



**Production and Characterization of Bio-char and Bio-oil**

**From Rice Husk**

DISSERTATION-2 REPORT

Submitted by

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In partial fulfillment for the award of the degree of  
MASTER OF TECHNOLOGY  
IN  
BIOTECHNOLOGY

Under the guidance of

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**TOPIC APPROVAL PERFORMA**

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Overall Remarks: Approved

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Approval Date: 21 Nov 2017

## **DECLARATION**

I hereby declare that the project entitled “**Production and Characterization of Bio-char and Bio oil From Rice Husk** ” is an authentic record of our own work carried out at School of Bioengineering and Biosciences, Lovely Professional University, Phagwara, for the partial fulfillment of the award of Bachelors of Technology in Biotechnology, under the guidance of Er. Ajay Kumar. This work is our original work and has not been submitted for any degree/diploma in this or any other University. The information furnished in this report is genuine to the best of our knowledge and belief.

**Monika**  
**(11306953)**

## **CERTIFICATE**

This is to certify that Monika (11306953), has completed dissertation II project (BTY783) entitled **“Production and Characterization of Bio-char and Bio oil From Rice Husk”** under my guidance and supervision. To the best of my knowledge, the present work is the result of their original investigation and study. No part of the report has ever been submitted for any other degree at any University. The report is fit for submission and the partial fulfillment of the conditions for the award of B. Tech. Biotechnology.

(Supervisor's signature)

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# INTRODUCTION

Bio-char is considered as the charred organic matter, which is produced with the objective to be purposely applied to soils to confiscate C and recover soil properties (Lehmann and Joseph, 2009). Biomass conversion into bio char is done either by hydrothermal conversion or pyrolysis. It has been illustrated as a significant potential tool for soil amendment and carbon sequestration (Day et al., 2005).

## 1. Bio-char

Bio-char is considered as the charred organic matter, which is produced with the objective to be deliberately applied to soils to confiscate C and recover soil properties (Lehmann and Joseph, 2009). Biomass conversion into bio char is done either by hydrothermal conversion or pyrolysis . It has been illustrated as a significant potential tool for carbon sequestration and soil amendment (Day et al., 2005). The International Bio-char Initiative (IBI) states that bio-char is a solid substance which is obtained from biomass carbonization. Bio-char could be added as a carbon sink or modifier for the reduction of greenhouse CO<sub>2</sub> emissions from the decaying biomass. Bio-char exists as a soil alteration and carbon black exists from wildfires in Terra Preta sites (Lehmann et al., 2011; Lehmann, 2007; Brewer et al., 2009). Bio-char usage in carbon sequestration, carbon farming, climate change mitigation, and soil remediation have been critically reviewed (Sohi et al., 2009; Lehmann, 2007; Ahmad et al., 2013b; Lehmann et al., 2006).

Bio-char generally helps to increase (1) soil organic matter (2) microbial activity (3) nutrient accessibility (4) water retention (5) crop yields in soils, while decreases its fertilizer needs, erosion, greenhouse gases emission and nutrient leaching (Woolf et al., 2010; Sohi et al., 2009). Bio-char is lesser carbonized than activated carbon. More oxygen and hydrogen remains in the structure (alongside ash) that originates from biomass. Bio-char absorb hydrocarbons along with other organic and some inorganic metal ions (Mohan et al., 2012; Hale et al., 2012) that exhibit potential for soil amelioration and water purification. Bio-char might replace wood, coal and coconut shell based activated carbons as a low-cost sorbent for both pathogens and contaminants. Bio-char may be used for the removal of contaminants from water. It is also being loaded with the nutrients to be used as a soil amendment. It has long-term sorption capacity and acts as a fertilizer (Bernd et al., 2013).

## **2. Recent technologies of biochar formation**

Biomass feedstock classification is important for the feasibility of pre-treatment. Feasibility also depends on the nature of feedstock (dry or wet).

### **2.1 Dry torrefaction**

In this process, biomass heating is done in an inert atmosphere with temperature range from 200-300°C with residence time from 30 min to 2-3 hours. This process is also called as mild pyrolysis (Rousset et al. 2012; Bergman et al. 2005). This account for a mass loss of 30% and only 10% of the energy is obtained from biomass which is lost in gaseous form. Thus, there occurs an increase in energy density of product which is a torrefied product (Pimchuai et al. 2010; Rousset et al. 2012). It is considered as an important pre-processing step as it improves physicochemical properties of biomass for combustion process (Rousset et al. 2012). A torrefied product is not considered as bio-char because of the presence of volatile organic compounds (biomass original compound). Torrefied biomass has properties of both biomass and raw biomass (Acharya et al. 2012; Nunes et al. 2014).

### **2.2 Hydrothermal carbonization**

It is a thermochemical process that converts organic feedstock into a solid product that has high carbon content. Hydrothermal carbonization (HTC) process is also called as wet torrefaction. It is performed in the temperature range from 180-260°C. During this process biomass gets submerged into water and heating occurs under system pressure which is kept confined (2-6 MPa) for 5-250 min (Hoekman et al. 2013; Libra et al. 2011). The reaction process cannot be controlled. It is an autogenic process with water of saturated vapor pressure which further corresponds to reaction temperature. It was proposed by Friedrich Bergius (1913) for the description of coalification process (Avola et al. 2012). As the severity of the reaction increases which accounts for the increase in temperature above 260°C, hydrothermal process gets classified into two categories (a) hydrothermal gasification (HTG) or hydrothermal vaporization (HTV) or super critical water gasification (SCWG) and (b) hydrothermal liquefaction (HTL) (Pavlovic et al. 2013, Petreson et al. 2008). Because in HTV and HTL rather than solid fuel more desired is gaseous or liquid fuel. This process remains unaffected by the high moisture content of the feedstock. Therefore, one step of wet biomass to be pre-treated gets eliminated like dry torrefaction and slow pyrolysis (Nunes et al. 2014).

## 2.3 Gasification

This process is termed as a partial combustion of biomass that occurs at an elevated temperature range (600-1200°C) with 10-12 seconds short residence time (Wiedner et al. 2013; Brewer et al. 2009). The production of bio-char process from a gasification process contains a large amount of alkalies as well as alkaline earth metals (Si, K, Mg, Ca etc.) and maybe polyaromatic hydrocarbons (PAHs) which appears to be highly toxic compounds. This makes a problem for soil amendment to be potentially problematic (Sivula et al. 2012; Laird et al. 2011). Whereas, in real practice, a small yield (<10%) of bio-char is produced (Batidzirai et al. 2013). A mixture of gases (CO<sub>2</sub>, H<sub>2</sub> and CO) is obtained as the primary product of gasification process, which is also referred to as syn gas i.e. synthetic gas. Most of the organic material present in the gasifier is converted into ash and gases; thereby no bio-char is produced by an ideal gasifier (Laird et al. 2011).

## 3. Bio-oil

Bio oil is known to be free flowing, organic liquid with 15-35% water, comprises of oxygenated compounds and is dark brown in color. Synonyms used for bio-oil includes bio-crude oil (BCO), liquid wood, pyroligneous acid, wood distillate, wood oil, liquid smoke, pyrolysis liquid, pyrolysis oil. It is a liquid generated by pyrolysis which is formed by depolymerizing and fragmenting biomass content (Peacocke, 1994; Teng and Wei 1998; Ren et al., 2009). Chemically, bio oil constitutes a chemical mixture of isoeugenol, furancarboxy aldehydes, pyrones, formic acid, acetic acid, water, catechols, vanillins, guaiacols, syringols and other carboxylic acids. Other major compounds present in bio-oils are sugars, phenolics, carboxylic acids, hydroxy aldehydes, hydroxy ketones. Upon fast pyrolysis, free water vaporizes easily. It aids heat transfer and spreads the feed particles (Scott et al. 1988; Wagner and Wu 2014). High pressure liquid chromatography, which is followed by electrospray mass spectroscopy (HPLC/ES-MS) or gas chromatography (GC), gas chromatography-mass spectroscopy (GC-MS), provides molecular mass distributions and some separation (Piskorz et al. 1988).

### 3.1 Properties of bio-oil

Bio-oil exact chemical nature is largely dependent on pyrolysis variables and the feedstock. Physical state of bio-oils multiphase structure is described as: “The multiphase complex structure of biomass pyrolysis oils can be recognized because of the presence of aqueous droplets, char particles, waxy materials, micelles and droplets formed of heavy compounds” (Brennan et al. 2010). Phase separation and variation may also occur after bio-oil was first recovered. The instability caused is believed to be a result of chemical reactions proceeding in the bio-oil (Veses et al. 2014). Several compounds present in pyrolysis oils like ketones, aldehydes can react with aldol condensations that occur during handling or storage to form larger molecules in the

pyrolysis oil (Shao et al. 2013). Due to these reactions, undesirable changes occur in physical properties. Water content and viscosity may also tend to increase, but the volatility will decrease (Abubakar et al. 2013). Bio-oil production occurs with 25 wt % water (which cannot be readily separated) and high oxygen content of 45%-50%. Therefore, the elemental composition resembles the biomass from which it was obtained (Yemis et al. 2011). Oxygen amount is the major reason for the variation in the behavior and properties between pyrolysis oils and hydrocarbon fuels. Bio-oil is immiscible with liquid hydrocarbons, as it is hydrophilic and polar in nature (Yoshikawa et al. 2014).

Bio-oil physical properties includes water content, pH value, stability, viscosity, lower heating value (LHV), higher heating value (HHV) (Choi et al. 2014). The LHV means the energy that does not include vaporization energy present in water vapor while the HHV refers to the total amount of the energy released when a fuel is burnt in the presence of oxygen (Ozbay et al. 2008). Oxygen bomb calorimeter is used to measure HHV of bio-oil (Bilgen et al. 2012). All the referred properties also called as proximate analysis with the elemental analysis is shown in table 1 with different biomass sources.

The HHV and LHV of the bio-oils can be approximately calculated from the following empirical correlation (Channiwala and Parikh 2002; Kan et al. 2016):

$$\text{HHV (MJ/kg)} = 0.3491 \times C + 1.1783 \times H + 0.1005 \times S - 0.1034 \times O - 0.0151 \times N - 0.0211 \times A$$

where C, H, S, O, and N are considered as the weight percent of carbon, hydrogen, sulphur, oxygen, and nitrogen, and A is weight percent of ash.

$$\text{LHV (KJ/Kg)} = \text{HHV (KJ/Kg)} - 218.3 \times H$$

where H means the mass percent of hydrogen.

## REVIEW OF LITERATURE

### 4. Bio-char

Bio-char yield was enhanced when pyrolysis is completed under the influence of higher pressure rather than ambient pressure. In an experiment it was shown that due to the presence of volatile substances that leads to tar formation then the char formation may be enhanced by either by enhancing pressure or by reducing the heating rate. Enhancement in residues of carbon content is also reported by some scientists by increasing the pressure (Manya et al. 2013). Carbon content present in bio-char also helps to influence high pressure inside the bioreactor. The rise in carbon content is due to pyrolysis of biomass which concludes increase in an energy density of char (Antal 2003).

#### 4.1 Parameters concerned with bio-char

The heating rate is considered to play a key role in biomass pyrolysis rate. It makes an influence on the composition and nature of the final product up to a certain limit. At the low heating rate, the chances of secondary pyrolysis reactions can be reduced. This also insures to prohibit the chances of thermal cracking that will further lead to more bio-char yield. But in contrast, high heating rate process backs the biomass fragmentation thereby, increasing the liquid and gaseous yield which reduces the chances of bio-char production. The effect of heating rate on bio-char yield is potent at low temperatures (Demirbas 2004)

In an experiment, performed on bio-char yield on pyrolysis of *Ferula orientalis* L, safflower seed and *Charthamus tinctorius*, the heating rate was increased from 30 -50°C/min while considering different temperatures from 400-600°C (Aysu et al. 2013, Angin 2013). Different types of biomass used for bio-char production are shown in table 1.

An increase in flow rate reduces bio-char yield but the effect is not observed to be huge because flow rate reduces char yield marginally. In an experiment, it was observed to have small decrease in rate from 24.4 to 22.6% in bio-char yield by increasing nitrogen flow rate from 1.2 to 4.5 L/min (Zhang et al. 2009). It was concluded by several experiments performed that low flow rate is sufficient to carry most vapors out from the reacting zone that further results in bio-char yield. Thereby, concluding that high carrier flow rate of the gas is not necessary for producing bio-char (Onay et al. 2001). To elevate bio-char production, low temperature associated with long vapor residence time is required (Encinar et al. 1996). When the vapor residence time is increased, it helps biomass constituents to be repolymerized, thus giving them required time to react. But if repolymerization does not get completed it leads to the reduction of bio-char yield (Park et al. 2008). In an experiment, it was observed that though residence time affects gaseous and liquid product composition, it does not affect yield of bio-char significantly. It is observed that at elevated temperatures, when residence time is increased, it also increases bio-char yield. But at

low temperatures, when residence time increases, it reduces bio-char yield (Fassinou et al. 2009). Longer residence time also keeps bio-char pore size to be enhanced (Tsai et al. 199). Various other characterization techniques are viewed in table 2.

Particle size controls the heat transfer rate for the input biomass. When the particle size has increased, the distance between the surface of core and input biomass also increases. This temperature gradient helps to favor char yield (Encinar 2000). In an experiment performed on the olive husk and tea waste at 677°C, the particle size was increased from 0.5 mm to 2.2 mm with an increase in bio-char yield from 19.5 to 35.7% (Demirbas 2004). Although most reports have shown that bio-char yield increases with increase in particle size but few research papers have claimed reduction in yield of bio-char by increasing biomass particle size (Sensoz and Kaynar 2006)

**Table 1: Elemental(C,H,O,N,S) and proximate(MC,volatile, HHV) analysis of biomass**

Biomass	C	H	O	N	S	MC (wt%)	Volatile (wt %)	HHV (MJ/kg)	Analysis method of HHV	Temperature (°C)	Reference
Wheat straw	58.4	6.0	38.20	0.1	nd	nd	75.00	nd	Calorimeter	750	Ren et al. 2009
Almond shell	47.63	5.71	44.48	nd	nd	7.90	24.00	nd	Calculation	750	Braz et al. 2014; Rapagna et al. 2000
Coconut shell	47.97	5.88	45.67	0.29	nd	14.75	nd	7.4	Calorimeter	950	Fagbemi et al.2001; Tang et al. 2008
Corn	43.04	6.42	49.27	1.03	nd	7.8	28.54	-	Calorimeter	-	Ren et al. 2009; Ioannidou et al. 2009
Corn cob (fruits part)	42.90	6.41	49.23	0.70	nd	6.44	nd	nd	Oxygen bomb calorimeter	923	Yanik et al. 2007; Ioannidou et al. 2009
hardwood	55.3	6.6	51.29	0.4	nd	nd	85.58	19.9	Calorimeter	950	Singh et al. 2016; Demirbas et al. 2004
Cottonseed	48.28	5.69	38.77	1.33	nd	nd	nd	18.3	Calorimeter	700	Ozbay et al. 2001, Demirbas 2001
Pine sawdust	44.80	6.56	48.49	0.05	0.1	18.76	80.2	17.13	Oxygen bomb calorimeter	nd	Ronsee et al. 2013; Gao et al. 2013
Groundnut shell	48.27	5.70	39.40	0.80	nd	nd	54.58	nd	Calorimeter	nd	Perez et al. 2002

Hazelnut shell	49.94	5.65	42.81	0.27	nd	5.73	nd	2.21	Calculation	600	Bermudez et al. 2015; Yang et al. 2009
Hazelnut shell	51.07	5.12	40.89	1.29	nd	nd	nd	nd	Calculation	nd	Demirbas, 2006
Microalgae	50.00	7.11	30.70	7.25	0.54	4.59	nd	21.10	Calorimeter	450	Ahmad et al. 2011
Hazelnut shell	51.24	5.74	42.23	0.41	nd	nd	64.54	nd	Calculation	650	Bonelli et al. 2003
Orange peel	38.7	6.10	52.89	0.39	0.61	nd	77.73	nd	Calculation		Bonelli et al. 2003
Scots	56.4	6.3	45.54	0.1	nd	nd	42.85	nd	nd	nd	Sipila et al. 1998
Peanut shell	46.59	6.00	53.65	2.06	nd	7.98	nd	16.52	Calculation	650	Safi et al. 2004; Braz et al. 2014
Pecan nutshell	47.3	6.60	45.58	0.80	nd	9.18	60.00	19.34	Calorimeter	700	Xiao et al. 2010; Mohamed et al. 2013
Rapeseed plant	57.29	6.63	34.08	1.03	nd	nd	nd	nd	nd	nd	Karaosmanoglu et al. 1999
Pine needles	45.81	5.38	46.11	0.98	nd	nd	78.54	nd	nd	900	Ren et al. 2009; Luo et al. 2009
Rice straw	45.14	5.85	46.69	0.62	nd	8.19	61.00	15.39	Oxygen bomb calorimeter	750	Ren et al. 2009; Braz et al. 2014
Rice husk	42.69	5.69	39.73	0.96	nd	nd	71.70	nd	nd	750	Xiao et al. 2010
Sunflower shell	47.40	5.80	41.40	1.40	nd	7.1	nd	20.25	Calorimeter	850	Demirbas, 2006; Zanzi et al. 2002
Walnut shell	50.59	6.42	42.12	0.3	nd	nd	65.58	nd	Calorimeter	850	Onay et al. 2004



Jute stick	47.18	8.36	44.1	nd	nd	nd	74.58	nd	Calorimeter	1000	Islam et al. 2005
Wheat straw	47.33	2.55	48.12	0.79	nd	8.5	75.00	18.25	Calorimeter	800	Ren et al. 2009; Ding et al. 2012

**Table 2. Bio-char characterization techniques**

Technique	Biomass source	Result			Importance	Property	References
<b>FTIR</b>	Pine sawdust	Bands at 120 cm <sup>-1</sup> and 875 cm <sup>-1</sup> represent C=C and strong =C-H bonding			For fuel storage and handling	Hydroxyl content decreased at 375°C	Srinivasan et al. 2015
<b>NMR</b>	Sewage sludge	consistent structure at very low C <sub>obs</sub> value of 3%			Solid bio-char as fuel	Increase in Hydro Thermal Carbonization temperature	McBeath et al. 2011; Smernik et al. 2000
<b>Carbonization</b>	Pine sawdust	Saturated hydrocarbon at C 1 s = 284.9 eV			For solid fuel production	Highest ignition index value(10.78) at 250°C	Srinivasan et al. 2015
		T <sub>i</sub> (°C)	T <sub>b</sub> (°C)	D <sub>i</sub> (×10 <sup>-2</sup> )			
<b>Combustion</b>	Coconut fiber	273	326	1.48	Improved fuel properties	High hydrophobicity and increased carbon content	Khan et al. 2009; Liu et al. 2013; Demirbas 2004
	C-300	400	478	0.42			
	C-375	393	580	0.11			
	Eucalyptus leaves	253	456	0.52			

	L-300	374	449	0.35			
	L-375	428	581	0.11			
<b>% yield with HTC and pyrolysis</b>		HTC (at 300°C)		Pyrolysis (at 300°C)			
	Pine	49.51		32.91		Naturally favor the formation and retention of solid products	Viable to use as soil amendments
	Peanut	50.07		38.67			
	Bamboo	32.72		33.28			
<b>Adsorption isotherms</b>		Freundlich		Langmuir			
		$K_f$ (mg/g)	$\eta$	$K_L$ (L/mg)	$q_{max}$ (mg/g)		
	Rice straw	24.6	2.08	0.11	179.4	Adsorption similar to monolayer “chemical sorption process”	Maximum adsorption capacity by the adsorbents for color removal
Spirulina	16.3	2.01	0.066	151.6			
<b>Wet torrefaction</b>		T(°C)	Mass yield (%)	Energy yield (%)	Energy densification		
	lignocellulose	200	87.2	93.5	1.07	Increase in energy densification with increase in temperature	Hydrochar formed with fuel values
		260	53.6	66.3	1.25		
							Gao et al. 2013; Lynam et al. 2015

Bio-char yield is affected in a negative way by elevating the temperature. This occurs when heavy hydrocarbon materials are thermally cracked which causes an increase in gaseous and liquid. Thereby, cause a decrease in bio-char yield. Low temperature is considered suitable for bio-char yield because at high temperature, energy provided to biomass may exceed the bond cessation energy which works in support for biomass volatile components to be released. Exact

temperature range needed for the biomass depends upon concentration and type of biomass product used (Shabhangu et al. 2014).

Catalyst helps to affect the pyrolysis product among all the three phases i.e. solid, liquid and gas. When catalyst is used in the pyrolysis process, it helps to eliminate the formation of tar (Sutton et al. 2001). Catalyst increases the product yield of bio-char formation by either reducing the gaseous yield or by enhancing the liquid yield. Ash present in the constituents can also play the role of catalyst (Samolada et al. 2000). Different types of catalyst used are ZSM-5,  $\text{Na}_2\text{CO}_3$ , MgO, NaOH, NiO, NaCl, alumina, Al-MSM-41,  $\text{Na}_2\text{SiO}_3$  (Stefanidis et al. 2011; Wang et al. 2006). Bio-char yield was compared with different catalysts like LiCl, NaCl,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , KCl, and  $\text{ZnCl}_2$ . It was observed that in the presence of  $\text{ZnCl}_2$  yield increased by 44% (Yu et al. 2014). Generally, acid catalysts are used than basic catalyst because they increase the bio-char yield.

Heavy metals are reported to pose health issues even at low concentrations. Few of them can be poisonous, capable of assimilation, concentration, and storage by the organisms which are exposed for long interval of time at reduced concentrations. Harmful physiological effects in tissues can be caused by metal built-up. Heavy metals appear to be among the major pollutants of this century (Davydova, 1999). Heavy metals being discharged acts as a serious threat both to natural water and human health. Vital biochar adsorption studies are made with As, Zn, Hg, Pb, Cu, Cd, Fe and Cr ions. Activated C is used for the removal of metal ions, but some absorption (in milligrams) has occurred on activated carbon. Due to this activated carbon becomes expensive for wastewater treatment. Therefore, its use in the developing countries is problematic.

#### **4.2 Reactors for biomass**

This makes the requirement of materials with low cost and adsorption capacities as compared to activated carbon. Solid biomass-derived waste is also a trouble. Biochar constitutes as a byproduct in bio-oil production with 15–25% yields. If bio-oil production gets widespread, then the resulting char will be extensively available for usage of water remediation. Slow pyrolysis process on bio-chars also helps to convert lignocellulosic wastes to bio chars. Industrial wastewater and surface/ground water can then be broadly treated with bio-chars to reduce metal ion removal costs (Pellera et al., 2012).

In an experiment, the bio-char obtained from waste biomass obtained progressive depletion in functional groups of cellulose, hemicellulose and lignin structures. Presence of aromatic carbon was observed above  $300^\circ\text{C}$ , with aromaticity degree increasing with the increase in temperature. At  $375^\circ\text{C}$  after carbonization, at 35 ppm broad peak disappeared. This indicated C-375 to be purely aromatic char with few hydrogen and organic oxygen substituents (Liu et al. 2013). Srinivasan et al. 2015 suggested spin counting method for the quantification of total signals

detected in every NMR spectrum. Spin counting method helps to compare the total amount of signal that is detected per unit C against the standard in a sample and is further expressed as NMR observability ( $C_{obs}$ ). In ablative pyrolysis process, wood is being pressed against the heated surface. It leaves behind an oily layer which evaporates (Yuan et al. 2011). Heat rate supplied is the limiting factor in this reactor. When biomass gets in contact with hot solid, ablation occurs and fresh biomass is exposed to the hot surface. Process control is done by measuring temperature directly. Continuous mode of operation is required for indirect heating method process (Ozer et al. 2012; Sun et al 2013).

## MATERIALS AND METHODS

### 5. Materials

Rice husk was selected as the feedstock biomass. The biomass was crushed and FTIR analysis was performed.

Name (chemicals)	Company's Name	Cas no.
Nitric acid	Lobachemie	7697-37-2
Potassium dichromate	Lobachemie	7778-50-9
Cadmium nitrate	Lobachemie	C10217
Sodium sulphate	Lobachemie	7778-80-5
Barium chloride	Lobachemie	10326-27-9
Sodium chloride	Lobachemie	7757-82-6
Concentrated HCL	Lobachemie	7647-01-0
Glycerol	Lobachemie	56-81-5
Isopropyl alcohol	Lobachemie	123-57-3
Concentrated Sulphuric Acid	Lobachemie	7664-93-9

Table 3: Chemicals list

Name (Materials)	Company's Name
Rice Husk	Food Corporation of India
Distilled Water	---
Brown Paper	---
Foil Paper	Mirage
Watt man Filter Paper	---
Zip Packets	---
Stickers	---

Table 4: Materials required

Name (Apparatus/Instrument)	Company's name	Catalog Number
Crucible	Perfit	---
Tong	---	---
Muffle Furnace	---	---
Weighing Balance	Shimadzu	---
Glass Beaker	Borosilicate	---
Steel Tray	---	---
Heating Mantel	Popular India(PI)	101/20
Fume Hood	---	---
Spatula	---	---
Conical Flask	Perfit India	---
Funnel	Borosilicate	---
China Dish	Borosilicate	---
Hot Air Oven	Narang Scientific Work	NSW-143
Syringe Filters	Mediplus	---
Standard Flask	Borosilicate	---
Holding Stand	----	---
Pipette	Perfit	---

Table 5: List of apparatus and instruments required

### 5.1 Bio-char preparation

Rice husk was sieved to 50 mm. Around 1500 gm of biomass was used to prepare bio-char. Bio-char was prepared in the laboratory in an autoclave which consisted of automatic temperature control. Biomass was allowed to heat from 125°C till rice husk starts to form bio-char. The autoclave was turned off after reaching at 300° C temperature. Rice husk was kept in the autoclave for 30 min to produce bio-char.



Figure 1 :autoclave used for bio-char formation

Simultaneously; bio-oil was collected which was received from the small opener present on the autoclave. Bio-oil being thick in nature was diluted with ethanol to collect the whole amount and for further analysis. The instrument was kept at final temperature and then allowed to cool to bring it back to the room temperature. Both bio-char and bio-oil samples were subjected for FTIR for the presence of functional groups present on the surface.

(Modifications performed on proposed methodology by Roberts et al. 2009)

## **5.2 Characterization techniques**

Fourier transform infrared (FTIR) analysis of both bio-char and bio-oil was performed on FTIR spectrophotometer at room temperature for the determination of functional groups. The flow rate of gas in FTIR was 100ml/min. Prior to surface analysis of bio-oil, it was diluted with ethanol (Yu et al. 2014).

Surface characterization of bio-char will be analyzed by scanning electron microscope (SEM). It uses a focused beam where the electron will be allowed to pass on the surface of the sample. This technique helps to reveal the composition and topography of the sample. In our case, both bio-char and bio-oil sample will be considered (Mohan et al. 2012).

To observe the features of extremely small sample obtained from bio-char and bio-oil, transmission electron microscopy (TEM) technique will be used. This technique helps for the

observation of features like morphology and structure. This also helps to view the sample at atomic level (which can be less than 1nm) (Chen et al. 2011).

Chen et al. 2011 suggested that for the determination of molecular and atomic structure, X-ray crystallography (XRD) will be performed.

For elemental analysis of bio-char and bio-oil, ICP will be used. It helps to reveal the carbon (C), oxygen (O), hydrogen (H), nitrogen (N) composition present in the biomass sample. Brosse et al. 2012 suggested that for the pore size determination, volume analysis and the specific surface area of bio-char and bio-oil, Brunauer Emmett and Teller (BET) meter is be used. Nitrogen is used as an adsorbate for the surface area determination in BET technique for both bio-oil and bio-char sample. It is an automatic apparatus, therefore only sample requirement is to be fulfilled. In the first assumption, all adsorbing surfaces are energetically homogenous. While in second assumption, vertical interaction takes place between adsorbent surface and adsorbent molecules. Thus, horizontal interactions between adsorbed molecules are neglected (Seri and Avnir, 1993).



## RESULTS and DISCUSSIONS

### 6. Bio-char formation

The final bio-char was allowed to cool down at room temperature. Bio-char obtained was then collected from the autoclave. Approximately 15gm of bio-char is used as sample. Bio-char was then used for characterization techniques.



Figure 2. bio-char formed by burning of rice husk



Figure 3. bio-char collected sample

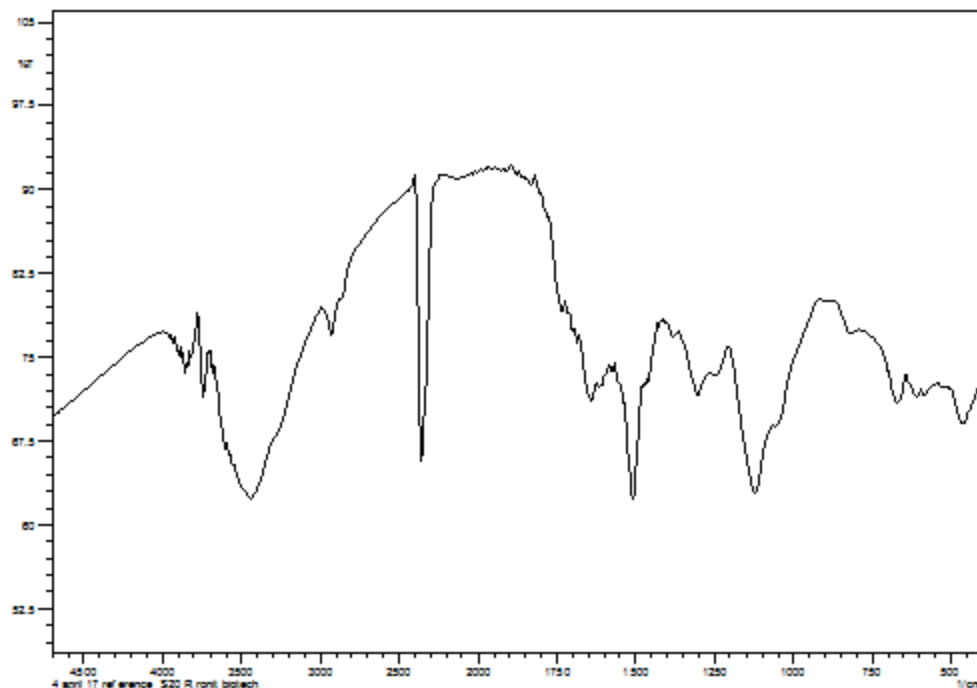


Figure 4. Bio-oil obtained from autoclave

To study the characteristics of both the samples, standards are being taken from data present in review of literature.

### **6.1 FTIR analysis**

Rice husk was taken as a biomass sample for bio-char production. Rice husk is abundantly composed of cellulose and silica (Liu et al. 2014). Previous performed analysis on bio-char revealed that FTIR with  $\text{SiO}_2$  should lie above the range of  $300 \text{ cm}^{-1}$ . Recent study shows presence of silica in rice husk to be amorphous in nature as the peaks lie between  $300 \text{ cm}^{-1}$  -  $1000 \text{ cm}^{-1}$ . In our procured FTIR sample, we can see a wide range of peaks lying in the range of  $350$ - $670 \text{ cm}^{-1}$  which clearly indicates the presence of amorphous silica in our sample. The graph below represents the FTIR graph showing the relevant peaks for recognition of predominant silica molecules present in raw biomass of rice husk.



**Figure 5 : FTIR interferogram for raw rice husk**

On conversion of rice husk biomass into bio-char, functional groups were changed. The peaks at  $3597\text{ cm}^{-1}$  and  $3743\text{ cm}^{-1}$  were assigned for C-H stretching. The peak at  $1512\text{ cm}^{-1}$  indicated aromatic carbon. The peaks at  $1556\text{ cm}^{-1}$  indicated C-N stretching. It is found that bio-char significantly has lost hydroxyl and aliphatic groups and gains the aromatic character.

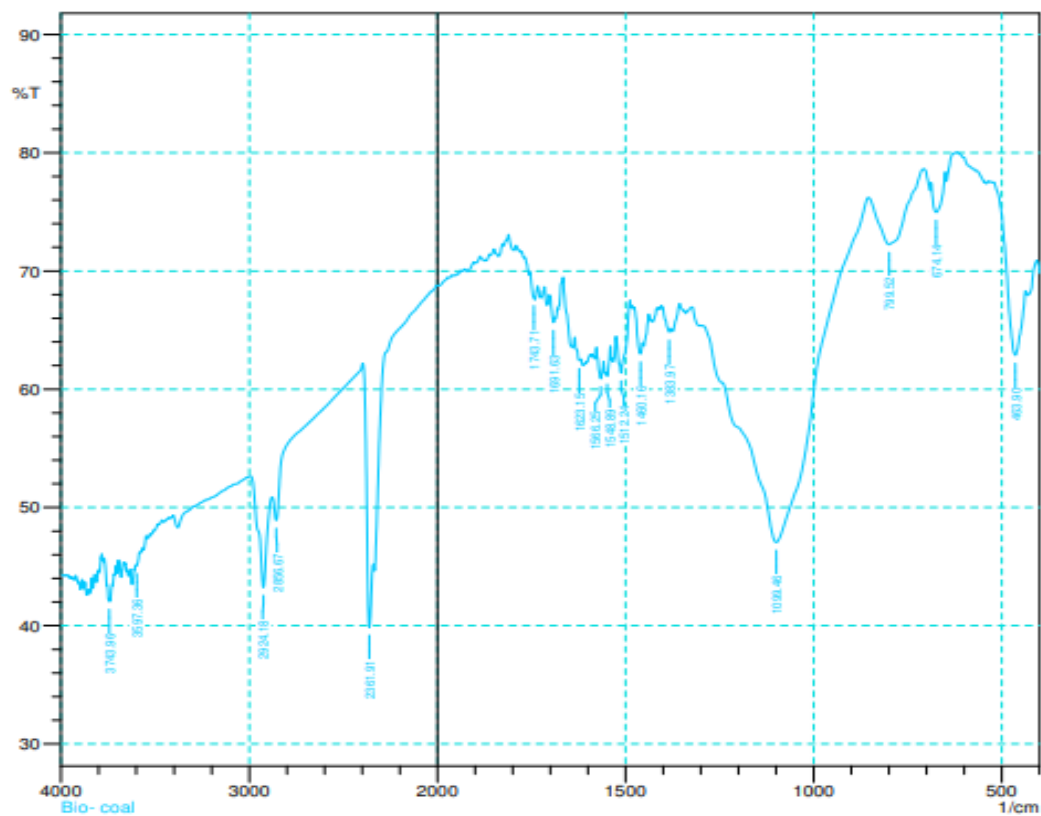


Figure 6. FTIR interferogram of bio-char

No.	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	463.9	62.865	8.406	520.8	436.89	13.558	1.972
2	674.14	74.97	2.824	687.65	650.03	4.498	0.422
3	799.52	72.24	4.886	854.49	707.9	18.554	2.261
4	1099.46	47.046	19.278	1242.2	854.49	89.908	24.817
5	1383.97	64.819	0.636	1402.3	1380.11	4.054	0.058
6	1460.16	62.986	1.715	1476.56	1454.38	4.248	0.158
7	1512.24	61.372	4.184	1525.74	1488.13	7.429	0.633
8	1548.89	61.104	1.003	1552.75	1540.21	2.611	0.054
9	1566.25	60.883	1.932	1577.82	1558.54	4.028	0.149
10	1623.15	62.425	0.484	1628.94	1618.33	2.155	0.022
11	1691.63	65.654	0.891	1703.2	1687.77	2.718	0.036
12	1743.71	67.738	0.199	1753.35	1742.74	1.743	0.021
13	2361.91	39.864	11.77	2396.63	2340.7	17.719	2.299
14	2856.67	48.906	2.47	2877.89	2396.63	115.933	-4.328
15	2924.18	43.238	8.353	2993.62	2877.89	36.584	3.486
16	3597.36	45.072	0.281	3601.22	3581.93	6.594	0.03
17	3743.96	42.058	0.427	3754.56	3741.06	5.018	0.047

Table 6: data of peaks obtained in FTIR analysis from bio-char

Bio-oil is also formed with bio-char from rice husk. Various peaks are present with strong, weak, medium intensity which corresponds to different bonds present in the bio-oil. The strong peak present at  $3739\text{ cm}^{-1}$  signifies the N-H stretch. The peak at  $3391\text{ cm}^{-1}$  indicates the presence of O-H stretch with the presence of alcohols and phenols. Weak peaks observed in  $1200\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$  proves weak C-O and C-N stretch.

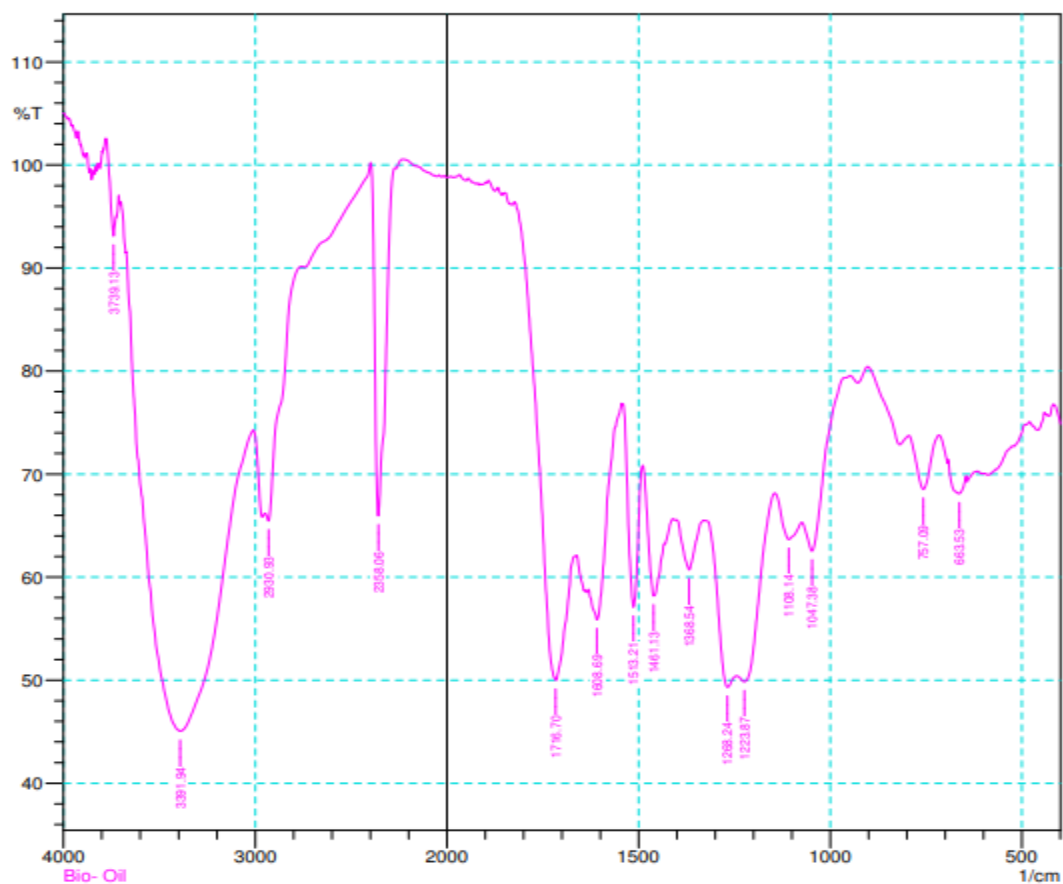


Figure 7: FTIR interferogram of bio-oil

No.	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	663.53	68.103	2.348	692.47	645.21	7.664	0.525
2	757.09	68.522	5.243	794.7	716.58	11.534	1.211
3	1047.38	62.529	6.172	1074.39	962.51	17.243	1.274
4	1108.14	63.656	3.023	1144.79	1074.39	13.12	0.748
5	1223.87	49.862	4.166	1244.13	1144.79	24.526	1.481
6	1268.24	49.323	5.523	1326.1	1244.13	20.953	1.225
7	1368.54	60.706	4.83	1401.33	1330.93	14.021	1.1
8	1461.13	58.187	8.858	1489.1	1433.16	11.526	1.774
9	1513.21	57.08	16.526	1541.18	1489.1	9.714	2.833
10	1608.69	55.877	7.598	1630.87	1545.03	16.333	1.533
11	1716.7	50	23.174	1823.76	1665.59	27.318	9.691
12	2358.06	65.944	34.118	2397.6	2271.26	10.214	10.195
13	2930.93	65.453	3.033	2949.26	2758.3	19.818	-1.595
14	3391.94	45.041	39.203	3673.55	3010.02	158.325	102.824
15	3739.13	93.085	3.918	3778.68	3724.67	0.709	0.401

Table 7: data of peaks obtained in FTIR analysis from bio-oil

## CONCLUSION

In this study, rice husk was used for the production of bio-char. The results indicated that bio-char significantly has lost hydroxyl and aliphatic groups and gains the aromatic character. Bio-oil is also formed with bio-char from rice husk. Various peaks are present with strong, weak, medium intensity which corresponds to different bonds present in the bio-oil. The rice husk when pyrolysed at high temperature ranging from 400-600 °C, is converted into biochar with a significant change in its morphology and other physio-chemical properties. The rice rusk components specifically lignin, cellulose and hemicellulose are converted into different compounds when subjected to high temperature in oxygen controlled environment. Future studies should focus on the bio-char application with its optimization for both environmental agronomic and purposes and carbon budget for agricultural systems which are enriched with bio-char.

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