CARBONIZATION OF EUCALYPTUS WOOD AND CHARACTERIZATION OF THE PROPERTIES OF CHARS FOR APPLICATION IN METALLURGY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF TECHNOLOGY

IN

METALLURGICAL & MATERIALS ENGINEERING

BY

SAURABH AGRAWAL
ROLL NO-212MM1413

DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA, ORISSA-769008
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Under the guidance of
Prof. M. KUMAR

DEPARTMENT OF METALLURGICAL & MATERIALS ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
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National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"CARBONIZATION OF EUCALYPTUS WOOD AND CHARACTERIZATION OF THE PROPERTIES OF CHARS FOR APPLICATION IN METALLURGY"** submitted by **Mr. Saurabh Agrawal** in partial fulfillment of the requirements for the award of **Master of Technology** Degree in Metallurgical and Materials Engineering with specialization in **"Metallurgical and Materials Engineering"** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Prof. M. Kumar
Dept. of Metallurgical & Materials Engineering
National Institute of technology
Rourkela – 76900

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Saurabh Agrawal

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ABSTRACT

In view of the prominent energy & environmental problems associated with the use of fossil fuels, an increasing attention is now being paid by the metallurgists for the alternate energy sources which are renewable and environment friendly in nature. Biomass (i.e. wood) obtained by fast growing trees appears to be highly beneficial and found suitable for plantations under Indian conditions. Charcoal obtained from these energy crops can be used as a reducing agent for iron-ore reduction. The aims of the present project work is i) Characterization of the properties of different components of eucalyptus tree, such as wood, bark, branch and leaves, and ii) Characterization of the physical and chemical properties of charcoals obtained at different carbonization conditions such as, temperature, heating rate and soaking time. It is found from the proximate analysis that the ash content of different components of eucalyptus wood is very low as compared to coal. It is also found that the calorific value of eucalyptus wood is higher than the other components of eucalyptus tree. The results shows that yield of char and their physical & chemical properties depends on the carbonization conditions, viz. temperature, heating rate and soaking time. The char yield decreases gradually with the increasing carbonization temperature and most of the volatilization occurs up to 800°C. The fixed carbon content increases while volatile matter decreases with increase in carbonization temperature. The calorific value of charcoals increases marginally with increase in carbonization temperature. Reactivity of Eucalyptus wood chars towards CO_2 was measured and the effects of carbonization conditions were determined. It is found that the reactivity decreases with increasing carbonization temperature. Charcoals obtained under rapid carbonization were found to be more reactive than the chars obtained under slow carbonization. Results indicate that apparent porosity increases while apparent density of charcoals decreases with increase in

temperature. It has also been found that ash fusion temperature of leaves is maximum followed by bark, branch & wood respectively. Higher ash fusion temperatures indicate the higher concentration of refractory oxides. The objective is to study the effects of carbonization conditions on wood charcoal and characterization of the properties of wood chars for the application in metallurgical industries.

Chapter 1

INTRODUCTION

1.1 INTRODUCTION

The prominent energy and environmental problems associated with the use of fossil fuels have made technocrats to think for alternate energy sources which are non-polluting and renewable in nature. Serious consideration should be given to biomass as a source of energy especially for iron-making industries. Also, use of biomass as an energy source for iron-making industries will certainly help in easing the greenhouse effect to some extent. The possible reductants (i.e. reducing agents) for iron ore reduction are coal, coke, charcoal, carbon monoxide (CO) gas and hydrogen (H_2) gas. The production of iron using charcoal as reductant is followed in many countries. In Brazil, wood char pig iron production accounts for about 30% of its annual iron production [1]. For using charcoal as reductant for Iron-ore reduction, the properties that need to be studied are: proximate analysis, ultimate analysis, calorific value, apparent densities and porosity, reactivity, etc. Also it has been studied that carbonization conditions such as heating rate, soaking time, carbonization temperature influences charcoal properties [1]. In the present project work, influence of carbonization conditions on the char yield and its properties has been investigated.

1.2 HISTORY OF IRONMAKING

History of Iron making started by the use of wood charcoal and before pre-industrial era (i.e. 1850), almost all the irons were being produced by the use of charcoal. Later on (i.e. after 1850), the use of charcoal as a reducing agent and source of energy was slowly & slowly abandoned because of the scarcity of wood charcoal and environmental problems. The position of charcoal in iron making was soon taken up by coal and coke. Coke is used in iron blast furnace whereas coal is used for iron making in Direct reduced iron (DRI) processes. Presently

around 70% of the iron is produced by using iron blast furnace and the remaining 30% by other processes.

1.3 COMPARISON BETWEEN CHARCOAL, COAL AND COKE:

The introduction, properties, advantages and disadvantages of these carbonaceous materials in context to iron making can be summarized in tabular form as shown in Table 1.

Table 1: Charcoal, coal and coke – A comparison

S.no.	Charcoal	Coal	Coke
1.	It is obtained by carbonization of wood at temperatures in the range of 400°C-1000°C. ***Biomass*** **Carbonization** → ***charcoal + wood gas***	It is directly obtained carbonaceous material from the mines. ***No carbonization***	It is obtained by the carbonization of coking coal at temperature of 1250°C-1300°C. ***Coking coal*** **Carbonization** → ***coke + coke oven gas***
2.	Charcoal contains very less amount of ash (2-5%).	Indian coals contain high amount of ash (20 - 50%).	Coke contains ash in the range of 20-28%.
3.	Volatile matter content in charcoal is higher than that in coal.	High volatile matter content in coal (25-35%).	Coke contains very low amount of volatile matter (≈2%).
4.	Charcoal has highest fixed carbon content.	Fixed carbon content of coal is less.	Coke contains less amount of volatile matter.
5..	Highest calorific value	Lower calorific value	Higher calorific value
6.	Highest reactivity towards CO_2 gas.	Intermediate reactivity	Lowest reactivity
7.	Lowest density	Lower density	Higher density

8.	Highest porosity (>50%)	Lower porosity	Intermediate porosity (38-45%)
9.	Highly amorphous structure	Amorphous structure	Semi crystalline structure
10.	Lowest mechanical strength	Intermediate mechanical strength	Higher mechanical strength
11.	Very poor abrasion resistant	Poor abrasion resistance	High abrasion resistance
12.	Highest reduction potential for Iron-oxide.	Intermediate reduction potential for Iron-oxide	Lower reduction potential
13.	Highest calorific value	Lower calorific value	Higher calorific value
14.	Approximately nil sulphur and phosphorus contents	Sulphur content is in the range of 0.5-2%	Sulphur content is around 0.7% and phosphorus content is around 0.5%.
15.	Lowest C-C bond strength	Intermediate C-C bond strength	Highest C-C bond strength
16.	Presently being used in the extraction of Au & Ag, in the manufacture of Indian ink and in the manufacture of medicines.	Presently being used in Iron-making in DR processes, power plants, brick kilns, cement industries etc.	Coke is presently used in iron-blast furnace for the manufacture of pig iron.
17.	Highest adsorption capacity	Lower adsorption capacity	Lower adsorption capacity

1.4 RESERVES OF COKING & NON-COKING COAL IN INDIA

Coal reserves in India are one of the largest in the world. As on April 1, 2012, India had 293.5 billion metric tons (323.5 billion short tons) of the resource [2]. The reserves of coking & non-coking coal in India have been outlined in Table 2:

Table 2: Reserves of Coking and Non-Coking coal in India

Type of coal	Coal Reserves (in Million tons)			
	Proved	**Indicated**	**Inferred**	**Total**
Coking Coal	17933.35	13653.47	2101.91	33688.73
Non-Coking Coal	99617.65	128416.04	30282.09	258315.78
Tertiary Coal	593.81	99.34	799.49	1492.64
Grand Total	**118144.81**	**142168.85**	**33183.49**	**293497.15**

Sources: Indian bureau of mines

1.5 PRODUCTION OF COAL IN INDIA

The total production of coal in 2011-12 was around 540 million tons [2]. India is third largest producer of coal in world. The production of coal in India in last ten years has been shown in Fig.1.

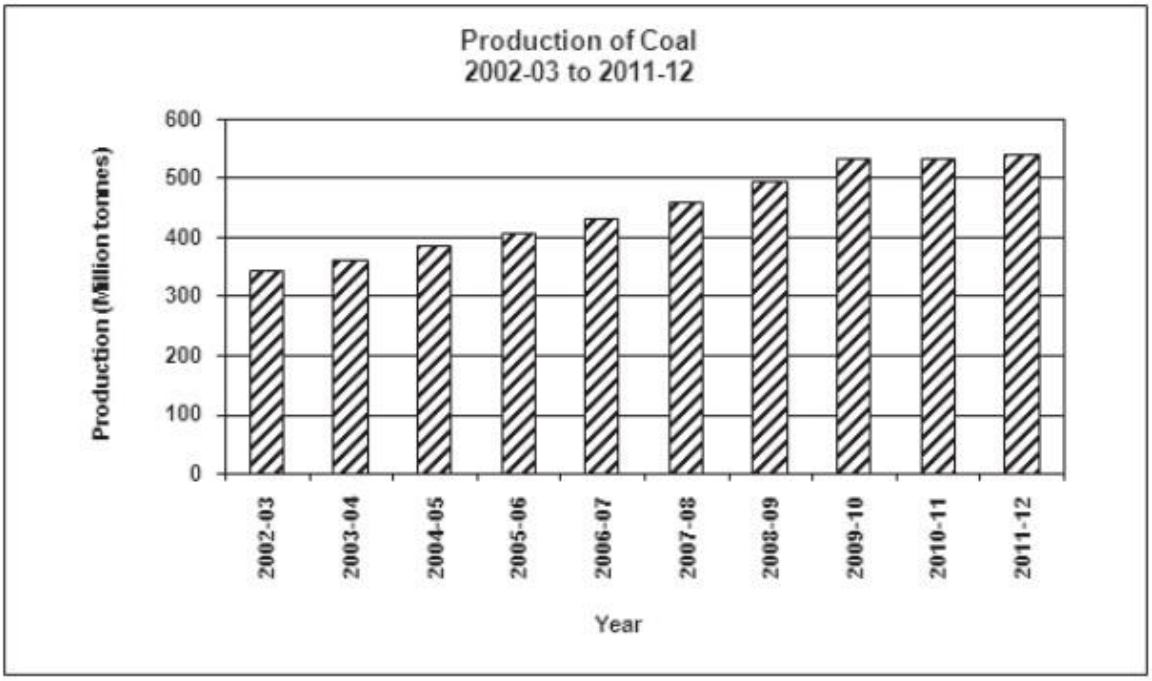


Fig.1: Year wise production of coal in India

1.6 MAJOR CONSUMERS OF COAL IN INDIA

Coal is a major source of energy for electricity generation as well as steel and iron industry. Table 3 outlined major coal consumers sector in India as well as we can see the gap between supply and demand of coal in recent years and in future estimates [2,3]. It is evident from the data outlined in Table 3, that to fill this gap of demand and supply we have to think for alternative energy source.

Table 3: Major coal consumers in India

Sector/Year	**2012-13 Budget estimates (in million tonnes)**			**2016-17 Projection by planning commission (in million tonnes)**		
	Demand	**Supply**	**Gap**	**Demand**	**Supply**	**Gap**
Coking Coal						
Steel industry	52	20	32	67	35	32
Non-Coking Coal						
Power	555	450	105	738	594	145
Cement	30	15	16	47	23	24
Sponge iron	35	24	11	50	57	-7
others	100	71	29	77	85	-8
Non coking sub total	721	560	161	913	760	154
Total raw coal demand	**773**	**580**	**193**	**981**	**795**	**186**

1.7 WOOD CHARCOAL: A POSSIBLE REDUCTANT AND ENERGY SOURCE FOR IRON MAKING

The current basis of utilization of coal in various industries, as shown in Table 3, indicate that iron & steel industries rank second among all these coal consuming industries in India and hence contribute significantly in damaging by greenhouse effect. Not only this, the reserves of coal are limited and are expected to contribute up to 100 more years. In view of energy & environmental problems associated with the use of fossil fuels, attempts must be made to develop an alternative source of energy/reductant for iron & steel industries. This will be a positive step towards mitigating the environmental problems associated with the use of fossil fuels. The properties of charcoal, coal & coke outlined in Table 1, clearly indicates that charcoal is the best among all these three materials so far as proximate analysis, reactivity, calorific value etc. are concerned.

The utilization of charcoal in iron & steel industries does not suggest the harvesting of existing forest carbon. The industrial use of charcoal should be based on "grow and utilize" principle, as is being practiced in Brazil. Brazil is presently producing nearly 70% of its pig iron by using Eucalyptus wood charcoal [4].

1.8 AIMS AND OBJECTIVES OF PRESENT PROJECT WORK

The aims and objectives of the present project work are as follows:

1. Determination of proximate analysis (moisture, volatile matter, ash and fixed carbon contents) and ultimate analysis of different components of Eucalyptus tree, such as wood, branch, bark and leaves.
2. Determination of calorific values of these components.

3. Carbonization of Eucalyptus wood at four different temperatures like 400, 600, 800 and 950°C for different time periods, such as 1, 2 and 3 hours under two different heating rates of slow (7°C min^{-1}) and rapid (30°C min^{-1}).
4. Determination of proximate analysis, ultimate analysis & calorific values of these eucalyptus wood charcoals.
5. Determination of density and porosity of these eucalyptus wood chars.
6. Determination of reactivity towards CO_2 gas of these charcoals.
7. Analysis of the results to access their suitability for metallurgical industries.

Chapter 2

LITERATURE SURVEY

Ravindranath et al. (2009) analyzed sustainable bioenergy for India in terms of technical, economic and policy analysis. India has to create quality energy for large section of population thus renewable energy is considered as one of the most promising alternatives. A large number of innovative programs and policies are being developed to promote bioenergy technologies including biomass stoves, biogas, biomass combustion and gasification. In this work potential of bioenergy has been considered to meet the need of rural area 1) for electricity production biomass combustion and gasification 2) for electricity as well as cooking energy bio-methantation 3) for cooking efficient wood-burning devices. This paper basically focuses on analyzing the potential and effectiveness of bioenergy for rural energy access for economic and technical development [5].

To reduce the impacts of global warming we have to use renewable energy sources. The most common form of renewable energy is biomass but the type of biomass required is determined by energy conversion process. In this paper production (in European climate) and plant properties is examined. It has been found that by using renewable forms of energy up to 10% of the UK's electricity needs is generated by 2010 which helps in reducing global warming. Woody plants, herbaceous plants and grasses are generally used for producing energy with attention on the C4 plant. Cellulose, hemicellulose and lignin components of the plant contain chemical energy and their proportions vary with the type of plant and they are the important factors in determining the optimum energy . Thermo conversion plant is used to burn biomass i.e. combustion to produce steam which is used in turbo generator to produce electricity and some species can be used to produce gaseous or liquid fuels by biochemical conversion. Growth rate, ease of management, harvesting and intrinsic material properties are primary criteria for selection of biomass species . For all plant species the energy content of biomass is

similar lying in the range 17-21 MJ/kg. In UK the biomass species of interest are wood species, willow and poplar and C_4 herbaceous species, switch grass and miscanthus [6].

For a developing country like India demand of energy is increasing tremendously due to which fossil fuels reserves are continuously depleting. So to meet this increasing demand renewable energy sources are the best solution. This paper investigates the main renewable energy sources used for power generation and their availability in various areas of Punjab. Various technologies are discussed to use dry or wet biomass for power generation. For different crop samples collected from different areas of Punjab proximate analysis, gross calorific value and ultimate analysis is done. It was concluded through various technologies that there are mainly two types of biomass conversion technique: thermochemical & biochemical conversion. Thermo chemical conversion techniques include firing, co-firing, gasification & pyrolysis whereas biochemical conversion includes anaerobic conversion & fermentation. In many parts of the world biomass to electricity conversion techniques are used. Calculation of values of moisture content, ash content, fixed carbon and GCV has been done and concluded that biomass is a clean source for producing energy and has same potential to generate electricity [7].

Animal manure, crop residues, municipal solid wastes (MSW), industrial waste water and biomass fuels can be conserved and can be utilized to produce energy through efficiency improvements. In 1997 the total potential energy from these sources is estimated to be around 5.14 EJ which contributes to a little more than a third of total fossil fuel used in India and in 2010 it is analyzed about 8.26 EJ [8].

In this paper monolithic wood structures are converted to carbon that possesses the cellular structure of wood without the formation of cracks and other defects. To manufacture the material a variety of wood species are carbonized and are characterized using TGA, SEM, mechanical testing, density, acoustic velocity, dimensional changes. Through the method of pyrolysis monolithic carbonized wood can be prepared without cracks. Linear relationship was established between the bulk densities of the precursor wood and acoustic velocity ranged from 4.7 ti 7.3 mm/ps and mechanical testing showed carbonized wood to be 28% stronger than the precursor [9].

In this paper production and properties of charcoal has been summarized. Charcoal has many fascinating features such as it contains no necessary and sulphur and contains no mercury and sulphur and contains low nitrogen and ash. Reactivity of charcoal is high but in spite of that it is easy to store & handle. Charcoal can be used as a good absorbent with large surface area. Regarding production new pressurized equipment have been develop to improve the yields of charcoal. Around the world researchers are focusing their attention on manufacturing pyrolytic liquid fuels due to energy crisis [10].

To produce electricity and heat, UK is considerably trying to utilize woody biomass. Using biomass for producing energy is advantageous for environment and consequently reduces carbon emissions. Eucalyptus is well suited for production of biomass but they cannot withstand the climate of UK. But there are some species which can withstand the extreme winter climate of UK. This paper provides information about the constraints for using Eucalyptus as a tool for biomass production in UK and a tentative list of species recommended [11].

Leading producer as well as consumer of charcoal is Brazil around 75% of charcoal is utilized by steel industry. Carbonization processes are basically small-scale technologies with low gravimetric yields. Currently new technologies are being developed and pressurized pyrolysis is one such technique. Recent studies reveal that by using pressure gravimetric yields can be increased by 50% and correspondingly carbonization time is reduced. This paper basically investigates the impact of pressure on the quality of charcoal and this statistical analysis was performed by using random factorial design and general linear system. Eucalyptus grandis at three relative working pressures was used for experimental analysis. Five variables such as charcoal yield, fixed carbon yield, bulk density, and fixed carbon content and gross calorific value were analyzed. The best steel quality charcoal seemed to be obtained with an anhydrous wood at a pressure of 10 bar and temperature of 600°C [12].

Due to global warming we need to use renewable sources of energy rather than fossil fuels for production of energy and biomass can be considered as one of the best alternative for this. Biomass is renewable source of energy and is used for producing electricity as well as can be used as fuel in internal combustion engine. This paper gives information about the conversion process as well as finding a suitable fuel for S.I. engines. To convert biomass into energy two technologies have been employed thermo-chemical & biochemical and for producing liquid fuels use pyrolysis, fermentation & mechanical extraction [13].

Biomass pyrolysis occurred in to step first is low temperature step (T = 360°C) until loss of mass of solid reached around 50% and second step is high temperature step (T>600°C) optimized yielding of charcoal up to 40%. In this paper we investigated thermo gravimetric analysis on eucalyptus and its three constituents i.e. cellulose, xylon and lignin. The experiment was conducted in two steps, first step is slow carbonization with heating rate of 2°C min^{-1}

followed by fast step with heating rate of 100°C min^{-1} and it was found that the char yields from eucalyptus wood increased from 18.8% to 22.8% when there was change in heating rate. Similarly in case of cellulose it increased very slightly but inverse situation occurred in case of xylon so it was concluded that pyrolysis of eucalyptus could not be regarded as the result of sum of the pyrolysis of its constituents [14].

Michael Jerry Antal, Jr. et al. (2003) reviewed methods for improving the yield of charcoal from biomass and found that increase in yield is obtained when the operation is done at elevated pressure in a gaseous environment free from vibration [15].

Sherif S.Z. Hindi analyzed effect of wood material & pyrolytic conditions on bio carbon production. Eucalyptus, Casuania, Tamarisk and Acacia outer and inner zone wood were pyrolyzed in flowing nitrogen atmosphere [16].

Using two different heating-cooling cycles Acacia and Eucalyptus wood were carbonized in the temperature range between 400 and 1200°C. Chemical composition and yielding of char was found to be dependent on carbonization temperature, rate of heating, soaking time and wood species. Higher yield of char was investigated during slow carbonization than rapid carbonization. As compared to the acacia wood char yield was in eucalyptus wood. Under similar carbonization conditions carbon content in eucalyptus wood char is higher as compared to Acacia wood char and the thus Eucalyptus wood is having a higher lignin content [17].

Lisardo Numez Reguieus et al. determined calorific values of forest waste biomass by static bomb calorimetry. Wastes originating from forests are collected and their calorific values are measured by static bomb caloriemetry and these waste materials are utilized to be used as an

alternative fuel. This paper analyses about two forest species Eucalyptus and Pine. Since the calorific values are exceeding 20000 KJ Kg^{-1}, these materials can be used as alternative fuels [18].

Changdong sheng et al. estimated the higher heating value of biomass fuels from basic analysis data. For design calculations or numerical simulations heating value is one of the most primary properties. Higher heating values of biomass fuel were estimated using proximate, ultimate and chemical analysis and it was concluded that correlations based on ultimate analysis has the highest accuracy [19].

M. kumar et al. studied the influence of carbonization conditions and wood species on CO_2 reactivity of resultant wood char powder. By using thermogravimetric analysis measurement of CO_2 reactivity's of powdered samples of Acacia and Eucalyptus have been done and the effects of carbonization conditions were determined on these samples. It was concluded that Acacia wood chars shows higher reactivity [20].

Mithlesh kumar et al. analyzed the influence of carbonization conditions on the gasification of acacia and eucalyptus wood chars by Co_2 gas. Using thernmogravimetric analysis gasification rates of acacia and eucalyptus wood chars were measured in carbon dioxide environment. Carbonization condition and effects of wood species were determined. Carbonization conditions such as temperature, heating rate and soaking time strongly influenced the reactivity and the activation energy of both acacia and eucalyptus wood chars. It was concluded that reactivity of acacia wood chars are higher as compared to eucalyptus wood chars [21].

Nestor Tancredi investigated CO_2 gasification of eucalyptus wood chars produced at different carbonization temperature. Eucalyptus grandis wood chars were gasified with CO_2 in thermo gravimetric experiments using isothermal & non-isothermal conditions. Reactivity at low and high temperature was observed and it was found that at low temperature, reactivity can be explained in terms of development of surface due to gasification area whereas at high temperature a steep increase is observed which is due to the catalytic effect of metallic constituents. Activation energies are found in the range of 230-261 KJ mol^{-1} [22].

Nicholas Standish et al. analyzed gasification of single wood charcoal particles in CO_2. The primary features of the gasification of wood charcoal particles in the environment of CO_2 gas has been studied using Kinetic studies and SEM analysis. The variables which were investigated during the studies are particle size (10-34mm), Temperature (900-1100°C), gas concentration (20-100% of CO_2), and Gas velocity (1-9cm /s). Shrinkage core –reaction model was used for the overall gasification process and relationship was investigated for the rate of gasification as a function of variables [23].

M. kumar et al. studied the influence of carbonization conditions on physical properties of acacia and eucalyptus wood chars. The manner in which physical properties of Acacia and Eucalyptus wood are changing is studied using apparent and true specific gravities in both of the species specific gravity is increasing with increase of heat treatment. It was found that under slow carbonization Eucalyptus wood chars have lower porosity and high apparent specific gravity as compared to Acacia under similar conditions [24].

Gulham Oz baygoolgu predicted a new approach for the ash fusion temperatures. With the use of chemical composition, determination of ash fusion temperatures has been previously

conducted. New technique has been discussed in this paper for predicting fusibility temperatures. By using chemical composition and coal parameters non-linear correlations are developed. Regression coefficients and variances are compared of linear and non-linear correlations. It has been concluded that for estimating ash fusion temperatures non-linear correlations are superior as compared to linear correlations [25].

Chapter 3

EXPERIMENTAL WORK

3.1 SELECTION OF MATERIAL

- Eucalyptus wood was collected from the local area and their different components like wood, branch, leaves and bark were separated for further procedure.
- Separated components were then air dried for around fifteen days.

3.2 PROXIMATE ANALYSIS

Proximate Analysis consists of determination of ash, moisture, fixed carbon and volatile matter contents were carried out on different components of eucalyptus tree and wood chars ground to fine powder of -72 mess size as per Indian standard method [26]. Following are the details of this analysis:

3.2.1 Moisture content determination

One gram of air dried powdered sample was taken in borosil glass crucibles and kept in furnace at temperature of 105°C ± 5°C for 1 hour. Then the crucibles were taken out of the oven and the samples were weighed. The loss in weight expressed as moisture content in the sample.

*%moisture = loss in weight *100/Wt. of sample taken*

3.2.2 Volatile Matter content

One gram of air dried powdered (-72 mess size) sample was taken in crucible. The crucible is covered with silica lid. Then crucible was kept in a furnace for 7 minute at the temperature of 925°C ± 5°C. The crucible was then taken out from the furnace and allowed to cool in air. The % volatile matter content in the sample was calculated by using the formula given below:

% volatile matter = % loss in weight - % moisture

3.2.3 Ash Content determination

One gram of air dried powdered sample was taken in a shallow disc of silica and kept in furnace at the temperature of 770°C ± 10°C. The samples were heated at this temperature till complete burning. The percentage ash content in the sample is calculated by the following formula:

$$\% \text{ Ash} = (\text{Wt. of residue obtained} / \text{Initial wt. of simple}) \times 100$$

3.2.4 Fixed Carbon determination

The fixed carbon content in the simple was determined by using the formula given below:

$$\% \text{ Fixed Carbon} = 100 - (\% \text{ Moisture} + \% \text{ Volatile Matter} + \% \text{ Ash})$$

3.3 ULTIMATE ANALYSIS

The ultimate analysis of eucalyptus wood samples giving carbon, hydrogen and nitrogen contents were carried out with a C-H-N analyzer. All the experiments were carried out at Punjab technical university, Chandigarh through my personal contacts.

3.4 CALORIFIC VALUE DETERMINATION

The calorific values of the samples were measured as per Indian standard method [27] by using Oxygen bomb calorimeter (shown in Fig.2). For the determination of the calorific value pellets are prepared from the fine powder of the different component. These pellets were taken in a crucible. A 15 cm long cotton thread was placed over the pellet in the bomb to facilitate in the ignition. Both the electrodes of the calorimeter were connected by a fuse wire. Oxygen gas was supplied in the bomb at a pressure of around 25kgf/cm^2. The water (2 litre) in

the bucket was continually starred to homogeneous the temperature. The sample was ignited by switching on the current through the fussed wire and the rise of temperature was noted down after every one minute till the attainment of maximum temperature. To calculate the calorific value of the sample formula given below is used.

Gross calorific value (GCV) = [{1987 × (ΔT+.04)} / (Initial wt. of simple)]

Where, 1987 kcal/°C is the water equivalent and,

ΔT is the difference between maximum and minimum temperature.

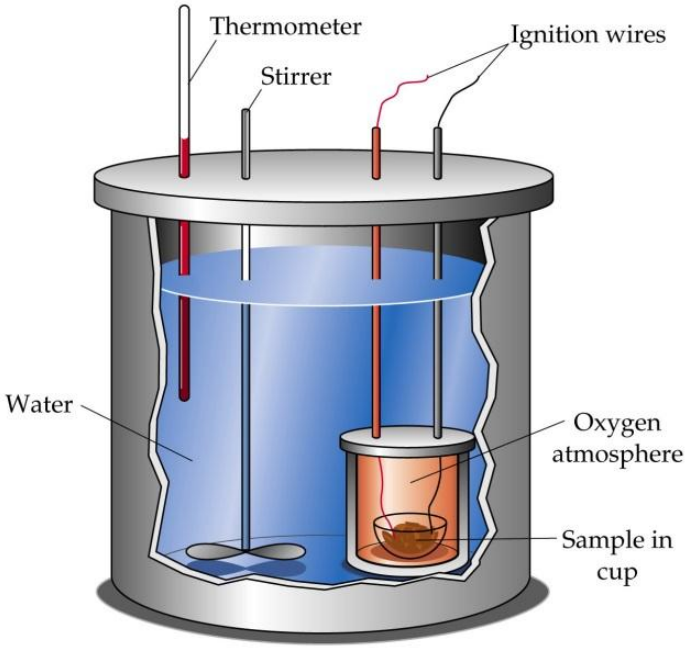


Fig. 2 Oxygen Bomb calorimeter

3.5 ASH FUSION TEMPERATURE DETERMINATION

The ash fusion temperature test consists of four different characteristics i.e., Initial deformation temperature (IDT), Softening Temperature (ST), Hemispherical temperature (HT) and Flow temperature (FT) of all the ash samples obtained from different components of Eucalyptus tree selected were determined by using Leitz Heating Microscope (shown in Fig. 3).

Ash samples obtained from different components of eucalyptus tree were taken and cubes of about 3 to 4 milligram was prepared and prepared sample was heated in a heating microscope at the heating rate of 10ºC $min^{-1}$and maximum temperature up to 1600ºC [28]. The temperature at which initial shrinkage in the shape was observed was noted down i.e. known as initial deformation temperature (IDT). Heating was continued till rounding of corners of prepared sample was observed and that temperature was noted down i.e. known as Softening temperature (ST).There after cubic sample was changed into hemisphere at a temperature, that was also noted down this temperature is known as hemispherical temperature (HT). Finally, this hemispherical form of sample flow as fluid and this temperature was temperature is known as flow temperature (FT). The shapes of ash samples at four different characteristics are shown in Fig.4.

Fig. 3 Leitz Heating Microscope

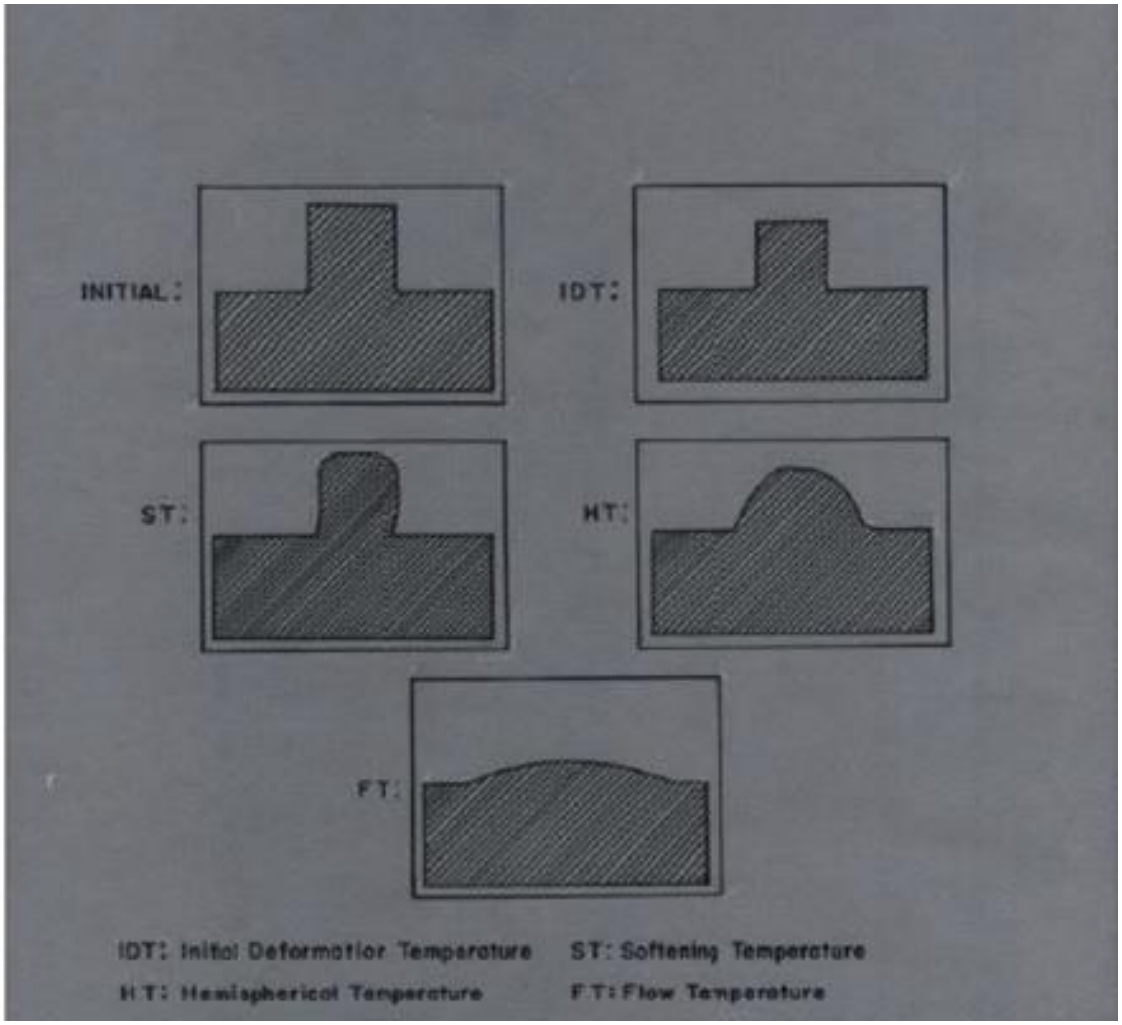


Fig. 4 Shapes of Ash Samples at Four Different Characteristics of Ash Fusion Temperature

3.6 APPARENT DENSITY AND APPARENT POROSITY DETERMINATION

Apparent density and apparent porosity of eucalyptus wood and chars samples were determined by using hot boiling water method [29]. A sample of 10-15 mm size was dried in an air oven at a temperature of 110°C ± 5°C and the weight of this dried sample is taken. This dried sample is suspended or hanged in hot boiling water with the help of thread and metal stand. The sample is kept in the hot water for around 20 minutes. Now the suspended weight of sample plus thread while immersed in water is recovered in a chemical weighing balance. The

sample is then removed from the thread and the weight of the thread only while immersed in water is recorded. Finally the weight of water saturated sample is taken in air and the below mentioned formulae are used to determine the apparent density and apparent porosity of wood.

$$\text{Apparent density} = D/ \{D-(S-s)\}$$

$$\text{Apparent porosity} = (W-D)*100/ \{D-(S-s)\}$$

Where, D = dried weight of wood sample

W = weight of water saturated sample in air

S = suspended weight of sample + thread while immersed in water

s = suspended weight of thread only while immersed in water

3.7 CARBONIZATION OF EUCALYPTUS WOOD

Chars were prepared by carbonization of the weighted amount of cubic shaped of Eucalyptus wood samples at four different temperatures like 400, 600, 800 and 950°C for different time periods, such as 1, 2 and 3 hours under two different heating rates of slow (7°C min^{-1}) and rapid (30°C min^{-1}) heating. For slow carbonization, air dried pieces of wood samples was placed in a stainless steel retort (130×38 mm) and closed with a lid and having an outlet for the exit of the volatile matter. The steel retort was then kept in a furnace and heated from room temperature to the carbonization temperature of 400, 600, 800 and 950°C. After attaining the final temperature, the samples were soaked for 1 hour and then allowed to cool in the furnace. For rapid carbonization, the air-dried eucalyptus wood pieces were taken in a stainless steel retort which was then kept in a furnace maintained at the predefined carbonization temperature of 400, 600, 800, and 950°C. The container was kept in the furnace for one hour soaking time

and then taken out and cooled in air. For the influence of soaking time on char yield and their properties, the eucalyptus wood samples were carbonized slowly at 800°C and 950°C with different soaking period i.e. 1, 2 and 3 hours.

3.8 DETERMINATION OF REACTIVITY OF CHARS TOWARDS CO_2

The set up for determination of reactivity is shown in Fig. 5. The reactivity of wood char was measured as per Indian standard [30]. The reaction tube (Quartz Tube) is made of transparent silica of 25mm (inside diameter). A eucalyptus wood char sample of 5 gm. of -16 and +500 micron size is taken in the quartz tube, sealing both ends of sample. The tube is so kept in the furnace that the sample is in the uniform temperature zone and the nitrogen gas is passed at the rate of 50c.c. min^{-1} and the test sample is preheated to 1000°C ± 50°C. After the temperature has stabilized carbon dioxide gas is passed at the rate of 100c.c. min^{-1} for 25 minutes. After completion of 25 minutes, carbon dioxide flow is stopped and instead nitrogen gas is passed at the rate of 50cc min^{-1} until the temperature of reacted sample is brought down to 150°C. While passing nitrogen care should be taken that no ash particle is blown off from the quartz tube. The remaining sample is then taken out and weighed. The below mentioned formulae are used to calculate the reactivity of different char samples.

$$\text{Reactivity} = 11.61*W/ (5*C_{fix} - W/2) \text{ c.c. /gm. Sec.}$$

Where, W = weight loss or reacted part of sample

C_{fix} = fixed carbon content of the char.

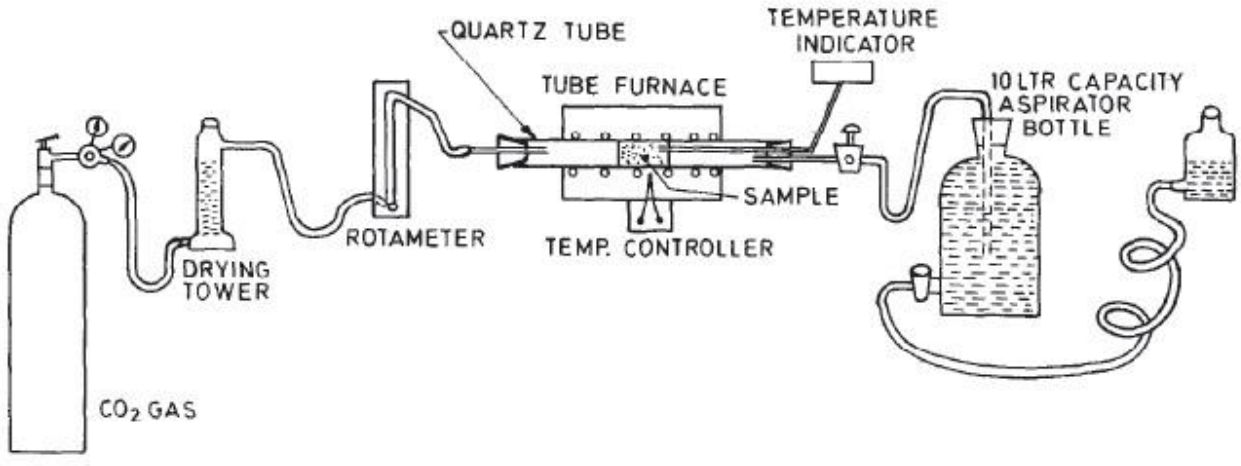


Fig. 5 Apparatus for determination of reactivity of wood char towards CO_2

3.9 X-RAY DIFFRACTION STUDIES

X-Ray Diffraction machine is a very useful device to characterise materials for the following information such as phase analysis (elemental phase/ inter-metallic phase/ crystalline phase/ non-crystalline phase) , lattice parameter determination, strain determination, texture and orientation analysis, order- disorder transformation. A phillips Pan analytical PW3040/00 X-ray diffractometer was used to characterise the ashes of different components of Eucalyptus tree. The scanning range of 2θ was from 20° to 80° with a scanning speed of 2° min^{-1} and accelerating voltage of 30 KV. The peak was analysed by using X-pert high score software to identify different types of phases.

Chapter 4

RESULTS & DISCUSSION

4.1 CHARACTERIZATION OF THE PROPERTIES OF DIFFERENT COMPONENTS OF EUCALYPTUS TREE:

The physical and chemical properties of different components of Eucalyptus tree such as wood, leaves, bark and branch have been summarized in Table 4.The Proximate Analysis of the different component of Eucalyptus reveals that the biomass components have a very low ash content compared to that of coal. It is also found that the moisture content of the biomass is very low that is less than 12 % and studies reveal that it can be further reduced to a very low level of around less than 3% through air drying in the sun and oven drying. Ash content and the moisture content are the most undesirable component of a fossil fuel and since Eucalyptus possesses a very low ash and moisture content and hence it can be used economically in place of fossil fuels.

Calorific values in Table 4 clearly indicate that among the different studied Eucalyptus components, Stump and leaves have the highest energy values. The pattern of variation of calorific value in the components like stem, bark, leaves and trunk is not identical for all the presently studied biomass species. The elements which are responsible for imparting calorific value to the fuel are carbon, hydrogen and sulphur. The calorific values of carbon; hydrogen and sulphur are 8,080 K cal/kg, 34,500 K cal/kg, and 2,200 K cal/kg respectively. Therefore variations in calorific values of these four components are clearly due to the difference in the contents of these elements.

From the above results it is found that eucalyptus have very high volatile matter content, low ash content, appreciable calorific value. It can be economically used in Iron Making by converting into charcoal, i.e. its carbon content can be improved by carbonization.

Table 4: Proximate analysis and heating values of different components of Eucalyptus tree

Component	Proximate Analysis (Wt.%, air-dried basis)				Calorific value (Kcal/Kg)
	Moisture	Ash	Volatile Matter	Fixed Carbon	
Wood	9	7	77	7	4653.76
Branch	11	6	76	7	4024.94
Bark	11	9	70	10	3900.40
Leaf	12	6	78	4	4576.12
Lingraj mines coal [31]	8.9	41.2	21.7	29	4237

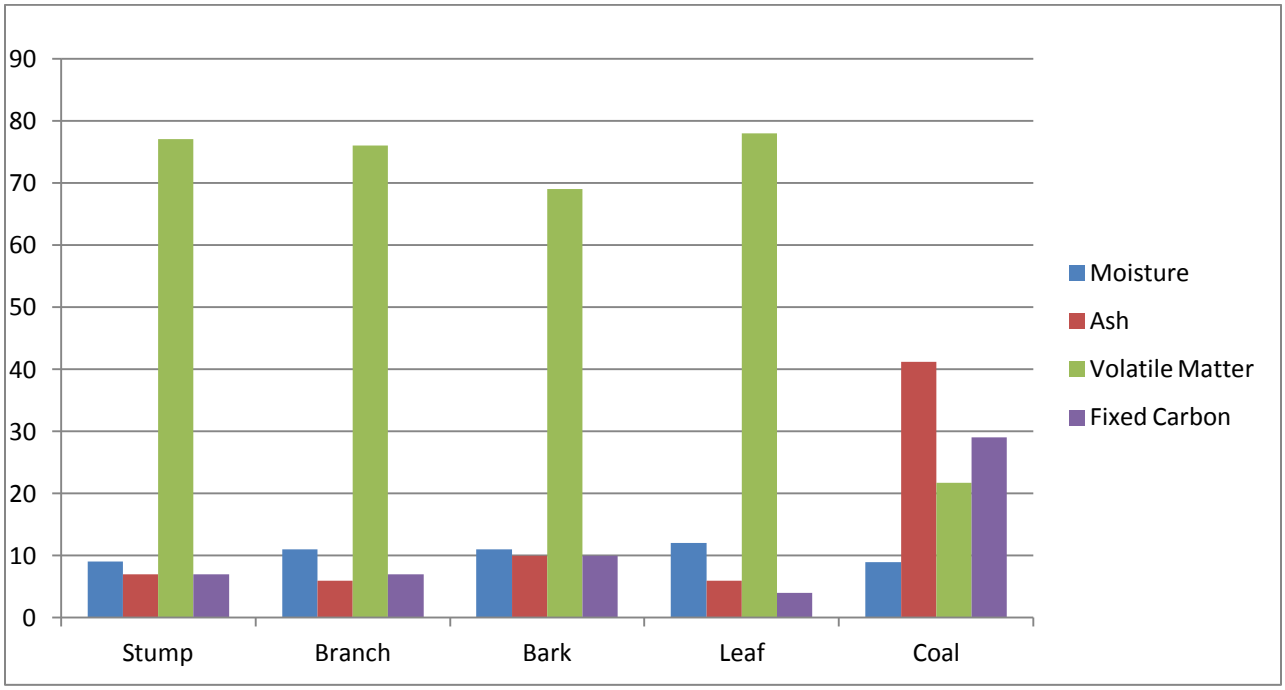


Fig. 6 Variation of Proximate Analysis of different components of Eucalyptus

Table 5: Chemical composition and physical properties of Eucalyptus wood

Component	Ultimate analysis (Wt.%, dry basis)					Apparent density	Apparent porosity (%)
	C	H	S	N	O		
Eucalyptus wood	50.12	6.12	ND	Nil	43.76	1.3144	50.56

4.2 CARBONIZATION OF WOOD SAMPLES UNDER DIFFERENT CONDITIONS SUCH AS TEMPERATURE, HEATING RATE, AND SOAKING TIME:

Table 6: Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization at 1 h soak

Carbonization Temperature	Soaking time (hours)	% Char yield	Proximate analysis (Wt.%, air-dried basis)				Calorific value (Kcal/Kg)
			Moisture	Ash	Volatile Matter	Fixed Carbon	
400	1	24.56	6	6	34	54	6402
600	1	17.20	9	6	30	55	6348
800	1	15.48	10	7	20	63	6897
950	1	14.58	10	7	19	64	6900

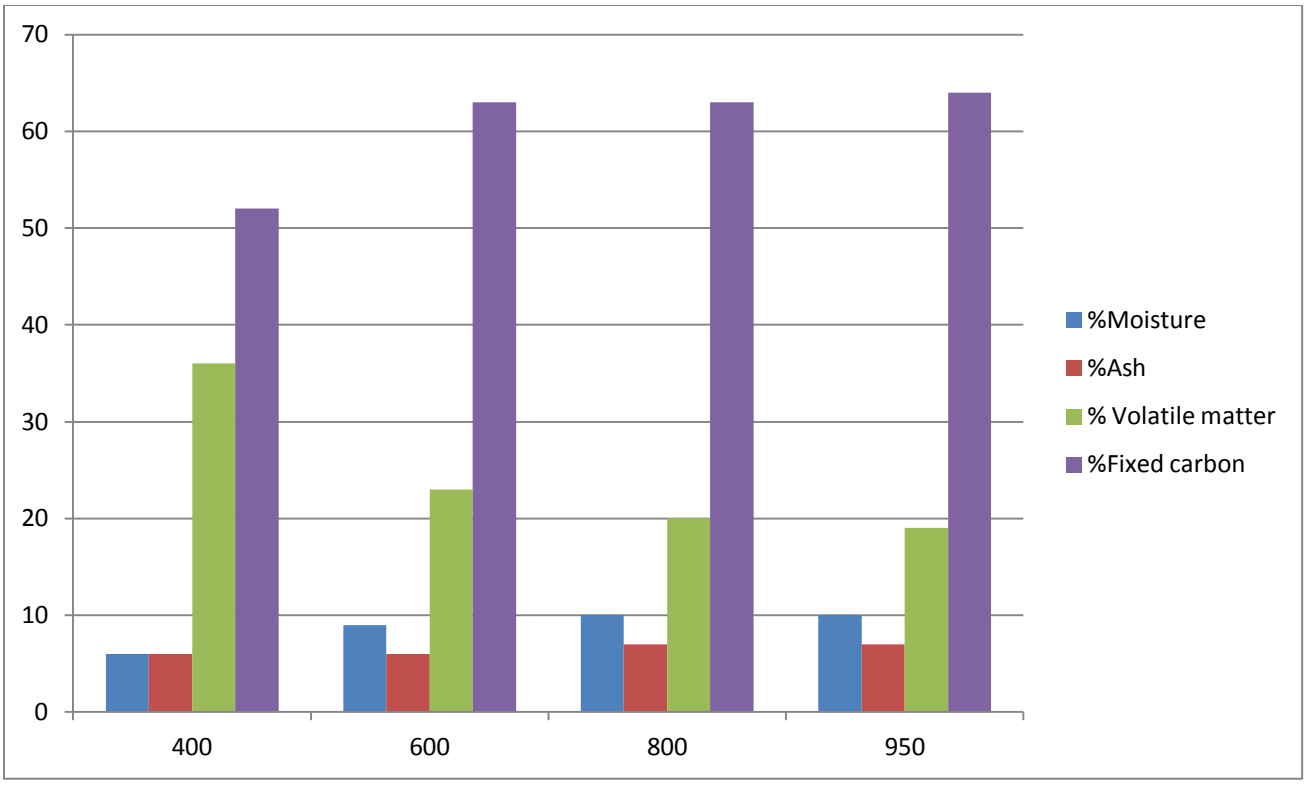


Fig. 7: Variation of Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization

Table 7: Proximate Analysis of chars obtained from Eucalyptus wood under rapid carbonization

Carbonization Temperature	Soaking time (hours)	% Char yield	Proximate analysis (Wt.%, air-dried basis)				Calorific value (Kcal/Kg)
			Moisture	Ash	Volatile Matter	Fixed Carbon	
400	1	23.48	6	6	35	53	6621
600	1	15.03	9	7	15	69	6341
800	1	13.33	10	8	12	70	6845
950	1	12.97	10	8	11	71	6754

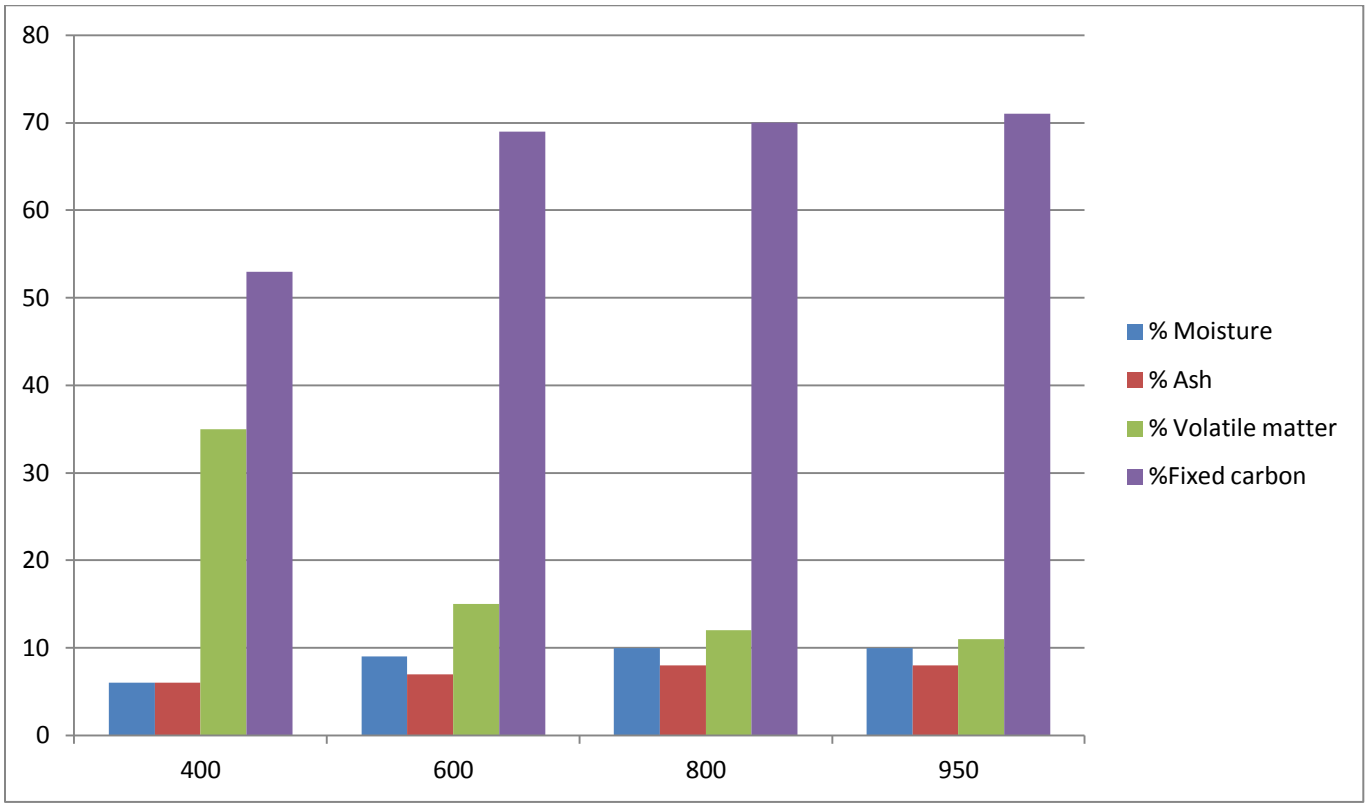


Fig. 8: Variation of Proximate Analysis of chars obtained from Eucalyptus wood under rapid carbonization

Table 8: Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization for different time periods and a temperature of 800°C

Carbonization Temperature	Soaking time (hrs)	% Char yield	Proximate analysis (Wt.%, air-dried basis)			
			Moisture	Ash	Volatile Matter	Fixed Carbon
800	1	15.48	10	7	20	63
800	2	15.23	11	6	13	70
800	3	14.98	11	6	12	71

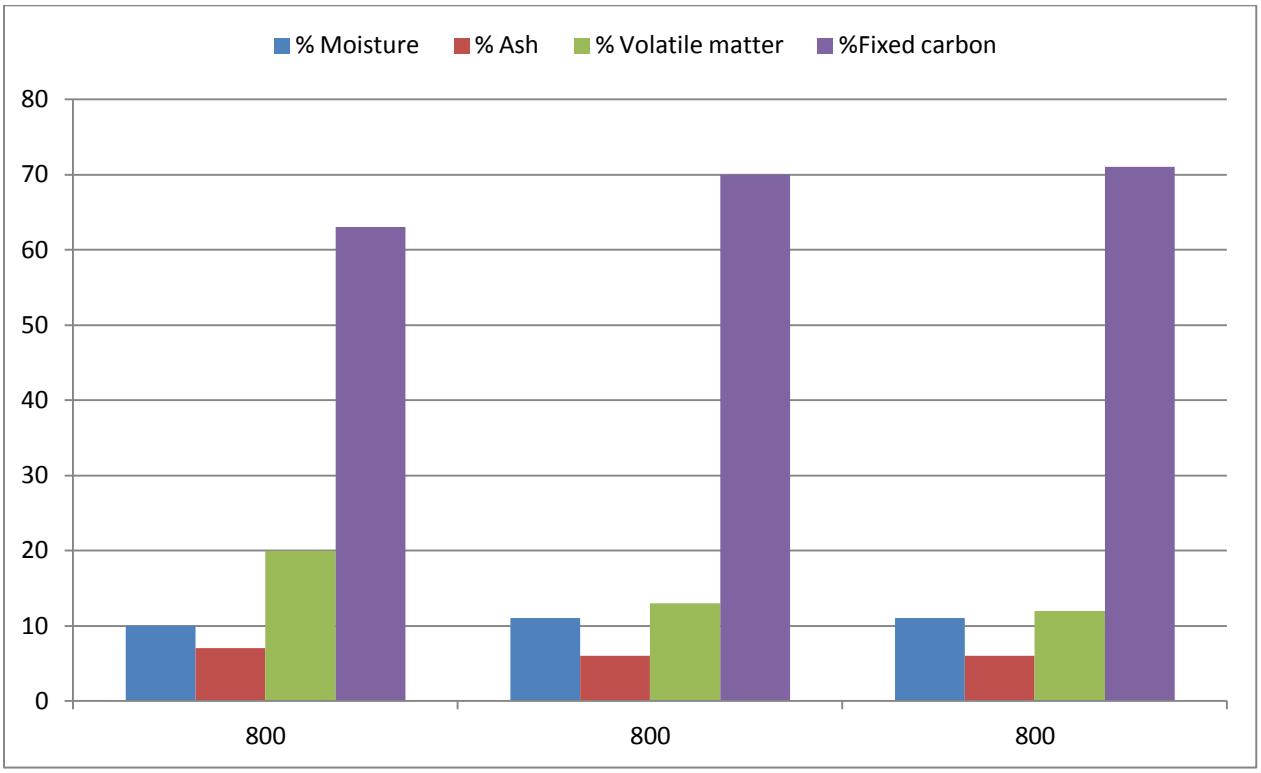


Fig. 9: Variation of Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization for different time periods and a temperature of 800°C

Table 9: Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization for different time periods and a temperature of 950°C

Carbonization Temperature	Soaking time (hours)	% Char yield	Proximate analysis			
			Moisture	Ash	Volatile Matter	Fixed Carbon
950	1	14.58	10	7	19	64
950	2	14.21	11	6	13	70
950	3	13.92	11	6	12	71

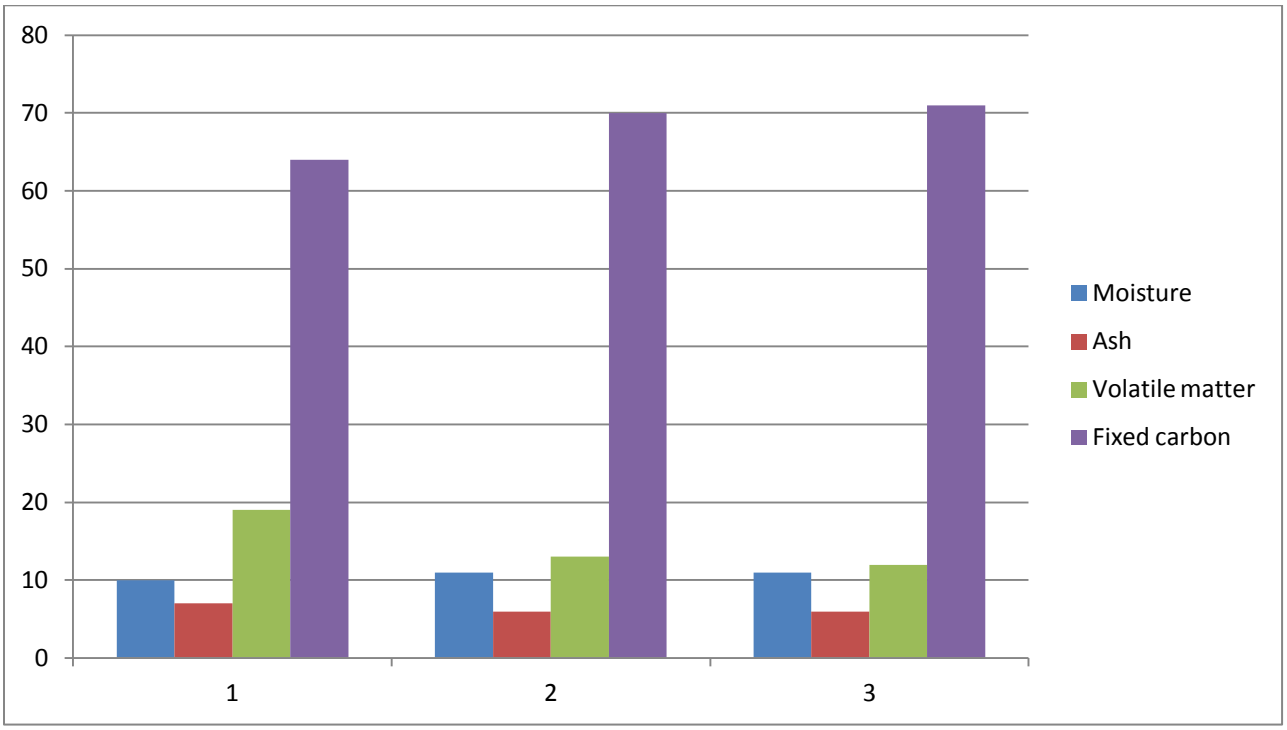


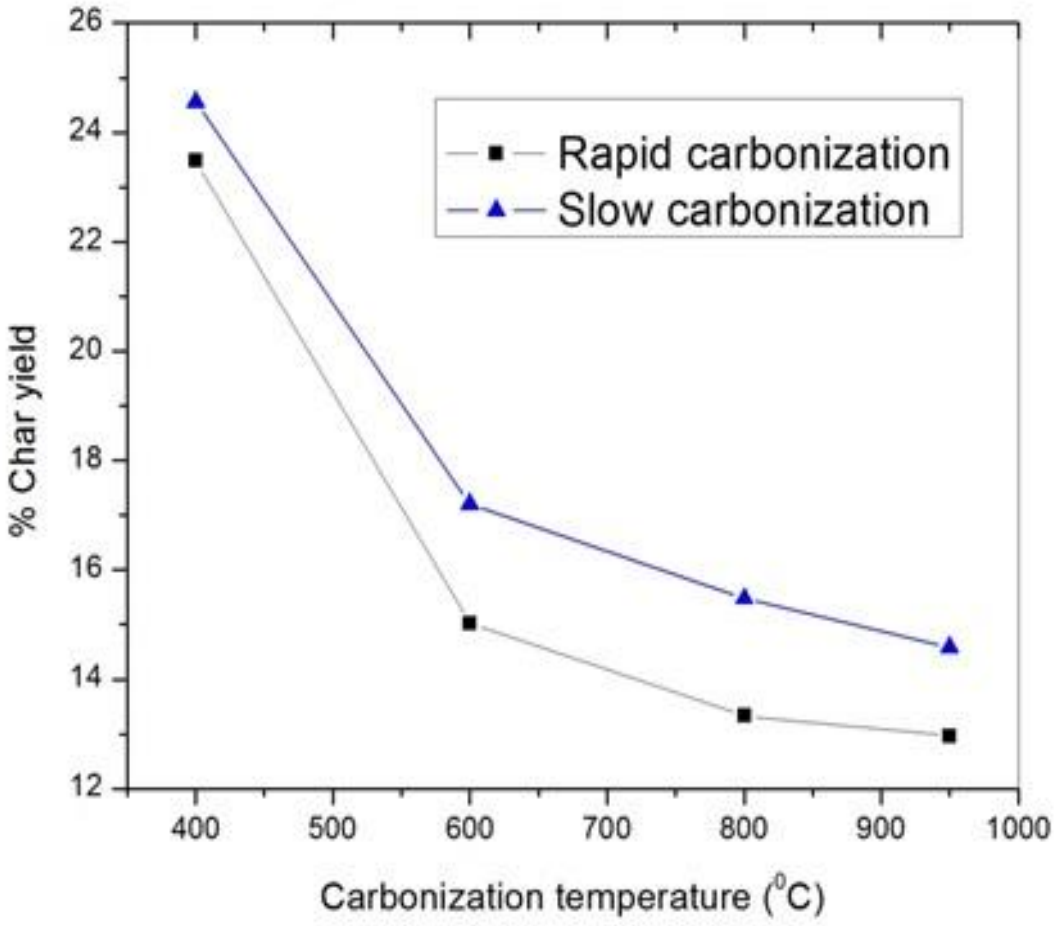
Fig. 10: Variation of Proximate Analysis of chars obtained from Eucalyptus wood under slow carbonization for different time periods and a temperature of 950°C

Table 10: Ultimate analysis of Eucalyptus wood char under different carbonizing conditions

Carbonization conditions			Ultimate analysis (% dried basis)				
Carbonization temperature (°C)	Heating rate	Soaking time (hours)	C	H	S	N	O
800	slow	1	86.23	Nil	ND	Nil	13.77
950			85.12	Nil	ND	Nil	14.88
800	rapid		89.67	Nil	ND	Nil	10.33
950			85.65	Nil	ND	Nil	14.35
800	slow	2	90.27	Nil	ND	Nil	9.73
950			88.97	Nil	ND	Nil	11.03

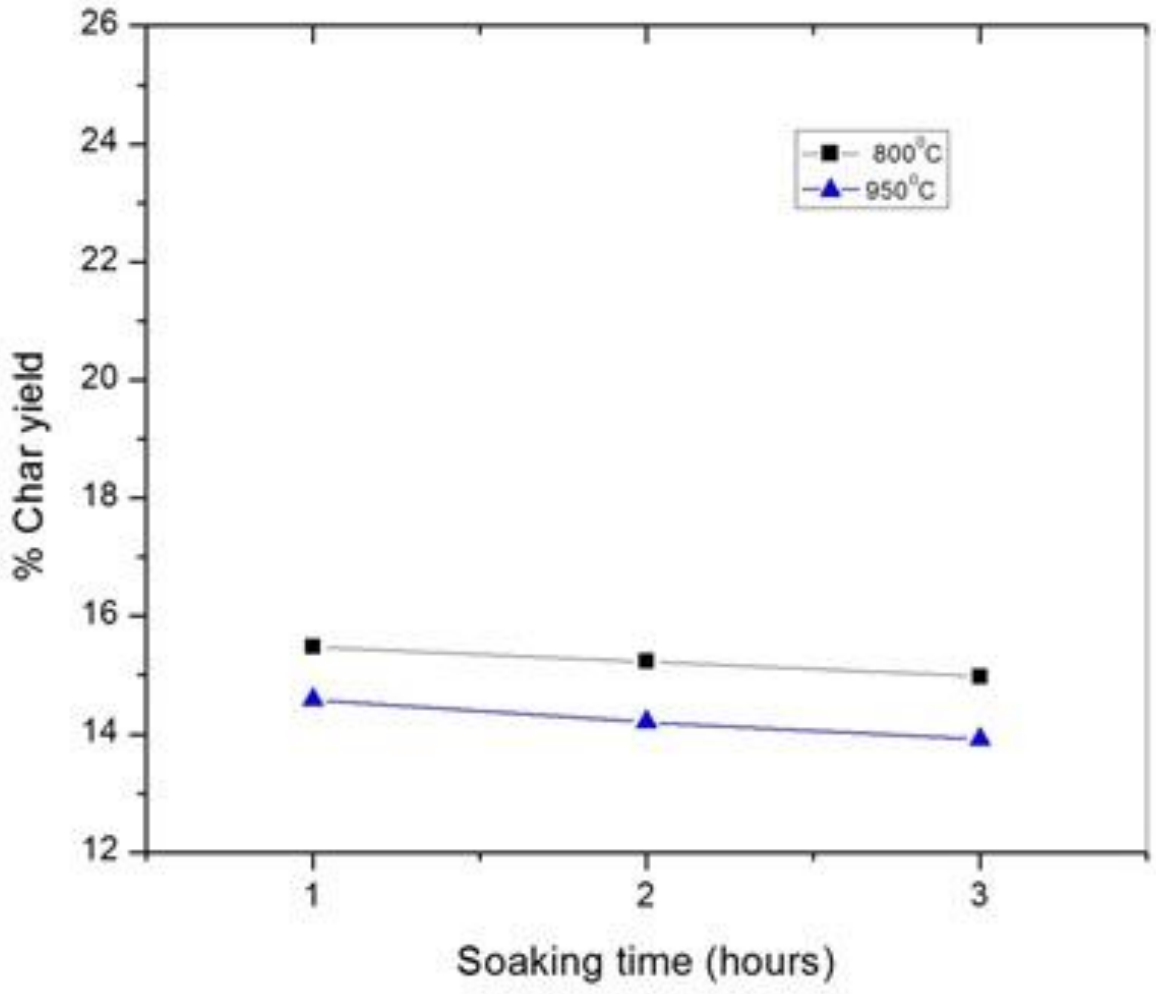
4.2.1 EFFECTS OF DIFFERENT CARBONIZATION CONDITIONS ON CHAR YIELD:

The results obtained for the wood char yield at different carbonization temperature under different heating rate i.e. slow and rapid have been outlined in Table 2 & 3. Also, Table 4 & 5 shows the char yield at 800°C and 950°C under slow heating rate at different soaking time. From the Fig.11 it can be seen that the %char yield decreases gradually with increasing carbonization temperature. It is due to the removal of volatile matter. This decrease in char yield is more rapid up to temperature 800°C where most of the volatile matter was removed.



Fig, 11: Graph plotted between % Char yield Vs Carbonization temperature at different heating rate

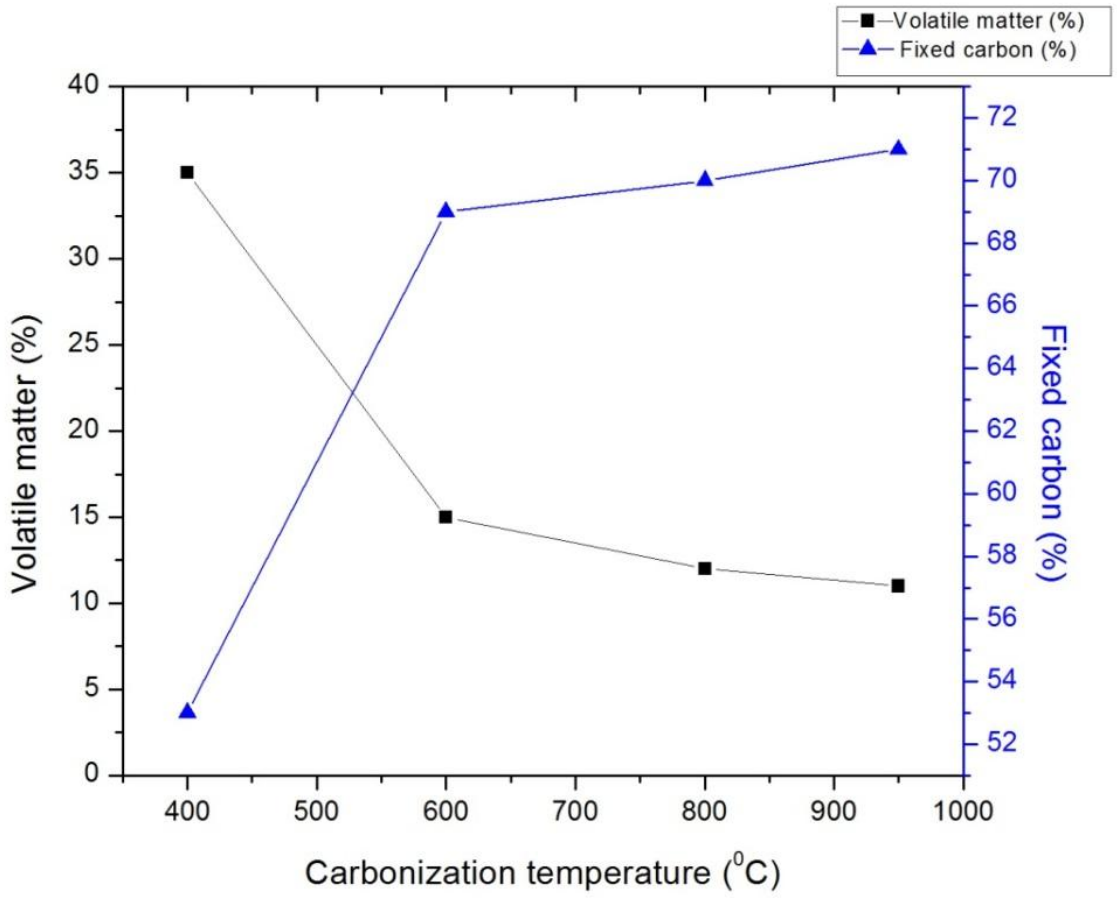
Also, as heating rate increases, char yield decreases. It is due to the removal of volatile matter higher rate and providing less time for the deposition of carbon. It is evident from the Fig. 12 that with increase in soaking time from 1 to 3 h there is only marginal decrease in char yield. It means increasing soaking time above 1 hr at 800°C and 950°C leads to very little loss of volatile matter.



Fig, 12: Graph plotted between % Char yield Vs soaking time at different carbonization temperature

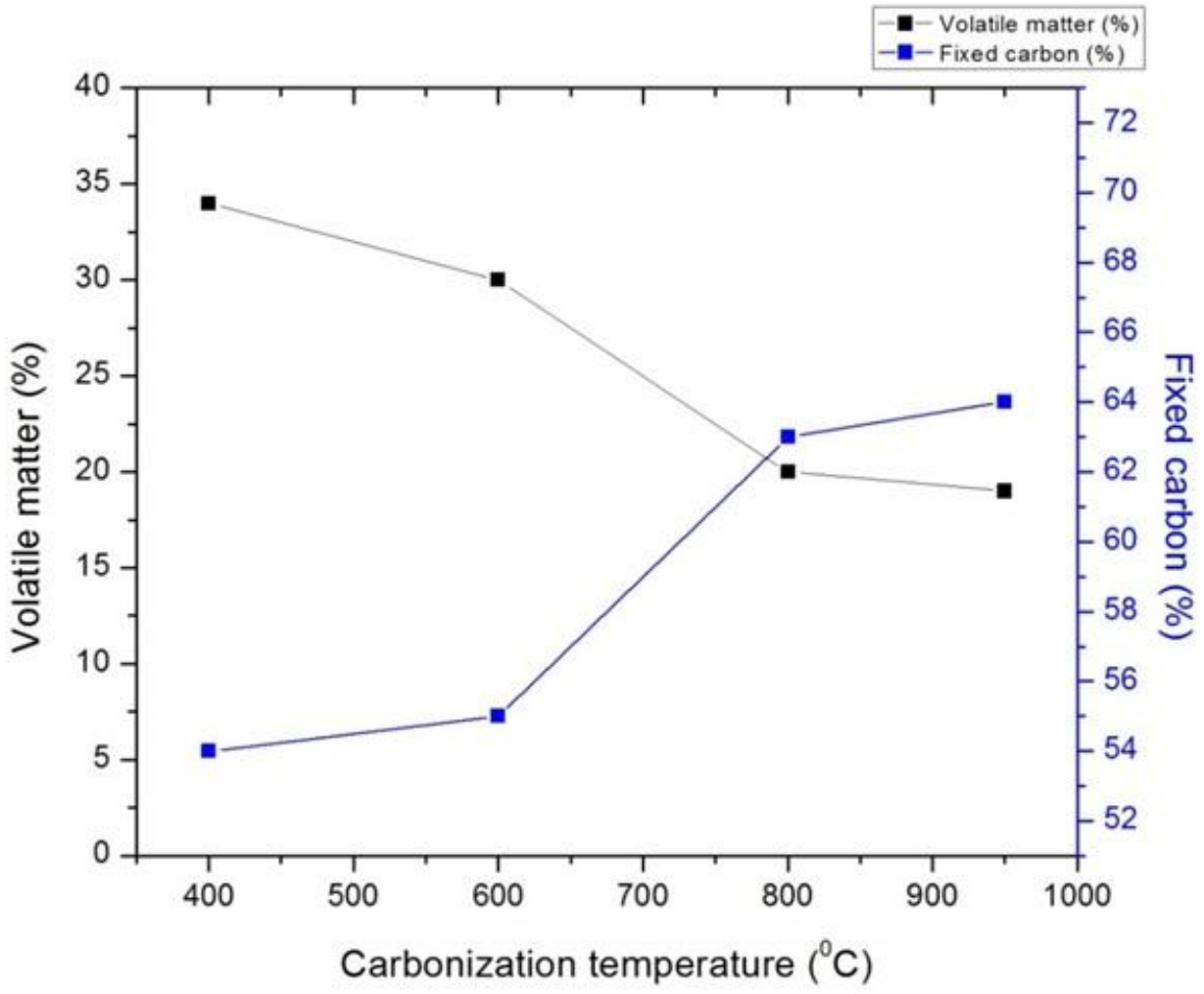
4.2.2 EFFECTS OF DIFFERENT CARBONIZATION CONDITIONS ON CHEMICAL COMPOSITION OF EUCALYPTUS WOOD CHARS OBTAINED:

The results obtained for chemical composition of wood chars yield at different carbonization temperature under different heating rate i.e. slow and rapid have been outlined in Table 2 & 3. Also, Table 4 & 5 shows the chemical composition of wood char yield at 800°C and 950°C under slow heating rate at different soaking time. From the Fig. 13 it can be seen that fixed carbon content of eucalyptus wood chars increases gradually with increase in carbonization temperature while volatile matter content decrease.



Fig, 13: Graph plotted between Carbonization temperature Vs Volatile matter and fixed carbon content of chars at under slow carbonization

In Fig. 14, a graph was plotted between carbonization temperature and volatile matter and fixed carbon content of chars under rapid carbonization. It is evident from the Fig. 14 that fixed carbon content under rapid carbonization is lower compare to slow carbonization.



Fig, 14: Graph plotted between Carbonization temperature Vs Volatile matter and fixed carbon content of chars under rapid carbonization

4.2.3 EFFECT OF DIFFERENT CARBONIZATION CONDITIONS ON PHYSICAL PROPERTIES OF WOOD CHARS OBTAINED

The results obtained for apparent density and apparent porosity of wood chars prepared under different heating rate have been outlined in Table 10. It is clear from the results that the apparent porosity of wood charcoals, in general, increased with increase in carbonization temperature. The increase in apparent porosity of carbonized eucalyptus wood with temperature is due to volatile matter release and formation of voids and cracks.

The results, as shown in Fig. 15, indicates that heating rate of carbonization has significant effect on the apparent porosity of the wood charcoals. The apparent porosity of charcoals prepared under rapid carbonization is higher than that of charcoals prepared under slow carbonization because in rapid carbonization amount of carbon deposited is less than that in slow carbonization process.

Table 10: Physical properties of wood chars prepared under different carbonization conditions.

Carbonization conditions			**Apparent Density**	**Apparent Porosity (%)**
Carbonization temperature (°C)	**Heating rate**	**Soaking time (hours)**		
400	slow	1	1.29	58.92
600			1.26	66.31
800			1.27	64.45
950			1.24	68.60
400	rapid		1.26	62.36
600			1.23	68.12
800			1.22	69.32
950			1.20	70.1

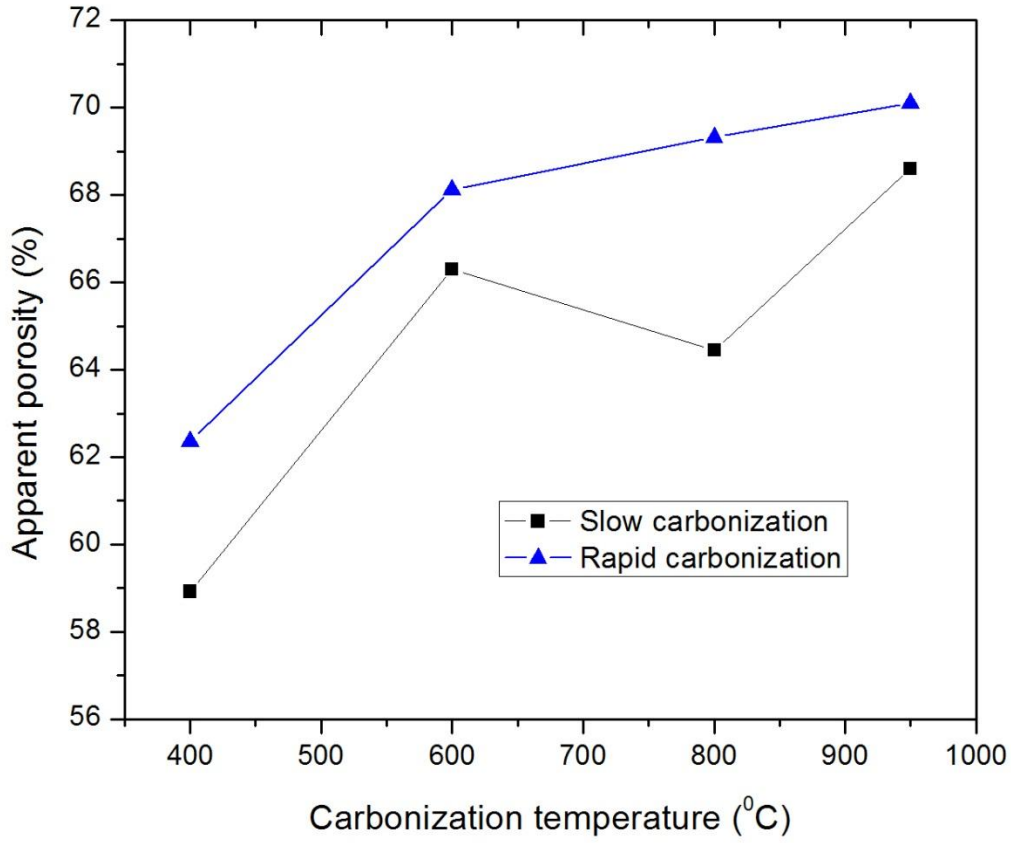


Fig. 15 Graph plotted between apparent porosity Vs Carbonization temperatures under different heating rate

4.2.4 EFFECT OF DIFFERENT CARBONIZATION CONDITIONS ON REACTIVITY TOWARDS CO_2 OF WOOD CHARS

The results obtained for the reactivity of wood chars towards CO_2 have been outlined in Table 11. For better reduction of iron-ore, reactivity should be high. As evident from the results, with increase in carbonization temperature, reactivity of wood char decreases marginally up to 800°C after that there is a substantial decrease in reactivity. The reason behind this

decrease in reactivity is the increase in structural ordering of carbon matrix which is by the results of hydrogen gas release which ends at 800°C.

In Fig 16, a graph is plotted between carbonization temperature and reactivity at different heating rate. It can be seen in Fig. 16, that reactivity of chars prepared under rapid carbonization is higher than that of the chars prepared at slow carbonization. The reason behind this is the defective carbon mono crystallites having active carbon sites in them which occur due to rapid heating and cooling of chars [32].

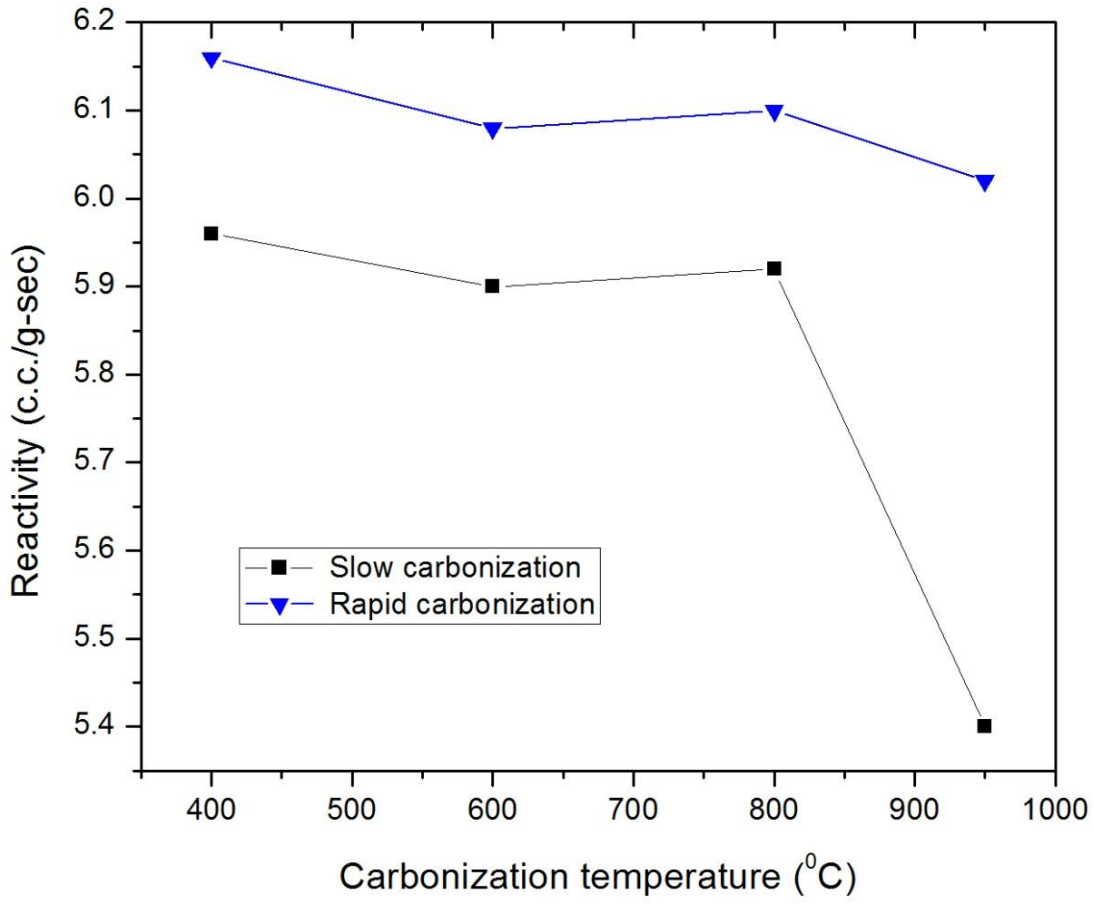


Fig.16. Graph plotted between Reactivity Vs Carbonization temperatures at different heating rate

Table 11: Reactivity values of wood chars prepared under different carbonization conditions.

Carbonization conditions			Reactivity
Carbonization temperature (°C)	**Heating rate**	**Soaking time (hours)**	**(c.c./g-sec)**
400	slow	1	5.96
600			5.90
800			5.92
950			5.40
400	rapid		6.16
600			6.08
800			6.10
950			6.02

4.4 STUDIES ON ASH FUSION TEMPERATURE OF DIFFERENT COMPONENTS OF EUCALYPTUS TREE:

The results obtained for the ash fusion temperatures (IDT, ST, HT & FT) of different components of Eucalyptus tree have been outlined in Table 12. As shown in the Table 12, the IDT, ST, HT & FT of leaf were found to be maximum followed by bark, branch & stump respectively. The ash fusion temperatures are related to the chemical compositions of ashes. Higher ash fusion temperatures indicate the presence of higher concentration of refractory oxides. Higher the ash fusion temperatures, greater is the prefer ability of the material for industrial ashes.

Table 12: Ash fusion temperature of different components of Eucalyptus

Component	Ash fusion temperatures (°C)			
	IDT	ST	HT	FT
Wood	1185	1211	1351	1383
Branch	1209	1245	1322	1380
Bark	1202	1278	1321	1391
Leaf	1358	1378	1425	1438

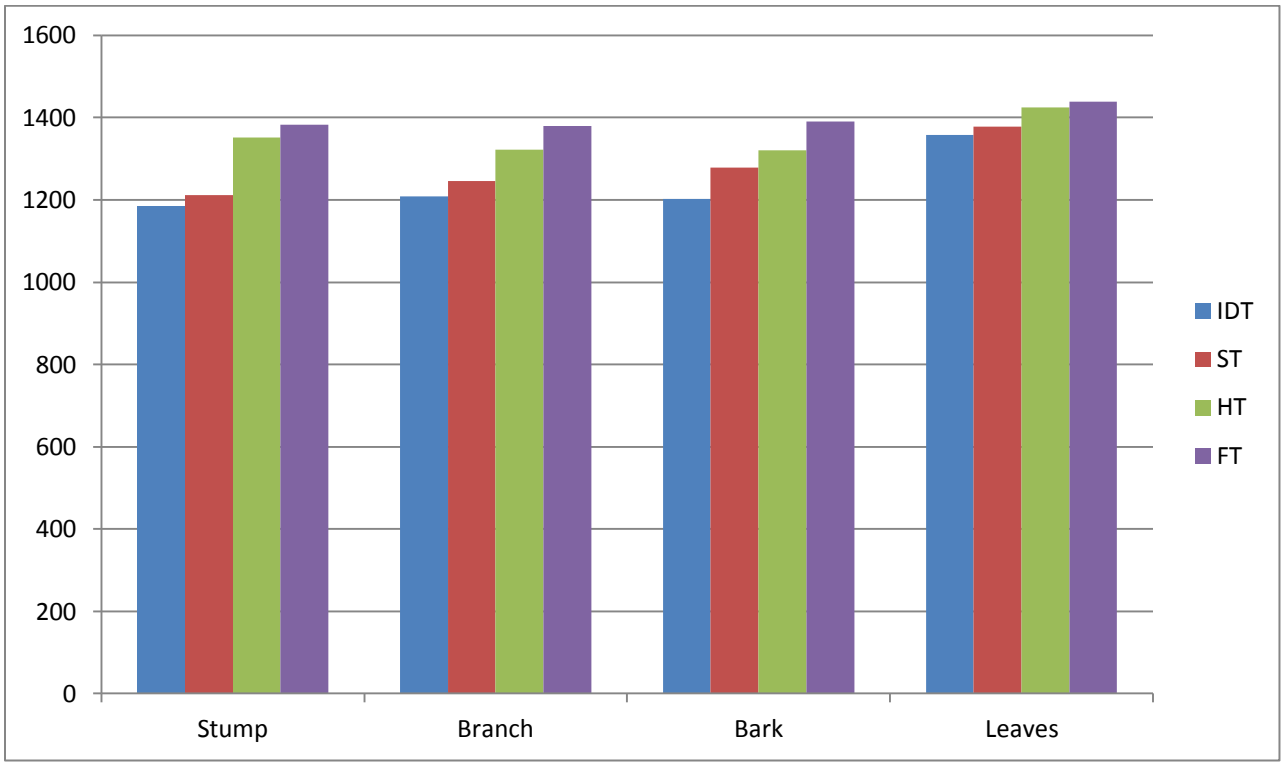


Fig. 17: Variation of Ash fusion temperatures (IDT, ST, HT & FT) of different components of Eucalyptus tree

4.5 X-RAY DIFFRACTION ANALYSIS OF ASHES OBTAINED FROM DIFFERENT COMPONENTS OF EUCALYPTUS TREE:

The X-ray diffraction patterns of Eucalyptus wood, bark, branch and leaves are shown in Fig. 18. As evident from this Fig.18, the major phases in Eucalyptus are Calcite, calcium carbonate and Calcium phosphate carbonate. The minor phases have been detected to be calcium, calcium phosphate and potassium nitrate.

Table 13: Phases detected in ashes of different components of eucalyptus tree by X-ray analysis

Sample	Major phase	Minor phase
Eucalyptus wood	Calcium phosphate carbonate	Potassium nitrate, Carbon
Eucalyptus leaves	Calcite	Calcium
Eucalyptus branch	Calcium carbonate	Calcium phosphate
Eucalyptus bark	Calcite	Calcium

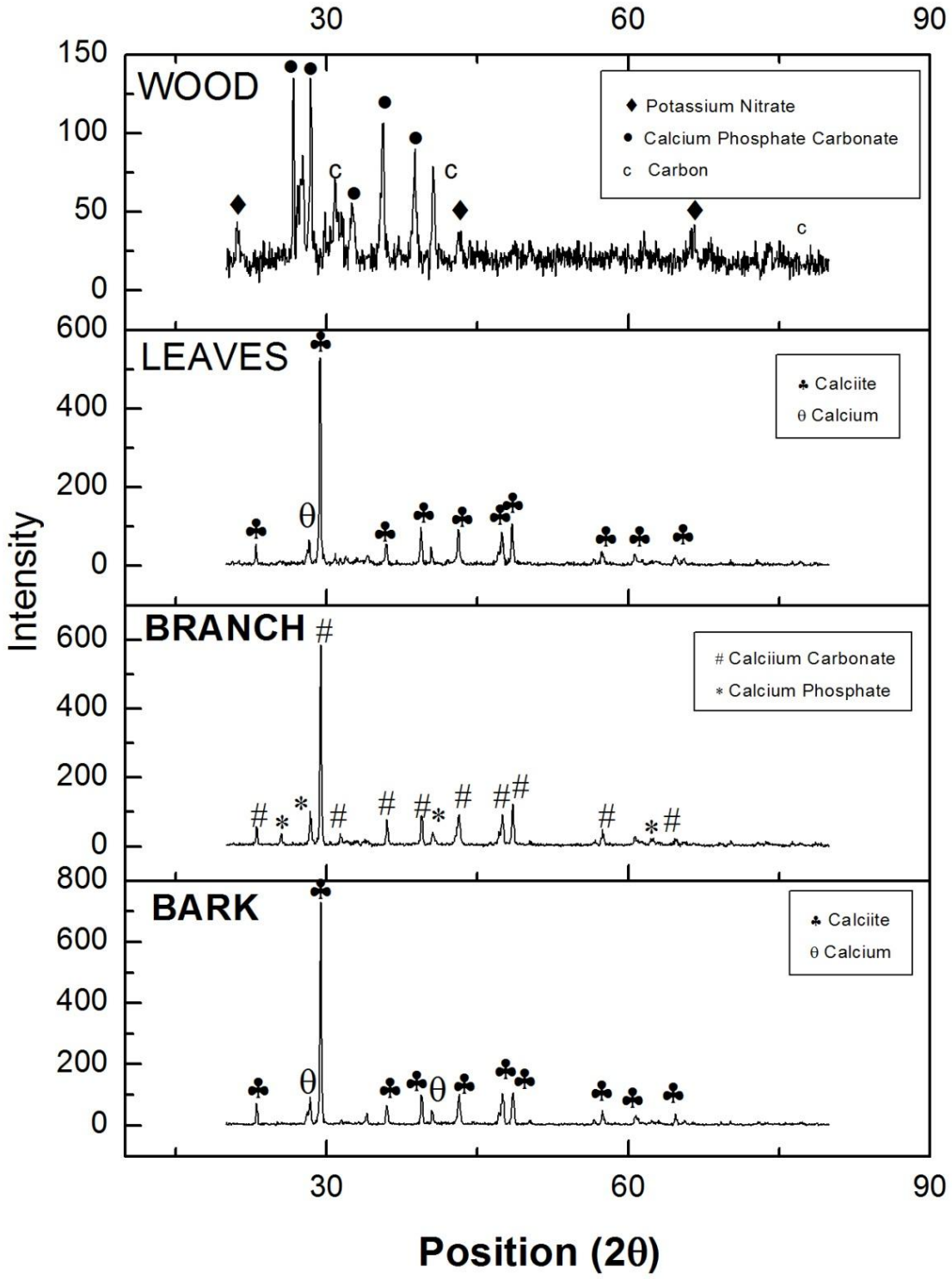


Fig.18. X-ray diffraction analysis of ashes of different components of Eucalyptus tree

Chapter 5

CONCLUSION

5.1 CONCLUSION

In the present work different components of Eucalyptus tree were collected from the local area of Rourkela. Experiments to determine the various physical and chemical properties were done on each of the components of the Eucalyptus tree such as wood, branch, bark and leaves were performed. Also, Carbonization of eucalyptus wood was done under different condition and experiments performed to determine their properties. The following are the different conclusions drawn from the present project work:

1. From the above results it is found that Eucalyptus wood have very high volatile matter content, low ash content and appreciable calorific value.
2. Due to low carbon content of Eucalyptus it will not be economical for the iron making industries as it cannot be used for the reduction of iron ores. But its carbon content can be improved from its carbonization.
3. With increase in carbonization temperature, % char yield decreases significantly up to 800°C, after that there is marginal decrease in char yield with further rise in temperature.
4. Also heating rate of carbonization has significant effect on yield of char. At slow heating rate there is a marginal increase in char yield.
5. There is only marginal decrease in char yield with an increasing soaking time.
6. Fixed carbon content increases with increase in carbonization temperature while volatile matter content decreases.
7. Apparent porosity of wood char increases with increase in carbonization temperature while apparent density decreases.
8. Also, heating rate of the carbonization process has significant effect on apparent porosity of wood char. Under rapid carbonization apparent porosity is higher.

9. Reactivity towards CO_2 of wood char decreases marginally with increase in carbonization temperature up to 800°C. After 800°C, further increase in carbonization temperature decreases reactivity value substantially.
10. Also, heating rate of carbonization has substantial effect on reactivity values. Reactivity values of wood char obtained from rapid carbonization of wood towards CO_2 gas is higher than that of slow carbonization.
11. Ash fusion temperature is determined for different components of eucalyptus tree and it is found that leaves having maximum ash fusion temperatures.
12. Also, ash fusion temperature of Eucalyptus wood is 1185°C. So it can be used in industries operations working under this temperature range.

5.2 SUGGESTIONS FOR FUTURE WORK

The present study was concentrated on different components of Eucalyptus tree. The following works are suggested to be carried out in future.

1. The studies on mechanical properties and other chemical and physical properties may be done in future.
2. Iron-ore reduction studies by using these biomass species should be carried out in future.
3. Similar type of study need to be extended for another woody biomass species available in the local area such as Acacia, Casuarina and Subabul.

Chapter 6

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