Chapter 2

Literature Review

2.1 Introduction

The processes used in cryogenic air separation plants almost remained same in basic principle. In the present scenario, air separation processes improving in terms of purity of products, recovery of the products, specific power consumption, ease of maintenance, multi utility applications and ease of installations.

A second revolution is expected with the use of oxygen in coal or biomass gasification. As compared to existing applications of air separation, gasification requires huge quantity of medium purity oxygen. Oxygen production by cryogenic air separation process consume huge amount of energy. Therefore, a thorough understanding is required on the minimum work of separation and finding out various ways to minimize specific power consumption of the cryogenic air separation plants. In gasification ultra pure oxygen (99.99 % mole) is not needed. The medium purity oxygen (80-98 % mole), cryogenic plants can be economically used for coal or biomass gasification for production of quality syngas.

The literature review of the cryogenic air separation is focused on the following points.

i. History of cryogenic air separation by distillation
ii. Development in the process cycle
iii. Power consumption in cryogenic air separation
iv. Biomass gasification
v. Use of oxygen in gasification
vi. Exergy analysis

2.2 History of cryogenic air separation by distillation

A cryogenic process with distillation has long been used for producing industrial gases like oxygen, nitrogen and argon. Distillation is the cascading of several evaporations and condensations carried out in counter flow. In the year 1902, Linde recovered for the first time pure oxygen from air in his new works in Hoellriegelskreuth near Munich. This was achieved by single column apparatus for air separation. In this case compressed air cooled against the separation products, liquefy it by reboiling the bottom of a distillation column and throttle it as reflux to the top of the distillation column. The concept of single column apparatus for cryogenic air separation is shown in **Fig. 2.1.**

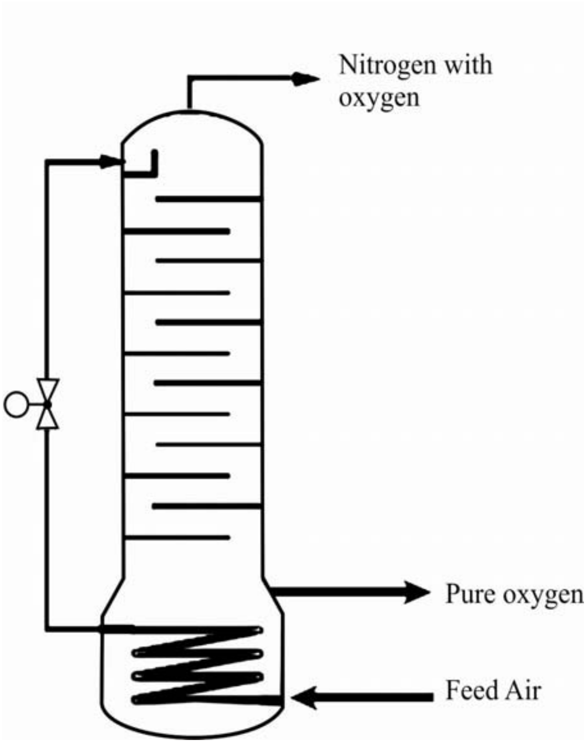

Fig. 2.1: Single column apparatus for air separation

This oxygen production by air distillation was motivation for Claude to do something better. The schematic diagram of single column with reflux heat exchanger is shown in **Fig. 2.2.** He placed a reflux heat exchanger with straight vertical tubes at the bottom of distillation column as reboiler. The reflux condensate somewhat enriched with oxygen was fed to the middle of the distillation column. The remaining gas somewhat enriched with nitrogen was condensed in the other tubes flowing downward and throttled as reflux to the top of the column. Using this scheme the oxygen recovery was improved, but it was still not possible to produce pure nitrogen. This concept of cryogenic air separation caused wakeful to the people working in this area until they found an even better solution.

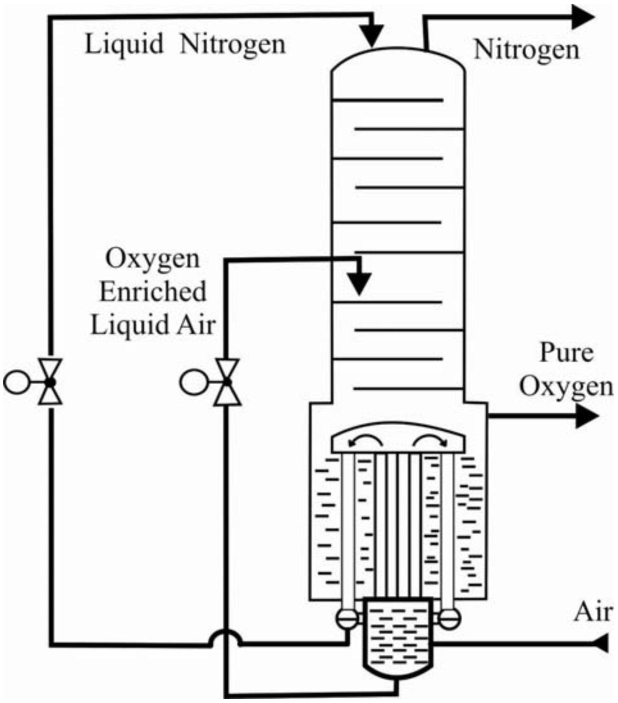

Fig. 2.2: Single column with reflux heat exchanger for air separation

In 1910, Linde sets the basis for the cryogenic air separation principle with the development of double column distillation system. Now it was possible to produce pure oxygen and pure nitrogen simultaneously. In this double column air separation system, below the low pressure column a high pressure column was installed. At the top of this column pure nitrogen was drawn off, liquefied in condenser and fed to the low pressure column serving as reflux. At the top of this low pressure column pure gaseous nitrogen was withdrawn as product while liquid oxygen evaporated at the bottom of this column to deliver the pure gaseous oxygen product. This principle of double column distillation combining the condenser and evaporator to form a heat exchanger called as combined condenser and reboiler which are still used today. The arrangement of double column system for air separation is shown in **Fig. 2.3.**

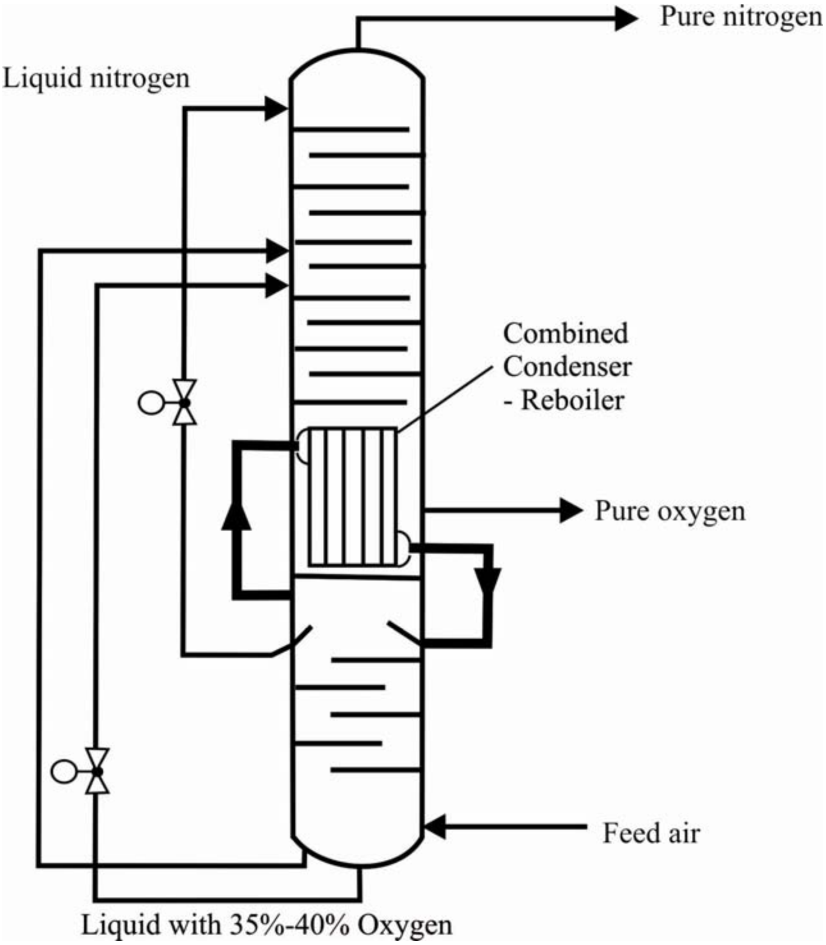

Fig. 2.3: Double column system for air separation

In 1925, a very significant invention took place in the field of steel production from iron ore. It was the LD process that needed a huge quantity of gaseous oxygen to oxidize the impurities of the ore to recover steel. German Company, Linde developed its Linde-Frankle process system to meet the demand of gaseous oxygen for the steel plants.

In 1939, Peter Kapitza of USSR formed an experimental air liquefier operating at 6 bar pressure using an expansion turbine which produced 15,000 Nm^3/hr GOX. As already noted, the cryogenic air separation plants grew in size, therefore the demand for argon has considerably increased during these years. Thus, older cryogenic air separation plants were equipped with third column for argon production at highest possible recovery. The history of cryogenic presented by Wolfgang [Wol 02], illustrates significant inventions in the development of cryogenic air separation. Grenier et al. [GP 86] have articulated the review of the salient points like air separation processes, plant size, air purification technology, new absorber design, and distillation column performance which have marked the last 20 years in the field of cryogenic air separation and liquefaction.

2.3 Development of air separation technology

Process cycles are somewhat different depending upon how many products are desired (either nitrogen or oxygen; oxygen and nitrogen; or nitrogen, oxygen and argon); the required product purities; gaseous product delivery pressures; and whether one or more products will be produced and stored in liquid form. There has been a continuous development of air separation techniques took place which is presented in following sections.

2.3.1 Main components of cryogenic ASU

The complexity of the cryogenic air separation process, the physical sizes of equipments, and the energy required to operate the process all vary with the number of gaseous and liquid products, required product purity, and required delivery pressures. Most of the equipments involved in air separation plants are dedicated to the liquefaction process. The main basic equipments required in cryogenic air separation plants are as compressors, equipment for separation of moisture, CO_2 and hydrocarbons, heat exchangers, expansion devices and cryogenic pumps etc.

2.3.1.1 Compressors

In this section the types of compressors used for ASUs, with their special application considerations are discussed. Compressors are widely used in industries to transport fluids. It is a mechanical device that compresses a gas. There are many types of compressors, thus a proper selection is needed to fulfill the typical necessity of each industry. Generally, the compression of gases may be accomplished in device with rotating blades or in cylinders with reciprocating pistons. Rotary equipment is used for high volume flow where the discharge pressure is not too high, while the reciprocating compressors are required for high pressures. Therefore, there are two major types of compressors used are dynamic, which include axial and centrifugal compressors, and positive displacement machines, which include reciprocating, diaphragm, rotary, and screw types. The compressor selection and sizing for engineering applications are reported in [Sch 72], [Lap 82], [WM 92], [Cho 98], [Cok 94] and [Mul 11]. Some of the important types of compressors are discussed here.

1. Axial compressors

Axial compressors are commonly used for the main air compressor on large air separation units and used for applications where the head required is low and with the high intake volume of flow. The axial flow compressor consist of the rotating element that construct from a single drum to which are attached several rows of decreasing-height blades having aerofoil cross sections. Between each rotating blade row is a stationary blade row. All blade angles and areas are designed precisely for a given performance and high efficiency. One additional row of fixed blades (inlet guide vanes) is frequently used at the compressor inlet to ensure that air enters the first stage rotors at the desired angle. Also, another diffuser at the exit of the compressor might be added, known as exit guide vanes, to further diffuse the fluid and control its velocity. Axial flow compressors do not significantly change the direction of the flow stream; the fluid flow enters the compressor and exits from the gas turbine in an axial direction (parallel with the axis of rotation). It compresses the gas fluid by first accelerating the fluid and then diffusing it to increase its pressure. The fluid flow is accelerated by a row of rotating aerofoil (blades) called the rotor, and then diffused in a row of stationary blades (the stator). Similar to the centrifugal compressor, the stator then converts the velocity energy gained in the rotor to pressure energy. One rotor and one stator make up a stage in a compressor. The axial flow compressor produces low pressure increase, thus the multiple stages are generally use to permit overall pressure increase up to 30:1 for some industrial applications. Driver of axial flow compressor can be steam turbines or electric motors. In the case of direct electric motor drive, low speeds are unavoidable unless sophisticated variable frequency motors are employed. The efficiency in an axial flow compressor is higher than the centrifugal compressor.

2. Centrifugal compressors

Centrifugal compressors are widely used for main air compressor duty as well as oxygen product, nitrogen product, and nitrogen recycles service. The centrifugal compressor is a dynamic machine that achieves compression by applying inertial forces to the gas (acceleration, deceleration, and turning) by means of rotating impellers. Centrifugal compressors can be driven by electrical motor, steam turbine, or gas turbines. It is made up of one or more stages; each stage consists of an impeller as the rotating element and the stationary element, i.e. diffuser. In centrifugal compressor, the fluid flow enters the impeller in an axial direction and discharged from an impeller radially at a right angle to the axis of rotation. The gas fluid is forced through the impeller by rapidly rotating impeller blades. The gas next flows through a circular chamber (diffuser), following a spiral path where it loses velocity and increases pressure. Briefly, the impeller adds energy to the gas fluid, and then the diffuser converts it into pressure energy. The maximum pressure rise for centrifugal compressor mostly depends on the rotational speed (RPM) of the impeller and the impeller diameter. But the maximum permissible speed is limited by the strength of the structural materials of the blade and the sonic velocity of fluid; furthermore, it leads into limitation for the maximum achievable pressure rise. Hence, multistage centrifugal compressors are used for higher pressure lift applications. A multistage centrifugal compressor compresses air to the required pressure in multiple stages.

3. Reciprocating compressors

Reciprocating compressors are widely used for oxygen, nitrogen, crude argon product, and high pressure air service. The reciprocating, or piston compressor, is a positive displacement compressor that uses the movement of a piston within a cylinder to move gas from one pressure level to another higher pressure level. Reciprocating compressors might be considered as single acting, when the compressing is accomplished using only one side of the piston and double acting when it is using both sides of the piston. They are used mainly when high-pressure head is required at a low flow. Generally, the maximum allowable discharge-gas temperature determines the maximum compression ratio. Reciprocating compressors are furnished in either single-stage or multistage types. For single stage design, the entire compression is accomplished with a single cylinder or a group of cylinders in parallel. Intercoolers are provided between stages on multistage machines. These heat exchangers remove the heat of compression from the gas and reduce its temperature to approximately the temperature existing at the compressor intake. Such cooling reduces the volume of gas going to the high-pressure cylinders, reduces the power required for compression, and keeps the temperature within safe operating limits. The intake gas enters the suction manifold into the cylinder because the vacuum condition is created inside the cylinder as the piston moves downward. After the piston reaches its bottom position it begins to move upward. The intake valve closes, trapping the gas fluid inside the cylinder. As the piston continues to move upward it compresses the gas fluid, increasing its pressure. The high pressure in the cylinder pushes the piston downward. When the piston is near the bottom of its travel, the exhaust valve opens and releases high pressure gas fluid.

4. Diaphragm compressor

Diaphragm compressors are normally used when high pressures and contaminant-free compression are required. The running gear, cooling, and monitoring requirements are similar to the reciprocating compressor requirements. Consideration should be given to systems for detecting leaks in the diaphragm. When a diaphragm compressor is used in oxygen service, the hydraulic fluid under the diaphragm should be a soap-water solution or halogenated fluid that is safe for use in oxygen. As diaphragms may develop fatigue cracks and the hydraulic fluid will come in contact with the oxygen gas, a detection device to detect fluid leakage is desirable.

2.3.1.2 Compressor power

To find out the power of the compressor, actual polytropic efficiencies of the compression stages have been used. The work done on the gas in a polytropic compression process is given in the form of a polytropic head, H_p (kN-m/kg) [Sap 02].

$$H_p = \frac{ZRT_1}{M_w}\left(\frac{n}{n-1}\right)\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right] \qquad \text{--- (2.1)}$$

Further, compressor power (kW) is determined using equation,

$$Compressor\ Power = \frac{H_p \times \dot{m}}{\eta_p} \qquad \text{--- (2.2)}$$

Where:

Z = Compressibility factor

R = Universal gas constant, (8.314 kJ/kmol K)

M_w = Molecular weight, kg/kmol

T_1 =Inlet temperature, K

P = Pressure, bar

η_p= Polytropic efficiency

m = Mass flow rate, kg/s

Polytropic coefficient (n) and heat capacity ratio ($k= C_p/C_v$) are related by

$$\frac{n-1}{n} \times \eta_p = \frac{k-1}{k} \qquad \text{--- (2.3)}$$

2.3.1.3 Air contamination removal

There are various ways to remove air contamination like water, carbon dioxide, hydrocarbons, carbon monoxide etc. which must be removed from the air, so that they do not freeze up in the main heat exchanger and the distillation column [Lat 67]. The typical concentrations of contamination in air have reported by [Han 86] and [Isa 89]. The some methods of removal of air contamination are addressed as follows.

1. Pre-purification processes

Pre- Purification Units (PPUs) consist of two or more vessels filled with adsorbent. One vessel is online removing the contaminants from the air while the other vessel is offline being regenerated. There can be one, two, or more layers of adsorbents tailored to remove specific components. Typical adsorbents used are alumina for water removal and 13X molecular sieve for water, carbon dioxide, and hydrocarbon removal. PPUs remove all of the water contained in the air, over 99.9 % of the carbon dioxide, and many hydrocarbons. A few of the light hydrocarbons are not removed, and must be dealt with in the cold box with a combination of liquid purge and cryogenic adsorbers.

2. Reversing heat exchangers (REVEX)

It consists of one or more Brazed Aluminum heat exchangers (BAHXs) (Plate- fin type). Sze [SC 59] has reported such heat exchangers for the application of air separation. The design and construction of concentric type and plate- fin type heat exchangers are addressed in various references texts like [KL 64], [Gre 86], [TF 89], [Bar 85], and [KB 86]. Air with all of the contained contaminants is sent into the BAHXs. Water, 99+ % of the carbon dioxide, and the higher boiling hydrocarbons are frozen out and removed in the REVEX. After a period of time (2 min to 15 min) the air passage is depressurized and waste gas from the process is sent through the same passage counter currently to the air. The impurities are removed by the low pressure waste gas stream and the passages are cleaned. Two sets of alternating passages are periodically switched to keep a constant flow of purified air to the distillation columns. Some of the contaminants are not removed in the REVEX, primarily trace amounts of carbon dioxide and low boiling hydrocarbons including acetylene. Cryogenic adsorbers and a liquid purge prevent those compounds from concentrating to unsafe levels in the downstream equipment.

3. Regenerators

Regenerators are similar to the REVEX except that instead of BAHXs, vessels filled with quartzite pebbles are used and act as a heat sink. As the air is cooled by the refrigeration stored in the pebbles, the contaminants are frozen on the pebbles and removed from the air stream. After a period of time (2 min to 15 min), the vessels are switched and the waste gas removes the frozen contaminants and cools the pebbles to the operating temperature. Two sets of alternating regenerators are periodically switched to keep a constant flow of purified air to the distillation columns. Tubes containing product oxygen or nitrogen are sometimes routed through the bed of pebbles, warming the gases to ambient temperature. Also, a portion of the air can bypass the regenerators and is cleaned up by high pressure driers, REVEX, caustic scrubbers, or any combination of these. Some of the contaminants are not removed in the regenerators, primarily trace amounts of carbon dioxide and low boiling hydrocarbons including acetylene. Cryogenic adsorbers and a liquid purge prevent those compounds from concentrating to unsafe levels in the downstream equipment.

4. Caustic Scrubbers

Caustic scrubbers are typically used in older high pressure ASUs. Intermediate pressure air from the air compressor is first passed through the caustic scrubber, where all of the carbon dioxide is removed by chemically reacting with the circulating aqueous sodium hydroxide solution in an absorption tower. This air is further compressed to high pressure in the multi stage air compressor (MAC). Any oil and high boiling point hydrocarbons are removed in an oil adsorber and the air is sent to the alumina driers, which remove the water. The air stream then passes to the main heat exchanger and the remaining hydrocarbons are removed in the cryogenic adsorbers and liquid products.

5. Catalytic Oxidizers

Catalytic oxidizers located on an air compressor stage discharge have been used to oxidize contaminants such as hydrocarbons, hydrogen, and carbon monoxide. Acetylene requires temperatures in the range of 152 °C to 157 °C. Other contaminants can require temperatures as high as 427 °C. Analyzers should be provided to verify proper performance of the catalytic oxidizers.

6. Direct contact after coolers (DCACs)

Direct contact after coolers are used in some installations after the MACs. The primary purpose of these units is to cool the hot air before it enters the PPU or REVEX. DCACs can also help to clean the air of dust and water-soluble contaminants such as sulphur dioxide, hydrogen sulphide, and ammonia.

7. Front end purification

Modern ASUs utilize Pre purification Unit (PPU), which removes moisture, CO_2 and most hydrocarbons from the air. Moisture and CO_2 must be removed to prevent ice and dry ice from forming later in the process. A PPU is typically made up of a chiller to cool the air to 4-10 ^{0}C, a condensate separator to remove free water and two vessels filled with desiccant and mole sieve material, which adsorbs the contaminants while allowing the air to pass through. One bed is always on line to the process, while the other bed is regenerated with heated waste nitrogen to remove accumulated contaminants. Beds automatically switch every 5-8 hours. The air from the PPU is very close to moisture and CO_2 free. Some older ASUs utilize reversing heat exchangers to accomplish front end clean up. These systems contain special cryogenic heat exchangers that freeze out the moisture and CO_2, allowing clean air to flow to the distillation process. The passes in the heat exchanger are switched every 3-10 minutes by a series of butterfly and check valves. One pass removes contaminates while the other is regenerated by outgoing waste gases.

2.3.1.4 Plate fin heat exchangers (PFHE)

A heat exchanger is a device that is used to transfer thermal energy (enthalpy) between two or more fluids, between a solid surface and a fluid, or between solid particulates and a fluid, at different temperatures and in thermal contact. In heat exchangers, there are usually no external heat and work interactions. Typical applications involve heating or cooling of a fluid stream of concern and evaporation or condensation of single or multi component fluid streams. The plate-fin exchanger has become the most common type used for cryogenic service. This results from its relatively low cost and high concentration of surface area per cubic foot of exchanger volume. It is made by clamping together a stack of alternate flat plates and corrugated sheets of aluminum coated with brazing flux. This assembly is then immersed in molten salt where the aluminum brazes together at points of contact. After removal from the bath the salt and flux are washed from the exchanger paths, and the assembly is enclosed in end plates and nozzles designed to give the desired flow arrangement. Usually the exchanger is roughly cubic, and is limited in size by the size of the available salt bath and the ability to make good braze seals in the center of the core. The core can be arranged for countercurrent flow or for cross flow. Aluminum plate-fin heat exchangers are key components in many process plants. Especially the compactness of this exchanger type is one of the most favorable possibilities to save installation space and costs. The typical PFHE is shown in **Fig. 2.4.**

The characteristics of Linde PFHE are:

- Aluminum alloys provide best possible heat exchange between clean gases and liquids in the low temperature service
- Favorable for simultaneous heat exchange between several streams
- Treatment of many process streams in one unit only
- Suitable for single phase and for mixed phase fluids
- Arrangement of streams in counter-flow, cross-flow or combinations
- Large choice of fin types with different surface areas ensures optimized equipment design
- Proven vacuum brazing technology (no use of flux)

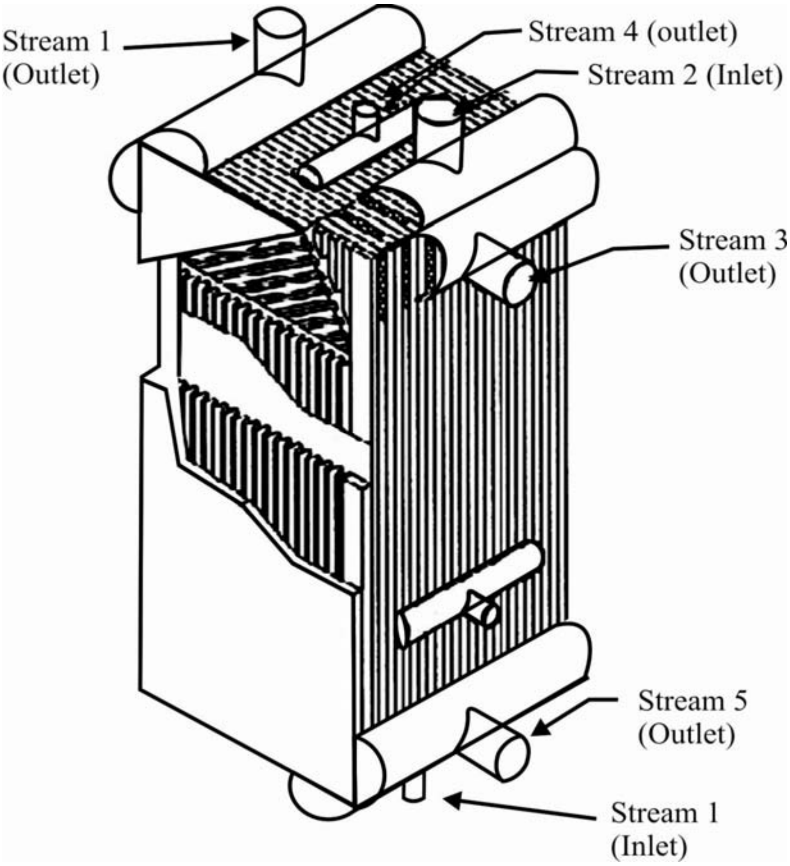

Fig. 2.4: Plate fin heat exchanger

2.3.1.5 Distillation and distillation columns

Distillation is the most widely used separation process in the chemical industry. It is also known as fractional distillation or fractionation. It is normally used to separate liquid mixtures into two or more vapor or liquid products with different compositions.

Distillation is an equilibrium stage operation. In each stage, a vapor phase is contacted with a liquid phase and mass transfer is from vapor to liquid and from liquid to vapor. The less volatile, "heavy" or "high boiling", components concentrate in the liquid phase; the more volatile, "light", components concentrate in the vapor. By using multiple stages in series with recycle, separation can be accomplished. Various kinds of devices such as random or structured packings and plates or trays are used to bring the two phases into intimate contact. Trays are stacked one above the other and enclosed in a cylindrical shell to form a column. Packings are also generally contained in a cylindrical shell between hold-down and support plates. The basic concepts, design, construction and working of a distillation column are illustrated in the reference texts [Bar 85], [PGM 97], [TF 89], and [Cok 10]. A typical tray-type distillation column with major external accessories is shown schematically in **Fig. 2.5.**

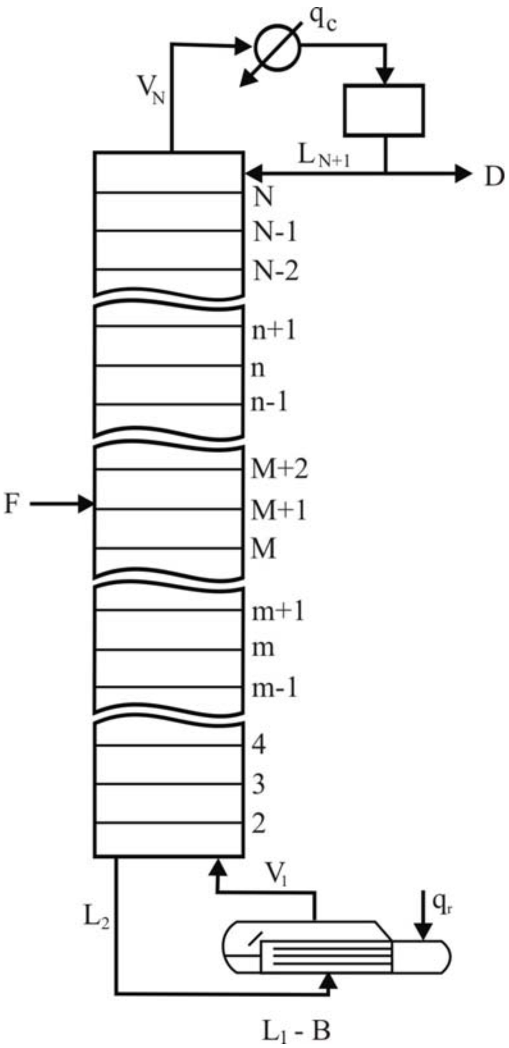

Fig. 2.5: Schematic diagram of simple distillation column

1. Principles of distillation

Separation of components from a liquid mixture via distillation depends on the differences in boiling points of the individual components. Also, depending on the concentrations of the components present, the liquid mixture will have different boiling point characteristics. Therefore, distillation processes depends on the vapor pressure characteristics of liquid mixtures. The feed material, which is to be separated into fractions, is introduced at one or more points along the column shell. Because of the difference in gravity between vapor and liquid phases, liquid runs down the column, cascading from tray to tray, while vapor flows up the column, contacting liquid at each tray. Liquid reaching the bottom of the column is partially vaporized in a heated reboiler to provide boil-up, which is sent back up the column. The remainder of the bottom liquid is withdrawn as bottoms, or bottom product. Vapor reaching the top of the column is cooled and condensed to liquid in the overhead condenser. Part of this liquid is returned to the column as reflux to provide liquid overflow. The remainder of the overhead stream is withdrawn as distillate, or overhead product. In some cases only part of the vapor is condensed so that a vapor distillate can be withdrawn. This overall flow pattern in a distillation column provides countercurrent contacting of vapor and liquid streams on all the trays through the column. Vapor and liquid phases on a given tray approach thermal, pressure, and composition equilibriums to an extent dependent upon the efficiency of the contacting tray. The lighter (lower-boiling) components tend to concentrate in the vapor phase, while the heavier (higher-boiling) components tend toward the liquid phase. The result is a vapor phase that becomes richer in light components as it passes up the column and a liquid phase that becomes richer in heavy components as it cascades downward. The overall separation achieved between the distillate and the bottoms depends primarily on the relative volatilities of the components, the number of contacting trays, and the ratio of the liquid phase flow rate to the vapor-phase flow rate. If the feed is introduced at one point along the column shell, the column is divided into an upper section, which is often called the rectifying section, and a lower section, which is often referred to as the stripping section. These terms become rather indefinite in multiple feed columns and in columns from which a liquid or vapor side stream is withdrawn somewhere along the column length in addition to the two end-product streams.

Distillation columns are designed to achieve this separation efficiently. Distillation is the most common separation technique it consumes enormous amounts of energy, both in terms of cooling and heating requirements. It can contribute to more than 50 % of plant operating costs. The best way to reduce operating costs of existing units is to improve their efficiency and operation via process optimization and control. To achieve this improvement, a thorough understanding of distillation principles and how distillation systems are designed is essential. The purpose of this set of notes is to understand the terminology used in distillation practice and to give a very basic introduction too.

2. Types of distillation columns

A distillation column can use either trays or packings; therefore columns are of two types as plate or tray distillation column or packed distillation columns. Their mechanisms of mass transfer differ, but the key for both is a good approach to equilibrium through the generation of large amounts of interfacial area. This interfacial area results from the passage of vapor through the perforations of trays, or the spreading of liquid on the surface of packings. In a trayed column, liquid flows down the column through down comers and then across the tray deck, while vapor flows upward through the liquid inventory on the tray. There are many types of tray designs, but the most common ones are bubble cap trays, valve trays and sieve trays. The performance of a tray also depends upon the type of tray deck. The simplest is a sieve tray, it has a perforated tray deck with a uniform hole diameter of from less than a millimeter to about 25 mm. Trays with valves, which can be fixed or floating, also are very common; bubble caps still are used, but infrequently and usually only for extreme turndown. **Fig. 2.6** shows the different type of trays. The pressure drop per stage in a distillation column depends on many factors like vapor velocity and the type of trays or type of structural packing used. Bennet et al. [BW 89], Lockett [Loc 89] and Agrawal et al. [AW 91a] have reported that minimum pressure drop is 435 pa per stage in a sieve tray distillation column.

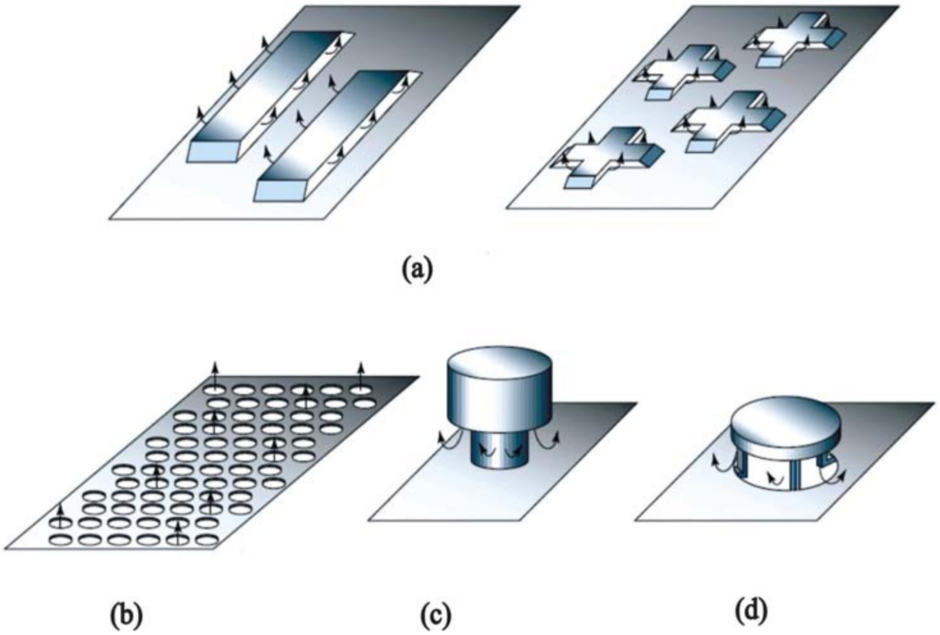

Fig. 2.6: Types of trays

(a) Fixed valve tray, (b) Sieve tray, (c) Bubble cap tray and (d) Floating valve tray

Packed distillation columns can be divided into two major groups based on the type of packing used, either random (dumped) packing, or structured (ordered) packing. Packings are passive devices that are designed to increase the interfacial area for vapor liquid contact. Structural packings in current use are composed of

i. Wire- mesh weavings
ii. Corrugated sheet or crimped sheet
iii. Grid type; open, heavy bar grid shapes stacked together

For most efficient performance, the fabricated sections of the structured packing usually are placed in a specific rotating pattern in the column to ensure uniform liquid flow, and vapor cross mixing. Fitz et al. [FKS 99] have reported performance evaluation of structured packing in commercial scale column. Bennet et al. [BW 89], Lockett [Loc 89] and Agrawal et al. [AWLB 94] have reported that with structured packing the pressure drop is only 10 to 20 % that of the sieve tray pressure drop.

3. Vapor pressure and boiling

The vapor pressure of a liquid at a particular temperature is the equilibrium pressure exerted by molecules leaving and entering the liquid surface. Here are some important points regarding vapor pressure: Energy input raises vapor pressure. Vapor pressure is related to boiling. A liquid is said to 'boil' when its vapor pressure equals the surrounding pressure. The ease with which a liquid boils depends on its volatility. Liquids with high vapor pressures (volatile liquids) will boil at lower temperatures. The vapor pressure and hence the boiling point of a liquid mixture depends on the relative amounts of the components in the mixture. Distillation occurs because of the differences in the volatility of the components in the liquid mixture. The boiling point diagram (**Fig. 2.7**) shows how the equilibrium compositions of the components in a liquid mixture vary with temperature at a fixed pressure.

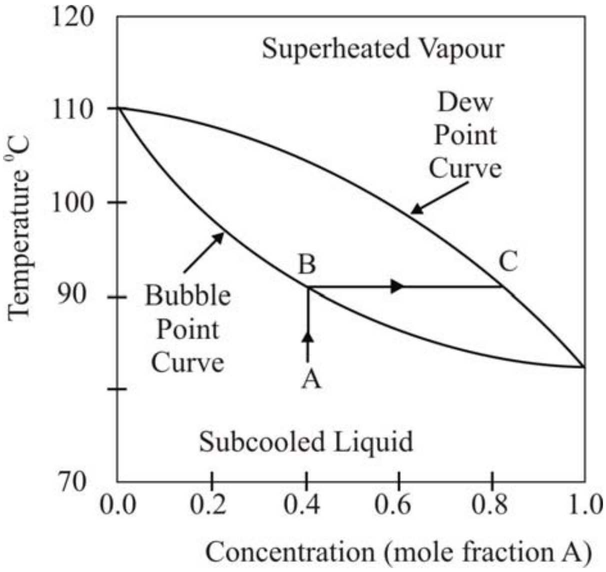

Fig. 2.7: Boiling point diagram of a binary mixture

Consider an example of a liquid mixture containing two components (A and B) - a binary mixture. The boiling point of 'A' is that at which the mole fraction of A is 1. The boiling point of 'B' is that at which the mole fraction of 'A' is 0. In this example, 'A' is the more volatile component and therefore has a lower boiling point than 'B'. The upper curve in the diagram is called the dew-point curve while the lower one is called the bubble-point curve. The dew point is the temperature at which the saturated vapor starts to condense. The bubble-point is the temperature at which the liquid starts to boil. The region above the dew-point curve shows the equilibrium composition of the superheated vapor while the region below the bubble-point curve shows the equilibrium composition of the sub cooled liquid. For example, when a sub cooled liquid with mole fraction of component 'A' is 0.4 (point A) is heated; its concentration remains constant until it reaches the bubble-point (point B), when it starts to boil. The vapors evolved during the boiling have the equilibrium composition given by point ‘C’, approximately 0.8 mole fractions of component ‘A’. This is approximately 50 % richer in component ‘A’ than the original liquid. This difference between liquid and vapor compositions is the basis for distillation operations.

4. Vapor- Liquid Equilibrium

Vapor- Liquid equilibrium (VLE) data form the basis for evaluation of distillation operations; the most useful form of this data is boiling point diagrams. An ideal liquid or gas solution is one for which the activity coefficient is unity. There are few liquid systems that behave ideally at any pressure, and the assumption of ideal liquid behavior is generally correct only for members of homogeneous series that have similar molecular weight. At low pressure, the vapor phase of a mixture approaches ideal behavior and follows the ideal gas law. For these conditions, the fugacity is equated with the partial pressure and the standard state fugacity of the liquid become equal to the vapor pressure.

2.3.1.6 Condenser - Reboiler

The condenser-reboiler thermally integrates the distillation column system. It is used to condense high pressure nitrogen by evaporating oxygen rich liquid. The reboiler is typically a BAHX. A BAHX consists of alternate fluid passages as shown in **Fig. 2.8.** The passages are separated by parting sheets. Within each passage are corrugated fins, which serve two purposes:

- They separate the parting sheets, while providing the mechanical integrity to hold the heat exchanger together.
- They promote heat transfer between the fluids.

The BAHX is built up like a sandwich with alternating passages of differing fluids. To introduce and remove the streams from each passage, at the feed and product end of the exchanger, the fins are angled towards a specific point. The performance of the reboiler can be most effectively characterized by the temperature difference between the boiling and condensing streams. Air compressor power is directly dependent on the pressure of the HP column, which in turn, depends on reboiler temperature difference. There are two type of reboilers used in cryogenic air separation plants which are thermosyphon reboiler and down flow reboiler addressed by Schimidt [Sch 06].

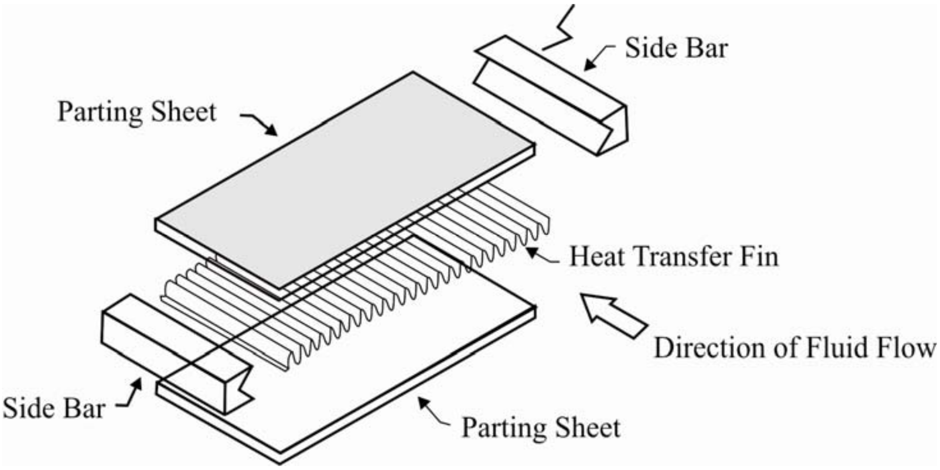

Fig. 2.8: BAHX passage construction

2.3.1.7 Cold box

The cold box contains the cryogenic heat exchangers, distillation columns and associated valves and piping. As parts of this system are very cold, all components are mounted inside the cold box and then encased in insulation. Cold boxes can be rectangular or cylindrical and are usually tall, some over 200 feet, depending on capacity and type of argon system. Modern cold boxes are filled with perlite insulation, which is light and easy to install and remove, when necessary. Older cold boxes may be tightly packed with cryogenic rock wool, which is hand packed to 14 pounds per cubic foot. It is very time consuming to install and remove.

2.3.1.8 Expanders

All ASUs except some very small units have expanders. Expanders provide the required refrigeration to produce liquids in the distillation column system. Air, nitrogen or waste nitrogen is fed to the expander, causing the wheel to turn and transfer energy to a compressor, generator or oil dynamometer. This transfer of energy causes the gas to cool. As the process continues, the outlet temperature of the expander eventually reaches design temperature while cooling the column system.

2.3.1.9 Cryogenic pumps

The functional design and operation of an air separation plant can depend on the application of one or more cryogenic liquid pumps. The type of pump used can vary depending on the requirements of the process or the end user. These pumps can be required to:

- Transfer process liquids from one distillation column to another;

- Circulate LOX through a reboiler;
- Circulate process liquids through an adsorber;
- Pump liquid products between the process and storage tanks;
- Pump liquid products to a higher pressure for vaporization in the main heat exchanger of ASU;
- Pump liquid products from LP storage into HP storage tanks and/or back-up vaporizers; and
- Pump liquid products between storage tanks and trailers or railcars.

All cryogenic pumps shall be constructed with materials suitable for the intended process conditions to ensure safe and reliable service. When designing and installing a cryogenic pump, care shall be taken to ensure that piping stresses due to pipe cool down shrinkage, liquid weight, ice formation, and pump operating dynamic forces are isolated from the pump housing to prevent damage. This can be accomplished by designing flexibility into the pump's suction and discharge piping system and by providing proper support for these lines. The preferred design method of isolation is to use flexible connections such as braided flexible hoses at pump tie-in points to the piping system. A pump inlet screen shall be installed in the suction line to prevent particles from damaging the pump. The recommended inlet screen mesh size shall be determined by the pump manufacturer (AIGA 055/08). It is preferable to install the inlet screen between the pump and the flexible connection. The piping system for cryogenic pumps shall be designed to be leak free by minimizing the use of threaded and flanged connections. Leaking cryogenic fluids can crack carbon steel enclosures, mounting frames, and motor housings and can also freeze motor bearings.

2.3.1.10 Product handling equipments

The hazards associated with product handling equipment depend on the properties of the products and the conditions under which they must be handled. Each system shall be suitable for the temperatures, pressures, and fluids involved.

Liquid storage

Because, of the very low temperature of this service, cryogenic tanks require special design and insulation techniques. Cryogenic tanks are generally constructed with the inner tank made up of material suitable for cryogenic temperatures and the outer tank of carbon steel. The annular space between these two vessels is filled with insulation to minimize heat leak and boil off of the cryogenic fluid.

The two types of cryogenic tanks used most are:

- LP flat-bottomed tanks or spheres with the annular space filled with insulation and purged with dry nitrogen. This type of tank design is generally used for large, field-erected storage tanks in stationary service and
- Vacuum-insulated tanks with powder/vacuum or super insulation/vacuum in the annular space. This type of tank design is generally shop fabricated and operated at either medium or high pressures

Hazards associated with the operation of cryogenic liquid storage vessels include:

- Cryogenic liquid leaks within the annular space;
- Loss of vacuum in the annular space (vacuum-insulated tank only);
- Loss of purge gas to the annular space (flat-bottomed tank only);
- Overfilling the inner tank;
- Over pressurization of the inner tank;
- Over pressurization of the annular space;
- Creation of vacuum in the inner tank;
- Creation of vacuum in the annular space (flat-bottomed tank only);
- Liquid spill and vapor cloud formation; and
- Mechanical stresses caused by rapid cool down

2.3.2 Cryogenic air separation cycle

Cryogenic air separation cycles are used to produce purified components of air like oxygen, nitrogen and argon in the form of gas, liquid or both. The cryogenic air separation is the only method to produce a large quantity of industrial gases economically, though initial investment is high. Cryogenic air separation plants consist of many unit operations. Most of the equipments involved in air separation plants are dedicated to the liquefaction process.

2.3.2.1 Steps in cryogenic air separation process

Following are the steps for producing liquid gases. These steps are shown schematically in chapter one in **Fig. 1.1.**

- Filter and compress the feed air up to required pressure. The compressed air is then cooled to close-to ambient temperature by passing through water-cooled or air-cooled heat exchangers.
- Remove the remaining water vapor and carbon dioxide. These components of air must be removed to meet product quality specifications. In addition, they

must be removed prior the air entering the distillation portion of the plant. If they were not, very low temperatures would cause the water and carbon dioxide to freeze and deposit on the surfaces within the process equipment.

- The next step is additional heat transfer against product and waste gas streams to bring the air feed to cryogenic temperature (approximately -185 ^{0}C). This cooling is done in brazed aluminum heat exchangers which allow the exchange of heat between the incoming air feed and cold product and waste gas streams exiting the separation process.
- Distillation columns are used to separate the air into desired products. To make oxygen as a product, the distillation system will have both “high” and “low” pressure columns. Nitrogen plants may have only one column, although many have two. Nitrogen leaves the top of each distillation column; oxygen leaves from the bottom. Argon has a boiling point very close to that of oxygen and will preferentially stay with the oxygen product. If high purity oxygen is required, argon must be removed from the distillation system at an intermediate point. Impure oxygen produced in the initial (high pressure) column is further purified in the second, low pressure column.
- The cold gaseous products and waste streams that emerge from the air separation columns are routed back through the front end heat exchangers. As they are warmed to near-ambient temperature, they chill the incoming air. Thus required liquid gases are produced for commercial application.

The different air separation cycles are explained in the following section.

2.3.2.2 Linde single-column system

Linde single column system is one of the most simple air separation systems as shown in **Fig. 2.9.** It consists of compressor, multichannel heat exchanger, distillation column and a J-T valve. The feed air is first compressed to a pressure depending on whether the oxygen product is desired as a gas (GOX) or Liquid (LOX). The compressed air is then purified for removal of water vapors, carbon dioxide and traces of hydrocarbons, if any, by adsorption and the air is passed through a multichannel heat exchanger for cooling by return streams. If the oxygen is desired as a gas the heat exchanger is a three-channel type. If the oxygen product is desired as liquid, the returned oxygen is omitted, and the heat exchanger is simple two-channel type. The liquid oxygen is then withdrawn from the lower section of the column called the kettle. The cool air is further cooled and partially condensed by exchanging energy with the liquid in the kettle, the incoming air is further cooled, which allows a greater liquid yield; and the heat is made available to boil some of the liquid in the kettle to furnish the upward flowing vapor in the column without the addition of heat from the ambient temperatures.

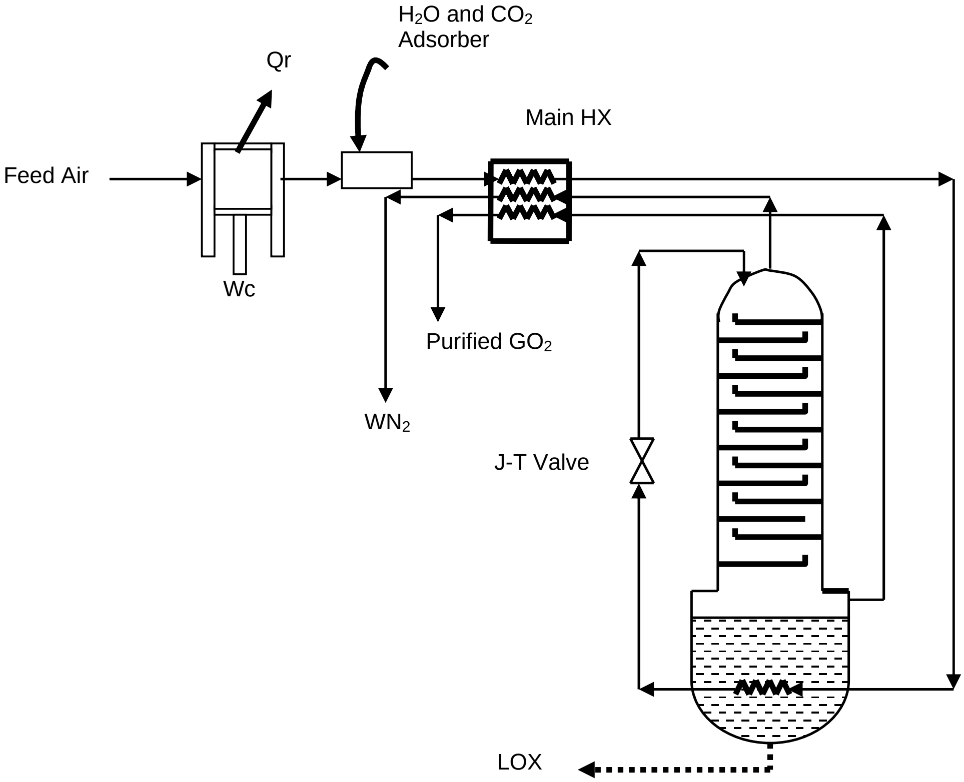

Fig. 2.9: Linde single-column system [Bar 85]

The cold air is expanded through a Joule-Thomson valve, after which some liquid is formed. This liquid is then passed to the top of the column, where it begins to travel down the column across the plates. As the liquid flows down the column over the plates, it is enriched in oxygen by exchange with the upward- flowing vapor. When the liquid reaches the bottom of the column, a portion is evaporated by the incoming air. This vapor flows up the column bubbling through the liquid layer and picking up nitrogen on its way. The other portion of the liquid is drawn off to a storage vessel, or some of the vapor is withdrawn and passed back through the three-channel heat exchanger to storage. The gas at the top of the column is removed and passed through three-channel heat exchanger (or two channel heat exchanger, if the oxygen is used as a liquid) to cool the incoming feed air. When the oxygen is desired as a gas, the air need be compressed only to pressure on the order of 3 MPa to 6 MPa; however if liquid oxygen is desired, the air must be compressed to approximately 20 MPa for the effective operation. The pressure within the column itself is usually on the order of 130 kPa to 200 kPa.

2.3.2.3 Linde double column system

The Linde single column has two serious disadvantages: (1) only the pure oxygen is produced and (2) large quantities of oxygen are wastages in the impure nitrogen exhaust gas. The nitrogen leaving the column had a composition of 10 percent oxygen and 90 percent nitrogen. This is not a very good level of purity for the nitrogen if it is to be used as an inert gas shield or any other application in which a little oxygen can be dangerous. In the early days of the air separation, the nitrogen was a waste product and was dumped into the atmosphere. Today however, liquid nitrogen is as an important cryogenic fluid. Thus, it is important to have a system that can produce relatively pure nitrogen as well as pure oxygen.

In this system two rectification columns are stacked one on top of the other, hence the name double column system. The double column system is shown in **Fig. 2.10.**

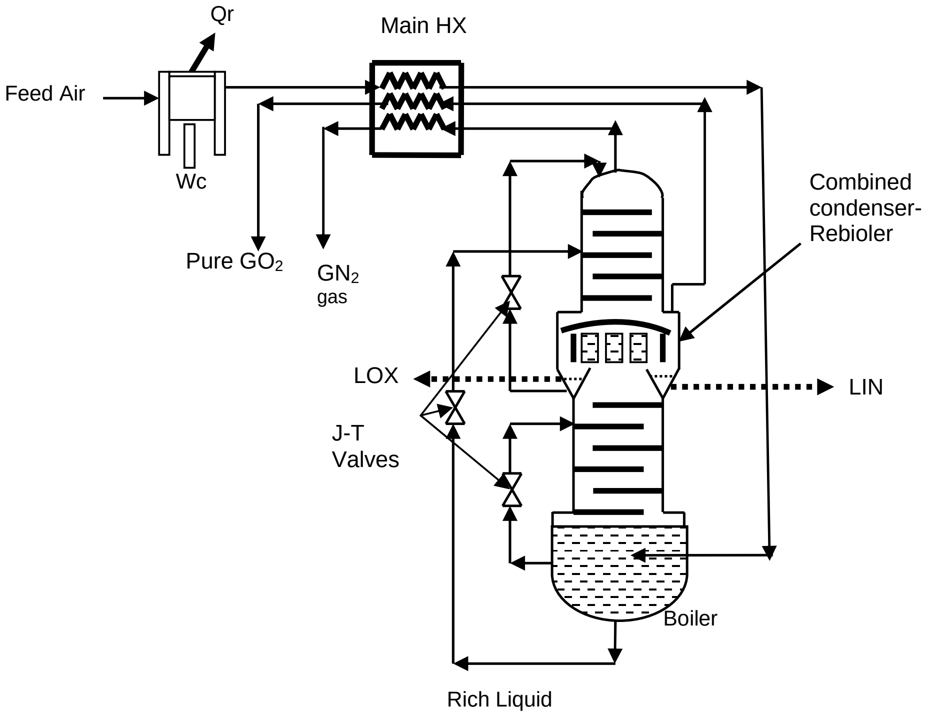

Fig. 2.10: Linde double column system [Bar 85]

The LP column operating at near atmospheric pressure is placed over the HP column, which operates at pressure of about 5 to 6 bar (500 to 600 kPa). This difference of pressures in the columns provides the much needed temperature difference across the condenser-reboiler. The boiling liquid oxygen in the base of the LP column provides the cooling effect to condense the vapor N_2 in the HP column. Depending on the number of stages in the LP column, any purity of either or both the products can be practically achieved. When extremely high purity products are desired, the argon component must also be separated.

2.3.2.4 Linde-Frankl system

In the 1930s the steel and chemical industries needed large quantities (by large quantities, we mean approximately 8 or 10 m^3/s or a million standard cubic feet per hour of air handled) of oxygen and nitrogen in quite pure form. To meet this demand, the Linde Company developed the separation system shown in **Fig. 2.11,** called Linde-Frankl system because it utilizes regenerators developed and patented by Frankl in 1925. Through the use of ammonia pre-cooling and an expansion engine the power consumption for this system was reduced to approximately one half of the Linde double column system. The liquefaction part of the separation system corresponds closely to an ammonia- precooled dual pressure Claude liquefaction system.

The air is first filtered and compressed to approximately 560 kPa in rotary compressor. Rotary compressors are well suited to large flow rates and rather small pressure ratios. Approximately 96 % of the total flow is diverted and passed through two pair of the regenerators, in which the air is cooled by the outgoing pure nitrogen and oxygen gaseous streams. Water vapor and carbon dioxide are removed from the air in the regenerators during the first half of the cycle, the air and cold nitrogen and oxygen streams are switched. The water vapor and carbon dioxide are evaporated while the air is cooled in the other regenerator of the pair.

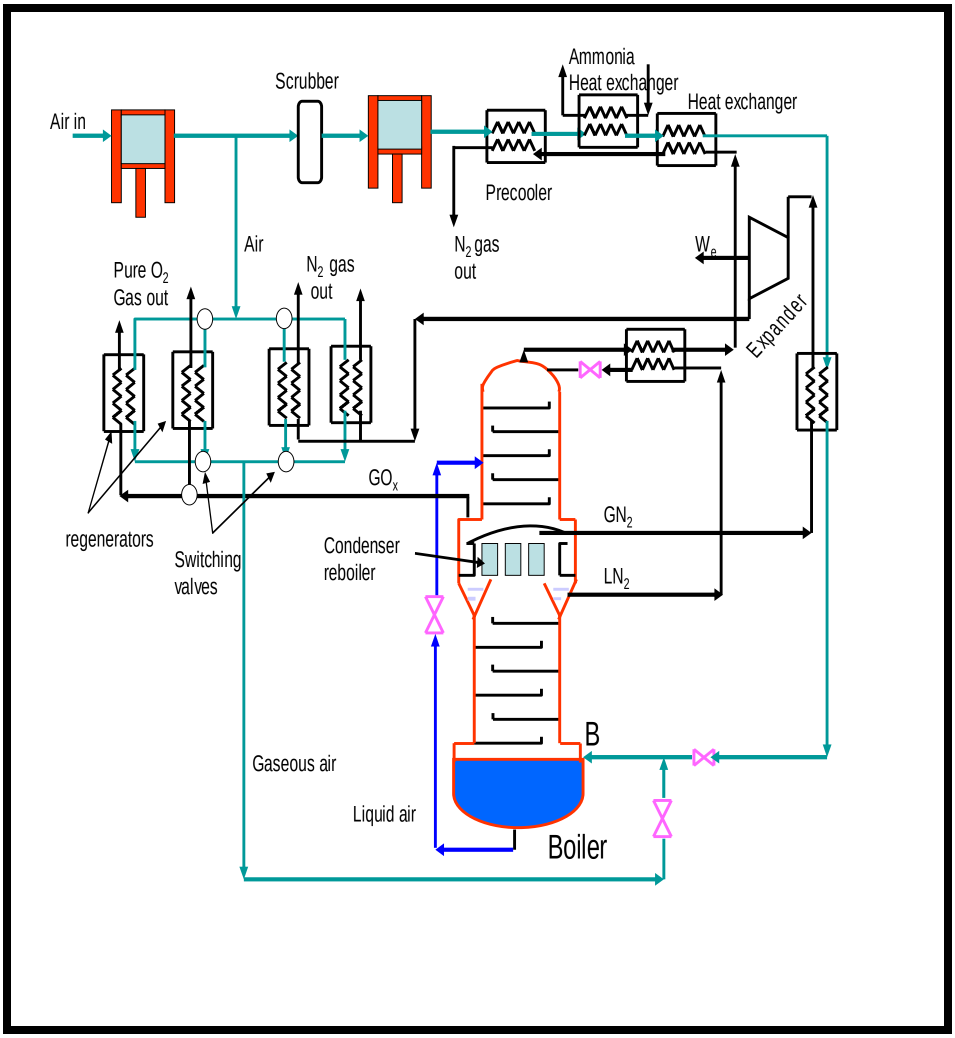

Fig. 2.11: Linde- Frankl system [Bar 85]

The cold saturated air is introduced into the lower part of the lower column. The remaining 4 percent of the total air flow is passed through a scrubber or separator in which CO_2 in the air stream is removed. The air is next compressed to 12.7 MPa and passed through a series of heat exchangers. The cold air is expanded through a Joule-Thomson valve and introduced with the regenerator stream into the lower portion of the lower column. This lower column operates at approximately 500 kPa.

2.3.2.5 Heylandt system

One of the air separation system commonly used in the United States today is the Heylandt system shown in **Fig. 2.12.** Usually products from this system are liquid nitrogen and liquid oxygen. The incoming air is compressed to 10 MPa in the four stage reciprocating compressor. Water vapors in the air are removed in the intercoolers and after cooler of the compressor. After removal of the water vapors, the air is compressed further to 13.7 MPa in a compressor driven by an expansion engine. The air is then passed through a precooler and ammonia forced cooler and cooled to –40 °C before the air stream is passed through the main heat exchanger. About half of the air is bypassed through an expansion engine and expand to 700 kPa and leave the expander at 110 K. The other half of the air stream pass through the main heat exchanger and is expanded through an expansion valve to 700 kPa. The two air streams are united and passed through a scrubber, in which carbon dioxide and hydrocarbons are removed by contact with liquid air. The gaseous air from the scrubber is introduced near the bottom of the lower column, and the liquid air from the scrubber is passed through a filter to remove the carbon dioxide, hydrocarbons and ice particles. The filtered air is united with kettle liquid from the lower column.

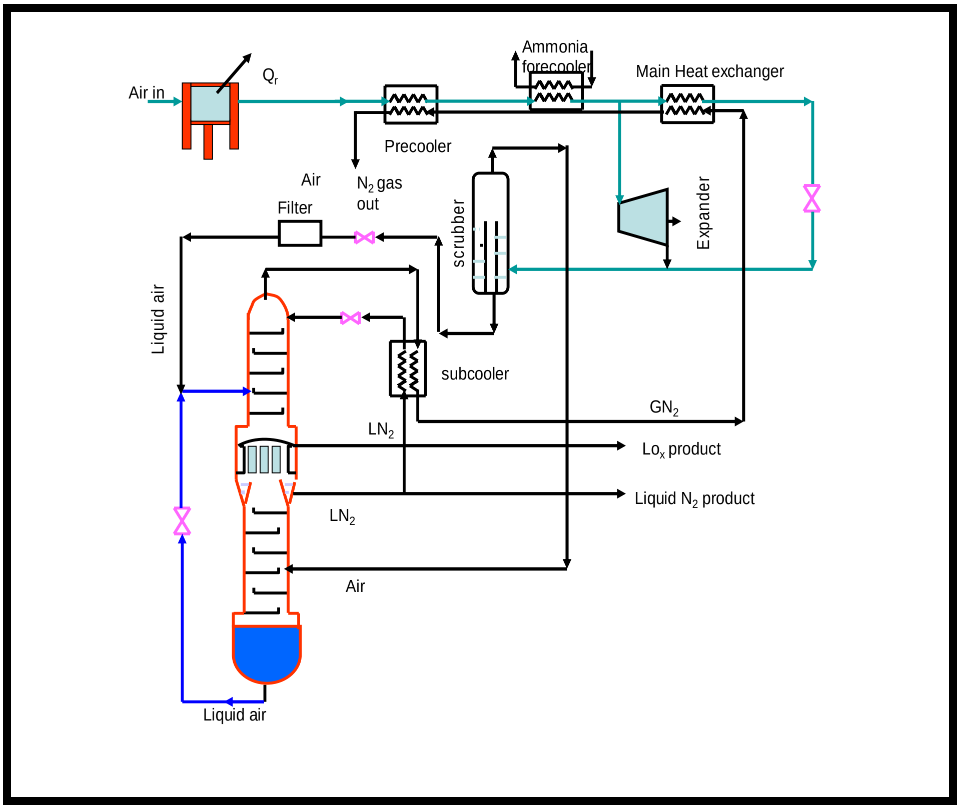

Fig. 2.12: Heylandt system [Bar 85]

To provide reflux for the upper column, liquid nitrogen is removed from the condenser in the lower column, sub cooled by the leaving gaseous nitrogen from the upper column and then introduced at the top of the upper column after expanding through an expansion valve. Liquid oxygen is removed from the reboiler of the upper column passed through the sub cooler, the main heat exchanger, and the pre cooler to the atmosphere.

In the Heylandt system, the lower column operates at approximately 700 kPa, and the upper column operates at less than 200 kPa. The nitrogen product usually contains less than 7 ppm of oxygen as an impurity, while the oxygen can be obtained with a purity level of 99.6 % oxygen. The impurity in the oxygen product is mostly argon. The waste nitrogen gas usually contains about 2 percent oxygen as impurity. By using a sufficient number of plates in the upper column, nitrogen gas can be obtained with less than 100 ppm oxygen as impurity and the nitrogen gas can be utilized instead of venting to atmosphere. The additional number of plates required to further purify the nitrogen gas adds to the cost of the system.

2.4 Power consumption in air separation plant

Cryogenic air separation process is high energy intensive process. The continuous development took place in terms of the performance improvements in components to provide less energy for separating products by this process. It is needed to understand thermodynamics of the process cycles for further improvement and analyze the nature of losses which took place in the components of the process cycle. The thermodynamic irreversibilities are divided into three categories as

1. Irreversible expansion or compression
2. Irreversible heat transfer
3. Irreversible mass transfer

2.4.1 Irreversible expansion or compression

Isothermal compression and isentropic expansion are limiting processes which are ideal for giving good performance. A gas flowing through a pipe experiences a pressure drop due to friction. Although the pressure falls, there is no recovery of energy and so the work, which was spent in increasing the pressure, is irreversibility loss. Similar losses occur in the compressors and expanders. The minimum work required to compress a unit mass of air from pressure P_1 to pressure P_2 isothermally as given below.

$$W_{Min} = RT_1 \ln\left(\frac{P_2}{P_1}\right) \qquad \text{--- (2.4)}$$

2.4.2 Irreversible heat transfer

Entropy increases in heat exchangers is due to two reasons as mentioned below.

i. Friction losses

ii. Temperature heads, including temperature unbalance

Such losses occur in a column where warm stream mix with colder stream on a tray, in sub coolers heat transfer between finite temperatures and in main heat exchangers heat transfer between finite temperatures. In a heat pump transferring heat Q from a temperature T_c to T_w, the work is given by the expression

$$W = Q\left(\frac{T_w - T_c}{T_c}\right) \qquad \text{--- (2.5)}$$

2.4.3 Irreversible mass transfer

Sometimes in air separation plant, waste nitrogen is produced and vented to atmosphere. The mixing of waste nitrogen with air is loss, since energy has been spent to separate nitrogen stream from air. In addition to this losses occur when streams, which are not in thermodynamic equilibrium, are mixed on distillation trays.

2.4.4 The thermodynamically ideal air separation system

The ideal system of air separation would be one in which all processes are reversible and require minimum work. The concept of minimum work requirement for separation of a gas mixture was reported by Haselden [Has 89] and Flower et al. [FJ 64]. Mixing of two gases together is ordinarily an irreversible process, because the gases would not unmix themselves without some external assistance. The method of separation using semi permeable membrane which allow the complete free passage of one gas but completely block the passage of all other gases can be considered as reversible process of separation. The idea of semi permeable membranes is not a completely theoretical concept because materials do exist in nature that is semi permeable for certain gases. The work requirement can be determined for mixture gas at a temperature T_m and P_m as

$$\frac{-W_{\min}}{m} = T_m\left(S_1 - S_2\right) - \left(h_1 - h_2\right) \qquad \text{--- (2.6)}$$

Let us consider the separation of mixture of two gases A and B in the double cylinder arrangement as shown in **Fig. 2.13.**

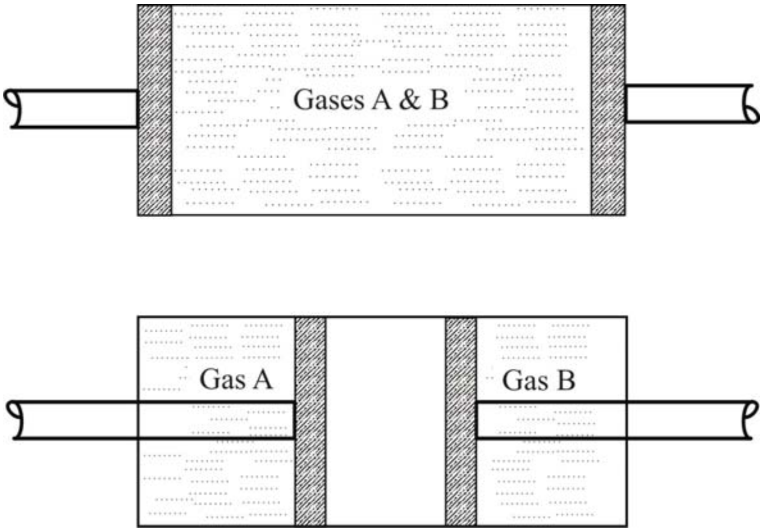

Fig. 2.13: Ideal separation process of two gases A and B

The total work required to separate a unit mass of mixture would be

$$\frac{-W_{\min}}{m_m}=T_m\left[\left(\frac{m_a}{m_m}\right)(S_{1a}-S_{2a})+\left(\frac{m_b}{m_m}\right)(S_{1b}-S_{2b})\right]-\left[\left(\frac{m_a}{m_m}\right)(h_{1a}-h_{2a})+\left(\frac{m_b}{m_m}\right)(h_{1b}-h_{2b})\right]$$

--- (2.7)

Let us consider, this separation process as an isothermal process and then the ideal work of separation for an ideal gas mixture is given by

$$\frac{-W_{\min}}{m_m}=T_m\left[\left(\frac{m_a}{m_m}\right)R_a\ln\left(\frac{p_m}{p_{1a}}\right)+\left(\frac{m_b}{m_m}\right)R_b\ln\left(\frac{p_m}{p_{1b}}\right)\right] \quad \text{--- (2.8)}$$

The entire process is carried out at constant temperature and constant total volume V_m, therefore, the individual pressure ratios can be expressed in terms of the mass ratios as

$$\frac{p_m}{p_{1a}}=\frac{m_m R_m T_m / V_m}{m_a R_a T_a / V_m}=\frac{m_m R_m}{m_a R_a} \quad \text{--- (2.9)}$$

Here, it becomes more convenient to use unit moles instead of unit mass. The above expression may be written as

$$\frac{p_m}{p_{1a}}=\frac{n_m}{n_a}=\frac{1}{y_a} \quad \text{--- (2.10)}$$

Therefore, the work requirement for separation per unit mole of fraction is given by

$$\frac{-W_{\min}}{n_m}=\bar{R}T_m\left[y_a\ln\left(\frac{1}{y_a}\right)+y_b\ln\left(\frac{1}{y_b}\right)\right] \quad \text{--- (2.11)}$$

It is observed that from above equation the thermodynamic minimum work of separation of a binary mixture as a function of feed composition. The work requirement for the complete separation of a mixture of several ideal gases as

$$\frac{-W_{\min}}{n_m} = \bar{R}\, T_m \sum_j y_j \ln\left(\frac{1}{y_j}\right) \qquad \text{--- (2.12)}$$

Where $\bar{R}$ is a universal gas constant (8.314 kJ/kmol K), T_m is temperature of mixture and y_j is mole fraction of the jth component. As per Timmerhaus [TF 89] the reversible work required for separating gaseous component from other component in air at 300 K is given in **Table 2.1.**

Table 2.1: Work required for reversible separation of air at 300 K [Sap 02]

Gas	**Mole (%)**	**Work per mole of mixture (kJ/kgmol)**	**Work per unit mass of separated gas (kJ/kg)**
Nitrogen	78.084	1311.6	60.0
Oxygen	20.946	1280.2	191.0
Argon	0.934	132.1	353.9
Carbon dioxide	0.033	7.42	511.1
Neon	$1.818\text{x}10^{-3}$	0.54	1472.5
Krypton	$1.14\text{x}10^{-4}$	0.404	438.1
Xenon	$8.6\text{x}10^{-6}$	0.0037	328.1
Hydrogen deuteride	$3.12\text{x}10^{-2}$	7.06	7485.0
Deuterium	$1.56\text{x}\ 10^{-2}$	3.80	6090.0
Helium	$1.0\text{x}10^{-5}$	0.00427	14,220.0

Energy required in the cryogenic air separation plant is utilized for the following purposes.

i. To separate the component gases from the mixture
ii. To provide cooling for off-setting the heat in-leak losses
iii. To compress the product gases
iv. To get the products in liquid form, as per requirement of the application

Air is separated into its components, in a distillation column, which is an energy intensive process. The continuous development is taking place in improvement in process cycle to minimize the work of separation.

In their paper Agrawal et al. [AEW 89] have discussed about several ways of improvement in the conventional dual pressure distillation process. The various more efficient distillation configurations for the conventional double column high purity oxygen process have been explained to provide substantial improvement either as reduced energy or as increased yield of valuable products. The important developments in the air separation, cryogenic and non-cryogenic in context of power consumption over the past few years are reviewed by Thorogood [Tho 91]. The power consumption and irreversibilities of low temperature distillation column are found on the basis of thermodynamic analyses [GS 57]. A method of calculation was developed by Thorogood [Tho 90], for the ideal energy consumption for binary gas separation, a single stage plug flow/cross flow membrane and their combination. The continuous development took place in thermodynamic cycle for cryogenic air separation plant, in order to improve its performance. The process cycle of cryogenic air separation plant analyzed and studied by mathematical modeling and software simulations for prediction of its performance.

Zhu et al. [ZLL 10] have developed a rigorous optimization model of cryogenic distillation system with argon column is presented and detail simulation is carried out. The simulation result shows that through optimization oxygen extraction percentage increases considerably and argon extraction percentage is also greatly improved. It indicates that optimization of this work is promising and feasible in improving productivity and profit of cryogenic distillation system. Castle [Cas 02] and [Cas 85] took review of modern developments in air separation and liquefaction systems. It is observed that earlier advances in air separation and liquefaction include improvements in overall product recovery, feed air purification, more efficient heat exchange, optimum plant control, gradual improvement in efficiency of compressors and expanders. More recent improvements include use of structured packing in distillation columns, molecular sieve adsorbents for air purification, computer simulation and control of plant and increased machinery efficiency. Advances in fabrication and construction techniques are aimed at reducing capital costs. Mandler [Man 00] has presented a summary over a decade of work in the modeling, simulation and control of cryogenic separation and liquefaction processes. The work includes not only successful applications but also the development of tools to facilitate the construction of the simulation flow sheets and their effective use in control system analysis and design. The use of these tools and of two commercial dynamic simulation packages is reviewed. Smith et al. [SK 97] reviews basic integration principle and describes next generation concepts based on advanced high pressure ratio gas turbines and integration of compression heat and refrigeration sources from the ASU. Continuing advancements in both air separation and gas turbine technologies offer new integration opportunities to improve performance and reduced costs. Operability issues associated with integration are reviewed and control measures are described for the safe, efficient, and reliable operation of these facilities.

Cryogenic air separation systems mainly involve interfacial mass and heat transfer as well as mixing. Distillation is a major separation system by means of heat supplied from a higher temperature level at the reboiler and rejected in the condenser at a lower temperature level. Therefore, it resembles a heat engine producing a separation work with a rather low efficiency. Thermodynamic analysis of air separation systems in context of lost work (energy) in separation systems is due to irreversible processes of heat, mass transfer, and mixing, and is directly related to entropy production discussed by Demirel [Dem 04]. In many separation systems of absorption, desorption, extraction, and membrane separation, the major irreversibility is the mass transfer process. Zhiong [Zhi 03] in his thesis, simulation of cryogenic air separation unit for liquid oxygen production is carried out. Separation of air is achieved by first expanding part of the compressed air to a low pressure into expander so that it cools to a low enough temperature to condense the balance of the air. The air after expander is directly fed to the low pressure distillation column. The low temperature, or cryogenic, air is subsequently separated in distillation units into its components of N_2 and O_2. The core of this process is a set of two columns, which are thermally connected at the center through a dual-function heat exchanger. This heat exchanger serves as a reboiler for the upper column and as a condenser for the lower column. The upper column operates at low pressure of about 0.6 atm while the lower column operates at middle pressure of about 5 atm. Sapali [Sap 01] has prepared process models of various cryogenic air separation units, like HP column, Double column, Crude argon column and double column integrated with crude argon column, low pressure gas plant and medium pressure liquid plant and carryout parametric evaluation including exergy analysis. Cryogenic air separation plants are continuously improvising in terms of power consumption and productivity with desired quality. Zhu et al. [ZLZ 06] have attempted to develop optimization model for cryogenic air separation plant including argon column and perform simulation to produce desired product with more profit. It is well known that cryogenic air separation require large amount of power to liquefy air by cooling. One novel concept of cryogenic air separation process that reduces energy consumption by self recuperation is reported by Kansha et al. [KKNT 11].

2.5 Biomass gasification

2.5.1 Biomass

Biomass refers to any organic materials that are derived from plants or animals. A generally accepted definition is difficult to find. However, the one used by the United Nations Framework Convention on Climate Change (UNFCCC, 2005) is relevant here:

“Non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes.

Common sources of biomass are:

- **Agricultural:** food grain, bagasse (crushed sugarcane), corn stalks, straw, seed hulls, nutshells, and manure from cattle, poultry, and hogs
- **Forest:** trees, wood waste, wood or bark, sawdust, timber slash, and mill scrap
- **Municipal:** sewage sludge, refuse-derived fuel (RDF), food waste, waste paper, and yard clippings
- **Energy:** poplars, willows, switch grass, alfalfa, prairie bluestem, corn, and soybean, canola, and other plant oils
- **Biological:** animal waste, aquatic species, biological waste

2.5.2 Introduction to gasification

The gasification of coal and biomass began in about 1800. The first commercial use of gasification started with the foundation of the London Gas, Light and Coke Company in 1812. The detail historical developments in gasification are explained by Hingman et al. [HB 03] and Basu [Bas 05]. Town gas was produced through pyrolysis of coal or by the water gas process, where coke was converted into a mixture of hydrogen and carbon monoxide. The town gas was first used for illuminating and later on also for space heating. But the use of town gas for lighting became unnecessary when the light bulb was introduced in the early 1900s. Later on cheaper natural gas made the use of town gas for space heating redundant. Still, the technology of gasification was useful for producing a raw material for synthesis of ammonia or methanol.

Gasification involves the production of gaseous fuel mainly consisting of Carbon monoxide (CO), Carbon dioxide (CO_2), Hydrogen (H_2), and with traces of Methane (CH_4); with useable heating value by partial combustion of solid fuel. The gasification process can be represented schematically as shown in **Fig. 2.14.**

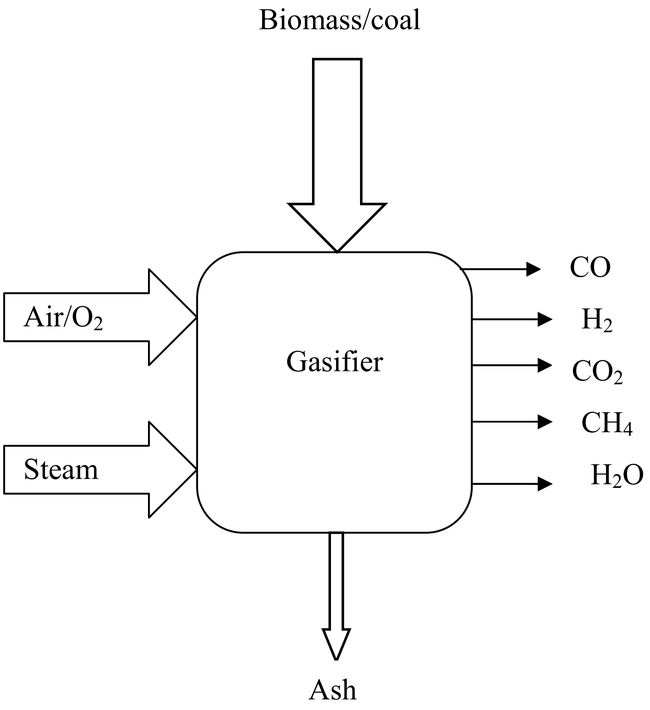

Fig. 2.14: Schematic diagram of gasification process

The combustion cannot be regarded as gasification since the product gas lacks heating value. It is normally carried out by reacting fuel such as coal, biomass, oil or coke with a minimal amount of oxygen often in combination with steam. It's a central process between combustion (thermal degradation with excess oxygen) and pyrolysis (thermal degradation in the absence of oxygen); it proceeds at temperatures ranging between 600 to 1500 ^{o}C. Depending upon the process type and operating conditions, low- or medium-value producer gas (which is a combination of combustible and non-combustible gases) is created. The heat liberated from the exothermic reactions of fuel and oxygen maintains the gasifier at the operating temperature and drives the endothermic gasification reactions taking place inside the gasifier. In comparison, "combustion" may be defined as the rapid high-temperature oxidation (burning) of a solid, liquid, or gaseous material. The main product of combustion is heat, whereas the main product of gasification is medium energy gas. This gas can be utilized directly as a fuel for power generation in gas turbines, etc. or as a feedstock for the production of chemicals otherwise produced from fossil fuels.

2.5.3 Importance of gasification

Clean gas obtained from a gasifier can be used as fuel for a large combined cycle system for electricity generation, where the gasified fuel is first burnt in a combustion turbine - generator unit, and then the hot exhaust gas from its gas turbine is used for generating steam to produce further power in a steam turbine - generator unit. The combination of a gasifier and a combined cycle is called the integrated gasification combined cycle (IGCC). Such a system results in a greater reduction in emissions from coal-based energy systems compared to that with direct combustion of the coal for power generation. An IGCC system offers a generating efficiency (40 %), higher than that for a conventional direct combustion pulverized coal fired plant (34 %). Another emerging application of gas from solid fuels is high-efficiency production of electricity using fuel cells. Coal/biomass can be gasified to produce syngas- a gas containing CO and H_2. This gas, after a high degree of purification can be substituted for natural gas in fuel cells, which could help enhance the power generation efficiency to above 50 %.

Gasification is a time-tested, reliable, and flexible technology that converts carbonaceous materials, biomass, municipal waste, scrap tires and plastics into a clean high energy gas. Gasification does not involve combustion, (or burning), but instead is a thermal chemical process that uses high temperature in a controlled environment, with limited oxygen, to convert carbon-based materials directly into a high energy ‘producer gas’. The gasification process breaks these materials down to the molecular level, so impurities can be easily and inexpensively removed. Gasification produces electricity with significantly reduced environmental impact compared to traditional technologies. Therefore compared to the old coal-burning plants, gasification can capture carbon dioxide much more efficiently and at a lower cost. Gasification has been reliably used on a commercial scale for more than 50 years in the refining, fertilizer, and chemical industries, and for more than 35 years in the electric power industry.

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, in an economically viable way, methanol - an extremely attractive chemical which is useful both as fuel for heat engines as well as chemical feedstock for industries. Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas where only selected biomass materials can produce the fuel. The multitude applications of syngas can be shown in **Fig. 2.15.**

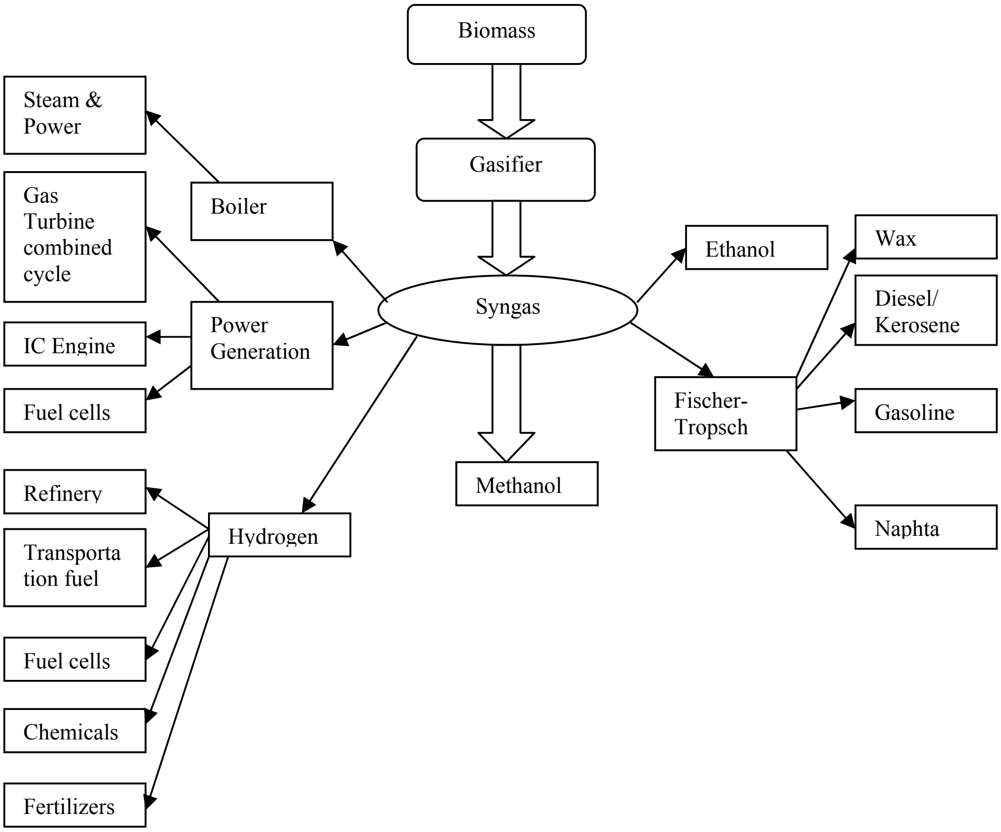

Fig. 2.15: Star diagram of syngas applications

2.5.4 Gasification process

During gasification of biomass/coal, the material is heated to a high temperature, which causes a series of physical and chemical changes that result in the evolution of volatile products and carbonaceous solid residues. The main steps of gasification process can be schematically shown in **Fig. 2.16.**

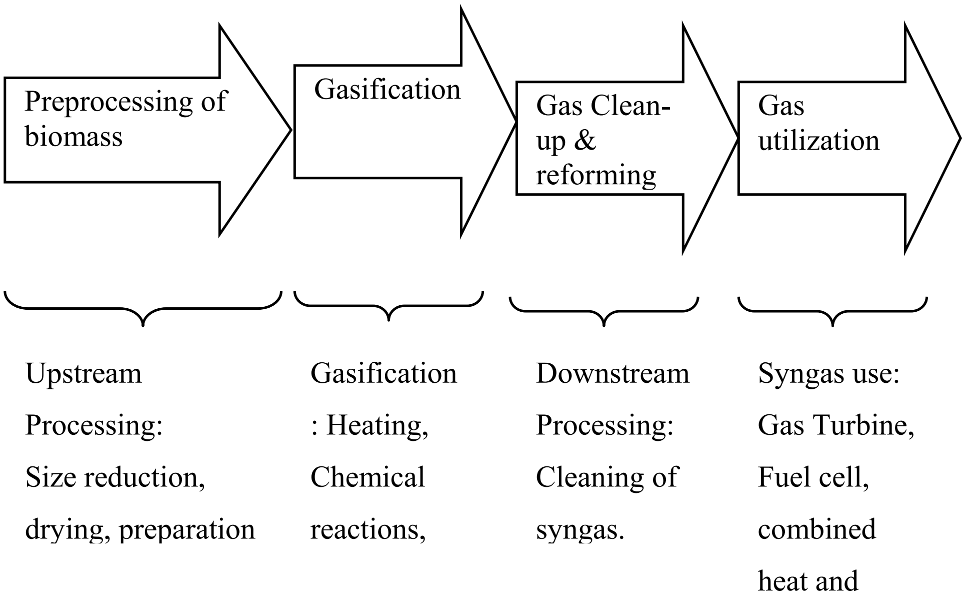

Fig. 2.16: Principal steps of gasification

The amount of volatiles produced and their compositions depend on the reactor temperature, type, and characteristics of fuel material. The gasification process uses an agent, air or oxygen, hydrogen or steam to convert carbonaceous materials into gaseous products as shown in **Fig. 2.17.**

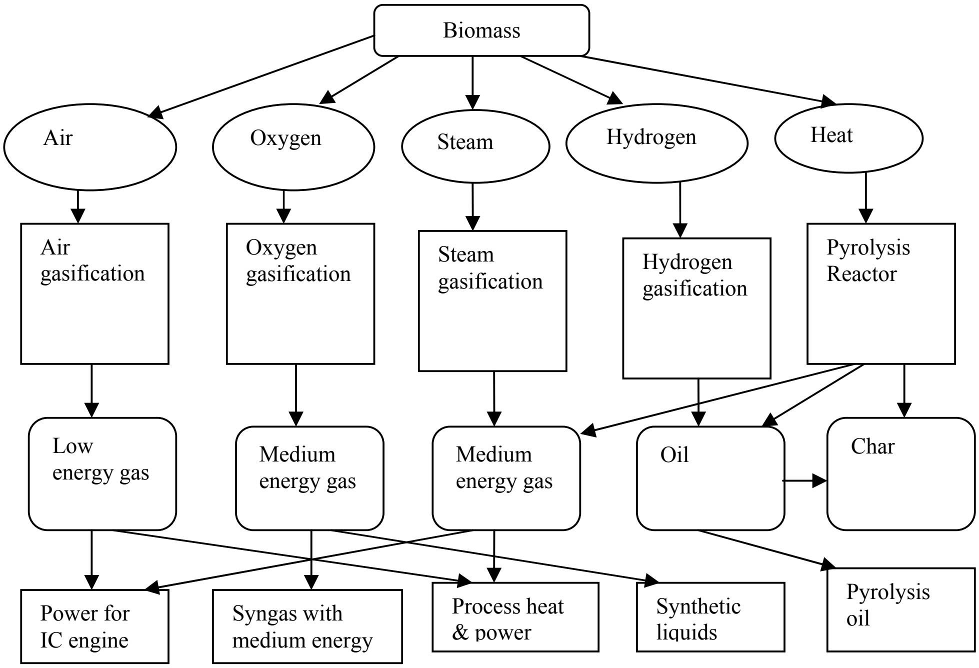

Fig. 2.17: Gasification process with different gasifying agent

2.5.5 Air gasification

The simplest gasification process is in which air is used as gasifying agent. The syngas produced is a low-energy gas containing primarily hydrogen and carbon monoxide diluted with the nitrogen from air. The lower heating value of the syngas is in the range of 4-7 MJ/Nm^3, which makes it suitable for boiler and engine applications. Due to its simplicity, air gasification technology is being studied by many researchers for various types of biomass.

2.5.6 Oxygen gasification

If the pure or enriched oxygen air is used as gasifying agent for gasification process, the product gas will not contain nitrogen and thus, have medium energy is in the range of 10-20 MJ/Nm^3. Such a gas can be economically distributed in pipeline network systems and therefore, be conveniently used for process heat or possibly as synthesis gas to produce chemical and fuels. However, the industrial production of oxygen for the gasifier, usually based on cryogenic air separation processes, also requires work, which should be included in the analysis. In this case, an oxygen plant or a nearby source of oxygen is required, which may elevate the capital cost necessary for the plant installation.

The use of oxygen does have other advantages such as operation at lower equivalence ratio, smaller equipment size of gasifier and downstream equipment, and possibly savings in compression cost of produced gas, but also disadvantages such as the investment cost for an oxygen plant and safety aspects related to storage and production of oxygen. Therefore, the choice of gasifying medium is not only determined by energetic considerations, but also by process economics, which depend on the scale of the gasification process.

2.5.7 Steam gasification

In steam gasification an external heat source is required if steam is used as a sole gasifying agent. In regular practice steam and air mixture is used as gasifying agent and such gasification process has been studied by many researchers. Oxygen in the air will help to provide the required energy due to exothermic nature of burning of biomass. The elevated temperature will help in the devolatilization process of biomass to produce various gases. Steam takes parts in water shift reaction in which steam reacts with carbon monoxide to produce hydrogen and carbon dioxide.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{--- (2.13)}$$

Steam gasification produces a higher energy content syngas as compared to air gasification.

2.5.8 Hydrogen gasification

In this route of gasification, the fuel feedstock is converted to gaseous fuels in the presence of hydrogen under high pressures. With this process, it is critical that stringent reaction conditions are maintained since the majority of the products are normally in the gaseous phase. This process is unfavorable because of the degree of control necessary as well as the fact that hydrogen must be readily available.

The composition of the product gas is dependent on several different factors such as, gasification temperature, oxidation agent, and reactor type and biomass feedstock. The choice of oxidizing agent strongly influences the lower heating value (LHV) of the produced gas. If air is chosen as oxidizing agent it will result in a low calorific value of gas (4-7 MJ/Nm^3), can be used in gas engines or turbines. Oxygen or steam as oxidizer leads to a medium calorific value gas (10-20 MJ/Nm^3). The later one is more appropriate as a feedstock for e.g. synthesis of liquid fuels and chemicals while the previous is more suitable where the heat content is not critical, for example in large boiler systems. Gasification with steam is more commonly called reforming and results in a syngas rich with hydrogen. Klosek et al. [KSS 86] have reported the role of oxygen in coal gasification and compared air gasification and oxygen gasification.

2.5.9 Gasification techniques

There are several different generic types of gasification techniques have been developed for conversion of biomass feedstock into syngas for the production of heat and power. These gasification techniques are having main differences as mentioned below.

- How the biomass is fed into the gasifier and is moved around within it - biomass is either fed into the top of the gasifier, or into the side, and then is moved around either by gravity or air flows.
- Whether oxygen, air or steam is used as an oxidant- using air dilutes the syngas with nitrogen, which adds to the cost of downstream processing. Using oxygen avoids this, but is expensive, and so oxygen enriched air can also be used.
- The temperature range in which the gasifier is operated.

- Whether the heat for the gasifier is provided by partially combusting some of the biomass in the gasifier (directly heated) or from an external source (indirectly heated).
- Whether or not the gasifier is operated at above atmospheric pressure - pressurized gasification provides maximum capacities, promotes hydrogen production and leads to smaller, cheaper downstream cleanup equipment. Furthermore, since no additional compression is required, the syngas temperature can be kept high for downstream operations and liquid fuels catalysis. However, at pressures above 25 - 30 bar, costs quickly increase, since gasifiers need to be more robustly engineered, and the required feeding mechanisms involve complex.

2.5.10 Indirect (Pyrolitic) gasification

Indirect (pyrolitic) gasification is accomplished when a portion of the fuel or char is burned in an external vessel with air, and the resulting heat is used to supply the energy necessary to pyrolyze the biomass. The principal advantage of this process is that a medium energy gas is produced without using oxygen. The disadvantage is that a significant fraction of tar may be produced and indirect heat or mass transfer is required which complicates the process. It is only practical in large installations and is not well developed as direct gasification with air or oxygen.

2.5.11 Direct gasification

Pyrolysis and gasification processes are endothermic, so heat must be supplied in order to carry out the process. The heat required to accomplish pyrolysis and raise the products to 600 ^{0}C is about 1.6- 2.2 kJ/gm, representing 6 % to 10 % of the heat of combustion of the dry biomass. In direct gasification, this heat is supplied directly by partially combusting the volatile tars in gasifiers; it comes from the sensible heat of the gases of partial combustion. This combustion then dilutes the product gas with CO_2 and H_2O, the products of combustion with oxygen. If the combustion is accomplished with air, the gas is also diluted with about 50 % nitrogen from the air. The principal advantage of direct gasification is that process is very simple, the direct heat transfer from the gases to the biomass is very efficient and the process is self regulating.

2.5.12 Gasification reactors

There are various types of reactors used in gasification process which can be classified according to the movement of the fuel and gasifying medium as either fixed bed (Updraft, downdraft and cross draft) or fluidized beds (Bubbling, circulating and swirling).

2.5.12.1 Fixed bed reactors

Fixed bed reactors are those in which solids move either countercurrent or concurrent to the flow of a gas as reaction takes place, and the solids are converted to gases. The fixed bed gasifiers are discussed below.

1. Updraft gasifier

Updraft gasifier is the oldest and the simplest design of all gasifiers. Here the gasifying agents (air, steam or oxygen) flow from the bottom and the biomass flows from the top in a concurrent stream as shown in **Fig. 2.18.** The gasifying medium enters through a grate and comes in contact with the hot ash. The grate is provided to facilitate removal of ash. Sometimes a vibratory or an oscillating grate is provided when high ash removal rate is required.

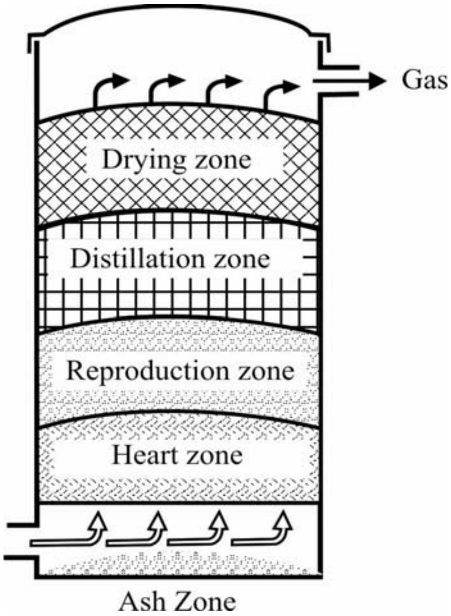

Fig. 2.18: Updraft gasifier

In this gasifier, the fuel descends through three zones (drying, pyrolysis and oxidation) of progressively increasing temperatures. Temperature in the oxidation zone can exceed 1500 ^{o}C. The oxidation zone lies at the bottom of the gasifier and the combustion gas passes through this zone reacting with the char, thereby releasing the required process heat. The produced gases, tar and other volatiles disperse at the top while ashes are removed at the bottom of the reactor. Part of the fuel is burned in the oxidation zone. The gas produced by an updraft gasifier usually exits at low temperatures (approximately 400 ^oC) and thus is rich in hydrocarbons and has high tar content. The tar contains as much as 30 % of the energy in the original crop biomass. The high tar content is not a major problem if the producer gas is used for direct heat applications. However, it requires thorough cleaning for internal combustion engine applications. The product gas from an updraft gasifier contains more CO, but less CH_4, ethane and acetylene than gas from other gasifiers. Updraft gasification of biomass using particulate fuels has been used widely in agricultural and industrial applications. The use of an endothermic agent (usually steam) has been the traditional approach for controlling the oxidation zone temperature of updraft gasifiers. Exhaust gas re-circulation is another approach to control the temperature of an updraft gasifier. Updraft gasifiers have several advantages, including simple design and construction, low gas exit temperature, high charcoal burnout and high thermal efficiency. However, slagging can be very severe in updraft gasifiers, especially with high ash-content fuels like cereal straws and corn cobs. Other disadvantages include high tar content and unsuitability for use with fluffy, low density feedstock.

2. Downdraft gasifier

Reaction zones in a downdraft gasifier are similar to those in the updraft unit, except the locations of the oxidation and reduction zones are interchanged as shown in **Fig. 2.19.** The most important difference is that the pyrolysis products in the downdraft type are allowed to pass through the high temperature oxidation zone. Hence, they undergo further decomposition. Also, the moisture vaporized from the biomass enters the gasification zone and serves as a gasifying agent. The final product gases, which leave the gasifier from the bottom at a fairly high temperature (700 ^oC), contains substantially less tar than the updraft gasifiers. In a downdraft gasifier, feedstock is introduced at the top and the gasifying agent is introduced through a set of nozzles located on the sides of the reactor. The benefit of the downdraft gasifier lies in its ability to produce gas with low oil and tar contents, which means less cleaning before use in internal combustion engines. The gas can, therefore, be used with minimal filtering as a fuel for spark ignition and diesel engines. However, due to slag and clinker formation problems, this type of gasifier has been found unsuitable for fuels with high ash content and low ash fusion temperatures, such as crop residues. A major drawback is its inability to handle fine and fluffy (low density) crop residues materials.

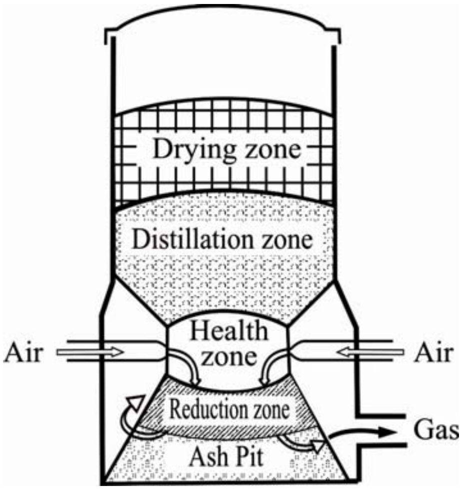

Fig. 2.19: Downdraft gasifier

3. Cross draft gasifier

Cross-draft gasifiers exhibit many operating characteristics of the down draft units. Air or air/steam mixtures are introduced in the side of the gasifier near the bottom while the product gas is drawn off on the opposite side. Normally an inlet nozzle is used to bring the air into the center of the combustion zone as shown in **Fig. 2.20.** The velocity of the air as it enters the combustion zone is considerably higher in this design, which creates a hot combustion zone. The combustion (oxidation) and reduction zones are both concentrated to a small volume around the sides of the unit. Cross-draft gasifiers respond rapidly to load changes. They are normally simpler to construct and more suitable for running engines than the other types of fixed bed gasifiers. However, they are sensitive to changes in biomass composition and moisture content.

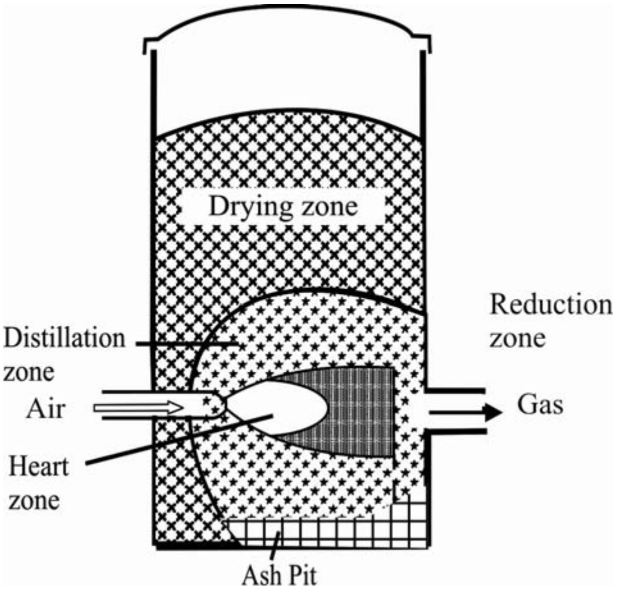

Fig. 2.20: Cross draft gasifier

2.5.12.2 Fluidized bed reactors

Unlike fixed bed reactors, models with a fluidized bed have no distinct reaction zones - drying, pyrolysis and gasification occur simultaneously in the reactor as the reactor is mixed and, thus, closed to isothermal. Fluidized bed reactors can be classified by configuration and the velocity of the gasifying agent, e.g., bubbling, circulating, spouted, and swirling fluidized beds.

2.6 Gasification reactions

The gasification reactions are reversible. The direction of the reaction and its conversion are subjected to the constraints of thermodynamic equilibrium and reaction kinetics. The combustion reactions essentially go to completion. The thermodynamic equilibrium of the rest of the gasification reactions are relatively well defined and collectively impose a strong influence on the thermal efficiency and the produced syngas composition of a gasification process. Thermodynamic modeling has been a useful tool for estimating key design parameters for a gasification process, for example:

- Calculating of the relative amounts of oxygen and/or steam required per unit of biomass/coal feed
- Estimating the composition of the produced syngas
- Optimization of the process efficiency at various operating conditions

Other deductions concerning gasification process design and operations can also be derived from the thermodynamic understanding of its reactions. Examples include:

- To produce a syngas with low methane content, a high temperature and substantial amount of steam in excess of the stoichiometric requirement is required
- Gasification at very high temperature will increase oxygen consumption and decrease the overall process efficiency
- To produce a syngas with a high methane content, gasification needs to be operated at low temperature (~700 °C), but the methanation reaction kinetics will be poor without the presence of a catalyst

There is considerable advantage to carry out gasification under pressure. At a typical entrained flow gasifier operation temperature of ~1500 °C, the syngas composition shows very little change as a function of operating pressure, but significant savings in compression energy and cost reduction from using smaller equipment can be realized.

2.6.1 Major reactions

Within a gasification process, the major chemical reactions are those involving carbon, CO, CO_2, H_2, H_2O and CH_4, as follows:

The combustion reactions:

1. $C + \frac{1}{2} O_2 \rightarrow CO$ (-111 MJ/Kmol)* --- (2.14)
2. $CO + \frac{1}{2} O_2 \rightarrow CO_2$ (-283 MJ/Kmol)* --- (2.15)
3. $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (-242 MJ/Kmol)* --- (2.16)

Other important gasification reactions include:

4. $C + H_2O \leftrightarrow CO + H_2$ (+131 MJ/Kmol)* --- (2.17)
   ("the Water-Gas Reaction")
5. $C + CO_2 \leftrightarrow 2CO$ (+172 MJ/Kmol)* --- (2.18)
   ("the Boudouard Reaction")
6. $C + 2H_2 \leftrightarrow CH_4$ (-75 MJ/Kmol)* --- (2.19)
   ("the Methanation Reaction")

Combustion reactions will result in completion under normal gasification operating conditions. Under the condition of high carbon conversion, the three heterogeneous reactions (reactions 4 to 6) can be reduced to two homogeneous gas phase reactions of water-gas-shift and steam methane-reforming (reactions 7 and 8 below), which collectively play a key role in determining the final equilibrium syngas composition.

7. $CO + H_2O \leftrightarrow CO_2 + H_2$ (-41 MJ/Kmol)* --- (2.20)

("Water-Gas-Shift Reaction")

8. $CH_4 + H_2O \leftrightarrow CO_2 + 3H_2$ (+206 MJ/Kmol)* --- (2.21)

("Steam-Methane-Reforming Reaction")

2.7 Thermodynamic equilibrium model of gasifier

Thermodynamic equilibrium calculation is independent of gasifier design and so is convenient for studying the influence of fuel and process parameters. Though chemical or thermodynamic equilibrium may not be reached within the gasifier, this model provides the designer with a reasonable prediction of the maximum achievable yield of a desired product. However, it cannot predict the influence of hydrodynamic or geometric parameters, like fluidizing velocity, or design variables, like gasifier height.

Chemical equilibrium is determined by either of the following:

1. The equilibrium constant (Stoichiometric)
2. Minimization of the Gibbs free energy (Non-Stoichiometric)

1. Stoichiometric equilibrium models

In the stoichiometric method, the model incorporates the chemical reactions and species involved. It usually starts by selecting all species containing C, H, and O, or any other dominant elements. If other elements form a minor part of the product gas, they are often neglected. Reaction rate constants can be used for balancing known and unknown variable.

2. Non-stoichiometric equilibrium models

In non-stoichiometric modeling, no knowledge of a particular reaction mechanism is required to solve the problem. In a reacting system, a stable equilibrium condition is reached when the Gibbs free energy of the system is at the minimum. So, this method is based on minimizing the total Gibbs free energy. The only input needed is the elemental composition of the feed, which is known from its ultimate analysis. This method is particularly suitable for fuels like coal, biomass, the exact chemical formula of which is not clearly known.

3. Kinetic models

Gas composition measurements for gasifiers often vary significantly from those predicted by equilibrium models. This shows the inadequacy of equilibrium models and underscores the need of kinetic models to simulate gasifier behavior.

A kinetic model gives the gas yield and product composition a gasifier achieves after a finite time or in a finite volume in a flowing medium. Thus, it involves parameters such as reaction rate, residence time of particles, and reactor hydrodynamics. For a given operating condition and gasifier configuration, the kinetic model can predict the profiles of gas composition and temperature inside the gasifier and overall gasifier performance. The model couples the hydrodynamics of the gasifier reactor with the kinetics of gasification reactions inside the gasifier. At low reaction temperatures, the reaction rate is very slow, so the residence time required for complete conversion is long. Therefore, kinetic modeling is more suitable and accurate at relatively low operating temperatures (<800 °C). For higher temperatures, where the reaction rate is faster, the equilibrium model may be of greater use.

Kinetic modeling has two components:

i. Reaction kinetics and
ii. Reactor hydrodynamics

Reaction kinetics must be solved simultaneously with bed hydrodynamics and mass and energy balances to obtain the yields of gas, tar, and char at a given operating condition. As the gasification of a coal particle proceeds, the resulting mass loss is manifested either through reduction in size with unchanged density or reduction in density with unchanged size. In both cases the rate is expressed in terms of the external surface area of the coal char. Some models, where the reaction is made up of char alone, can define a reaction rate based on reactor volume.

2.7.1 Thermodynamic equilibrium model for biomass/coal gasification

Let A denote the air supply in kg of dry air/kg dry fuel, F the amount of dry fuel required to obtain one normal cubic meter of the gas, and X_C the carbon content of the fuel (kg carbon/kg dry fuel). Carbon is split between CO, CO_2, and CH_4. For one normal cubic meter of gas produced, one can write the carbon molar balance between inflow and outflow streams [Bas 06].

Carbon balance:

$$\frac{F*Xc}{12}=\frac{(Vco+Vco_2+Vch_4)}{22.4} \quad \text{Or } 1.866*F*Xc=Vco+Vco_2+Vch_4$$

--- (2.22)

Where V represent the volumetric fraction of a constituent gas.

Hydrogen balance:

Let S represent the total steam supplied as humidity associated with air and added steam (kg steam/kg of dry fuel), and W represent the moisture content of fuel (kg water/kg dry fuel).

We write the molar balance of H_2 as follows:

$$F\left(\frac{S}{18}+\frac{X_H}{2}+\frac{W}{18}\right)=\frac{(Vh_2+Vh_2o+2*Vch_4)}{22.4} \quad \text{Or}$$

$$1.24*F*S+(11.21*F*X_H+1.24*F*W)=Vh_2+Vh_2o+2*Vch_4$$

--- (2.23)

Where X_H = Hydrogen content of the fuel (kg hydrogen/kg dry fuel)

Oxygen balance:

If O_a represents the mass fraction of oxygen in air and X_O is the oxygen content of the fuel (kg oxygen/kg dry fuel), hence the molar balance of O_2 as follows:

$$F\left(\frac{S}{36}+\frac{Xo}{32}+\frac{W}{6}+\frac{A*O_a}{32}\right)=\frac{(0.5*Vco+Vco_2+0.5*Vh_2o)}{22.4} \quad \text{--- (2.24)}$$

Where A is kg air/kg dry fuel, or,

$$0.623(F*S+F*W)+0.701(F*Xo+F*A*O_a)=0.5*Vco+Vco_2+0.5*Vh_2o$$

--- (2.25)

Nitrogen balance:

If X_N is the nitrogen content of the fuel (kg nitrogen/kg dry fuel) and Na is the mass fraction of nitrogen in air, the molar balance of N_2 gives:

$$F\left(\frac{Xn}{28}+\frac{A*Na}{28}\right)=\frac{Vn_2}{22.4} \quad \text{Or,} \quad 0.8*F*Xn+0.8*F*A*Na=Vn_2$$

--- (2.26)

The volume fractions of all constituents of the product gas add up to 1.0. We, therefore, also have:

$$Vco+Vco_2+Vh_2+Vch_4+Vh_2o+Vn_2=1 \quad \text{--- (2.27)}$$

To estimate the values of the seven unknowns: V_{co}, V_{co2}, V_{h2}, V_{h2o}, V_{n2}, V_{ch4}, and F, seven equations are required. For this purpose, besides the above five equations (Equation 2.22 to Equation 2.27), any two of the equations can be assumed from the water-gas reaction, Boudouard reaction, shift conversion and methanation to be in equilibrium. Working with Water-gas reaction and Boudouard reaction was chosen. For the Boudouard reaction, the equilibrium constant is:

$$Kpb = \frac{P^{2}co}{Pco_{2}} \qquad \text{--- (2.28)}$$

Where P_{CO} is the partial pressure of CO, which is equal to volume fraction of CO, (V_{CO} x the pressure of the reactor, P)

$$Kpb = \frac{(Vco*P)^{2}}{Vco_{2}*P} = \frac{(Vco)^{2}*P}{Vco_{2}} \qquad \text{--- (2.29)}$$

Similarly, for the water–gas reaction:

$$Kpw = \frac{Ph_{2}*Pco}{Ph_{2}o} = Vh_{2}*Vco*\frac{P}{Vh_{2}o} \qquad \text{--- (2.30)}$$

Solving above equations, equilibrium concentrations of gases are found.

In this case seven equations (2.22-2.27, 2.29, and 2.30) can be solved simultaneously. Aspen plus is used for solving these seven simultaneous equations. The input parameters are as follows.

Xc = 0.5961	kg of carbon / kg of dry fuel
Xh = 0.038	kg of hydrogen / kg of dry fuel
Xo = 0.0643	kg of oxygen / kg of dry fuel
Xn = 0.0077	kg of nitrogen / kg of dry fuel
S = 0.5	kg of steam / kg of dry fuel
A = 1.5	kg of dry air / kg of dry fuel
W = 0.059	kg of moisture in fuel / kg of dry fuel
Oa = 0.233	mass fraction of oxygen in air
Na = 0.767	mass fraction of nitrogen in air
Kpb = 60.17	Bouduard reaction equilibrium constant (bar)
Kps = 42.878	Steam gasification equilibrium constant (bar)
P = 30	Operating pressure (bar)
T = 1200	Operating temperature (K)

Carbon balance

$$1.866 * F * Xc = Vco + Vco_2 + Vch_4 \quad \text{--- (2.31)}$$

Hydrogen balance

$$1.24 * F * S + (11.21 * F * X_H + 1.24 * F * W) = Vh_2 + Vh_2o + 2 * Vch_4 \quad \text{--- (2.32)}$$

Oxygen balance

$$0.623(F * S + F * W) + 0.701(F * Xo + F * A * O_a) = 0.5 * Vco + Vco_2 + 0.5 * Vh_2o \quad \text{--- (2.33)}$$

Nitrogen balance

$$0.8 * F * Xn + 0.8 * F * A * Na = Vn_2 \quad \text{--- (2.34)}$$

$$Vco + Vco_2 + Vh_2 + Vch_4 + Vh_2o + Vn_2 = 1 \quad \text{--- (2.35)}$$

Boudouard reaction

$$Kpb = \frac{(Vco * P)^2}{Vco_2 * P} = \frac{(Vco)^2 * P}{Vco_2} \quad \text{--- (2.36)}$$

Steam gasification reaction

$$Kpw = \frac{Ph_2 * Pco}{Ph_2o} = Vh_2 * Vco * \frac{P}{Vh_2o} \quad \text{--- (2.37)}$$

Seven Unknowns: F, Vh_2, Vh_2o, Vch_4, Vco, Vco_2, Vn_2

Equilibrium constant for Boudouard and Steam gasification reaction are calculated from Gibbs free energy and equilibrium constant relation.

$$\Delta G = -RT \ln K \quad \text{--- (2.38)}$$

Where,

ΔG – Change in Gibbs free energy for the reaction

R – Gas Constant = 8.314 KJ / Kmol.K

T – Reaction Temperature, K

K – Rate Constant

2.8 Performance analysis of gasifier

There are various performance parameters quoted for gasification process. The most commonly applied parameters are discussed below.

2.8.1 Energetic efficiency

This efficiency is also called as first law efficiency. The gasification process is similar to any thermodynamic process and it has to satisfy first law of thermodynamics, which describes energy conservation. According to the first law of thermodynamics, we can write.

$$\sum_{R} H - \sum_{P} H = Q_{lost} \qquad \text{--- (2.39)}$$

Where H- enthalpy

Q_{lost}-heat lost during gasification process.

R and P- Reactants and products.

Two forms of energetic efficiencies are defined as follows.

$$\eta_1 = \frac{En_{H_2}}{En_{biomass} + En_{steam}} \qquad \text{--- (2.40)}$$

$$\eta_2 = \frac{En_{gas} + En_{tar} + En_{Char}}{En_{biomass} + En_{steam}} \qquad \text{--- (2.41)}$$

2.8.2 Cold gas efficiency

$$CGE = \frac{Heating\ value\ in\ the\ product\ gas\ (MW)}{Heating\ value\ in\ feedstock\ (MW)} \times 100 \qquad \text{--- (2.42)}$$

It is important to clarify that whether heating values on the basis of higher heating value or lower heating value.

2.8.3 Carbon conversion

$$Carbon\ \ conversion\ (\%) = 1 - \left[\frac{carbon\ \ in\ gasification\ \ residue}{carbon\ feedstock}\right] \qquad \text{--- (2.43)}$$

2.8.4 Effects of operating Parameters on gasification process

Several variables seem to affect the gasification process and product composition including temperature, pressure, bed height, gasifying medium, equivalence ratio, feed material moisture content, particle size, and air/oxygen to steam ratio. These parameters are quite interrelated and each of them affects the gasification rate, process efficiency, product gas heating value and product distribution.

The composition of the product gas of gasification, which is a mixture of carbon monoxide, methane, hydrogen, nitrogen, carbon dioxide etc., depends on its operating parameters as well as on the characteristics of the feedstock. Among the operating parameters, the temperature and the pressure of the gasifier have the greatest effect on the product composition.

1. Boudouard reaction

Fig. 2.21a shows the variation of volumetric carbon monoxide concentration with temperature for the Boudouard reaction ($C + CO_2 = 2CO$) at a pressure of 1 atm. It can be seen from the figure that high temperature favors carbon monoxide formation. Pressure has the opposite effect. **Fig. 2.21b** shows that at a given temperature, carbon monoxide formation is favored by low pressure. Thus, these figures suggest that if high carbon monoxide content gas is desired, the gasifier should be designed to operate at a high temperature and low pressure.

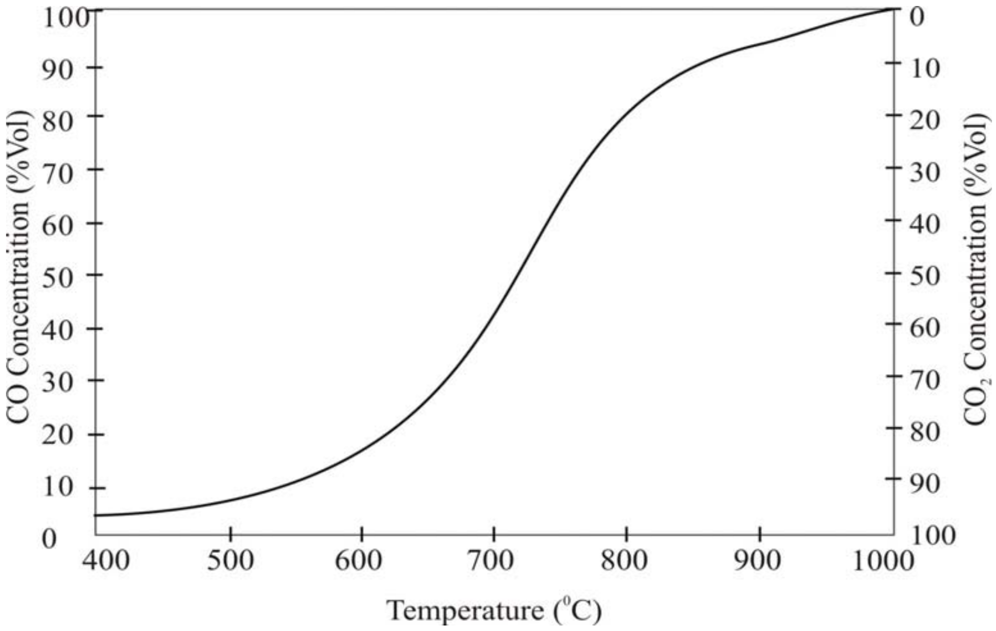

Fig. 2.21a: Effect of temperature on CO concentration [Bas 06]

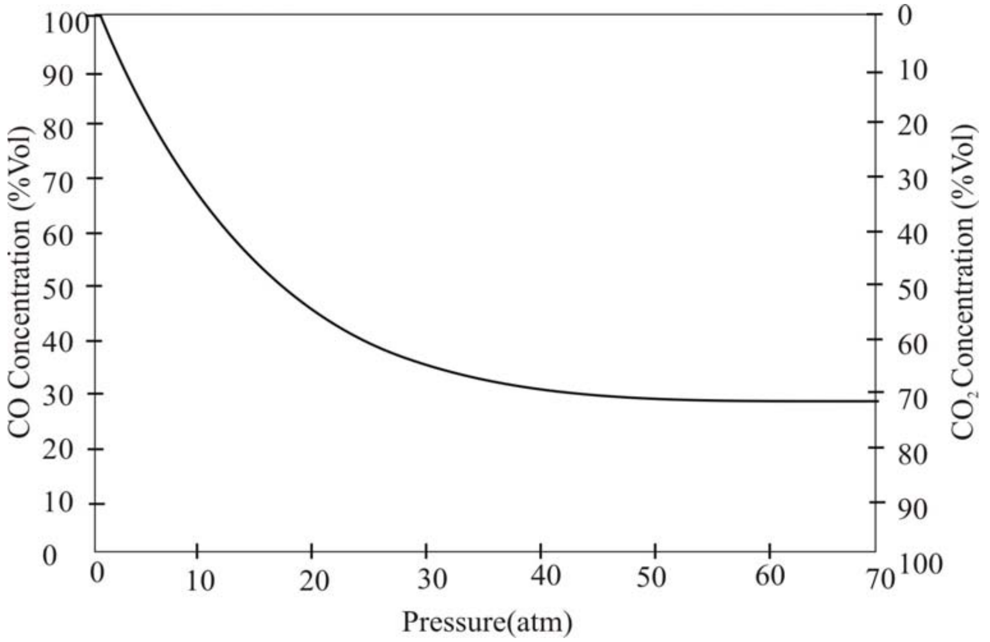

Fig. 2.21b: Effect of pressure on CO concentration [Bas 06]

2. Water–gas reaction

Fig. 2.22a, **b** shows the variation of carbon monoxide and hydrogen with temperature at a pressure of 1 atm, and with pressure at a temperature of 800 ^{0}C, respectively, for the water - gas reaction ($C + H_2O = CO + H_2$). It can be seen that the forward reaction is favored by high temperature and low pressure. Since hydrogen and carbon monoxide are produced at the same molar rate, they have the same molar (or volumetric) concentration in the gas mixture at equilibrium. Thus the concentration of steam in the mixture can be estimated by subtracting the concentrations of hydrogen and carbon monoxide (two times the value obtained from **Fig. 2.22a or b**) from the whole.

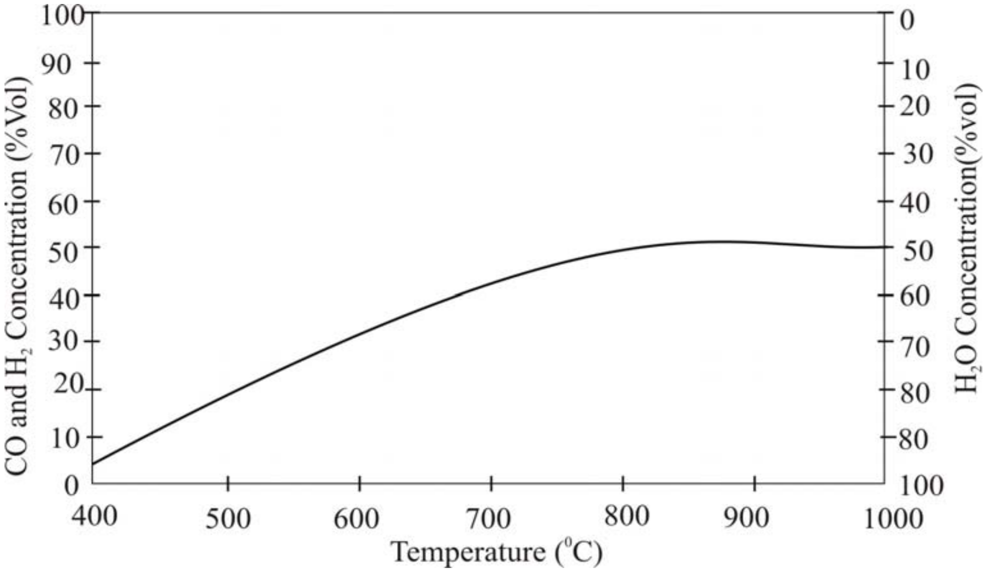

Fig. 2.22a: Effect of temperature on CO and H_2 concentration [Bas 06]

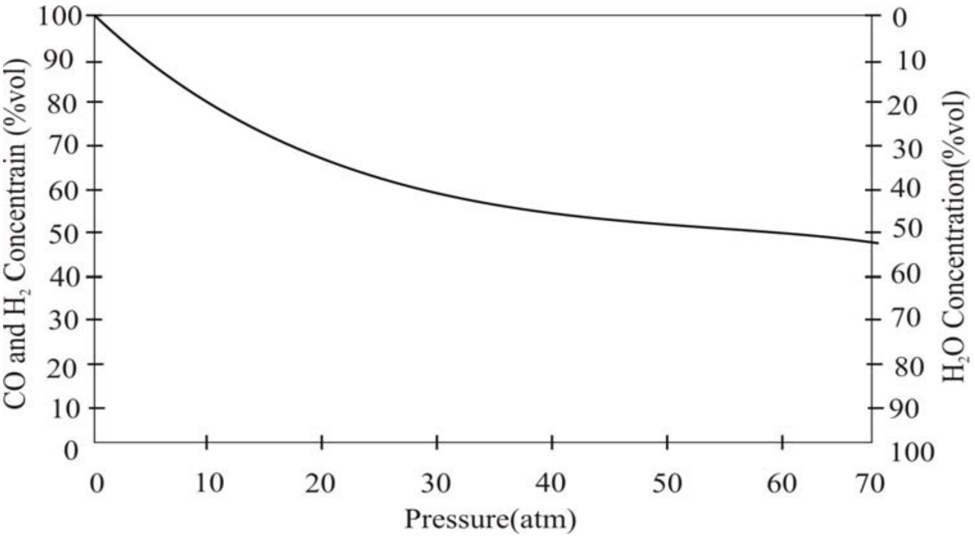

Fig. 2.22b: Effect of pressure on CO and H_2 concentration [Bas 06]

3. Methanation reaction

Fig. 2.23a, b shows the variation of methane in the flue gas with temperature at a given pressure (1 atm), and with pressure at a given temperature (800 ^{0}C), respectively. From these figures for the methane formation reaction ($C + 2H_2 = CH_4$), it can be noted that high methane concentration is favored by low temperature and high pressure.

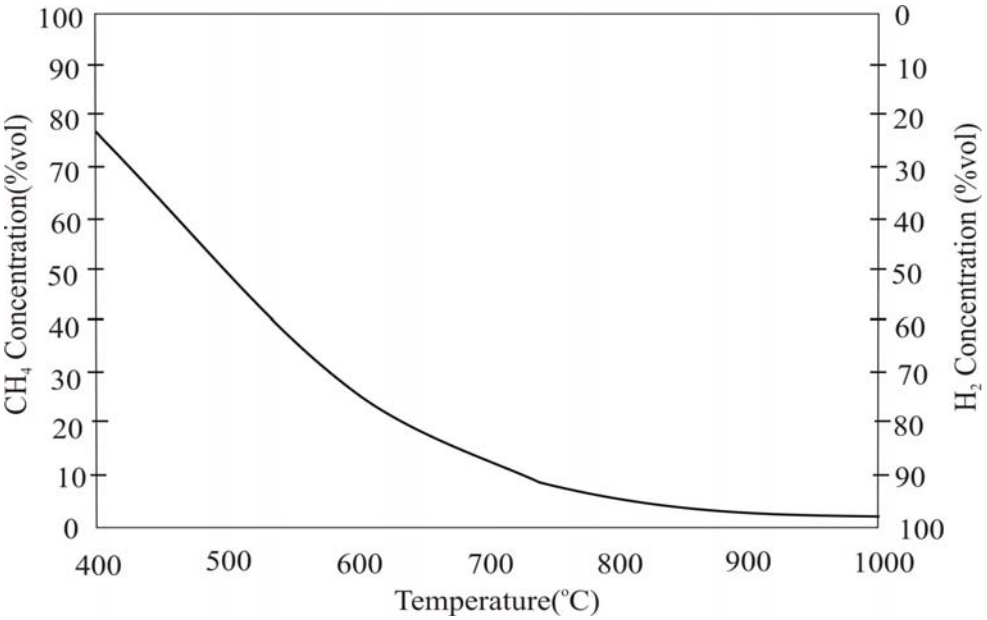

Fig. 2.23a: Effect of temperature on CH_4 concentration [Bas 06]

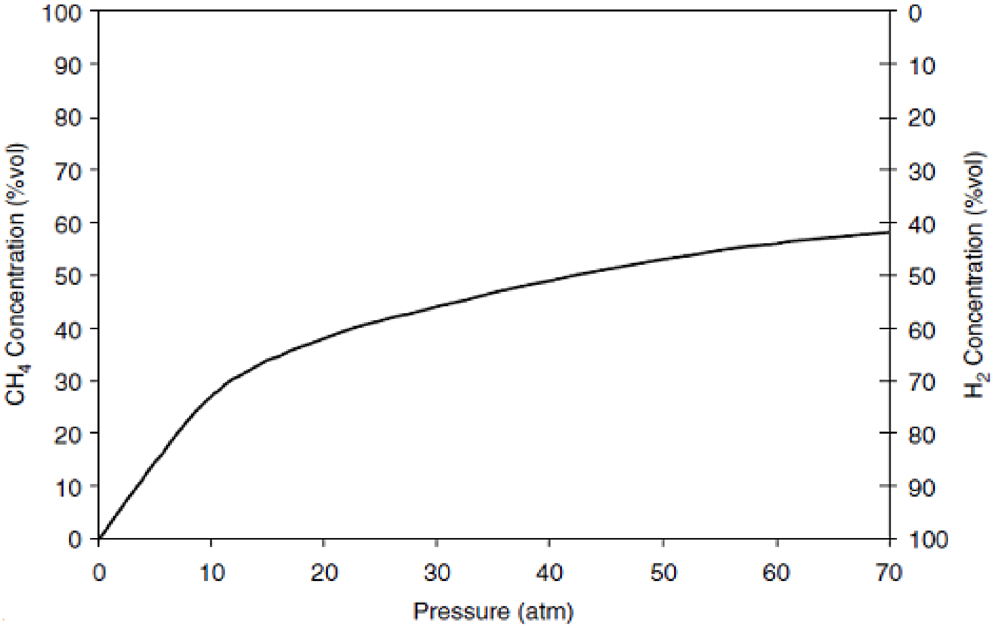

Fig. 2.23b: Effect of pressure on CH_4 concentration [Bas 06]

2.8.5 Effect of feed properties on gasification

The following section describes the effect of feed properties on the composition of the product gases.

1. Fuel reactivity

In general, the reactivity of coal decreases with its rise in rank. Physical properties of coal, such as particle size and porosity also have significant effects on the kinetics of coal gasification. As the particle size becomes smaller, the specific contact area between the coal and the reaction gases increases, resulting in faster reactions. For low and medium-rank coals, the reactivity in gasification increases with an increase in pore volume and surface area, but for high rank coal (C- 85 %); the reactivity is not affected by changes.

2. Volatile matter

On a dry basis, the volatile matter content of a fuel varies from less than 5 % in the case of anthracite to more than 75 % in the case of wood. The reactivity of a solid fuel and its conversion to char inside the gasifier depend on its volatile matter content. Fuels with higher volatile matter content are more reactive and therefore can be converted more easily into gas, producing less char. In the case of high-rank coals, which are less reactive and have low volatile matter content, char is the major product of pyrolysis. Thus, an efficient utilization of the char inside the gasifier is a major concern for the gasification of high-rank coal. Biomass feedstock, such as wood, is highly reactive and characterized by high volatile content. Thus, these fuels produce relatively small amounts (25 % of the weight of the original dry fuel) of char. Also, the char is more porous and reacts relatively fast. For this reason, fuels with high volatile matter content are easier to gasify. However, they produce gas with a high tar content, which makes gas clean-up more difficult.

3. Ash

The ash content of the fuel does not have much direct influence on the composition of the product gases, but it affects the practical operation of the gasifier. For example, in a gasifier operation, ash is an unavoidable nuisance that has to be separated from the product gases and suitably disposed of. Depending on the design, the ash is removed from a gasifier in either solid or liquid form. In the case of fixed and fluidized bed gasifiers, the ash is normally removed as a solid, requiring the peak temperature to be well below the melting point of the ash. Some units like slagging gasifiers are deliberately operated at sufficiently high temperatures to remove the ash as liquid slag. Fuels used in a gasifier designed to remove ash in dry solid form should have high ash-melting/ softening temperatures to avoid ash agglomeration inside the gasifier.

4. Moisture

The moisture content of solid fuels varies widely depending on their type, ranging from below 5 % for anthracite to about 40 % for low-rank sub-bituminous coal and lignite. The moisture content of wood from a freshly harvested tree is typically around 50 %. High moisture content of the feed lowers the temperature inside the gasifier since evaporation as well as the chemical reaction of steam with char is endothermic. Therefore, an upper limit of moisture content is set for satisfactory gasification. For example, in a typical fixed bed this limit is about 35 % for a good quality coal (moderate rank and ash content), and about 25 % for wood. Fluidized and entrained bed gasifiers, with their lower tolerance of moisture content, normally require moisture content of the feedstock to be reduced to 5 to 10 %.

2.9 Use of oxygen in gasification

There is large demand of oxygen for gasification for producing quality syngas, with lesser cost of oxygen production. Gasification is the process of converting carbon based fuels into a gaseous product with useable heating value.

Gasification occurs in a high temperature environment in the presence of an oxidation agent. Typical oxidation agents are air, steam, oxygen or a combination of these. Heat is added to the process either direct or indirect. The combination of heat and an oxidizer makes the large polymeric molecules of which the biomass consist to decompose into lighter molecules and finally into permanent gases. The product gas, or syngas, consists mainly of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2).

Bajareborn et al. [BA 10] in his thesis, the work was carried out in two steps, the first step was a literature survey and the second step was to model an integrated gasification combined cycle plant. The literature survey covered different gasification technologies, gas turbine operation, gas cleaning, fuel drying etc. Equilibrium modeling of the gasification process was also investigated in the literature survey. From the survey the concept of pressurized indirect gasification was chosen for the second part of the work. The models and simulations are made with the software IPSEpro, which is a simulation environment for energy engineering. Biomass gasification is one of the important energy conversion processes in context to limit global CO_2. The work carried out by Ruggiero et al. [RM 99] describes the simulation of biomass gasification process using equilibrium reactions and prediction of performance like syngas composition and its heating value. The majority past biomass gasifier demonstrations has been for the generation of process heat, steam and electricity, but Ciferno [CM 02], reported the use of syngas produced from biomass gasification for fuels, chemicals and hydrogen production. Biomass has high potential to contribute to energy needs of modern society worldwide. The physical and chemical characteristics of biomass, capacity of gasifier and its intended application decides the choice of gasification system. These all gasification systems are reviewed by authors [Raj 86], and [RD 98]. There are different types of gasifiers to produce syngas with the help of various gasifying agents. One of the important types is fixed bed gasifiers which are classified as updraft, downdraft and cross draft gasifiers. A complete review of fixed bed gasification systems for biomass is reported by Chopra et al. [CJ 07]. The gasification process uses an agent, air, oxygen, hydrogen, steam to convert carbonaceous materials into gaseous products. Sirigudi [Sir 05] has developed process model of gasifier in which air is used as gasifying agent and bioreactor to produce ethanol from switch grass in Aspen plus software. Using the developed model he studied the performance of the gasifier by manipulating the process variables and characterizing the effect on gas quality and composition. Gautam [Gau 10] has presents thermodynamic model of process inside the gasifier and syngas composition is predicted assuming thermodynamic equilibrium condition inside the gasifier. He has also experimentally studied effect of selected parameters like moisture content and biomass flow rate on syngas composition in downdraft gasifier.

In the work of Ponzio [Pon 08] primarily focus on fundamental aspects like mass conversion, heating and ignition. The analysis started from thin beds of fuel particles inserted into highly preheated agents and then thermal analysis carried out for whole gasification system. Thermo chemical equilibrium model of a biomass gasification process using Aspen plus has developed by Paviet et al. [PCT 09]. They modeled a downdraft gasifier and validated their result experimentally. Also they analyzed the effect of air fuel ratio on the syngas composition. Equilibrium model for biomass gasification have studied various fuels on the basis of the calorific value of generated synthetic gas proposed by Khadse et al. [KPAG 06]. Also the gasification model simulated using MATLAB and effect of various gasification parameters and adiabatic gasification temperature is determined. Sahu [Sah 11] has discussed about the effect of oxygen and steam enrichment on biomass gasification. Equilibrium model for a downdraft gasifier is solved using Engineering equation solver. The effect on calorific value of the producer gas is studied in detail. Ahmad et al. [AIYS 11] have focused on hydrogen production via gasification using equilibrium model of Empty fruit bunch. Simulation was done using iCON PETRONAS simulation software while studying the temperature variation effect from 600-1000 ^{0}C and Steam to feed ratio 0.1 to 1. Chawdhury et al. [CM 11] have developed a small model of downdraft biomass gasifier. Engineering Equation Solver (EES) is used to obtain syngas composition, heating value and cold gas efficiency. In his work, designing, developing and testing of the model are involved. In present scenario, hydrogen becomes more attractive clean fuel. Inayat et al. [IAMU 09] have highlighted gasification process for hydrogen production. Kinetic model based on chemical reactions analyzed using MATLAB for the prediction of syngas composition. Doherty et al. [DRK 08] have developed computer model of atmospheric circulating fluidized bed by using Aspen plus. The model predicts syngas composition, heating value and conversion efficiency in good agreement with published experimental data. Chen et al. [CCCY 10] have presents a simulation model for converting coal to methanol based on gasification process by commercial software Pro II V8.1.1.

2.10 Literature review of exergy analysis

In case of energy analysis, an energy balance is always closed as stated in the first law of thermodynamics. There can never be an energy loss, only energy transfer to the environment in which case it is useless. Exergy analysis is based on first and second law of thermodynamics, which shows the thermodynamic imperfectness of the process, including all quality losses of material and energy. Exergy analysis is needed for pinpointing and quantifying the irreversibilities in thermodynamic processes.

2.10.1 Introduction

The idea of available energy was first understood by the French Engineer Sadi Carnot for the specialized case of heat engines. In the next decades this concept developed theoretically by especially Herman Helmhotz and J. Willard Gibbs, but only recently standard definition has been formulated and termed as exergy [Rant 1956; Wall 1977; Suzargut et al. 1988]. The concept of exergy is extensively discussed in the books by Kotas [Kot 85], Brodyansky et al. [BSLP 94], Moran and Shapiro [MS 95] and Bejan et al. [BTM 96]. Keenan [Kee 32] has defined the concept of physical exergy, which is also called availability and uses it for the analysis of a steam turbine. Szargut [Sza 86] introduced the concept of chemical exergy and its associated reference states. Rosen [Ros 02] discussed the relation of exergy with economics, and many methods for performing economic analysis on the basis of exergy. The focus on linkage between exergy and environment also addressed elaborately. Cengel [Cen 02] addressed the exergy of mixing and splitting thermodynamic process by giving day to day life examples like merging and breaking up of families, companies etc. using the concept of entropy generation and exergy destruction. The mixing process is discussed elaborately by giving various examples in the light of exergy by Cengel et al. [CWD 02]. It shows that uniting or combining systems to form larger, more powerful system is good only if the systems work in harmony in the new larger unit and thus there is little or no exergy destruction. This can happen only if the combined system can act like a single homogeneous system. Therefore it is concluded that combining systems that are identical or almost identical will result in larger system with larger exergy content, but combining two systems that are at different states will yield a system that is larger in energy content with smaller in exergy content. So to avoid waste of work potential such systems should operate separately. Wall et al. [WG 01] have discussed sustainable development in the light of exergy. If there is no potential for work, i.e. no exergy, natural or artificial systems cannot work. This is a thermodynamic dead state, although energy still exists. If a society consumes the exergy resources at a faster rate than they are renewed, it will not be sustainable. The present industrial society is obliviously not sustainable and facing a collapse.

2.10.1.1 Exergy analysis of cryogenic air separation process

Exergy analysis can be applied to unit operation by first quantifying the exergy loss due to mixing, temperature difference, pressure drops, etc. and then evaluating the possible reduction in exergy loss for improvement in the equipment design. In cryogenic air separation process, the important equipment types are the distillation column, the heat exchanger, the driver system (turbine and compressor), and the pressure reducing devices, such as the J-T (Joule Thompson) valve and expander. In distillation column, the internal irreversibilities due to the stage mixing, valve, and heat transfer can be quantified by exergy analysis and then reduced through better feed tray location, increase in the number of stages, and reduction of reflux ratio. In heat exchangers, the reduction of temperature approach and pressure drop may reduce the irreversibilities. However, lower pressure drop may also lower the heat transfer coefficient and, offer no net reduction in irreversibility. The driver systems in cryogenic air separation process like compressors and turbines are also optimized by exergy analysis. Yong et al. [YMY 02] have performed exergy analysis of cryogenic air separation process for generating nitrogen. It was found that structural packings distillation columns gives better exergy efficiency than sieve tray distillation column. Chiu [Chi 82] has reviewed exergy analysis of cryogenic process and equipment optimization. Both the iterative comparative and analytical approaches are discussed in terms of their advantages and limitations. Shukuya et al. [SH 02] have presented mathematical formulation of exergy calculation to various processes like air conditioning, space heating and cryogenic air separation. Cornelisson [Cor 97] has presented the difference between energy analysis and exergy analysis and shows that for carrying out exergy analysis, an energy analysis has to be performed first. Tuo et al. [TL 11] have presented a novel idea of combined cycle of air separation and natural gas liquefaction. In a simulation of this combined cycle, exergy analysis was also performed. Yan et al. [YYLZ 10] have simulated a large scale air separation plant on the basis of industrial process and exergy efficiency of major equipments was analyzed.

2.10.1.2 Exergy analysis of gasification process

Gasification is a chemical process of converting any solid fuel into gaseous products having useable heating value. In the gasification process, exergy loss occurs due to instantaneous chemical reaction, internal thermal energy exchange and product mixing. Basically gasification is more efficient than combustion because in gasification internal thermal energy exchange loss reduced from 14-16 % to 5-7 %, while the chemical reactions are relatively efficient for both processes. Dudgeon [Dud 09] has presented equilibrium modeling in Aspen plus to develop methodology for evaluating different fuels for gasification based on exergy analysis. It is shown that by increasing equivalence ratio resulted in slight increase in exergetic efficiency of the gasifier. Internal combustion engine model was also developed based on closed system thermodynamics. Prins [Pri 05] has presented the gasification process in the light of exergy. He mentioned that thermodynamic efficiency of gasification processes should be defined based on exergy content of biomass feed and gaseous and solid products. It is observed that oxygen- blown gasification of fuels produces syngas with better quality than air-blown gasification of fuels. In the second part of his work, the pretreatment processes like Torrefaction of the gasification feedstock are required to produce quality syngas. Spyrakis et al. [SPK 09] have presents the modeling and exergy analysis of atmospheric air-blown gasification process for F-T synthesis which is second generation biofuel. Abuadala et al. [ADN 10] have addressed the hydrogen production from biomass gasification on the basis of first and second law of thermodynamics. It also shows the parametric analysis of biomass gasification for production of hydrogen.