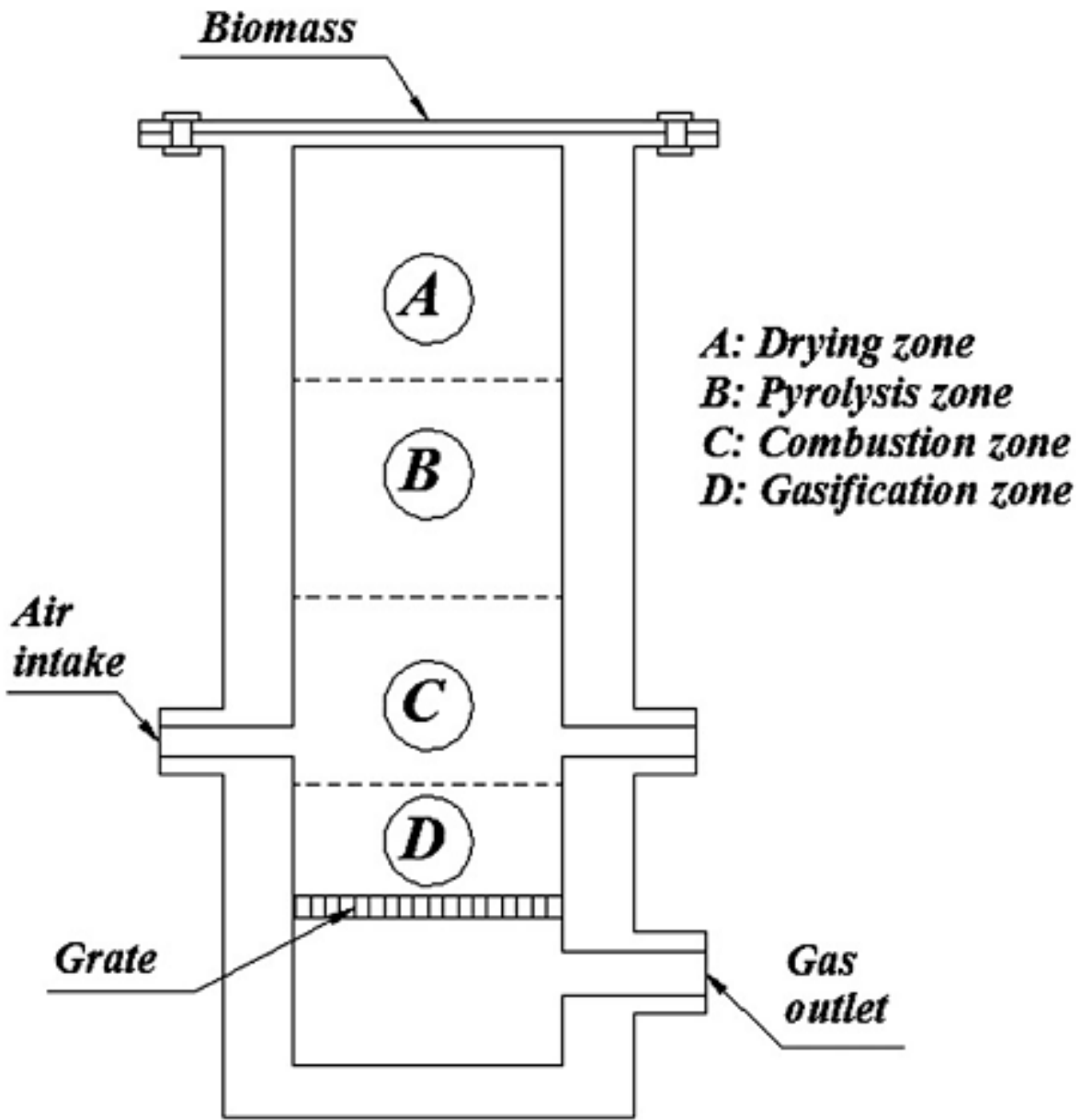


Fig. 7.4 b Downdraft gasifier with closed top (conventional design) (source: Juan *et al*)

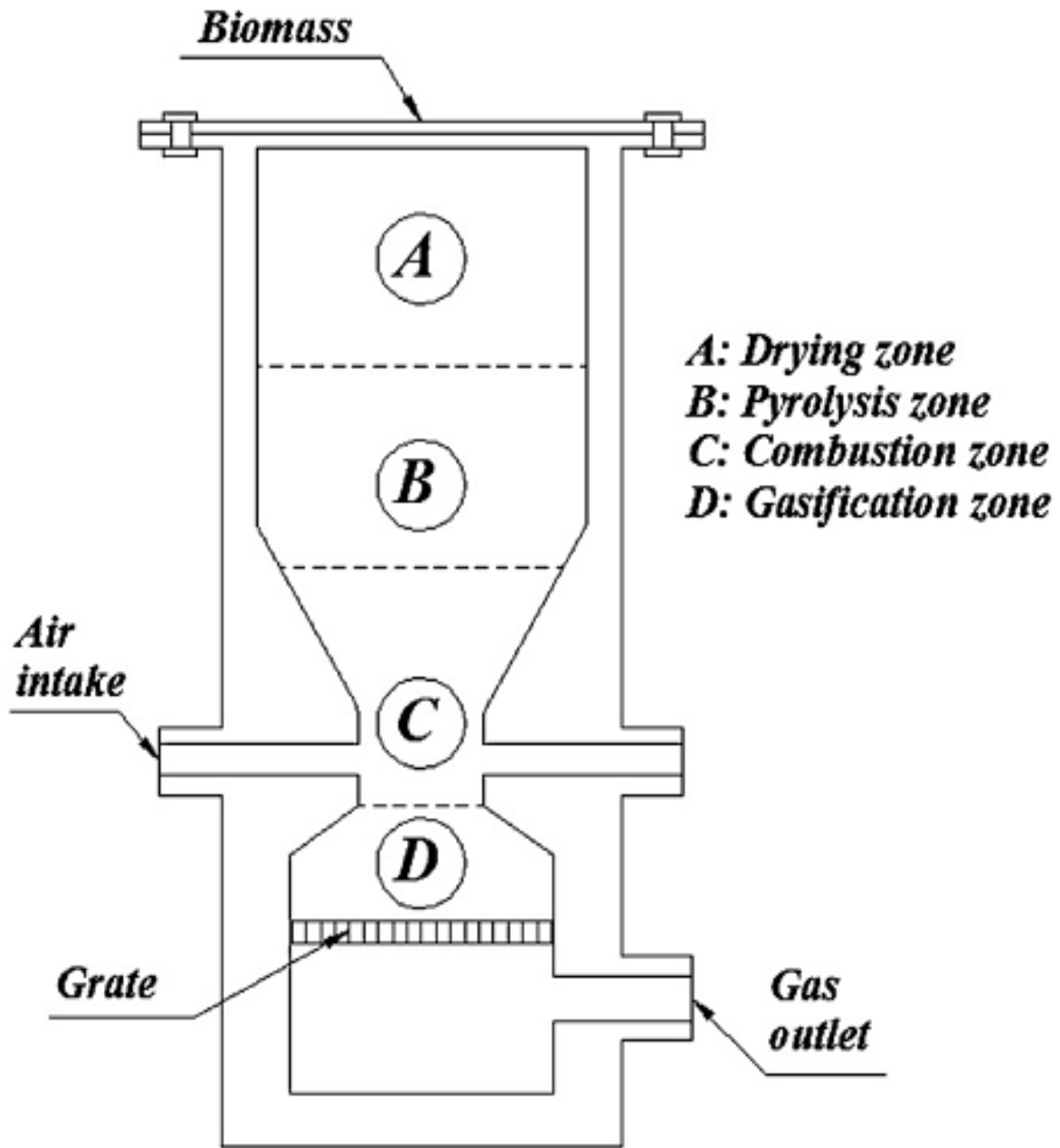


Fig. 7.4 c Downdraft gasifier with closed top (throated: Imbert gasifier) (source: Juan *et al*)

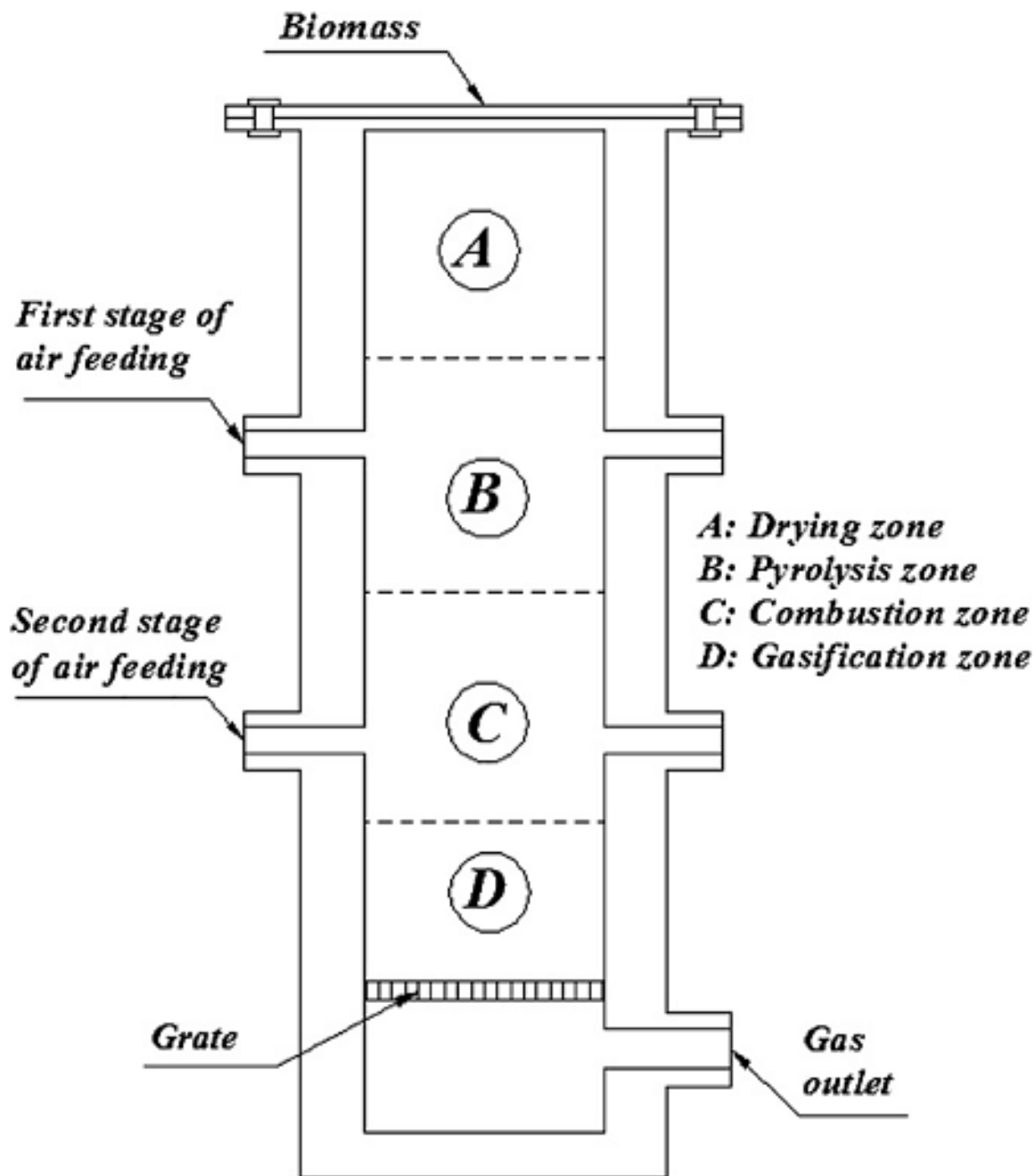


Fig. 7.4 d Downdraft gasifier with double stage air supply (source: Juan *et al*)

Cross draft Gasifier:

A typical arrangement of a crossdraft gasifier (also known as side draft) is shown in Fig. 7.5. It is a co-current moving-bed reactor, in which the fuel is fed from the top and air is injected through a nozzle as shown in Fig. 7.5. It is primarily used for gasification of charcoal with very low ash

content. It is also suitable for small scale biomass gasification units. In this type of reactor product gas is released from its side wall opposite to the entry point of the air for gasification.

Heat exchange amongst the zones of cross draft gasifier

Air (at relatively higher velocity) enters the gasifier through a nozzle set at a certain height above the grate. Excess oxygen in front of the nozzles facilitates combustion (oxidation) of part of the char, creating a very-high-temperature zone (more than 1500 °C). The remaining char is then

gasified to CO downstream in the next zone. The product gas exits from the opposite side of the gasifier. Heat from the combustion zone is conducted around the pyrolysis zone, so the fresh biomass is pyrolyzed while passing through it.

Some favourable features of cross draft gasifier:

One of its important features is a relatively small reaction zone with low thermal capacity, which gives a faster response time than that of any other moving-bed type. Moreover, startup time (5– 10 minutes) is much shorter than in downdraft and updraft units. These features allow a side

draft gasifier to respond well to load changes when used directly to run an engine (use of producer gas in engine is discussed later in this unit). Because its tar production is low (0.01– 0.1 g/Nm³), a crossdraft gasifier requires a relatively simple gas cleaning system (the need of gas

cleaning system for engine operation is also discussed later in this unit).

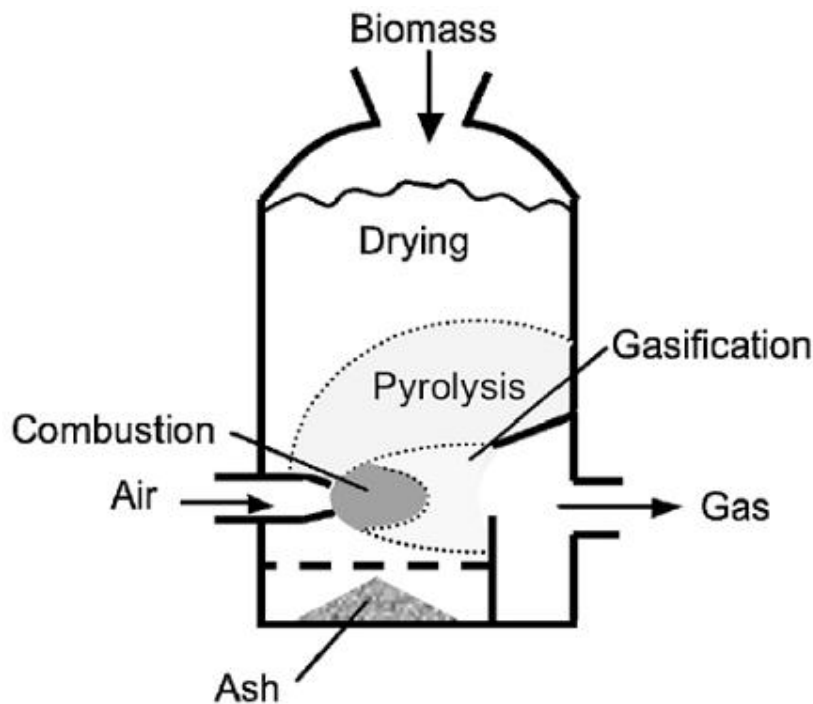


Fig. 7.5 Arrangement of a crossdraft gasifier
(source: Biomass gasification and pyrolysis, Prabir Basu)

Fluidized-Bed Reactor:

This is an improved version of gasifier to improve the performance *i.e.* increased conversion efficiency (energy output of gas per unit energy of input fuel is the overall thermal efficiency of the gasifier) and better gas quality (higher calorific value and lesser tar and other foreign matter

content is considered better gas quality) even with inferior quality of fuel (calorific value, density and size of fuel particle should be as per the requirements of the design).

Why do we need Fluidized-Bed Reactor

Regulation of temperature and mixing of the gases as per the requirements of the gasification chemistry have been the major challenges of gasifier design. We have already discussed several gasifier designs where feedstock (*i.e.* fuel) is provided inside the reactor and does not have

motion of its particles during reaction. Non-uniform temperature and inadequate mixing of gases are considered drawbacks of such gasifier design. Fluidized bed reactor is a design to address some of such challenges.

How does Fluidized-Bed Reactor work?

In this design fuel are made granular in size. The granular solids (fuel), called bed materials are kept in a semi-suspended condition (fluidized state) by the passage of the gasifying medium through them at the appropriate velocities (Fig. 7.6). Fluidized-bed gasifiers are reported to have excellent mixing and temperature uniformity.

Features of Fluidized-Bed Reactor:

The temperature uniformity greatly reduces the risk of fuel agglomeration (fuel agglomeration is a specific problem where fuel undergoing undesirable higher temperature at certain points can melt and solidify when passing through colder zone. Some of the fuels are more susceptible to this problem due their chemical composition and physical nature, therefore, are considered not suitable for conventional design of gasifier). Therefore, relatively poor quality of fuel can also be used with this reactor. The fluidized-bed design is advantageous for gasification of loose

biomass. Its tar production lies between 50 g/Nm³ (that for updraft) and 1 g/Nm³ (downdraft gasifiers), with an average value of around 10 g/Nm³.

Types of Fluidized-Bed Gasifier:

There are different types of fluidized bed gasifiers available. (i) Bubbling Fluidized-Bed Gasifier and (ii) Circulating fluidized bed Gasifier are two commonly used designs. The mode of fluidization is varied to achieve better performance depending upon the nature of the fuel. Schematic diagram of these two types of designs are provided in Figs. 7.6a and b. In a bubbling fluidized bed (Fig. 7.6a), the fuel fed from either the top or the sides mixes relatively fast over the whole body of the fluid bed. The gasifying medium (air, oxygen, steam, or their mixture) also serves as the fluidizing gas and so is sent through the bottom of the reactor. In a typical fluidized-bed gasifier, fresh solid fuel particles are brought into contact with hot bed solids that quickly heat the particles to the bed temperature and make them undergo rapid drying

and pyrolysis, producing char and gases. In a circulating fluidized bed (Fig. 7.6b), fuel circulate around a loop where intense mixing and longer solid residence time are achieved within its solid (fuel) circulation loop. The absence of any bubbles avoids the gas-bypassing problem of bubbling fluidized beds (gas-bypassing is a problem of Bubbling Fluidized-Bed Gasifier).

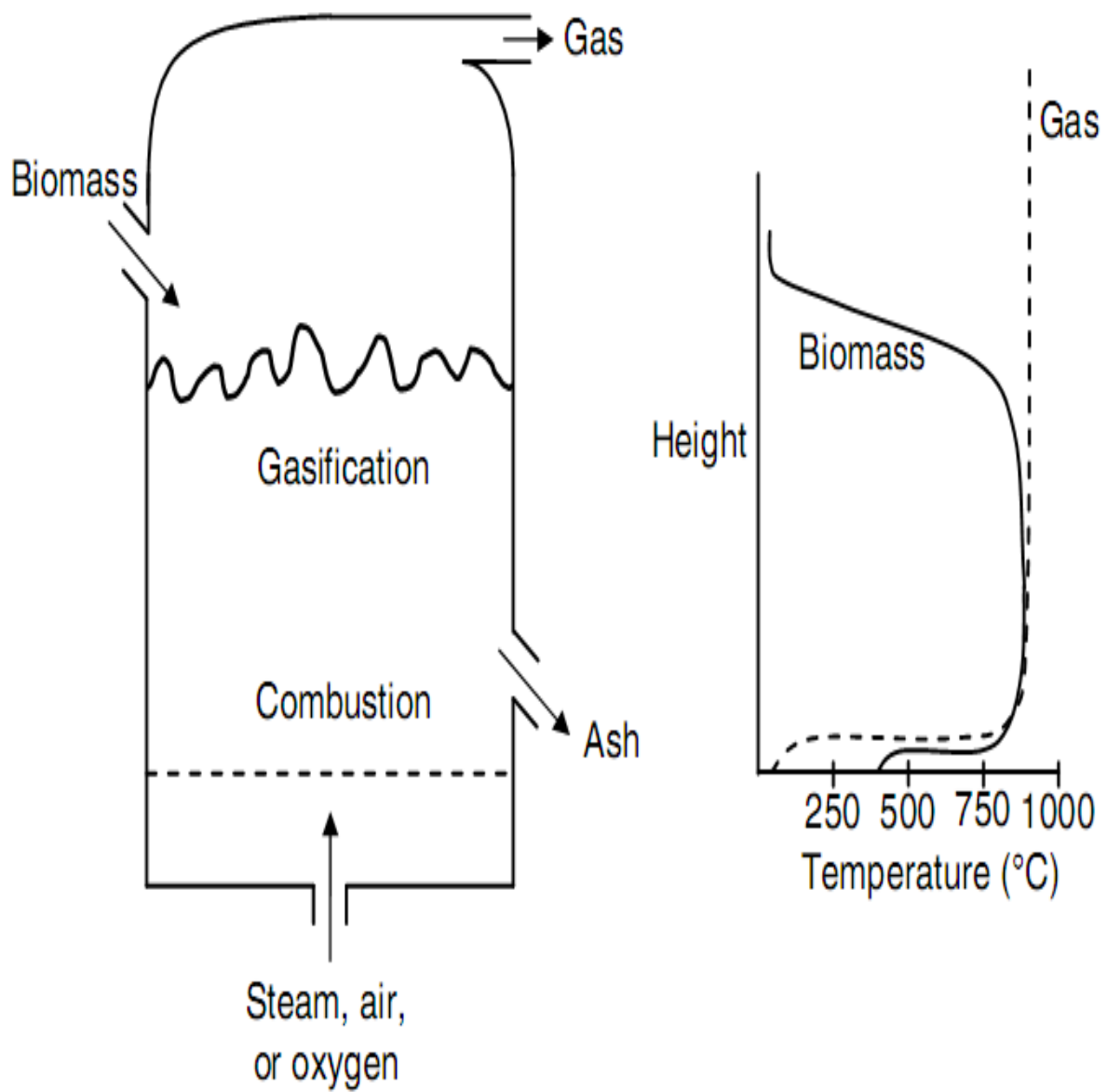


Fig. 7.6a Bubbling Fluidized-bed Gasifier (Source: Higman and van der Burgt, 2008, p. 106.)

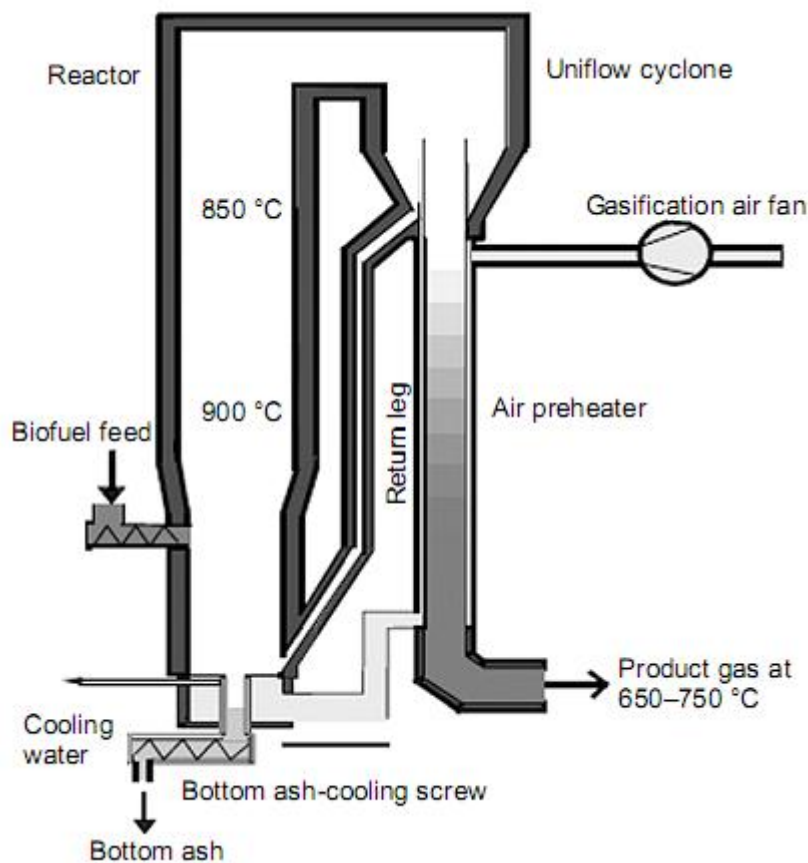


Fig 7.6b Circulating Fluidized-bed Gasifier (Source: Foster Wheeler)

7.6 THE UTILITIES OF PRODUCER GAS

Till now, we have discussed about the gasification reactions and gasifier reactors used for generation of producer gas. The utilization of producer gas has not been discussed yet. Evidences of use of producer gas for thermal (heat) and mechanical (engine) power generation are not new.

However, as indicated at the beginning of this unit, the biomass generated producer gas has got renewed attention due to problems associated with fossil based energy system. Uses of producer gas can be classified into two broad classes, viz., (i) production of chemicals and (ii) generation of energy. The content of this unit is focused on the energy aspect. There are again three specific energy applications. These are (i) thermal, (ii) mechanical and (iii) electrical. These are highlighted below.

Thermal applications of producer gas:

We know that LPG, natural gas etc are used for cooking, drying etc as source of thermal energy. It is found that burning producer gas is similar to the burning of liquefied petroleum gas (LPG) or natural gas. Therefore, producer gas can be used as a substitute of LPG for cooking and similar applications.

Burning characteristics of producer gas and flame temperature:

We have discussed earlier details about the combustion of fuel. Producer gas is a gaseous fuel having CO and H₂ as major constituent (LPG and natural gas has other constituent). Air (or oxygen) requirement for complete combustion (i.e. oxidation) depends upon the nature of the constituents. Similarly, the maximum flame temperature generated during burning also depends upon the composition. Stoichiometric air fuel ratio and flame temperature for some common fuel gases are provided in Box 7.10.

Box 7.10

Stoichiometric air fuel ratio and flame temperature for some common fuel gases
(source: Understanding Clean Energy and Fuels From Biomass, Mukunda, H S)

Item	Stoichiometric air-fuel ratio		Flame temperature, K
	Mass basis	Volume basis	
Natural gas-air	17	10	2300
Natural gas-oxygen	4	2	3500
Biogas (60% CH ₄)-air	10	8	2100
LPG-air	15	5	2300
Producer gas-air	1.2-1.4 (both mass and volume)		1900-2100
Producer gas-oxygen	0.3-0.4 (both mass and volume)		2800-3000

Producer gas is composed of CO that has oxygen in it. Hence the value of stoichiometric ratio for producer gas is lower. Due to its lower calorific value, producer gas is not a suitable option for higher temperature demanding situations like in glass melting furnaces (need nearly 2000 K).

However, with suitable modifications to generate higher flow rates of producer gas, it can be used in such conditions also. The only technical issue that may be flagged with regard to the use of producer gas is safety because the gas has a significant fraction of CO. This also can be addressed through the use of CO monitors and additives to cause a smell when producer gas leaks as it is done for LPG. It is also seen from the Box 7.10 that higher flame temperature can be achieved, if burning can be done in oxygen environment instead of air – which is true for all

the gaseous fuel shown in the Box.

Use of producer gas for mechanical and electrical power:

We know that internal combustion engine which are run either on diesel (CI: compression ignition) or petrol (SI: spark ignition) used for mechanical power generation to do shaft work. Moreover, the shaft power is also used for generation of electrical power through generator. Now-a-days people are also attempted to use producer gas as feedstock for fuel cell. These aspects are detailed below.

Use of producer gas in diesel engine:

Conventional diesel engine uses liquid diesel fuel. Such diesel engine varying in sizes and specification are available in market. Some features of commercially available diesel engine are provided in Box. 7.11.

Box 7.11:

Some technical facts of diesel engine

Number of cylinder and CR of diesel engine:

Diesel engines have variations in terms of number of cylinders and also in terms of compression ratio (CR). We know that CR is an important parameter which affects the performance of diesel engine performance. Most small power diesel engines are multi-cylinder direct injections with CR between 15 and 21 (most common CR is about 17).

Sizes and efficiency of diesel engine:

Engines of 3.7 to 60 kWe are available in naturally aspirated mode; those with power levels from 60 to 150 kWe on both naturally aspirated and turbo-supercharger mode; and beyond 150 kWe most usually in turbosupercharger mode. Use of turbo-supercharger will increase the power output on the same basic frame. Most small diesel engines generate electricity at 230 to 270 g/kWh at power levels less than 150 kWe. These correspond to diesel-to-electricity efficiencies of 30% to 35%. Even small engines provide the efficiencies of 25%.

Scope of supplementing biomass generated producer gas for diesel engine:

The only issue is that the cost of diesel has gone high and so cost of electricity per unit. That is the reason, operating on duel fuel mode becomes an attraction if the industry/institution is being serviced by diesel electricity solely substantially since biomass in off-city areas may be available at price that make duel fuel operations economically attractive.

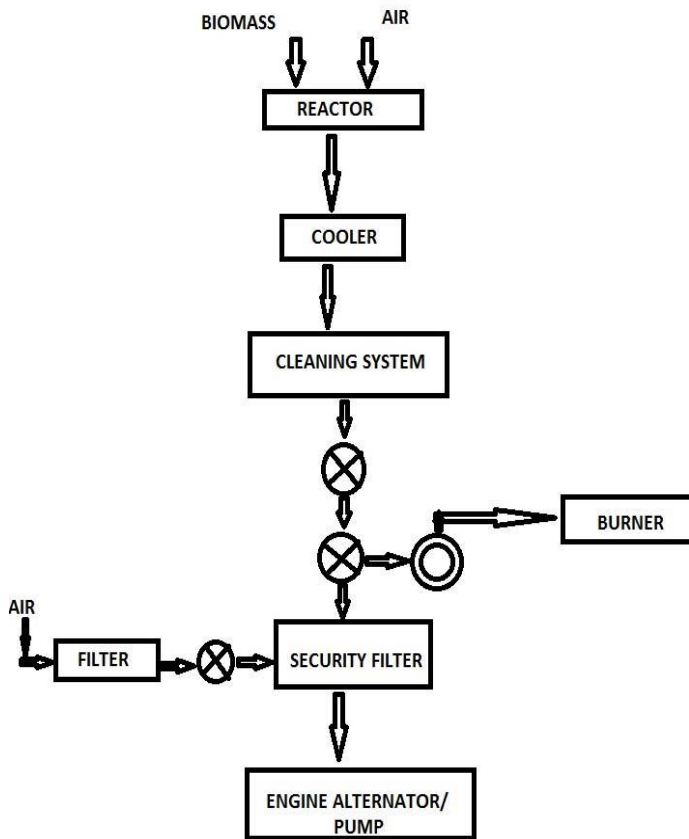


Fig. 7.7 A scheme of gasifier-engine for dual-fuel operation

A gasifier can be coupled with a diesel engine as shown in Fig. 7.7 for running under dual fuel mode (diesel and producer gas). The producer gas coming out of the gasifier should be properly monitored to check (i) cooling, (ii) cleaning and (iii) composition before allowing to enter into

the diesel engine. The operation of dual fuel engine using producer gas is briefly highlighted below.

The engine air inlet is connected to a piping that draws air (from atmosphere) and gas (from gasifier passed through cooler and cleaner). Piping is provided with filters and control valves. To begin with, the gasifier operation is stabilized with the gas going to a flare (or a burner).

Oxygen fraction in the producer gas outlet should be below 1% for engine application. The engine is started in diesel mode during which period the control valve from the air filter only kept open. After both engine and gasifier operations are normal, the flare (or burner) line from the gasifier is closed and the control valve to the engine is opened. The engine will draw both air and gas depending on the relative resistances. Since the resistance from the gas line is larger, it will begin to draw small amount of gas. At this stage, the control valve on the air line can be turned down slowly. This will enable more gas to be drawn into the engine. It is also known that dual-fueling will make the engine more quietly and this transition to dual fuel mode is very distinct. The engine can then loaded suitably. By reducing the air flowing into the engine, the proportion of power from the gas can be enhanced. It is reported that using dry wood and proper conduct of gasifier operations, diesel replacements up to 85% (at around 80% of the rated load) in engines could be achieved.

Use of producer gas in gas engines:

The producer gas can also be used in gas engine as used for natural gas. These are spark ignition engine and proper mixture of air with fuel is critical for trouble free operation. Mixing valve with appropriate control is provided to take care of optimum air fuel ratio. As discussed earlier,

cooling of producer gas (as the gas temperature at the outlet of the gasifier remains high) is very essential for engine application. Moreover, the cleaning is also another essential aspect to ensure successful operation in engine.

Use of producer gas in Gas turbine:

Producer gas can be used in gas turbines to generate electricity. Gas turbines operate generally on gaseous fuels like natural gas and liquid fuels like kerosene, alcohols or diesel. Air from the ambient is drawn into the rotating compressor, compressed to the desired pressure which is

typically 5 to 10 atmosphere in the case of small power systems and delivered to the combustion chamber. Fuel is injected at high pressure into the combustion chamber.

Use of producer gas in Fuel cells:

Fuel cells are electro chemical cells. They perform the function which is reverse of electrolysis where if one pumps electricity, one decomposes the fluid, say water into hydrogen and oxygen. If one pumps hydrogen and oxygen into a fuel cell that breaks these into ions, they combine to

produce water. Since they need to move between electrodes, the movement the of charge between electrodes creates electric current. Unlike thermal engines, fuel cells can operate at a fixed temperature. The high-temperature fuel cells can accept a combination of fuels including

producer gas. When methane is used it is passed through a reformer to produce CO-H₂ mixture to enable use in fuel cells. The possibility of using producer gas in fuel cells (like Solid Oxide Fuel Cell – SFOC, and Molten Carbonate Fuel Cell – MCFC) is realistic technically, but it is

difficult to conceive of economically meaningful possibilities except in niche applications.

7.7 QUESTIONS:

Q1. Why biomass is getting attention as a source of energy? Write about the major processes of biomass to energy conversion? 10

Q2. Combustion is essentially an oxidation process takes place under certain conditions. Discuss the above statement describing the requirements of the combustion process? 10

Q3. Is it true that nitrogen present in air affects inevitable evil of combustion process? Justify your answer. 5

Q4. Biomass combustion takes place in certain stages. Explain the statement indicating the temperature profile of the stages. 5

Q5. What are the major constituents of biomass fuel? List the chemical reactions involved in combustion of these constituents?

Q6. What do you mean by Stoichiometric air fuel ratio? What are the practical limitations of achieving complete combustion at stoichiometric air fuel ratio? What is the purpose of providing excess air for biomass combustion? 10

Q7. Calculate stoichiometric air requirement for burning a biomass sample having 65% carbon, 10% hydrogen and 15% oxygen by mass. Also determine the mass of air required if 10% excess air is supplied for combustion. 10

Q8. What is the purpose of biomass carbonization? What should be the desirable properties of biomass for carbonization? Describe a typical carbonization process. 10

Q9. What do you mean by yield of carbonization? Is the information on yield is sufficient to judge the quality of carbonization product? Substantiate your answer. 10

Q10. What are major products of a typical carbonization process? Does the temperature of carbonization chamber affect the end product? Substantiate your answer. 10

Q11. Describe two commercial methods of charcoal production. 10

Q12. What is biomass gasification? How does gasification differ from combustion? Mention the major constituents of a biomass gasification reaction. 10

Q13. What are the medium used for biomass gasification? Do you believe that calorific value of producer gas depends upon the gasifier medium? Substantiate your answer. 10

Q14. With the help of neat sketch describe the gasification process indicating the different steps involved in it. 10

Q15. Entire gasification can be expressed in terms of 14 reactions. Discuss. 15

Q16. Do you believe that quality of biomass feedstock affect the performance of gasification? Substantiate your answer. 10

Q17. Char gasification is an important step of gasification process. Explain. 5

Q18. With the help of neat sketch describe the different types of gasifier reactors used for biomass gasification. 25

Q19. How does the working of fluidized bed gasifier reactor different form the fixed bed reactor? 5

Q20. What are the major applications of producer gas? Discuss the technologies used for each of the applications. 20

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UNIT STRUCTURE

8.0 INTRODUCTION

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8.0 INTRODUCTION

Currently, the total biomass of 421×10^6 tonnes from the world's forests is distributed over a total area of 3869 Mha; 95% of this is in natural forest and 5% in plantation forest [1].

Terrestrial biomass, both from wood and non-wood sources, has been used as a source of energy for cooking, heating and other purposes since prehistoric time. Bioenergy from accounts for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries, besides being the source of more than 90% of the total rural energy supplies in some developing countries [2]. However, the extent of use of biomass energy both in traditional and modern ways varies geographically depending upon (i) availability and types of biomass resources, (ii) access to other form of energy, (iii) technological status and (iv) socio-economic condition. Although the contribution of biomass to overall energy consumption is much lesser in developed countries than the developing ones, the use of biomass as modern energy source has been re-emphasized all over the world mainly due to (i) fast depletion of convention fuels, (ii) rising price of petroleum and (iii) environmental consequences of fossil fuels. There are certain advantages of biomass over other forms of renewable energy which includes carbon neutral nature, widespread distribution, use of by-products for range of applications including pharmaceutical, chemicals, fibres, catalysts.

Taking into account illegal and unrecorded fuelwood collections, fuel-wood consumption in India is estimated at about 380 million cubic MT[3]. The consumption of fuel-wood in India is about five times higher than sustainable level. Fuel-wood meets about 40% energy needs of the country in India. About 70% of the fuel-wood consumption is accounted for by households and the rest is by commercial and industrial units. Fuelwood alone accounts for more than 60% of the total fuel consumption in the rural areas.

8.1 OVERVIEW OF ENERGY PLANTATION

Biomass has to play a crucial role to attain energy security by utilizing renewable resources and by minimize dependency on fossil fuels,. However, large production of biomass energy could be achieved only if certain species of fast growing, high energy yielding plants are grown at large scale. Energy plantation means growing select species of

trees and shrubs, specifically meant for fuel. The essential characteristics of this would be to be harvestable in a comparably shorter time.. Fuel from these can be either directly used in burning stoves or boilers or processed into methanol, ethanol and producer gas. Biomass derived from short rotation high density energy plantation (HDEP) can be used in the same ways as wood waste. General advantages of wood derived from HDEP are: they are largely sulphur free, renewable, non polluting, high yield and low impact per unit of land, and show a quick return on investment [3]. Above all their production and use will be carbon neutral and will not adversely affect the global CO₂ balance. Some of the attractive features of energy plantations, for example, woody energy crops are:

- (i) Thermal equivalent of wood is similar to that of low grade coal
- (ii) sulphur content is low,
- (iii) ash from burnt wood is a valuable fertilizer,
- (iv) utilization of erosion prone land for raising these plantations helps to reduce wind and water erosion, thereby minimizing hazards from floods, siltation, and loss of nitrogen and minerals from soil,
- (v) help in rural employment generation, and
- (vi) selection of multipurpose species provides a number of by-products like oils, organic compounds, fruits, edible leaves, forage for livestock, etc.

Energy crops currently contribute a relatively small proportion to the total energy produced from biomass each year, but the proportion is set to grow over the next few decades. Some estimates have suggested a technical potential for energy crops of approx. 400 EJ per year by 2050. However, a new analysis based on energy crop areas for each of the IPCC SRES scenarios in 2025, more conservative dry matter and energy yield estimates and an assessment of the impact on non-CO₂ greenhouse gases estimates the realistically achievable potential for energy crops by 2025 is between 2 and 22 EJ per year [4].

Energy crops can take many forms and can be converted to a number of different products. Many crop species are multipurpose in that they can be used to produce more than

one type of energy product, for example, hemp (both oil and solid biomass) and cereals (ethanol and solid biomass from straw). Some of the more common energy crops are listed below [4].

(i) Oil crops: (e.g. oilseed rape, linseed, field mustard, hemp, sunflower, safflower, castor oil, olive, palm, coconut and groundnut). Vegetable oils can be used directly as heating fuels or refined to transport biofuels such as biodiesel esters.

(ii) Cereals: (e.g. barley, wheat, oats, maize and rye): The grain can be used to produce ethanol and the straw can be used as a solid fuel. They can also be grown and harvested as a whole crop (grain plus straw) before the grain has ripened and used as a solid fuel or for biogas production feedstock.

(iii) Starch and sugar crops (e.g. potato, sugar beet, Jerusalem artichoke and sugarcane): Ethanol can be produced from the starch and glucose by fermentation then used directly as a fuel, as in Brazil, or more normally in blends with gasoline.

(iv) Cellulose crops (e.g. straw, wood, short rotation coppice (SRC), etc.): The hemicellulose can be reduced to sugar by acid or enzymatic hydrolysis and then fermented to produce ethanol.

(v) Solid energy crops (e.g. cardoon, sorghum, kenaf, prickly pear, whole crop maize, reed canary grass, miscanthus and SRC willow, poplar and eucalyptus): These crops can be utilized whole to produce heat and electricity directly through combustion or indirectly through conversion for use as biofuels like methanol and ethanol.

8.1.1 ENERGY PLANTATION IN INDIA

Recently, energy plantation has got much boost in India also. Government of India has started many plans, for example, social forestry, silviculture, agro-horticulture practices, and afforestation in waste lands. Afforestation and forest management systems will have to be developed to get maximum biomass,. These must include social forestry, silviculture (short-rotation forestry) tree-use systems, coppicing system, drought, salt-tolerant, pollutant - resistant plantations and high density energy plantations (HDEP).

8.1.2. ENERGY PLANTATION THROUGH SOCIAL FORESTRY

Plantation through social forestry is attractive option to meet the demand of fuel and fodder in the rural areas. It will certainly decrease the gradually increasing pressure on the forests. This includes planting trees along road sides, canals, railway lines and waste lands in villages. Some of important plants are: *Acacia nilotica*, *Albizia lebbek*, *A. procera*, *Anthocephalus chinensis*, *Azadirachta indica*, *Bauhinia variegata*, *Butea monosperma*, *Cassia fistula*, *Dalbergia sissoo*, *Eucalyptus globulus*, *E. citriodora*, *Ficus glomerata*, *Lagerstroemia speciosa*, *Madhuca indica*, *Morus alba*, *Populus ciliata*, *P. nigra*, *Terminalia arjuna*, *Toona ciliata*, *Salix alba* and *S. tetrasperma*.

8.1.3 ENERGY PLANTATION THROUGH SILVICULTURE ENERGY FARMS (SHORT ROTATION FORESTRY)

Silviculture energy farms employ techniques more similar to agriculture than forestry. The chief objective is to produce biomass from the selected trees and shrub species in the shortest possible time (generally 5-10 yrs) and at the minimal cost, so as to satisfy energy needs.

Eucalyptus tereticornis has been planted in India in almost every state for large scale afforestation and plantation programmes both to cover denuded and barren areas as well as for converting poor or derelict forest growth into fast growing monocultures of high productivity [5]. Of the several species/varieties of *Eucalyptus* so far tried in India, *E. tereticornis* hybrid stands out as the most outstanding species for the afforestation purposes. The following characteristics of the tree have contributed to its popularity under Indian conditions:

- (i) It is a fast growing species capable of quickly outgrowing weeds and grass in afforestation areas, due to its indefinite shoots and naked buds.
- (ii) It has the ability to adapt to a wide range of edaphic and climatic conditions and can grow in degraded soils, barren denuded areas and even on the soils of deficient nutrient status.
- (iii) It coppices very well and produce vigorous shoots increasing the yield up to 1.5 times at coppice rotation.

(iv) It is fire hardy and browse resistant and even capable of surviving severe drought conditions.

(v) The tree as such has good end use. The wood is used mainly for rayon grade pulp and paper pulp and also used as firewood having high calorific value of 4800 cal/g [6]. Dry fallen leaves are also used as source of fuel.

Amongst the countries in South America, Africa and Asia, India is the one with the largest potential for *Jatropha*. India has taken the *Jatropha* plantation scheme to the highest level of national discussions with a large number and variety of institutions already involved in the pilot scale experiments of *Jatropha* for biodiesel production [3]. Further, with one third of the agricultural lands degraded and another 50 to 150 million Ha of wastelands that are underused and degraded due to overuse, deforestation, drought and erosion, technically the land area available for *Jatropha* is high. *Jatropha curcas* (*physic nut*) is a quick maturing plant species that starts bearing fruits within a year of its planting and following the extraction and transesterification the oil can be blended with petroleum diesel for use. *Jatropha* can exist upto age of 40–50 years. The oilseed crop in good conditions rises from 0.75 tonnes/ha in the first year to a maximum of 12.5 t/ha after 5 years, being proportionately less in poor conditions.

It is a very hardy plant and grows in a wide variety of agro-climatic conditions from arid (200 mm of rainfall) to high rainfall areas and on lands with thin soil cover to good lands. It is also not browsed by cattle and so its plantation can be easily under taken in the farmers' fields and their boundaries, understocked forests, public lands and denuded lands facing increasing degradation. Its planting, seed collection, oil extraction etc. will create employment opportunities for a large number of people, particularly the tribal people of central India and the poor, and will help rehabilitate unproductive and wastelands and save precious foreign exchange by substituting for imported crude.

8.1.4. DESIGNING ENERGY PLANTATION

While designing energy plantations, focus should be on to capture maximum of

sunlight energy and hence increasing the productivity of the ecosystems. The main emphasis in these techniques is to introduce fast growing species combined with short rotation thus harvesting more solar energy. Energy fixation in forest crops can be optimized as follows [7]:

8.1.4.1. CANOPY MODELING FOR MULTI-STOREYED PLANTATIONS:

One of the concepts for improving the energy fixation efficiency by forest plants is development of multi-storeyed plantations. Such plantations consist of different species at different heights, which may differentially intercept solar radiation at different times of the day, thus reducing the competition for sunlight. Such multi-storeyed structures would intercept maximum amount of solar radiation by their leaves which obviously will result in more dry matter production per unit area. Investigation carried out in some *Pinus roxburghii* plantations ("Open bunch" canopy) revealed that during the course of 50 years two other species of trees developed under the plantations naturally. Thus such plantations consist of three clearly distinguishable structures. They are, top structure of *Pinus roxburghii* with "open bunch" canopy, middle structure of *Michelia champaca* with "column canopy" and a lower structure of *Cinnamomum camphora* with "Umbrella" shaped canopy.

8.1.4.2. HIGH DENSITY ENERGY PLANTATION (HDEP)

This concept is based on the principle that yield of dry production, in certain fast growing species of forest crops, is independent of spacing during the first few years of growth. This method would also help in rapid closure of canopy at a very early stage, resulting in more dry matter production per unit area. A Number of species like *Acacia nilotica*, *Acacia tortilis*, *Albizia lebbek*, *Cassia siamea*, *Casuarina equisetifolia*, *Eucalyptus spp.*, *Leucaena leucocaecephala*, *Prosopis juliflora*, *Sesbania grandiflora* are capable of producing very high yield when planted at the rate of 10,000 plants/ha.

8.1.5. MANAGEMENT OF ENERGY PLANTATION

Management of energy plantation can be achieved through following measure [7].

(i) Determination of the optimum rotation is very critical, because the production drops rapidly mainly due to development of competition between individuals once the optimum age has reached.

(ii) The maximum growth at close spacing tends to concentrate on the stem. Stand density is therefore the best means available to the forester for regulating growth and yield of the fuel wood.

(iii) There is a positive relation between leaf production and plant biomass production. The net increased photosynthetic leaf surface increases the efficiency of capturing solar energy, and this leads to increase in dry weight productivity.

(iv) Control of crown size and shape by pruning and singling of stems results in redistribution of growth on the stem, and thus stem form and taper can be altered. Trees can, thus, be stimulated to greater growth and controlled to grow in a more desirable way.

(v) Effectiveness of leaves for photosynthesis varies with the age of branches and their position on the crown.

(vi) Energy plantations of single species, race or clone at a time, therefore, are exposed to a greater risk of disease and insect susceptibility and hence damage. It is, therefore, necessary to use disease resistant species or mixture of clones in energy plantations.

8.2. BASIS OF SELECTING THE PLANTS FOR ENERGY PLANTATION

Burley, 1978 [8] reported some criteria while selecting plants energy plantation. These are given below.

(i) High Specific Gravity: Combining specific gravity with volume gives dry-weight yield per unit area; probably the most important single criterion for fuelwood quality. When making

initial estimates, it should be noted that specific gravity in fast growing short rotation crops would be different from that in mature or over-mature stands.

(ii) High Calorific Value of Wood: Calorific value is inversely proportional to the moisture of the wood and directly related with its content of extractives. Where there is fuel wood famine, plantation fuelwood is likely to be burnt soon after harvesting and the calorific value of the green wood will be more important than calorific value of the dry wood. Where there is an opportunity to dry the wood before its use, natural durability during the drying period will be of importance.

(iii) Strong coppicing ability: It will reduce the cost of establishment over a number of rotations.

(iv) Short rotation cycle between planting and harvesting (not exceeding ten years)

(v) Adaptation to variable microclimates

(vi) Local Acceptability: Trees free of thorns are easier to handle and transport; wood that burns without excessive sparking and odour is more agreeable to use. Species that will provide additional products or services, such as food, fodder, shelter and soil amelioration or protection should be given preference.

8.2.1. IDENTIFICATION OF SUITABLE TREE SPECIES FOR ENERGY PLANTATION IN NORTH-EAST INDIA

Although the north-eastern Himalayan region comprising of eight states is rich in flora and fauna but due to prevailing shifting cultivation and large scale deforestation due to various factors including heavy dependence on fuelwood for cooking, space heating, animal feed preparation by tribal communities, the region is experiencing severe ecological threats in the form of loss of forest cover. This has led to a blanket ban on tree felling by the Apex Court of India. Apart from that, there is lack of data about rural energy supply and consumption patterns, which is a shortcoming in rural energy planning (Bhatt and Sachan, 2004). Energy planners overlook this most essential energy use sector and planning priorities are usually met in favor of the industrial and agricultural sectors' commercial energy demand.

Keeping this fact in view, extensive farming for firewood could be the only alternative to bridge the gap between the demand and supply. The region has also a characteristic feature that the all most entire population belongs to the different tribal communities, and their traditional dependence on tree biomass for different purpose. Animal husbandry is closely linked with agricultural activities and pig, poultry, rabbit, goat, mithun, etc. are some of the important livestock reared by the tribes. Since food is also cooked for livestock reared by the tribes, the firewood consumption increases many fold compared to other parts of the country [Bhat *et al*, 2010].

In view of the above discussion, screening and exploration of various indigenous tree species for their fuel value evaluations are necessary to establish farming on energy plantation to avert the fuelwood crisis of the region. Recently, fuelwood characteristics of some indigenously grown tree species of North-East India have been investigated (Kataki *et al.*, 2001, 2002a; 2002b; Kataki & Konwer, 2007, Deka *et al.*, 2007; 2011; Bhatt *et al.*, 2010). The works on screening of fuelwood species of north-east India are summarized in the table ..

Table No 1: Fuelwood species and their calorific value and FVI

Sl. No.	Name of the fuelwood spp.	CV (KJ/g) on ash free dry wt basis	Fuelwood Value Index (FVI)
1	<i>A. auriculiformis</i>	20.44 ± 0.63	1851 ± 2.45
2	<i>A. nilotica</i>	19.67 ± 0.88 0	2089 ± 3.97
3	<i>A. excelsa Muell.</i>	16.85 ± 0.45	370 ± 1.12
4	<i>A. polycephala</i>	18.43 ± 0.75	554 ± 1.35
5	<i>A. assamicus</i>	17.63 ± 0.65	1008 ± 2.69
6	<i>A. chinensis</i>	18.95 ± 0.47	477 ± 1.10
7	<i>A. lebbeck</i>	19.02 ± 0.35	1329 ± 1.93
8	<i>A. procera</i>	18.84 ± 0.72	1793 ± 3.79
9	<i>A. nepalensis</i>	15.44 ± 0.44	780 ± 3.40
10	<i>C. seamea</i>	19.00 ± 0:70	1062 ± 2.49

11	<i>C. serrata</i>	20.36 ± 0.90	1050 ± 3.24
12	<i>E. umbellata</i>	21.91 ± 0.87	1082 ± 3.13
13	<i>G. robusta</i>	19.96 ± 0.86	742 ± 1:09
14	<i>L. parvi8ora</i>	13.90 ± 0.50	448 ± 1.67
15	<i>L. camara Linn.</i>	19.23 ± 0.60	516 ± 1.01
16	<i>L. polyantha</i>	17.53 ± 0.49	369 ± 1.79
17	<i>M. azedarach</i>	20.93 ± 0.39	968 ± 2.52
18	<i>P. kesiya</i>	19.23 ± 0.64	1308 ± 3.19
19	<i>P. wallichiana</i>	19.63 ± 0.42	560 ± 1.11
20	<i>P. ceredoides</i>	19.65 ± 0.45	760 ± 2.14
21	<i>Q. delbata</i>	19.89 ± 0.51	661 ± 3.11
22	<i>Q. glauca</i>	19.90 ± 0.70	725 ± 2.03
23	<i>Q. semicaprifolia</i>	19.50 ± 0.93	748 ± 2.79
24	<i>R. parviflora</i>	18.44 ± 0.70	370 ± 1.15
25	<i>S. tetrasperma</i>	20.11 ± 0.75	687 ± 2.10
26	<i>S. laurifolius</i>	19.85 ± 0.48	388 ± 1.20
27	<i>S. mukorossi</i>	21.04 ± 0.37	801 ± 1.55
28	<i>S. robusta</i>	19.73 ± 0.57	1027 ± 1.35
29	<i>T. arjuna</i>	19.21 ± 0.39	714 ± 1.66
30	<i>T. bellerica</i>	18.47 ± 0.78	460 ± 1.15
31	<i>T. chebula</i>	20.69 ± 0.30	602 ± 1.87
32	<i>T. ciliata</i>	19.85 ± 0.60	445 ± 1.21
33	<i>V. contifolium</i>	21.81 ± 0.71	991 ± 2.39
34	<i>P. obovatum</i>	19.63 □□0.18	1413.76
35	<i>D. peregrina</i>	18.64 □□0.51	0854.64
36	<i>S. wallichii</i>	19.87 □□0.13	1092.48
37	<i>A. procera</i>	20.35 □□0.58	3134.99

38	<i>T. belerica</i>	19.91 □□0.14	1732.51
39	<i>C. siamea</i>	19.87 □□0.08	0875.58
40	<i>Castanopsis indica</i>	20.15	1,178.67
41	<i>Eriobotrya dubia</i>	20.38	911.26
42	<i>Phoebe attenuata</i>	17.71	1,113.64
43	<i>Manglietia insignis</i>	17.92	587.78
44	<i>Macropanax undulatum</i>	17.54	781.81
45	<i>Litsea laeta</i>	17.37	1,134.77
46	<i>Ixonanthes khasiana</i>	17.14	892.51
47	<i>Cunninghamia lanceolata</i>	17.01	1,133.66
48	<i>Michelia cathcartii</i>	16.98	1,062.58
49	<i>Sapindus mukorossi</i>	17.11	531.67
50	<i>Cinnamonum camphora</i>	16.04	769.52
51	<i>Altingia excels</i>	15.56	805.68
52	<i>Livistonia jenkinsiana</i>	15.47	1,084.40
53	<i>Caryota urens</i>	15.45	684.40
54	<i>Engelhardtia spicata</i>	15.13	430.30
55	<i>Bischofia javanica</i>	15.12	306.90
56	<i>Lithocarpus elegans</i>	14.66	478.00
57	<i>Elaeocarpus lanceaefolius</i>	14.43	576.20
58	<i>Morus laevigata</i>	14.22	465.76

8.3 WASTELAND UTILIZATION THROUGH ENERGY PLANTATION

Several studies have argued that the use of degraded soils for the production of perennial energy crops could reduce competition with food production, as perennial energy crops would be less susceptible for soil degradation compared to (annual) food crops [9-13]. In other words, the option of growing perennial bio-energy crops could significantly increase the productivity of these lands. Bioenergy production on these soils would potentially have

little negative impacts on biodiversity and the GHG balance. In fact, authors have argued that cultivation of perennial energy crops could increase the carbon sequestered in degraded soils [14-16], increase the quality of these soils [17-18] and improve wildlife habitat and restore natural ecosystem functions [19-20]. Where surplus land is available, dedicated bioenergy crops can be grown on surplus cropland, agriculturally marginal lands and degraded or drastically disturbed lands.

8.3.1. GLOBAL POTENTIAL OF ENERGY CROPS IN DEGRADED LANDS

In a recent study, Nijsen *et al.*, 2011 [21] reported that the total global area of degraded land equals 1836 MHa. The degraded area is spread across all regions in the world. Most of the degraded land can be found in China (15%). Other regions that have significant areas of degraded land are the Middle East (9%), India, Brazil and the region Rest of South America (RSAM). The last three regions each account for 6% of the global area of degraded land. About 46% of the degraded land is moderately degraded, 37% is lightly degraded and 15% and 0.5% are strongly and extremely degraded, respectively.

Hoogwijk *et al.* [22] estimated that, out of the global potential of biomass energy production of 33–1135 EJ per year, that of growing energy crops on surplus agricultural land is 10–988 EJ per year. Kort *et al.* [23] estimated that up to 60 million hectares (MHa) of land could be devoted to bioenergy crop production in the US by conversion of agriculturally marginal soils to production of biomass crops. Pacala and Socolow [24] reported that production of ethanol can be one of the 15 viable options to mitigate the climate change by off-setting 1 Pg C per year by 2054. This would require production of about 34 million barrels per day of ethanol by 2054, or 50 times the rate of ethanol production in 2004. The biomass required as a feedstock for ethanol production would require 250 MHa of land worldwide to establish high yielding (10–15 Mg per ha per year) bioenergy plantations.

Study conducted by Nijsen *et al.*, [21] reported that the total potential of the production of perennial energy crops on moderately, strongly and extremely degraded soils was estimated at 193 EJ per year for woody crops and 151 EJ per year for grassy species,

respectively. In these estimates, lightly degraded soils have been excluded, as these soils are potentially still suitable for the production of food. Within the total potential for woody crops, moderately degraded areas account for 86% (or 166 EJ per year), strong degraded areas for 26 EJ per year and extremely degraded areas for 0.4 EJ per year. The bulk of the potential was calculated for Asia (45%), Africa (18%) and Central and South America (19%). The largest potential, 16% of the total global potential or 30 EJ per year, was projected for China, whereby 16% of this potential came from ‘other land’, while 33% and 34% came from cropland and pastures, respectively, and the remaining from forests. But the potentials of other regions were also considerable. The USA, Brazil, West Africa, East Africa, Russia and India each have potentials above 10 EJ per year. The procedure used to estimate energy potential from energy crops through utilizing degraded land is presented in Fig. 1.

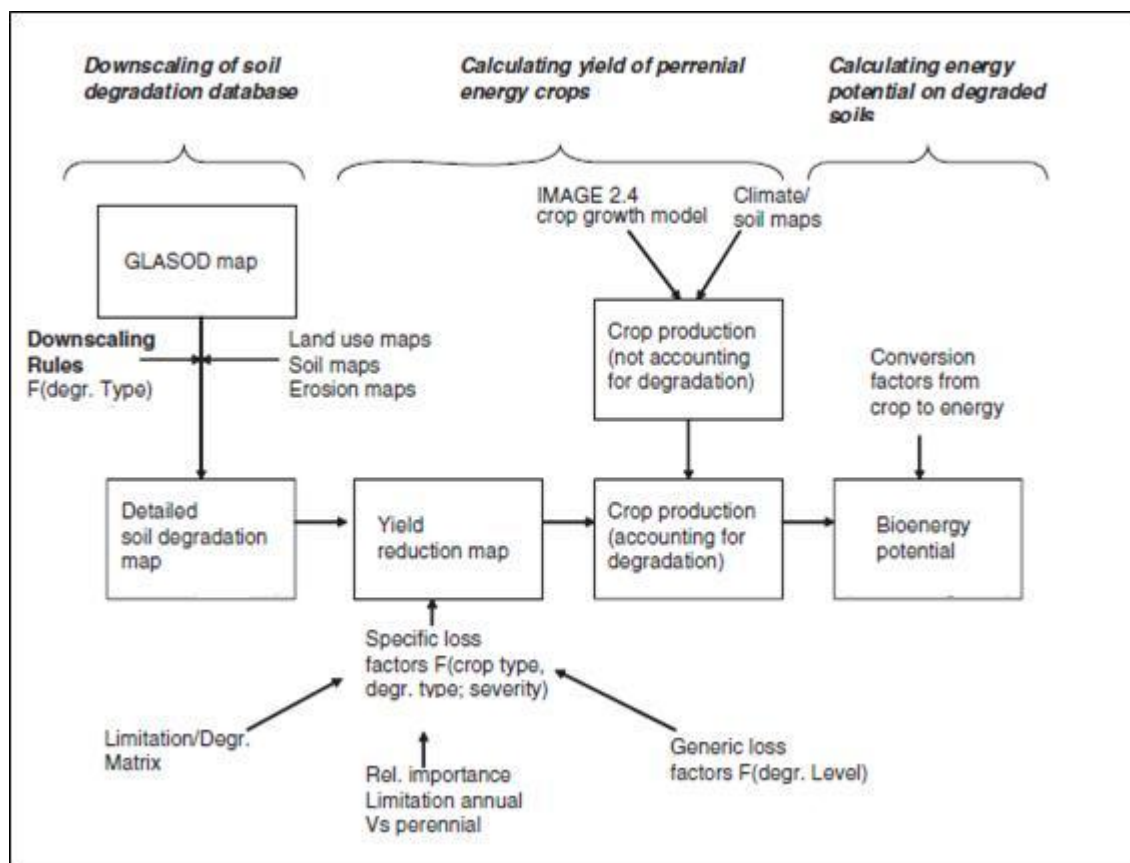


Fig.1. Methodology for estimation of the potential perennial energy crops production on degraded soils [21].

8.3.2. INDIA'S POTENTIAL OF ENERGY CROPS PRODUCTION IN DEGRADED LANDS

India has large tracts of degraded / wastelands, both in forest and non-forest areas. This could be used for raising dedicated plantations of fast growing high yielding plant species suitable for supply of biomass for meeting decentralized electricity and other energy demands on sustainable basis in rural areas. In addition, small megawatt biomass power plants could be set up for feeding power at the grid. These plants would ensure power to many villages. In this context, the Ministry of New and Renewable Energy (MNRE) has planned to initiate programme from 12th Plan period (2012-2017) on raising dedicated energy plantations and utilization of forest residues linking with biomass power projects with the objective to formulate a strategy to provide sustainable and reliable energy solutions at an affordable cost at the grass root level in an integrated and environment friendly manner [25].

India has approximately 50 million hectares of degraded wasteland that lie outside the areas demarcated as national forests, and another 34 million hectares of protected forest area, in much of which tree cover is severely degraded. A massive program of energy plantation consisting of fast-growing tree crops such as bamboo, casurina, *Eucalyptus* etc. can serve as the raw material for a national network of small, decentralized biomass power [25]. Plantation of high yielding short rotation plant species for 4-6 year cycle has the advantage of reducing rate of carbon sequestration as plants store maximum carbon during initial growth up to 5-10 years as against long rotation cycle. For example, bamboo store 12 tonne per hectare per year as compared to 0.30 to 1.5 tonne per hectare per year expected for other plant species [25]. There are crops, which can be grown in arid and saline areas like Sea Coasts, Rajasthan, and Gujarat etc. Some promising tree species suitable for arid land such as *Cassia siamea*, *Acacia nilotica*, *Leucaena leucocephala*, *Casuarina equisetifolia*, *Prosopis juliflora* etc are also capable of yielding 20-25 ton per hectare per year in a rotation of 4-6 years.

8.4. CONCLUSION

Energy crops plantation has the potential to meet the growing energy demand as well as to offset carbon emission from conventional fuels. Several tree and shrubs species have been already identified and cultivated successfully in different parts of the world including India. Many species have been also identified as suitable candidates for plantation in wastelands/degraded lands. In future, role of biotechnology will be crucial to develop high yielding, short life cycled, and disease resistant energy crops.

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