"Production of Bio-fuel & Bio-char from Sugarcane Bagasse by Thermal Pyrolysis"

M. Tech Thesis

Submitted by

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NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "***Production of Bio-fuel & Bio-char from Sugarcane Bagasse by thermal Pyrolysis***" submitted by Sowhm Swain Mohapatra **,** Roll No.- 211CH1261 for the award of the Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela. The candidate has fulfilled all prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere.

(Prof. R. K. Singh)

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Abstract

Bio-fuel & bio-char from sugarcane bagasse thermal pyrolysis has the potential to replace the fossil fuel derived energy sources. The various process of conversion although has been put into view like gasification, Torre-faction & Pyrolysis, the pyrolysis has gained a lot of importance because of its viability as compared to other processes discussed above. The conversion of the bio-mass by pyrolysis was conducted at various pyrolytic temperatures starting from (300-500^{0}C) at a heating rate of 25^{0}C/min and the optimum temperature was found at 450^{0}C which was found to be 53.3% of bio-oil. The liquid product i.e., the bio-oil was analyzed by various characterization techniques like CHNS, 1H-NMR, physical properties, GC-MS etc. The properties of the bio-oil were found suitable for being used as a fuel. The effect of temperature on the yield of bio-oil, bio-char, bio-gas & reaction time were studied & plotted which showed that the bio-char yield decreased with increase of the pyrolytic temperature. The potential of the bio-char produced from biomass was analyzed by proximate, ultimate, BET surface area, SEM-EDX, anion chromatography, pH, Electrical Conductivity& Zeta Potential studies. The carbon percentage was high enough to be used as a soil amendment, the surface areas were also found to be more with low surface area as 132m^2/gm for 300^{0}C bio-char to 510 m^2/gm for highest temperature bio-char. This high surface area attributed towards application of the bio-char in soil amendment purpose. The ion-chromatography results also showed the presence of anions that are required as nutrients for plants for their metabolic activities. It will also serve as a good source of plant nutrients since it contains less toxic elements. The bio-char had a slightly acidic surface as found from the pH study. Thus from the above studies we found that the bio-fuel and the bio-char can serve as a source of energy as well as chemical feedstock for the future to depend on.

Keywords: Sugarcane bagasse, bio-oil, bio-char, TGA, XRD, Proximate analysis, CHNS analysis, BET surface area, Electrical Conductivity.

CHAPTER - 1

INTRODUCTION

1. INTRODUCTION:

From the very earlier times people used to be depend upon the biomass for their energy requirement. The introduction of the crude oil led to advancement of industrialization. Biomass is the biological material from the living organism mostly referring to flora of the ecosystem which refers to the plants and generally plant derived materials. Since biomass are renewable source of energy they can be used directly or indirectly when once they are converted to valuable products .The energy demand is mainly comes from the conventional energy sources like coal, petroleum and natural gas. As petroleum sources are getting depleted, and also there is a demand for petroleum products, so we have to develop economical and energy-efficient processes for the production of fuels. Thus, a dire need to put a control over its consumption has been felt by environmentalists and economists as well, , to examine renewable and less cost substitute to fossil fuel to meet their energy demand. In regards to this, a lot of research work is going on around the globe on various alternative sources of energy such as solar, wind, geothermal, hydrogen, nuclear, bio fuel or biomass etc.

The main source of biomass generally comes from the forestry products, agricultural crops and residues and biological wastes. The energy derived from the biomass generally helps reducing the carbon dioxide emission from the atmosphere thereby reducing the global warming effect. Since the carbon dioxide acts as a green house gas and increases the temperature of the atmosphere. Biomass is all biologically produced materials made of carbon hydrogen and oxygen. Biomass can be converted to energy by various process or means which include biological, thermal, mechanical or physical process .Biological process uses biological catalysts to produce selective products on the other hand thermal conversion of biomass gives a very large products within short reaction times. The three main thermal processes for converting biomass to a more useful energy form is pyrolysis, gasification and combustion. The most suitable form amongst the three was found to be pyrolysis since it gave valuable product yield that to at low reaction times whereas on the other hand gasification involves heating the biomass in controlled supply of oxygen to produce syn gas (CO ,H_2) and involves a high temperature heating . The energy rich compounds prepared from biomass are called bio-fuels. The bio-fuels obtained from different biomass are classified into solid, liquid and gases. ***(a) Solid Bio-fuels:*** They are solid biomass that is combustible such as wood, compressed peat and dry bagasse etc, these can be burnt to get heat as a form of energy.

***(b) Liquid Bio-fuels*:** This basically consists of liquid extracted from biomass and used as fuel and for production of other useful products. This liquid stream consists of bio-oils and other organic chemicals mainly ethanol, methanol, acetone, acetic acid, bio-oils and bio-diesel (fatty acid methyl ester).

(c) *Gaseous Bio-fuels:* Gaseous product obtained from biomass decomposition contains primarily hydrogen, methane, carbon monoxide, carbon dioxide, ammonia and other gases depending upon the organic nature of biomass and process condition.

Energy produced by burning of the biomass is also known as endothermal energy. Biomass also has the potential to be converted to multiple commodity chemicals. The biomass power generating industry in USA is consists of approximately 11,000 MW summer operating capacity supplying to the grids and produces about 1.4% of electricity supply. The 140 MW facilities uses sugar cane fiber bagasse and recycled urban wood as fuel to generate enough power for its large milling and refining operations as well as to supply renewable electricity for nearly 60,000 homes. Biomass like Sugarcane bagasse are also used in manufacture of paper and simultaneously used in generation of electricity and simultaneously used as fuel. Biomass, such as corn and sugar cane, can be fermented to produce the bio-fuel which can be used in transportation, production of ethanol. Biodiesel, which is being used as a transportation fuel, can be produced from left-over food products like vegetable oils and animal fats. The Energy Information Administration projected that by 2017, biomass is expected to be about twice as expensive as natural gas, slightly more expensive than nuclear power, and much less expensive than solar panels. Biomass consists of cellulose and hemicelluloses and an aromatic lignin molecule. The lignocellulosic biomass is useful in paper and pulp industry. One barrier to the production of ethanol from biomass is that the sugars necessary for fermentation are inside the lignocelluloses. These tend to resist the change due to their strength in the cell wall which. This robustness or "recalcitrance" is attributable to the cross-linking between the polysaccharides (cellulose and hemicellulose) and the lignin via ester and ether linkages.

CHAPTER 2

MODES OF BIOMASS CONVERSION

2. BIOMASS CONVERSION PROCESS:

Biomass is in general converted to useful products mainly by two process:

1. Thermo-chemical process.

2. Bio-chemical processes.

2.1. THERMOCHEMICAL PROCESS:

The thermo-chemical process include mainly process like

1. Torrefaction

2. Pyrolysis

3. Combustion

4. Gasification

5. Hydrogenation

The method which was found to be suitable and is used is the pyrolysis of the biomass to produce the bio-oil, bio-char & the volatile components.

2.1.1. PYROLYSIS:

Pyrolysis is the thermal decomposition of biomass at modest temperatures in absence of oxygen. The steps in pyrolysis includes: feedstock preparation and introduction of the feed into the reactor, carrying out the reaction by absorption of heat or other addition of agents such as air, oxygen, steam, hydrogen, post combustion or processing of the gases produced during the reaction step, and proper guidance of the resulting liquids, char, and ash .Pyrolysis product basically consists of gases like CH_4, CO_2 ,and NH_3 and liquids like ethanol, bio-oils, acetone, acetic acid etc. and solid as char .The relative proportion of the output depends upon the process and process condition, characteristics of biomass, optimum temperature and residence time of material. In this process the biomass is heated to a temperature range with low residence time and rapidly cooled to collect the condensed liquid which is otherwise known as bio-oil. This is done to avoid the decomposition of the intermediate products during pyrolysis. When cooled, most volatiles condense to from bio-oil. This process is a very popular process which makes a good quantity of liquid fuel from biomass, which is very

similar to commercial transportation fuels and can be upgraded or modified to replace transportation fuel. Longer residence times and High temperatures increase biomass conversion to gas, and short vapor residence time and moderate temperatures are optimum for producing liquids. The most important features for pyrolysis to occur to give proper bio oil yield are:

1. A Temperature of around (400-500^{0}C) in order to produce bio oil in maximum.

2. Finely ground biomass with about less than 3mm size with high heating rates.

3. Vapor residence times of about less than 2 sec to lessen the secondary reactions to occur.

4. The remaining bio-char must be removed so as to prevent the secondary cracking reactions.

5. The vapors are rapidly cooled to produce the bio oil as the intermediate product.

During the pyrolysis process the heat transfer occurs between the biomass particles from the bottom of the reactor to the top thereby following the decomposition of the cell wall of biomass and releasing the moisture, volatiles and thereby leaving behind the ash. Before the process to occur the biomass particles are dried for some hours to eliminate the water content of the biomass in the bio oil. The feed i.e., the biomass is grounded so that easy to be separated as the char particles and rapid quenching of the biomass materials to obtain the bio oil. There are various changes occurring in the process are as follows:

1. The increase of temperature of the reactor so as to increase the temperature inside the fuel.

2. With the increase of the pyrolysis temperature the release of volatiles occur and thereby converting into the bio-char.

3. The flow of hot volatiles towards cooler solid in the upper chamber leads to heat transfer between them.

4. There occurs condensation in the cooler parts of the fuel thereby producing tar in opening of the condenser which sticks to the condenser.

5. Further thermal decomposition, reforming, water gas shift reaction, dehydration occurs which are the function of the residence time of the process.

FAST PYROLYSIS:

The products of fast pyrolysis include gases, bio-oil, and char which depend on the process temperature, pressure, and residence time of the given out pyrolysis vapors. The production of bio-oil is maximized by fast pyrolysis, typically performed at temperatures (~450-500ºC) at atmospheric pressure, high heating rates (i.e., 500ºC/sec) and short residence times (1-2 sec) .

SLOW PYROLYSIS:

Here the temperature maintained for pyrolysis reaction is 300 - 500ºC and the rate of heating is slow i.e. around 20 - 30ºC/sec and the residence time allowed. In this case, the yield of gaseous product and solid residue is more as compared to fast pyrolysis. The amount of liquid product obtained is upto the mark and the quality of the liquid product obtained is good .

2.2. BIO-CHEMICAL PROCESS:

The biochemical process involves anaerobic digestion and alcoholic fermentation are involved for biochemical conversion of the biomass like animal manure and bio waste. Sometimes it also deals with energy crops and paper mill residues. It combines methods like pre-treatment, enzymatic action & hydrolysis.

The other types of biochemical process involve anaerobic digestion &alcoholic fermentation process. The former process involves the decomposition of the organic material in presence of microbes in the absence of oxygen to produce the so called biogas which comprises of methane and carbon dioxide as the prime components .Biogas is generally a product from manure of cow, It is used in producing electricity since the biogas produced from the manure has a higher calorific value .On the other hand the alcoholic fermentation process involves the production of wines from the biomass like sugar crops and starch crops. It involves the action of organisms like yeast that helps in yield of high quality fuel for transportation purpose .For this process initially the compounds needed to be broken down by hydrolysis as it contains longer chains of Polysaccharide. In the production process of ethanol, It can be distilled and can be used as fuel as petrol.

CHAPTER 3

LITERATURE REVIEW

3. LITERATURE REVIEW:

Biomass such as lignocellulosic biomass can be used as as a source of starting materials for many industrial processes. The advantage of using the biomaterial is that the processing will become less expensive than petroleum and will certainly not affect the food supplies and all the chemicals derived from it will have lower environmental impact than the petrochemicals Lucian. A. Lucia et al (1). The advancement in thermo chemical process use for bio fuel production has gained a lot of importance for the production of clean and efficient energy substitute. The choice of process depends upon the type of desirable product; Fast pyrolysis leads to high yield of bio-oil whereas the slow and vacuum pyrolysis process gives a good choice for production of bio-char and bio-oil furnishing high yields and simultaneously superior quality of bio-char A.V Bridgewater et al (2). It is recognized that biomass exceeds many other renewable energy sources because it is plentily available, high energy values and it is versatile, and sugarcane bagasse is the most abundant crop waste found in the world J.M Encinar et al (3) .Biomass pyrolysis products are the complex combination of the products from individual pyrolysis of cellulose, hemicelluloses and extractives each having its own kinetic characteristics. In addition to that the secondary products come from the cross reactions of primary pyrolysis products between pyrolysis products and the original feedstock molecules, Pyrolysis of each constituent is itself a complex process which is dependent on many factors Dinesh Mohan et al (4) .

The pyrolysis characteristics of sugarcane bagasse hemicellulose were found out using a tubular furnace, the pyrolysis experiment was conducted at various elevated temperatures starting from 550,600,650,700,750,800,850 & 900 ^{0}C in a homemade tubular furnace. The main objective of the project was to investigate the effect of temperature on the various product yields and to characterize the products with various analytical techniques. The liquid products were analyzed by GCMS and it was found that the main gas products were (CO, CO_2, CH_4& H_2) respectively Peng et al (5) .The biomass pyrolysis was carried out using Thermo gravimetric analyzer and packed- bed pyrolyser. It inferred that there were no detectable interactions among the components during pyrolysis in either of the above two process on the other hand the ash present in the biomass had a strong influence on both pyrolysis characteristics and the product distribution . It also inferred that the cellulose decomposition took place between the temperature range of (573-703 K) , Lignin on the other hand was found to be decomposing between the temperature ranges of (523-823) , the char

yield by lignin decomposition was the highest in the region of (45-50 wt%) (6) .Thermal decomposition of sugarcane bagasse was carried out at different heating rates (10,20, 40,60^{0}C/min) . In the above process the thermal decomposition kinetic parameters were determined. Various kinetic studies were useful in detecting the interactions between cellulose, hemicelluloses and lignin during the biomass decomposition process. The study also detected that the structural changes in the biomass was noticed between 200-300^0 C while carrying out the solid FTIR of the biomass sample. These were shown by decrease of (C-O, C=C, & O-H) peaks intensities and formation of alkyl bonds (7) .The agricultural waste i.e., the sugarcane bagasse was pyrolysed between a temperature range of 375-575 and the highest bio-oil yield was found to be obtained at 475^{0}C. The pyrolytic bio-oil obtained had a GCV of about 15-38 MJ/Kg with some advantages of transportation, storage, combustion, retrofitting and flexibility in production and marketing. The feed particles prior to pyrolysis were dried for duration of 3 hours at 110^{0}C. The pyrolytic oil obtained at maximum temperature was well mixed in order to obtain homogeneity before the analysis being made, The liquid was put under analysis by density , viscosity , flash point ,GCV , were determined using standard methods (8).

In another study carbonization of sugarcane bagasse was conducted in a fixed bed reactor which was done from 250-700^0 C, with heating rates from 5-30^{0}C with nitrogen gas sweep rate of 350 cc/min. The reduction in yield was rapid upto 500^0 C and thereafter again slows down showing decreasing trend and simultaneously the optimum temperature also. The studies inferred that the ash content as well as the fixed carbon increased with temperature. They also studied that with the increase of pyrolytic temperature yield of char decreased with a corresponding increase in volatiles (9). With the help of induction heating reactor the fast pyrolysis was carried with 3 biomass (Rice husk, Sugarcane Bagasse & Coconut shell) and the maximum yield of 50% of the pyrolytic product was obtained under proper conditions , The biomass materials after being pyrolysed were cooled to room temperature using cryogenic system(-10 ^{0} C)with ethylene glycol solution and then taken for holding crucible and the and condensable collectors in order to weigh the weight of the residual solid and liquid tar (10). This study inferred that sugarcane bagasse is a high thermal value fuel only when it is dried. The lower heating value of bagasse is about 5.4MJ/Kg. In the above process it used a two stage process is favoured which comprised of heating of biomass stage upto 350 ^{0} C and the other is charcoal glowing stage with a peak temperature of about 475-500^{0}C , the biomass carbonization is divided into 3 stages drying , heating up , pyrolysis and glowing in

which the residual tars are eliminated at 450-500 ^{0}C during the glowing stage (11). From the pyrolytic experiments conducted in slow and vacuum manner the results obtained were the optimal bio-oil for vacuum pyrolysis was obtained at 400-500^0 C with heating rates of about (15-24)^0 C/min whereas on the other hand slow pyrolysis led to an high bio-char yield . The yield differs from vacuum pyrolysis due to short residence times in vacuum pyrolysis (12). The fresh bio-char was digested anaerobically at 600^0 C to produce methane in nitrogen environment. The digested bagasse bio-char and the undigested bagasse bio-char were characterized to determine their physical properties. The bio-char produced from digested bagasse was 18% by weight whereas those from raw bagasse were 23%, this is attributed to perhaps reduction in carbon content after the digestion (13). This process used a fluidized bed for pyrolysis of biomass where the maximum oil yield was found at 793 K and the yield was 45% from bagasse as the temperature increased further the secondary reaction became predominant leading to a lower bio oil yield. On the other hand lower temperature leads to biomass incomplete decomposition, moreover it was also noticed that there was no change in product yield when partice size was less than 1mm (14).

Pyrolysis is one of the most promising ways to convert the biomass to energy. One of the promising approaches for lowering the CO_2 emission in the atmosphere is while producing bio-char bio-energy based on low temperature pyrolysis. In soil the bio-char are the better source to retain cations than any other source of organic matter; moreover the cation retention of fresh bio-chars is less than those of aged bio-chars (15). The balance between char, gas, and oil and tar products in pyrolysis depends considerably to an extent on rate of heating. The character of the char product is dependent on the extent of pyrolytic temperature. Pyrolysis engineers have sought to minimize the char production since it is viewed a problematic low value waste fraction, after the pyrolysis of the biomass particles 30-40% of the feedstock material is recovered as bio-char (16). Vacuum pyrolysis furnishes bio-oil and bio-char in similar quantities. Vacuum pyrolysis has the potential to produce high quality char for waste water treatment as well as soil amendment. The bio-char after acidic treatment becomes activated carbon which inferred a surface area of about 418 m^2/g . The electrical conductivity was very low of 0.17 ds m^{-1} .The water soluble ions in the bio-char is the indication of available plant nutrients like (P ,K ,Ca ,S) (17). The pyrolysis experiments were conducted at a temperature of 500^{0}C, under a pressure of 5kpa. Among the total amount of liquid collected in the form of bio-oil was found to have a dew point of about 60-65^0 C and were collected in an ice bath of (5-7^0 C) (18) . The pyrolysis of corn stover gave a yield of 60 % (mass/mass)

and a higher heating value of oil of 20MJ/Kg. The amount of water content was determined by Karl fischer process. Overall ash content of the bio-char was found to be 13.1 and 32.4 from corn cob & corn stover pyrolysis. Bio-char pH was found to be slightly alkaline. Bio-char produced at lower temperatures will have higher content of plant available nutrients since it had the functional groups of (C=O & C-H) functional groups. The bio-oil & bio-char constitute about energy efficiency of 70% for both the feedstock (19). The application of bio-char to soil has proved to be advantageous for the atmospheric sink for a long duration of time. Conversion of biomass to bio-char carbon leads to sequestration of about 50% of the initial carbon after low amount left after decomposition and burning. The conversion of carbon conversion to bio-char is highly dependent on type of feed stock and also pyrolysis temperature of (300-500^0 C) (20). Bio-energy produced from biomass can replace fossil fuel based energy resources. Biomass can be converted to bio-energy either through direct combustion or any other thermo-chemical process. In terms of emission reduction bio-char is more valuable than fuel application. It reduces the emission like (N_2O, CH_4) when added to soil (21). Studies were conducted at various pyrolytic temperatures starting from 300-500^{0}C for pitchpine as the bio-mass. The experimental studies revealed that the bio-chars obtained at 300 & 500^0 C were composed of highly branched aromatic structures. The bio-char yield decreased from 60.7% to 14.4 % , the bio-char was analyzed for BET surface area and also for ^{13}C NMR (22).The pyrolysis of the biomass was conducted t various elevated temperatures ranging from (300-500^{0}C) in order to study the various forms of alkalis that were present in the biomass and they inferred that with the increase of the pyrolytic temperature the carbonates fraction in the bio-char increased to a level & from the FTIR studies it was concluded that the carboxyl & phenolic groups were noticed which were found responsible for the negative surface charge of the bio-chars. The XRD spectra of the bio-char samples showed that the carbonates were found for high temperature bio-char samples (23). The experiment was conducted at different pyrolytic temperatures and with different heating rates while the carbonization techniques which are operating at low heating rates resulted in high bio-char yields, since the biomass has low thermal conductivity the biomass which has particle size less than 2mm has the highest pyrolysis regimes. Both the bio-oil & bio-char values increase in the energy values when the pyrolytic temperature increases since the energy value of both increases (24).

CHAPTER 4

MATERIALS & METHODS

4. MATERIALS AND METHODS:

4.1. COLLECTION OF RAW MATERIAL:

The precursor is collected from the nearest sugar industry namely (SHAKTI SUGAR INDUSTRIES) as they are used for power generation inside the sugar mill. The raw material is in the form of fibres.

Fig.1. Sugarcane bagasse (Bio-mass used)

4.2. PYROLYSIS PROCEDURE:

Pyrolysis of the biomass is carried out with a system which comprises of a reactor, a furnace and a condenser that is being used to condense the gas and thereby collect the bio-oil. It is carried out using a reactor which is made up of stainless steel (SS 316) material having diameter of about 4.5cm and a elevation of 18.5cm. The reactor is the one inside which the precursor is being filled and certainly inserted vertically inside the furnace. Once the reaction is started the precursor is pyrolysed and the moisture is eliminated with next volatiles and thereby remaining with ash (bio-char). The bio-oil is collected in the measuring flask which lies below the condenser. There also lies a temperature controller inside the furnace which is PID controller. The furnace has a maximum temperature reach ability of 1200^0C.

Fig 1. Shows the experimental set-up for pyrolysis. The process is carried out at a heating rate of 25^0 C/min and the pyrolysis is done at regular intervals of 50^0 C starting from (300^0-500^0 C). During the process the various parameters are being studied such as yield of bio-oil, yield

of bio-char with the increase of temperatures upto 500^0C .The optimum temperature of yield was noted to be 400^0C .

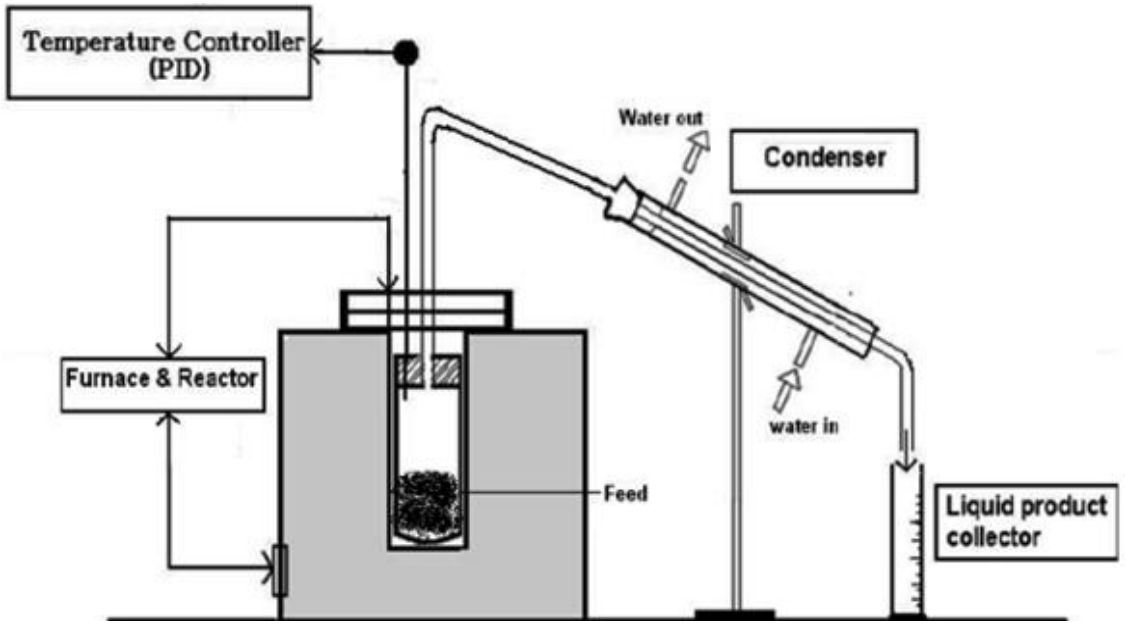

Fig.2. Schematic diagram of the experimental set-up for Pyrolysis.

4.3. CHARACTERIZATION OF THE MATERIAL:

4.3.1. PROXIMATE ANALYSIS:

It is done in order to calculate the moisture content, ash content, volatile matter content and the fixed carbon content of the biomass sample. The experiment was conducted by ASTM D3173-75. The fixed carbon is calculated by difference, after the calculation of moisture content, volatile content and ash content. It is the quantitative analysis which separates all the above 3 components from any material. The ash content of the material doesn't contribute to the calorific value of the fuel. The proximate analysis was done for the bio-mass as well as bio-char samples.

4.3.2. ULTIMATE ANALYSIS:

The Ultimate analysis was carried out using an CHNSO elemental analyser. It is otherwise known as elemental analysis which determines the carbon, hydrogen, nitrogen, sulphur and

the oxygen content in the material. The oxygen component of the material is calculated by difference after the calculation of carbon, hydrogen, nitrogen &sulphur content .The elemental analysis was done for bio-mass, bio-oil as well as the bio-char also.

4.3.3. THERMO-GRAVIMETRIC ANALYSIS (TGA):

It is a method of thermal analysis in which the physical and chemical properties changes with the increase of temperature.TGA is used to determine either the mass loss or gain during the decomposition, oxidation or due to loss of volatiles. It is also used to study the characterization of the material by the decomposition pattern of the material. The process continuously weighs the sample till it attends a temperature of about 2000^0C for coupling with FTIR and mass-spectroscopy and determines the weight percentage of each resulting mass change . It is done by SHIZMAZDU TGA 60-H with a constant nitrogen flow rate . The TGA was carried out for the raw bio-mass sample then for the bio-char also.

4.3.4 FTIR:

The FTIR of the bio-oil as well as the bio-char was conducted for the analysis of the functional groups present. The absorption of infrared radiation causes excitation of the atoms or molecules thereby causing to vibrational bands which is calculated as wave number cm^{-1}. There showed the different ranges for bio-oil as well as bio-char samples which mostly were in the mid infrared regions which correspond to ($400\text{-}4000cm^{-1}$) .The FTIR was carried out with (PERKIN EMLER RX). The ominc software is used to correct the medium's background material used during analysis. Samples are dried prior to analysis and then were mixed with (1:200) (w/w) and then hydraulically pressed and then set for analysis.

4.3.51H –NMR:

The NMR is a research technique that is used to determine the magnetic properties of atomic nuclei present within the material. It also determines the physical and chemical properties of the molecules in which they are present. In order to determine the structure of the molecules 1H NMR is being used. NMR is generally recorded in solution state for which it is first dissolved in solvent ($CDCl_3$). Tetra methyl silane is used to determine the shift in proton, it is a tetrahedral molecule with all the protons give one signal uniting as a single entity and it defines the chemical shift as zero. 1-H NMR is carried out with a 400 MHz, BRUKER DPX-400. When the sample placed in NMR analysis it absorbs the electromagnetic radiation at a

frequency which is the characteristics of the isotope. NMR of the bio-oil was carried by using the above procedure.

4.3.6 GC-MS ANALYSIS:

This analysis is done to determine the chemical compounds present in the bio-oil. In this process the components are separated for the analysis to be done easily. In GC-MS analysis the mobile phase is the gas phase generally helium gas is being considered. During the analysis a column is being used the mixture of compounds in mobile phase interacts with the stationary phase and thereby causing the separation based on the rate of interaction which interacts first will analyzed and then the next. The column used in the analysis is 0.25 µm in diameter and has a length of 30m. The bio-oil was analyzed using(QP2010SHIMADZU).

4.3.7 SEM–EDX:

SEM is used to determine the morphology of the material under view whereas the EDX or energy dispersive X-ray is used to determine the inorganic compounds or components present in the material under view. SEM –EDX are united singly in equipment and thereby both of them are determined at a glance. The elements present in the sample absorbs the X ray beam and results in movement is the electrons from the ground state thereby disclocating the electrons and thereby creates a hole but electron from the other higher energy state fills it and a difference in energy is created which results in determination of peaks . The analysis of the sample is done by JEOL (JSM -6480 LV) operating with a voltage of 15 KV.

4.3.8 XRD (X ray Diffraction):

X-ray diffraction (XRD) is the principal technique used to investigate long and short-range order of atoms and molecules in the solid state, respectively. The XRD of the bio-char sample was conducted using SRM 640 D. It measures the average spacing between two layers or rows of atoms, in order to determine the orientation of the grains and to determine the crystal structure of the sample under view. The X- rays are produced when high beam electrons collide with the sample and thereby characteristics spectrum is generated. The crystal is mounted on a goniometer and then rotated while the the X- rays falls generating different patterns of regularly spaced reflections giving the characteristics spectrum.

4.3.9 ELECTRICAL CONDUCTIVITY:

The electrical conductivity of the bio-char samples were conducted using (AMBER SCIENCE 800 SERIES). The electrical conductivity meter measures the electrical conductivity of the bio-char solution. The electrical conductivity is the measure of total number of water soluble ions in it. The electrode used is made up of platinum metal. An alternating current is applied to the outer surface of the electrodes and the potential of inner electrode helps to calculate the conductivity of the sample. The Model 3084 is a bench top, line powered, microprocessor based, multi-function EC meter designed to precisely determine the conductivity of aqueous solutions. It covers six ranges (auto or manual) with a maximum full scale of 3300 counts. Measurement data is displayed on a 2 line by 20 characters each, backlit dot matrix (LCD) liquid crystal display.

4.3.10 BET SPECIFIC SURFACE AREA:

The surface area of the bio-char was determined using multipoint BET analysis on a Micrometrics ASAP 2010 system. The degassing was done at about 280^0C and after the sample being degassed suddenly being introduced into N_2 atmosphere inside the adsorption equipment.

4.3.11. SURFACE ACIDITY AND ALKALINITY USING BOHEM TITRATION:

Bohem titration provides the total surface acidity and alkalinity of the surface of the bio-char , A 0.2 gm of subsample of bio-char was added to 15ml of either 0.1N NaOH /0.1N HCL and shaken for a duration of about 30 hours . The bio-char slurry was then filtered using (WHATMAN NO. 40) filter paper. An aliquot of 5ml of NaOH was transferred to 10 ml of 0.1N HCL which neutralized the unreacted base. The solution was back titrated with 0.1N NaOH with phenolphthalein indicator. In the similar manner surface basicity was also measured. The acid /base uptake was converted to ($mmolg^{-1}$) for both the cases.

4.3.12. pH DETERMINATION:

The determination of pH indicates the active (pH in water) and reserve (pH in KCl) acidity in the bio char. pH of a bio-char can have a substantial effect on soil by changing the soil pH, therefore it could be a solution for soil acidity and aluminium toxicity. Potassium chloride

solution was used because KCl could release the exchangeable protons from bio-char into the solution due to its ionic nature. Two grams of bio-char was shaken with 40 mL distilled water or 1 M KCl (99% purity) (Merck Chemicals Ltd.) solution for 30 min on an IKA®KS 260 basic shaker. The suspension was allowed to stand for 10 min before measuring the pH with a pH electrode, 827pH Lab, Metrohm (Cheng & Lehmann, 2009). The pH values of raw materials were measured with the same procedure in a distilled water suspension.

4.3.13 ION CHROMATOGRAPHY:

Ion chromatography is a method to separate charges and polar molecules based on their charge. It can be used for any kind of charged molecules including proteins .the solution to be injected is usually called the sample and the individual separated components are called analytes. Ion chromatography is used to separate cations, anions and polar compounds (Ammonia in smoke stream) for analysis based on the charge properties of the molecules .It has a suitable cation exchange analytical column (250 mm X 4 mm) and Suitable anion exchange analytical column (250 mm X 4 mm) . The binding capacity should be 0.5–2 mg/cm^2 with 95% recovery at 10 ml/min irrespective of the concentration up to 10 mg/ml. Ion-exclusion separation and pre-concentration of impurity anions is performed using Dionex AS6-ICE and AS11-HC (4 mm) columns, respectively, with water eluent. Final separation is performed using Dionex AG11-HC and AS11-HC (2 mm) columns, KOH gradient elution, and suppressed conductivity detection.

4.3.14 ZETA POTENTIAL:

Zeta potential is a physical property of material which is exhibited by any particle in suspension form. About 0.50 g of coarse (0.25 – 2 mm) bio-char sample was placed in a cylindrical cell with perforated Ag/AgCl electrodes attached to two sides of the cell. An electrolyte solution flows through the cell carrying the sample particles and causing charge transport along the length of the cell. Depending on the flow resistance of the sample, a pressure drop is also detected along cell. The measured pressure drop and streaming potential are used served to calculate the zeta potential. The ZP of coarse bio-char samples was determined using an Anton Paar Electro-Kinetic Analyzer (EKA) , the solution pH was measured using an inline pH meter . About 0.5 g of fine bio-char sample was added to 50 mL double distilled water and then sonicated for 30 min. The resulting solution was filtered

(What man42 filter paper) and the filtrate was placed in a plastic cell between a positive and a negative palladium electrode of a PALS Zeta Potential Analyzer (Ver. 3.16). An electric field was applied across the electrophoresis cell, causing the particles to move towards the electrodes with a velocity proportional to the ZP and in a direction determined by the sign of their charge. The pH of the solutions was recorded immediately after measuring the ZP of the bio-char samples. Then the pH of the samples was adjusted using 0.1 M NaOH or 0.1 N HCL. The zeta potential values as reported for bio-char samples for various materials give an indication of sample surface charge which then finds its applications.

CHAPTER 5

RESULTS & DISCUSSIONS

5. RESULTS AND DISCUSSION:

5.1. PROXIMATE AND ULTIMATE ANALYSIS OF BIOMASS:

TABLE 1. Proximate and Elemental analysis of the Sugarcane Biomass:

PROXIMATE ANALYSIS	
Content	**Weight percentage (%)**
MOISTURE CONTENT	1.94
VOLATILE MATTER	71.48
FIXED CARBON	15.57
ASH CONTENT	11.01
ULTIMATE ANALYSIS	
Elements	**Weight percentage (%)**
CARBON	56.160
HYDROGEN	3.512
NITROGEN	6.213
SULPHUR	2.380
OXYGEN	31.73
H/C	0.750
O/C	0.560
OIL CONTENT (%)	53.3
GROSS CALORIFIC VALUE	2754.32
ELEMENTAL FORMULA	$CH_{0.75}N_{0.0946}S_{0.015}O_{0.560}$

The proximate analysis and ultimate analysis gave their result with highest volatile matter in the biomass of about 71.48% and the lowest moisture of 1.94 whereas the ultimate analysis showed the highest presence of carbon of about 56.16 %. The elemental formula of the biomass is also predicted above.

5.2. THERMOGRAVITRIC ANALYSIS (TGA):

The TGA curve of the biomass gave the decomposition stages of the biomass and the temperature between which the thermal pyrolysis would be done so as to get the optimum temperature. It is conducted at gas flow rate of 35 ml/min and the amount of sample taken during TGA analysis was 2.926gm and within a temperature range of $(0\text{- }600)^0$ C. The decomposition occurs in 3 stages the first stage shows the removal of moisture from the bio-mass , the 2^{nd} stage gives the removal of volatile matter present in the biomass sample and in the 3^{rd} stage the total combustion of the material takes place with the weight loss from the material giving rise to decomposition of the hydrocarbons . From the 3 stage process the rapid decomposition occurs during the volatiles are eliminated and so the stage is considered to be important for pyrolysis. The pyrolysis is performed according to the information from TGA between 300-500 ^{0}C.

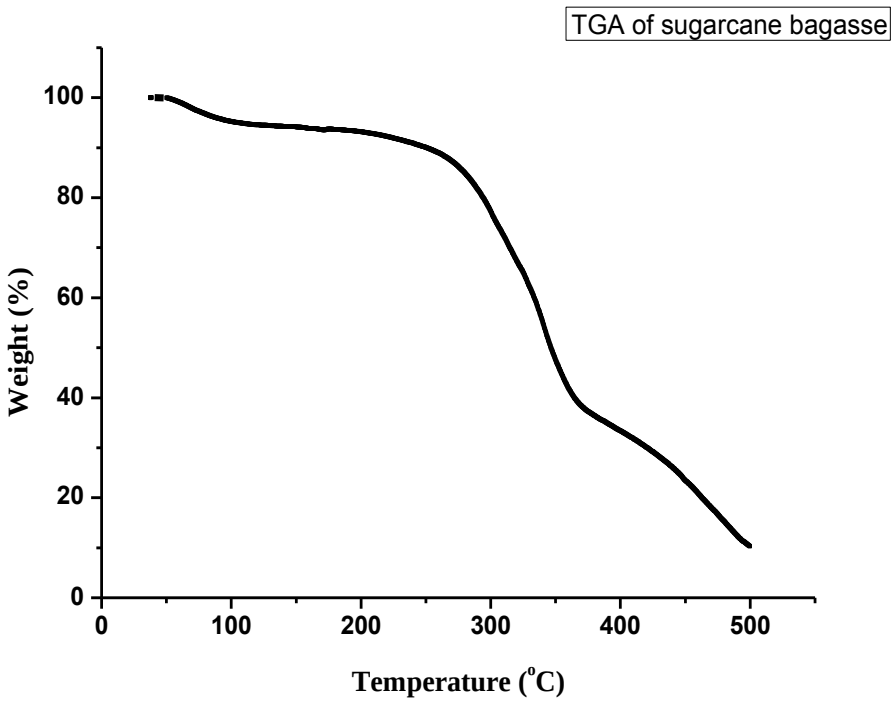

Fig3.TGA of Sugarcane Bagasse

5.3 EXPERIMENTAL RESULTS:

Table 2. Experimental result of Sugar Bagasse pyrolysis

CHARACTERISTICS	SUGARCANE BAGASSE								
TEMPERATURE (^{0}C)	300	325	350	375	400	425	450	475	500
LIQUID PRODUCT (%)	20.32	25.66	44.46	45.46	46.21	50.66	53.30	51.13	41.33
BIO-CHAR (%)	49.54	46.73	40.8	34.7	33.05	31.90	29.78	25.0	20.12
VOLATILES (%)	30.14	27.61	22.74	19.84	18.62	17.44	16.92	23.87	38.55
REACTION TIME(MIN)	48	45	38	32	29	25	22	20	17

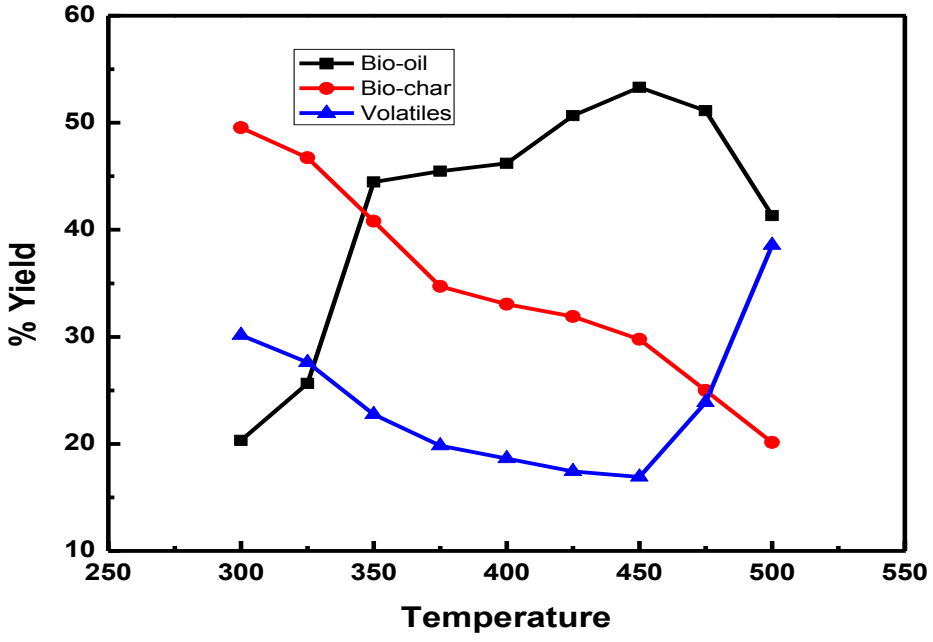

Fig4. Pyrolysis of Sugarcane bagasse at various temperatures

The conclusion drawn from the above figure is that with the increase of temperatures the bio-oil yield increases with the decrease in bio-char yield. The oil yield was maximum at 450^{0}C and was 53.30% &

the bio-char descended to a value of 20.12 % and the volatiles upto optimum reduced and then after culminates with the decrease of bio-oil yield.

5.4 .CHNS OF THE BIO-OIL:

Table 3. Elemental analysis of the bio-oil

No of sample	N%	C%	H%	S%	O%	Elemental formula	GCV (MJ/Kg)
1	4.586	44.125	3.65	2.47	45.16	$CH_{0.992}N_{0.0889}S_{0.00241}O_{0.7674}$	25.31

5.5 FTIR ASSIGNMENT OF SUGAR BAGASSE BIO-OIL AT 450^{0}C:

Table.4 FTIR assignment of bio-oil at 450^{0}C

Frequency range(cm-^{1})	Groups	Class of compounds
3412.57	O-H GROUP	Polymeric O-H , Water Impurity
2354.05	C-H STRECHING GROUP	Alkanes
2105.10	C-H STRECHING GROUP	Alkanes
1711.25	C=O STRETCHING GROUP	Ketones, Aldehyde & Carboxylic acid
1691.65	C=O STRECHING GROUP	Ketones, Aldehyde & Carboxylic acid
1659.57	C=C STRECHING GROUP	Alkenes

1642.95	C=C STRECHING GROUP	Alkenes
1391.54	C-H bending	Alkanes
1274.87	C-O & O-H STRECHING	Alcohols , Phenols, Esters &Ethers for O-H Bonding
1052.56	C-O &O-H STRECHING	Alcohols , Phenols, Esters &Ethers for O-H Bonding
665.30	O-H BENDING	Aromatic compounds

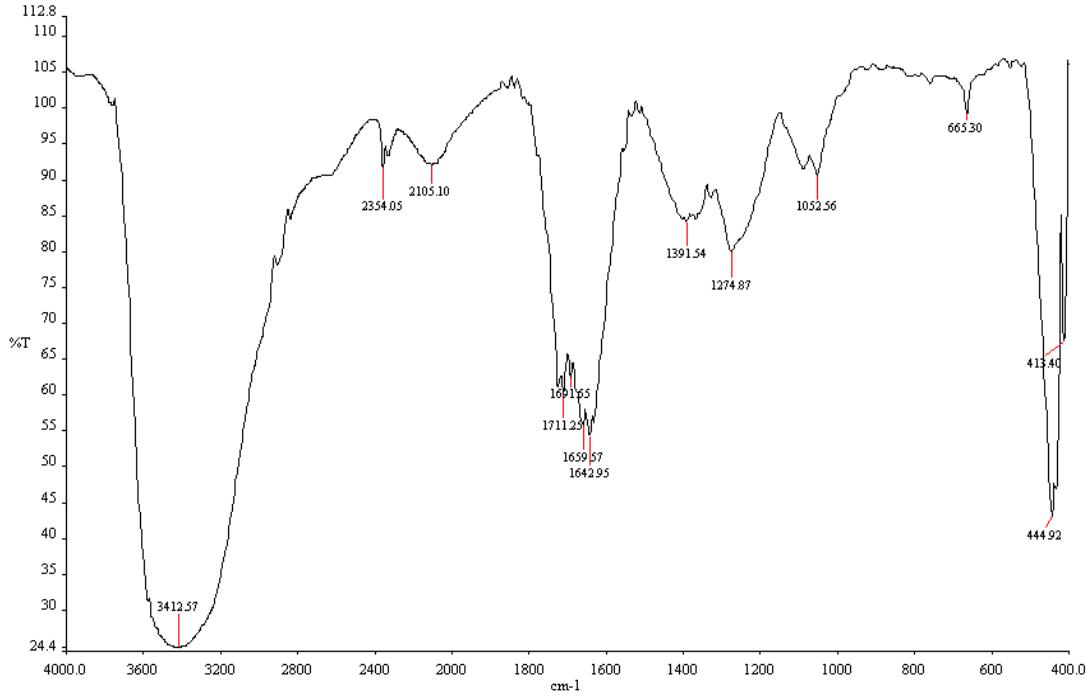

Fig.5. FTIR spectroscopy of the bio-oil at 450^{0}C

5.6 GC-MS OF BIO-OIL SAMPLE:

The GC MS of the bio-oil sample was used to detect the compounds present in the bio-oil from sugarcane bagasse is composed of mostly aliphatic carbon and aromatic compounds starting from (C_4-C_{11}). The compounds are mainly p-cresol, Phenol, Maltol, Creosol etc. The difference in chemical properties of the molecules will separate as the molecules move along

the column. The molecules are held in the column and then eluted from the column. Maltol is a naturally occurring organic compound which is used as a flavor enhancer-cresol is soluble in hot water chloroform and other organic solvents and phenol is used in production of Bakelite, Detergents, Herbicide and Pharmaceutical drugs. Many other compounds are detected which have their uses in various fields .The volatile components are then withdrawn onto a trap and then the volatile components

Table5. GC-MS analysis of the bio-oil

R. Time	Area%	Name of compound	Molecular formula
3.363	0.65	Furan ,tetrahydro-2,5-dimethoxy-	$C_6H_{12}O_3$
3.508	1.33	1,2-Hexanediol	$C_6H_{14}O_2$
3.552	1.05	2-Cyclopenten-1-one,2-methyl-	C_6H_8O
3.668	3.63	2(5H)-Furan one	$C_4H_4O_2$
3.726	1.66	3-Methoxy-2,2-Dimethyl Oxirane	$C_5H_{10}O_2$
3.828	4.32	1,2-Cyclopentane dione	$C_5H_6O_2$
4.075	0.90	2(5H)-Furan one ,5-Methyl	$C_5H_6O_2$
4.365	1.51	4-Amino-6-hydroxy pyrimidine	$C_4H_5N_3O$
4.438	0.93	3-Hexane-2-one,3-Methyl-	$C_7H_{12}O$
4.481	2.91	2-Furancarboxyldehyde,5-methyl	$C_6H_6O_2$
4.786	2.92	Phenol	C_6H_5OH
4.888	0.52	Pentatonic acid,4-oxo-methylester	$C_6H_{10}O_3$
5.091	0.65	Oxazolidine,2-butyl,2-ethyl,3-methyl	$C_{11}H_{23}NO$
5.149	0.82	Cyclohexane,3-Methyl-	$C_7H_{12}O$
5.236	0.55	1-Hydroxy-2-pentanone-	$C_5H_{10}O_2$

5.614	5.81	2-Hydroxy-3-methyl-	$C_6H_8O_2$
5.817	0.45	1H-Pyrazole,1,3,5-trimethyl-	$C_6H_{10}N_2$
5.919	1.68	1-Butene,3-3 Di-methyl-	C_6H_{12}
6.093	1.54	Phenol,3-Methyl-	$CH_3C_6H_4OH$
6.195	1.03	1,3-Dioxirane-2-propanol,2-Methyl	$C_8H_{16}O_3$
6.335	1.88	1H-Pyrrole,1-Methyl	C_5H_7N
6.442	1.90	p-cresol	C_7H_7OH
6.616	1.11	4-Hydroxy-2,5-dimethyl,3(2H)-furan one	$C_6H_8O_3$
6.776	4.36	N-Methyl-1,3-diaminePropane	$CH_3NH(CH_2)_3NH_2$
7.095	1.48	Maltol	$C_6H_6O_3$
7.197	1.16	2-Cyclopenatne-1-one,3-ethyl-2-hydroxy	$C_{10}H_{28}$
7.981	3.75	Phenol, 4ethyl-	$C_2H_5C_6H_4OH$
8.286	0.83	2,6-Dimethyl- 2,6-Octadine	$C_{10}H_{18}$
8.388	3.07	Creosol	C_7H_8O
8.664	2.98	3-Aminopiperidin-2-one	$C_5H_{10}N_2O$
8.809	0.94	Catecholborane	$C_6H_5BO_2$
8.911	0.81	3-Hexanal	$C_6H_{10}O$
9.695	3.47	Phenol,4-ethyl-2-Methoxy	$C_9H_{12}O_2$
10.392	1.97	2-Methyl cyclohexanol	$C_7H_{14}O$
10.726	6.84	Hexahydropthalic Anhydrite	$C_8H_{10}O_3$
11.409	1.02	Vanillin	$C_8H_8O_3$
11.990	2.05	3-(Methyl Sulfonyl) Benzoic acid	$C_8H_8O_4$

13.079	1.66	Benzoic acid,2,6 Dimethoxy	$C_9H_{10}O_4$
13.224	2.66	Ethyl 4- Methyl Hexanoate	$C_9H_{18}O_2$
13.907	1.02	Benzoic acid,4-Hydroxy-Butyl Ester-	$C_{11}H_{14}O_3$
15.417	0.86	Methyl 3,5-Dimethoxy benzoate	$C_{10}H_{12}O_4$
15.809	1.53	3-4 Dimethoxy Benzoic acid	$C_9H_{10}O_4$

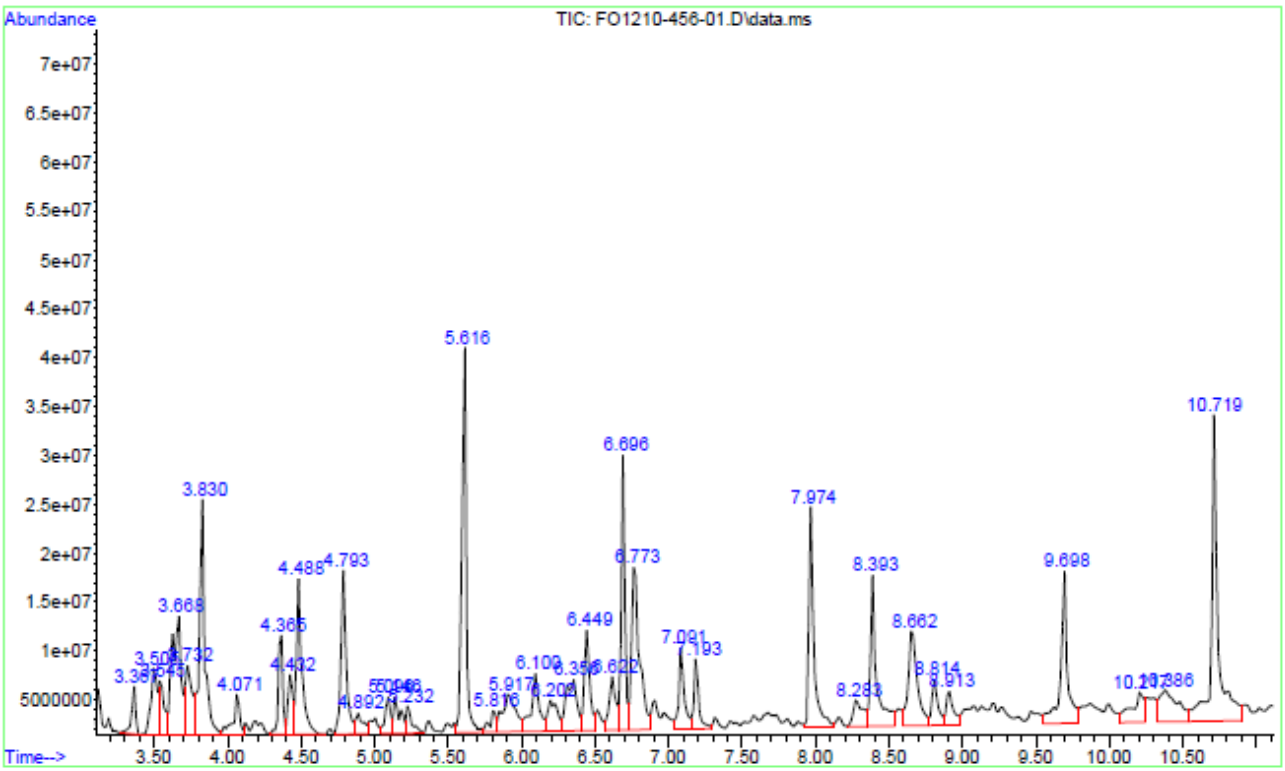

Fig6. GC-MS analysis of the bio-oil

5.7. PHYSICAL PROPERTIES:

The physical properties tests include the determination of pour point, cloud point , viscosity , density , flash point , fire point & gross calorific value of the bio-oil .

Table .6 Physical properties of the bio-oil

TESTS	RESULTS OBTAINED	TEST METHODS
Specific Gravity at 15^0 C	1.0856	IS:1448 P:16
Density @ 15^0C	1.0818	IS:1448 P:16
Kinematic Viscosity@40^0 C	1.60	IS:1448 P:25
KinematicViscosity@100^0C	Not possible	IS:1448 P:25
Condransons carbon Residue	2.25	IS:1448 P:122
Flash point by Abel method	52	IS:1448 P:20
Fire point	Sample boil in the cup without flashing at 80^0C	IS:1448 P:20
Cloud point	Not possible	IS:1448 P:10
Pour point	-12	IS:1448 P:10

Gross calorific value	1719 cal/gm 3094btu/lb	IS:1448 P:6

The physical properties of the pyrolytic oil were carried on with the instruments having standard as mentioned. The kinematic viscosity of the sample was unable to be determined since for the prediction of kinematic viscosity the oil needed to be first preheated at 60^0C, then methanol and KOH were mixed with it for a duration of 20-30 mins and then put in separating funnel and allowed to settle for 12-24 hours, but the problem is that in preheating stage it boils and turns into vapor so unable to predict values. The cloud point is also unpredicted since while determining the cloud point temperature the test oil needed to be seen in transparent layers .It is the temperature at which crystals first appear same problem also here when heated the sample boils and turns to vapor so unable to be predicted . For the prediction of flash point the samples are first to be taken in a cup and then heated to see the temperature at which the sample catches fire , but it is seen that the sample boils at 80^0 C in the cup in which it is taken . From the above studies it is predicted that as the water content in the bio-oil increases the viscosity decreases and thereby the energy content for the bio-oil .For the prediction of the sulphur content the procedure was followed and it was found to be negligible in the sample. The negligible sulphur content in the bio-oil is attributed to low pollution by reducing the SO_X emission to the atmosphere. The gross calorific value calculated are good from the fuel point of view as it will give good output and the carbon residue calculated, it is actually the coked material left after the sample has been exposed to high temperatures . It is the tendency of the fuel to form carbon deposits under high temperature conditions. The higher the carbon residue value may cause increased fouling gas thereby necessity of more cleaning for the engine , here since the value is low it can be used as a efficient fuel .

5.8 1H- NMR OF THE BIO-OIL:

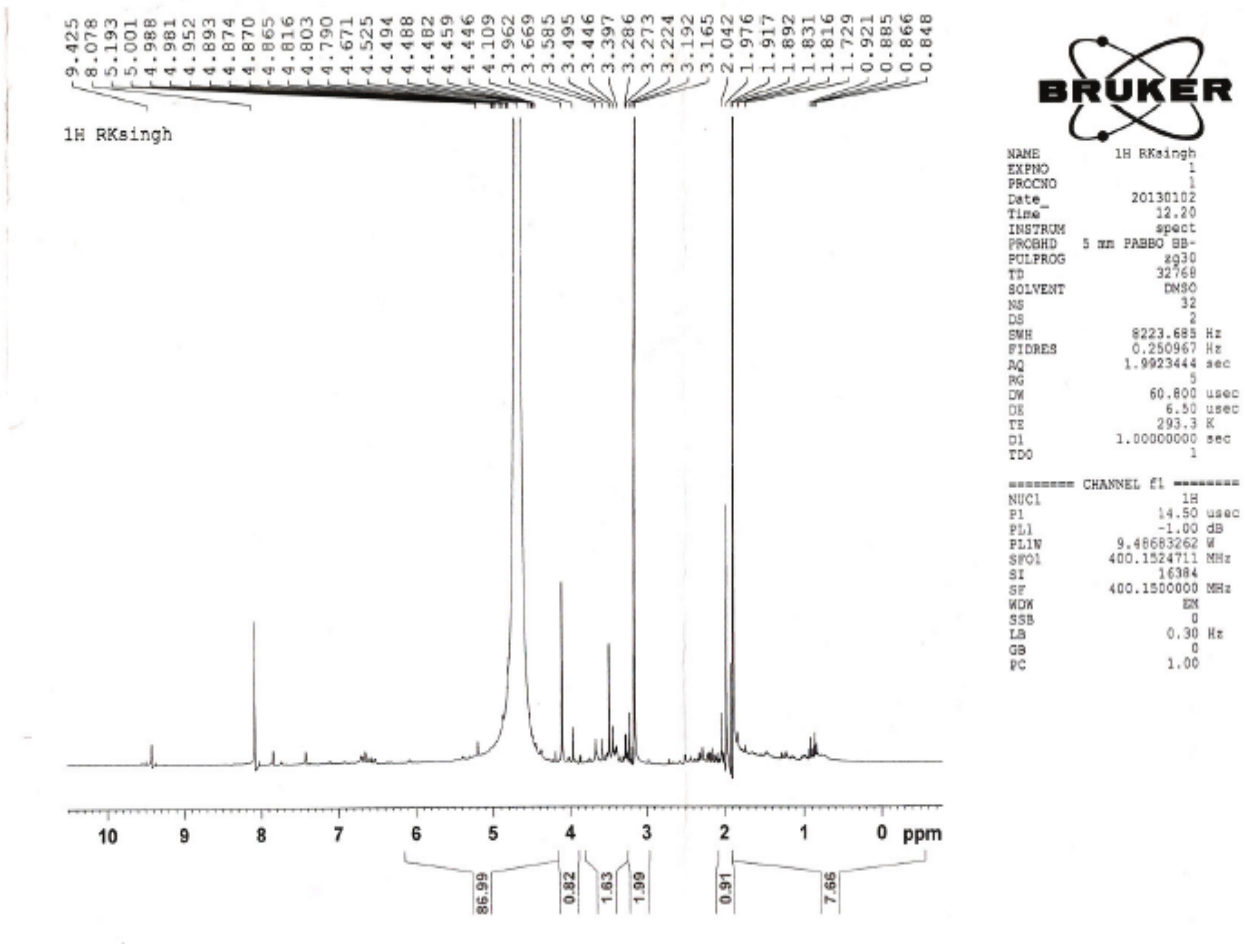

Fig .7 1H NMR of the bio-oil

Fig 7.1H NMR of the bio-oil

Types of hydrogen	Chemical shift	Percentage of total hydrogen
Phenolic or olefin Proton	6.5– 5.0	86.99
Hydroxyl groups or ring-join methylene(Ar–CH2–Ar)	4.5– 3.3	0.82

CH_3 CH_2 and CH to an aromatic ring	3.3-2.0	1.63
CH_2 and CH β to an aromatic ring (naphthenic)	2.0-1.6	1.99
β-CH_3, CH_2 and CH γ to an aromatic ring	1.6-1.0	0.91
CH_3γ or further from an aromatic ring	1.0-0.5	7.66

1H NMR of the sugar bagasse pyrolytic oil was conducted using DMSO as the solvent which is known as dimethyl sulfoxide it is an organic solvent that dissolves both polar and non polar molecules.

The above table represents the results of NMR which indicates that Phenolic or olefinic proton are found to about 86.99 % as compared to other groups they are found in abundance whereas Hydroxyl groups or ring join methylene are found in low quantity of about 0.82 % . The solvent used is weakly acidic that is why it dissolves all types of bases. Because of its high boiling point it slowly vaporizes at high pressures. The NMR results of the bio-char gives the isotopes in other sense that are present within the sample & will thereby help us to eliminate the unwanted or harmful isotope from the oil fraction so that we can use it for fuel purpose or other useful work.

6.0 ANALYSIS OF THE BIO-CHAR:

6.1 *PROXIMATE & ULTIMATE ANALYSIS OF THE BIO-CHAR:*

The proximate and ultimate analysis of the secondary intermediate i.e., the bio-char is done in order to quantify the fixed carbon and the ultimate analysis carbon in dominant and the other compositions are also determined simultaneously . The fixed carbon in percentage was found to be 49.52 whereas the ultimate carbon content was determined to be 56.31 % , the other components were also determined simultaneously .

Table8. Proximate analysis results of the bio-chars produced at various pyrolytic temperatures

Temperature	Volatile matter	Ash content	Fixed carbon
300	61.52	7.46	31.02
350	53.23	10.43	36.34
400	46.48	13.25	40.27
450	36.60	18.82	44.58
500	30.36	20.12	49.52

Table9. Ultimate analysis results of the bio-chars produced at various pyrolytic temperatures

Sample name	N%	C%	H%	S%	O%	H/C (MOLAR RATIO)	GCV
300	3.21	54.12	2.82	1.74	39.85	0.625	15.98
350	3.78	57.88	3.01	1.08	34.52	0.624	18.37
400	4.45	58.74	2.77	1.24	32.80	0.566	18.60
450	3.66	58.21	2.24	1.60	34.29	0.461	17.43
500	2.86	56.31	2.55	1.41	36.87	0.543	16.81

6.2 SEM EDX ANALYSIS OF BIO-CHARS:

6.2.1. SEM- EDX OF BIO-CHAR AT 300^0C:

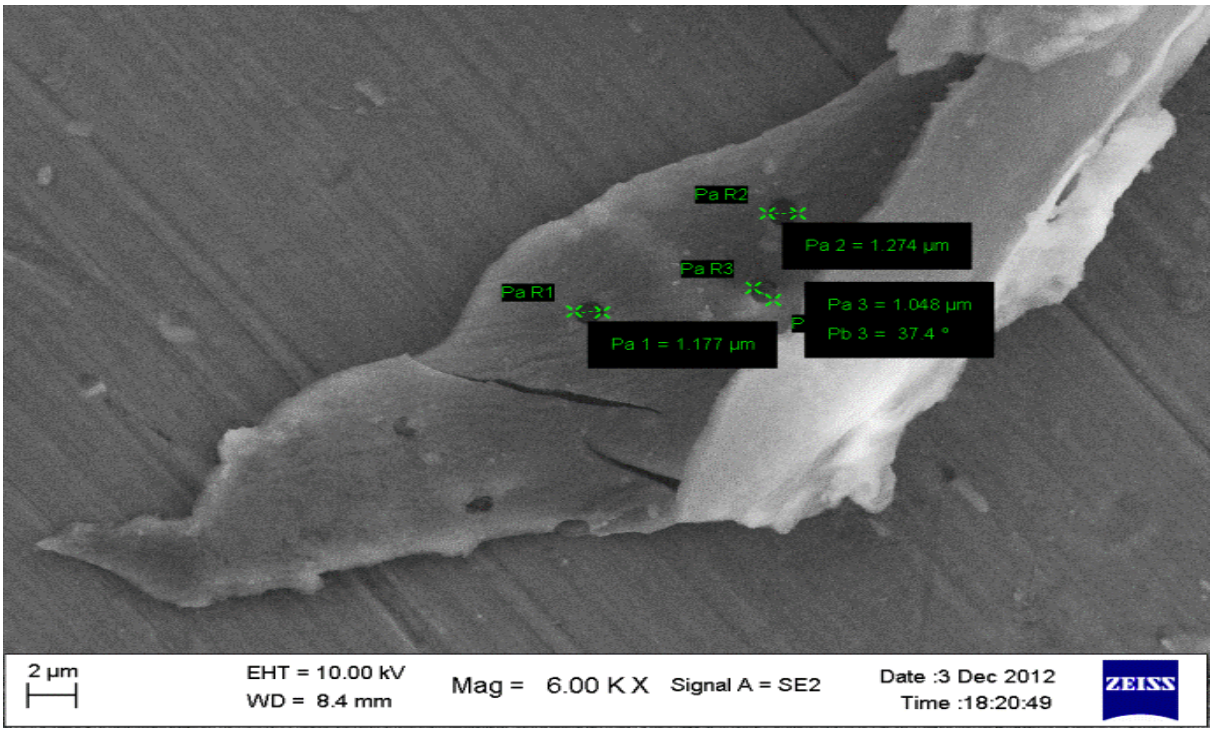

Fig8. SEM analysis of bio-char at 300^0 C

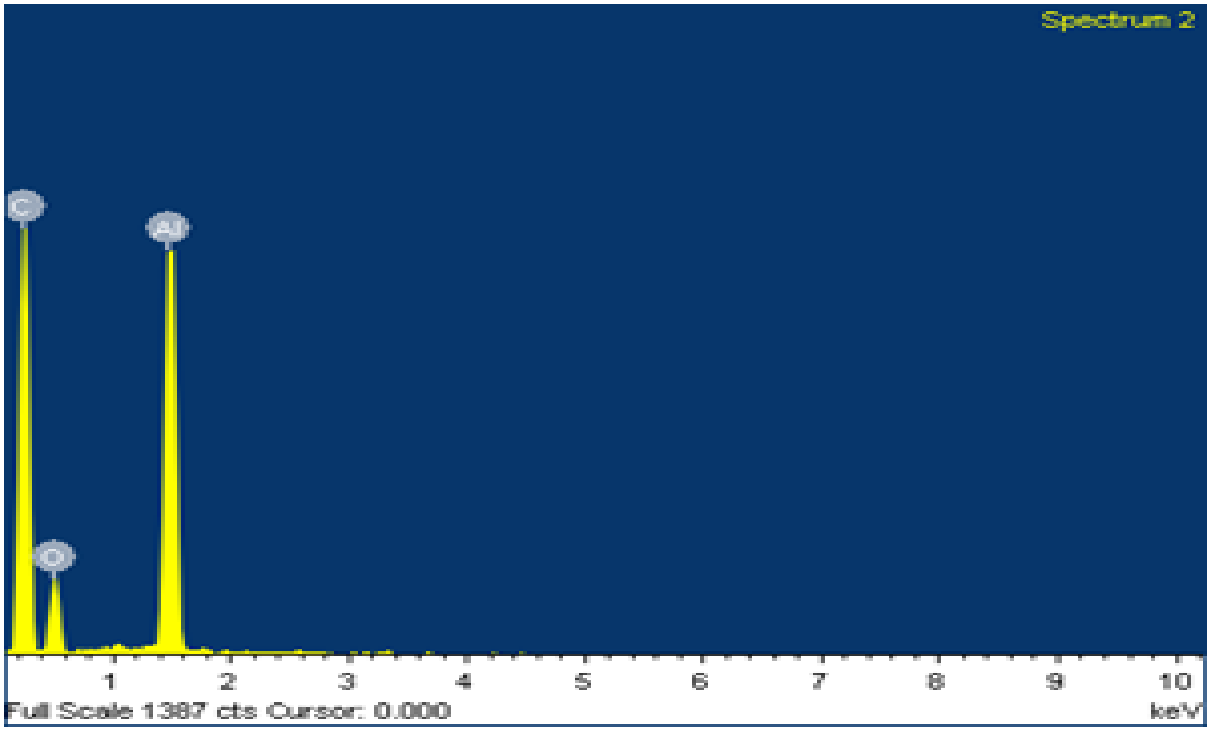

Fig9. EDX analysis of the bio-char at 300^0C

Table 10.EDX analysis of bio-char at 300^0 C

Element	App Conc.	Intensity Corrn.	Weight%	Atomic%	Compd%	Formula	Number of ions
C, K	3.47	1.1025	21.51	27.93	78.82	CO_2	3.41
Al, K	1.70	1.0385	11.21	6.48	21.18	Al_2O_3	0.79
O			67.28	65.59			8.00
Totals			100.00				
						Cation sum	4.20

6.2.2 SEM- EDX OF BIO-CHAR AT 350^0C :

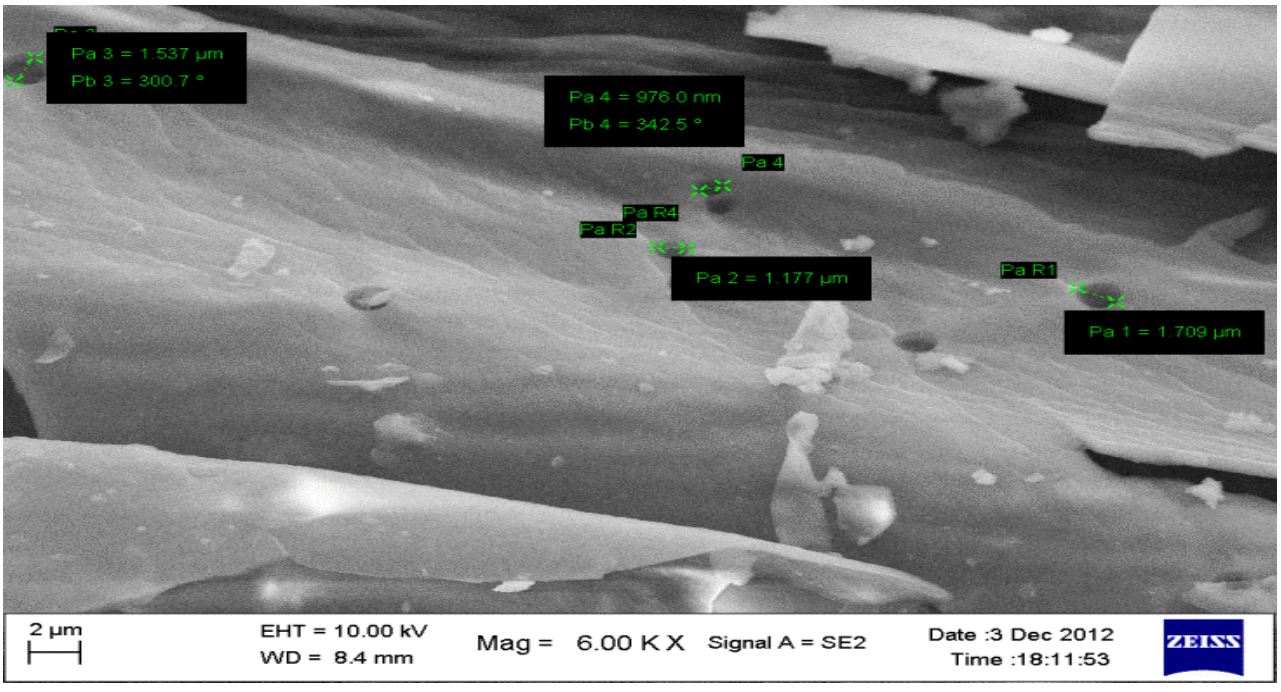

Fig10. SEM analysis of bio-char at 350^0 c

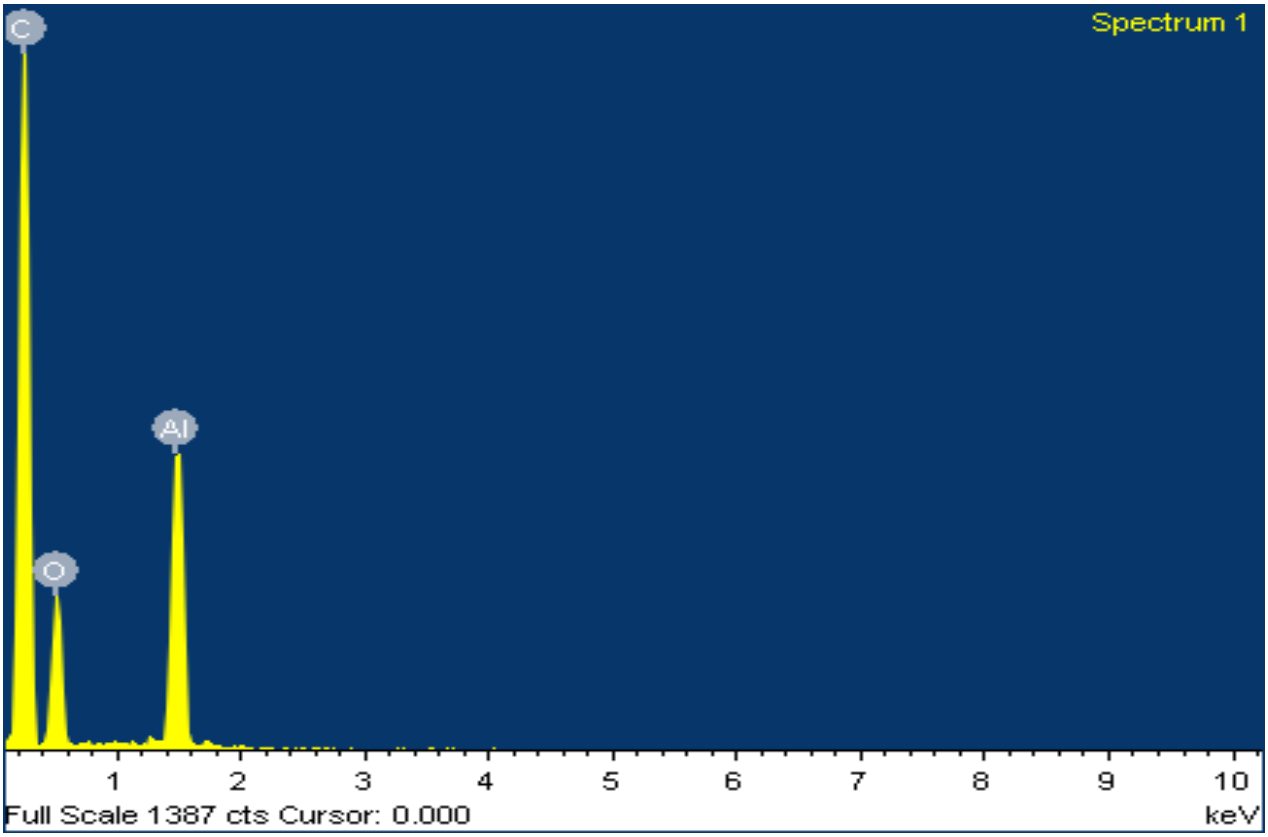

Fig 11. EDX Analysis of the bio-char at 350^0 C

Table 11. EDX analysis of bio-char at 350^0 c

Element	App Conc.	Intensity Conc.	Weight%	Atomic%	Compd%	Formula	Number of ions
C, K	4.93	1.2485	23.98	30.32	87.87	CO_2	3.67
Al, K	1.08	1.0247	6.42	3.61	12.13	Al_2O_3	0.44
O			69.60	66.06			8.00
Totals			100.00			Cation sum	4.11

6.2.3 SEM- EDX OF BIO-CHAR AT 400^0C :

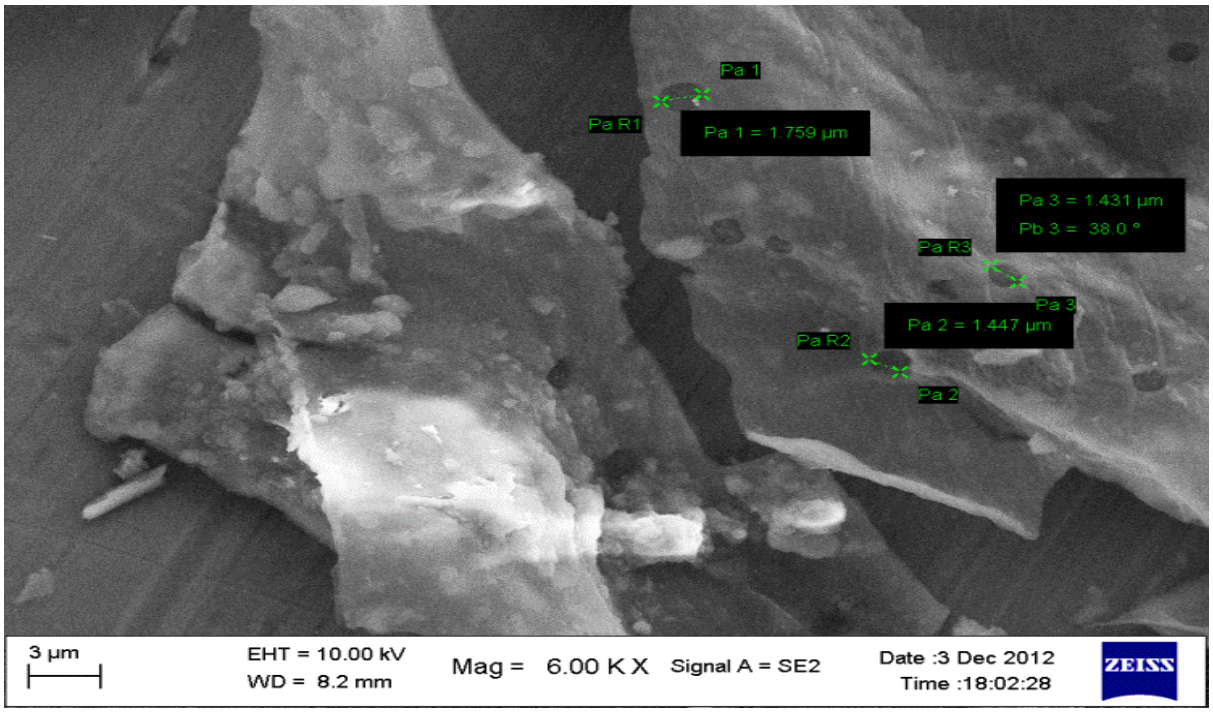

Fig12. SEM analysis of the bio-char at 400^0 C

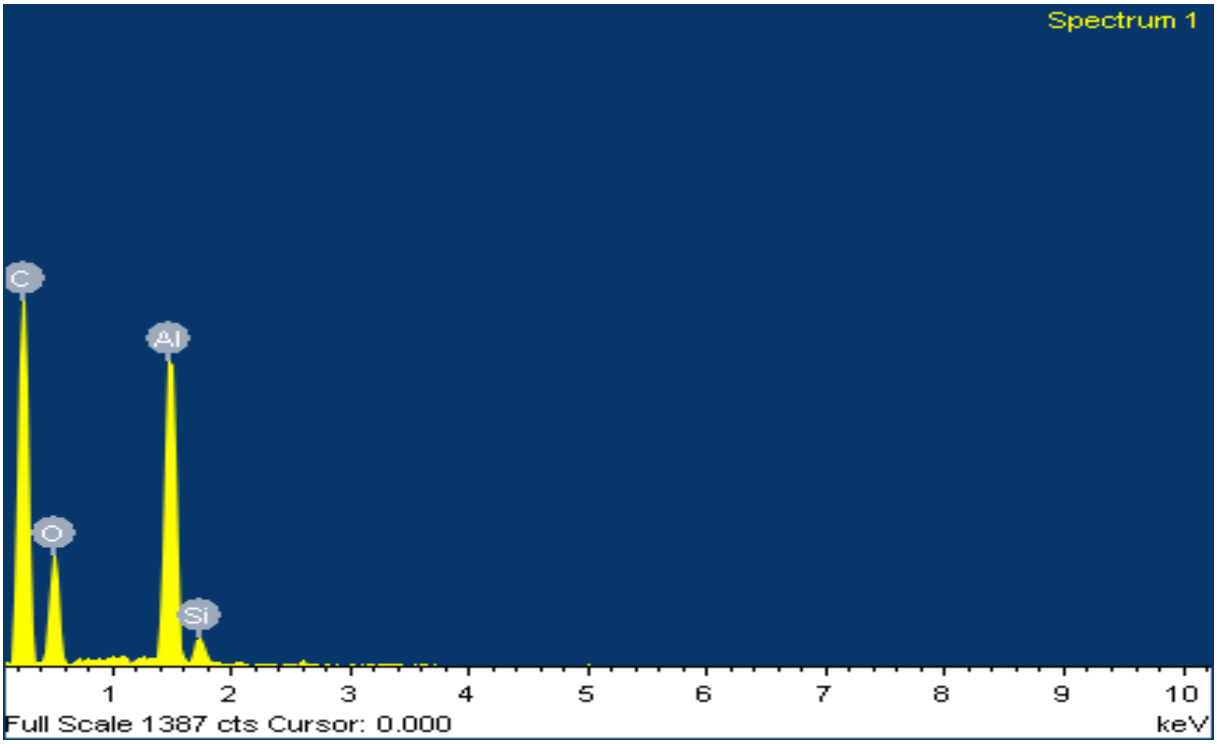

Fig13. EDX analysis of bio-char at 400^0 C

Table12. EDX analysis of bio-char at 400^0 C

Element	App	Intensity	Weight%	Atomic%	Compd%	Formula	Number of ions
	Conc.	Corr.					
C, K	2.86	1.0974	21.54	27.95	78.92	CO_2	3.40
Al,K	1.26	1.0379	10.02	5.79	18.92	Al_2O_3	0.70
Si, K	0.12	0.9817	1.01	0.56	2.16	SiO_2	0.07
O			67.44	65.70			8.00
Totals			100.00			Cation sum	4.18

6.2.4 SEM EDX OF BIO-CHAR AT 450^0C :

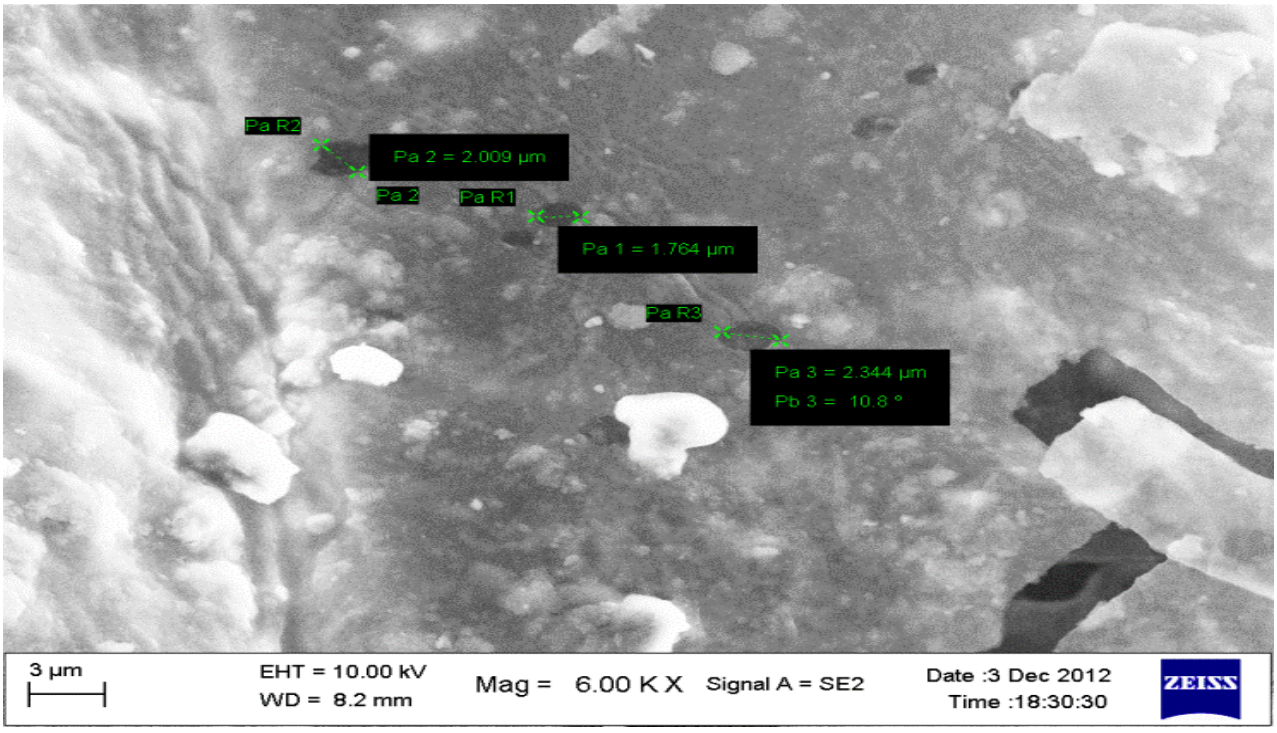

Fig14. SEM of bio-char at 450^0 C

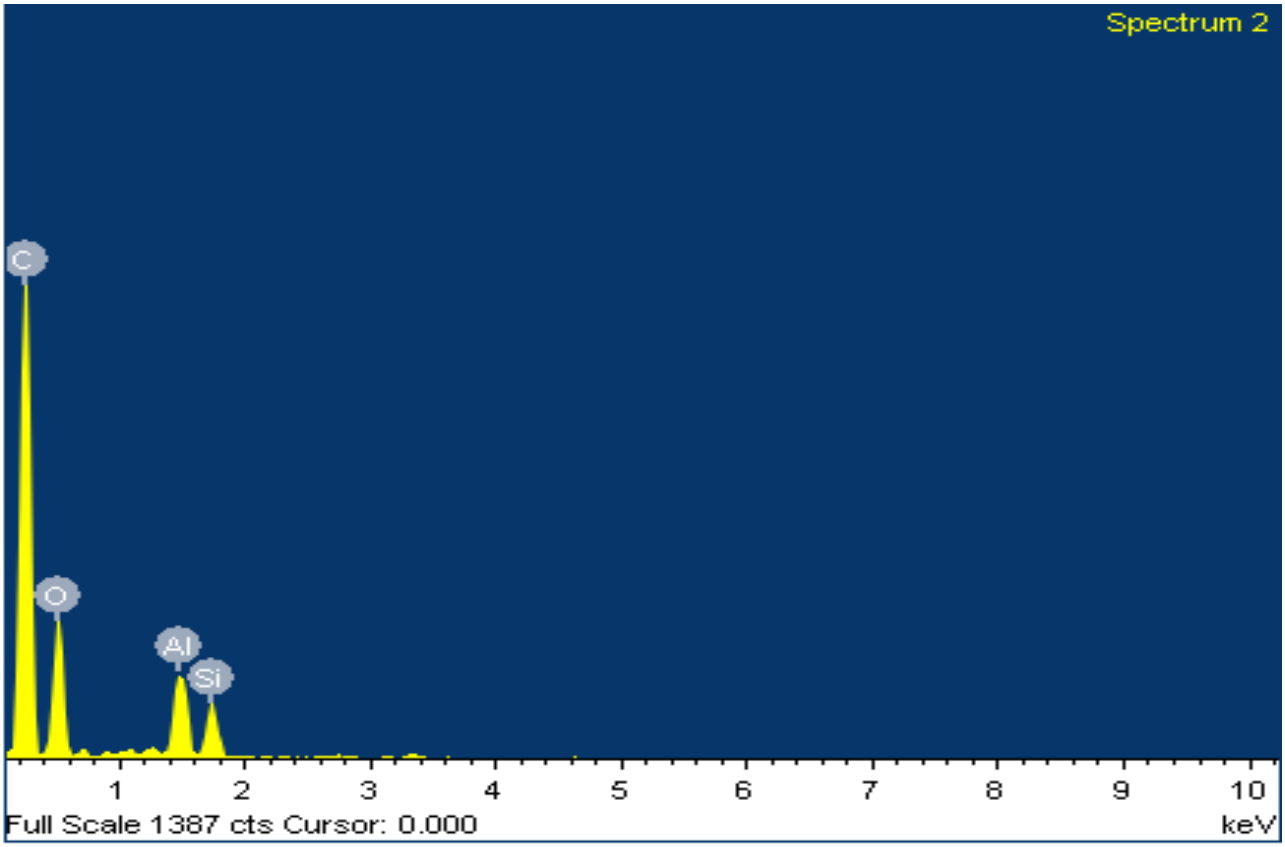

Fig15. EDX of the bio-char at 450^0 C

Table 13.EDX Analysis of the bio-char at 450^0 C

Element	**App**	**Intensity**	**Weight%**	**Atomic%**	**Compd%**	**Formula**	**Number of ions**
	Conc.	**Corr.**					
C, K	3.26	1.2848	24.76	31.03	90.72	CO_2	3.74
Al K	0.28	1.0196	2.68	1.50	5.07	Al_2O_3	0.18
Si K	0.20	1.0021	1.97	1.06	4.21	SiO_2	0.13
O			70.59	66.42			8.00
Totals			100.00			Cation sum	4.05

6.2.5 SEM EDX Of the bio-char at 500^0C :

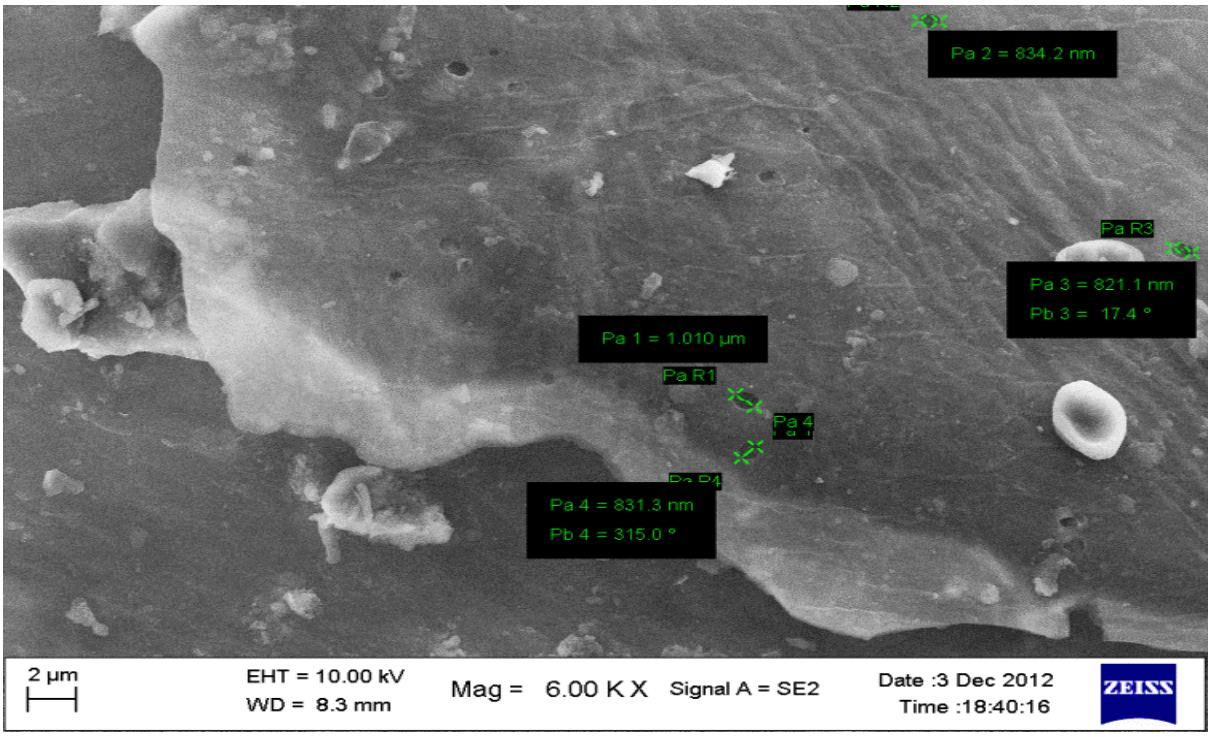

Fig16. SEM Of the bio-char at 500^0 C

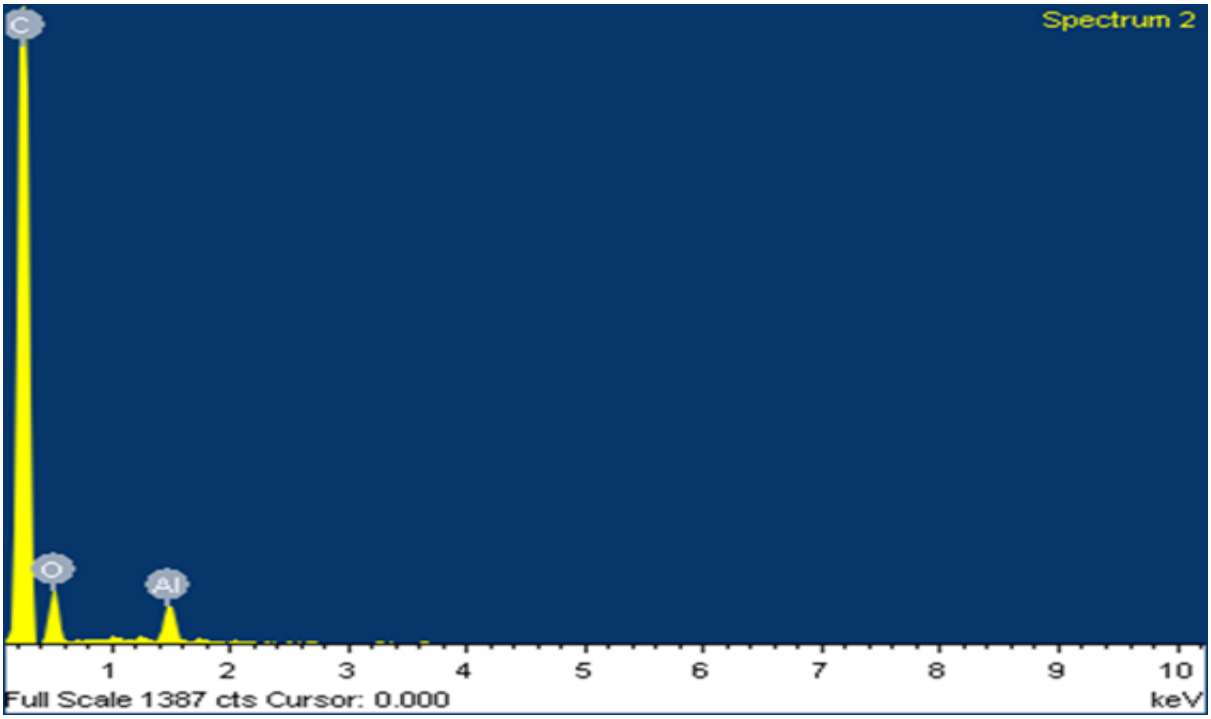

Fig17. EDX of the bio-char at 500^0 C

Table14. EDX Analysis of the bio- char at 500^0C

Element	App	Intensity	Weight%	Atomic%	Compd%	Formula	Number
	Conc.	Conc					of ions
C K	6.06	1.4541	26.80	32.90	98.21	CO_2	3.95
Al K	0.15	1.0093	0.95	0.52	1.79	Al_2O_3	0.06
O			72.25	66.58			8.00
Totals			100.00			Cation sum	4.02

6.3 TGA OF THE BIO-CHAR AT OPTIMUM PYROLYTIC TEMPERATURE:

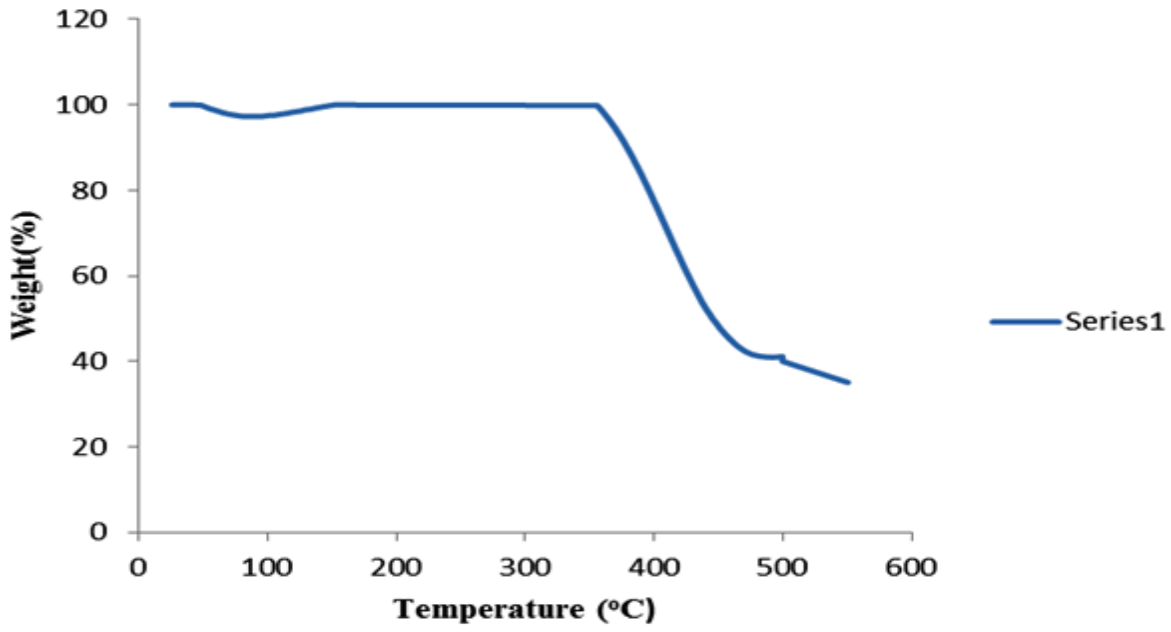

Fig18. TGA of the bio-char

The Thermo-gravimetric analysis of the bio-char analysis shows the amount of carbon content in percentage and which is approximate to those found from the elemental analysis of the bio-char at the optimum values. The decomposition of the biomass is as usual in 3 stages moisture loss, volatile loss and the ash at last. From the above fig we calculated that the carbon content in the bio-sample and those pre-calculated are approximately same. In the bio-char as we all know that nothing is left after the sample's ash content is found as the kinetic study is done through TGA method and here the TGA is used to study the kinetics as well as verification of the carbon content after the ash content being found .

6.4 ELECTRICAL CONDUCTIVITY OF THE BIO-CHARS:

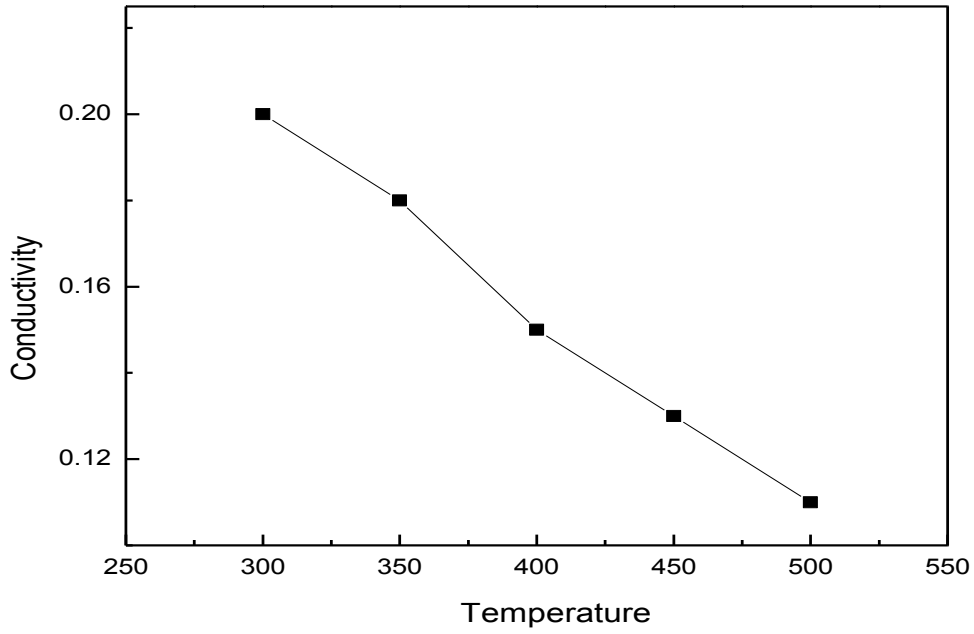

***Fig 19.Electrical Conductivity of the bio-chars at various temperatures*.**

The electrical conductivity is the measure of total amount of water soluble ions in the bio-char. In the above studies we conclude that with the increase of the temperatures of the pyrolytic bio-chars the electrical conductivity decreases, the bio-char at 300^0C showed a conductivity of about 0.18 & we observed that it showed a decreasing trend which indicates a lower conductivity value which in other sense means it has slow salinity means it can be

applied to soil for soil amelioration purpose. Low salinity shows that it can hold more nutrients and can also facilitate the transport of nutrients to the plants for their growth & metabolism.

6.5 BET SURAFCE AREAS OF THE BIO-CHARS AT VARIOUS TEMPERATURES:

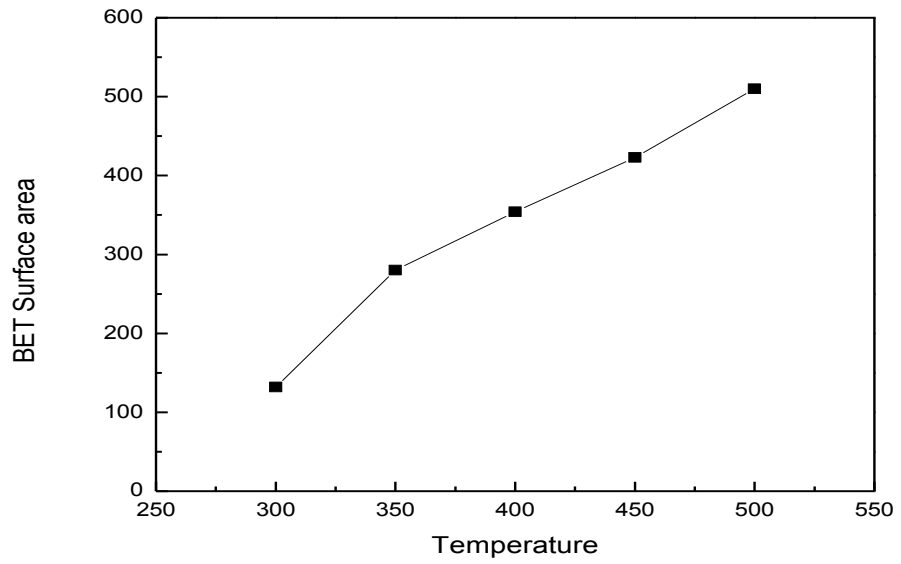

Fig 20. BET surface areas of the bio-chars

The BET surface areas of the bio-chars were calculated and were found that the surface areas showed an increasing trend with the increase of pyrolytic temperatures. It increased from 132 m^2/gm to 510 m^2/gm. The pyrolytic condition like temperatures and pressures perhaps affects the surface areas. The low surface areas for the inital pyrolytic temperatures bio-chars may be due to presence of alkaline earth metals in the bio-chars, but with the increase of the pyrolytic temperatures the surface areas of the bio-chars increased due to the volatization of the alkaline earth metal species . The bio-chars were placed in nitrogen atmosphere prior to surface areas calculation .During the calculation of the surface areas reduction in the burn-off was observed at high temperatures bio-char.

6.6. ANION CHROMATOGRAPHY OF THE BIO-CHAR:

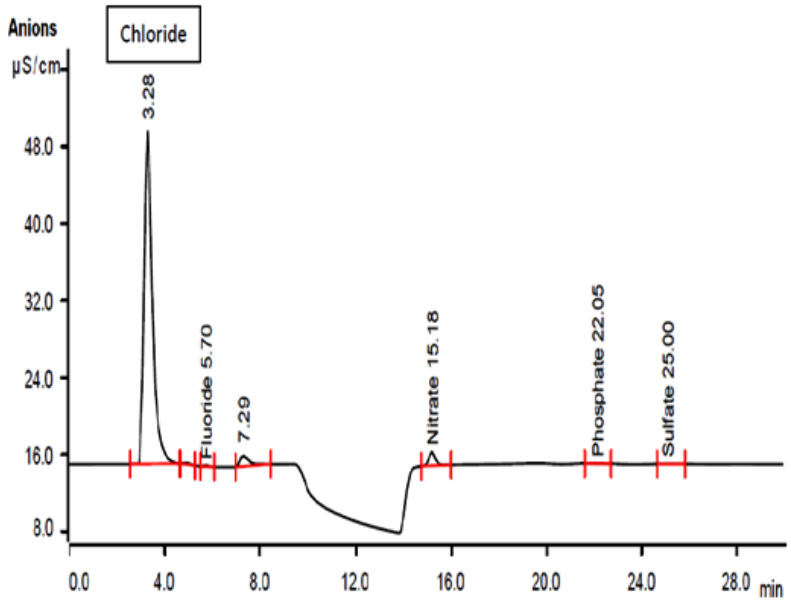

Fig 21. Anion chromatography results for the bio-char

Table 15. Tabulation for anion chromatography

Peak number	Retention time	Area (µS/cm)*min	Height	Concentration ppm	Component name
1	3.282	13.735	34.411	5.241	Chloride
2	5.702	0.0315	0.122	0.119	Fluoride
3	15.175	0.4342	1.434	4.492	Nitrate
4	22.047	0.0155	0.029	0.325	Phosphate
5	24.995	0.0070	0.012	0.052	Sulfate

6.7. XRD ANALYSIS OF THE BIO-CHAR :

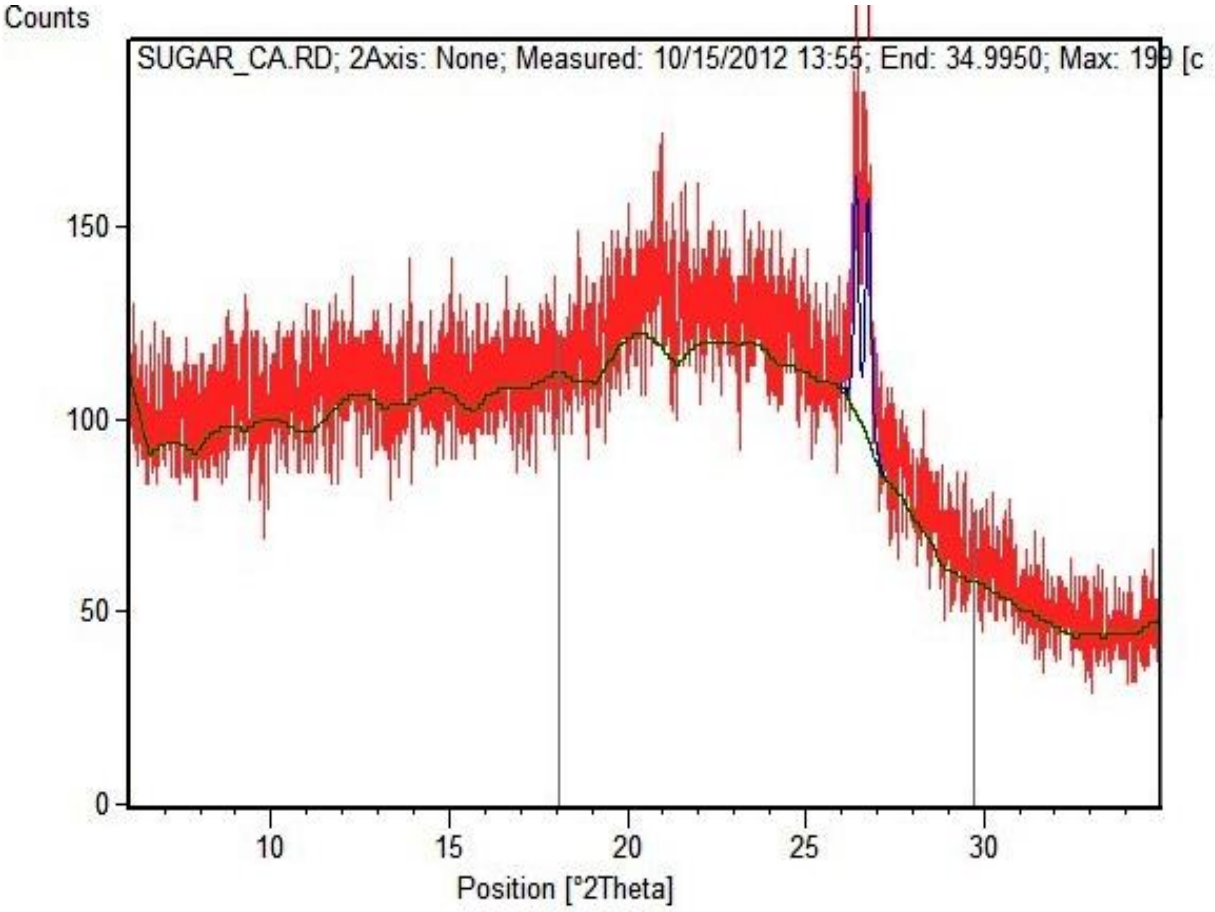

Fig22. XRD analysis of the bio-char

From the above study it was found that the bio-char structure was amorphous with the peaks found within the range where carbon phase was found out. The normal starting band of spectrum was misjudged as noise within the sample but later it was confirmed that those were not noise in the instrument rather those were the continuous spectrum. This was done with anCu alpha radiation having wavelength of 1.5418 A^0 which was used to study the structure of the bio-char. It was found that the sample wholly was existing in carbon phase. The step size followed here was 5-60^0. The crystallinty in the sample was found to be reduced due to the depolymerisation from the biomass sample.

6.8. pH OF THE BIO-CHAR SAMPLE:

The pH of the bio-char sample was calculated by 2 modes of operation firstly it is dissolved in distilled water and then pH was calculated and in the next stage the pH was calculated using KCL (Neutral salt) as the dissolving medium. It was found that the pH was slightly acidic when dissolved in distilled water, but the acidity again became more when dissolved in KCL , this showed that the acidity was found to be reserved. The sample acidity & alkalinity was also calculated by using Bohem titration as the method.

Table 16.pH of the bio-char sample

Biomass	pH(H_2O)raw	pH(H_2O)Bio char	pH(KCL)Bio char	Surface Acidity (mmol/gm)	Surface alkalinity (mmol/gm)
Sugarcane Bagasse	6.19	6.52	5.3	3.5	1.8

The pH of the bio-char sample was found to be acidic i.e, between (6-7). The pH of the bio-char sample finds its application in the soil. The pH of the sample can used to find its dynamics which is important as per soil amendment application of the bio-char. The alkalinity is low as compared to the acidity which virtues the bio-char for its application in the soil as soil amelioration / amendment purpose.

6.9. FTIR OF THE BIO-CHAR SAMPLE:

The FTIR of the sample in general indicates the functional group present and the absorbance of the function group in a particular wave number.

TABLE 17. FTIR assignment of the bio-char

Frequency range(cm^{-1})	**Groups**	**Class of compounds**
3948	O-H GROUP	Polymeric O-H , Water Impurity
3454	O-H GROUP	Polymeric O-H , Water Impurity
3400	O-H GROUP	Polymeric O-H , Water Impurity
3374	O-H GROUP	Polymeric O-H , Water Impurity
2982	C-H STRECHING GROUP	Alkanes
2920	C-H STRECHING GROUP	Alkanes
2334	C-H STRECHING GROUP	Alkanes
1674	C=O STRETCHING GROUP	Ketones, Aldehyde & Carboxylic acid
1608	C=O STRECHING GROUP	Ketones, Aldehyde & Carboxylic acid
1552	C=C STRECHING GROUP	Alkenes
1382	C-H bending	Alkanes
1202	C-O & O-H STRECHING	Alcohols , Phenols, Esters &Ethers for O-H Bonding

1092	C-O &O-H STRECHING	Alcohols , Phenols, Esters &Ethers for O-H Bonding
740	O-H BENDING	Aromatic compounds
526	O-H BENDING	Aromatic compounds
460		Visible region

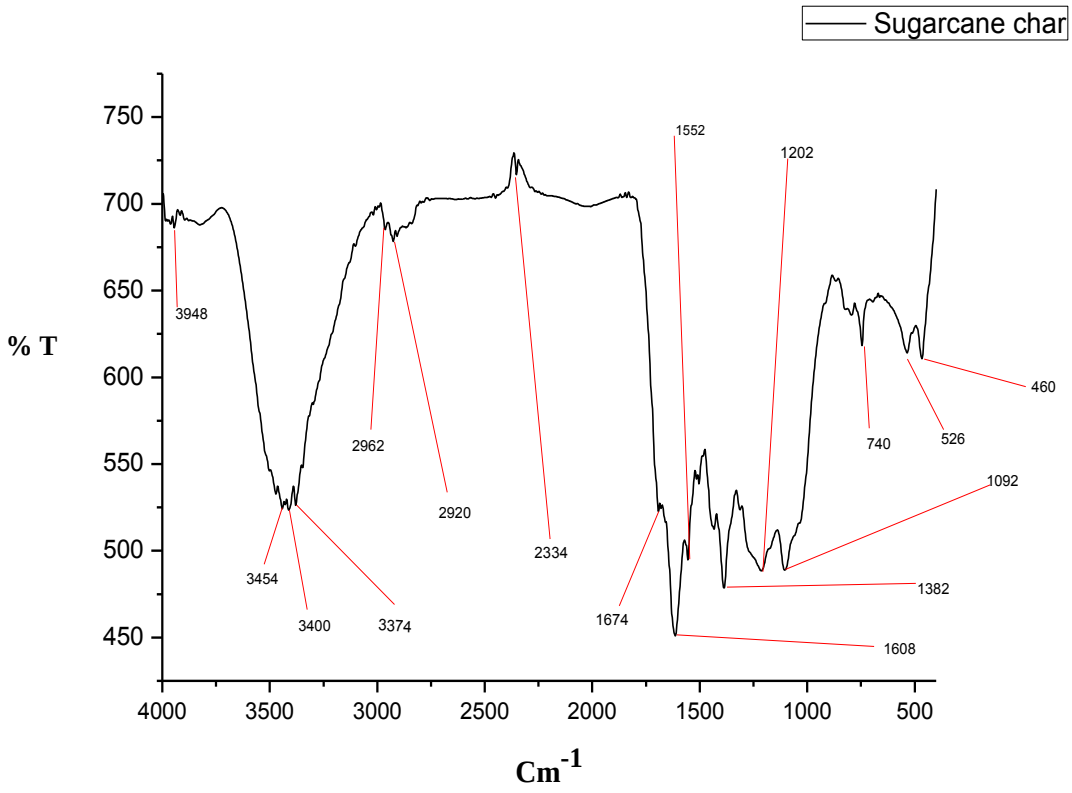

Fig 23. FTIR spectra of the bio-char sample

The FTIR spectra of the bio-char sample show the functional groups that are present. The absorbance at various wave numbers corresponds to various functional groups. The wave number near 1400 cm^{-1} is generally attributed to O-H bonding / C-O vibration. The wave

number near 1000 i.e., (1202 & 1092) shows the characteristics of C-H &O-H stretching. On the other hand the 740 & 526 wave number corresponds to O-H bending.

7.0. ZETA POTENTIAL ANALYSIS OF THE BIO-CHAR:

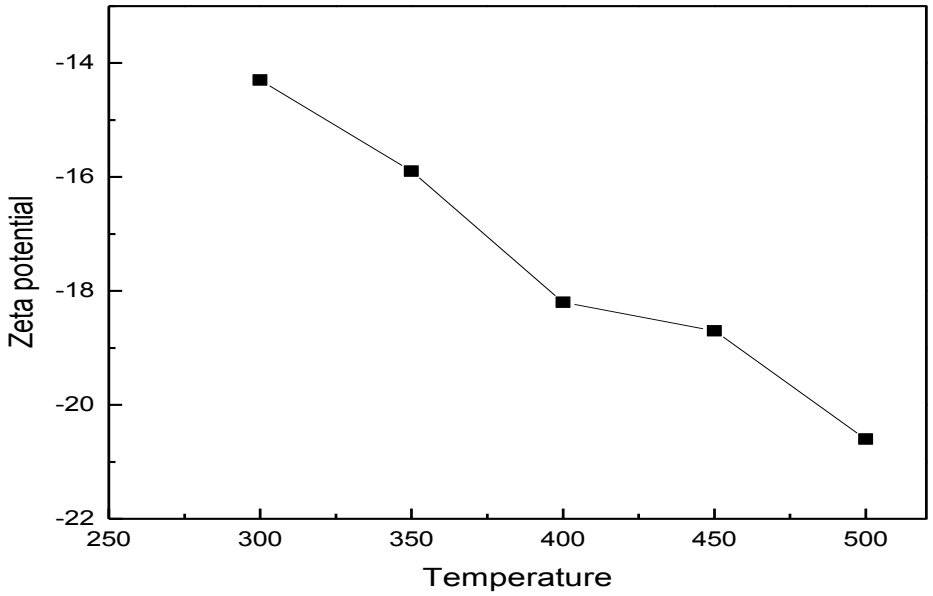

Fig24. Zeta potential analysis of the bio-chars at various pyrolytic temperatures

The zeta potential of the bio-char gives the values of the surface charge of the bio-char samples at various pyrolytic temperatures which in turn can specify the nutrient holding capacity of the bio-chars at various pyrolytic temperatures. The zeta potential values calculated from above showed that the values increased with increase of the bio-char temperatures which clearly indicate the presence of surface negative charge of bio-chars & which could be applied for soil amelioration purpose in order to reduce the acidity of the soil.

CHAPTER 8

CONCLUSION

8. Conclusion

Since the demand for energy is growing more and more the dependency on fossil fuel need to be reduced since they will get totally exhausted, the need for more and more efficient used of biomass by converting it to an efficient and clean source of energy, therefore the biomass conversion is done by pyrolysis technique to find efficient utilization of biomass to produce the energy in form of solid, liquid & gaseous fuels.

In this present work the pyrolysis of the sugarcane bagasse is conducted at various temperatures starting from 300^0C- 500^0C at 15^0 C rate of heating in the reactor thereby giving an yield of 53.3% which was found to be optimum at the temperature of 450^0C . On contrary the bio-char yield showed a decreasing trend and the volatiles in a similar manner showed increasing trend upto optimum temperature i.e, 450^0C, giving an yield of 53.3% bio-oil at 450^0C thereafter showing a decreasing trend.

The components present in the bio-oil sample were found suitable for its use as bio-fuel in turbines and other applications. Whereas on the other hand the bio-char produced by the pyrolysis of bio-char also has its applications as found by characterization of the bio-char like the nutrients present in it may help as a precursor in the soil amendment purpose. The weight loss from the TGA studies of the bio-char gave that the weight loss found was 35%. The surface area values of the bio-chars would suitably find its application in soil amendment purpose. The anion chromatography results also inferred various plant required nutrients which might find its applications. The proximate and ultimate analysis of the bio-chars produced at various pyrolytic temperatures revealed that the carbon content were upto the mark which can be used as a fuel , since the carbon composition in the bio-fuel plays a vital role. The FTIR analysis results showed negative functional groups on the surface of the bio-char like carboxyl groups and phenolic groups. Therefore with such tests conducted for the bio-oil and the bio-char were all found feasible for its application as bio-fuel as well as its application as bio-char and various other applications depending upon the properties of the sample, therefore the use of the bio-fuel in refinery was found feasible from properties study.

CHAPTER 9

FUTURE WORK

9. FUTURE WORK:

1. Engine performance of the bio-oil.

2. Soil amendment studies of the bio-char.

3. Bio-char applications as fuel & other applications.

4. Study of adsorption properties of the bio-char.

5. Study the distillation range of the bio-oil.

CHAPTER 10

BIBLIOGRAPHY

CHAPTER 10. BIBLIOGRAPHY:

1. Lucian A. Lucia, "Lignocellulosic biomass: A potential feedstock to replace petroleum", Bio Resources 2008, (4), 981-982.

2. A.V Bridgewater, Chemical Engineering Journal, 2003 (91) 87-102.

3. J.M Encinar, F.JBelatran, A. Bernalte, A.Ramrio, J.F Gonzalez, "Biomass and bio energy" 1995 (11) 397.

4. Dinesh Mohan, Charles. U.Pittman, Jr., Phillip. Steele, "Pyrolysis of Wood/ Biomass: A critical Review", 2006, (3) 848-889

5. Yun yunpeng & Shubin Wu, "Fast pyrolysis characteristics of sugarcane bagasse hemicelluloses", Cellulose Chem.Technol., 2011 (45) 605-612 .

6. K.Raveendran, Anuradda Ganesh, Kartic .C. Khilar, "Pyrolysis characteristics of biomass and biomass components" 1996, (75), 987.

7. M.Gracia- Perez, A. Challa, J. Yang, C.Roy "Co-pyrolysis of sugarcane bagasse with petroleum residue .Part 1: Thermo gravimetric analysis" , Fuel, 2001,(80), 1245-1258 .

8. Mohammad Rofiqul Islam, MomtazParveen, Hiroyuki Haniu "Properties of sugarcane waste derived bio-oil obtained by fixed- bed, fire-tube heating pyrolysis",2010, (101), 4162-4168 .

9. Surinder Katayal, Kelly Thambimuthu, Marjorie Valix, "Carbonization of bagasse in a fixed bed reactor: Influence of process variables on char yield and characteristics", 2003, (28), 713-725.

10. W.T.Tsai, M.K Lee, Y.M Chang, "Fast pyrolysis of rice straw, sugarcane bagasse & coconut shell in induction heating reactor", 2006 (76), 230-237.

11. J.Zandersons, J.Gravitis, A. Kokorevics, A.Zhurinsh, O.Bikovens, A.Tradenaka, B.Spince, "Studies of Brazilian sugarcane bagasse carbonisation process & product properties, 1999, (17), 209-219.

12. M.Carrier, T.Hugo, J.Gorgens, J.H.Knoetze, "Comparison of slow and vacuum pyrolysis of sugarcane bagasse", 2011, (90), 18-26.

13.Mandu Inyang , Bin Gao , P.Pullamannapallil ,Wenchuan Ding , Andrew.R.Zimmerman , “Biochar from anerobically digested sugarcane bagasse” , 2010, (101) ,8868-8872 .

14. Z.Luo, S.Wang, Y.Liao, J.Zhou, Y.Gu & Kefa Cen, “Research on biomass fast pyrolysis for liquid fuels”, 2004, 26, 455-462.

15. J.Lehmann, “Bio energy in the black, Frontiers in Ecology and the Environment”, 2007, (5), 381-387.

16. S.P Sohi, E. Krull, E.Lopez-Capel, R.Bol, “A review of bio-char and its use and function in soil”, 2010, (105) , 48-75 .

17. M.Carrier, A.G Hardie, U.Uras, J.Gorgens, J.Knoetze , “Production of char from vacuum pyrolysis of sugarcane bagasse and its characterization as activated carbon and bio-char”, 2012, (JAAP-2725), 1-9 .

18. P.Das, A.Ganesh, P.Wangikar , “ Influence of pre-treatment of deashing of sugarcane bagasse on pyrolysis products , Bio-mass and Bio energy , 2004 ,(27), 445-457 .

19. Charles A. Mullen, A.A Boateng, N.M Goldberg , I.M Lima , D.A Laird ,K.B Hicks ,“ Bio-oil and bio-char production from corn stover by fast pyrolysis” ,Biomass & Bio-energy , 2010 ,(34) ,67-74 .

20. J.Lehmann, J.Gaunt, M.Rondon, “Bio-char sequestration in terrestrial ecosystems – A Review”, Mitigation and adaptation strategies for global change, 2006, (11), 403-427.

21. J.L Gaunt & J .Lehmann, “Energy balance and emission associated with bio-char sequestration and pyrolysis bio-energy production, Environ.Sci.Technol, 2008, (42), 4152-4158.

22. K.H Kim , J.Y Kim , T.S Cho, J.W Choi , “Influence of pyrolytic temperature on physicochemical properties of bio-char obtained from fast pyrolysis of pitch pine ,Bio resource Technology, 2012 , (118), 158-162 .

23. J.H Yuan, R-K Xou, H. Zhnag , “The forms of alkalis in the bio-char produced from crop residues at different temperatures”,2011, (102), 3488-3497.

24. J.Yoder, S.Galinato, D. Granatstein, M.Gracia Perez, “Economic tradeoff between bio-char & bio-oil production via pyrolysis”, 2011, (35), 1851-1862.