DESIGN AND PARTIAL VALIDATION OF A SYSTEM FOR PROCESSING AND UTILISATION OF VEGETABLE PEELS, TRIMMINGS AND FLOWER WASTE TO BE USED IN IRON AND STEEL SECTOR

A Thesis submitted in partial fulfilment of requirements for the award of degree of

Master of Technology in Material Engineering

Jadavpur University

By

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2022-23

Declaration of Originality and Compliance of Academic Ethics

I, hereby, declare that this thesis contains literature review and original research work by the undersigned candidate, as part of studies: **"Design and Partial Validation of a System for Processing and Utilisation of Vegetable Peels, Trimmings and Flower Waste to be Used in Iron and Steel Sector".**

All the information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work and taken from different resources.

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This foregoing thesis is, hereby, approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as pre-requisite to the degree for which it has been submitted. It is understood by this approval the undersigned do not necessary endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

Committee on final examination for the evaluation of the thesis.

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Abstract

From the earlier days, in the world, Iron and Steel technology is the base of all development and infrastructure build-up, not only in economy, also in the human civilisation and daily life. Demand of this material is increasing with days, due to better properties and longer durability. Although the costing of reducing agent, Metallurgical coke is extremely higher. Coking process of lesser grade coal to produce coking grade coal is time consuming and relatively costlier. Also, the stock of coal and fossil fuel is in severe deterioration. In this situation, to execute the reduction process of iron ore (Hematite, Fe_2O_3), there is the higher need of alternative source of carbon rich reducing agent. In present day, in India, population is increasing in rapid rate. For this, as the demand of food and flowers is increasing, the amount of vegetable and flower wastes is also enhancing. The dumped peels and trimming of vegetables and flower wastes can be the potential source of carbon. In this context, study has been done on 4 vegetables: Potato, Pumpkin, Potal, Banana and 1 flower: Mary gold. The TGA-DTA analysis expresses that the peels and trimmings of vegetables and flower wastes contain about 85% water molecule as well as 15% pure form of carbon. In this study, from TGA-DTA plot, it is found that heating the vegetable and flower wastes for 30 minute at 350 deg. C, moisture content can be removed to obtain bio-dust containing pure form of carbon. This carbon containing bio-dust for each vegetable and flower is mixed with iron ore in stoichiometric basis, in presence of binding agent to produce nugget. Each of 5 nuggets are heating in raising hearth furnace at 1000 deg. C for 1 hour to reduce iron ore to metallic iron, the sign of reduction can be observed from X Ray Diffraction or XRD plot. Along with this, during heating the waste materials to generate bio-dust, huge amount of moisture can be lost. To prevent this, a design has been provided to condense the steam to get pure form water as well to reheat and pass the steam through the bio-dust at 900 deg. C to produce Syn-gas with the collection of excess steam content in form of water. This Syn gas can enhance extent of reduction by allowing it to pass through pre-reduced ore at 900 to 1000 deg. C. The water is potable and can be applied in laboratory and industrial purposes. The entire study signifies the vegetable (Potato, Potal, Pumpkin, Banana) peels and trimmings and flower wastes as the potential source of pure form of carbon to be applied in reduction in Iron ore (Hematite, Fe_2O_3), and the optimisation of moisture content released from the waste material to obtain Syn gas and allowing it through pre-reduced ore to enhance extent of

reduction as well as the degree of metallisation. Entire values, calculation and plots related to laboratory testing and design is provided in this study.

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Chapter: 1

Introduction

Introduction

Iron and Steel industries have shown remarkable growth from the last few decades. Iron is the pillar of human society. During the ancient period, after the discovery of this precious metal, human life and civilization became highly dependent on Iron. In today’s world, Iron and steel are the basic source of socio-economic progress and industrial development. India is quite fortunate since it is endowed with natural resources which are required for healthy and vigorous iron and steel making. India is in second position in crude iron and steel making in the world after china. With the liberalisation of import traffic on finished steel items, Indian steel manufacturers are able to decrease the cost of production and are competing in the world market. Private sectors are ready to invest in newer steel projects.

Steel industries derives its demand from other important sectors like- infrastructure, aviation, construction, road and transportation, automobile, real estate, pipes and tubes. With the economy of India posted for its next wave of growth under the reforms being unleashed in the last one year, there lays tremendous opportunity for Indian steel industry to prosper and grow exponentially. The steel sector contributes nearly 2% of the GDP of the country and employs over 6 lakh people. The per capita consumption of total finished steel in the country has been raised from 51 kg in 2009-2010 to about 77.2 kg in 2022-2023 financial year.

Simple look at the previous production figures over the last century attests a significant shift in the geography of Steel making. In 1990, USA was producing 37% of the world steel as against 14% at present, with post war industrial development Asian production now accounts for almost 40%, Europe (including former Soviet Union) for 36% and North America for 14.5%. Since the late 1960s, there has been a leveling up off of the rate of growth in steel production, which is partly attributable to greater efficiency in the use of steel and lesser wastage. Progress in iron and steel making technology is also indicated from the use of Bessemer converter at the turn of 19th century to the introduction of oxygen conversion processes in the 1950s and continuous casting in 1960s. Steel is one of the most recycled non-expandable industrial materials recycled. Material is used in all steel production. Even after decades of application, steel is salvaged and over 40% of steel production is based on recycled material including scraps.

The major steel producers in India are SAIL, Tata Steel, Arcelor-Mittal-Nippan Steel, Ispat Alloy.

There are some integrated steel sectors in India:

i. Tata Steel,
ii. SAIL: Bhilai steel (BSP),
    Bokaro steel (BSL),
    Durgapur steel (DSP),
    Rourkela Steel (RSP),
    Indian iron and steel (IISCO),
iii. Rashtriyo Ispat Nigam Limited (RINL),
iv. Arcelor-Mittal-Nippan Steel,
v. Jindal South West (JSW),
vi. Jindal Steel and Power Limited (JSPL)

Top 10 Steel-Producing Countries in the World - million tons (Mt) in 2021:

While steel is used extensively all over the world, only 64 of the world's 193+ countries manufacture steel in any significant quantity. These 64 countries produced 98% of the world's steel. Unlike many industries, steel production weathered the COVID-19 pandemic relatively well, with year-on-year production falling less than 1% in 2020. Global steel production reached 1,878.5 metric ton (MT) in 2022.

Sl. No.	**Country**	**Production of steel in 2022 (Metric Ton)**
1	**China**	**1013**
2	**India**	**125.32**
3	**Japan**	**89.2**
4	**USA**	**80.7**
5	**Russia**	**71.5**
6	**South Korea**	**65.9**
7	**Germany**	**36.8**

Integrated Steel Plant:

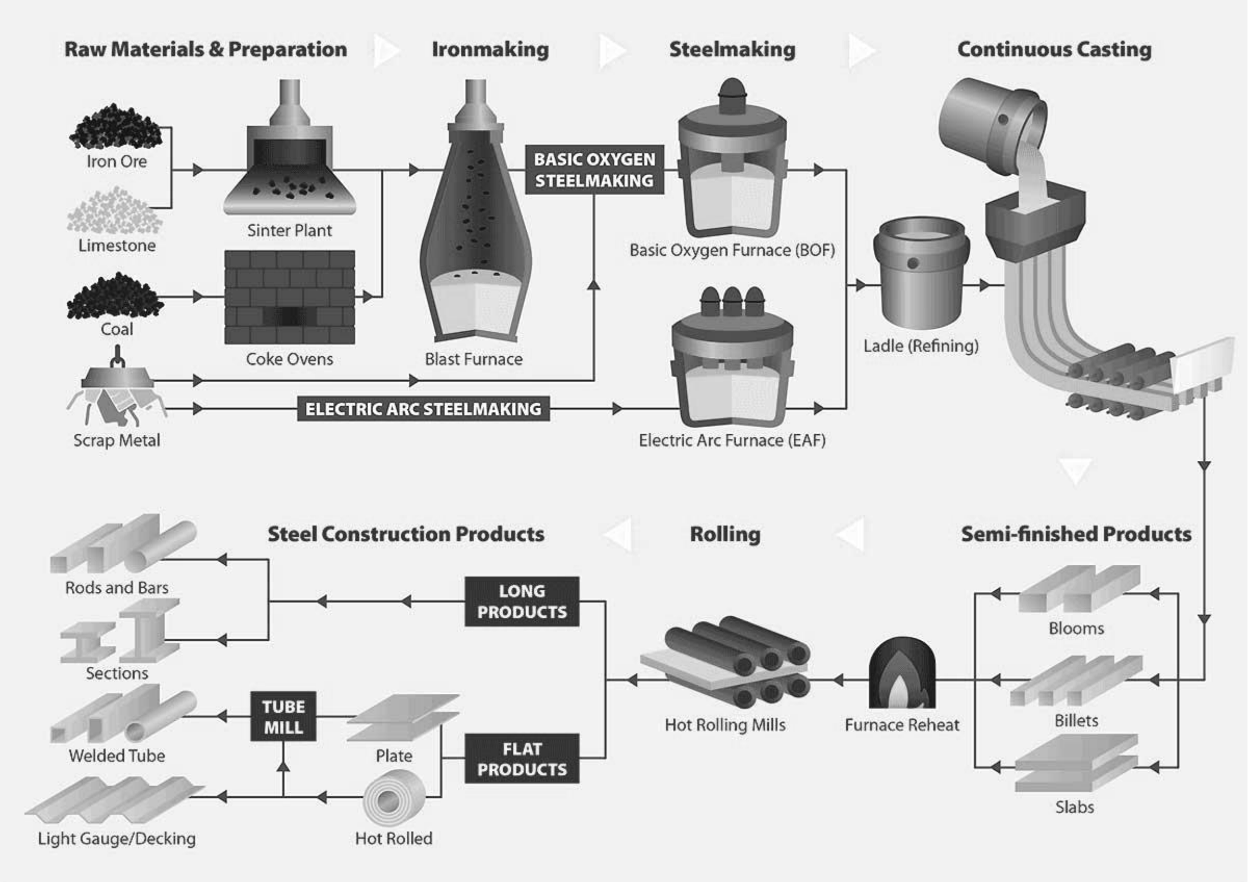


Fig:1.1, Integrated Steel Plant Flow Chart

The figure 1.1 shows a flowchart of the integrated manufacturing process for iron and steel using the blast furnace, basic oxygen furnace (denoted as LD convertor) and Secondary steel making (Ladle metallurgy) process, which is presently the most commonly used method (51% of world steel production). After the BF-BOF process, molten steel is controlled to a target composition and temperature and is then cast by continuous casting machine to produce slabs, blooms, and billets. These castings are rolled to the required dimensions by the rolling mill to produce steel products. The smelting and refining process for iron and steel in the BF-BOF process involves the carbon reduction of iron ore (Fe_2O_3) in the BF to make molten iron, and decarburization of molten iron in the BOF to make molten steel.

4 basic parts of Integrated Steel plant are:

i. Raw material beneficiation,
ii. Iron making,
iii. Steel making,
iv. Casting and finishing process

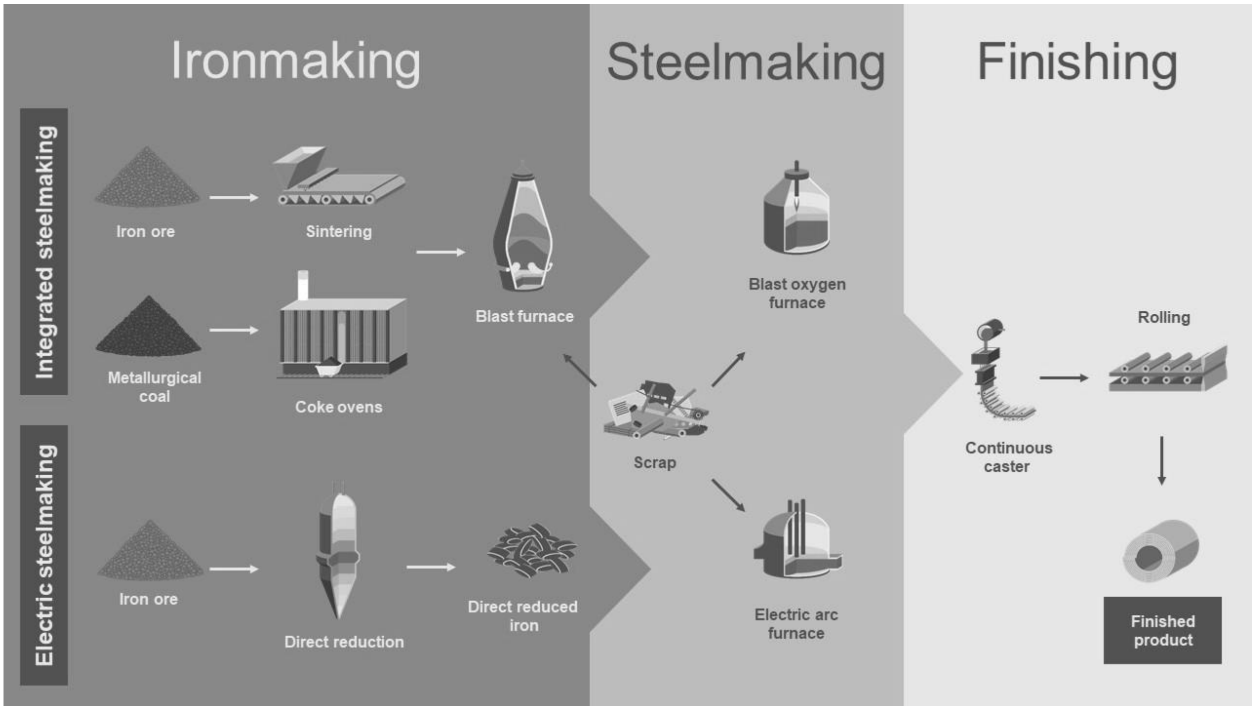


Fig:1.2, Processes in Integrated Steel Making

Raw material beneficiation:

In the initial stage of integrated steel making, raw materials, such as: metallurgical coke, coking coal, iron ore, flux material (dolomite, limestone) are arranged properly and these materials are properly beneficiated and blended. Agglomeration is one of the most essential process. Agglomeration includes sintering and pelletisation of raw materials, which increase the extent of reduction in higher extent.

Iron Making Process:

After proper beneficiation and agglomeration of raw material, iron making process starts. The primary objective of iron making is to release iron from chemical combination with oxygen, and, since the blast furnace is much the most efficient process, it receives the most attention here. Alternative methods known as direct reduction are used in over a score of countries and 45% of entire iron is produced by direct reduction (DR) process. A third group of iron-making techniques classed as smelting-reduction is still in its infancy. Iron making takes place in 2 manners: Smelting reduction and Direct reduction process.

- ### Smelting Reduction Process:

In this process, reduction of iron ore by Carbon Monoxide (CO) gas or coke takes place, after which melting starts, which gives pure form of carbon in molten condition. Blast furnace is the most essential and majorly used smelting reduction furnace, from longer time back, till now. Although activity of other smelting reduction processes be significant.

Blast Furnace Iron Making Process:

Blast furnace is basically a vertical shaft furnace that produces liquid metals by the reaction of a flow of air introduced under pressure into the bottom of the furnace with a mixture of metallic ore, coke, and flux fed into the top. Blast furnaces are used to produce pig iron from iron ore for subsequent processing into steel, and they are also employed in processing lead, copper, and other metals. Rapid combustion is maintained by the current of air under pressure.

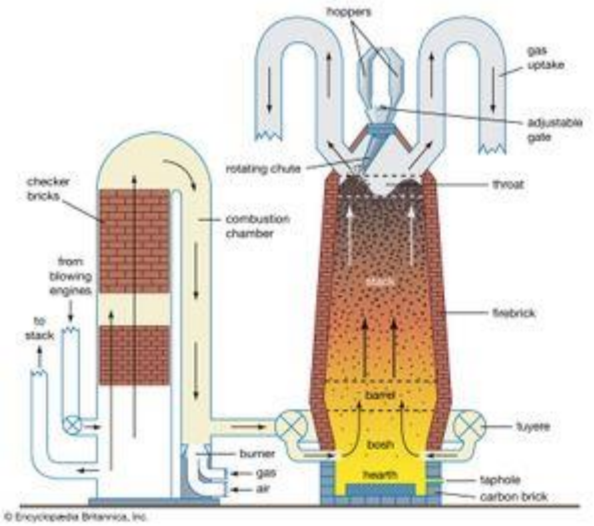


Fig:1.3, Blast Furnace and Hot Blast Stove

Blast furnaces produce pig iron from iron ore by the reducing action of carbon (supplied as coke) at a high temperature in the presence of a fluxing agent such as limestone.

Other Smelting Reduction Furnace:

Electric pig iron furnaces and induction furnaces are essential to produce hot molten iron. In older days, bath-smelting furnace was significant which is obsolete in present days. In Austria, Corex process was installed, which is also remarkable in alternative smelting-reducing iron making process. Also, Hismelt, Combismelt, Fastmelt, Technored, Finex, Cleansmelt and ITmk3 are the most important smelting reduction furnace as well as having significant degree of commercial application. China is specialised in designing and construction of multitude of smaller blast furnaces, called Mini Blast Furnace or MBF. Many other countries are installing this furnace, India has more than 70 number of this type furnace, from where 3 MT/year of hot metal can be obtained.

• Direct Reduction of Iron:

Direct reduced iron (DRI) is the product which is produced by the direct reduction of iron ore or other iron bearing materials in the solid state by using non-coking coal or natural gas. Processes which produce DRI by reduction of iron ore below the melting point of the iron are normally known as the direct reduction (DR) processes. The reducing agents are carbon monoxide (CO) and hydrogen (H_2), coming from reformed natural gas, syngas or coal. Iron ore is used mostly in pellet and/or lumpy form. Oxygen (O_2) is removed from the iron ore by chemical reactions based on H_2 and CO for the production of highly metalized DRI. Significant example of direct reduction (DR) processes, in present world, are: Rotary Kiln, Rotary Hearth furnace, Midrex, HyL process etc.

In the direct reduction process, the solid metallic iron (Fe) is obtained directly from solid iron ore without subjecting the ore or the metal to fusion. Direct reduction can be defined as reduction in the solid state at O_2 potentials which allow reduction of iron oxides, but not of other oxides (MnO, and SiO_2 etc.), to the corresponding elements. Since reduction is in the solid state, there is very little chance of these elements dissolving (at low thermodynamic activity) in the reduced iron, so the oxides which are more stable than iron remain essentially unreduced.

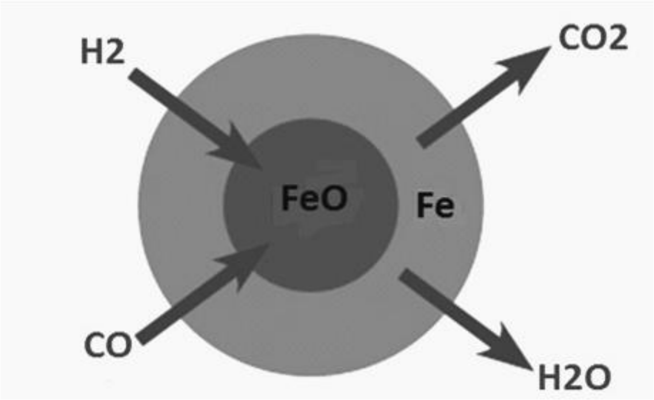


Fig 1.4, Principle of Direct Reduction of Iron Ore

The principle of the process of the direct reduction of iron ore is shown in Fig 1.5.

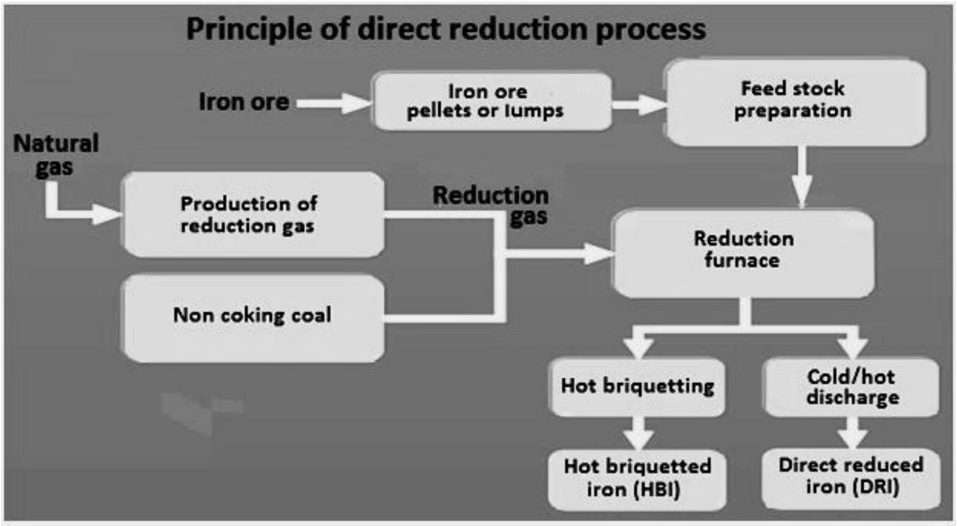


Fig 1.5, Principle of Direct Reduction Process

DRI Production in India:

India is the largest producer of Direct Reduced Iron in the world with annual capacity of nearly 10 Mt comprising coal and gas based DRI plants. India has the largest coal based DRI capacity. The industry is faced with problems relating to raw materials availability and their quality. An important consideration for overcoming this problem will be to install pelletising plants. Despite all odds, the outlook appears to be bright for the DRI industry as the steel production in India is expected to reach about 50 Mt by the year 2010. The paper deals with coal based DRI industry.

India is the largest producer of coal-based sponge iron. About 75% of the sponge iron capacity in India is coal based. To-day many of the plants are operating with raw materials of inferior grade and the sponge iron produced by many plants are of inferior quality mainly with regard to gangue content and to some extent metallisation. Such coal-based sponge iron is mainly used by induction furnace steel producers leading to technical deficiencies in the steel making process. Further, energy consumption wise, the coal-based sponge iron plants are not efficient which can be improved by co-generation using kiln off gas.

Coal based rotary kiln sponge iron plants have mushroomed in India, mainly in the states of Madhya Pradesh, West Bengal, Orissa, Jharkhand, Goa, Andhra Pradesh, Karnataka and in small numbers in other states mainly due to relatively low investment costs, scarcity and high cost of quality steel scrap and on the assumption that the technology is not sophisticated and could be operated by less experienced personnel. Many of these units have also put up their induction furnaces for steel making and some of them rolling mills mainly to produce construction bars and rods. That is how the use of sponge iron in steel making has become a regular practice mainly by induction furnace steel plants. Majority of the sponge iron units did not have final gas cleaning system to remove fine dust in the gas before letting out to the atmosphere, which are of course installed later/being installed. With the boom in export price of iron ore during last 2-3 years, iron ore suppliers have put up the rotary kilns with the objective of earning higher profits by sponge iron sales.

Steel Making Process:

Fig:1.6, Steel Making Process

In principle, steelmaking is basically, combination of melting, purifying, and alloying processes, carried out at approximately 1,600 deg. C (2,900 deg. F) in molten conditions. Various chemical reactions are associated, either in sequence or simultaneously, in order to arrive at specified chemical compositions and temperatures. Indeed, a number of reactions interfere with one another, requiring the application of process models in order to help in analysing options, optimising competing reactions, and designing efficient commercial practices.

The major iron-bearing raw materials for steelmaking are blast-furnace iron, steel scrap, and direct-reduced iron (DRI). Hot molten iron typically contains 3.8 to 4.5 % carbon (C), 0.4 to 1.2 % silicon (Si), 0.6 to 1.2 %manganese (Mn), up to 0.2 % phosphorus (P), and 0.04 % sulfur (S). Its temperature is usually 1,400 deg. to 1,500 deg. C (2,550 deg. to 2,700 deg. F). The phosphorus content highly depends on the ore used, since phosphorus is not removed in the blast-furnace process, whereas sulfur is usually picked up while iron making from coke and other fuels. DRI is reduced from iron ore in the solid state by carbon monoxide (CO) and hydrogen (H_2). It frequently contains about 3 % unreduced iron ore and 4 % gangue, depending on the ore used. It is normally shipped in form of briquettes and charged into the steelmaking furnace like scrap. Steel scrap is metallic iron containing residuals, such as copper, tin, and chromium, that vary with its origin. Of the 3 major steel making processes—basic oxygen, open hearth, and electric arc—the first 2, with smaller exceptions, use liquid blast-furnace iron and scrap as raw material and the latter uses a solid charge of scrap and DRI.

Casting and Finishing Process:

Fig:1.7, Casting and Finishing Process

At present, continuous casting is, by far, the most pre-dominant method of casting hot molten steel, through efficient manner. Bulk of the hot molten steel, after casting, is shaped by rolling either into several products, flat products: plates and sheets, or into longer products: rod, angles, rails etc.

Ingot casting is still effective, in much smaller volumes, particularly for casting special steel products. For forging of special shapes, ingot casting is much crucial route. Some smaller capacity steel plants, still exist in several parts of world, including India, where ordinary carbon steel and special alloy steels are, in smaller quantities, cast through traditional ingot casting method.

Environmental Management:

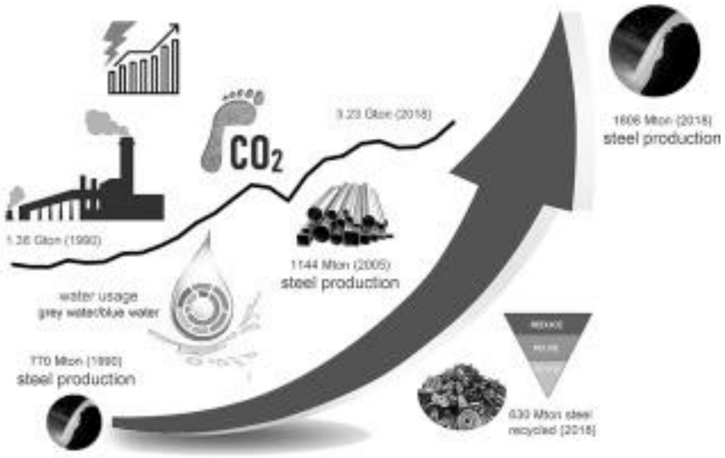


Fig: 1.8, Industrial Environmental Management

Iron and steel industries which comprises, mining of ores, preparation of raw materials, agglomeration of fines in sinter plant, feeding of burden to blast furnace, manufacturing of coke in the coke ovens, conversion of pig iron to steel, making and shaping of steel goods, granulation of slag due to its use in cement plant, recovery of chemicals from Benzoyl and tar products etc. All the above-mentioned operations add to air, water, land and noise pollution. The steel plant slag mainly includes blast furnace slag and steel melting slag (LD process slag). LD slag is a by-product of steel making which comes from pig iron refining process using LD converters and one of the most essential waste materials in all integrated steel plant. In India, the steel melting slag is over 4 million tonne per annum. The amount of steel slag from different steel industries is about 150 kg/ton to 180 kg/ton. The total generation per annum is about 1.28 million tonne in Steel Authority of India (SAIL), about .98 million tonne in Tata Steel. The slag contains variable substances like CaO, Fe and Mn. CaO is an essential oxide present in LD slag which can be used as flux material instead of lime. Blast furnace slag has longer term market in construction and fertiliser industries;

whereas LD slag is not suitable due to higher phosphorus content. Till date only 40%-50% of LD slag is possible to recycle in India. If removal of phosphorus is possible, LD slag can be recycled in steel making as flux material. Application of this LD slag not only replaces the lime but also avoid heat loss for calcinations of lime stone. Therefore, the removal of phosphorus from LD slag reduces not only steel making cost but also the disposal cost. The main co-products from iron and crude steel production are slag, scrap, dust and sludge.

One of the most essential factor related to Iron and Steel making is the pollution of environment due to emission of Carbon monoxide (CO) gas. During entire process, significant amount of Carbon Di-oxide (CO_2) emits to environment. Carbon Di-oxide (CO_2) is important green-house gas and enhances temperature of the atmosphere. To minimize emission of CO_2 is the main objective of World environment organisation. For this purpose, Green Steel Making is of greater importance.

To minimise environmental pollution by reducing CO emission as well as to decrease green-house effect by reducing CO_2 emission, Green Steel Technology is essential. In this process, iron ore (Fe_2O_3) is reduced by pure Hydrogen (H_2) gas. Due to having smaller atomic size and higher diffusivity, H_2 gas higher reducing power and iron ore can effectively reduce to metallic iron, without emission of CO and CO_2.

$$Fe_2O_3 + H_2 = Fe + H_2O$$

Although this process is environmentally favourable, it has some disadvantages, like it needs to produce pure Hydrogen gas, for which electrolysis of water is essential, which is much costly procedure.

Problems in Iron and Steel Making Process:

While, in producing metallic iron from iron ore applying coke, natural gas and other fossil fuels, the problem is not only related to environmental polluting effect due to emission of carbonaceous polluting gasses, also:

i. The amount of higher grade coal (coking coal) is reducing and present stock is much lesser in present world,
ii. Generation of carbon rich and lesser ash containing metallurgical coke and coking coal is not only time-consuming, also costly.
iii. During the entire procedure of iron and steel making, huge amount of dust particle and polluting gases (CO, CO_2 mainly) are emitted out and incorporated in the atmosphere to cause significant environmental degradation.

3R and Utilization of House-hold Waste:

Basically, Utilization of wastes has gained importance in iron and steel industry.

This can address some most urgent issues:

i. rising raw material input costs,
ii. scarcity of higher-grade raw materials and
iii. Abundant solid waste generated.

3R i.e., Reduce, Reuse and Recycle has become a Global Mantra present days for a clean, green environment. Reduce, reuse and recycling of the waste generated is solution towards sustainable development. Not only newer technologies are tried for utilization of wastes in the manufacturing of conventional products but also for conversion of the same into completely newer products.

To Demonstrate Alternating Source of Pure Form of Carbon:

Conventional iron making process (BF-BOF route) consumes a great quantity of carbon in the form of metallurgical coke, which is one of the indispensable raw materials used in blast furnace for Pig Iron production. Metallurgical coal is needed to produce coke along with by-product from Coke Oven and by-product plant (COBP). Subsequently coke is used as reducing agent. Carbon monoxide (CO) is the crucial ingredient for reduction of Fe_2O_3, the reaction can be given as:

$$\mathbf{Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2}$$

and this CO is produced in blast furnaces by burning coke. However, metallurgical coal reserves are depleting and coking process also have severe environmental consequences. Because of these reasons, alternative Iron-making process normally uses non coking coal. Indian non coking coal contains high amount of ash (>20%), the cleaning of which also adversely affects the environment. Moreover, usage of coal with higher ash generates a higher amount of slag. Therefore, it is of great significance for the interests of iron and steel manufacturers to explore alternatives to Coke as reductant in iron making process. In this perspective, domestic waste could have been a potential source and partial alternative for coke. In the present society, the population in increasing with days. The generation of huge amount of vegetable peels, trimmings and flower wastes can be effective, non-polluting source of pure form of carbon, which can be essential, lesser costly and alternative source of reducing agent in iron and steel technology. The basic objective of this project proposal is to evaluate the potentiality of vegetable peels and trimmings and flower wastes to be represented as an alternative source of reducing agent.

Potentiality of Vegetable and Flower Waste as Source of Reductant:

Vegetable wastes from domestic as well as commercial sources are produced in huge quantity every day. These wastes are generally dumped. This current project aims at utilizing vegetable wastes, like: potato peels and trimmings etc. as an alternate for coke. Wastes (peels and trimmings) from other vegetables and fruits such as gourd (Potal); bottle gourd (Jinga); sugarcane etc. will also be considered. These vegetable wastes contain considerable amounts of carbon in the form of starch / cellulose. Flower wastes, collecting from different sources, are also dumped. These flower wastes can be important source of carbon.

The major components of these vegetable wastes are moisture and starch. If the moisture can be removed, the remaining part would contain high amount of fixed carbon with virtually zero ash content. Moreover, the moisture content could be recycled to be used as make-up water in steel plant.

Evaluation of Syn Gas from Vegetable and Flower Waste:

Vegetable and flower wastes are generally dumped in landfill, which causes serious environmental problems. From the vision of volume, these dumped landfill wastes are the largest contributor methane gas production. There is the serious problem of odor when the decomposition of the wastes takes place, to cause public annoyance in addition to forming germs and microbes, and attracting flies and vermin. Another serious problem related to dumping of vegetable and flower wastes is the generation of landfill leachate. Landfill leachate is basically particular liquid that leaks from the landfill and enters the environment. Once it enters the environment, the leachate be at risk for mixing groundwater near the site which then travers to some distances. Furthermore, the liquid has the potential in adding biological oxygen demand (BOD) to the groundwater. BOD measures the rate of oxygen uptake by micro-organisms in a sample of water at a temperature of 20 °C and over an elapsed period of five days in the dark area.

Vegetable and flower wastes basically have higher energy content. Consequently, these wastes offer enough potential for feed stock for gasification in power plants. Gasification of wastes aids to solve 2 major matters at the same time. Gasification of wastes reduces landfill problems and favours to recover energy at the same time. Characteristics of this waste gasification process and pyrolysis have been investigated in terms of some factors:

i. Syn-gas yield,

ii. Hydrogen yield,

iii. Energy yield and

iv. Apparent thermal efficiency.

Entire evaluation can effectively represent that vegetable and flower wastes offer a gentle potential for thermal treatment of the waste with the specific aim of power generation.

In this thesis, an attempt has to be made to properly utilize vegetable peels, trimmings and flower wastes in iron and steel making technology as a partial substitute of reducing agent and demineralised water along with significant laboratory based plant design to generate syn gas.

Chapter: 2

Objective of the Project

As time goes on, there is found many changes in different procedures. These changes are the indications of rapid progress as well as systematic development of science and technology. Rejected vegetable peels, trimmings and flower wastes, having minimum costing, can be effectively processed through relatively lesser costly procedure, to produce most wanted pure form of carbon (C) with minimum ash content, to apply in iron ore reduction, to produce iron and steel, power as well as the moisture content can be accumulated to further apply in iron ore reduction by producing Syn gas, which are also the most remarkable as well as enthusiastic development in metallurgy.

2.1 Containing Pure Carbon in Bio-dust and Lesser Amount of Ash:

Demand of iron and steel, with the progress of human civilisation, is increasing day by day. For this, to come across increasing demand of iron and steel, requirement of reductant coke in increasing. Coal contains relatively higher amount of ash, which creates pollution and more consumption of energy in this process, reduction process would not reach to the value of efficiency. It is required to use some reductant, having lesser ash content. Though coking coal is of higher grade and contains relatively higher amount of free carbon, cost of coking coal is much higher. For this, carbon generated from waste vegetable and flowers can be used as reductant with economic feasibility.

2.2 Application in Sintering Process:

Iron ore can be pre-reduced using the bio-dust coming from dehydration of vegetable peels and trimmings as well as flower wastes. Pre-reduced ore has is already promoted to further reduction and as the activation energy barrier due to pre-reduction be lesser, the pre-reduced ore can be mixed with conventional hematite for charging as raw material in sinter plant. Thus, sinter produced, will contain more Fe% and relatively lesser amount of coke and thermal energy required to execute further reduction process, consequently the coke rate will be effectively reduced in Blast furnace compared to the conventional process.

2.3 Application in Pelletisation Process:

The carbon derived from vegetable wastes and flower wastes can be mixed with hematite (ore of iron) to form briquettes and pellets and are heated for iron ore reduction. Pelletisation is one of the most essential agglomeration processes, which is much remarkable in direct reduced iron (DRI) making process due to lesser surface area of the pellets, which indicates relatively lesser coke consumption as well as better thermal efficiency. Applying bio-dust, obtained from waste material, the pure form of carbon as reducing agent, would enhance the efficiency and degree of metallisation.

2.4 Reduction in Coking Coal Consumption:

The vegetable and flower wastes would effectively generate pure form of carbon, which can effectively replace the requirement of medium and lesser grade coal. The process, where coking coal is essential, the carbon rich bio-dust can partially replace the coking coal, as a reductant and source of heat. This would reduce the consumption of coking coal. Coking coal is costlier as well as the bio-dust rich of pure carbon is almost having no investment costing. For this, the entire procedure would be cost-effective.

2.5 Application in DRI Making:

In the generation of Sponge iron from hematite (Fe_2O_3), coal is the main reducing agent as well as source of additional heat. Coal is cheaper. Although it contains higher amount of ash, specifically the amount of pure carbon and volatile matter are much lesser. For this, in coal-based sponge iron making, the effectiveness of reduction of iron ore quite lesser. Degree of Metallisation (DoM) basically indicate the ratio of iron produced from specific amount of ore to the amount of total iron in the ore, which should be fractional and much lesser than 1 for relatively lesser grade of coal. Application of pure form of carbon, obtained from dehydration of vegetable wastes, peels and trimmings as well as flower wastes, can enhance the reduction of iron ore, DoM would increase and efficiency of DRI (Direct Reduction of Iron) will increase more.

2.6 Environmental Friendliness:

Vegetable wastes, peels and trimmings and flower wastes are dumped in the garbage area on land. Collection and processing of these wastes are not regular. These wastes are organic in nature and show bio-degradability. Due to be deposited on land, bio-degradation of the wastes be started. This has some toxic effects:

i. Bitter smell is found,
ii. Micro-organisms are effective and chance of spreading of disease may increase,
iii. Street animals (dogs, cats) and birds (crows) may gather there and may carry the wastes to the locality,
iv. Harmful insects, mainly mosquitoes, can accumulate their and can carry germs to locality.

This type of processing of vegetable and flower wastes can prevent environmental pollution as well as inconvenience in daily life. It will also be helpful to municipal corporation to regular remove these dumped wastes from garbage and lands.

2.7 Recycling of Moisture Content:

The vegetable and flower wastes contain massive amount of moisture in it. From TGA-DTA plot, it is clear that the wastes contain more than 80% moisture in it (in average 85%). To produce the bio-dust from the wastes, the moisture content should not be lost. Water coming from condensation of moisture, has significant purity as it is complete distilled in nature. The water content can be poured into bottles as well as be employed in laboratory testing purposes, to fulfil the requirement of demineralised water. Also, the water content can be used for drinking purposes. The pure form of water can be effectively supplied to different industrial purposes, in Iron and Steel making plant, thermal power plant, fertiliser plant etc.

2.8 Production of Syn Gas:

The moisture content can be used in quite different manner. The moisture content can be reheated in moisture-reheater to increase its temperature to 700 to 800 deg. C to pass through the preheated carbon as well as pure carbon rich pre-reduced bio-dust to react between them to produced Synthetic gas or Syn-gas, in vacuum condition:

$$\mathbf{C + H_2O = CO + H_2}$$

This would be quite optimisation of the application of huge amount of moisture, prevent its unwanted loss. The Syn gas can be supplied to the Gas Based Sponge Iron Plant, where consumption of costlier natural gas (CH_4) can be effectively reduced, through quite cheaper method. This will definitely help to enhance the costing optimastion of the entire reduction process to produce Gas-based DRI.

From the entire discussion, it can be expressed that vegetable peels, trimmings and flower wastes not only be the alternative source of pure form of carbon, as well as enough water content can be obtained from the waste materials. Also, the extent of reduction of Iron ore, using carbon-rich bio-dust obtained from these waste materials can be enhanced using by applying Syn gas (CO +H2), obtained by passing hot steam through the carbon rich bio-dust, with the method of optimisation of loss of steam. In the coming days, these domestic wastes will be the potential source of reducing agent in Iron and Steel Technology, to compensate the scarcity of fossil fuel and to optimise the costing of entire procedure.

Chapter: 3

Literature Review

2.1 Importance of Iron and Steel Industry:

Steel has had a major influence on human life, the cars, the buildings, the homes in which human being lives and countless other facets in between. Steel is used in our electricity-power-line towers, natural-gas pipelines, machine tools, military weapons-the list is endless. Steel has also earned a place in our homes in protecting our families, making our lives convenient, its benefits are undoubtedly clear. Steel is by far the most important, multi-functional and most adaptable of materials [1]. The development of mankind would have been impossible but for steel. The backbone of developed economies was laid on the strength and inherent uses of steel. Steel compared to other materials of its type has low production costs. The energy required for extracting iron from ore is about 25 % of what is needed for extracting aluminum. Steel is environment friendly as it can be recycled. 5.6 % of element iron is present in earth's crust, representing a secure raw material base [2]. Steel production is 20 times higher as compared to production of all non-ferrous metals put together. The steel industry has developed new technologies and has strived hard to make the world's strongest and most versatile material even better. There are altogether about 2000 grades of steel developed of which 1500 grades are high grade steels. There is still immense potential for developing new grades of steel with varying properties The large number of grades gives steel the characteristic of a basic production material Steel has enjoyed an important position in our lives and will continue to do so in the years to come [3]. However, the degree to which it maintains its dominant position will depend on if steel can exploit its potential by developing new higher grades and adaptable grades. This can be achieved by refining the structure and applying alloying techniques and thus furthering its utility value [4]. We will have to find out ways to use steel and be ready to face a stiff competition from Aluminum in the future.

2.2 Modification in Iron and Steel Making Technology in World:

The iron and steel industry has undergone a technological revolution in the last 40 years. In a relatively short time, the North American industry has observed the complete disappearance of basic open-hearth processing, as well as the wide spread adoption of continuous casting and the near complete shift of manufacturing long product to the electric arc furnace sector [5]. These and other developments have dramatically affected the way the steel is made, the price, quality and range of products generated, and changed the basic structure of the industry [6]. The same trends can be observed in other industrialized nations and are reflected in the global industry as well. Competitive forces and market globalization will continue to drive the development and adoption of new iron and steel-making technologies well into the 21st century [7]. Industry response to specific local and global technology drivers will effectively affect in both significant improvements in existing technologies, and in major developments in several key areas including direct iron making (DRI) and near net shape casting [8].

2.3 Modification in Iron and Steel Making Technology in Asian Countries:

Since the turn of the millennium, the world's steel industry has experienced significant change. First, global crude steel production per annum increased to around 120 million tons by 2006, after having fluctuated at around 80 million tons for nearly three decades from the early 1970s to around 2000 [9]. Second, a transnational restructuring of big steel firms has been taking place as exemplified by the acquisition in 2006 of Arcelor, the second largest steel firm in the world, by Mittal, the largest, and the takeover of Corus by Tata Steel in 2007. The backdrop to these phenomena was changes that took place during the period of long stagnation in steel production from the early 1970s to around 2000. One factor was changes in the international division of labor in steel production. In 1975 the USA, the EU, the USSR and Japan produced 78% of the world's total crude steel. In 2005 the share of these countries had decreased to 43% while the steel industries in developing countries increased their share of global crude steel production [10]. Steel production in Asian countries in particular has shown a significant rise, and in 2005 Asia's share of world crude steel production reached over 50%.3 Therefore, the paper highlights the steel industry in Asia and seeks to analyze the features and factors in the development processes of Asia's steel industry.4 In so doing, it also aims to study the relationship of industrial policy, economic development and the development of the steel industry, and to examine the changes in technology, demand and trade patterns [11]. In other words, the paper seeks to present the diversified development processes of the steel industry in each country and, at the same time, to extract the factors that are shared by each country as well as those factors that have brought about differences in the development processes of each country.

2.4 Modification in Iron and Steel Making Technology in Indian Scenario:

Since the start of economic liberalization in 1991, the structure of the Indian steel industry has undergone significant reorganization. Before liberalization the state-owned firm SAIL had played the core role in steel industry development. Since liberalization a triple structure of main, secondary and small-scale producers has appeared [12]. Amongst the main producers consisting of incumbent integrated firms, technological upgrading and institutional reform have been slow for SAIL, while Tata Steel has gradually upgraded its facilities as well as the quality of its products. Secondary producers Essar, Ispat and Jindal have introduced newly available technology such as DRI and CC and are endeavoring to make efficient use of domestically available raw materials. It is this sector that has principally contributed to the rapid growth of the industry since liberalization. Also, they are more export oriented than SAIL. Small-scale producers depend on induction furnaces which are considerably small-scale technology and utilize scrap steel. India's steel market is segmented geographically and in product quality, and this has enabled small-scale producers to grow [13]. The post-liberalization experience of the industry presents a unique example where newcomers have sought to utilize locally available raw materials with new technology.

Appreciable developmental activity in iron making is being observed in India in recent years the world over. In order to be responsive to market forces, there is drive to have processes which are flexible with regard to raw materials, energy and production tonnages. Such endeavours are being actively supported by the respective Governments of several nations. The efforts are spurred by need to bring down capital and fixed costs, utilize non coking coals and iron ore fines directly. The need for appropriate technologies with lower capital cost and without use of low ash coking coal is obvious in Indian context to further hone competitive edge of our country [14]. In current international scene, it is vital to develop technology locally to maximize wealth creation. The times is ripe for Indian researchers, designers and entrepreneurs to benefit from work done abroad and suitably synergize to take newer coal-ore fines and coal-ore agglomerate based DRI processes and coal-hot air- based smelting reduction processes to commercial stage with innovative indigenous efforts. Further improvements in Blast Furnace View publication stats designs to maximize direct injection of ore, coal and lime fines may also yield rich dividends [15].

2.5 Scarcity in Coal and Fossil Fuel:

Energy markets began to tighten in 2021 because of a variety of factors, including the extraordinarily rapid economic rebound following the pandemic. But the situation escalated dramatically into a full-blown global energy crisis following Russia's invasion of Ukraine in February 2022 [16]. The price of coal and natural gas reached record highs, and as a result so did electricity in some markets as well as in iron and steel industries. Higher energy prices have contributed to painfully high inflation, pushed families into poverty, forced some factories to curtail output or even shut down, and slowed economic growth to the point that some countries are heading towards severe recession [17]. Europe, whose gas supply is uniquely vulnerable because of its historic reliance on Russia, could face gas rationing this winter, while many emerging economies are seeing sharply higher energy import bills and fuel shortages. While today's coal and energy crisis share some parallels with the oil shocks of the 1970s, there are important differences. Today's crisis involves all fossil fuels, while the 1970s price shocks were largely limited to oil at a time when the global economy was much more dependent on oil, and less dependent on gas [18]. The entire word economy is much more interlinked than it was 50 years ago, magnifying the impact. That's why we can refer to this as the first truly global energy crisis. Some gas-intensive manufacturing plants in Europe have curtailed output because they can't afford to keep operating, while in China some have simply had their power supply cut. In emerging and developing economies, where the share of household budgets spent on energy and food is already larger, higher energy bills have increased extreme poverty and set back progress towards achieving universal and affordable energy access [19]. Even in advanced economies, rising prices of coal and fossil fuel adversely affect iron and steel industries, to let them use as reducing agent, along with costlier coking process.

2.6 Challenges to Green Steel Adoption:

Basically to decrease the participation of carbonaceous reducing agent (coke, coal, reformed natural gas) and to keep the environment cleaner from emission of polluting

And green-house gas, green steel technology is of greater necessity. In green steel making, iron ore hematite is allowed to be reduced by pure Hydrogen gas. This pure form of Hydrogen gas is difficult to produce as it is produced by electrolysis of water. The challenges facing the widespread adoption of green steel include high costs, limited availability of technology, and the need for a reliable supply chain of hydrogen generated by 100% renewables [20]. The cost of hydrogen-based direct reduction and molten oxide electrolysis is currently 20%-30% higher compared to conventional steel production, which corresponds to a carbon price of around \$70-\$100/tCO2. Additionally, the scale of change required is daunting, as the global economy consumes around 1,700 million tons of steel per year, and a 100-fold step-change in the pace of transition is needed for the steel industry to adhere to a 1.5°C pathway. However, as renewable power costs continue to plummet and new technologies enter the commercial pilot stage, low-carbon processes are starting to make economic sense [21].

For this, it is essential for Iron and steel plant, to find out the source of alternating reducing wastes, which has higher availability as well as cost is much lesser to reduce the expense of entire procedure. Also processing and application of the reducing agent are to be convenient and lesser time consuming.

2.7 Biomass Applications as Alternative Reducing Agent in Iron and Steel Industry:

The iron and steel industry accounts for about 20% of the annual industrial energy utilization. The intensive fossil fuel consumption in steel industry is associated with CO_2 emission. In the absence of economically feasible and efficient methods for capture and storage of enormous quantities of CO_2 emissions from steel industry, the use of biomass products as a source of energy and reducing agents provides a promising alternative solution for green steel production. However, the biomass application in iron and steel industry is still limited and it suffers strong competition from fossil fuels. The challenges of biomass usage in steel industry are included technical and economic aspects which required synergy between steelmaking and bio-energy sectors [22]. Although intensive work has been carried out separately, there is a lack of link between these two vital sectors. The present article provides a comprehensive review of recent research progresses which have been conducted on biomass upgrading and analysing the opportunities and obstacles for biomass implementation in iron and steel industry. In the first part, an overview on the energy consumption and CO_2 emissions in different iron and steel-making routes is clarified. Moreover, the potential approaches of bio-mass conversion processes and upgrading technologies are reviewed. In the second part, an attention has been paid to the utilization of torrefied / pyrolyzed biomass in the energy-intensive iron-making processes. Biomass addition to coal blend during coke-making and its influence on the product coke quality is discussed. The partial and complete substitution of coke breeze with bio-char in sintering process and its influence on the product sinter quality is explained [23]. The impact of charcoal top charging or injection into blast furnace has been elaborated. Benefits and limitations of biomass application in each process are thoroughly discussed. In the third part, an economic analysis of biomass implementation for low-carbon steel is addressed.

2.8 Effective Pyrolysis of Dried Vegetable Waste to Produce Bio-char:

In today’s world, generation of vegetable wastes and their environmental impact is a serious global issue. Scientists have studied to add value of these vegetable peels and wastes by converting into bio-char through pyrolysis and subsequent processing methods. Wastes of each type of vegetable were tested individually as well as combination of different vegetable wastes. Wastes coming from mainly cauliflower and banana provide better ingredient assessment to be used as proper raw material for bio-char, although combination of different vegetable wastes can be effectively employed. Pyrolysis temperature range from 300 °C to 600 °C and particle size fraction in the range of less than 75 µm, 75–125 µm are properly considered. Characterisation of bio-char is essential for various properties which can influence the effectiveness of bio-char as soil-amendment [24]. Basically, it is found that temperature for pyrolysis is the crucial factor for optimisation of properties of bio-char although characteristics of bio-char highly depend on individual feedstock. Properties of bio-char can be optimised with the pyrolysis temperature of feed stock about around 400 °C, though this differed slightly, 300°C to 500 °C depending on the distinct feature of feedstock. Basically bio-char application with optimal feature can be obtained with tiny particles. Bio-char yields can be obtained in the range of 20–30% at the particular temperature range, although there is exception for corn cobs where the ranges are higher [25]. This study precisely describes that effective pyrolysis of dried vegetable wastes is a suitable waste valorization approach to produce bio-char with reliable agricultural properties.

2.9 Shredded Residue Material (SRM) of the Mixture of Different Plastics as Reducing Agent:

In newer generation metallurgical area, non-ferrous bath smelting is one of the most essential processes, in which plastic containing shredder residue material can be used as effective reducing agent, along with the replacement of conventional fossil fuel as the amount of the fossil fuel is decreasing day by day. Also their use and burning is detrimental for the environment. End-of-life equipment parts are taken into hammer mills, the size range of all parts is reduced; these parts are effectively separated using the array of procedures, such as air classification, magnetic and eddy current separators into three major streams: ferrous, nonferrous scraps and a light fraction which mainly consist of plastics explained as SRM. Using SRM as reducing agent in metallurgical extraction process, not only reduces the dependency on fossil fuel as reducing agent, but also enhances efficiency of utilization of secondary sources. From the systematic scientific investigation, these secondary reducing agents can be compared with primary sources, from different points, such as: reactivity, devolatilization characteristics, combustion characteristics etc. Basically devolatilization characteristics are the most basic features of plastic-containing shredder residue material (SRM), which can be compared to those of coal using thermo-gravimetric analysis. Proximate analysis indicates that the volatile matter in the SRM and individual plastic material is higher than that of coke and coal which have relatively higher amount of fixed carbon. Shredded plastic material has higher amount of ash content than that of coal, which has essential catalytic effect during devolatilisation. During the volatilization, temperature reaches about 280–450 °C. Also the volatiles contain hydrocarbons, H_2, carbon monoxide etc. gases which have higher calorific values. Volatiles can be used as effective reducing agents. As Shredded materials have heterogeneous nature, during volatilization, DTG curve and volatiles show multiple number of stages. Basically, devolatilisation of shredded materials takes place at relatively lesser temperature range, for this, energy consumption during this process is much smaller. Analysis on devolatilisation characteristics of 3 different plastics- polyurethane, polyvinylchloride and polyethylene and their mixture are necessarily taken into account. Polyethylene consists of aliphatic hydrocarbon with lesser number of carbon, basically during decomposition, 94% volatiles are generated. For this, only volatile part of polyethylene would participate in the reduction reaction. In the other hand, polyvinylchloride and polyurethane consist of 12% and 14% fixed carbon. Due to this, during their devolatilisation, volatiles are formed along with some amount of char. For this, this char effectively participates in the reduction reaction along with the volatiles [26]. From this analysis, it is possible to reach to the point that during devolatilisation of shredded residue material (SRM) of the mixture of different plastics, volatiles generated from certain type of plastic would actively interact with the volatiles coming from other plastics.

2.10 Carbonaceous Waste as Reducing Agent and Source of Heat in Iron Making Process:

In the society, production of plastic has been increased in huge amount, which can cause significant amount of carbonaceous waste. These waste materials can be employed as reducing agent and source of heat in Iron making process. Plastic wastes have several essential physical properties, such as:

i. grain size,
ii. shape,
iii. porosity,
iv. free surface area.

These properties can affect its conversion stronger than chemistry. In spite of higher amount of volatile matter in the plastic wastes, during combustion of these waste materials, formation of char takes place, leaving the simulating raceway region. This char formation during combustion of plastic wastes depends on several conditions:

i. shorter residence time,

ii. higher rate of heating,
iii. larger particle size range.
iv. The reaction takes place almost only on the surface.

No circulation of coarse plastics particles was observed by WP injection into the pilot coke bed simulator [27]. The reaction takes place almost only on the surface. No circulation of coarse plastics particles was observed by WP injection into the pilot coke bed simulator The reaction takes place almost only on the surface. No circulation of coarse plastics particles was observed by WP injection into the pilot coke bed simulator The reaction takes place almost only on the surface.

Actually. reaction happens almost only on the surface portion and there is no circulation of coarser plastic particle at the time of waste plastic injection in the pilot coke bed simulator. Unburnt plastic particles are effectively consumed under the condition of bird's nest and shaft. Extension of secondary gasification reaction essentially depends on several factors: temperature, atmosphere, burn out rate and char size range.

Smaller particles can be converted faster in coke bed than the coarser particles. Plastic char has significant amount of ash content, basically the behavior and characteristics of char may affect the coke reactivity [28].

2.11 Plastic Waste Material as Metallurgical Raw Material with Spontaneity:

Scientists have tried to find newer ways to dispose plastic waste material as metallurgical raw material with spontaneity and flexibility in those countries, like China, where higher amount of plastic wastes are generated per day. In these countries, features of plastic wastes can be pointed as:

- Amount is larger,
- Various in type,
- Dispersive in the deposition.

Iron scale has some essential features, such as: higher ferrous content and lesser amount of impurity; for this, iron scale can be used as essential raw material to produce iron powder [29]. Among the different processes, Hoganas method is essential, in which, pure form of iron powder is produced after one or multi-stage reduction reaction. Investigations on these reduction reactions have introduced several important facts:

- Both chemical and thermal energy of the wastes are effectively utilized,
- Reduction conditions are significantly improved,
- Newer method is obtained to dispose plastic wastes.

Under the specific experimental conditions, thermal decomposition of waste plastics significantly takes place, which can increase the porosity in the reduction system. Better energy efficiency can be obtained [30]. Improvement in thermodynamic and kinetic condition in the reaction system is remarkable. Kinetic rate for reduction is effectively increased.

2.12 Process and Factors to Produce Syn Gas:

Pyrolysis and gasification are essential processes to reform solid and liquid hydrocarbons to clean gaseous fuel, which can be further processed to obtain clean and pure form of gaseous fuel or liquid fuel. Pyrolysis is basically thermal degradation process of organic compounds, in absence of oxygen or air, to produce various gaseous component yield as well as yield of tar and char residues. During pyrolysis, the evolved char product and their distribution effectively depend on several factors:

i. the heating rate of the sample,
ii. pyrolysis temperature, and
iii. particle size and distribution.

Gasification process is basically heating-up of solid or liquid carbonaceous material with particular gasifying agent in anaerobic condition to produce gaseous fuel [31]. The heating value of the gases produced is generally lower to medium. Basically, this definition be not able to include combustion, because the product flue gas contains no residual heating value from entire combustion of the fuel. It does include partial oxidation of fuel or fuel-rich combustion, and hydrogenation. In partial oxidation process, the oxidant or gasifying agent could be: steam (H_2O), carbon dioxide (CO_2), air or oxygen (O_2), or some mixture of two or more gasifying agents [32]. The gasifying agent is selected on the basis of the desired chemical composition of the syn-gas and efficiency.

Gasification of solid wastes includes a devolatilization process at initiation point of the process. At higher heating rates, the sample undergoes pyrolysis and gasification in parallel; however, at lesser heating rates, the sample undergoes pyrolysis and gasification in series, in the order of pyrolysis to bio dust then bio dust gasification. Percentage of overlap between bio dust gasification and pyrolysis can be observed by plotting the evolution of syngas flow rate for both gasification and pyrolysis [34].

The average proximate analysis of vegetable and flower wastes is: 82 to 83% volatile matter, 15% fixed carbon, and 2 to 3 % ash. The volatile matter can be effectively destructed in a relatively shorter period of time, extending from 8 to 12 min at reactor temperatures in the range of 700 to 1000°C. Recovery of energy from volatile components in wastes can be recovered applying pyrolysis process. However, in order to consume the residual fixed carbon after the pyrolysis, the sample must undergo a gasification process. Gasification of waste sample includes a pyrolysis part and a bio dust and char gasification part. Bio char gasification reactions are slower than that of pyrolysis and consequently, is the rate limiting step in the overall gasification process. The ash present in the sample would not react with the gasifying agent [35]. The ash can be collected after cooling and cleaning the syngas, and then recycled for its further use in industrial processes.

Since the char gasification process is the slowest step as well as rate limiting step, it is necessary to quantify the kinetic parameters of char gasification. Bio char gasification has been investigated by a large number of researchers. Some of the essential parameters investigated include:

i. origin of the char sample,
ii. gasifying agent,
iii. total pressure,
iv. variation of partial pressure of gasifying agents,
v. geometric changes of the sample during gasification, and
vi. catalysed char gasification.

One of the most important parameters which have been investigated is the catalytic effect of ash content on gasification of bio char. Catalytic effect of ash on char gasification has been investigated for several biomass samples. Kinetics of char gasification has not drawn the attention of researchers in this field. Since vegetable and flower wastes have considerable ash content, its catalytic effect must be investigated. Results show that ash has a positive effect on char reactivity. Kinetic parameters can be calculated for different degrees of conversion. Values of kinetic parameters are found to be affected by the degree of conversion. Analysis of kinetic parameters dependency on sample conversion has been examined here [36]. Quantifying the catalytic effect of ash on char kinetics will assist improving design gasifiers with better controlled parameters for input and operational conditions, such as:

i. operating temperature,
ii. condition for gasification,
iii. gasifying supporting media,
iv. rate of feedstock to the gasifier.

In conjunction with fluid dynamic simulations, improved expressions for reaction rates will be effective in providing better estimate on char particles residence time in the reactor by providing an accurate conversion-time relationship. Consequently, for desired rate of feeding the feed-stock into the reactor and for known gasifier operational conditions an accurate reactivity expression will lead to a close estimate of the gasifier size and configuration. If a constant reactivity value is employed in reacting flow simulations for feedstock having time-dependent reactivity, misleading information on char particles residence time will be obtained. This will consequently result in a departure gasifier size from the true design size and configuration. If a constant reactivity value is used for chars having ash catalytic effect, the designed gasifier size will be over-estimated since the reactivity of bio char is found to effectively enhance with the degree of conversion [37].

2.13 Necessity of Bio-energy in Modern Iron Making Process:

In today’s world, though energy science and reduction technology have progressed a lot, Iron and Steel making sectors are highly dependent on carbon as well as fossil fuels as raw material. In most of Iron making Units in India, in the blast furnaces, when hematite and magnetite are reduced to iron, larger amount of coke or coal is consumed.

The sources of fossil fuels are decreasing day by day. Procurement cost of these raw materials is increasing with motion. Also, pollution is the crucial global matter and rate of pollution using fossil fuels is much higher. Therefore, it is of greater significance for the interests of iron and steel sectors and social affairs to achieve a lesser-carbon, energy-efficient, emission-cutting and lower cost iron-making process. Bio-energy, which is basically renewable source of carbon, has several advantages:

- Energetically feasible,
- Economical usage,
- Conservation of resources,
- Sustainable development,
- Environment friendly.

Biochar, which is produced from effective pyrolysis of biomass, can be taken as essential solid fuel with excellent chemical and thermal properties. This fuel has:

- Higher reactivity,
- Purity,
- Lesser sulfur and ash content.

In metallurgical purpose, during reduction of ore in the reduction reactor, biochar can act as effective reducing agent to extract metal part from the oxide ore [37]. This fuel can effectively generate higher temperature which is suitable for the reaction to occur. Thermodynamic stability during reduction reaction can be effectively sustained. As cost of biochar is effectively smaller than that of coke, the reduction reaction, using biochar as reducing agent, becomes economical. From the view of availability, biomass can be obtained from nature easily with difficulty and higher capital costing and biochar can be produced in plenty amount without restraint. More essential point is during metallurgical reduction process using biochar, emission of polluting gases, CO_2, SO_2 and NO_x decreases in larger amount and balance in environment is sustained [38].

2.14 Effect of Residual Volatile Matter on Reduction of Iron Oxide:

Basically, semi-charcoal composite iron oxide pellets along with particular amount of residual volatile matter can be prepared as a reducing agent in the metallurgical reduction reaction and the effect of residual volatile matter on reduction of iron oxide (hematite or magnetite) has been investigated. Furthermore, semi-charcoal particle size has immense effect on the kinetics of reduction reaction. Some essential points can be summarized as follows:

- The semi-charcoal obtained at $T_{C,\ max}$ = 823 K retains much volatile matter, mainly H_2.
- Fractional reduction, F (%) of semi-charcoal composite pellet at $T_{C,\ max}$ = 823 K is about 19% for 60 minute and is actually larger than any other pellets by usually 7–8% at T_R= 1073 K.
- Fractional reduction F (%) of semi-charcoal composite pellet at $T_{C,\ max}$ = 823 K is over 40% for 60 minute of reaction and is also greater than any other pellets at T_R= 1173 K.
- Fractional reductions F (%) of semi-charcoal composite pellets at $T_{C,\ max}$ = 823, 1073 and 1273 K are over 90% for 60 minute of reaction. The effective reducibility of semi-charcoal composite pellets does not depend on residual volatile matter at T_R=1273 K.

Fractional reduction F (%) of semi-charcoal composite pellet at $T_{C,\ max}$ = 1073 K applying semi-charcoal type reducing agent with the particle size of 23–35 mm is about 38% for 60 minute of reaction and was higher than any other pellets. Basically, semi-charcoal particle size has much essential roles in controlling the rate of reduction of iron oxide burdens. When the size of semi-charcoal particle is smaller, the kinetic rate of reduction of iron oxide can be increased significantly [39].

2.15 Ethanol Production from Potato Peel Waste:

Food processing industries produce large amount of potato peels as waste material. Gathering these peel wastes for longer time may not be favourable for the environment. Although further processing of these wastes would cause further expenditure. For this, scientists have investigated on the particular composition of potato peels and potential application of them. Potato peel wastes contain significant amount of starch, cellulose, hemi-cellulose and fermentable sugars, for which, these peels can be effectively used as the feedstock material to produce bio-ethanol. Bio-ethanol is highly demanding material in chemical processing as well as can be used as fuel. Basically, to produce bio-ethanol from potato peel wastes, batch hydrolysis and thereby fermentation would be the essential method. After hydrolysis, fermentation takes place with the involvement of Saccharomyces cerevisae var. bayanus, which can help to identify the fermentability and ethanol production from feedstock material. Hydrolysis of the peel wastes becomes more effective during using enzymes than hydrochloric acid. Hydrolysis with enzyme produces relatively higher amount of fermentable reducing sugar. During hydrolysis, maximum 18.48 gr/lt of reducing sugar can be produced with particular combination of enzymes: Ternamyl 0.24 KNU + Viscozyme 12 FBGU + Celluclast 1%. After end of fermentation, the amount reducing sugar can be about 1.93 gr/lt. Therefore, the amount of sugar consumed is = (18.48 – 1.93) gr/lt or 16.55 gr/lt. Therefore, bio-ethanol production in the amount of 7.58 gr/lt can be obtained. The yield of ethanol production with 91.6% of the maximum theoretical yield can be obtained [40].

2.16 Investigation of Potato Peels as Raw Material Base for Bio-fuel Production:

Development of bio-refinery platform faces one crucial barrier,that is to find out actual energy potential of the feedstock material. Energy potential of the potato peels can be enhanced by different type of modification techniques. Concentration of fermentable sugar can be effectively upgraded by the proper pre-treatment, which, from the other side, can increase the efficiency of entire bioconversion process. For this, 2 essential substrate pre-treatment procedures are utilized:

i. hydrochloric acid hydrolysis at higher pressure and temperature,
ii. hydrolysis using enzyme at higher temperature using amylolytic complex.

For the hydrolysis, biochemical methane potential of the substrate potato peels enhances in different manner for different chemicals. For acidic modification, the potential increases about 24%, .33 dm^3 CH_4/gVSS and for enzymatic treatment, the potential enhances about 67%, .55 dm^3 CH_4/gVSS. Basically, the combination of 2 processes is followed to obtain the entire energy potential of the substrate potato peels, the 2 processes are:

i. alcohol fermentation,
ii. bio methanation,

Both the 2 processes are consecutive and anaerobic. Basically, the combination of processes can effectively support in expansion of spectrum of the prepared bio-fuels in acidic hydrolysis of the potato peels, on the other hand, for enzymatic modification, the combined method enhances the energy potential about 2.2 times [41]. Food processing industries can adapt this method of producing bio-fuel to obtain economic benefit as well as to execute waste management to keep environmental balance.

2.17 Sustainability and Economic Utilisation of Agricultural Waste:

In today’s world, due to increasing population rate, rate of agricultural activity and harvest of crops and foods has enhanced significantly. Along with the growth of technologies and rate of production of crops in agriculture, higher amount of wastes are generated. Managing of wastes is going to be difficult day by day due to larger amount. Scientists have investigated to find out the way to add value to the wastes and to utilize them in industrial and laboratory research purposes. The wastes can effectively be upgraded in other production purposes and are able to be used as essential resources for several bioactive compounds, such as: carotenoids, β-glucans, essential oils, phenolic compounds. These compounds have necessary application as additives or functional ingredients in the food processing industries for their health properties, antimicrobial activities and antioxidant along with ability of them to act as natural food colorant. Tissues, obtaining from the by-products, contain variation in concentrations of flavor volatiles, which would be recovered and utilised in food and beverage industries. Other essential ingredients would be the content in dietary fibers, which are polysaccharides and lignin or proteins which are possible to be used as functional food ingredient enhancing the nutritional value and imparting useful features and properties in food. Different compounds coming from wastes have antimicrobial or antioxidant effects, which are utilised in edible coating or active packaging to keep the shelf life of food products longer. With the example phenolic compounds such as hydroxytyrosols, which, contained in olive waste or wheat bran, can exert antioxidant properties. Oat husk residues coming from cereal processing would be effectively utilised as essential reinforcing material in producing bio-composites, needed for packaging purposes. The potential applications of waste streams are the use as plant fertilising, biogas material and composting or animal feed. In the other hand, they are landfilled or incinerated. With that, they cannot generate basic value for the farmers but have potential to lead to waste management and form an environmental burden. For different utilisation possibilities and its essential economic impact, the value addition of wastes has gained attention. The global production of food and with this, the particular amount of waste is generally tends to rise, specifying the increased attention. The state-of-the-art technologies and utilisations are represented specifically on mainstream sectors: pharmaceutical, nutraceutical and food processing industries [42]. In the entire sense, needful, sustainable and economic utilisation of agricultural wastes is investigated and facilitated effectively.

2.18 Production of Synthetic Gas by Gasification of Bio-Char:

Reduction of iron ore can initiate co-production of syn gas by the gasification of bio-char. This is basically synergic conversion of bio mass and iron ore. Iron ore basically acts as carrier of oxygen and catalyst for gasification of bio mass. Along with, bio mass acts as reducing agent for metallisation of iron ore. Essential factors can be:

- Temperature for conversion,
- Bio mass to iron ore ratio,

- Time of calcinations.

  Iron ore contain specific amount of lattice oxygen, which would provide catalytic activity, to promote conversion of bio mass into syn gas. There should be effective cracking of hydro-carbon to produce carbon monoxide (CO) and hydrogen (H_2) [43]. Volatiles coming from bio mass would enhance the rate of reduction of iron ore. Volatiles along with 35% char would react with iron ore in the first 10 minute to produce entire amount of H_2 in the syn gas with some amount of CO present in this. Remaining 65% of the bio mass is gasified with in 20 minute to produce remaining amount of carbon monoxide. Maximum amount of yield in producing syn gas about 72.6% with gasification ratio for carbon and hydrogen would be about 72.7% and 68.8%. This effectively takes place at 1000°C in 30 minute. In the reactant mixture, carbon to iron mole ratio about .8 can be obtained. Metallisation of 93.8% would be obtained. The entire process can have potentiality in application in green fuel gasification as well as in direct reduction of iron or DRI process [44].

2.19 Effective Utilisation of Reduction Property of Different Veggies Through Chemical Processing:

In the acidic aqueous solution, if Cr (3) and Cr (6) are present in sufficient amount, then to remove them, proper sorbent is required. Investigation implies that there are some veggies which are very effective in this purpose. These veggies not only, can act as sorbent, but also can show their reducing property. Yohimbe bark and grape stalks are the most suitable in this purpose. Basically, the pH of the aqueous solution should be 2 to 3. Grape stocks are found to be most effective. In this, 2 mechanisms are established, these are: adsorption of Cr (6) and reduction of Cr (6) to its trivalent state.

Some modification is required in this:

- kinetics of the sorption and reduction process,
- to find out whether bio-sorption and reduction process take place in parallel manner (at same rate) or at various rates.

Basically, Yohimbe bark and grape stalks have represented themselves as effective material in the purpose. There are some advantages regarding this:

- Efficient activity as sorbent and reducing agent at relatively lesser expense, which makes the entire procedure economic.
- Availability is better,

Due to presence of lesser toxicity, this method can be used for removal of Chromium from waste water, entire method is environment friendly [45].

2.20 Energy Efficiency in Iron and Steel Making using Bio-Mass:

The iron and steel industrial sector use about 20% of the total annual industrial energy. Coke and coal are the main sources of energy, but they also used as reducing agents for iron ores and consequently contribute to fossil CO_2 emission. Partial or full replacement of fossil fuel with neutral biomass products can significantly contribute to lowering the fossil CO_2 emission and provide a good opportunity for green steel production. The challenges of biomass usage in iron and steel industry can be generally classified into technical and economic aspects. This chapter will focus on technical issues of biomass implementations and the recent research progresses in iron and steel industry. The discussion will focus on biomass utilization in top charged burden materials into the iron-making blast furnace but also via tuyere injection at the lower part of the shaft. In addition, the potential of using the biomass in steelmaking will be addressed [46]. Benefits and limitations of biomass applications in each process will be comprehensively discussed and analyzed.

Gasification of Carbon-rich Bio-dust to Generate Syn Gas:

To enhance the extent of reduction and degree of metallisation of iron ore (Hematite) as well as to decrease the consumption of coke and fossil fuel, the pre-reduced ore by bio-dust can be further introduced in the reduction process, using syn gas as reductant. This syn gas can be obtained through the gasification process and this syn gas contains the mixture of Carbon Monoxide (CO) and Hydrogen (H_2), for this, effective gas-based reduction of pre-reduced ore using both the reducing gases would enhance the degree of metallisation. Along with this, pollution of environment would be smaller than the conventional procedure.

2.21 Catalytic Effect of Ash on Char Gasification for Eucalyptus Wood Chars:

Tancredi et al. investigated the catalytic effect of ash on char gasification for eucalyptus wood chars. The ash content in char was of the order of 1.45% on mass basis. The reactivity of the char increases monotonically with conversion. At low and intermediate conversion, it can be attributed to the increase in surface area as gasification proceeds. At high conversion levels a steeper increase in reactivity has been observed, which cannot be explained by the development of surface area. This region of the reactivity conversion curves can be better explained as the result of an increase in catalytic effect of the metallic constituents (mainly Na and K) present as inorganic matter in the chars. Here CO2 was used as the gasifying agent. Activation energies determined were found to vary within a narrow range of 230–257 kJ/mol. Arrhenius plots showed parallel lines for different degrees of conversion. Parallel line of Arrhenius plot indicates similar activation energies. The increase in reactivity was mainly due to an increase in pre-exponential factor. In a similar study by Montesinos et al., steam gasification and CO_2 gasification of grape fruit skin char were investigated. They also observed an increase in reactivity at high values of conversion [47]. However, a different trend of activation energies values was observed; in the case of CO_2 gasification, as the conversion increased, a decrease in activation energy was observed.

On the other hand, an increase in activation energy was observed in case of steam gasification. This increase in activation energy was also, observed by Marsh et al. The decrease in activation energy values in the case of CO_2 gasification was accompanied by a decrease in pre-exponential factor as well. This behaviour is called the compensation effect. Montesinos et al. obtained a value of isokinetic temperature of 1150 K. The isokinetic temperature is the temperature at which all reactivities are equal for different conversions. An isokinetic temperature of 1449 K was obtained by Dhupe et al. for CO_2 gasification using catalysed sodium lignosulfonate. Feistel et al. found this temperature to be 1425 K, obtained using potassium-catalysed steam gasification [48].

2.22 Gasification of Char Using Two Types of Catalysts and a Mixture of Both the Catalysts:

Gokarn and Muhlen investigated the gasification of char using two types of catalysts and a mixture of both the catalysts. The investigated catalysts were calcium lignosulfonate and sodium lignosulfonate. The carbon matrix was saturated by calcium lignosulfonate at 10% by weight. However, this saturation did not affect the catalytic effect of sodium lignosulfonate in the mixed catalytic system.

Li and Cheng investigated the catalytic gasification of coal char using Na_2CO_3 and K_2CO_3 as catalysts. Effect of catalyst loading was investigated. Increase in catalysts loading was found to be effective until 25% by weight of K_2CO_3 loading and 20% by weight of Na_2CO_3 loading. Further increase in catalysts loading resulted in a decrease in char reactivity. The results of reactivity versus conversion plots showed an increase in char reactivity initially. Further increase in conversion showed a decrease in char reactivity.

They attributed this decrease to the char pores blocking the catalyst at high degrees of conversion. A compensation effect was observed and an isokinetic temperature of 1289 deg. C for Na_2CO_3 and 1466 deg. C for K_2CO_3 were obtained. Food wastes, especially which have high percentage of vegetable oil and animal fat, provide a good potential for production of liquid fuels though transesterification. Transesterification is the process of exchanging the organic group R00 of an ester with the organic group R0 of an alcohol. The process is widely used to produce biodiesel fuels from vegetable oils and animal fats. The process is often catalysed by an acid or a base.

Other than acid or base catalysts, enzyme or heterogeneous catalysts might be used as well. Among the mentioned catalysts, alkali catalysts are more effective. However, if the oil has high free fatty acid (FFA) content, higher than 3% (approximately), acid catalyzed transesterification is used rather than a base catalyst.

Drawbacks of alkaline or acid catalysis process include: (a) it requires considerable amounts of energy; (b) separation of glycerol is difficult; (c) the alkaline catalyst has to be removed from the product, free fatty acid and water interfere with the reaction. On the other hand, enzymatic catalysts have the advantage of effectively acting as catalyst in the transesterification of triglycerides in either aqueous or non-aqueous systems. Besides, free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. However, production cost of enzymatic catalysts is significantly higher than that of an alkaline catalyst. It is to be noted that the conversion rate increases with reaction time and temperature [49]. At fixed reaction time the increase in temperature provides the same effect of increased conversion.

2.23 Investigation of the Transesterification of Waste Palm Oil into Bio-diesel Fuel:

Al-Widyan and Al-Shyoukh conducted an experimental investigation of the transesterification of waste palm oil into biodiesel fuel. Acidic catalyst has been used due to the high free fatty acid content of 10–15%. Effect of catalyst concentration and alcohol levels, amongst other parameters, has been investigated [50]. The results show that at any given catalyst concentration and reactor temperature, specific gravity decreases exponentially with time and ends up with an asymptotic value. However, higher catalyst concentrations, results in obtaining the terminal value of specific gravity in much shorter times. Higher the excess alcohol levels consistently led to desirable lower values of specific gravity throughout the reaction time [51].

2.24 Production of Biodiesel Fuel from Vegetable Oil Using Supercritical Methanol Process:

He et al. investigated the continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Reactor temperature, pressure, alcohol to oil ratio and residence time was varied in order to determine conditions for maximum production rate. The optimal reaction condition under constant reaction temperature process was found to be 40:1 molar ratio of alcohol to oil, 25 min of residence time, 35 MPa and 310 deg C. At these conditions, the maximum production yield was 77% for a constant reaction temperature. Side reactions of unsaturated fatty acid methyl esters (FAME) were observed when reaction temperature exceeded 300 deg C, which led to a loss in unsaturated fatty acid methyl esters (FAME). They proposed a new methodology to avoid the loss of FAME at high temperatures, through gradual heating of the reactants along the reactor to a high temperature. With the new reaction technology, the methyl esters yield reached more than 96% [52].

2.25 Thermal Effects in Cellulose Pyrolysis:

Milosavljevic et al. investigated thermal effects in cellulose pyrolysis. They investigated the effect of heating rate on char formation and pyrolysis heat absorption. A linear relationship between mass loss and heat absorption, observed at high heating rate, 60 K/min. They concluded that the processes responsible for net heat absorption are apparently quite constant throughout the process of rapid heating. In contrast to high heating rate the results obtained at lower heating rates show a deviation from a steady heat absorption curve, at some point. This deviation occurs at progressively lower extents of mass loss as the heating rate is lowered. They suggested that the heats of pyrolysis depend upon the exothermic nature of char formation. They concluded that a large portion of the exothermic char formation is delayed to progressively later times during the pyrolysis process at higher heating rates [53].

2.26 Kinetic Study of Thermal Decomposition of Bio-mass Waste:

Becidan et al. conducted a kinetic study of thermal decomposition of biomass wastes. Through their experiments they introduced the peak values of sample mass degradation rate dm/dt. They also, identified the temperatures at which peak dm/dt occurred in the range from 233 to 367 deg. C.

Li et al. and Banyasz et al. investigated gas evolution and mechanism of cellulose pyrolysis in a two-heating zone pyrolysis system. The two heating zone experiments indicated that a large portion of CO is formed from the decomposition of primary volatile products (aldehydes) during secondary reactions. However, CO_2 is formed at early stages of cellulose pyrolysis during the primary reactions. In the two-heating zone experiment, CO formation was found to be highly dependent on the temperature set at the second zone, while CO_2 was not affected by additional heating, thus indicating further decomposition of vapor products to produce CO [54].

2.27 Gaseous Products from Biomass by Pyrolysis and Gasification:

Demirbas investigated gaseous products from biomass by pyrolysis and gasification. In their study they introduced the effect of reactor temperature on gaseous, liquid and char yield for the pyrolysis process. Increasing the reactor temperature decreased the liquid and char yield. However, increasing reactor temperature increased the gaseous yield.

The general trend of increase in the steam to sample ratio is to increase the yield of total syngas, H_2, and CO_2, while the yield of CO and CH_4 decreases. The increase in H_2 and CO_2 yield and the decrease in CO yield are attributed to the acceleration of the forward reaction rate of the water gas shift reaction:

$$\mathbf{CO + H_2O \Leftrightarrow CO_2 + H_2}$$

On the other hand, the increase in steam to sample ratio increases the methane reforming reaction to cause a reduction in the yield of methane. Therefore, increase in steam to sample ratio results in a direct increase in the ratio of H_2/CO [55].

2.28 Effect of Pressure on Apparent and Intrinsic Reaction Kinetics:

Roberts et al. investigated the effect of pressure on apparent and intrinsic reaction kinetics. The apparent reaction rate at 10% conversion for the char-CO_2 reaction is a function of pressure. The results showed that pressure increases the apparent reaction rate of the char-CO_2. However, this increase is not constant over the pressure range 1–30 atm. As the pressure is increased to above 10 atm., effect of pressure is less and apparent reaction order is almost zero at pressures of 20–30 atm. However, the intrinsic reaction rate was not found to be affected by the pressure that much. This supports that the shift in apparent reaction order at high pressures is not due to fundamental change in the reaction mechanism. They attributed this decrease in reaction order due to the following: at atmospheric pressure the surface of the sample is not saturated and the reaction rate is proportional to the number of surface complexes. As the pressure increases, more surface complexes are formed to result in an increase in reaction rate. At high enough pressures the surface will be saturated with complexes, such that increases in pressure will not lead to the formation of further surface complexes and the reaction rate will not increase. Consequently, the apparent reaction order is zero.

Kaijitani et al. investigated the gasification rate of coal using a pressurized drop tube furnace to simulate two stages entrained flow gasifier. Specific surface areas of the investigated coal char increased rapidly with the progress of reaction and peaked at a conversion of 0.4. Carbon dioxide adsorption was used to precisely evaluate the micro pores surface area as compared to calculating the surface area using the analysis of nitrogen adsorption isotherm at 77 K by the BET method. They concluded that the examined char is considered to be dominated by micro pores because its specific surface area is nearly 10 times the size of the specific surface area resulting from nitrogen adsorption. They concluded that it is essential to measure the specific surface area of the char at the early stages of gasification with the use of carbon dioxide adsorption isotherm at 273 K. They also noticed the widening of pores from micro-scale to meso-scale with the progress of reaction.

Authors made a comparison between the grain model and a random pore model. The equation to calculate the specific surface area in the grain model is:

$$S = S_0(1-X)^{2/3}.$$

The specific surface area in the random pore model is:

$$S = S_0(1-X)\ (1-y)\ (1-X))^{1/2},$$

where x is the conversion and W is a dimensionless parameter that describes the initial pore structure as function of initial surface area, initial pore length and initial sample porosity. Based on their experiments they concluded that the random pore model was better for describing the evolution of char specific surface area [56]. Consequently, the reaction rate was described as:

$$dx/dt = A_0.\ (P_A)^{pi}.\ Exp(-E/RT).\ (1-x).\ \{1-y.\ ln(1-x)\}^{1/2}$$

2.29 Kinetics of CO_2 and Steam Gasification of a Grape Fruit Skin Char:

Montesinos et al. investigated the kinetics of CO_2 and steam gasification of a grapefruit skin char. They found that this agriculture wastes show a comparatively high reactivity and they attributed this to the catalytic effect of inorganic matter present in the sample. The reactivity (and also reactivity per unit area) of both steam and CO_2 gasification is found to increase with the increase in conversion, which supports their conclusion about the catalytic effect. However, lowering the catalytic effect by washing the sample with an acid leads to a decrease in reactivity thus confirming the catalytic activity of inorganic matter. Ash content in the tested char was 14.6% with potassium being the major metallic constituent. As gasification proceeds, potassium to carbon ratio increases and this consequently increases the catalytic effect of potassium. They also concluded that the reactivity versus conversion curve did not show a saturation of the catalytic effect even at a high conversion value of 0.9.

Bhat et al. investigated the kinetics of rice husk gasification using steam as gasifying agents. The investigated temperature range was from 750 to 900 deg. C. They used both the volume reaction model represented by the conversion–time relation;

$$\mathbf{\ln (1\text{-}x) = (k_v.C_{A0}).t}$$

and the shrinking core model represented as:

$$\mathbf{t = (d.R_p / k_v.C_{A0}).\{1 - (1\text{-}x)^{1/3}\}}$$

Their results show that the gasification reaction of rice husk char is chemically controlled up to a temperature of 850 deg. C. The activation energy obtained by volume reaction model and shrinking core model were close in agreement. The activation energy calculated was in the order of 180–200 kJ/ mol. This value is higher than the value obtained for paper char gasification in this study using the same reacting volume model [57]. This discrepancy may be attributed to the high ash content of paper which may have a catalytic effect on the process.

2.30 Catalytic Effect of Molten Carbonate Mixtures on Waste Paper Conversion:

Iwaki et al. investigated the catalytic effect of molten carbonates mixtures on waste paper conversion. Li, Na and K carbonates and their mixtures were used in their experiments. They found that the melting point is an essential factor to be considered. Usually, a mixture of carbonates has a lower melting point than a single carbonate compound. The results show that carbon conversion varies significantly with one, two and three carbonate components [58]. They attributed this variation in carbon conversion to a lower melting point associated with the mixture catalyst as compared to a single catalyst from the improved contact efficiency between the gasifying agent and wastepaper using a mixture.

Tomishige et al. investigated the cellulose gasification using Rh/CeO_2/SiO_2 catalysts. They investigated the dependence of carbon conversion (C-conversion) and cold gas efficiency in the gasification of cellulose on CeO_2 content in $Rh/CeO_2/SiO_2$ catalysts. There was a maximum in the C-conversion and the cold gas efficiency at 35 mass% CeO_2 content. The presence of a peak was justified as follows. The BET surface area decreased with increase in CeO_2 content in the catalyst. On the other hand, using Rh/SiO_2 with no addition of CeO_2 showed low performance of the gasification of cellulose and showed an elevated value of tar and solid carbon yield. However, addition of 10% CeO_2 decreased the yield of tar and solid carbon drastically, and this indicates that CeO_2 promoted the gasification reaction significantly. On the other hand, the addition of CeO_2 decreased the catalyst surface area, and this can make the particle size of Rh metal large and reduce the activity. So, the addition of CeO_2 has both positive and negative aspects to the gasifier performance. In a similar study by Asadullah et al. Rhodium metal loaded on CeO_2 (Rh/CeO_2) was found to be an excellent catalyst for cellulose gasification at low temperatures that resulted in 100% C-conversion to syngas.

Watanabe et al. investigated catalytic hydrogen generation from biomass simulated as glucose and cellulose with ZrO_2 in supercritical water. They found that gasification efficiency with zirconia was twice as much as that without catalyst at all the experimental conditions. For comparison, they conducted the experiments using alkali hydroxide (NaOH) for glucose and cellulose [59]. For all the experiments, the gasification efficiency with NaOH was the highest and the yield of CO was negligibly small. Negligible CO yield was attributed to the acceleration in the water gas shift reaction.

Work conducted by previous investigators reveals the behaviour of different samples during gasification or pyrolysis, separately. However, a quantitative study that isolates the differences and similarities between gasification and pyrolysis has not been well explored yet. From the available literature one can deduce general conclusions about the differences and similarities in behaviour of a certain sample when undergoing a gasification or pyrolysis process. However, no detailed quantification is available in the literature [60]. The objective of this paper is to illustrate and quantify the differences and similarities in behaviour of paper when undergoing a gasification or pyrolysis process.

Chapter: 4

Methodology

Flower wastes (Mary gold) were collected from gardens and nurseries as well as vegetable (such as: Potato, Potal, Banana, Pumpkin) wastes, peels and trimmings were taken from various sources such as restaurants, household domestic wastes, corporation wastes etc. Total 5 samples were employed there.

a. The collected wastes needed to be cleaned and dried. Thereafter, samples of these wastes were studied for compositional analysis. Proximate and ultimate analysis of the wastes were essential in this purpose. Based on requirement, the higher-carbon containing waste samples were separated to keep at safe place without wastage to be used further.

b. Peels and trimmings of the vegetables and the flower wastes comprise of high amount of moisture and carbon in the form of starch. Water content present in the molecular structure of the waste material, is the main constituent of the waste material. The moisture content in the peels and trimmings needs to be removed prior to utilizing it as a reductant. Upon heating, the moisture present in peels escapes leaving behind the carbon rich residue. Also, during dehydration by heating, some amount of volatile matter be removed and residue material is basically pure form of carbon.

c. Peels and trimmings of vegetables and flower wastes were shredded to smaller size, in the range 20 mm to 30 mm. It would be helpful to get enhanced surface area during heating and removal of moisture would properly take place, chance of retention of sample, without dehydration, be lesser. Mass measurement of the waste sample had been done by Digital Laboratory Balance, in vacuum. Practically, it was found that heating 90 to 100 gram of properly sized sample could be effectively dehydrated by heating to produce carbon rich bio-dust.

d. The heating temperature was determined by Differential Thermal Analysis (DTA)of wastes. From the DTA data, a suitable temperature would be chosen such that the moisture could be completely removed but there was chance of burning of the carbon residue in presence of air (Oxygen). For this, it was essential that at this temperature it should be ensured that the combustion of the carbon residue would not occur.

e. Each sample were properly marked, such that no sample of one vegetable or flower may mix with other. 1 conical flask of 500 ml. volume was taken for heating, placing it on heating plate, in which temperature could reach up to 400 deg. C temperature. The flask had 2 nozzles along with 1 opening mouth, in such manner that 1 nozzle was at the bottom part and the other nozzle was at the upper part. Such flask could be kept evacuated during heating as well as inert gas, during dehydration, could be allowed to pass through the bottom nozzle and steam would pass through the upper nozzle. Valve was mandatory to control the flow of inert gas and steam both.

f. The mouth was closed by a cork, after shredded sample was placed properly and distributed on the bottom surface of flask such that, sample was not allowed to be accumulated or gathered at particular region, which might prevent from complete dehydration and complete formation of bio-dust. The container for heating was preheated at the particular temperature range of 380 deg. C. Inert gas (Argon or Nitrogen) was allowed to enter the flask through bottom nozzle and steam along with inert gas was going out through the upper nozzle of flask.

g. The container was made of higher temperature glass as well as insulating cloth wrapped the container, even during pre-heating to prevent condensation of steam and to accelerate the removal of moisture from sample. The heating was done in 30 minute for each sample, to observe the bio-dust specimen from each sample. A gas analyser was connected at the upper nozzle of flask, from where steam along with inert gas (Argon or Nitrogen) was coming out. When the analyser detected only inert gas in the outcoming gaseous substance, it indicated that the entire process of removal of moisture content from waste sample was completed and bio-dust was formed.

h. After heating for sufficient time period, the each was collected and measured in Laboratory Balance, the data were written. The carbon residue after heating would be pulverized to powder. The bio dust sample of each vegetable and flower wastes was dusted in hand-mortar, to obtain the size range of 149 microns nearly. It was confirmed by sieve analysis, by allowing the the bio-dust sample to pass through sieve of 100 mesh size, the size of bio-dust was -100 mesh. The quantity of finer carbon required for a given amount of ore sample would be calculated on stoichiometric basis.

i. Agglomeration of ore fines with the pulverized carbon obtained from the wastes peels and flower wastes comprises the next step. Nugget preparation was done. Mixing of bentonite and molasses, during nugget preparation, was essential here around 2% and 3% respectively. The entire system was kept for 1 days.

j. These nuggets were then charged in the pre-heated raising hearth furnace keeping on alumina crucible. The crucible was already preheated at 900^0C. The pre-heating was started with the rate of increment of temperature about 5 deg. C per minute. Total 3 hours required to reach to the temperature range and 40 minute was holding time for reaction, in this manner, PNC of furnace was set. The crucible was already preheated cooled to keep it thermally stable at higher temperature range. After reaching to 900 deg. C, nugget sample was held about 40 minute to execute the entire reaction. After this time period, the furnace was allowed to drop its temperature as well as cooling of the sample containing crucible had taken place inside the furnace. After the entire system was cooled and reached to room temperature range, the container along with the sample was taken out and sample was collected. Then each sample is taken to XRD analysis, to detect the peaks of metallic iron, as the presence of peaks of metallic iron in each sample expresses the occurrence of reduction reaction of iron ore.

k. After this, plant design of producing syn gas with laboratory based equipments, using the steam loss, was started. Initially, the disadvantages of entire iron ore reduction process along with loss of steam was analysed and modification of these was planned.

l. On the basis of the modification, thermodynamic and kinetic design, to obtain the theoretical set up, to produce syn gas, by hot steam, to pass through carbon-rich bio-dust were prepared. Accordingly, laboratory scale plant design to produce syn gas was prepared.

m. In execute the design, loss of steam by heating the waste material was calculated and this particular amount of steam was planned to be condensed to produce pure water for drinking, laboratory use etc. purposes. Along with this, controlling parameters for this laboratory scale plant set up were analysed carefully.

n. The entire design procedure be completely free of any undesired element and causes no degradation of physical and mental health of human being. At the terminal part of this project, the environmental impact of the entire activity was properly analysed.

Chapter: 5

Apparatus and Instruments

5.1 Weighing Balance:

Weighing balance machine is measuring equipment for determining the weight of an object or sample with a digital display board. It is a class of balance designed to measure weights in the sub-milligram range. The capacity of the balance is 1000 gram as well as the readability is .01 gram. The measuring pan inside the weighing balance (.1 mg or better) is inside in a transparent enclosure with properly closing doors, in order to suppress the effect of dust and fluctuation due to air and current flow inside the room during operation. This enclosure is often called a draft shield.

Fig: 5.1, Weighing Balance

5.2 X-ray Fluorescence:

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analysers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays (“a fingerprint”) that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

Strengths and Limitations of X-ray Fluorescence:

Strengths:

X-Ray fluorescence is particularly well-suited for investigations that involve:

- bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment
- bulk chemical analyses of trace elements (>1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment.

Limitations:

In theory the XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength and intensity of incident x-rays.

- In practice, most commercially available instruments are very limited in their ability to precisely and accurately measure the abundances of elements with Z lesser than (<) 11 in most natural earth materials.
- XRF analyses cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments.
- XRF analyses cannot distinguish ions of the same elements in different valence states, so these analyses of rocks and minerals are done with techniques such as wet chemical analysis or Mossbauer spectroscopy.

Fig: 5.2, XRF Machine

5.3 XRD Analysis:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material is finely ground, homogenized, and average bulk composition is determined.

Principal of Analysis:

Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

Strengths and Limitations of X-ray Powder Diffraction (XRD):

Strengths:

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- In most cases, it provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

Limitations:

- Homogeneous and single-phase material is best for identification of an unknown
- Must have access to a standard reference file of inorganic compounds (d-spacing, *hkl*s)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur and worsens for high angle 'reflections'.

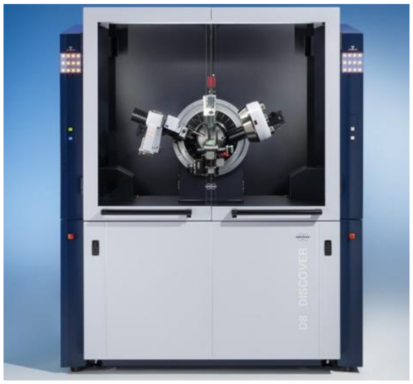


Fig: 5.3, XRD Analyser

5.4 TGA-DTA Analysis:

Thermo-gravimetric Differential Thermal Analysis or TG/DTA is a simultaneous thermal analyzer that can characterize multiple thermal properties of a sample in a single experiment. The TG component measures temperatures where decomposition, reduction or oxidation occurs. It simultaneously measures the weight changes associated with decomposition, oxidation and any other physical or chemical changes that result in sample weight loss or gain. The DTA component shows whether decomposition processes are endothermic or exothermic. The DTA also measures temperatures corresponding to phase changes where no mass loss occurs, such as melting, crystallization and glass transitions.

Fundamentally, the “TG” of TG/DTA is very similar to standard thermo-gravimetric analysis (TGA). A TG/DTA measures the change in sample weight as a function of temperature (and/or time) under controlled gas atmosphere and temperature. Graphing the percent weight change over a programmed temperature range enables the study of physical or chemical processes that have caused the sample to lose or gain weight.

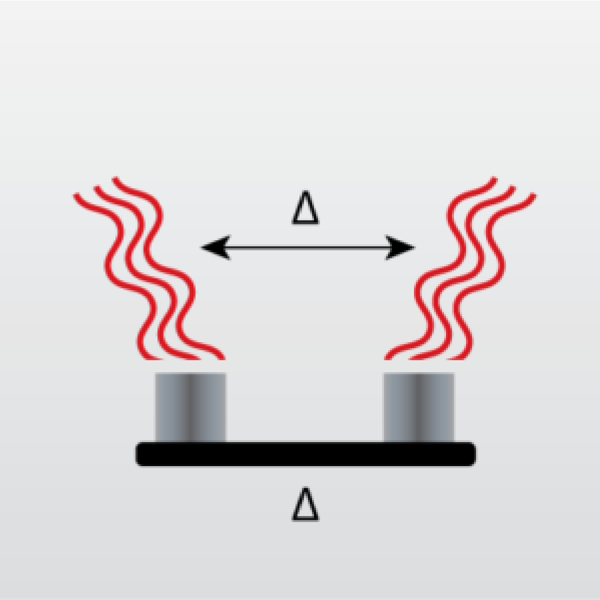


Fig: 5.4, TGA-DTA Analysis

The "DTA" refers to differential thermal analysis. The DTA technique measures the difference between the sample temperature (T_s) and the temperature of a reference (T_r). A plot of $T_s - T_R$ over a programmed temperature range will show a series of peaks or step changes that map the temperatures where thermal events occur. However, the amount of heat absorbed or released by the sample as it undergoes changes in temperature cannot be accurately quantified by the TG/DTA instrument. This heat quantity, known as change in enthalpy (delta H), can be accurately measured using differential scanning calorimetry (DSC).

Strengths and Limitations of TGA-DTA Analysis:

Strengths:

- Rapid screening of thermal properties of materials
- Simultaneous acquisition of thermo-gravimetry and phase transition data
- Small sample size
- Choice of atmospheres (inert or reactive)
- Used for high temperature analysis of phase transitions

Limitations:

- Does not measure heat capacity
- Not quantitative for enthalpy change (e.g. heat of fusion) measurement.

Fig: 5.5, TGA-DTA Analyser

5.5 Raising Hearth Furnace:

Raising Hearth Furnace with Hearth Lifting Arrangement (HLA), is suitable, executing heating or reduction activity in the range of 1400 deg. C to 1800 deg. C application. The Raising Hearth Furnace is a kind of user friendly operating system that comes with smooth hearth lifting arrangement. The Raising Hearth Furnace is widely used for firing and sintering of advanced ceramics and high temperature glass melting application. Raising Hearth Furnace with Hearth Lifting Arrangement offers high temperature accuracy in a range of +/- 1 deg. C.

Advantage of Raising Hearth furnace:

- Smooth hearth lifting arrangement
- Effective hearth sealing to minimize heat loss
- Rapid heating (maximum 20 deg. C/min)
- High temperature accuracy (+/- 1-degree C)

- Stirrer facility can also be provided
- Low skin temperature due to accelerated air circulation between insulation and outer case by means of exhaust fan
- Precise furnace temperature control with the help of a thyristor
- Essential heating elements, including: Ni-Chrome wire, Special alloy resistance heating wire, Silicon Carbide, Molybdenum Di- Silicide, Molybdenum, Tungsten, Graphite
- User friendly operating system.

Fig: 5.6, Raising Hearth Furnace

Chapter: 6

Results and Discussion

In present world, the iron and steel industries are significantly a faster growing sector. Although the stocking of higher-grade coal (coking coal) is decreasing in rapid manner. The entire procedure of coking is not only huge costly, but also time consuming. Al well as conventional iron and steel making process causes huge environmental pollution. For this, carbonaceous domestic wastes are employed in this project as potential source of pure form of carbon, to be used as reducing agent in iron and steel making technology.

In this activity, Iron ore, Hematite (Fe_2O_3) has to be effectively reduced to metallic iron by the action of carbonaceous agents, which is basically bio mass. This bio mass is effectively produced from dehydrated vegetable wastes and flower wastes. In this experiment, peels of some particular vegetables are taken for executing the mentioned reduction reaction. Most of the vegetables are commonly consumed by Indians. Day by day, the amount of these vegetable wastes is increasing, with population. The vegetables are basically: potato, potal, banana and pumpkin. The flower waste which is taken here is basically meri gold (hibiscus).

So, in this thesis, proper analysis of all the 4 vegetables and 1 flower wastes is needed to find out amount of bio-dust (pure form of carbon) and moisture produced, after heating the waste materials at some suitable temperature. The entire experiment is carried out in the laboratory. However, to initiate the experiment, some theoretical data about waste materials have been collected from different available literature, which are given as under. In this activity, the chapter is divided into 4 parts:

6.1. Ingredient Waste Material, their Source and Analysis,

6.2. Analysis of Iron Ore and Nugget Samples after Direct Reduction Using Bio-dust as Reductant,

6.3. Design of Gas-based Direct Reduced Iron (DRI) Plant Using Laboratory Based Equipments,

6.4. Environmental Impact Assessment and Risk Analysis

Chapter: 6.1

Ingredient Waste Material, their Source and Analysis

6.1.1 Source of Vegetable and Flower Waste:

According to director of IRAI, Dr. A. K. Singh, almost 30-40% of vegetables and fruits and almost 10% of the total agricultural product move to waste in India. Fruits and vegetables are the highly used food products amongst the horticultural crops. These items are consumed uncooked, nominally cooked or fully cooked, according to their nature and cooking process. With the change in diet habits and rising population, the production, as well as the processing of horticultural crops, has exponentially improved to meet its increasing demand. A large amount of peel waste is generated from fruit and vegetable-based industries and household kitchen and has led to a big nutritional and economic loss and environmental problems. Processing of fruits and vegetables alone generates a significant waste, which amounts to 25-30% of the total product. Most common type of wastes include pomace, peels, rind and seeds, which are highly rich in valuable bioactive compounds such as carotenoids, enzymes, polyphenols, oils, vitamins and many other compounds. These bioactive compounds show their application in various industries such as food to develop edible films, food industries for probiotics and other industries for valuable products. The utilization of these wastes with lesser costing, horticultural wastes can be effectively used as the source of carbon and bio mass. Producing the value-added product from these wastes' a novel step in its sustainable utilization.

Across the country, people bring flowers to temples daily—gifts for the God, blessings for life, for celebrations—to the tune of more than 800 million metric tons per year. These flowers are thrown into the Ganges and India's other sacred rivers, a beautiful religious ritual that is having an unfortunate effect. As the flowers rot, they fill the rivers with waste, dumping toxins like arsenic, lead, and cadmium from pesticides, thus causing pollution and enormous levels of water-borne diseases. Flowers, incense, and other religious items come in plastic packaging adorned with images of the gods. Devotees do not want to throw away this packaging, so they either leave the packaging under trees or immerse it into bodies of water. Collecting these flower wastes from the waste dumping and river bodies, these can be further processed to produce carbonaceous material, basically the source of carbon, to be used for different purposes.

6.1.2 Detailed Analysis:

In this analysis, effective reduction of Iron ore HMO, Hematite (Fe_2O_3) has been executed to metallic iron by the action of concentrated carbonaceous agents, which is basically bio mass. This bio mass was effectively produced from dehydrated vegetable wastes and flower wastes. In this experiment, peels of 4 particular vegetables are taken for executing the mentioned reduction reaction. Most of the vegetables are commonly consumed by Indians. Day by day, the amount of these vegetable wastes is increasing with increasing the population.

The vegetables are basically: Potato, Potal, Banana and Pumpkin. The flower waste which is taken here is basically Meri Gold (Hibiscus). 2 types of analysis were done regarding these ingredients:

a. Proximate Analysis
b. Elemental Analysis,
c. Thermo-Gravimetric and Differential Thermal Analysis (TGA-DTA),

6.1.2.a Proximate Analysis:

Proximate analysis of the vegetable and flower samples were taken place to find actual amount of volatile matter, ash content and fixed carbon present in the organic substances and it was essential to find out which waste contains maximum amount of fixed carbo which would help in analysing extent of reduction of iron ore applying the bio-dust obtained from heating and dehydration of the wastes. Ash content was undesirable during entire analysis.
Ultimate analysis is essential to obtain % amount of elements present in the waste material, in an extensive manner, such elements are: Carbon, Hydrogen, Oxygen, Sulphur etc.

Table 6.1:

Waste	**Volatile Matter**	**Fixed Carbon**	**Ash Content**
Potato Peel	76.5	14.2	9.3
Potal Peel	79.4	11.6	9.0
Pumpkin Peel	78.8	11.5	9.7
Banana Peel	79.36	14.6	6.04

Mary Gold	78.2	12.6	9.2

Ultimate Analysis of the wastes nearly gives following result (in %):

C - 43.78 ± 0.15%

H - 5.96 ± 0.12 %

N - 4.06 ± 0.01 % and

O - 46.21 ± 0.28%

Banana peel only contains Sulphur around 9.4%

6.1.2.b. Elemental Analysis of the Waste Material:

6.1.2.b.1. Potato Peels:

To find the physicochemical properties of potato peel, it is necessary to focus on its physical and chemical composition. The knowledge of these properties would help in developing an environmentally friendly approach for the utilization of potato peel. Following table illustrates different compounds present in potato peel Based on geographical cultivation areas, the composition, variety, colour and breed, of potatoes (and thus their peel) varies. Potato peel contains various polyphenols and phenolic acids which are responsible for its antioxidant activities, whereas fatty acids and lipids showed antibacterial activities. Potato peel also contains starch (25%), non-starch polysaccharide (30%), protein (18%), acid-soluble and acid-insoluble lignin (20%), lipids (1%) and ash (6%) on dry basis. The lipid fraction includes long-chain fatty acids, alcohols, triglycerides and sterol esters. In addition, lignin units have been found in the cell wall of potatoes. Potato peel is rich in starch (52% dry weight), but the content of fermentable reducing sugar is limited (0.6% dry weight). For this purpose, fermentation of potato peel is not practically possible, thus initial hydrolysis (enzymatic or acidic) of carbohydrates is required to increase the content of fermentable reducing sugar. Elemental analysis of potato peel shows that it contains (in % dry basis):

C - 43.78 ± 0.15,

H - 5.96 ± 0.12,

N - 4.06 ± 0.01 and
O - 46.21 ± 0.28.

The C/N ratio of potato peel is 10.7 and its pH 6.5. The calorific value of potato peel is 17.37 ± 0.38 (MJ/kg). Various phenolic acids, such as gallic acid (58.6–63.0 mg/100 g), proto-catechuic acid (216.0–256.0 mg/100 g), vanillic acid (43.0–48.0 mg/100 g), caffeic acid (278.0–296.0 mg/100 g), chlorogenic acid (753.0–821.3 mg/100 g), p-hydroxybenzoic acid (82.0–87.0 mg/100 g) and p-coumaric acid (41.8–45.6 mg/100 g) are found in the potato peel extract.

These values range from 0.17% to 0.21% (dry weight basis) and show that potato peel has a higher content of lipid than peeled potatoes (0.10%). Onyeneho and Hettiarachchy had an alike fatty acid composition and have higher quantities of PUFAS (polyunsaturated fatty acids). Variations in the comparative quantities of single fatty acids appeared to be affected by the colour of the potato peels.

Chemical composition of raw potato peel is given, g per 100 g, Table 6.2:

Compound	**Minimum and Maximum Values (%)**
Water	83.3–85.1
Protein	1.2–2.3
Total lipids	0.1–0.4
Total carbohydrate	8.7–12.4
Starch	7.8
Total dietary fibre	2.5
Ash	0.9–1.6
Total phenolic content	1.02–2.92
Total flavonoids	0.51–0.96

6.1.2.b.2 Potal Peels:

Trichosanthes dioica Roxb. is a climber of the Cucurbitaceae family, mainly found in tropical Asia. The fruit is widely consumed as a vegetable and different parts of this plant are used in the traditional medicine to treat various types of human ailments. Trichosanthes dioica is annual or perennial herbaceous vine commonly known as pointed gourd (English), Putulika (Sanskrit), Parval (Hindi) and Potol (Bengali). It grows up to 5–6 m. The stem is about 1 cm thick with simple tendrils. The leaves are cordate, oblong, acute, sinuate-dentate not lobed and dark green. The inflorescence is racemose and the flowers found in leaf axils are whitish green, sessile, solitary, bracteate with oblong-cylindrical calyx tube. Fruits are generally globose, oblong and smooth and the pericarp and mesocarp form the edible part. The shape, size and striation patterns of the fruit vary greatly giving rise of four categories:

i. 10–13 cm long fruit of dark green color with white stripes;
ii. 10–16 cm long and comparatively thick fruit with dark green color with very pale-green stripes;
iii. 5–8 cm long and roundish fruit of dark green color with white stripes; and
iv. 5–8 cm long fruit of green color, tapered at the ends, and striped.T. dioica has tuberous taproots. The propagation usually is done by root or stem cuttings rather than the seed because of poor germination and late flowering.

Chemical composition of raw potato peel is given, g per 100 g, Table 6.3:

Compound	**Minimum and Maximum Values**
Moisture	92
Protein	.7
Fibre	3
Total carbohydrate	2.2
Calcium	30
Phosphorus	40
Iron	1.7
Carotene	15.3

Thiamine	.05
Riboflavin	.06
Vitamin C	29

6.1.2.b.3 Pumpkin Peels:

The nutritional composition of the powdered pumpkin peel is presented in Table 1. The moisture content is found to be around 83.3% – 85.1% in peels. Protein content was more or less in peel about 12.5%. The ash content is high in peel, about 6.04% indicating high mineral content. The waste is found to be good source of phosphorus and iron. The vitamin C content of the peel is around 18.90 mg/100 g. This information about ingredients indicate that if the peel wastes were to be used for value addition, they would contribute considerable amounts of nutrients and effective elements to products. Identification and quantification of β-carotene in pumpkin peel was carried out by HPLC method. The ß-carotene is eluted after 8 mins and is identified with standard β-carotene. The peel waste is found to be a medium source of β-carotene.

Chemical composition of raw potato peel is given, g per 100 g, Table 6.4:

Compound	**Minimum and maximum values (%)**
Moisture	83.3–85.1
Protein	12.5
Crude fibre	13.91
Dietary fibre	28.81
Phosphorus	6.64
iron	14.44
Ash	6.04

Ascorbic acid	18.9

6.1.2.b.4 Banana Peels:

Banana peels are analysed properly to find specifically minerals, nutritional and anti-nutritional contents. The basic mineral content indicates the concentrations (mg/g) of potassium, calcium, sodium, iron, manganese, bromine, rubidium, strontium, zirconium and niobium to be 78.10, 19.20, 24.30, 0.61, 76.20, 0.04, 0.21, 0.03, 0.02 and 0.02 respectively. The percentage concentrations of protein, crude lipid, carbohydrate and crude fibre were 0.90, 1.70, 59.00 and 31.70 respectively. The results indicate that if the peels are properly exploited and process, they can be effectively high-quality and cheap source of carbohydrates and minerals for livestock.

Chemical composition of raw potato peel is given, g per 100 g, Table 6.5:

Compound	**Minimum and maximum values (%)**
Moisture	83.3 – 85.1
Protein	.9
Crude Fibre	37.1
Crude Lipid	1.7
Carbohydrate	59
Phosphorus	78.1
Sulphur	18.86 – 20.62
Iron	.61
Calcium	19.2
Sodium	24.3
Manganese	76.2
Bromine	.04
Rubidium	.21

Strontium	.03
Zirconium	.02
Niobium	.02
Ash	6.04

6.1.2.b.5 Mari gold Flower Waste:

Tagetes is a genus of annual or perennial, mostly herbaceous plants in the family Asteraceae. They are among several groups of plants known in English as Mari golds. The genus Tagetes was described by Carl Linnaeus in 1753.

These plants are native to Mexico, growing naturally since Mexico's valley down to the south and even reaching several other Latin-American countries, but some species have become naturalized around the world. One species, T. minuta, is considered a noxious invasive plant in some areas.

Tagetes species vary in size from 0.1 to 2.2 m tall. Most species have pinnate green leaves. Blooms naturally occur in golden, orange, yellow, and white colours, often with maroon highlights. Floral heads are typically (1-) to 4–6 cm diameter, generally with both ray florets and disc florets. In horticulture, they tend to be planted as annuals, although the perennial species are gaining popularity. They have fibrous roots.

Depending on the species, Tagetes species grow well in almost any sort of soil. Most horticultural selections grow best in soil with good drainage, and some cultivars are known to have good tolerance to drought.

6.1.2.c.TGA-DTA Analysis of the Waste Material:

Figure 1 to 5 represent the TGA-DTA curve for the Potato, Potal, Pumpkin, Banana peels and trimmings and Mary gold flower wastes. As expected, an enormous amount of moisture was lost (> 80%), for convenience in calculation, it is taken as 85%. These peels were pre-heated in an oven at 115^0C and DTA-TG study was done, it is evident that a strongly exothermic reaction occurs at around 450^0C to 500^0C.

Therefore, in the present study, 350^{0}C was chosen to be the optimum temperature to heat the peels and trimmings of 4 vegetables as well as west of 1 flower to completely remove the moisture without the combustion of carbon residue at all.

From the figures, it is also observed that by heating upto 900^{0}C, almost complete burning of carbon is achieved leaving behind hardly any residue. This shows that the fixed carbon content in pre-dried peels at 350^{0}C, is very higher, having little ash, which no doubt is highly desirable.

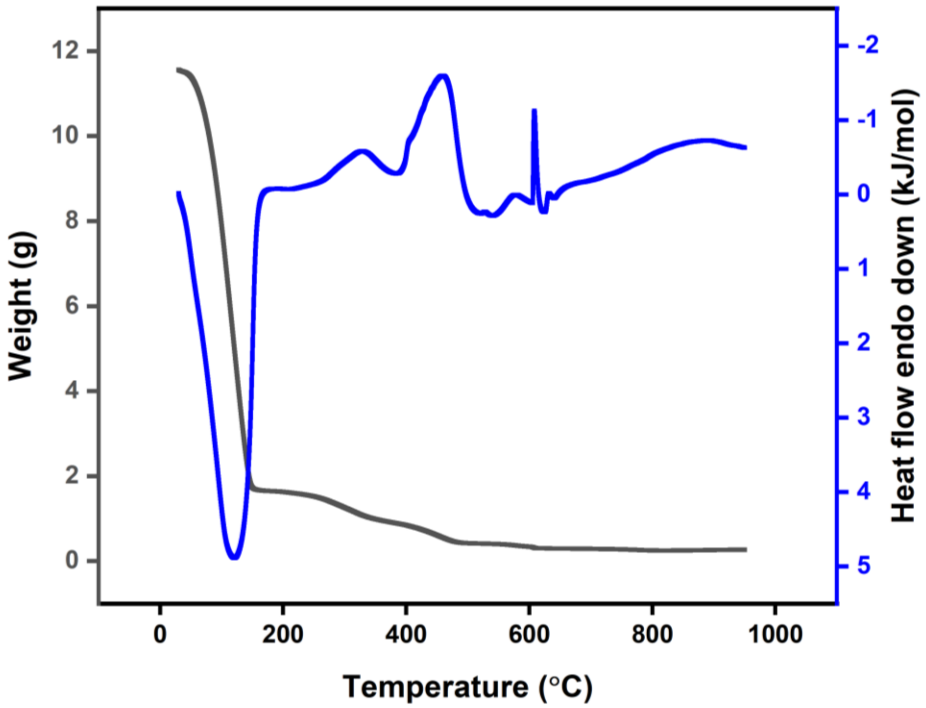


Fig:6.1, TGA-DTA Plot of Potato Peels

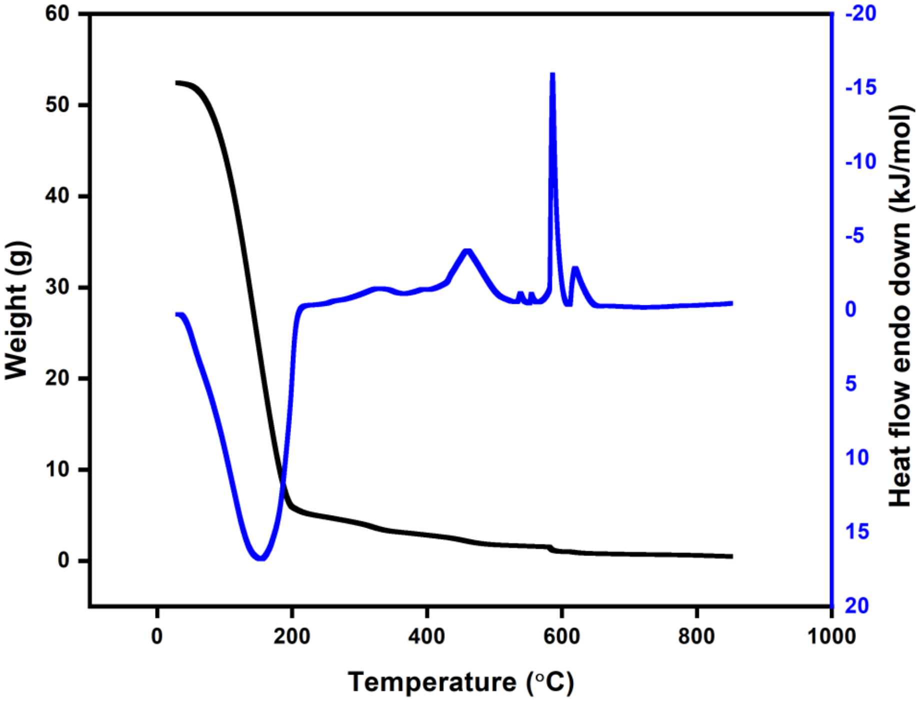


Fig:6.2, TGA-DTA Plot of Potal Peels

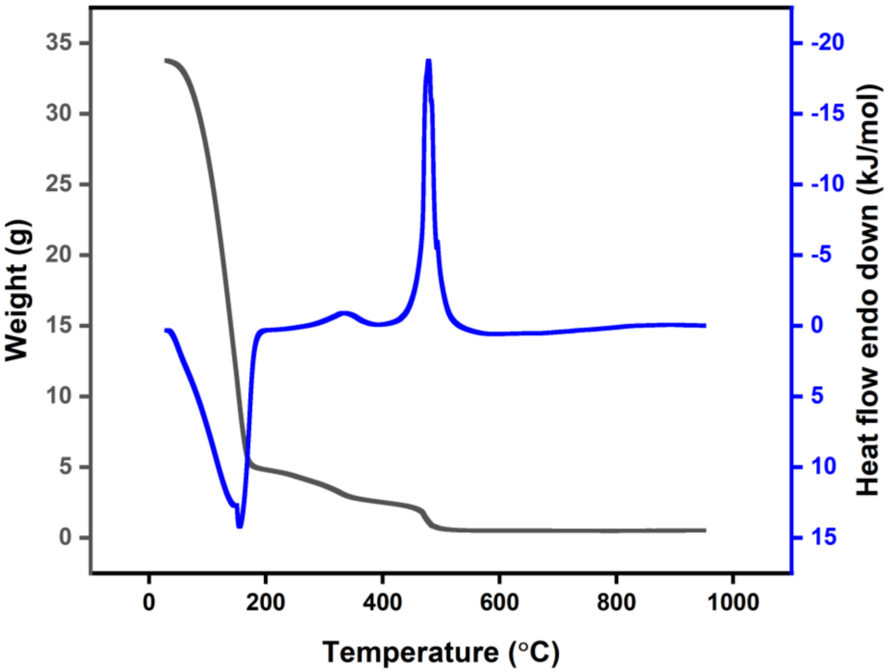


Fig:6.3, TGA-DTA Plot for Pumpkin Peels

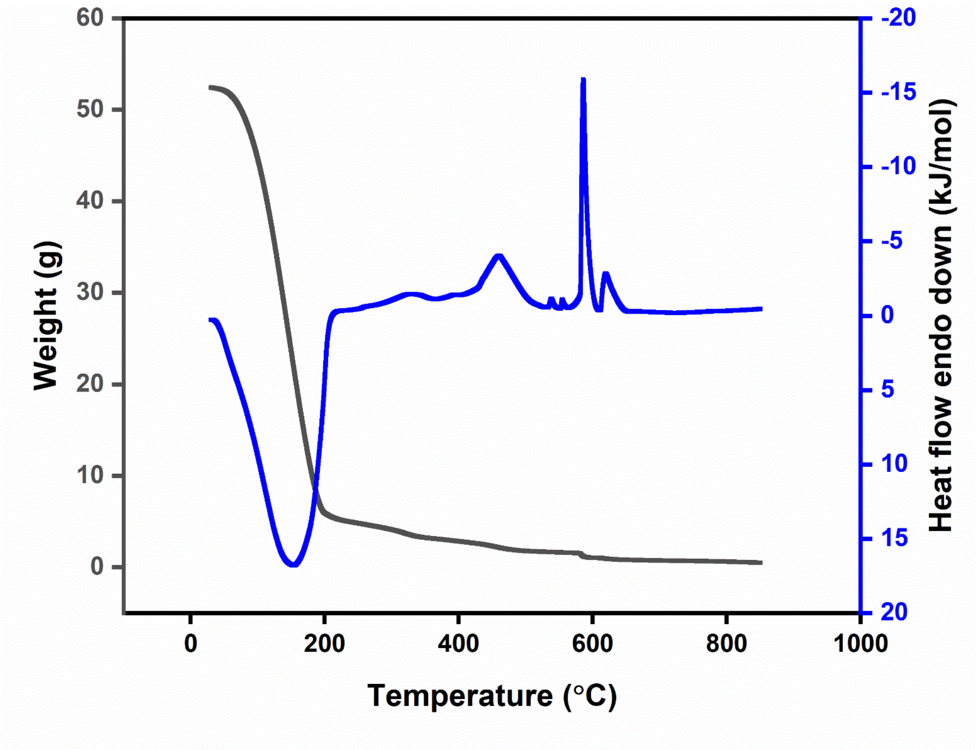


Fig:6.4, TGA-DTA Plot for Banana Peels

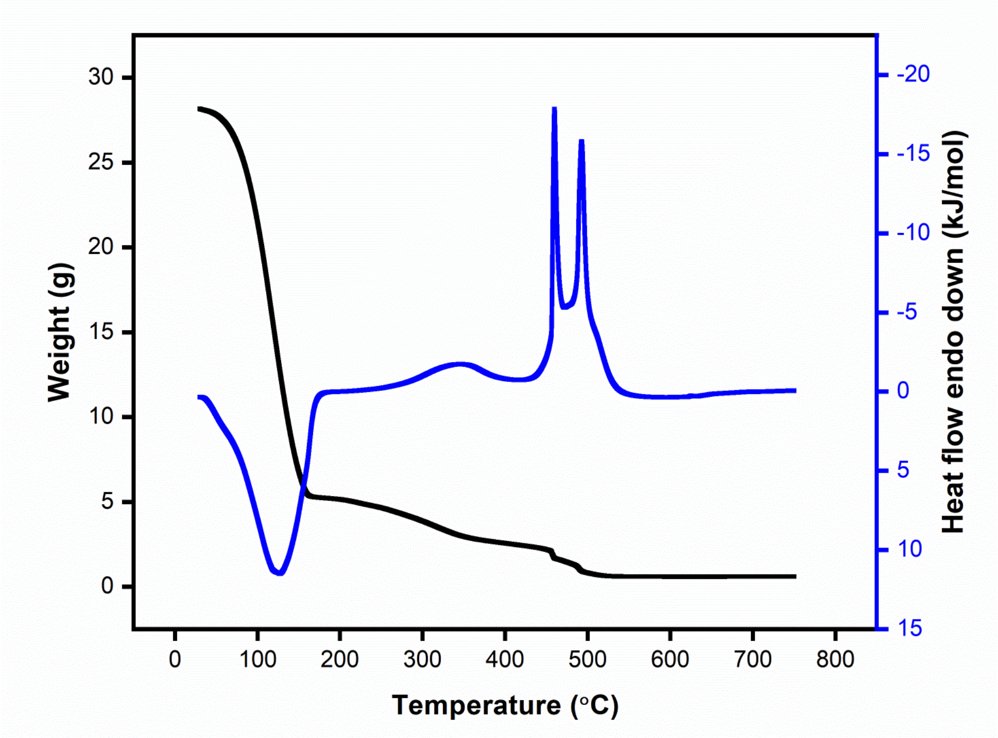


Fig:6.5, TGA-DTA Plot for Mary gold

Chapter: 6.2

Analysis of Iron Ore and Nugget Samples after Direct Reduction using Bio-dust as Reductant

6.2.1. X-Ray Diffraction (XRD) Analysis:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material is finely ground, homogenized, and average bulk composition is determined.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

XRD Analysis of the HMO (Hematite) Ore:

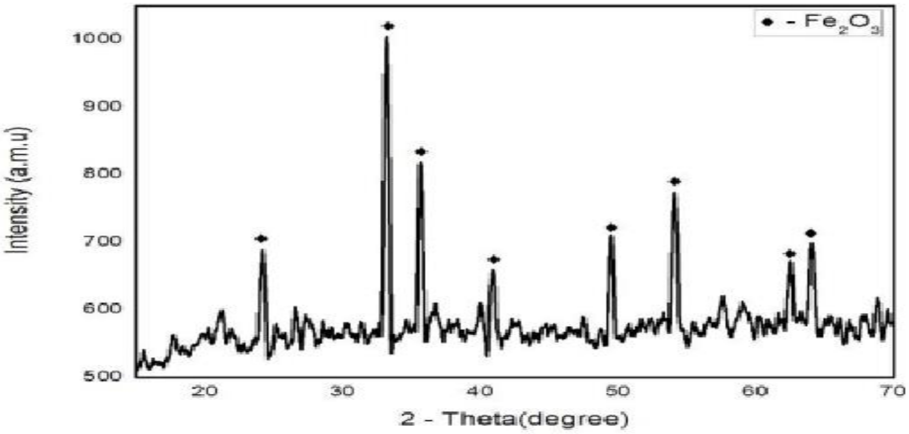


Fig: 6.6, XRD Analysis Report of Iron Ore

In the ore specimen, different phases are present, coexisting with each other. These phases are mainly oxide in nature, along with some other phases, like: sulphide, carbonate etc are present. Hematite is basically present as the major phase in the ore specimen. Also, SiO_2, Al_2O_3 are present as minor phases.

6.2.2. X-Ray Fluorescence (XRF) Analysis:

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analysers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

XRF Analysis of Iron Ore Specimen:

Iron ore, Hematite is present in dry dust form having significant amount of Fe_2O_3 which is the main ingredient.

XRF analysis of this Ore:

Table: 6.6

Ingredient	**Chemical Agent**	**wt. %**
total iron	total Fe	58.072
silica	SiO2	6.278
alumina	Al2O3	2047
phosphorus pentoxide	P2O5	0.067
sulphur	S	0.027
manganese	Mn	0.049
calcium oxide	CaO	1.465
magnesium oxide	MgO	0.361

From this XRF data, it can be expressed that the ore contains significant amount of total iron in it, about 58.072 %. Also, the ore would have acidic nature due to present of silica, about 6.278 %.

6.2.3. Reduction Analysis of Iron Ore with Waste Material:

6.2.3.a.Reduction Reaction:

At 1000 deg. C, Hematite (Fe_2O_3) would reduce to Metallic Iron (Fe), in step wise reaction, though formation of Magnetite (Fe_3O_4) and Wustite (FeO),

$$\mathbf{Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow \text{Metallic Fe}}$$

Essential reactions are:

i. $3Fe_2O_3 + C = 2Fe_3O_4 + CO$

ii. $Fe_3O_4 + C = 3FeO + CO$

iii. $FeO + C = Fe + CO$

iv. $CO_2 + C = 2CO$

The ultimate reaction will be:

$$Fe_2O_3 + 3C = 2Fe + 3CO$$

6.2.3.b. XRD of Samples after Reduction:

The vegetable and flower wastes contain considerable amount of carbon which can be obtained by heating at 350 deg. C for sufficient time period. The carbon rich bio-dust samples are mixed and blended with iron ore, in stoichiometric basis to produce nugget sample hematite to metallic iron. In this study, we will study this reduction process taken place by carrying the reduction of hematite with 5 different raw wastes: peels and trimmings of 4 vegetables and 1 flower waste samples.

The data shown in the table clearly expresses the amount of raw material were taken for the reduction reactions.

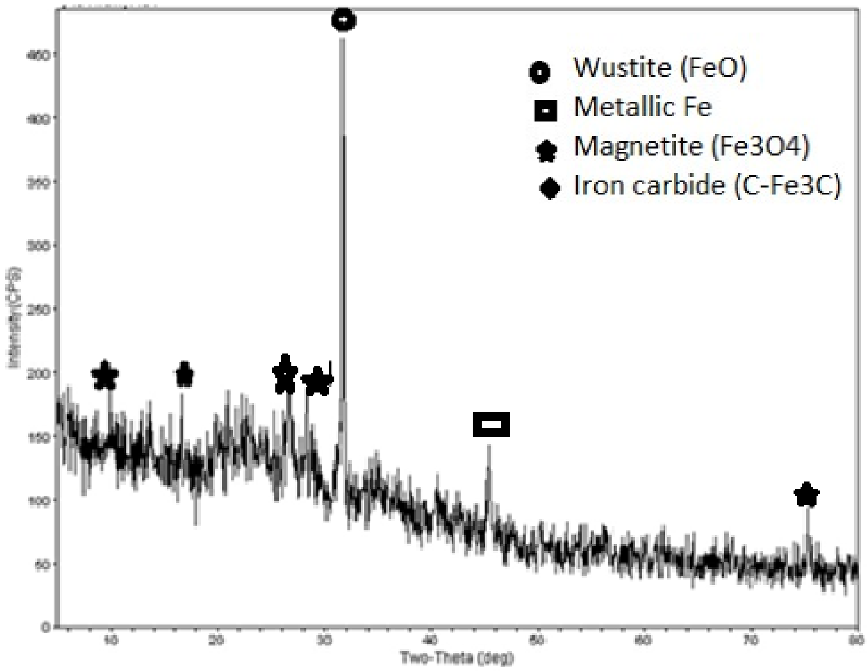


Fig:6.7, XRD Plot of Reduced Sample, Reduction Using Pumpkin Peels

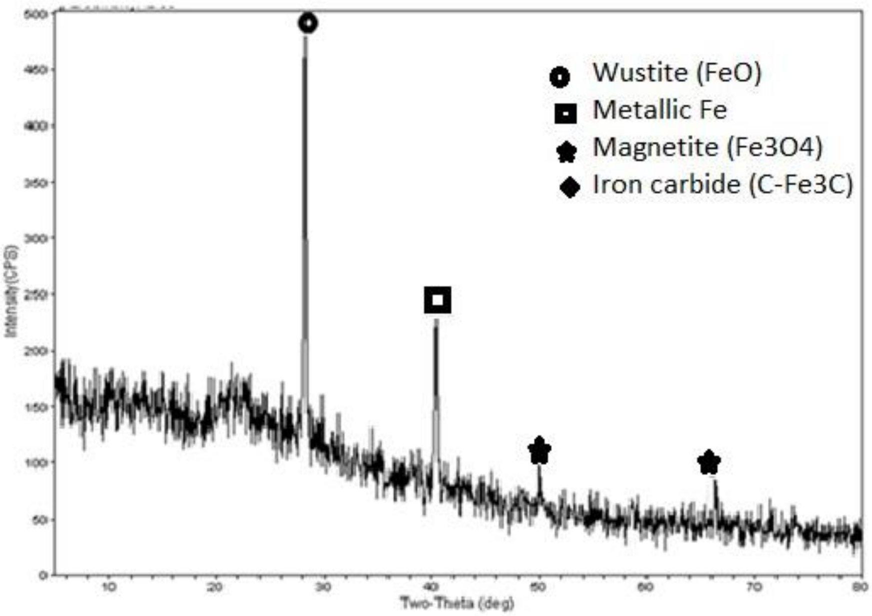


Fig:6.8, XRD Plot of Reduced Sample, Reduction Using Potal Peels

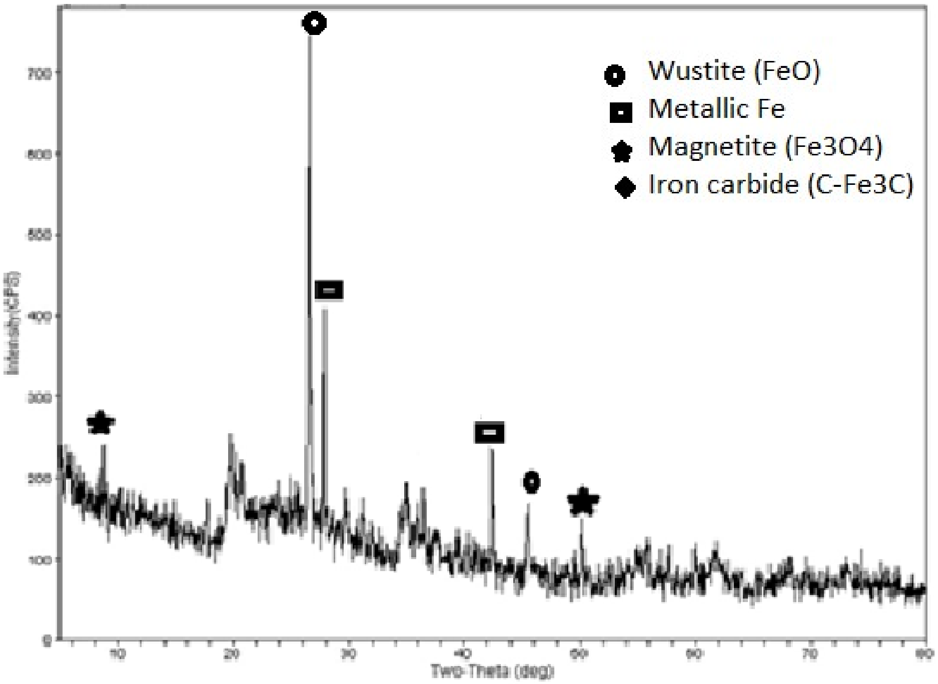


Fig:6.9, XRD Plot of Reduced Sample, Reduction Using Mary gold Waste

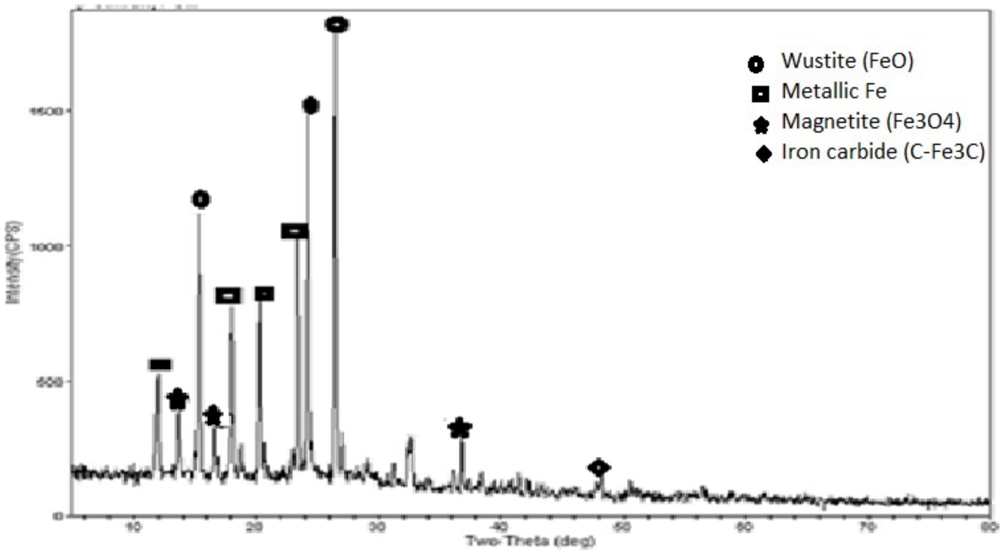


Fig:6.10, XRD Plot of Reduced Sample, Reduction Using Potato Peels

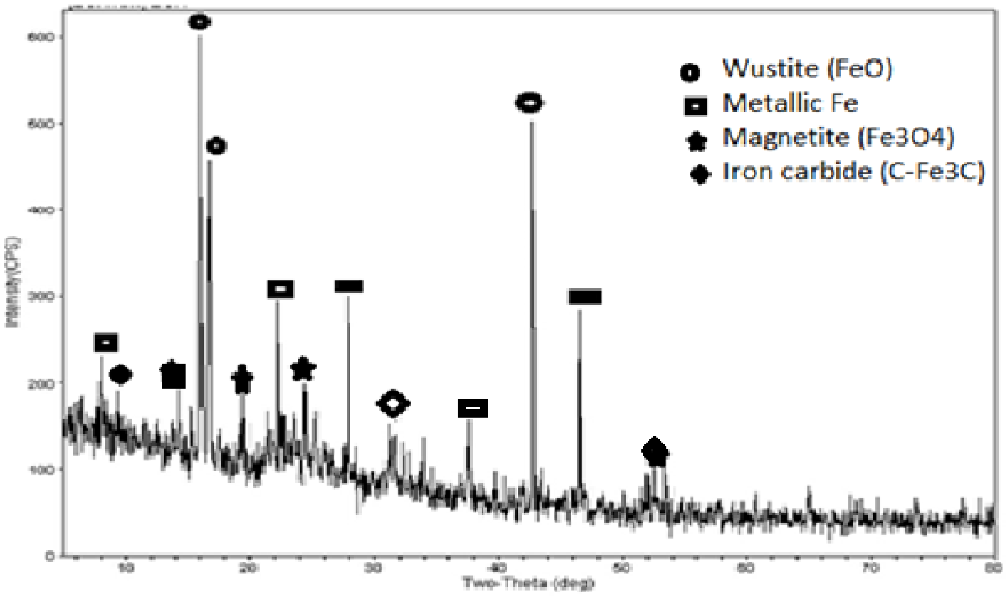


Fig:6.11, XRD Plot of Reduced Sample, Reduction Using Banana Peels

From the Intensity vs 2 Theta plot in XRD analysis of 5 samples after reduction at 1000 deg. C, it is clear that:

i. Maximum amount of metallic iron has been obtained from the sample where used bio-dust coming from banana peels, due to presence of greater number of peaks of metallic iron in the plot, extent of reduction is better for reduction reaction.

ii. After banana peels, potato peels and waste mary gold produced carbon rich bio-dust which could effectively produce metallic iron by reduction of iron ore, relatively lesser than banana peels. Basically, after reduction, intense peak of Wustite was found in the XRD plot of each sample, which indicates that the entire amount of iron ore was not reduced. Not only Wustite, also some number of peaks of Magnetite are also found. For samples containing bio-dust of Banana, Potato and Mary gold, the number of peaks of Magnetite be much lesser, where, in case of Potato and Pumpkin, the number of peaks of Magnetite be higher.

iii. In the plot of sample having bio-dust of pumpkin peels, the extent of reduction is much lesser as minimum number of peaks of metallic iron is found.

iv. In the plot of sample having bio-dust of potal peels, peak of metallic iron is much lesser as well as much number of peaks of Magnetite is found. It indicates that the extent of reduction be much lesser in case of Potal and Pumpkin peels and trimming than those of Potato, Mary gold and Banana.

v. It can be expressed that bio-dust coming from Banana peels has the most reducing capacity or reducibility, after that, bio-dust coming from Potato and Mary gold. Peels of Pumpkin and Potal produces the bio-dust which have minimum reducibility and during reduction of Iron ore, retention of Magnetite be significant.

vi. Peaks of some other phases are also observed, which indicate presence of some other elements in the samples. Due to executing reduction at 1000 deg. C, there is a higher chance of producing Iron-Carbide phase (Fe_3C) as carbon atoms tend to incorporate in the crystal structure of metallic iron, the reaction is:

$$3Fe + C = Fe_3C$$

Here, generally in case of carbon rich bio-dust sample of Banana and potato peels, the presence of peak of carbide phase is slightly observed.

vii. Although no sharp peak of carbon in the plot was observed during the XRD analysis of the samples after reduction, which indicates that pure carbon in bio-dust has involved predominantly as reducing agent in the reaction in the temperature range of 1000 deg. C.

6.2.4. Effect of Temperature:

During the reduction of Iron ore, Hematite (Fe_2O_3), selection of temperature is essential to obtain better degree of metallisation. In this context, iron ore can be reduced by 2 objects: volatile matter in bio-dust as well as pure carbon. Both can have sufficient reducibility.

When the temperature increases in the furnace and reaches to 570 deg. C, reduction reaction in nugget starts. Hematite starts to reduce to Magnetite (Fe_3O_4), with time. With increasing temperature, the extent of reduction increases. While samples heated up 600 °C, reached the values slightly higher than the theoretical reduction of hematite to magnetite. Up to 800 °C, the reduction advanced to the region close of the complete Magnetite reduction to Wustite (FeO).

During reduction at this temperature range, condensable liquid products (tars) are generated, which can condense on the surface of the iron ore particles and can cause crack, promoting carbon deposition according to reaction:

$$\mathbf{Tar \rightarrow H_2 + CO + CO_2 + CH_4 + \text{other light hydrocarbons} + C}$$

which is expected to be the major source of carbon detected on the iron ores.

The presence of constant carbon content in the pre-reduced iron ores at temperatures between 400 and 800 °C basically expresses that iron oxide reduction observed up to 800 °C, occurred mainly by non-condensable volatiles generated during biomass pyrolysis (CO, H2) or even by tar cracking reactions. Above 800 °C, solid carbon dominates the iron oxide reduction, which is evidenced by the carbon consumption at 1000 °C and no peak of carbon in the plot was observed during the XRD analysis of the samples after reduction.

6.2.5. Water Recovery and Usage:

Waste peeling and flower bodies contain higher amount of water, in their body, approximately 82 to 85% amount. For this, they can be the source of water. This can be achieved by heating the waste material at nearly 400 deg. C, for half an hour approximately as well as by condensing the moisture content into water. Also, the water has much significant purity. For this, water can be used in industrial, laboratory and farming purposes. Along with this, water can be poured into bottles for drinking.

The carbon produced from vegetable wastes and flower wastes can also act as a reductant in Coal based Sponge Iron Making Process. Beside this, the carbon produced from vegetable wastes and flower wastes can also react with moisture to generate Syn gas, which is basically mixture of CO and H_2 gases ($CO + H_2$) and that can be needed as reductant in Gas based Sponge Iron Making Process. A specific plant design to produce syn gas from the waste material with laboratory based equipments is introduced in this thesis, in the later part of this section. Application of syn gas in reducing iron ore, can enhance the application field of the waste material as well as better degree of efficiency in energy and reduction of iron ore to produce pure iron can be achieved.

Chapter: 6.3

Design of Gas-based Direct Reduced Iron (DRI) Plant Using Laboratory Based Equipments with Flow Chart

In this thesis, Iron ore, Hematite (Fe_2O_3) has been effectively reduced to metallic iron by the action of carbonaceous agents, which is basically bio mass, obtained by heating vegetable wastes and flower wastes at 400 deg. C separately. With time, the vegetable and flower wastes are enhancing, with population. In this experiment, the vegetables are basically: potato, potal, banana and pumpkin. Mary gold wastes are used in this experiment as flower waste as this flower wastes have higher availability.

6.3.1. Modification of Direct Reduction of Iron Ore Using Waste Material:

Basically, from this experiment, it can be cleared that peels and trimmings of vegetables, mainly Banana, Potato etc. and flower wastes (here Mary gold) would be the alternative source of carbonaceous reducing agent. The bio-dust obtained from the wastes contains pure carbon rich part. In the entire process, there are 2 points which can be effectively modified by proper design.

i. Modification Related to Steam:

During the dehydration process, by which the waste materials are heated to higher temperature (around 350 deg. C) to produce bio-dust sample, significant amount of moisture loss takes place, as the organic waste material contains around 85% of water. The molecular water content is to be removed to produce carbon rich bio-dust, although the water content is going out of the system without any usage. The system can be modified to collect the steam during the heating process and condensation of steam can provide pure distilled water. This water content can be collected into bottles, to use as potable water and pure water in the laboratory. This water content can be used in power plant, agricultural purposes etc.

ii. To Produce Syn Gas:

This steam can be reheated to higher temperature, around 800 to 900 deg. to react with pre-heated carbon in gasification reactor at 900 deg. C to produce Synthetic gas or Syn gas, which is the mixture of Carbon Monoxide (CO) and Hydrogen gas (H_2), the reaction is:

$$\mathbf{C + H_2O = CO + H_2}$$

This syn gas can be passed through pre-reduced ore to reduce to metallic iron. It will enhance the extent of reduction as well as degree of metallisation and higher will be the yield of iron.

6.3.2. Thermodynamic Design to Produce Syn Gas:

Vegetable wastes have main ingredients such as: water molecules, volatile matter, ash content and fixed carbon. Water content is present nearly 85 to 90% in the wastes. This water removes out in form of hot stream from the vegetable wastes while heating the wastes to particular temperature range, which is obtained by TGA-DTA analysis of vegetable wastes. Generally, the temperature is about 350 deg. C.

After removal of moisture content from the vegetable wastes, in the sample bed, there is present pure dry organic content, which is basically bio-mass. This bio-mass contents mainly fixed carbon, volatile matter and minimum amount of ash. From ultimate analysis, it is found that the bio-mass is basically the major source of carbon.

At higher temperature, hot steam, in presence of air (O_2) can react with carbon to produce mixture of reducing gases: CO and H_2. This gas mixture is synthetic gas or Syn gas.

6.3.2.a. Reaction and Temperature Selection:

$C + H_2O = CO + H_2$…. (1)

Thermodynamically,

$C (s) + O_2 (g) = CO_2 (g)$…. (2), del G= -394100 -.84T $J.mol^{-1}$

$CO_2 (g) + C (s) = 2CO (g)$…. (3), del G= 170700 – 174.46T $J.mol^{-1}$

From (2) and (3), it can be written:

$2C + O_2 (g) = 2 CO (g)$ …. (4), del G= -223400 – 175.3T $J.mol^{-1}$

And

$C (s) + .5 O_2 (g) = CO (g)$ …. (5), del G= -111700 -87.65T $J.mol^{-1}$

Now, water is produced by the reaction between H_2 and O_2:

$2H_2 + O_2 = 2H_2O$…. (6), del G= -492000 + 109.6T J.mol $^{-1}$

And

$H_2 + .5\ O_2 = H_2O$…. (7), del G= -246000 +54.80T J.mol $^{-1}$

And

$H_2O = H_2 + .5\ O_2$…. (8), del G= 246000 – 54.80T J.mol $^{-1}$

Now combining equation (5) and (8), it can be said that:

$C + H_2O = CO + H_2$…. (9), del G= 134300 – 142.45T J. mol (-1)……..+131 MJ/Kmol

The temperature to execute the reaction is, T= (134300/142.45)

= 942.78 Kelvin

The temperature in deg. C is= (942.78-273) deg. C

= 669.78 deg. C

- As this is the solid-gas phase reaction, extensivity of reaction will increase by enhancing temperature above 800 deg. C.
- Activation of carbon is also obtained properly for this reaction at this temperature range.
- Although increasing the temperature at 1000 deg. C or above, there is the major chance of rapid oxidation of carbon in bio-dust as well as higher carbon consumption will prevent the reaction to reach its efficiency.
- The temperature for this reaction should be kept around 900 deg. C to obtain better efficiency.

6.3.3. Kinetic Design to Produce Syn Gas:

In the overall gasification process, the char gasification reaction is slowest step. For this, it is necessary to quantify how faster this process is. The main constituent of bio char obtained from vegetable and flower wastes is carbon and main reaction in the char gasification process is the water gas reaction:

$$\mathbf{C + H_2O = CO + H_2}$$

The carbon-monoxide may undergo a water gas shift reaction:

$$\mathbf{CO + H_2O = CO_2 + H_2}$$

Therefore, the carbon reactivity in the char can be inferred from the molar flow rate of carbon monoxide (CO) and carbon dioxide (CO2). A mass spectrometer has been installed to calculate the CO2 and CO flow rate. From the flow rate of CO and CO2, the total carbon yield and carbon conversion history can be determined. In the plot between carbon conversion and time at several higher temperatures, the plots have to characterise by an initial constant slop. The results show that lower is the temperature longer is the conversion time.

Carbon reactivity was defined as:

$$\mathbf{r = - (1/m)\ dm/dt,}$$

where m is the mass at time (t). History of carbon mass inside the reactor can be calculated from the carbon flow rate history. While, dm/dt is the carbon mass flow rate measured by the mass spectrometer.

Carbon reactivity basically increases monotonically with conversion until conversion from solid to gas value of upto certain value, followed by a steeper increase in reactivity. The steepness at lesser temperature plots may not be observed because of the r values scale.

6.3.3.a. Importance of Ash Content:

The bio dust and char contain about 15 to 20% ash, most of which is salt. The inorganic components in the ash in char are the main reason of increase of reactivity, since they have significant catalytic effect.

From the information of reactivity, kinetic parameters, activation energy E and pre-exponential factor A, can be calculated.

In Arrhenius equation, $\mathbf{(1/t) = r = A^{*} \exp(-E/RT)}$

or, **ln (r) = ln (A) – (E/RT)**

A first order reaction model has been used. The following figure shows the Arrhenius plot from which the activation energies and pre-exponential factors at different degrees of conversion (X) can be calculated.

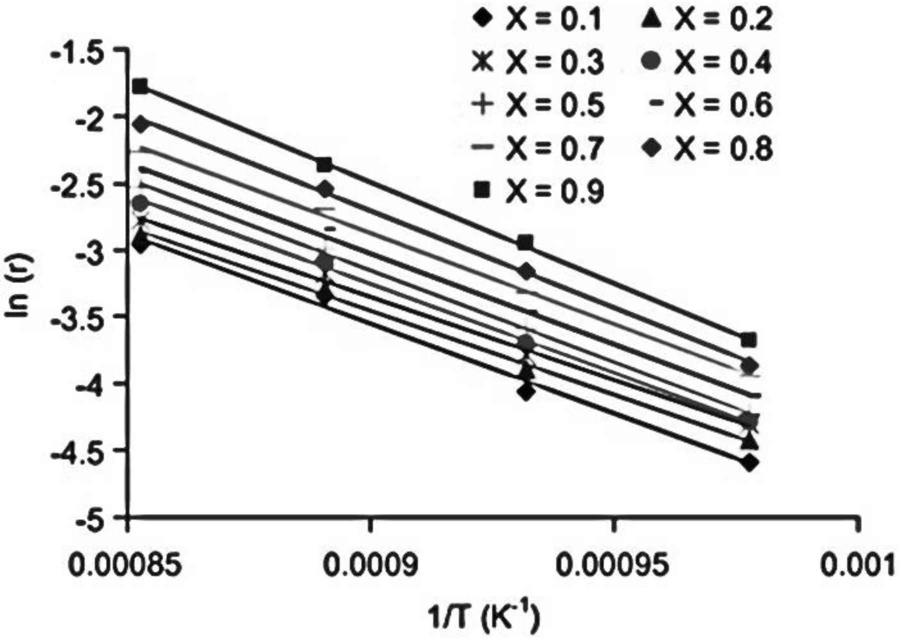


Fig 6.12: Arrhenius Plot for First Order Reaction Kinetics

From this figure 13.1, one can see that the Arrhenius plots show almost parallel lines with increasing intercept with conversion. Parallel lines indicate constant values of activation energy. However, values of pre-exponential factor increase with conversion. The general trend of activation energies and pre-exponential factors indicates that the increase in reactivity in this range of conversion is attributed to increase in pre-exponential factor. In theory, the pre-exponential factor or frequency factor, A, depends on what frequency the molecules effectively collide with each other and whether the molecules are properly oriented or not. Effective collision where distribution or exchange of energy takes place, be considered here. Although in solid reactions, the pre-exponential factor and activation energy do not have the physical significance, as in gas reactions [5], a logical reasoning can be introduced to explain the increase in pre-exponential factor. Ash may have increased the adsorption rate of steam to the char surface and consequently, raised the reaction rate.

6.3.3.b. Compensation Effect or Isokinetic Effect:

A compensation effect was observed here, where a simultaneous decrease in activation energy and pre-exponential factor with increase in conversion be observed. The simultaneous decrease in activation energy and pre-exponential factor is called ‘‘the compensation effect” or ‘‘isokinetic effect”.

In a compensation effect behaviour, Arrhenius plots should intersect at a single point at the isokinetic temperature and isokinetic reactivity. Since the plots do not intersect in the examined temperature range, an extrapolation for the linear fittings was used to find the isokinetic temperature and reactivity.

According to Agrawal, in order to validate the presence of correct compensation effect, the linear plot of ln(A) versus E should have a slop of 1/RTiso, were Tiso is the isokinetic temperature and an intercept of ln(riso), where riso is the isokinetic reactivity.

6.3.4. Design of Plant Set-up to Generate Syn Gas using Thermodynamic and Kinetic Data:

The entire procedure of producing Syn gas comprises of a number of nuclear sub-processes, such as:

a. Generation of steam,

b. Reheating of Steam,

c. Reposition bio-dust from heating round bottom flask to gasification reactor,

d. Gasification in reactor,

e. Filtering and drying of gas,

f. Gas chromatography

All these sub-processes combine to execute the entire gasification reaction. To set up the entire process, a number of equipment are required which are needed to be connected in sequential manner. Each equipment should be calibrated as well as should have proper function with minimum error and within specific tolerance.

6.3.4.1. Equipment:

During the entire process, the required equipments are:

i. Heating plate and round bottom flask (500 ml.) with 3 nozzles at upper side and 1 nozzle along with valve at bottom side, made of higher temperature glass,

ii. Nozzle, connecting glass tube, cork,

iii. smaller (6 to 8 mm) diameter higher temperature glass tube and larger diameter (20 to 30 mm) higher temperature steel tube with as well as without branch of almost similar diameter along with a valve, branch made of higher temperature glass

iv. Smaller unidirectional valve, flow meter, conveyer belt, steam flow meter

v. Steam Heater,

vi. Gasification Reactor,

vii. Non-returnable valve and Flow meter,

viii. Filter and Moister Absorber,

ix. Micro Gas Chromatograph

6.3.4.1.a. Steam Generating System:

The heating conical container made of higher temperature glass, with double nozzle is essential to heat the vegetable and flower wastes to the particular temperature for generating steam, 1 nozzle for Argon gas flow and another for removal of mixture of Argon and steam. The heating conical container made of higher temperature glass, with connecting glass tube or nozzle should be covered with insulation material, glass wool during entire procedure. There should be cork of particular size to close the opening of mouth of glass container.

Fig:6.13, Heating Plate

Fig:6.14, Heating Round Bottom Flask

Fig:6.15, Glass Tube with Cork

6.3.4.1.b. Reheater of Steam:

Steam generated is then introduced into the superheater section to form the gasifying agent by reheating at the desired condition. The temperature of the gasifying agent heater is kept at the similar temperature as that of the main reactor in which sample bio-char and bio-dust material is allowed to undergo gasification.

Fig:6.16, Steam Reheater

6.3.4.1.c. Gasification Reactor:

Reheated steam is then introduced into the main reaction chamber that contained the bio-dust sample. The temperature during the process should be properly maintained in the particular range at which forward chemical reaction between bio dust (C) and hot steam (H_2O) takes place to produce syngas ($CO + H_2$).

Fig:6.17, Gasification Reactor

6.3.4.1.d. Collection:

The impure syngas flowing out from the main reaction chamber, is allowed to be cooled and then is sub-divided into two paths; one passes to the sampling line while the other is passed through the exhaust system.

6.3.4.1.e. Non-Returning valve and Flow Meter:

The bypass line has a non-return valve for which the obtained gas cannot have a trend to return to the reaction system and the reaction would proceed to forward direction. A flow meter should be present in the line to assure the desired unidirectional flow out of syn gas at particular flow rate from the reactor.

Fig:6.18, Non-Return Valve

6.3.4.1.f. Filter and Moister Absorber:

Basically, the produced syn gas is impure and unwanted steam can be present in it. The syngas sample is then introduced to a condenser followed by a lower pressure filter and a moister absorber. Anhydrous calcium sulphate can be used as to absorb the moisture from the syn gas. This procedure assures that the sample is dry prior to its introduction into a gas analyser.

Fig:6.19, Filter and Moister Absorber

6.3.4.1.g. Micro Gas Chromatograph:

The syngas characteristics were determined using a Micro gas chromatograph (GC). The filtered and dried syngas flow is introduced to allow for either filling sampling bottles or introducing the syngas directly to the micro-GC for detailed analysis of the gas. The sampling bottles are used only when shorter sampling intervals are needed (0.5–1 min). Direct sampling and analysis were carried out by the GC when longer sampling time intervals were required.

Fig:6.20, Micro Gas Chromatograph

6.3.4.1.h. Mass Spectrometer:

mass spectrometry, also called mass spectroscopy, analytic technique by which chemical substances are identified by the sorting of gaseous ions in electric and magnetic fields according to their mass-to-charge ratios. Mass spectroscopes consist of five basic parts: a high vacuum system; a sample handling system, through which the sample to be investigated can be introduced; an ion source, in which a beam of charged particles characteristic of the sample can be produced; an analyser, in which the beam can be separated into its components; and a detector or receiver by means of which the separated ion beams can be observed or collected. Mass spectrometer helps to detect actual presence of syn gas in the produced, out-coming gas.

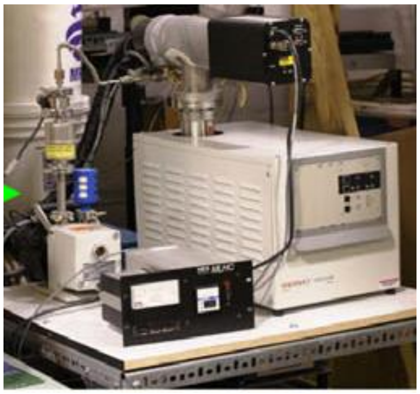


Fig:6.21, Mass Spectrometer

6.3.4.1.i. Application of Nitrogen gas:

A constant flow rate of inert gas, mainly Nitrogen, is introduced with the oxygen flow, in case of gasification. The nitrogen (N_2) is detected by the GC and used to determine the flow rate of different syngas species by comparing the species mole fraction to that of the nitrogen mole fraction. As Helium (He) gas is inert, relatively cheaper, having higher availability and very lighter in weight, flow of He gas along with N_2 is essential.

6.3.4.2. Design Steps:

a. Generation of Steam:

Basically, the initial process is to collect the washed and dried vegetable and flower wastes. The ingredient material should be properly cleaned and washed otherwise contamination of impurity would prevent to meet the efficiency of producing Syn gas. The vegetable and flower wastes should be kept in the container when the container prior heated to steam generating temperature keeping it on heating plate and the container should be properly covered by insulating material to prevent loss of heat. Temperature should be kept at the value for generating steam, which is already obtained from TGA-DTA of vegetable and flower wastes, at about 350 deg C for 30 minutes. As the container is round bottom flask, the distribution of heat through the whole body of container can be obtained to uniformly heat the wastes sample. Connecting tube (for out-coming of steam) through nozzle of container should be also covered with insulating material, such that the entire system of steam generation can be kept heated and condensation of steam cannot take place. The heating container should be heated to steam generating temperature, prior to pour the vegetable and flower wastes in it. Through the most left nozzle, Argan (Ar) gas is allowed to enter the flask during heating process. During heating, keeping the container on heating plate, the container or flask should be kept slightly tilted, fact is:

i. Placing the flask on heating plate would be convenient as there is a smaller diameter nozzle with valve at the bottom of the flask, to allow to pass the bio-dust, after proper heating as well as removal of water content from wastes.

ii. Inert gas can be entered from the lower side as it is heavier than steam and entering from lower side will help Ar to cover the entire flask as well as after heating, the gas can move forward with steam passing nozzle present at upper side.

iii. Due to this tilting of flask, the steam along with Ar can conveniently pass through upper side nozzle of flask.

The vegetable and flower wastes should have preferable size range about 10 to 40 mm. It is easier to get the particular size range as well as this smaller size of raw waste material would increase the surface area in the flask and during heating, the removal of moisture will be effective from entire waste material through their uniform heating. A funnel will be inserted through rubber cork, placed at the opening of the middle nozzle of flask. After pouring the raw material in flask, the funnel will have to remove and a temperature sensor is inserted into the flask through the same cork present in the middle mouth of flask.

b. Condensation of Steam in First Stage:

In the initial stage, there is no bio-dust in the gasification reactor to execute gasification reaction. For this, the steam produced in the first stage is allowed to pass through Calcium Chloride dust. After entire steam is absorbed into $CaCl_2$ dust, the dust would have to remove from system and should be heated. The steam will be removed from $CaCl_2$ dust. The steam has to pass through condensing system, to obtain water from this. The water is effectively pure to use as potable water, which can be saleable item as well as the loss of steam can be prevented. A branched smaller diameter line is to be connected with main steam line to the gas analyser to detect the presence of steam in the flowing line. If the gas analyser detects only Argan gas, it would indicate that the team generation from the vegetable and flower wastes is completed.

c. Reheating of Steam:

After generating the steam, it should be reheated, otherwise, after reaching the gasification reactor, the steam cannot effectively react with bio-dust (carbon) specimen, heat as well as steam loss will take place. Although, it is found that, the steam, which is generated from particular amount of vegetable and flower wastes, is basically excess to react with such amount of bio-dust obtained from the particular amount of wastes, the extra amount of steam might cause loss. To prevent this, there should be present 1 branched line of similar diameter, which is connected to the condensing system. In the initial portion of branched line, a valve should be present, which controls the flow of steam, in such manner, the steam flow through the branched line should be at such value that, the steam excess than the requirement of generating syn gas should entirely pass through the channel to be condensed to produced distilled water.

In the branched line, after the valve, a steam flow meter is to be connected to measure the flow of excess steam through the branch. The water collected from each step of entire procedure, is significantly higher and effectively optimise the entire procedure.

Reheating of steam should be done to the temperature at which gasification reaction take place. This temperature can be obtained from thermodynamic data analysis of syn gas reaction, which is about 700 to 800 deg. C. Basically, this reheating of steam takes place in steam heater which is directly connected to the system of generating steam. Temperature sensor should be connected to the system of reheating steam. A branched smaller diameter line is to be connected with main steam line to the gas analyser to detect the presence of steam in the flowing line. If the gas analyser detects only Argan gas, it would indicate that the team generation from the vegetable and flower wastes is completed and bio-dust is formed.

d. Relocation of Bio-dust:

When generation of steam is completed, in the flask, bio-dust is present as residue material. The valve at the bottom of flask, is opened. The bio-dust from the flask, moves down on the conveyor belt and dust moves through the running belt, with the chain speed of 50 mm/second, toward gasification furnace and takes place inside already heated furnace. Belt speed is justified because the length of belt will be approximately 1 metre and the bio-dust will reach to gasification furnace from steam generating system within 20 second, which would be enough to again pour the vegetable and flower wastes into the steam generating flask as well as to start the generation of steam. Furnace is prior heated to gasification temperature as it would decrease the activation energy barrier for the reaction and enhance the kinetic of the reaction.

e. Gasification Reaction:

Reheated steam is then introduced into the main reaction chamber that contained the bio-dust sample. The temperature during the process should be properly maintained in the particular range at which forward chemical reaction between bio dust (C) and hot steam (H_2O) takes place to produce syngas ($CO + H_2$), which is in the range of 700 to 800 deg. C. During the reaction, there should be a temperature sensor, to monitor the reaction would execute in the particular temperature range. After reaction, the ash is deposited at the bottom of flask. During the reaction, there is the flow of Nitrogen (N_2) inside the reactor. The flow rate of N_2 is about 2.6 LPM. During reaction, the rate of flow of steam is basically 8 g/minute. Presence of Helium gas, along with N2 can be effective to obtain better flowability. The efficient time of gasification reaction is 40 minutes.

f. Collection:

The impure syngas flowing out from the main reaction chamber is sub-divided into two paths; one passes to the sampling line while the other is passed through the exhaust system.

g. Non-Return Valve and Flow Meter:

The bypass line has a non-return valve for which the obtained gas cannot have a trend to return to the reaction system and the reaction would proceed to forward direction. A flow meter should be present in the line to assure the desired unidirectional flow out of syn gas at particular flow rate from the reactor.

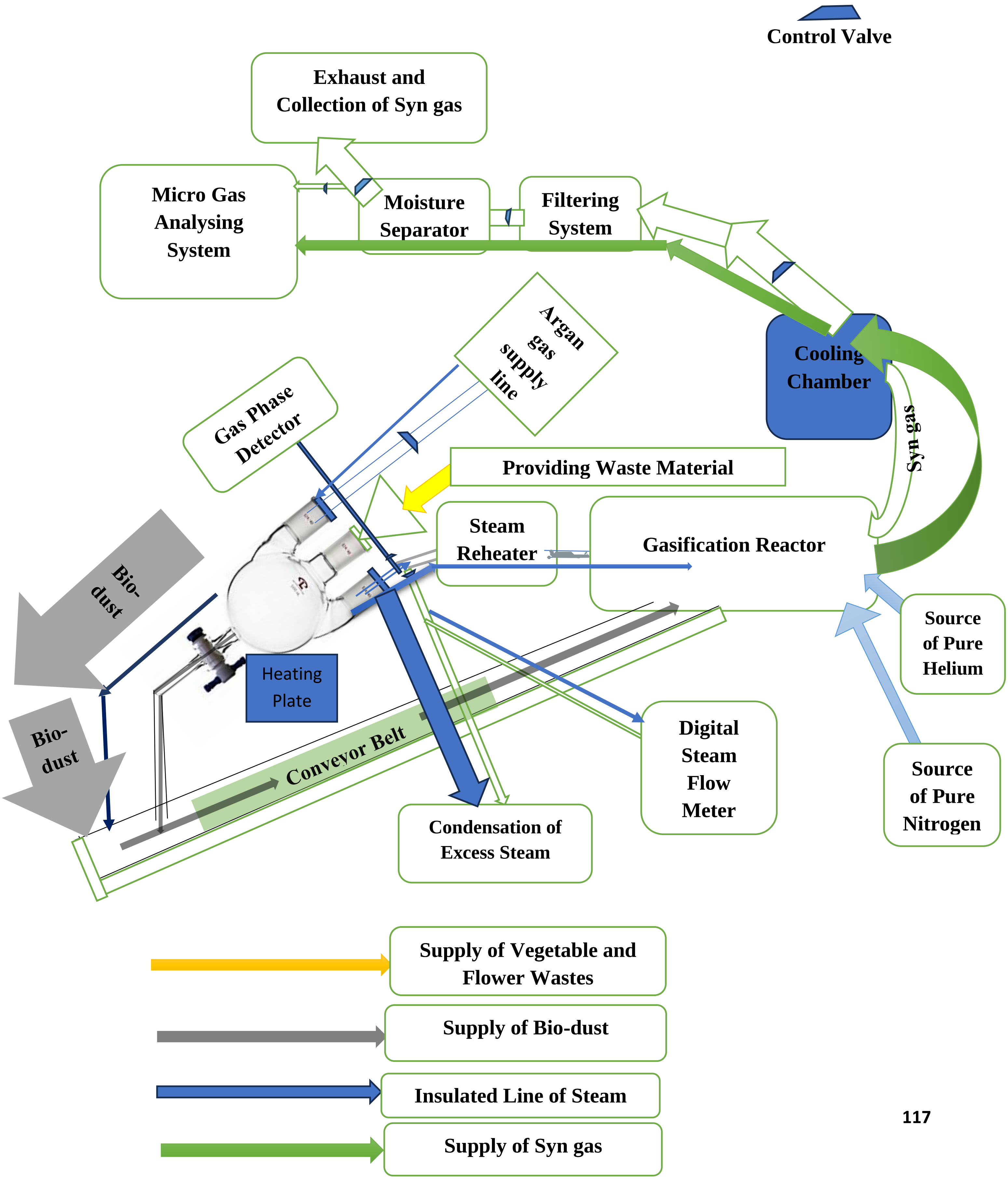
h. Filter and Moister Absorber:

Basically, the produced syn gas is impure and unwanted steam can be present in it. Cooling of impure syn-gas is essential. The syngas sample is then introduced to a condenser followed by a lower pressure filter and a moister absorber. Anhydrous Calcium Sulphate ($CaSO_4$) can be used as to absorb the moisture from the syn gas. This procedure assures that the sample is dry prior to its introduction into a gas analyser. After the moisture separator, there be present a valve and the line is then sub-divided into 2 line: 1 main line is going to tube furnace for reduction of iron ore or stacking. The other smaller diameter line is connected to micro gas analyser. There should be a valve in the smaller diameter line. Before going to stacking or gasification furnace, there should be a unidirectional valve. After obtaining positive indication from the analyser, the valve is opened and the produced gas is allowed to pass to the stacking unit.

i. Micro Gas Chromatograph:

The syngas characteristics were determined using a Micro gas chromatograph (GC). Before entering the gas chromatograph, a valve should be present to control the movement of gas. The filtered and dried syngas flow is introduced to allow for either filling sampling bottles or introducing the syngas directly to the micro-GC for detailed analysis of the gas. When, in analyser, only Nitrogen (N_2) as well as Helium (He) gas be detected, it indicates that the reaction has come to the end. The entire process can be present by particular flow chart separately.

6.3.4.3. Design Flow Chart:



6.3.4.3. Design Parameters:

Generation of syn gas through the chemical reaction is basically combined for number of sub procedures. The most essential sub steps of the entire design process are:

a. The generation of steam from the vegetable as well as flower wastes,

b. Producing bio-dust containing about 90% free carbon with volatile matter,

c. Selection and adjustment of temperature,

d. Flow control of inert gas as well as steam,

e. The presence of inert gas and the purification of raw and impure syn gas.

In the entire system of producing syn gas, there are some essential factors, which effectively control the process.

i. Temperature,

ii. Pressure,

iii. Ingredient material,

iv. Purification of syn gas,

v. Inert gas

These controlling factors can be described as follows:

i. Temperature:

The effect of reactor temperature on syngas generation rate is essential. The temperature is the main controlling factor during the generation of steam. If the temperature is lesser than the water molecule removal temperature obtained from TGA – DTA diagram, the production of steam from vegetable and flower wastes would be delayed, the entire process would be delayed as well as loss of steam would be higher which would decrease the efficiency of the process.

The syn gas yield can increase with the increase in gasification temperature. The reaction for generating syn gas is basically first order reaction with the reaction rate, such that:

$$\textbf{Reaction rate, } r = A.\ \exp(-E_A/RT)$$

$$\textbf{or, } \ln(r) = \ln A - (E_A/RT)$$

As the reaction of producing syn gas (CO + H_2) his highly endothermic reaction with the consumed energy about 206.12 KJ/Mol, increasing temperature from 700 deg C to 1000 deg C, the rate of reaction increases in rapid manner. However, increasing temperature to 900 and 1000 deg C, production and flow rate of syn gas would be extremely higher which may cause loss of efficiency of process due to loss of produced gas. While temperature is higher about 900 deg to 1000 deg. C, the stability of CO is effectively higher than CO_2 as well as rate of Boudouard reaction would obtain a significant rate, chance of producing CO_2 will decrease and CO_2 will convert to CO in maximum amount. In the syn gas, there is present maximum concentration of CO along with H_2 and the volume ratio of CO to CO_2 (V_{CO}: V_{CO2}) would be much higher. It is observed from previous experiment that, at about 1000 °C, devolatilisation accounts for more than 50% of the syngas yield. This has pronounced effect on the desired quality and quantity of syngas produced from the feedstock material. When temperature increases from 1000 deg. C, the first order reaction kinetics may tend to be hampered, a compensation effect was observed here, where a simultaneous decrease in activation energy and pre-exponential factor with increase in temperature may be observed. Along with this, at higher temperatures, hydrogen is allowed to escape in the form of volatile hydrocarbons due to the higher heating rate of the sample. However, at lower temperatures, hydrogen is trapped in the bio-dust specimen and is released later by steam-char reactions. The mole fraction of H_2 in the produced syn gas decreases with increasing temperature. For this, the effective temperature for gasification reaction to obtain effective composition of syn gas with sufficient mole fraction of CO along with H_2 is basically 700 deg. C to 800 deg. C.

ii. Pressure:

Basically, the entire system should be in vacuum, otherwise generation of steam would be effectively hampered. Vacuum would help to obtain effective flow of higher temperature steam to gasification furnace to react with bio-dust, the adequate temperature range.

In the other hand, from Le Chatelier's principle, during the generation of syn gas, when at specific temperature, the pressure would be higher, rate of production of CO and H_2 would be prevented. The vacuum is essential for the entire reaction, flowing and filtering.

iii. Ingredient Material:

In the bio-dust material, the volatile matter should be present in sufficient amount along with fixed carbon. Volatile matter be main source of H_2 in syn gas. If the amount of volatile matter is lesser than the required valued, in the produced syn gas, ratio of mole fraction of CO to H_2 be much higher, which has 2 adverse effects. Initially, the desired composition of syngas with signification CO to H_2 molar ratio cannot be obtained, which indicates generation of higher amount of CO_2 after further oxidation of syn gas, mainly during reduction of iron ore. The gasification rate of bio-dust, due to lesser effectivity of volatile matter, is much higher, which causes loss of efficiency. The loss of heat would be effectively higher during the application of syn gas as oxidation of syn gas containing higher amount of CO provide higher exothermic effect.

iv. Filtering System:

Syn gas, after produced from gasification reactor is in impure condition. Unwanted substances can be present along with syn gas. Impure substances can be some hydrocarbon gas, finer dust particles and moisture content. The raw syn gas is required to pure by passing it through proper filtering. Also, steam can be present as an impurity with the gas. For this, the raw gas should be allowed to pass through the filter, with lesser amount of pressure. Pressure should be kept lesser to obtain better flow of gas during its processing. To remove moisture content from gas, different type of moisture absorbing material dust can be used and the syn gas is allowed to pass through the material dust. Anhydrous Calcium Chloride, Calcium Sulphate etc. can be used.

v. Inert Gas:

Inert gas has some essential purposes. First of all, inert gas helps to execute the process of steam generation and producing syn gas by keeping the entire atmosphere inert and prevent to exist any other unwanted gaseous substances. During heating of vegetable and flower wastes at about 350 to 400 deg. C to produce steam, Argan gas is allowed to enter the conical flask. This Argan gas prevents the oxidation of the ingredient waste material as well as helps to obtain better flow of steam with minimum loss. There should be particular rate of flow of Argan gas during generating steam, if it is about 6.4 g/min better efficiency can be obtained. There is a steam or gas analyser before entering to gasification after steam reheating to detect the presence of steam in gasifying age. If only Argan is detected in detector, it would be clear that the steam generation process is completed. Flowmeter should be installed nearer to gasification reactor to obtain specific steam flow rate. Steam flow rate should be 8 g/minute, better to obtain desired efficiency of the syn gas producing process.

During syn gas generation, flow of Nitrogen (N_2) gas is essential to prevent oxidation of bio-dust as at higher temperature, bio-dust has higher chance to be oxidised. Presence of N_2, helps to execute the reaction between steam and bio-dust without any adverse activity of O_2. A flow of Helium is essential to prevent confusion between CO and N_2 during detection in analyser. Mass spectrometer helps to measure the flow rate of CO and CO_2 obtained by relating the partial pressure of CO and CO_2 with the partial pressure of Helium. For this purpose, the flow rate of Helium should be kept constant at a known flow rate, better flow rate of Helium should be 1.1 g/minute.

Chapter: 6.4

Environmental Impact Assessment and Risk Analysis

Safety and the environment are one of the most essential issues in any activity. When research works and industrial activities go on, there might be higher chance of environmental degradation as well as physical and mental hazards, which can affect community life adversely. For this, to maintain proper living standard, pollution, risk factors and safety precautions should be analysed effectively. Each successfully developing project has proper intimacy with safety and environment.

The entire processes be completely environment friendly as well as safe and free of hazard. There is no such process step and equipment which can adversely affect the environment and safety. The generation of bio-dust from vegetable and flower wastes, reaction between bio-dust and hot steam completely takes place within the gasification system. Outcoming gas after reduction reaction, contains negligible amount of polluting Carbon Monoxide (CO). After the entire procedure, lesser amount of ash be present as residue in system as from vegetable and flower wastes, after heating to specific temperature range, pure form of carbon can be obtained. The entire steam lines and round bottom flask be completely insulated and no chance to come in contact the body part of flask and lines to atmosphere. During the process, no such gas is emitted which can pollute the atmosphere.

Here the bio-dust, which contains significantly pure form of carbon (C) as well as unwanted gangue material without carbon is minimum. Coal contains some amount of sulphur, although in bio-dust, there is found no sulphur as well as any polluting agent.

The vegetable peels, trimming and flower wastes are dumped in different places. As these wastes are organic in nature, they show bio-degradability and this is by temperature, air as well as micro-organisms in atmosphere. This causes several indecent effects:

v. Micro-organisms are effective and chance of spreading of disease may increase,
vi. Bitter smell is found,
vii. Street animals (dogs, cats) and birds (crows) may gather there and may carry the wastes to the locality,
viii. Harmful insects, mainly mosquitoes, can accumulate their and can carry germs to locality.

This type of processing of vegetable and flower wastes can prevent environmental pollution as well as inconvenience in daily life. It will also be helpful to municipal corporation to regular remove these dumped wastes from garbage and lands.

For having purest form of carbon, during reduction of iron ore with carbon rich bio-dust, CO and CO_2 can be generated, which can be controlled or further processed to prevent air pollution and environmental degradation due to emission. The amount of ash content, which is difficult to control, is much lesser in amount, for this environmental pollution is much lesser.

During this process, as in raw material, amount of gangue content is much lesser, volume of slag is found minimum. As according to the laboratory-based plant set up design to produce syn gas, the carbon rich bio-dust is allowed to react with hot steam and the generated syn gas ($CO + H_2$) is transferred to react with pre-reduced iron ore, effective reduction of iron ore can be found and higher amount of metallic iron can be achieved, along with minimum amount of CO gas is obtained from exhaust gas and this gas contains mainly CO_2, which is non-polluting, the entire procedure of reducing iron ore becomes environmentally compatible.

Chapter: 7

Conclusion and Future Scope of Work

In today's world, the root of human development is Iron and Steel technology, not only in economy, but also the growth in civilisation as well as future technology. Rapid rate of growth of this sector is very significant. Better physical and mechanical properties and longer durability build up huge demand of this material. Along with this, among all the material, applied in constructional purpose, this Iron and Steel is the cheaper as well as higher availability of Iron ore, enhance the feasibility of this material. Production of this material is relatively convenient as well as more straight-forward.

Conventionally, from Hematite (Fe_2O_3) ore, Iron can be obtained by effective reduction, in which Metallurgical coke is the main reducing age. Not only Metallurgical Coke, also carbon rich higher-grade coal and other fossil fuels (Natural gas) can effectively reduce the ore, to produce metallic iron:

$$\mathbf{Fe_2O_3 + 3C \rightarrow 2Fe + 3CO}$$

and

$$\mathbf{Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2}$$

Blast furnace is the main reduction reactor, from the previous time, even in recent days. Obviously different modification of this counter current reduction reactor has been done, although the basic issue of consumption of coke and pollution in environment still remain there. During the Direct Reduction of Iron or DRI making, requirement of carbonaceous fossil fuel still remains.

In present day, the reduction of stock of coal as well as fossil fuels is the fearing issue. Also coking process to enhance carbon content taking lesser grade coal is quite costlier. Without such strong carbon rich reducing agent, reduction of iron ore is much difficult. Also, from a number of sources, generation of carbon rich part is quite difficult. Technology requires some different source of carbon, alternative way to produce carbon rich part which can be applied in the reduction of Iron ore and the entire method would be cost effective and economically viable.

In present day, in India, the population is increasing at higher rate. Demand of food is also increasing, along with this. Also in Indian civilisation, use of flowers is significant. For this, per day in India, huge amount of vegetable peels, trimming and flower wastes be generated. As these are bio-degradable organic wastes, these can be effective source of carbon.

From the TGA-DTA analysis, it is clear that in the peels of vegetables: Potato, Potal, Pumpkin, Banana and Mary gold flower wastes, 85% of water content is present as in vegetable body part, major portion contains water molecule. The rest 15% is completely pure form of carbon, and there is negligible amount of ash. Heating the waste samples at 350 deg. for 30 minute, as obtained from TGA-DTA plot, water content can be removed totally, which is an exothermic process. After that, the pure form of carbon is effectively mixed with iron ore in stoichiometric basis, along with particular amount of binder material, to produce nugget. The reduction has, in this context, taken place at 1000 deg. C for 1 hour, in the raising hearth furnace, keeping each sample in Alumina crucible.

Basically, reducing power of carbon-rich bio-dust slightly varies from one waste sample to another. The extent reduction i.e., the XRD peak of reduced sample of different vegetables and the flower waste express this clearly.

- In reduced sample of Banana, the number of peaks of iron is higher, after that, Potato and Mary gold peels come.
- Lesser number of peaks of iron is found for sample of Pumpkin.
- For Potal, the significant number of peaks of Magnetite are found in reduced sample of Potal peels.

This indicates that bio-dust coming from peels and trimmings of Banana has better ability in reducing Iron ore (Hematite), after that, peels of Potato and Mary gold flower wastes come. Bio-dust samples coming from peels of Potal and Pumpkin are quite lesser efficient in this context, as in the peels, amount of pure carbon is relatively lesser, volatile matter and ash content is relatively higher.

In this procedure, it is found that the vegetable peels and trimming and flower wastes contain significant amount of moisture in it. This moisture can be effective utilised by simple condensation process, the collect the pure form of water for drinking and laboratory activity. This water content can be utilised in industrial purposes, due to its consistent purity.

The steam coming from heating the vegetable and flower wastes at particular temperature range for particular time period, can be reheated and processed further, pass through the heated bio-dust in stoichiometric basis at 900 deg. C, to produce syn gas:

$$\mathbf{C + H_2O = CO + H_2}$$

This syn-gas can effectively be passed though the pre-reduced iron ore, at 800 to 1000 deg. C, to effectively reduce Wustite (FeO) to metallic Iron. Syn gas has better reducibility and higher rate of diffusion of Hydrogen gas can cause effective dis-bondment in Fe-O to enhance amount of metallic Iron, as well as higher degree of metallisation can be obtained.

Theoretical design of producing Syn-gas from the bio-dust and steam coming from waste sample has been introduced in the context. According to stoichiometric calculation, it is found that, from particular amount of vegetable and flower waster, the amount of steam content obtained, is excess to react with the bio-dust coming from same amount of wastes. For this, in the design, in the main steam flowing line, there is a branch, after the nozzle of the heating round bottom flask, from where, excess steam can be removed from system, to condense it to pure water. In such manner, the loss of moisture can be effectively minimised, in the design.

This entire activity is free of any undesired ingredient and causes no degradation of physical and mental stability of human life. The environment-friendliness of the project is prominent as minimum exhaustion of Carbon Monoxide (CO), no emission of sulphur and nitrogenous oxides during reduction of iron ore as well as bio-degradation of vegetable and flower wastes can be completely prevented.

As a part of improvement in the entire design, a software can be built up by design, as essential future scope, by which, the entire procedure of generating steam, generation of Syn-gas and reduction of iron ore can be effectively controlled. Software base activity will enhance the efficiency of entire procedure. Also, amount of water obtained by condensation of excess steam during the entire procedure, can be prominently obtained.

Therefore, it can be remarkable for the iron and steel manufacturers to explore alternatives to Coke as obtained from coal, as reductant in iron making process. In this way, domestic wastes can be effectively removed from being deposited, environmental pollution can be prevented as well as a potential source and partial alternative for coke in iron and steel making plants can be obtained.

Chapter: 8

Reference

1. https://blog.mwpbnp.com/necessity-of-the-iron-and-steel-industry/
2. https://www.agnisteels.com/Post/the-role-of-iron-in-the-steel-manufacturing-industry
3. https://sail.co.in/en/learning-center/importance-steel#:~:text=Steel%20is%20used%20in%20our,its%20benefits%20are%20undoubtedly%20clear.
4. https://www.reuters.com/article/idINIndia-53521120101213#:~:text=*%20India's%20iron%20and%20steel%20industry,world%20after%20China%20and%20Japan.
5. https://www.iea.org/reports/iron-and-steel-technology-roadmap
6. https://www.nipponsteel.com/en/tech/report/nsc/pdf/NSTR101-13_tech_review-2-2.pdf
7. https://www.sciencedirect.com/science/article/pii/S0959652620346023?casa_token=eVGBb6-VUPAAAAAA:Qj0kzYwRLmn11Fsmjd4hbZc76iJdN49my6NnxeLf7ccqxSBhurX9kNTKExZNuMH6Et4LkcSAhUsa
8. https://link.springer.com/article/10.3103/S0967091215090077
9. https://www.researchgate.net/publication/32938288_The_Iron_and_Steel_Industry_in_Asia_Development_and_Restructuring
10. https://www.oecd.org/industry/ind/latest-developments-in-steelmaking-capacity-2021.pdf
11. https://www.sciencedirect.com/science/article/pii/S0954349X00000254?casa_token=dAIzTnpCickAAAAA:VSh24sVURg2SnT8W_z_lc-aM_1pFXTphdbcAIyLlUn3Avcqy6WdBNo-1C2pBI7Q1rTrnfUu-ZQhI
12. https://carboncopy.info/indias-iron-and-steel-industry-capable-of-emitting-less-and-producing-more-report/
13. https://www.ias.ac.in/article/fulltext/sadh/007/03/0181-0202
14. https://steel.gov.in/en/make-india#:~:text=Crude%20steel%20production%20grew%20at,MT%2C%20up%20by%208.9%25.
15. https://www.toppr.com/ask/question/what-are-the-main-problems-faced-by-the-iron-and-steel-industry-in-india/#:~:text=a)%20High%20cost%3A%20Limited%20availability,b)%20Low%20productivity%20of%20labour.

16. https://idp.springer.com/authorize/casa?redirect_uri=https://link.springer.com/article/10.1007/s10584-013-0902-5&casa_token=wjwx-ONc1EMAAAAA:rmJ-rS4hkThHRNBSxhnO9zLpA0HEw9THyg6YcGxuOgYKyjXbp0O1BH4LwlO7J8wZzTEyxlET2mO_HDEK_TU

17. Iron and charcoal the industrial fuelwood crisis in Minas Gerais
Author links open overlay panelFrank Ackerman, Paulo Eduardo Fernandes de Almeida

18. Alleviating dependency on fossil fuel by using cow-dung during iron ore pelletization; Assessment of pellet physical and metallurgical properties
Author: panel Sachida Nanda Sahu, Surendra K. Biswal

19. The impact of climate targets on future steel production – an analysis based on a global energy system model☆
Author panel Johannes Morfeldt, Wouter Nijs , Semida Silveira

20. Opportunities and challenges for decarbonizing steel production by creating markets for ‘green steel’ products
Author: panel Hasan Muslemani, Xi Liang, Katharina Kaesehage, Francisco Ascui, Jeffrey Wilson

21. A comprehensive review on energy efficient CO2 breakthrough technologies for sustainable green iron and steel manufacturing
Author: M. Abdul Quader, Shamsuddin Ahmed, Raja Ariffin Raja Ghazilla, Shameem Ahmed, Mahidzal Dahari

22. Biomass applications in iron and steel industry: An overview of challenges and opportunities
Author: Elsayed Mousa, Chuan Wang, Johan Riesbeck, Mikael Larsson

23. Utilization of biomass as an alternative fuel in iron and steel making
Author: Elsayed Mousa, Hesham Ahmed

24. Production and characterization of bio-oil and bio-char from pyrolysis of potato peel wastes
Shaobo Liang, Yinglei Han, Liqing Wei & Armando G. McDonald
Biomass Conversion and Biorefinery volume 5, pages 237–246 (2015) Cite this article
https://link.springer.com/article/10.1007/s13399-014-0130-x

25. Critical analysis of pyrolysis process with cellulosic based municipal waste as renewable source in energy and technical perspective
Author: Manu Agarwal, James Tardio, S. Venkata Mohan

26. Alternative Reducing Agents in Metallurgical Processes: Gasification of Shredder Residue Material
Samira Lotfian, Hesham Ahmed, Abdel-Hady A. El-Geassy & Caisa Samuelsson

27. Alternative emerging ironmaking technologies for energy-efficiency and carbon dioxide emissions reduction: A technical review
Author: Ali Hasanbeigi, Marlene Arens, Lynn Price

28. A technical review on coke rate and quality in low-carbon blast furnace ironmaking
Author: Behnaz Rahmatmand, Arash Tahmasebi, Hannah Lomas, Tom Honeyands, Pramod Koshy, Kim Hockings, Apsara Jayasekara

29. Composite Pellets – A Potential Raw Material for Iron-Making
Hesham M. Ahmed, Nurni Viswanathan, Bo Bjorkman

30. Plastics—Villain or Hero? Polymers and Recycled Polymers in Mineral and Metallurgical Processing—A Review by Sheila Devasahayam, R. K. Singh Raman, K. Chennakesavulu and Sankar Bhattacharya

31. Equilibrium Simulations of Coal Gasification – Factors Affecting Syngas Composition
Author: Alina Żogała

32. Clean syngas from biomass—process development and concept assessment
Pekka Simell, Ilkka Hannula, Sanna Tuomi, Matti Nieminen, Esa Kurkela, Ilkka Hiltunen, Noora Kaisalo & Johanna Kihlman

33. Biomass Gasification for Synthesis Gas Production and Applications of the Syngas
Reinhard Rauch, Jitka Hrbek, Hermann Hofbauer

34. A review of advanced catalyst development for Fischer–Tropsch synthesis of hydrocarbons from biomass derived syn-gas
Hessam Jahangiri, James Bennett, Parvin Mahjoubi, Karen Wilson and Sai Gu

35. Clean syngas from small commercial biomass gasifiers; a review of gasifier development, recent advances and performance evaluation
Author: Richard Thomson, Philip Kwong, Ejaz Ahmad, K.D.P. Nigam

36. Hydrogen-rich synthesis gas production from waste wood via gasification and reforming technology for fuel cell application
Wei Wu, Katsuya Kawamoto & Hidetoshi Kuramochi

37. Biomass Energy and Bio-energy Trade: Historic Developments in Brazil
and Current Opportunities
Arnaldo Walter1, Paulo Dolzan, Erik Piacente

38. Recent Developments in Bio-Energy Recovery Through Fermentation
R. Braun, B. Drosg, G. Bochmann, S. Weiß & R. Kirchmayr

39. Effect of Residual Volatile Matter on Reduction of Iron Oxide in Semi-charcoal
Composite Pellets
Hirokazu Konishi, Kazuhira Ichikawa, Tateo Usui

40. Ethanol production from potato peel waste (PPW)
Author: D. Arapoglou, Th. Varzakas, A. Vlyssides, C. Israilides

41. Biofuel Generation from Potato Peel Waste: Current State and Prospects
by Omojola Awogbemi, Daramy Vandi, Von Kallon and Adefemi O. Owoputi

42. Agricultural waste: Review of the evolution, approaches and perspectives on alternative uses
Author: Mónica Duque-Acevedo, Luis J. Belmonte-Ureña, Francisco Joaquín Cortés-García, Francisco Camacho-Ferre

43. Hydrogen-Rich Gas Production from Steam Gasification of Bio-char in the Presence of CaO
Jun Dong, Ange Nzihou, Yong Chi, Elsa Weiss-Hortala, Mingjiang Ni, Nathalie Lyczko, Yuanjun Tang & Marion Ducousso

44. Hydrogen production from high temperature steam catalytic gasification of bio-char
Author: Qari M.K. Waheed, Chunfei Wu, Paul T. Williams

45. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals
Author: Francesco Cherubini

46. Energy Efficiency and Sustainability in Steel Production
L. E. K. Holappa

47. Gasification of lignocellulosic biomass char obtained from pyrolysis: Kinetic and evolved gas analyses
Author: D. López-González, M. Fernandez-Lopez, J.L. Valverde, L. Sanchez-Silva

48. Catalysed and uncatalysed steam gasification of eucalyptus char: influence of variables and kinetic study
Author: José M. Encinar, Juan F. González, Juan J. Rodríguez, María J. Ramiro

49. Influence of char composition and inorganics on catalytic activity of char from biomass gasification
Author: Naomi B. Klinghoffer, Marco J. Castaldi, Ange Nzihou

50. Biodiesel production via transesterification of palm olein using waste mud crab (Scylla serrata) shell as a heterogeneous catalyst
Author: Peng-Lim Boey, Gaanty Pragas Maniam, Shafida Abd Hamid

51. Process intensification of transesterification for biodiesel production from palm oil: Microwave irradiation on transesterification reaction catalyzed by acidic imidazolium ionic liquids
Author: Hui Ding, Wei Ye, Yongqiang Wang, Xianqin Wang, Lujun Li, Dan Liu, Jianzhou Gui, Chunfeng Song, Na Ji

52. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process
Author: Huayang He, Tao Wang, Shenlin Zhu

53. Thermal Effects in Cellulose Pyrolysis: Relationship to Char Formation Processes
Ivan Milosavljevic, Vahur Oja, and Eric M. Suuberg

54. Thermal Decomposition of Biomass Wastes. A Kinetic Study
Michaël Becidan, Gábor Várhegyi, Johan E. Hustad, and Øyvind Skreiberg

55. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield
Author: Ayhan Demirbaş

56. Char Gasification with O2, CO2, and H2O: Effects of Pressure on Intrinsic Reaction Kinetics
D. G. Roberts and D. J. Harris

57. CO2 and steam gasification of a grapefruit skin char☆

Author: F. Marquez-Montesinos, T. Cordero, J. Rodríguez-Mirasol, J.J. Rodríguez

58. Wastepaper gasification with CO2 or steam using catalysts of molten carbonates

Author: Hiroyuki Iwaki, Shufeng Ye, Haruo Katagiri, Kuniyuki Kitagawa

59. Study on the gasification of wastepaper/carbon dioxide catalyzed by molten carbonate salts

Author: Gong Jin, Hiroyuki Iwaki, Norio Arai, Kuniyuki Kitagawa

60. CO2 Reforming of Methane in a Molten Carbonate Salt Bath for Use in Solar Thermochemical Processes

T. Kodama, T. Koyanagi, T. Shimizu, and Y. Kitayama

Appendix 1

Numerical Calculation of Reducing Iron Ore by Bio-dust of Vegetable and Flower Wastes

Initially, 10 gram of iron ore is taken. It is necessary to calculate the particular amount of ingredient material including total iron present in it.

Ingradient	name	wt %	amount in gram
total iron	total Fe	58.072	5.8072
silica	SiO2	6.278	0.6278
alumina	Al2O3	2047	204.7
phosphorus pentoxide	P2O5	0.067	0.0067
sulphur	S	0.027	0.0027
manganese	Mn	0.049	0.0049
calcium oxide	CaO	1.465	0.1465
magnesium oxide	MgO	0.361	0.0361

From this, it is found that in 10 gram hematite ore, 5.8072 gram total iron is present, which is the major according to the amount.

From TGA-DTA diagram, it can be told that from 350 deg C to 400 deg C, maximum amount of moisture is removed.

From the plot, it is found that potato peels contain about 85% water and rest 15% is carbon at ambient condition.

Stoichiometric Calculation:

Here dehydrated vegetables and flower wastes are the main source of carbon, which is essential reducing agent in the reduction of iron ore (Fe_2O_3) to produce metallic iron.

As dust of iron ore is reduced to metallic Fe in solid condition by the action of carbon at higher temparature, this is direct reduction of iron or DRI.

Reaction is:

Fe2O3 + 3C = 2Fe + 3CO

In 10 gram ore, metallic iron is present: 5.8072 gram

Therefore, the amount of Fe_2O_3 in the ore is = (5.8072 *160 /100) gram

= 8.296 gram

Therefore, the amount of cabon required for effective reduction of iron ore is

= (5.8072 *36 /112) gram

= 1.8666 gram

Normally, each waste material contains around 85% moisture and 15% pure carbon content in it

Therefore, in 100 gram of vegetable or flower waste contains 85 gram of water content as well as 15 gram of pure carbon in it in form of bio-dust

In this consequence, when pure carbon is around 1.867 gram, then the requirement of waste material will be = (1.867*100/15) gram

= 12.44 gram

Therefore, during the reduction process, in preparing each nugget, with 10 gram of iron ore, 1.86 gram pure form of carbon is required, which basically comes from 12.44 gram of waste material.

Appendix 2

Numerical Calculation of Syn Gas Generation

Calculation of Ingredients in Ore:

Initially, 10 gram of iron ore is taken. It is necessary to calculate the particular amount of ingredient material including total iron present in it.

Ingredient	Name	Wt. %	Amount in gram
total iron	total Fe	58.072	5.8072
silica	SiO_2	6.278	0.6278
alumina	Al_2O_3	2047	204.7
phosphorus pentoxide	P_2O_5	0.067	0.0067
sulphur	S	0.027	0.0027
manganese	Mn	0.049	0.0049
calcium oxide	CaO	1.465	0.1465
magnesium oxide	MgO	0.361	0.0361

From this, it is found that:
in 100-gram hematite ore, 58.072-gram total iron is present, which is the major according to the amount.

Calculation amount of Iron in Ore:
Then, in 10 gram of iron ore, the iron is= (10/100) *58.072
= 5.8072 gram

The reduction reaction between iron ore (Fe_2O_3) and Syn gas ($CO+H_2$) is:

$$Fe_2O_3 + CO + 2H_2 = 2Fe + CO_2 + 2H_2O$$

Molecular weight of elements:

Iron, Fe = 56

Carbon, C = 12

Oxygen, O = 16

Hydrogen, H = 1

Calculation of Carbon Monoxide (CO) in Syn gas:

(2*56) gram Fe is produced from (12+16) gram or 28 gram CO

To obtain 5.8072-gram Fe, the required amount of CO will be

= 28* 5.8072/ (2*56)

= 1.4518 gram

Calculation of hydrogen (H2) in Syn gas:

4 gram of H2 gas is required to produced (2*56) gram Fe

To obtain 5.8072-gram Fe, the required amount of H2 will be

= 4*5.8072/ (2*56)

= .2074 gram

The required reaction to produce syn gas is:

$$C + H_2O = CO + H_2$$

Requirement of Carbon or Bio-dust:

(12+16) gram or 28 gram CO is generated from 12 gram Carbon (here Bio-dust as it contains pure form of carbon)

To obtain 1.4518 gram of CO, the required amount of bio-dust will be

= 12*1.4518/28

= .6222 gram

Requirement of Steam:

(12+16) gram or 28 gram CO is generated from 18 gram hot steam (H_2O)

To obtain 1.4518 gram of CO, the required amount of hot steam (H_2O) will be = (18*1.4518/28) gram
= .9333 gram

Calculation of Vegetable and Flower Waste Material:

From TGA-DTA plot, it is found that approximately 15% of pure form of carbon in form of bio-dust and 85% of steam can be obtained from vegetable as well as flower wastes.

This indicates that 15 gram bio-dust in generated from 100 gram of vegetable and flower waste material

To obtain .6222 gram Carbon, the required amount of ingredient waste material = (100*.6222/15) gram
= 4.148 gram

Calculation of Loss of Steam:

Also, to obtain .9333 gram steam, the amount waste material required, will be = (.9333*100/85) gram
= 1.098 gram

For convenience in design as well as calculation, in both purposes, amount of vegetable and flower wastes are multiplied by 100

The amount of wastes is = 1.098*100 or 109.8 gram
and
= 4.148 * 100 gram or 414.8 gram

In the initial process step, entire amount of steam is turned into water by condensing to prevent the loss of steam

The amount water obtained is= (414.8*85/100) gram
= 352.58 gram

The amount of waste material for which steam loss has taken place is = (414.8 – 109.8) gram
= 305 gram

The amount of loss of steam is = (305*85/100)
= 259.25 gram

Optimisation in Steam Loss:

For this, in the steam line, through which steam is moving to steam reheater, there should be a branched line of similar with a valve.

The valve should be adjusted in such manner that, steam should be flowed in a particular value with minimum tolerance and this value is obtained from the digital steam flow meter.

Basically, in single step, heating of vegetable and flower wastes requires 30 minute to execute complete dehydration to entire produce bio-dust.

The maximum value of flow of waste steam through the branched line is
= (259.25/30) gram/minute
= 8.64 gram/minute

The steam flow meter will have to show the value of flow of 8.64 gram/ minute digitally, with minimum tolerance, to obtain exact vale of steam loss during entire dehydration of vegetable and flower wastes process step and it will help to optimise the process with minimum loss and wastage.

This extra amount of steam is not allowed to be loosed. The steam is condensed to pure distilled water.

From the entire calculation, it is found:

i. From 414.8 gram of vegetable as well as flower wastes, (.6222*100) gram or 62.22 gram of bio-dust or pure form of carbon can be obtained,

ii. In the initial process step, entire amount of steam is turned into water. The amount of water obtained by condensing the steam is 352.58 gram,

iii. In the process, from 414.8 gram of waste material, 145.18 gram CO can be produced,

iv. In the process, from 414.8 gram of waste material, 10.37 gram CO can be produced,
v. The amount of entire syn-gas is = (145.18+10.37) gram
= 155.55 gram

vi. From the entire calculation, it can be cleared that from this amount of syn gas, 580.72 gram of iron ore can be produced from reduction.

vii. From the waste material of 414.8 gram, 352.58 gram steam is generated although to react with 62.22 gram carbon or bio-dust obtained from 414.8 gram wastes, 93.33 gram steam is enough. The extra steam is 259.25 gram, which is allowed to be condensed to produce distilled water.

viii. In the extra steam branch line, the valve should be controlled in such manner that the steam flow though the branch line is 8.64 gram/ minute, obtained from steam flow meter, with minimum tolerance.