OPTIMIZATION OF PROCESS PARAMETERS FOR CONVERSION OF PINE NEEDLES TO BIO-OIL, BIOCHAR AND PRODUCT GAS THROUGH BATCH AND CONTINUOUS PYROLYSIS

Thesis

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Pantnagar (**Sandip Mandal**)

April, 2018 Author

CERTIFICATE - I

This is to certify that the thesis entitled "**Optimization of Process Parameters for Conversion of Pine Needles to Bio-Oil, Biochar and Product Gas through Batch and Continuous Pyrolysis**", submitted in partial fulfillment of the requirements for the degree of **Doctor of Philosophy** with major in **Farm Machinery and Power Engineering** and minor in **Mechanical Engineering** of the college of Post Graduate Studies, G.B. Pant University of Agriculture and Technology, Pantnagar, is a record of *bona fide* research carried out by **Mr. Sandip Mandal, ID No.- 32845,** under my supervision, and no part of the thesis has been submitted for any other degree or diploma.

The assistance and help received during the course of this investigation have been duly acknowledged.

Pantnagar
April, 2018

(**T.K. Bhattacharya**)
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CERTIFICATE - II

We, the undersigned, members of the Advisory Committee of **Mr. Sandip Mandal, ID No. 32845**, a candidate for the degree of **Doctor of Philosophy** with major in **Farm Machinery and Power Engineering** and minor in **Mechanical Engineering**, agree that the thesis entitled **"Optimization of Process Parameters for Conversion of Pine Needles to Bio-Oil, Biochar and Product Gas through Batch and Continuous Pyrolysis"** may be submitted in partial fulfillment of the requirements for the degree.

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LIST OF NOMENCLATURES/SYMBOLS

μm	:	micron
°C	:	degree Celsius
°C s^{-1}	:	degree Celsius per second
°C min^{-1}	:	degree Celsius per minute
α	:	alpha
β	:	beta
γ	:	gamma
θ	:	theta
AC	:	Alternating current
AISI	:	American Iron and Steel Institute
ANOVA	:	analysis of variance
ASAE	:	American Society of Agricultural Engineers
ASTM	:	American Society for Testing and Materials
C	:	Carbon
Ca	:	Calcium
CEC	:	Cation Exchange Capacity
CFB	:	Circulating Fluidized Bed
CH_4	:	Methane
cm	:	centimeter
cm^2	:	centimeter square
CO	:	Carbon monoxide
CO_2	:	Carbon dioxide
cSt	:	centi stoke
df	:	degree of freedom
ESP	:	electrostatic precipitator
et al.	:	and others
Eqn.	:	equation
FID	:	flame ionization detector
Fig.	:	figure
g	:	gram
GC/MS	:	Gas chromatography mass spectrometry

GI	:	galvanized iron
H	:	Hydrogen
h	:	hour
ha	:	hectare
HHV	:	High heat value
H_2SO_4	:	Sulphuric acid
Hz	:	hertz
i. e.	:	that is
K	:	Potassium, Kelvin
K min^{-1}	:	Kelvin per minute
kg	:	kilogram
kg m^{-3}	:	kilogram per cubic meter
kg h^{-1}	:	kilogram per hour
kg ha^{-1}	:	kilogram per hectare
kJ	:	kilo joule
kJ mol^{-1}	:	kilo joule per mole
kPa	:	kilo Pascal
kWe	:	kilowatt equivalent
LHV	:	low heating value
lph	:	litre per hour
m	:	meter
m^3	:	cubic meter
m^2 g^{-1}	:	square meter per gram
m^3 h^{-1}	:	cubic meter per hour
m.c.	:	moisture content
ml	:	mililitre
MJ kg-$mole^{-1}$	:	mega joule per kilogram mole
mmolc kg^{-1}	:	millimole concentration per kg
ms	:	mild steel
mg	:	milligram
mg kg^{-1}	:	milligram per kilogram
Mg	:	mega gram, magnesium
Mg m^{-3}	:	mega gram per cubic meter

MJ kg^{-1}		mega joule per kilogram
MJ m^{-3}	:	mega joule per cubic meter
min	:	minute
ml min^{-1}	:	millilitre per minute
mm	:	millimeter
mm^2	:	millimeter square
mm^3	:	millimeter cube
MPa	:	Mega Pascal
N	:	nitrogen
Na	:	sodium
NaOH	:	Sodium hydroxide
Nm	:	Newton meter
Nm^3 kg^{-1}	:	Normal cubic meter per kilogram
O	:	oxygen
P	:	phosphorous
PPM	:	parts per million
RSM	:	Response Surface Methodology
s	:	second
S	:	Sulphur
S/N	:	signal to noise
t	:	tonne
TCD	:	thermal conductivity detector
TG	:	thermogravimetry
wt.	:	weight
wb	:	weight basis
t ha^{-1}	:	tonne per hectare

Chapter – 1

INTRODUCTION

INTRODUCTION

The depletion of fossil fuel sources and emission of green house gases from them have called for search of alternate fuel sources. Biomass is considered as renewable, sustainable and carbon neutral fuel source (**Goyal *et al.*, 2008; Kaygusuz, 2009**). Currently, numerous studies are being carried out to find suitability of different biomass as potential fuel sources in different routes (**IEA, 2006; Efika *et al.,* 2012**). Pine needles are the abundantly available biomass of pine forests which are present in almost entire globe. These are product of regular leaf shedding from fast growing pine forest. The *chir* pine (*Pinus roxburghii*) has a forest cover of 7.62 million hectares in North Western Himalaya consisting India, Nepal and Bhutan. Estimation in hills of Uttarakhand, India has shown pine needle productivity of 6.3 t ha^{-1} per year (**Singh *et al.,* 2016**). Decaying process of pine needles is very slow and they are seldom removed from forest bed. Thick layer of dry pine needles is a fire hazard and stops the growth of grass which the cattle feed upon (**Dwivedi *et al.,* 2016**). Large scale forest fires caused by thick layer of pine needles contribute to significant air pollution with devastating environmental impacts (**Tzamtzis *et al.,* 2006**). Therefore, finding of an alternate use of pine needles is utmost important to reduce risk of forest fire.

Pine needles are locally used as bedding material for poultry and cattle during winter and as fuel by rural household. These uses are not to its fullest potential considering its availability. Being a ligno-cellulosic biomass, it has huge potential as an energy source. Ligno-cellulosic biomass can be converted to energy products by different routes such as high pressure briquetting, gasification for producer gas, fermentation for ethanol, anaerobic digestion for biogas production and thermochemical conversion for bio-oil and biochar production (**Mandal *et al.*, 2017**). All these processes have their relative merits and demerits. Among these processes briquetting, gasification and pyrolysis processes are particularly advantageous with energy conversion efficiency of 88%, 52% and 74%, respectively (**Mahmood *et al.*, 2016; Mandal *et al.*, 2017**). The best route can only be decided based on the detail scientific study of the conversion processes and kinetic study of the biomass material.

The kinetic studies suggest that pine needles can be good source for conversion to bio-oil and biochar through pyrolysis (**Saâdaoui *et al.*, 2008**). Bio-oil is a mixture of complex organic compounds and can be converted into higher value added materials, such

as phenols, ketones, aldehydes, alcohols, besides energy and fuel (**Torri *et al.,* 2016**). Also, it can be stored for longer period reducing the requirement of storing voluminous biomass and helps in utilization of biomass of distant locations (**Bordoloi *et al.,* 2015**). It has been a growing interest of scientists and industries in the last decade to produce bio-oil and biochar from different ligno-cellulosic biomass. Few among these biomass are also from forest and grass lands such as spruce, birch, pines (**Mohan *et al.,* 2006**), switchgrass (**Boateng *et al.,* 2006**), elephant grass (**Strezov *et al.,* 2008**), napier grass (**Lee *et al.,* 2010**), wheat straw, timothy grass and pine wood (**Nanda *et al.,* 2014**).

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen or in presence of limited amount of oxygen. Pyrolysis occurs over a range of temperatures from 400°C – 600°C, and usually at atmospheric pressure. In the process, heat is transferred from a heat source to the fuel which releases volatiles and forms char. Quick condensation of the volatiles leads to formation of bio-oil. The uncondensed gases thus produced are a mixture of H_2, CO, CH_4 and CO_2, called product gas or pyrolysis gas, is another fuel product of pyrolysis (**Haykiri-Acma and Yaman, 2007**). The distribution of these three products (bio-oil, biochar and product gases) from any biomass is the function of process parameters as well as the pyrolysis reactor configuration. The common pyrolysis reactor configurations are fixed bed; circulating fluidized bed; bubbling fluidized bed; rotating drum kiln and auger (screw) reactor (**Mohan *et al.,* 2006**). Batch type reactors or fixed bed reactors are mostly laboratory scale and widely used to find out the thermal behaviour of biomass under varying process parameters. By varying the parameters like pyrolysis temperature, inert gas flow rate, heating rate, holding time, particle size of biomass and vapour cooling temperature, product distribution of pyrolysis process from different biomass is studied. Control and variation of the process parameters are much easier with bench scale batch type reactor.

Among many reactor configurations, screw reactor is particularly advantageous due to its simple design, requirement of low carrier gas flow and suitability for large biomass particles (**Brown and Brown, 20**12). In a screw reactor, biomass is heated externally while being transported by a rotating screw inside a cylindrical reactor. It may be equipped with a single screw or twin screw. As vapor products evolve, they exit the reactor due to pressure differences, and the biochar exits at the end of the reactor. The previous studies with single screw auger reactor have reported good recovery of bio-oil and biochar with different biomass (**Puy *et al.,* 2011; Brown and Brown, 2012; Liaw *et al.,* 2013;**

Ferreira *et al.,* 2015) Considering these factors, the single screw reactor configuration was adopted for the pyrolysis of pine needles which would also simulate the bio-refinery concept for large scale industrial production of bio-oil and biochar.

A screw reactor runs continuously and can only be utilized as an industrial setup. For the people of hilly and rural areas in India, a large scale batch type reactor can be helpful for production of biochar and product gas from limited quantity of biomass. This kind of units can be utilized for fulfilling the daily needs of cooking and space hating by utilizing the product gases. Biochar can be used for soil application and for making charcoal briquettes. Many batch type designs have been proposed to convert biomass to biochar (**Srinivasarao *et al.*, 2013)**. In such designs, the cylindrical reactor is placed horizontally or vertically. Biomass is placed inside it and ignited for an initial burning which might continue up to 60 min depending on the configuration. Although, available designs are efficient in conversion of woody materials like wood chips, branches and twigs into char, they are not quite suitable for loose biomass which mostly burn in the process. Further, due to lack of insulation and process control, heat loss is very high which affects the biochar quality. Therefore, a biochar reactor for loose biomass is required which can readily convert loose biomass to biochar without much pre-treatment and losses.

Bio-oil yield from biomass feedstock is greatly affected by the process conditions such as pyrolysis temperature, feedstock size, inert gas flow rate, heating rate and vapour cooling temperature. Optimization of these parameters through complete randomized design needs a huge number of experimental runs whereas, optimization tools like Response Surface Methodology (RSM) generates statistically validated results with fewer experimental runs (**Montgomery, 2005; Mazaheri *et al.,* 2010**).

Yield and properties of pyrolysis products from a continuous screw reactor are affected by various parameters which include temperature, heating rate, biomass particle size and its properties, sweeping gas flow rate and catalyst loading. Finding the effect of these parameters by factorial design needs a huge number of experimental runs which is costly and time consuming. Therefore, to reduce the number of experimental runs, Taguchi's Orthogonal Array was used to perform a number of representative experiments. Taguchi's Orthogonal Array had been utilized in various fields, such as the medical industry, pollution control, therapeutic, pharmaceutical industries, machine design and briquette production (**Chou *et al.,* 2009; Chan *et al.,* 201**4).

Considering the threat of pine needles as fire hazard and its higher availability in India, the aim of the present study was to utilize pine needles through pyrolysis process to produce bio-oil and biochar which otherwise would only be burnt to add pollution in environment. Although thermogravimetric analysis of pine needles has been conducted but none has been done on optimization of pyrolysis parameters of pine needles. With RSM a wide range of variables can be studied with less number of experimental runs and seldom applied on pyrolysis experiments. Further, there is no reported study on pyrolysis of pine needles using a screw reactor and not many investigations have utilized Taguchi's Orthogonal Array to determine the optimum conditions for bio-oil production with screw reactor. Hence, objectives of this research work were:

- To optimize the pyrolysis process parameters of pine needles for production of bio-oil through batch and continuous pyrolysis processes.
- To develop a batch type biochar and producer gas production unit and evaluate its performance with pine needles.
- To study the fuel and chemical properties of produced bio-oil, biochar and product gases.

Chapter – 2

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Pyrolysis process and its product distribution are highly dependent on the process parameters, reactor configuration and biomass types. Various studies have been carried out to understand its basic mechanism and optimum conditions with different types of biomass. The methodology, instrumentation and experimental design were thus decided after critically reviewing the vast database already published in various forms. This chapter contains the summary of the relevant literatures, definitions of processes, experimental methodologies, statistical designs and analytical procedures followed in this study.

2.1 Introduction to Biomass Pyrolysis

Demirbas and Arin (2002) defined pyrolysis as the thermo-chemical decomposition of organic material to carbon-rich solid and volatile matter in the absence of oxygen. The process is normally conducted in a closed container with presence of some inert gas. The solid is termed variously as char, biochar or charcoal, is highly recalcitrant and contains high amount of carbon. The volatiles are partly condensed to produce a liquid fraction called 'bio-oil' or 'pyrolysis oil'. It is a complex mixture of numerous organic compounds with high density, viscosity, low acidity and smoky odour. Non-condensable gases are termed as 'Syn gas' or 'Product gas' or 'Producer gas' and can be used in internal combustion engines.

Brownsort (2009) reported that prior to the development of petrochemicals, pyrolysis, or 'wood distillation', was a source of many valuable organic compounds for industrial and medicinal uses like some high value added liquid products, such as flavouring agents which are still produced by pyrolysis. Pyrolysis processes had also been used to extract liquid and gas products from coal since Victorian times and the technology for producing a synthetic crude oil from coal is well established. It is only more recently that biomass and organic wastes have become a focus as feeds for pyrolysis and related thermal treatment processes for energy recovery or bio-fuel production which are still relatively undeveloped. Char has also been used in agriculture for thousands of years. The fertile *terra preta* (dark earth) soils of the Amazonian region result from incorporation of char into otherwise poor soils. The resulting soils have long-lasting fertility that has been related to the stability of carbon in soil. He suggested the depiction of the pyrolysis process as shown in Fig. 2.1.

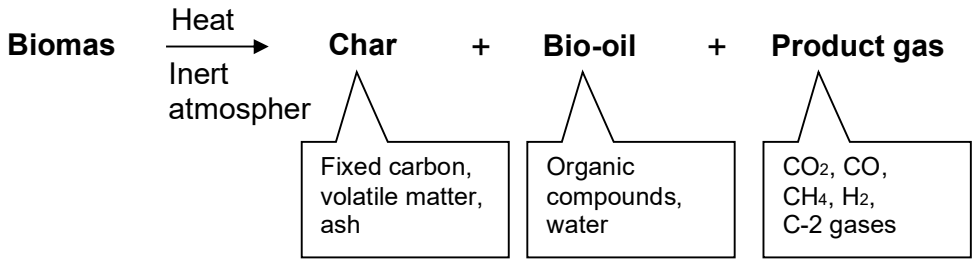

Fig. 2.1 Schematic of Pyrolysis Process

2.2 Types of Pyrolysis

Pyrolysis processes can be classified in two categories which are conventional or slow pyrolysis and fast pyrolysis depending on the operating conditions that are used.

2.2.1 Slow pyrolysis

Mohan *et al.* (2006) characterized slow pyrolysis by slower heating rates, relatively long solid and vapour residence times and usually a lower temperature than fast pyrolysis. The target product is often the char, but this will always be accompanied by liquid and gas products although these are not always recovered. They also reported that conventional slow pyrolysis had been applied for thousands of years to produce charcoal. The temperature is usually ~500°C and vapour residence time varies from 5 min to 30 min. Vapours do not escape as rapidly as they do in fast pyrolysis. Thus, components in the vapour phase continue to react with each other, as the solid char and any liquid are being formed. The heating rate in conventional pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock is held at constant temperature or slowly heated.

Brownsort (2009) reported that slow pyrolysis could be divided into traditional charcoal making and modern processes. Traditional processes include pits, mounds or kilns where wood is directly combusted as heat source in the kiln. Liquid and gas products are often not collected but escape as smoke with consequent environmental issues. Developments through the late 19th and early 20th centuries led to industrial scale processes using large retorts operated in batch or continuous modes. These allow recovery of organic liquid products and recirculation of gases to provide process heat, either internally or externally. Prior to the widespread availability of petrochemicals, such processes were used to generate important organic liquid products, in particular acetic acid and methanol. Other developments in the later 20th century led to slow pyrolysis technologies for biochar production. These are generally based on a horizontal tubular kiln where the biomass is

moved at a controlled rate through the kiln; these include agitated drum kilns, rotary kilns and screw pyrolysers. In several cases these have been adapted for biomass pyrolysis from original uses such as the coking of coal with production of 'towns gas' or the extraction of hydrocarbons from oil shale. Although some of these technologies have well-established commercial applications, there is as yet little commercial use with biomass in biochar production.

2.2.2 Fast pyrolysis

Bridgwater *et al*. (1999) characterized fast pyrolysis by high heating rates and short vapour residence times. It uses much faster heating rates than conventional pyrolysis. The processes are carefully controlled to give high yield of bio-oil. Heating rates of 1000 °C s^{-1} to even 10000 °C s^{-1} has been reported. Rapid heating and rapid cooling of vapour produces the intermediate pyrolysis liquid products which condense before further reactions break down of higher-molecular-weight species into gaseous products. Fast pyrolysis generally requires a small particle size of feedstock and quick removal of vapours from the reactor. Fast pyrolysis processes produce 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of non-condensable gases, depending on the feedstock used.

Bridgwater and Peacocke (2000) defined fast pyrolysis as a high temperature process in which the feedstock is rapidly heated in the absence of air, vapourises and condenses to a dark brown liquid with a heating value of about half of conventional liquid fuel. While it is related to the traditional pyrolysis processes used for making charcoal, fast pyrolysis is a more advanced process that can be carefully controlled to give high yields of liquid. The essential features of a fast pyrolysis process are: very high heating and heat transfer rates that requires a finely grinded biomass feed; carefully controlled temperature of around 500°C; rapid cooling of the pyrolysis vapours to give higher liquid yield. Bio-oil is obtained up to 80% wt. of dry feed together with char and gas which are used within the process.

2.3 Types of Pyrolysis Reactors

The heart of a pyrolysis process is its reactor. Several different reactor designs have been explored in last two decades that meet the rapid heat-transfer requirements. These reactor configurations have been shown to achieve liquid-product yields as high as 70%-80%, based on the starting dry biomass weight. There are five main types of pyrolysis

reactors which were (a) Bubbling fluidized-bed reactors; (b) circulating fluidized-bed reactors (both dilute and dense types); (c) ablative reactors, both cyclonic and plate type; (d) vacuum pyrolysis reactors and (e) auger reactors (slow pyrolysis)**.** These are discussed here in brief:

2.3.1 Bubbling fluidized bed

Mohan *et al.* (2006) described configuration of bubbling fluidized bed reactors which are usually referred as fluidized bed reactors as shown in Fig. 2.2. These are simple in operation and construction. They provide good temperature control and very efficient heat transfer to biomass particles. Sand is often used as heat transfer medium. The residence time of solids and vapours is controlled by the fluidizing gas flow rate. Char has a higher residence time than the vapours and acts as an effective vapour cracking catalyst. Therefore, rapid and effective char separation is important which is achieved by cyclone separators. For separation of very fine char particles hot gas filtration system is employed at the outlet.

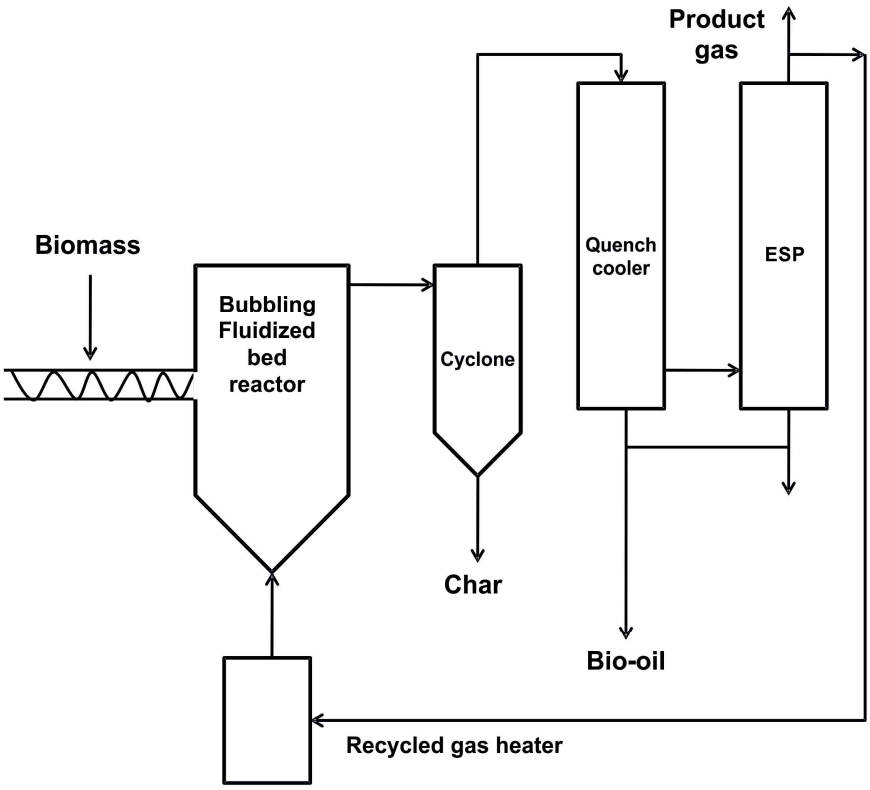

Fig. 2.2 Bubbling Fluidized Bed Reactor (Mohan *et al*., 2006)

2.3.2 Circulating fluidized bed

Mohan *et al.* (2006) also reported that Circulating Fluidized Bed (CFB) reactors were same as of bubbling fluidized beds, except that the residence time for the char was almost the same as that for the vapours (Fig. 2.3). The gas velocity is quite high which leads to more char appearing in the condensed bio-oil. Heat transfer rate is not particularly high, because it is dependent primarily on gas-solid convective transfer. In some designs, CFB common twin-bed reactor is used, with the second reactor employed as a char combustor to reheat the circulating solids. This leads to ash buildup in the circulating solids. Ash acts as a cracking catalyst for the organic molecules in the volatile pyrolysis products causing lesser yield of bio-oil yield and higher yield of product gas. Main advantage of CFBs is that they are suitable for very large throughputs.

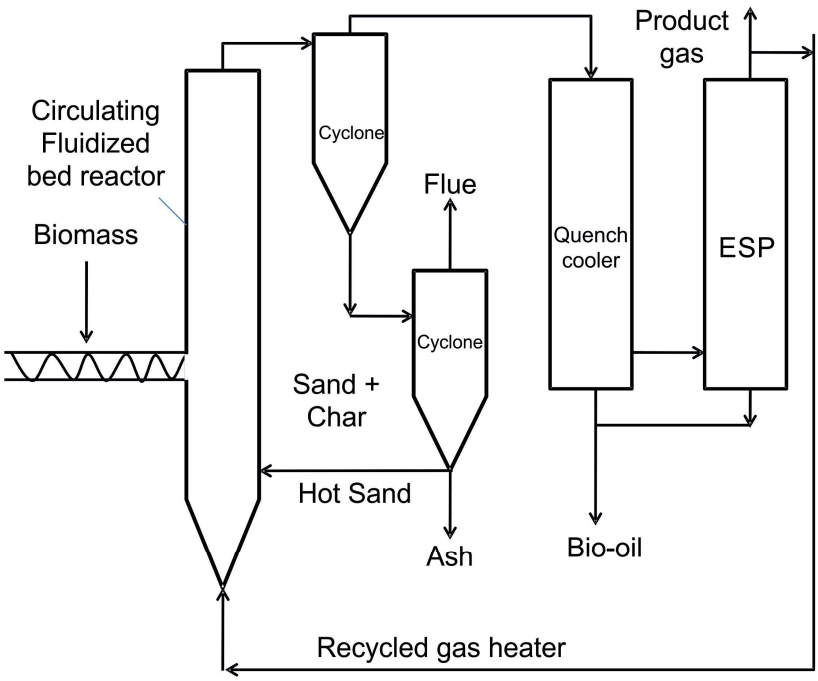

Fig. 2.3 Circulating Fluidized Bed Reactor (Mohan *et al*., 2006)

2.3.3 Ablative reactors

Ringer *et al.* (2006) introduced ablative reactors where biomass particle was melted/vapourised from one plane or side of reactor plate (Fig. 2.4). This design approach had the potential to use particle sizes up to 20 mm in contrast to the 2 mm particle size required for fluidized bed designs. Biomass particles are accelerated to very high velocities by an inert carrier gas (steam or nitrogen) and then introduced tangentially to the vortex

(tubular) reactor. Under these conditions the particle is forced to slide across the inside surface of the reactor at high velocities. Centrifugal force at the high velocities applied a normal force to the particle against the reactor wall. The reactor wall temperature is maintained at 625°C, which effectively melts the particle in a fashion similar to butter melting on a hot skillet. Vapours generated at the surface are quickly swept out of the reactor by the carrier gases to result in vapour residence times of 50-100 milliseconds. So, this design is also able to meet the requirements for fast pyrolysis and gives yield of 65% liquid.

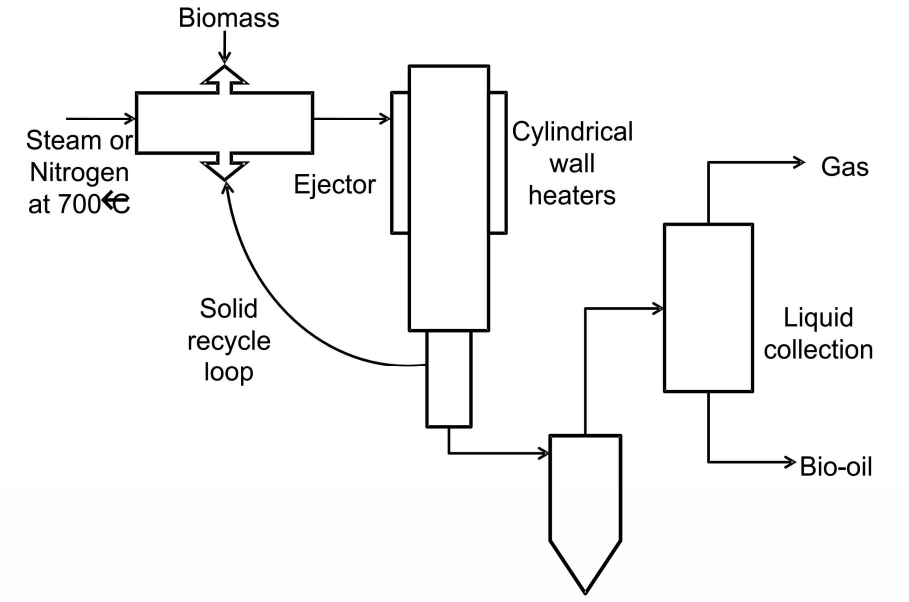

Fig. 2.4 Vortex Ablative Bed Reactor (Ringer *et al.*, 2006)

2.3.4 Vacuum pyrolysis reactors

Yang *et al.* (2001) demonstrated an industrial vacuum pyrolysis reactor of size 14.6 m long and 2.2 m in diameter (Fig. 2.5). The operation of the pyrolysis reactor had been successful, with the reactor capacity reaching feed rate of 3000 kg h^{-1} on a biomass feedstock anhydrous basis. Vacuum pyrolysis is typically carried out at low pressure of 2-20 kPa and a temperature of 400-500°C. The vacuum condition allows the pyrolysis products to be rapidly withdrawn from the hot reaction chamber, thus preserving the primary fragments originating from the thermal decomposition reactions. A limitation of vacuum pyrolysis technology is heat transfer. The main feature of the vacuum pyrolysis process is that a very short residence time for volatiles is easily achieved. Rapid volatilization of biomass fragments under vacuum minimizes the extent of secondary decomposition reactions.

Thus, the chemical structure of the pyrolysis products more closely resembles the original structures of the complex biomolecules that constitute the original organic material.

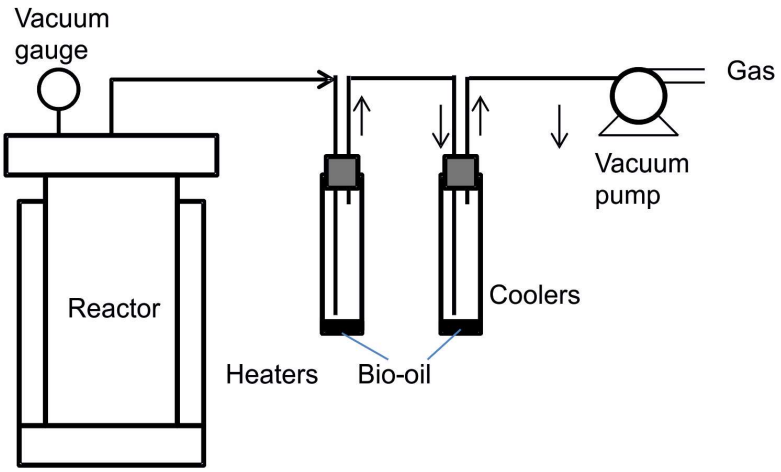

Fig. 2.5 Vacuum Pyrolysis Reactors (Yang *et al.*, 2001)

2.3.5 Auger reactors

Mohan *et al.* (2006) described auger reactors or screw reactors as shown in Fig. 2.6. These are compact and require less carrier gas. They operate at lower process temperatures (400 °C) as a continuous process. Augers move biomass feedstock through an oxygen-free cylindrical tube where it is heated to the desired pyrolysis temperature causing it to devolatize and gasify. Char is produced and gases are condensed as bio-oil and noncondensables are collected as biogas. This design consequently reduces energy costs. Also, the vapour residence time can be modified by increasing the length of the heated zone through which the vapours pass prior to entering the condenser train.

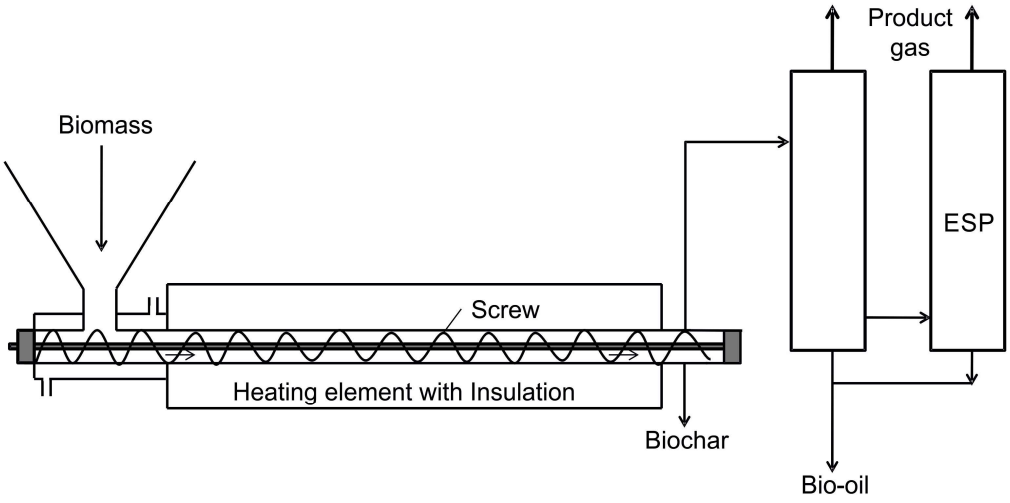

Fig. 2.6 Auger or Screw Pyrolysis Reactor

2.4 Bio-oil and Its Properties

Mohan *et al.* (2006) defined bio-oil as a complex mixture of numerous organic compounds which are mostly oxygenated. It is synonymously called pyrolysis oil; pyroligneous acid; wood oil or bio-crude oil (BCO). Based on the Ultimate Analysis, the chemical formula for wood can be represented by $CH_{1.4}O_{0.6}$. What this formula implies is that on a weight basis wood is composed of almost 42% oxygen. When biomass undergoes pyrolysis, bonds are cleaved to produce fragments of the original macro polymers: cellulose, hemicellulose, and lignin. During this process most of the original oxygen is retained in the fragments that collectively comprise bio-oil. Chemically, biooil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. Content in the bio-oil can be broadly classified as hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. The phenolics are primarily derived from the lignin component of biomass. Through GC/MS more than 300 compounds have been identified in bio-oil. They also stated that aging of bio-oil continued after it was first recovered which was marked by its viscosity increase and phase separation. The instability in bio-oil is believed to result from a breakdown in the stabilized microemulsion and to chemical reactions, which continue to proceed in the oil. Biomass pyrolysis oils contain aldehydes, ketones, and other compounds that can react via aldol condensations during storage or handling to form larger molecules. These reactions cause undesirable changes in physical properties. Viscosity and water content can increase, whereas the volatility will decrease. The most important variable driving this “aging” is temperature. Bio-oil is produced with 25 wt % water, which cannot readily be separated.

Ringer *et al.* (2006) produced bio-oil from three different types of biomass: birch, pine, and poplar. The birch and pine bio-oils were produced in Finland using a circulating fluidized bed reactor while the poplar bio-oil was produced in a vortex reactor. The chemical properties of these bio-oils are presented in Table 2.1. The column labeled “various” is a compilation of over 150 bio-oil samples produced from a variety of feedstocks. While there is a rich mixture of known compounds in bio-oil, the vast majority are found in low concentrations. The highest concentration of any single chemical compound (after water) is hydroxyacetaldehyde at levels up to 10 wt%. This is followed by acetic and formic acids, at about 5 wt% and 3 wt%, respectively. This is the primary reason why bio-oils exhibit a pH in the range of 2.0-3.0.

2.5 Biochar and its Properties

Biochar production by pyrolysis process from different biomass and amendment in soil had been proposed by many researchers as one effective countermeasure to increase soil organic carbon stock while improve soil fertility and climate change mitigation in agriculture.

Table 2.1 Chemical and Physical Properties of Bio-Oil from Different Feedstocks

Property	Birch	Pine	Poplar	Various
Solids (wt%)	0.06	0.03	0.045	0.01-1
pH	2.5	2.4	2.8	2.0-3.7
Water (wt%)	18.9	17.0	16.8	15-30
Density (kg m^{-3})	1.25	1.24	1.20	1.2-1.3
Viscosity, cSt @ 50°C	28	28	13.5	13-80
LHV (MJ kg^{-1})	16.5	17.2	17.3	13-18
Ash (wt%)	0.004	0.03	0.007	0.004-0.3
CCR (wt%)	20	16	N/M	14-23
C (wt%)	44.0	45.7	48.1	32-49
H (wt%)	6.9	7.0	5.3	6.9-8.6
N (wt%)	<0.1	<0.1	0.14	0.0-0.2
S (wt%)	0.00	0.02	0.04	0.0-0.05
O (wt%)	49.0	47.0	46.1	44-60
Na + K (ppm)	29	22	2	5-500
Ca (ppm)	50	23	1	4-600
Mg (ppm)	12	5	0.7	N/M
Flash Point (°C)	62	95	64	50-100
Pour Point (°C)	-24	-19	N/M	-36 -9

Lehmann *et al.* (2006) stated that "From the Amazonians' primitive technology called "Terra-Preta" of enhancing soil productivity with charred biomass, biochar has emerged as a viable technique for carbon sequestration in soil". The application of bio-char (charcoal or biomass-derived black carbon) to soil had been proposed as a novel approach to establish a significant and long-term sink for atmospheric carbon dioxide in terrestrial ecosystems. Apart from positive effects in both reducing emissions and increasing the sequestration of greenhouse gases, the production of bio-char and its application to soil

will deliver immediate benefits through improved soil fertility and increased crop production. Conversion of biomass C to bio-char C leads to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and biological decomposition (< 10–20% after 5–10 years), therefore yielding more stable soil C than burning or direct land application of biomass. This efficiency of C conversion of biomass to bio-char is highly dependent on the type of feedstock, but is not significantly affected by the pyrolysis temperature (within 350–500 °C common for pyrolysis).

Lehmann (2007a) defined biochar as a predominantly stable, recalcitrant organic carbon compound produced by incomplete combustion of biological materials in absence of oxygen or with limited amount of oxygen usually between 300 and 1000 °C. It is believed that biochar can store carbon in soil for hundreds to thousands of years and thus level of green house gases like CO_2 and methane can be reduced significantly while concurrently improving soil properties and functions. Properties of three different biochar are presented in Table 2.2.

Table 2.2 Properties of Biochar Prepared at 600°C from Three Different Biomasses

Properties	Oak wood biochar	Corn stover biochar	Poultry litter biochar
pH	7.90	9.42	10.33
CEC (mmolc kg^{-1})	75.7	252.1	58.7
C (%)	87.5	70.6	23.6
C/N ratio	489	66	25
Total P (mg kg^{-1})	29	2114	23,596
Ash (%)	1.3	16.7	55.8
Volatiles (%)	27.5	23.5	44.1
Fixed C (%)	71.2	59.8	0.1
H/C ratio	0.33	0.39	0.18
O/C ratio	0.07	0.1	0.62
Aromatic C (% of total)	86.6	88.2	Non-detectable
Aromatic clusters	37	40	Non-detectable
SSA (m^2 g^{-1})	642	527	94

Haefele *et al.* (2011) suggested that biochar can be produced by incomplete combustion from any biomass and is a by-product of modern technologies for bioenergy

production such as gasification and pyrolysis. Therefore, crop residues could be used to produce energy, and the biochar by-product could serve to recycle nutrients and maintain or even improve soil fertility. The supposedly high stability of carbonized residues could help to reduce green-house gas emissions from rice-based systems and sequester carbon in soils.

Jeffery *et al.* (2011) concluded that along-with carbon sequestration, biochar is intended to improve soil properties and functions relevant to agronomic and environmental performance mainly enhanced water and nutrient retention as well as improved soil structure and drainage. Furthermore, there is experimental evidence that soil microbial communities and their activity, which hold key roles in sustaining soil health and functioning, are directly affected by the addition of biochar to soils. However, it is likely that changes in soil microbial activity, community structure and functional diversity could impact on crop productivity.

Tsai *et al.* (2012) evaluated exhausted coffee residue (ECR), a processing by-product from the soluble coffee industry, as a potential feedstock for preparing biochar fuel. Its thermochemical characteristics were first investigated using the standard methods, showing that the biomass obviously comprises a large percentage of volatile matter and less amount of ash. Its molar ratio of hydrogen to carbon (H/C) is about 1.59, which is close to the cellulose (H/C = 1.67) and hemicellulose (H/C = 1.60). Under the pyrolysis temperature of 673–973 K and the heating rate of about 10 K min^{-1} studied, the yields and calorific values for the resulting biochar products reached to the maximum at the condition of around 673 K. The calorific value (around 31.9 MJ kg^{-1}) of the optimal biochar from ECR was relatively high as compared to that of coal. However, the resulting biochar has greater nitrogen content, which may contribute to greater nitrogen oxides (NOx) emissions during combustion or co-firing. On the other hand, the resulting biochars were characterized using helium-based solid density (true density), showing that the density increased with increasing pyrolysis temperature in accord with the conversion of low-density disordered carbon to high-density turbostratic carbon.

2.6 Product Gas and Its Composition

Rajvanshi (1986) defined product gas or producer gas or syn gas as the mixture of noncondesable gases of pyrolysis and gasification process. Pyrolysis gas mainly comprises of CO, CO_2 and CH_4. The other components present are H_2, propane, propylene, butane,

butenes, C_5, ethane, etc. It can be used to run internal combustion engines (both compression and spark ignition), can be used as substitute for furnace oil in direct heat applications and can be used to produce methanol in an economically viable way. It was reported that properties of producer gas are greatly affected by the reactor configuration, feed type and reaction temperature and the Table 2.3 lists the composition of gases produced from various sources. The governing reactions responsible for production of combustible gases are:

$$C + CO_2 = 2CO \ (- 164.9 \text{ MJ kg-mole}^{-1}) \quad \ldots (2.1)$$

$$C + H_2O = CO + H_2 \ (- 122.6 \text{ MJ kg-mole}^{-1}) \quad \ldots (2.2)$$

$$CO + H_2O = CO + H_2 \ (+ 42 \text{ MJ kg-mole}^{-1}) \quad \ldots (2.3)$$

$$C + 2H_2 = CH_4 \ (+ 75 \text{ MJ kg-mole}^{-1}) \quad \ldots (2.4)$$

$$CO_2 + H_2 = CO + H_2O \ (- 42.3 \text{ MJ kg-mole}^{-1}) \quad \ldots (2.5)$$

Table 2.3 Composition of Producer Gas from Various Fuels

Fuel	**Gasification method**	Volume Percentage (%)					Calorific value (MJ m^{-3})
		CO	H	CH_4	CO_2	N_2	
Charcoal	Downdraft	28-31	5-10	1-2	1-2	55-60	4.60-5.65
Wood	Downdraft	17-22	16-20	2-3	10-15	55-50	5.00-5.86
Wheat straw pellets	Downdraft	14-17	17-19	-	11-14	-	4.50
Coconut husks	Downdraft	16-20	17-19.5	-	10-15	-	5.80
Coconut shells	Downdraft	19-24	10-15	-	11-15	-	7.20
Pressed Sugarcane	Downdraft	15-18	15-18	-	12-14	-	5.30
Charcoal	Updraft	30	19.7	-	3.6	46	5.98
Corn cobs	Downdraft	18.6	16.5	6.4	-	-	6.29
Rice hulls	Downdraft	16.1	9.6	0.95	-	-	3.25
Cotton stalks cubed	Downdraft	15.7	11.7	3.4	-	-	4.32

Sridhar *et al.* (2001) experimented on the use of producer gas in reciprocating engines at high compression ratio (17:1), which otherwise had been restricted to lower compression ratio (up to 12:1). This restriction in compression ratio had been mainly attributed to the auto-ignition tendency of the fuel. The work indicated the breakdown of

compression ratio barrier and it was shown that the engine run smoothly at compression ratio of 17:1 without any tendency of auto-ignition. Experiments had been conducted on multi-cylinder spark ignition engine modified from a production diesel engine at varying compression ratios from 11.5:1 to 17:1 by retaining the combustion chamber design. As expected, working at a higher compression ratio turned out to be more efficient and also yielded higher brake power. A maximum brake power of 17.5 kWe was obtained at an overall efficiency of 21% at the highest compression ratio. The maximum de-rating of power in gas mode was 16% as compared to the normal diesel mode of operation at comparable compression ratio, whereas, the overall efficiency declined by 32.5%. A careful analysis of energy balance revealed excess energy loss to the coolant due to the existing combustion chamber design.

Sheth and Babu (2009) conducted studies on producer gas generation from wood waste in a downdraft biomass gasifier with Dalbergia sisoo, generally known as sesame wood or rose wood. The range of air-to-fuel ratio varied was 1.37–1.64 $Nm^3\ kg^{-1}$ and that of equivalence ratio varied was 0.262–0.314. The optimum operation of the gasifier was found to be between 1.44 and 1.47 $Nm^3\ kg^{-1}$ of air-to-fuel ratios at the values of 4.06 and 4.48 kg h^{-1} of wet feed rate, which produced the producer gas with a calorific value of about 5 MJ m^{-3}. The optimum equivalence ratio was 0.205 for the downdraft biomass gasifier studied.

2.7 Pine Needles as Feedstock for Pyrolysis

Pappa *et al.* (2006) used Thermogravimetry-mass spectrometry (TG-MS) to study the effect of the inorganic salts $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, as forest fire retardants, on the pyrolysis of *Pinus halepensis* needles and their main components (cellulose, lignin and extractives). These salts seemed to affect the pyrolysis of cellulose by increasing significantly the char residue, decreasing the pyrolysis temperature and changing the composition of the evolved gases, that is, increasing levoglucosenone and decreasing oxygen containing volatile products. $(NH_4)_2SO_4$ seemed to have negligible effect on the pyrolysis of lignin, while $(NH_4)_2HPO_4$ increased the char residue and decrease the relative contribution of guaiacols in the evolved gases. No effects of the inorganic salts on the extractives were observed. Finally, the inorganic salts seemed to affect the pyrolysis of pine-needles, mainly the cellulose component, but the effects were not as intense as in the pyrolysis of cellulose.

Tzamtzis *et al.* (2006) studied a new method called TG-bridge/mass spectrometry for the on-line monitoring of the pine needles combustion emissions in a common lab furnace. The TG-bridge (thermogravimetry-bridge) system had been developed in-house as a TG–MS (thermogravimetry–mass spectrometry) interface, for TG–MS analysis. In this work, TG-bridge was used for directly sampling of the combustion emissions from the inside of the furnace and transferring them into the mass spectrometer (MS), without disturbing the sub-pressure conditions inside the MS ion source. They concluded that thick layer of pine needles was considerable threat for forest fire in Mediterranean basin and many other parts of the globe.

Font *et al.* (2008) conducted kinetics of pyrolysis and combustion of pine needles and cones. A wide kinetic study was carried out under different conditions in TG and TG–MS for each material, at different operating conditions. Runs were carried out at three different atmospheres: N_2, N_2:O_2 4:1 and N_2:O_2 9:1. In addition to the dynamic runs carried out at constant heating rate, other runs were performed in an isothermal regime (constant heating rate until the set temperature was reached and then the set temperature was maintained constant). In addition, a study of the thermal decomposition for both materials was also carried out in a dynamic run using TG–MS in order to observe the evolution of the major compounds and to discuss the information that could be obtained. There was an initial small fraction (volatile fraction around 0.06), whose volatiles evolved around 300–370 K, with a small apparent activation energy (43–44 kJ mol^{-1}), corresponding mainly to the humidity of the sample. After the evolution of volatiles corresponding to the first fraction, a second fraction decomposed at 470–600 K, with apparent activation energy around 130–140 kJ mol^{-1}, and probably corresponding to mainly hemicellulose. The following fraction decomposed in the range 550–700 K with an apparent activation energy around 200–240 kJ mol^{-1} which was cellulose. There was a fourth fraction that decomposed in a wide temperature interval (550–800 K), with apparent activation energy around 190–200 kJ mol^{-1} that corresponds mainly to lignin. This study was an excellent directive to find the temperature regime of pine needles for pyrolysis under inert atmosphere.

Ahmad *et al.* (2013) conducted studies on Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. Pine needles were converted to biochar at different pyrolysis temperatures of 300, 500, and 700 °C to sorb trichloroethylene and the changes in biochar properties with each temperature were

evaluated. Pyrolysis temperature showed a pronounced effect on biochar properties. Decreases in molar H/C and O/C ratios resulted from removing O- and H-containing functional groups with increasing temperature, and produced high aromaticity and low polarity biochars. Biochars produced at higher temperature showed greater trichloroethylene removal efficiency from water due to their high surface area, micro-porosity, and carbonized extent.

Fateh *et al.* (2016) studied flammability of pine needles (*Pinus pinaster*, representative of Mediterranean vegetation) in a cone calorimeter under air atmosphere with piloted ignition and self-ignition for different heat fluxes, from 10 to 50 kW m^{-2}. The main objective was to measure the yields of the gaseous emissions released during the experiments because one of the major risks during the fire is from the smoke and products of combustion. Identification of exhaust gaseous compounds and concentration measurements had been done by FTIR, NDIR, chemiluminescence and paramagnetism gas analyzers for assessing the fire behavior and identifying the decomposition chemistry. Among the 15 different gaseous compounds quantified simultaneously (with the 2 analyzers), main species concentrations and emission yields were CH_4, CO_2, CO, H_2O, NO and O_2. HCN and light-weight hydrocarbons (C_2H_2, C_2H_4, C_3H_6 and C_3H_8) had been observed at low concentrations. They concluded that bed of pine needles behaved as a thermally thick material and temperature of ignition was 639K.

2.8 Batch Pyrolysis of Different Biomass

Most batch pyrolysis experiments are conducted in a horizontally laid cylindrical stainless steel reactor which is heated externally. The configurations of reactor varied widely in the previous researches. Some of the relevant experiments have been reported here.

Özçimen and Karaosmanoğlu (2004) performed pyrolysis of rapeseed cake under static and nitrogen atmospheric conditions in a Heinze retort 316 stainless steel fixed bed reactor which has a length of 104 mm and an inner diameter of 70 mm. The reactor was heated externally by an electrical furnace in which the temperature was measured by a thermocouple erected inside the bed. The experimental results of pyrolysis, which were conducted at 7°C min^{-1} heating rate, 500°C final temperature under static atmosphere showed 27.4% biochar, 59.7% bio-oil and 12.8% yield of gas. The biochar obtained were

carbon rich, with high heating value and relatively pollution-free potential solid biofuel. The bio-oil product was presented as an environment friendly green biofuel candidate.

Özçimen and Ersoy-Meriçboyu (2010) performed carbonization experiments in a Jenkner type retort which was a cylindrical stainless steel fixed bed reactor with a length of 270 mm and an inner diameter of 130 mm. The reactor was heated externally by an isolated electrical furnace where temperature was measured by a Ni–Cr–Ni thermocouple inside the bed. During the carbonization the inner and outer temperatures of the reactor were controlled continuously. Before heating, the system was flushed with dry nitrogen for 30 min to remove all traces of oxygen. After carbonization at final temperature value, which lasted 30 min, the final weight of samples was determined to calculate the biochar and bio-oil yields. In this study, the characteristics of bio-oil and biochar samples obtained from the carbonization of apricot stone, hazelnut shell, grape seed and chestnut shell were investigated. The maximum biochar yields were found as 34.65%, 51.53%, 52.98% and 58.80% for apricot stone, hazelnut shell, grape seed and chestnut shell samples, respectively. The maximum bio-oil yields, on the other hand, were determined for those conditions as 35.82%, 41.95%, 49.11% and 36.11% for apricot stone, hazelnut shell, grape seed and chestnut shell samples, respectively. It was found that the biochar products can be characterized as carbon rich, high heating value and relatively pollution-free potential solid biofuels.

Uzun *et al.* (2010) carried out pyrolysis of tea waste in a stainless steel tubular reactor of 90 cm height and 2.5 cm internal diameter. A stream of nitrogen was introduced at the top of the reactor and its flow rate was adjusted with a rotameter. Heating rate and pyrolysis temperature were controlled with PID controller. Investigated process variables were temperature (673–973 K), heating rate (5–700 K min^{-1}) and nitrogen gas flow rate (200–800 cm^3 min^{-1}). The maximum oil and char yields are 30.4 (773 K) and 43.3% (673 K), respectively. The liquid and its aliphatic sub-fraction were characterized by elemental analysis, FT-IR, 1H NMR, and GC/MS. The char was characterized with elemental analysis, SEM, BET, and FT-IR techniques. The aliphatic sub-fraction of the obtained bio-oil contains predominantly n-alkanes and alkenes, and branched hydrocarbons. According to the experimental results the liquid products can be used as liquid fuels, whereas the solid product seems to be not suitable for adsorption purposes, due to having low surface areas.

Das *et al.* (2008) pyrolyzed poultry litter and pine chips in the batch reactor of 255 mm diameter and 230 mm long heated to 500°C with a 30400 thermolyne furnace. Then, 1.4 kg of biomass was converted per test. The pyrolysis vapours were evacuated across the biomass bed and condensed in four ice cooled traps connected in series. The 2 l min^{-1} of nitrogen was used as carrier gas. The resulting char was cooled under nitrogen at the end of each test to avoid oxidation. Oil phase yield of 8.8 to 16.2 % was recorded.

Bordoloi *et al.* (2015) conducted pyrolysis of *Mesua ferrea* seed cover (MFSC) and *Pongamia glabra* seed cover (PGSC) to investigate the characteristics of bio-oil and its sub fractions. The effect of temperature (range of 350–650 °C) on product yield and quality of solid product were monitored. The pyrolysis experiments were conducted in a fixed bed tubular reactor system in which the temperature was controlled by Ni–Cr thermocouple which was placed in the center of pyrolysis reactor. The fixed-bed tubular reactor had a length of 30 cm and an internal diameter of 2.47 cm and was made of quartz. At the outlet of reactor, a condenser was attached to condense the vapours coming out of it. The condensed liquid was collected in a container at the end of condenser. The maximum bio-oil yield of 28.5 wt.% and 29.6 wt.% for PGSC and MFSC respectively was obtained at 550 °C at heating rate of 40 °C/min. The chemical composition of bio-oil and its sub fractions were investigated using FTIR and 1H NMR. GC–MS was performed for both PGSC and MFSC bio-oils and their corresponding n-hexane fractions. The results showed that bio-oil from the feedstocks and its subfractions might be a potential source of renewable fuel and value added chemicals.

Saikia *et al.* (2015) conducted pyrolysis experiments of perennial grass species *Arundo donax* L. in a fixed-bed reactor and characterized the liquid and the solid products. Biomass samples were pyrolyzed in a lab scale quartz fixed-bed reactor with a length of 30 cm and an internal diameter of 3 cm, equipped with an inert gas (nitrogen) connection. The effect of process parameters such as temperature (350–650 °C), heating rate (10 °C and 40 °C min^{-1}) and sweeping gas flow rate (50–250 ml min^{-1}) was also investigated. Maximum bio-oil yield of 26% was observed at 500 °C for the heating rate of 40°C min^{-1}. Chemical composition of the bio-oil was analysed through NMR, FTIR and GC–MS. The biochar was characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy along with elemental analysis (CHN).

2.9 Continuous (Screw) Pyrolysis of Different Biomass

Previous studies shows that there are two types of auger (continuous) reactors, namely single screw and twin screw in pyrolysis of biomass. Majority of the works are focused on single screw reactors, as it is simpler in design and operation.

Puy *et al.* (2011) described a single screw system without heat carrier (that is, heat is delivered externally through the reactor shell) by using pine wood. The operating parameters were auger speed, biomass flow rate, temperature, sweep gas flow rate and feedstocks. Results showed that the greatest yields for bio-oil production (59%) and optimum product characterization were obtained at a 500°C temperature and solid residence times longer than 2 min.

Brown and Brown (2012) worked in an auger reactor heated by an externally supplied heat carrier for pyrolysis of red oak wood biomass. A statistically designed set of experiments was performed in order to optimize the process conditions for maximizing bio-oil yield. This systematic, simultaneous investigation of multiple variables (heat carrier temperature and mass flow rate, auger rotational speed, and sweep gas volumetric flow rate) allowed the identification of interaction effects among the variables. It was concluded that the conditions for maximum bio-oil and minimum char yields were high flow rate of sweep gas (3.5 standard L min^{-1}), high heat carrier temperature (600°C), high auger speeds (63 RPM) and high heat carrier mass flow rates (18 kg h^{-1}).

Liaw *et al.* (2013) investigated the effect of pyrolysis temperature on the yield and composition of bio-oils obtained from the auger pyrolysis of Douglas Fir wood. The maximum yield of bio-oil at 500 °C was about 59% while the yield of char was 13%. The results confirmed that the auger reactor was able to achieve good yields of both bio-oil and bio-char, but the overall oil composition obtained was affected by the slower heating rates and the intensification of secondary reactions in gas phase.

Efika *et al.* (2012) investigated a two-stage continuous screw-kiln reactor for the production of synthesis gas (syngas) from the pyrolysis of biomass in the form of waste wood and subsequent catalytic steam reforming of the pyrolysis oils and gases. Pyrolysis of the biomass at a rapid heating rate of approximately 40°C s^{-1}, was carried out at a pyrolysis temperature of 500°C and the second stage reforming of the evolved pyrolysis gases was carried out with a catalytic bed kept at a temperature of 760°C. The screw kiln

reactor was 54 cm long × 6.2 cm diameter, constructed of stainless steel and heated by an electrical furnace to a fixed pyrolysis temperature of 500°C. The reactor design was shown to be effective for the pyrolysis and catalytic steam reforming of biomass with a maximum syngas yield of 54.0 wt.% produced with NiO/SiO_2 catalyst.

Sirijanusorn *et al.* (2013) studied behaviour of counter-rotating twin screw reactor unit for pyrolysis of cassava rhizome biomass. The two screws were designed to rotate on the opposite direction and referred to as a ‘‘counter-rotating twin screw’’. Purpose of their work was to examine the behavior of the counter-rotating twin screw reactor in the production of bio-oil in the pyrolysis temperature range of 500–700 °C, biomass particle size of <0.6 mm, sand as heat transfer medium, nitrogen flow rate of 4–10 L/min and nitrogen pressure of 1–3 bar. It was found that the pyrolysis temperature of 550°C could maximise the bio-oil yield (50 wt.%). The other optimum parameters for maximising the bio-oil yield were the biomass particle size of 0.250–0.425 mm, the nitrogen flow rate of 4 L/min and the nitrogen pressure of 2 bar. The use of the heat transfer medium could increase the bio-oil yield to a certain extent. Moreover, the water content of bio-oil produced with the counter-rotating twin screw reactor was relatively low, whereas the solids content was relatively high, compared to some other reactor configurations.

Ferreira *et al.* (2015) evaluated a pilot scale reactor with screw conveyor for pyrolysis of Medium Density Fiberboard (MDF) wastes at two reaction temperatures (450 and 600°C) and, for each one, three solid residence times (9, 15 and 34 min). Products (char/bio-oil/fuel gas) of the pyrolysis process were characterized and quantified. Results revealed that the products yields were influenced by pyrolysis temperature, as well as by solid residence time. Char yield ranged between 17.3 and 39.7 (wt.%), the bio-oil yield ranged between 23.9 and 40.0 (wt.%), while the fuel gas yield ranged between 34.6 and 50.7 (wt.%). The char surface area at 450 and 600°C in 15-min residence time were surprisingly high, 415 and 593 $m^2\ g^{-1}$, respectively, which were compatible with the superficial area of commercial activated carbons. Energetic efficiency of process was estimated from energetic content present in the reaction products and the energetic content of MDF wastes, and the following results were obtained: 41.4% (fuel gas), 35.5% (char) and 29.2% (bio-oil). The contribution of the work was the development of a detailed study of the MDF pyrolysis in a pilot reactor with screw conveyor that supported the biorefineries concept.

Morgano *et al.* (2015) investigated pyrolysis of beech wood chips by means of intermediate pyrolysis in a screw reactor with integrated hot gas filtration (STYX). The STYX reactor was developed by the Institute for Technical Chemistry (ITC) at the Karlsruhe Institute of Technology, in Germany. It was a through screw reactor, which measures approximately 2 m in heated length and has a diameter of 0.15 m. The screw had the advantage of well-defined residence time of the solids, which could be varied in the range of 5–25 min by adjusting the rotational speed of the screw. The operating temperature of the STYX could be regulated in the range of 350–550°C via external independent electrical heaters. On the one side, the filtered vapours were extracted from the reactor and conveyed together to the condensation unit. The other side served as inlet for the recleaning gas. Heated nitrogen was injected for online recleaning by using the coupled-pressure-pulse technology. The condensation train was composed of three condensers displaced in series and an electrostatic precipitator (ESP) at the tail, just before the gas analytics. The condensate was collected at a temperature of 15°C. it was observed that the yield of the char decreased with increased temperature from 31 wt.% to 18 wt.% whereas, the yield of the oil phase reached a maximum value of 13.2 wt.% at 450°C. The configuration of the reactor allowed sequential filtration and extraction of the vapours, as well the direct access to the partially pyrolyzed char. The sequential extraction appeared as a promising route to concentrate valuable products. Among the results, it had been found that the heating rate in the range of 100°C min^{-1} to 210°C min^{-1} did not play a major role on the characteristics of the produced char.

Kelkar *et al.* (2015) conducted fast pyrolysis of spent coffee grounds (SCG) using a compact, transportable, screw conveyor reactor for producing bio-oil. The pilot-scale screw-conveyor pyrolysis reactor used in this study was capable of processing 1–6 kg of biomass per hour, depending upon the flowability of the feedstock. The major parts of this reactor were gravimetric pre-feeder, screw-conveyor reactor, char trap, bio-oil condensers and traps, electrostatic precipitator (ESP) and a flame calorimeter. A variable speed motor controlled the rotation rate of the screw and hence the residence time of the solid biomass. The gravimetric pre-feeder enabled consistent biomass input and helped to minimize undesired solids bridging. Each reactor run was conducted with approximately 1–1.5 kg of SCG in the temperature range of 450–550 °C. Bio-oil yields increased with screw speed and decreasing residence time. In addition to containing oxygenated organic compounds typical of bio-oils, spent coffee bio-oil also contains more hydrophobic compounds (N20%

peak area) such as fatty acids, fatty acid esters, medium-chain paraffins, olefins, and caffeine. Because of the abundance of spent coffee grounds and the quality of its bio-oil, this waste stream was found potent as a valuable bioenergy feedstock.

Henrich *et al.* (2016) designed a process development unit (PDU) with 10 kg h^{-1} biomass capacity for fast pyrolysis of biomass. A twin-screw type reactor, in earlier applications used for treatment of coal, oil shale, oil sand and oil refinery residues, was used. The intertwining screws were rotated in the same direction and permanently cleaned each other as well as the inner reactor walls. Radial mixing with a rotation speed was in the range of Froude number one: $Fr = (2n)^2 r/g = 1$ with $n = 3.53\ s^{-1}$ (n rotational frequency, r=0.02m outer screw radius, g=9.81m s^{-2} gravitational acceleration) where centrifugal forces at the outer screw radius and gravitational forces of the heat carrier just compensate each other, proved to be a suitable design criterion for scale-up. Test campaigns with a variety of biomass types were performed. The results with hard-wood, softwood, wheat straw and wheat bran were reported and discussed to verify the suitability of the twin screw reactor along with a new product recovery procedure. Liquid pyrolysis condensate, termed bio-oil, was the main product of fast pyrolysis and the yields were about 65 ± 10 wt.% for wood but only about 50 ± 10 wt.% for cereal straw, which was a typical result for all fast growing types of biomass with higher ash content.

2.10 Batch Type Biochar Production Reactors

Venkatesh *et al.* (2013) developed a low-cost charring kiln by modifying oil drums at Central Research Institute on Dryland Agriculture, , Hyderabad, India. A square shaped hole of 16 cm × 16 cm was made on the centre of top side of the drum for loading the crop residues. On the opposite side (bottom) of the oil drum, a total of 36 holes each measuring 4 cm^2 were made in concentric circles to facilitate uniform circulation of air from bottom. After loading of crop residues a fire is started and allowed to burn for 15 minutes. After that all holes are closed by clay to stop air flow and carbonization process to complete.

Srinivasarao *et al.* (2013) reported that researchers at Central Institute of Agricultural Engineering, Bhopal had developed a 'CIAE Portable Charring Kiln'. It was also made of 200 litre oil drum. It was laid horizontally and has a 30 cm × 30 cm opening at the centre which could be closed by a door. In operation, after putting a small charge of biomass a fire is started and biomass is added in small quantity until it is full. After 30 min, the door is closed and left for 6 hours to cool down. It converts crop-residues into char through pyrolysis process for

smokeless kitchen fuel (briquettes) production. It can be used for different bioresidues including soybean straw, pigeonpea and cotton stalks etc as input material. It consists of mild steel drum, handle and a door. Similarly, a modified portable metallic kiln was used at ICAR (Indian Council of Agricultural) Research Complex for North Eastern Hilly Region to make biochar from weed biomass. The kiln was made from 200 litre used oil-drum. It had a conical grate at the bottom extended to the top of the drum by a cylinder of 120 mm diameter. The cylinder was further extended to a chimney of same diameter up to a height of 1.2 m. A pipe of 60 mm diameter was provided below the drum to supply air by a blower. After putting a small charge of dry biomass, it is ignited at the top and air is blown from bottom of the drum. Once the biomass catches sufficient fire, addition of charge in small quantities is continued till the drum is filled. The chimney is put on the conical grate extension after ignition. When the colour of smoke fades, the chimney is taken out and a lid is put over the drum which completely seals the smoke. Blower is taken out and the bottom pipe is closed by using mud. In one batch, 30-40 kg biomass can be converted to biochar within two hours with a conversion efficiency of 25-35% depending on the type of biomass. All these inventions require constant involvement of a person to feed the biomass. The operator also has to face the smoke produced during the process which is harmful to health as it contains CO, CO_2, H_2S and many other hydrocarbons.

Murcia (2002) invented a portable kiln for making charcoal from wood waste which was patented with number **US20020148716A1**. It included three main parts—a bottom cylinder, an upper cylinder and a cover—is assembled while being loaded with the wood waste. The kiln can be placed on the ground or on a vehicle, such as a flatbed truck. Once the kiln is assembled and filled, the wood is consumed to make charcoal. During the carbonization process, the kiln can be transported. Once the carbonization process is completed, the kiln can be easily emptied of both the charcoal and byproducts.

Shepard (2011) designed a Biochar Retort Kiln for pyrolysis of waste biomass to produce biochar under patent number **US20110252699A1**. It comprises a firebox through which passes a cylindrical retort chamber. The fire in the firebox directly heats the retort chamber. Biomass is placed inside the retort chamber wherein it is subjected to temperatures reaching 750° C in the absence of oxygen for enough time to be fully pyrolyzed and turned into biochar. The synthesis gasses which are driven out of the biomass during pyrolysis, exit the retort chamber and are directly burned in the firebox, further fueling pyrolysis. Both these units had no control unit for air flow supply which in

turn controls the reaction temperature and specifically made for converting woody materials.

Aupperle *et al.* (2015) patented a Controlled Kiln and Manufacturing System for Biochar under patent number **US20150136581A1**. It includes a drum, a lid and a floor together forming a combustion chamber configured to contain feedstock for conversion into biochar. A catalytic converter is coupled with an outlet of the kiln and a conversion process completion detection subsystem to issue notifications. It also includes a feedstock filling station for providing feedstock to kiln, a firing line for receiving the kiln containing feedstock, a tipping station for receiving biochar from the kiln, a biochar sizing station, and an automated handler configured to move the kiln between the feedstock filling station, the firing line and the tipping station. This unit requires sophisticated instrumental setup and higher initial cost.

2.11 Response Surface Methodology and Its Application for Process Optimization

Carley *et al*. (2004) defined Response Surface Methodology (RSM) as a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. The most extensive applications of RSM are in the particular situations where several input variables potentially influence some performance measure or quality characteristic of the process. Thus performance measure or quality characteristic is called the **response**. The input variables are sometimes called **independent variables,** and they are subjected to the control of the scientist or engineer. The field of response surface methodology consists of the experimental strategy for exploring the space of the process or independent variables, empirical statistical modeling to develop an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response. In general, the response variable y may be related to k regressor variables. The model

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + ... + \beta_k x_k + \varepsilon \qquad \text{... (2.6)}$$

is called a multiple linear regression model with k regressor variables. The parameters, β_j, $j=0,1,...k,$ are called the **regression coefficients**.

The second-order response surface model in two variables is expressed as:

$$y = \beta_0 + \sum\beta_i x_i + \sum\beta_{ii} x_i^2 + \sum\sum\beta_{ij} x_i x_j + \varepsilon \qquad \text{... (2.7)}$$

RSM has been employed in number of industrial processes for optimization. Some of the relevant studies are presented here.

Mazaheri *et al.* (2010) used RSM for optimisation for subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide. The study used experimental design and process optimisation tools to maximise the liquid product yield using response surface methodology (RSM) with central composite rotatable design (CCRD). The independent variables were temperature, residence time, particle size, specimen loading, and additive loading. The mathematical model that was developed fit the experimental results well for all of the response variables that were studied. The optimal conditions were found to be a temperature of 551 K, a residence time of 40 min, a particle size of 710–1000 μ, a specimen loading of 5 g, and a additive loading of 9 wt.% to achieve a liquid product yield of 76.16%.

Isa *et al.* (2011) conducted studies to optimize bio-oil yield from rice husk pyrolysis using RSM. The effects of pyrolysis temperature, heating rate, particle size, holding time, and gas flow rate were investigated. The optimisation process was analysed by employing central composite design (CCD) in RSM using Design Expert Version 7.5.1 (StatEase, USA). A two-level fractional factorial was initially carried out and followed by RSM. The statistical analysis showed that pyrolysis temperature, heating rate, particle size and holding time significantly affected the bio-oil yield. By utilising response surface method, these four factors were investigated, analysed and optimal conditions were obtained at pyrolysis temperature of 473.37 °C, heating rate of 100 °C/min, particle size of 0.6mm and holding time of 1 min. Confirmation runs gave 48.30% and 47.80% of bio-oil yield compared to 48.10% of predicted value.

Kelkar *et al.* (2015) conducted pyrolysis of spent coffee grounds using a screw-conveyor reactor. A two-factor, five-level, central composite response surface experiment was used to formulate a statistical model that related reactor temperature (429–550 °C) and residence time (23–42 s, controlled by the screw rotation rate) to bio-oil yield and quality. Regression analysis of model fitted with experimental data showed that temperature and residence time had a significant effect ($p<0.05$) on bio-oil yield. Highest biooil yield (61.8%) was observed at 500 °C while the highest char yield (20.6 % w/w) was produced at the lowest temperature of 429 °C. The model predicted a maximum liquid yield of 61.7% and an accompanying char yield of 17.1% at 505 °C (778 K) and 70 rpm.

2.12 Taguchi Method and Its Application for Process Optimization

Dr. Genichi Taguchi developed a new method of conducting the design of experiments (Taguchi method). The most important feature of the Taguchi method is the use of an orthogonal array. The orthogonal array stipulates the way of conducting the minimal number of experiments which could give the full information of all the factors that affect the performance parameter. Although the Taguchi method is not a full factorial one that can pinpoint the exact optimal conditions, it can obtain the best trend using less experimental data, and thus in practice is more feasible than a full factorial approach. In addition to the main effect of each factor, the Taguchi method can also study the interactions between the factors to optimize the output response. It is thus a widely used strategy for the optimization of industrial processes.

In the Taguchi method, the term "signal" (S) represents the desired value for the output characteristic, while "noise" (N) represents an undesirable value for the output characteristic. The S/N ratio is thus the ratio of the signal to the noise, and the Taguchi method uses this to measure how a specific quality characteristic deviates from the desired value. The S/N ratio is defined as

$$\frac{S}{N} = -10\log[M.S.D.] \qquad \ldots (2.8)$$

where, M.S.D. is the mean-square deviation for the output characteristic. The S/N ratio characteristics can be divided into three categories, i.e. NTB (nominal is the best), the STB (smaller the better), and the LTB (larger the better). To obtain the maximum yield of pyrolytic oil, the larger the better is used in the study, and the related S/N ratio can be expressed as follows:

$$\frac{S}{N}_{HB} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right] \qquad \ldots (2.9)$$

where, n is the number of repetitions under the same experimental conditions, and Y represents the yield of bio-oil in i^{th} experiment. The design of an experiment by Taguchi method involves the following steps

1. Selection of the output response
2. Selection of S/N ratio characteristics
3. Selection of independent variables

4. Selection of number of level settings for each independent variable

5. Selection of orthogonal array

6. Assigning the independent variables to each column

7. Conducting the experiments

8. Analyzing the data

9. Conducting confirmation experiments

In the Taguchi method, the most important step is the use of orthogonal arrays, which are created on the basis of the statistical approach developed by C.R. Rao in 1947. Orthogonal arrays are mainly used to design experiments, and these are matrices related to the experimental factors and levels of interest. Because all the columns in such matrices are independent from each other, they are called orthogonal arrays. The key advantage of these is that they can reduce the number of experiments that are needed to obtain the optimal condition, and thus significantly reduce the costs of the analysis. The orthogonal array in Taguchi method is often labeled as $L_a(b^c)$. Where 'a' is the total experiment number, 'b' is the level number of each factor and 'c' is the number of control factor. 'L' represents the orthogonal array matrix comes from the Latin square. For each control factor with two levels, commonly used orthogonal arrays are $L_4(2^3)$, $L^8(2^7)$, $L^{16}(2^{15})$ and $L^{32}(2^{31})$. For each control factor with three levels, commonly used orthogonal arrays are $L_9(3^4)$ and $L_{27}(3^{13})$. Therefore, in the choice of the orthogonal array, the number of control factor must be considered in combination with the level.

Chou *et al.* (2009) found optimum conditions for preparing solid fuel briquette of rice straw by a piston-mold process using the Taguchi method. The controllable factors used in the study consisted of the following: (1) the type of binder (such as the rice bran, the soybean residue, and the sawdust of Acacia confuse), (2) the hot pressing temperature (such as 110, 130, and 150 °C), (3) the size of the smashed rice straw (such as 10–5mm, 5–2mm, and <2mm), and (4) the percentage ratio of rice straw to binder in a briquette (such as 100/0, 80/20, and 60/40). The percentage contribution of each controllable factor was also determined. The confirmation experiment was carried out according to the optimum conditions. Most interestingly, the size of the smashed rice straw was the most influential factor to solidify fuel briquette, and its value was up to 43.0%.

Chen *el at.* (2014) conducted study of thermal pyrolysis for castor meal using the Taguchi method. The effects of different parameters on castor meal pyrolysis were

investigated, namely the pyrolytic temperature, residence time, heating rate and nitrogen flow rate. The pyrolysis control factors were selected and categorized into three levels. Based on the Taguchi design concept, an L_9 orthogonal array was chosen for the experiments. The results show that the maximum yield of 19.61% (g-pyrolytic oil/g castor meal) pyrolytic oil was obtained when the castor meal was subjected to a pyrolytic temperature of 400 °C, residence time of 120 min, heating rate of 20 °C/min, and the nitrogen flow rate of 200 mL/min. The effective sequence of different parameters on castor meal pyrolysis was the nitrogen flow rate, pyrolytic temperature, residence time and heating rate, respectively. The results of the experiment confirmed that there were some differences between the theoretical and experimental yields because of certain assumptions in the Taguchi method and the non-uniformity of castor meal.

Chan *et al.* (2014) conducted studies on catalytic pyrolysis of empty fruit bunch (EFB) using Taguchi's L_9 Orthogonal Array. They investigated the effects of four reaction parameters that included type of catalyst, catalyst loading, reaction temperature and nitrogen gas flow rate on the liquid (bio-oil) yield from the catalytic pyrolysis of EFB. The experimental design was based on Taguchi's L_9 Orthogonal Array in which the reaction parameters are varied at three levels. The maximum liquid yield was predicted based on systematic experimental runs, and was found to be at 5 wt-% of H-Y catalyst, 500 °C and at nitrogen flow rate of 100 ml min^{-1}. The predicted maximum liquid yield was validated with an experimental run at the corresponding predicted conditions.

The past researches on the subject therefore indicate that higher bio-oil yield can be achieved by rapid heating and rapid cooling of vapour. It produces the intermediate pyrolysis liquid products which condense before further reactions break down of higher-molecular-weight species into gaseous products. Fast pyrolysis generally requires a small particle size of feedstock and quick removal of vapours from the reactor. Batch pyrolysis experiments are mostly conducted in a horizontally laid cylindrical stainless reactor which is heated externally by electrical heaters.

There are five main types of pyrolysis reactors which were (a) Bubbling fluidized-bed reactors; (b) circulating fluidized-bed reactors (both dilute and dense types); (c) ablative reactors, both cyclonic and plate type; (d) vacuum pyrolysis reactors and (e) auger reactors (slow pyrolysis)**.** Screw or auger reactor is advantageous due to its simple design, requirement of low carrier gas flow and suitability for large biomass particles.

Biooil is a complex mixture of water, hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. It is heavier than water and has a colorific value equivalent to 2/3rd of diesel fuel. Biochar is a predominantly stable, recalcitrant organic carbon compound produced by incomplete combustion of biological materials in absence of oxygen or with limited amount of oxygen. It can store carbon in soil for hundreds to thousands of years and reduces level of GHGs while concurrently improving soil properties. Product gas or producer gas or syn gas is the mixture of noncondesable gases of pyrolysis and gasification process. Pyrolysis gas mainly comprises of CO, CO_2 and CH_4. The other components present are H_2, propane, propylene, butane, butenes, C_5, ethane, etc. It can be used to run internal combustion engines.

The bed of pine needles behaved as a thermally thick material and temperature of ignition was 639K. However, pine needles had been found as suitable biomass for thermochemical conversion to bio-oil, biochar and product gases. Temperature regime of pine needles for pyrolysis is 550–800 K.

Highest bio-oil yield in batch pyrolysis of most biomass had been achieved within the temperature range of 450 – 550 °C, at higher heating rate and small particle size. The operating parameters such as auger speed, biomass flow rate, temperature, sweep gas flow rate) and feedstock size affected yield of bio-oil in a screw reactor. The greatest yield of biooil production was obtained at 500°C temperature and solid residence time longer than 2 min.

Batch type biochar production units are suitable for woody biomass of varying sizes. They can achieve a conversion rate of 30%. Control of temperature is difficult and the product gases are not usable.

RSM is a strong optimization tool which develops an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response. Taguchi method is specially designed orthogonal array which stipulates the way of conducting the minimal number of experiments which could give the full information of all the factors that affect the performance parameter. It can obtain the best trend using less experimental data, and thus in practice is more feasible than a full factorial approach.

Chapter – 3

MATERIALS AND METHODS

MATERIALS AND METHODS

This chapter describes the standards followed for characterisation of pine needle biomass and its derived products. It also deals with the experimental procedures followed for pyrolysis. The batch pyrolysis experiments were carried out at the Department of Farm Machinery and Power Engineering, College of Technology, G.B. Pant University of Agriculture and Technology, Pantnagar, India whereas, the continuous pyrolysis experiments were carried out at The Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, Slovak Republic. In both institutes fuel properties of bio-oil and biochar were determined using ASTM standard methods. Chemical characterization of bio-oil was conducted using Fourier Transform Infrared (FTIR) spectroscopy and gas chromatographic/mass spectroscopy (GC/MS). Composition of pyrolysis gas was determined by gas chromatography and higher heating value (HHV) was calculated theoretically.

Process parameters such as pyrolysis temperature, gas flow rate, vapour cooling temperature, heating rate and holding time in batch experiment were optimized by employing central composite design (CCD) in RSM. In continuous pyrolysis experiment pyrolysis temperature, biomass particle size, solid residence time and gas flow rate were optimized by employing Taguchi's L_9 Orthogonal Array. All the scientific procedures, experimental designs and instrumentation have been discussed in this chapter.

3.1 Experimental Procedures for Batch Pyrolysis

3.1.1 Batch pyrolysis setup

Pyrolysis of *Pinus roxburgii* needle was carried out in batch type reactor. Pyrolysis experiments were run following the fractional factorial and central composite design. The reactor was fabricated from 14 gauge stainless steel sheet with an internal diameter of 100 mm and length of 400 mm. In each run 200 g of dried biomass was loaded. Temperature was recorded by a Ni-Cr-Ni thermocouple fitted inside the reactor (Fig. 3.1). Before loading of biomass, CO_2 was purged inside the reactor with a flow rate of 3 l min^{-1} and then adjusted to required flow rate of experimental design. CO_2 flow rate was measured using gas flow meter with a range of 0.1 to 3 l min^{-1} having least count of 0.1 l min^{-1}. Once the gas flow rate has been stable, the temperature controller was switched on and the

required temperature was set. After attaining the set temperature at required heating rate it was held for the specific time according to the fractional factorial (Table 3.1) and CCD design. The vapour produced was immediately cooled by a tube-tube heat exchanger by flowing ice chilled water of desired temperature. A high flow rate of water was used to reduce the temperature fluctuation. The condensate was collected in a pre-weighed and dried beaker. The condensate consisted of two phases: aqueous and organic phase. The oil from this mixture was dissolved with dichloromethane. Equal volume of dichloromethane was added to the mixture of aqueous and organic phase. The organic phase dissolved in the dichloromethane and settled below the water due to higher density. Two layers were separated with a separating funnel and filtered. Dichloromethane from the organic phase was then separated using a rotary evaporator at a temperature of 40ºC. The residual was then weighed and considered as bio-oil recovered (**Bordoloi *et al.*, 2015**).

Table 3.1 Matrix of Fractional Factorial Design Experiments

Expt. run	A. Pyrolysis Temp. (°C)	B. CO_2 flow (l min^{-1})	C. Cooling temp. (°C)	D. Heating rate (°C min^{-1})	E. Holding time (min)
1	450 (-1)*	1.5 (-1)	5 (-1)	20 (-1)	30 (+1)
2	550 (+1)	1.5 (-1)	5 (-1)	20 (-1)	10 (-1)
3	450 (-1)	2.5 (+1)	5 (-1)	20 (-1)	10 (-1)
4	550 (+1)	2.5 (+1)	5 (-1)	20 (-1)	30 (+1)
5	450 (-1)	1.5 (-1)	15 (+1)	20 (-1)	10 (-1)
6	550 (+1)	1.5 (-1)	15 (+1)	20 (-1)	30 (+1)
7	450 (-1)	2.5 (+1)	15 (+1)	20 (-1)	30 (+1)
8	550 (+1)	2.5 (+1)	15 (+1)	20 (-1)	10 (-1)
9	450 (-1)	1.5 (-1)	5 (-1)	40 (+1)	10 (-1)
10	550 (+1)	1.5 (-1)	5 (-1)	40 (+1)	30 (+1)
11	450 (-1)	2.5 (+1)	5 (-1)	40 (+1)	30 (+1)
12	550 (+1)	2.5 (+1)	5 (-1)	40 (+1)	10 (-1)
13	450 (-1)	1.5 (-1)	15 (+1)	40 (+1)	30 (+1)
14	550 (+1)	1.5 (-1)	15 (+1)	40 (+1)	10 (-1)
15	450 (-1)	2.5 (+1)	15 (+1)	40 (+1)	10 (-1)
16	550 (+1)	2.5 (+1)	15 (+1)	40 (+1)	30 (+1)
17	500 (0)	2.0 (0)	10 (0)	30 (0)	20 (0)
18	500 (0)	2.0 (0)	10 (0)	30 (0)	20 (0)
19	500 (0)	2.0 (0)	10 (0)	30 (0)	20 (0)
20	500 (0)	2.0 (0)	10 (0)	30 (0)	20 (0)

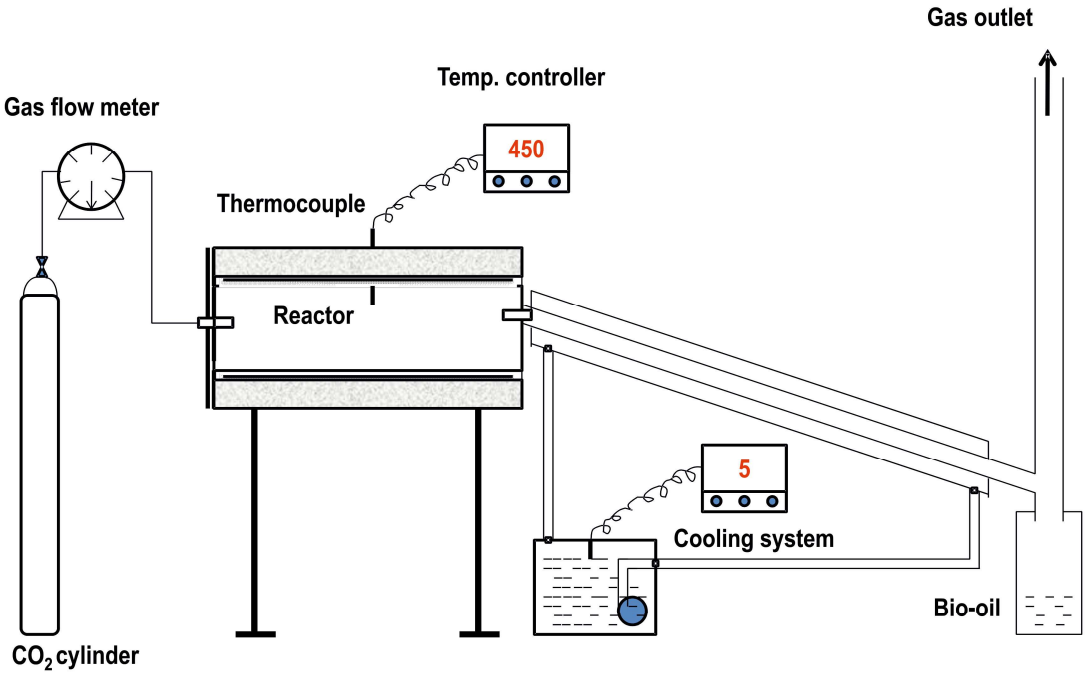

Fig. 3.1 Schematic Diagram of Laboratory Scale Bio-oil Production Unit

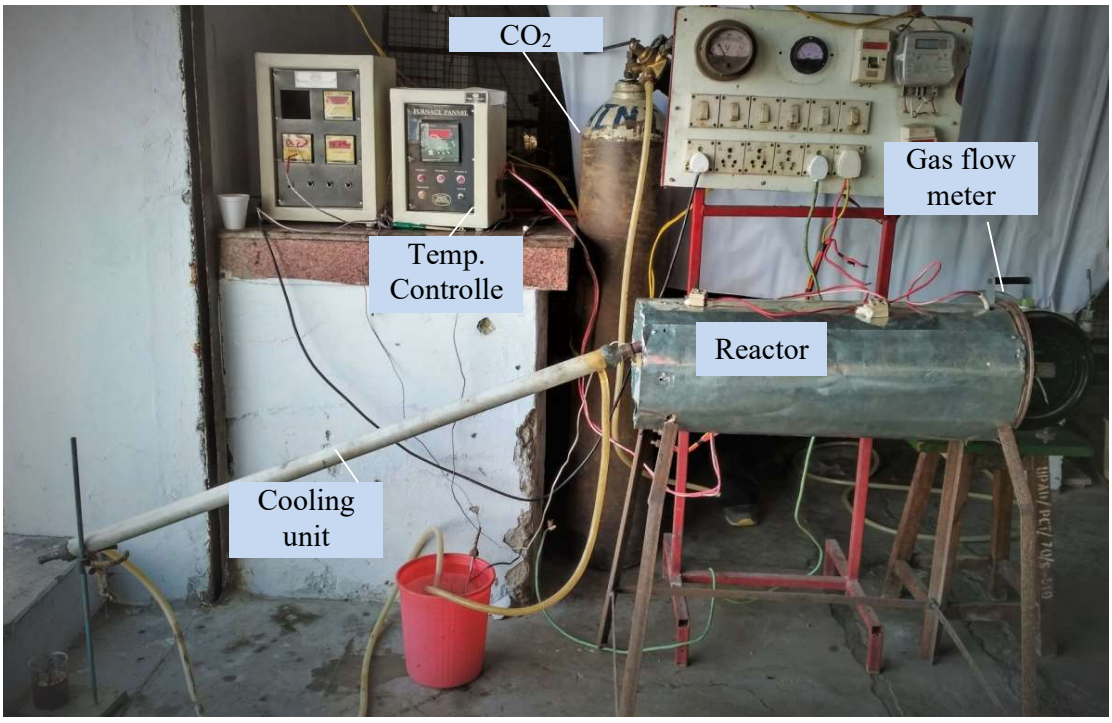

Plate 3.1 Laboratory Scale Batch Type Bio-oil Production Unit

3.1.2 Preparation of raw material

Pine needles (*Pinus roxburgii*) in this study were collected from pine forest of Bhowali, Nainital, India (coordinates: 29.3823°N 79.5196°E). Samples for pyrolysis were prepared by chopping to an average size of 25 mm by a straw reaper followed by sun-drying. Prior to pyrolysis, these samples were grinded to small particle size using a hammer mill and subsequently sieved to a size ≤0.841 mm (I.S. sieve No. 20). The samples were stored in sealed plastic bags at ambient temperature (23–30°C) for the whole duration of experiment (60 days). Moisture content of grinded pine needle was found to be 7.78% which was determined by oven drying at 105°C for 2 hours (ASTM D 3173).

3.1.3 Proximate analysis

Proximate analysis was carried out to determine the moisture, volatile matter, fixed carbon and ash content of the pine needle and its biochar. Moisture content, volatile matter and ash content were determined according to ASTM D 3173, ASTM D 3175 and ASTM D 3174 protocols, respectively on dry basis. Volatile matter was determined by establishing the loss in weight resulting from heating a coal or coke under rigidly controlled conditions. For analysis, 1 g of sample was placed in ceramic crucible with a cover which fitted closely enough so that the carbon did not burn away and kept in a muffle furnace (make: Sonar, Associated Scientific Technology, New Delhi) at 950°C for 7 min. The weight loss was calculated which represented the volatile matter. Ash was determined by weighing the residue remaining after burning the biomass samples under rigidly controlled conditions. In a similar way, 1 g of sample was kept in muffle furnace at 750°C for 4 h and remaining weight was the ash content. The fixed carbon content was calculated by difference of weight.

3.1.4 Elemental analysis

Elemental analysis (EA) refers to the process of determination of mass fraction of carbon, hydrogen, nitrogen and sulphur to find out the structure of an unknown compound. EA of pine needle (*Pinus roxburgii*) and its derived biochar and bio-oil was carried out in a CHN analyzer (Carlo Erba 1108, CE Elantech Inc., NJ, USA). Bio-oil recovered at optimum condition was used for all characterization study. Oxygen content was determined by difference of weight considering that the whole biomass was made of C, H, N, O and ash.

3.1.5 Composition analysis

Hemicelluloses, lignin and cellulose content of pine needle (*Pinus roxburgii*) were determined by direct methods described by **Lin *et al.* (2010)**. Before determination of cellulose, hemicelluloses and lignin, extractives in pine needle were determined using a Soxhlet extractor for 5.0 g of biomass sample by adding 300 ml acetone. Sample was kept in a cellulose thimble placed inside the receiver of Soxhlet apparatus and acetone was poured into the heating flask. Acetone was heated at a temperature of 90°C for 2 h during which many cycles of extraction were repeated. The extracted sample was then oven dried at 105°C to constant weight. The extractives content was taken as the difference in weight between the raw biomass and extractive-free biomass.

In order to determine hemicelluloses content**,** 30 ml 0.5 M NaOH solution was added to 1 g of extractive free biomass in a 100 ml erlenmeyer flask and heated at 80°C for 3.5 h as hemicellulose is soluble in 0.5 M NaOH solution. It was then filtered and washed with de-ionized water until pH reached 7.0. The residue was dried at 105°C in a hot air convective oven for two hours. The difference between the sample weight before and after this treatment was the hemicellulose content.

The lignin content was determined by adding 30 ml, 98 wt.% H_2SO_4 to 1 g of dried extractive free biomass in a 100 ml erlenmeyer flask. The sample was kept at ambient temperature for 24 h with periodic shaking for complete hydrolysis of cellulose and hemicellulose. After that it was boiled at 100°C for 1 h in a water bath. Residue was filtered through a filtering crucible. The residue was then washed with de-ionized water until neutral pH and dried to constant weight at 105°C. Obtained content was incinerated in a muffle furnace at 575°C for ash content. The difference weight after ash deduction from residue was taken as lignin content. The cellulose content was calculated by difference, assuming that extractives, hemicellulose, lignin, ash, and cellulose are the only components of the entire biomass.

3.1.6 Determination of high heating (HHV) value and other fuel properties

HHV of pine needle (*Pinus roxburgii*) and its biochar and bio-oil was determined by using an automatic micro-processor controlled isothermal bomb calorimeter (WISWO Instruments, New Delhi, India) according to ASTM D 240. For bio-oil, 1.0 g of sample was placed in a pre-weighed crucible which was further placed in an adiabatic bomb. It was then oxidized by combustion in an adiabatic bomb containing oxygen at 3.4 MPa

pressure. For pine needle biomass and biochar, pellets of 1.0 g of finely ground biomass were prepared using a screw press mechanical pelletizer. This pellet was used for determination of HHV following the procedure described above. Test for each was carried out in triplicates and the mean value was reported.

Density of bio-oil was determined as per ASTM D1217-15 using pycknometers of 50 ml capacity kept inside an orbital shaker at 15°C. Pour point and cloud points were measured according to ASTM D5853-05 and ASTM D2500, respectively using testing jars of specified dimensions. Flash and fire points were determined by ASTM D93 using a Pensky Martin Flash Point apparatus. Kinematic viscosity as 40°C was determined using a Redwood Viscometer (make: Toshniwal, New Delhi). Acid value was determined following ASTM D974 method by Colour-Indicator Titration. Carbon residue in bio-oil was determined using a Conradson Carbon Residue Apparatus which conforms to ASTM D189.

3.1.7 Determination of pH

The pH of pine needle (*Pinus roxburgii*) bio-oil and biochar was measured using a digital pH meter (EUTECH Instruments pH 700). It consists of an electronic meter and a potentiometric probe. The sample for pH determination of biochar was measured by adding 20 ml de-ionized water to 1 g of biochar in a test tube. The solution was then hand shaken and allowed to stand for 5 min followed by measurement of pH with the probe (**Bordoloi *et al.*, 2015**). Bio-oil ph was measured directly by dipping the probe in the samples.

3.1.8 FTIR analysis

FTIR analysis provides information about presence of different chemical classes. FTIR of pine needle (*Pinus roxburgii*) biomass, bio-oil, biochar was carried out in an IR spectrometer (Bruker Alpha, Eco ATR, Germany) in a spectral range of 4000 – 600 cm^{-1}.

3.1.9 GC/MS analysis

Gas chromatography – mass spectrometry of pine needle (*Pinus roxburgii*) bio-oil was carried out using Shimadzu QP-2000 Plus GC/MS analyzer equipped with Rxi - 5ms column (30.0 m × 0.25 mm × 0.25 μm). Sample was prepared by adding 50 mg of bio-oil in 10 ml dichloromethane followed by filtration with 0.22 micron filter. Temperature of the column was held at 50ºC for 2 min. Then it was heated up to 210ºC with a heating rate of

3ºC min^{-1} and then up to final temperature of 280°C with a heating rate of 8°C min^{-1} and held for 16 min. Helium was used as carrier gas with a flow rate of 1.21 ml min^{-1}.

3.1.10 Design of experiments for batch pyrolysis

A two level fractional factorial design (2^{5-1}) with highest resolution (resolution V) was used to screen the non-significant variables affecting bio-oil yield from pine needles. This design helps to reduce the number of experimental runs. The variables in this study included pyrolysis temperature (*A*), gas flow rate (*B*), vapour cooling temperature (*C*), heating rate (*D*) and holding time (*E*). Bio-oil yield was the single response analysed. The significant factors affecting bio-oil yield were identified in factorial design and further investigated in response surface methodology (RSM) for optimization. Significant factor optimization was carried out using central composite design (CCD) in RSM using Design Expert software (Version 7.0.0). For prediction of optimum conditions the following quadratic equation was used:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum\sum \beta_{ij} x_i x_j + \varepsilon \quad \text{... (3.1)}$$

Where, y is the bio-oil yield (%); β_0 is the intercept coefficient; β_i, β_{ii} and β_{ij} are first order, second order and interaction quadratic model coefficients, respectively; x_i and x_j are the coded independent variables and ε was the standard error (**Mazaheri *et al.*, 2010; Isa *et al.*, 2011**). Overall predictive capability of the model was explained by the multiple coefficient of determination, R^2.

3.2 Experimental Procedures for Continuous Pyrolysis

3.2.1 Continuous pyrolysis experimental setup

Pyrolysis of grinded pine needle (*Pinus cembra*) was carried out in a screw type continuous reactor. The reactor is made of AISI 316 stainless steel and has an effective length of 0.8 m, internal diameter of 44 mm, external diameter of 50 mm. The reactor is externally heated by an electric heating unit which consists of two sets of heating elements, a PID controller to vary the rate of heating and maintain the desired temperature. A thermocouple has been positioned at the centre of the reactor to monitor the reaction temperature. Before experiment, temperature at various location of the reactor was measured to find any variation through the length and found within ±3% of the set temperature. Inside the reactor fitted is a screw made of AISI 316 stainless steel with diameter of 40 mm and pitch of 40 mm. Diameter of Screw conveyer shaft is 20 mm.

Screw is rotated by an AC motor coupled to speed reducer. Speed of the screw can be varied between 1 to 15 rpm by a variable frequency drive. The complete schematic of the reactor is shown in Fig. 3.2 and plate 3.2 to 3.3.

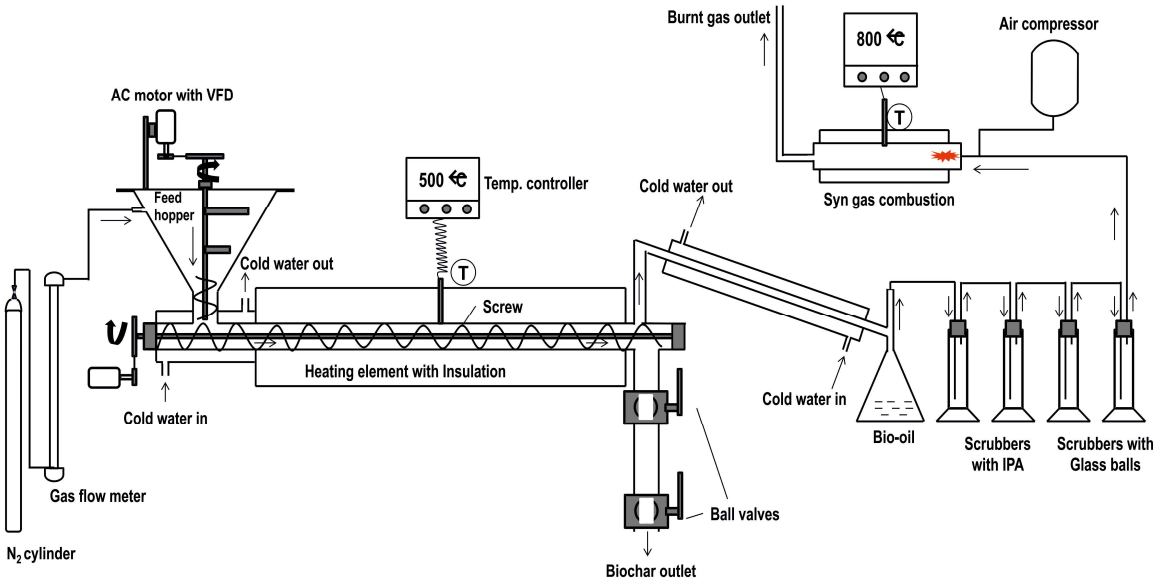

Fig. 3.2 Schematic of Continuous Pyrolysis Experimental Setup

Feeding section of the screw reactor is 250 mm long and provided with an annular jacket to circulate water at ambient temperature to prevent pyrolysis at entrance and a feeding hopper to hold biomass for a single run. Feeding hopper is sealed during the experiment to prevent any entry of air. Another screw, of which shaft is vertically mounted on the lid of the hopper, driven by the second motor with reducer and variable frequency drive, controls the rate of feeding. The char outlet section is attached vertically downward at the end of the screw and provided with two consecutive ball valves to prevent air entry. Closing the first valve, second valve can be opened to remove char. Vapour outlet is attached vertically upward and immediately connected with the cooling unit by silicon hose. The cooling unit is a tube-tube glass heat exchanger and cooled by water circulation at ambient temperature. Major part of the pyrolysis vapour is condensed in this cooler and collected in a flask attached at the end. Gas outlet of cooling unit is further connected with four scrubbers of which first two are filled with iso-propyl alcohol (IPA) and other two with glass balls to trap any residual heavy hydrocarbons. Uncondensed gases are then mixed with air and burnt inside a tube heated up to 800 °C.

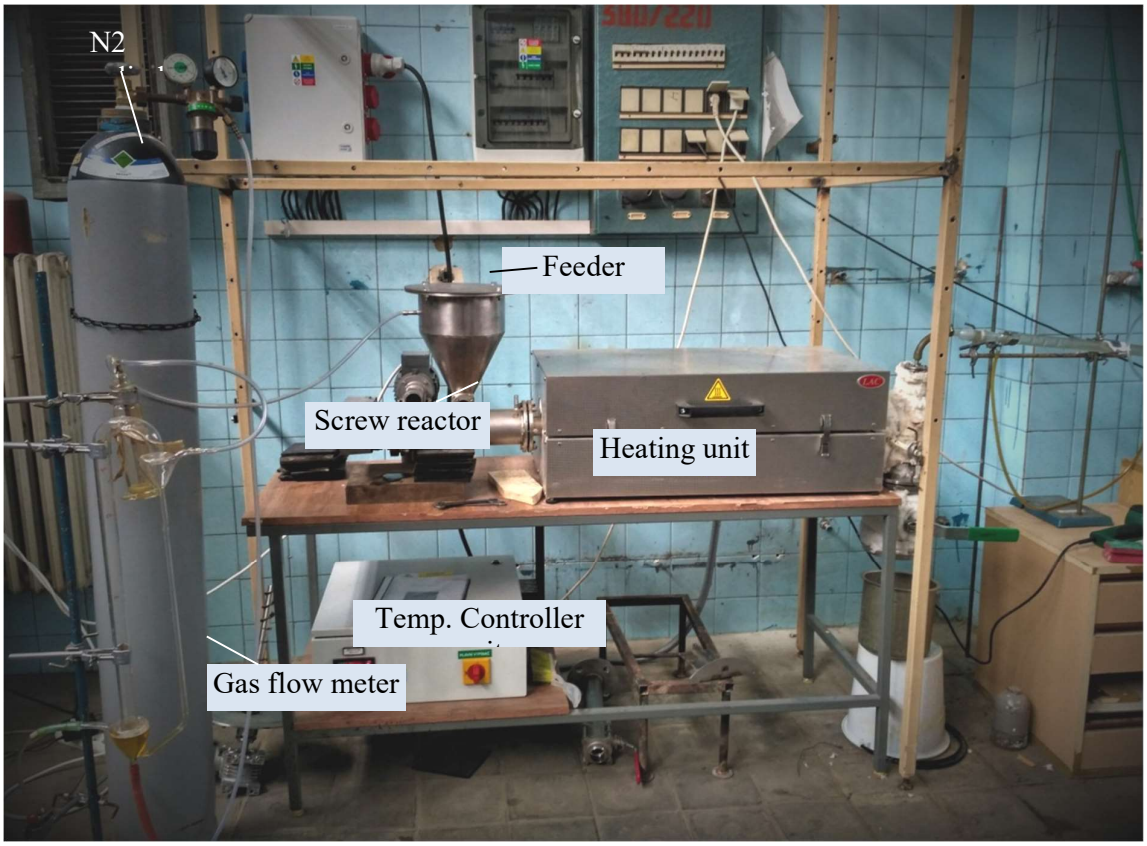

Plate 3.2 Continuous Pyrolysis Experimental Setup – Reactor Unit

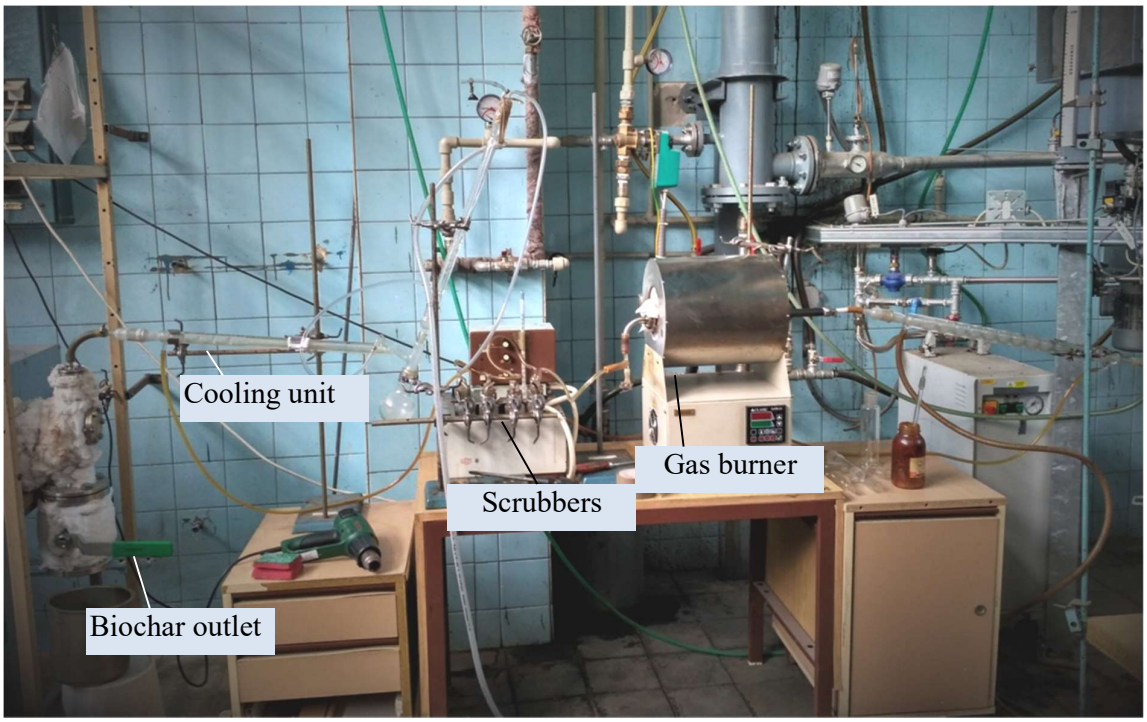

Plate 3.3 Continuous Pyrolysis Experimental Setup – Condenser and Scrubbing Unit

Cold tests were conducted to determine the solid residence time. In this experiment, operational low frequencies were used (3, 5 and 8 Hz) which correspond to 15, 10 and 5 min residence time, respectively. This range of residence time refers to conventional slow pyrolysis (**Demirbas, 2009**). Levels of experimental factors are presented in Table 3.2. In operation, feeding hopper is filled with weighed biomass and sealed with the lid. Nitrogen is then allowed to flow inside the whole unit while reactor is heated up. Once temperature reaches to the set temperature, both the screw conveyors are started. Nitrogen flow is measured by a glass flow meter connected to the nitrogen cylinder. Most of the heavy compounds are condensed to liquid form in the cooling unit and rest are trapped by the four consecutive scrubbers filled with IPA and glass balls. Liquid yield in the cooling unit was recorded by a digital balance. Liquid yields of scrubbers were determined by difference weight before and after the experiment. The total liquid recovery was then calculated by summing up liquid yields of cooling unit and scrubbers. Recovered liquid of cooling unit was then added with the IPA inside first two scrubbers. Liquid collected in scrubbers with glass balls are recovered by washing them with IPA. IPA from the oil is then separated by a vacuum evaporator at temperature of 55 °C and pressure of 10 kPA. In the process, water was also separated which was dissolved in IPA. In industrial scale, IPA can be further separated by vacuum distillation for recycling. The liquid thus collected by this process is referred as bio-oil in this study. Once the reactor cooled down to ambient temperature, char was collected from the char outlet by opening the ball valves and weighed. Gas yield was determined by the weight balance.

Table 3.2 Experimental Layout for Continuous Pyrolysis of Pine Needles (*Pinus cembra*) using $L_9(3^4)$ Orthogonal Array

Treatment	Temp (°C)	Particle size (mm)	Residence time (min)	N_2 flow, (lph)
T_1	400	<1.25	15	30
T_2	400	1.25 - 2.0	10	45
T_3	400	2.0 -3.0	5	60
T_4	500	<1.25	10	60
T_5	500	1.25 - 2.0	5	30
T_6	500	2.0 -3.0	15	45
T_7	600	<1.25	5	45
T_8	600	1.25 - 2.0	15	60
T_9	600	2.0 -3.0	10	30

3.2.2 Preparation of materials

Pine needles were collected from pine forest of Lozorno which is the part of Little Carpathians (48°20′04″ N and 17°02′30″ E) near Bratislava, the capital of Slovak Republic. Pine in this area belongs to Swiss pine (*Pinus cembra*) and has short needles. Collected needles were sun dried and grinded in a cutting mill with a screen size of 5 mm. Moisture content of grinded pine needle was determined by oven drying at 105°C for 2 hours (ASTM D 3173). The grinded material was then sieved to three different size groups: <1.25 mm, 1.25 – 2.0 mm and 2.0 – 3.0 mm by standard sieves. The elemental composition of different size groups was carried out to check the homogeneity. Grinded samples were then kept in sealed polyethylene bags at ambient condition (25 °C) for the whole duration of experiment (30 days).

3.2.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA/DTG) of pine needles (*Pinus cembra*) was carried out using a Netzsch STA (Model: 409 PC Luxx, Selb, Germany) under N_2 atmosphere with a flow rate of 50 ml min^{-1} and heating rate of 10 °C min^{-1}. Diameter of samples of less than 0.4 mm was used with an initial mass of approximately 10 mg. Heating of the samples was continued from ambient temperature up to 800 °C.

3.2.4 Proximate and elemental analysis

Proximate analysis of pine needle (*Pinus cembra*) biomass and its derived char was carried out following the ASTM/D-5373/2008 standard method using a Thermogravimetric analyzer (Netzsch STA 409 PC Luxx, Selb, Germany) for determination of moisture, volatile matter, fixed carbon and ash content. The elemental analysis was carried out in a Vario Macro Cube ELEMENTAR Elemental analyzer. A CHNS (Carbon, hydrogen, nitrogen and sulphur) module with combustion tube temperature of 1150 °C and reduction tube temperature of 850 °C was used. All runs were carried out in triplicates and 1 g of sample was used for each run.

3.2.5 Determination of higher heating value (HHV)

Higher heating value of pine needle (*Pinus cembra*) biomass, biochar and bio-oil was determined using an FTT isoperibolic calorimetric bomb (Fire Testing Technology Limited, UK). Sample combustion took place in a calorimetric bomb under oxygen atmosphere at 3 MPa. In every experiment approximately 300 mg sample was used.

3.2.6 Composition analysis

Extractives in pine needle were determined using an Accelerated Solvent Extractor model Dionex 350. Laboratory analytical procedure was made by National Renewable Energy Laboratory (NREL) TP-510-42619 for Determination of Extractives in Biomass. The extraction pressure (10.34 MPa) was imposed by the ASE 350 apparatus. Samples, typically 10 g, were placed into stainless steel extraction chambers. Parameter of static time (time for reaching final temperature) was 7 min for 100°C. The sample in stainless steel cell was flushed with 100% volume of used solvent and extract was collected in vial after static time. Samples were sequentially extracted three times for each solvent i.e. first three times with de-ionized water and second three times with 96.9% ethanol. Compositional analysis, was done following the method described in Section 3.1.5.

3.2.7 Determination of pH

The pH of pine needle (*Pinus cembra*) bio-oil was directly measured using a digital pH meter (Metler Toledo). For determination of biochar pH, 20 ml de-ionized water was added to 1 g of sample in a test tube. The solution was then hand shaken and allowed to stand for 5 min before measuring the pH with the pH meter.

3.2.8 Surface area

Specific surface area of produced biochar was first determined by nitrogen adsorption in Thermo Scientific Surfer Gas Adsorption Porosimeter (static volumetric gas adsorption). Before the measurement, char samples were activated in vacuum at 20°C. Results provided by nitrogen adsorption porosimeter claimed that all analysed biochar samples had no specific surface area. This indicates that there are no micropores in produced bio-char or that they are obstructed by residual tar. Therefore, specific surface area of produced biochar was then determined by Mercury porosimetry using Pascal Mercury Porosimeter (Thermo Fisher Scientific, USA). Three samples of biochar produced at optimized conditions were analysed. Specific surface area of bio-char in form of larger mesopores and macropores was provided by mercury porosimetry.

3.2.9 GC/MS analysis

Gas chromatography – mass spectrometry of pine needle (*Pinus cembra*) bio-oil was carried out using GC 7890A gas chromatograph (Agilent Technologies, Wilmington, USA). The separation was made on a 30 m × 250 μm × 0.25 μm internal diameter fused

silica capillary column HP-5MS. The oven temperature was held at 40°C for 4 min and then heated by ramp at 10 °C min^{-1} to 100°C, then heated by ramp 20 °C min^{-1} to 300°C. The final temperature was kept for 4 min. The injector temperature was 280°C with split mode. Helium was used as the carrier gas with flow 2 ml min^{-1}. The end of the column was introduced into the ion source of the mass selective detector model 5975C (Agilent Technologies, Wilmington, USA) operated in electron impact ionization mode. The data acquisition system used was ChemStation software (E.02.02.1431, Wilmington, USA) and analysed compounds were identified with NIST and Wiley electronic libraries.

3.2.10 Design of experiment using Taguchi L_9 Orthogonal Array for continuous pyrolysis

Taguchi method is the specially designed orthogonal array to reduce the number of experimental run in an optimization study. Prediction of optimum condition can be accurately determined by using full factorial design of experiment with regression or soft computing based models. However, interactions of all the independent parameters may not have the significant effect on all the dependent parameters. But this method would lead to unnecessary time, cost and energy for the identification of the optimal solutions. The orthogonal array specifies the way of conducting the minimal number of experiments which could give the full information of all the independent parameters that affect the dependent parameters. Taguchi method can give the best trend using fewer experimental data and study the interactions between the factors to optimize the output response (**Ghani *et al.,* 2004; Chou *et al.,* 2009; Chan *et al.*, 2014; Chen *et al.,* 2014**).

In this study, four factors were considered which would affect the bio-oil yield and each factor had three levels. Hence, an L_9 (3^4) orthogonal array was used for optimization of four factors. Taguchi method uses an S/N ratio, where S stands for "signal" which represents the desired value for the output characteristic and N stands for "noise" which represents an undesirable value for the output characteristic, to measure how a specific quality characteristic deviates from the desired value (**Chen *et al.,* 2014**). There are three types of S/N ratios: lower is better (LB), nominal is best (NB) and higher is better (HB). As the target of this study was to get the maximum bio-oil yield from pine needles, the S/N ratio of HB characteristics was chosen which is expressed as follows:

$$\frac{S}{N_{HB}} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right] \quad \text{... (3.2)}$$

where, n is the number of repetitions under the same experimental conditions, and Y represents the yield of bio-oil in i^{th} experiment. In orthogonal experimental design, it is possible to separate out the effects of each factor at different levels which is done by averaging the S/N ratios for the experimental runs. This process is called Analysis of mean (ANOM) and the following equation is used to calculate the mean S/N ratio:

$$M_{Factor=l}^{Level=i} = \frac{1}{n_{li}}\left[\sum_{j=1}^{n_{li}}\left(\frac{S}{N}\right)_{Factor=l}^{Level=i}\right]_j \quad \text{... (3.3)}$$

where, $M_{Factor=l}^{Level=i}$ is the mean of the S/N ratio of factor l in level i, n_{li} is the number of appearances of factor l in level i and $\left[\left(\frac{S}{N}\right)_{Factor=l}^{Level=i}\right]$ is the S/N ratio of factor l in level i (**Chou *et al*., 2009; Chen *et al*., 2014**). From the mean S/N ratio table, optimal conditions were identified. Confirmation experiments were then conducted at the optimum conditions. Further, analysis of variance (ANOVA) was carried out to find the influence of each factor on bio-oil yield. The percentage contribution (ρ_F) of each factor is expressed as:

$$\rho_F = \frac{SS_F - DOF_F V_{Er}}{SS_T} \times 100 \quad \text{...(3.4)}$$

where, SS_F is the factorial sum of square and is given by

$$SS_F = \frac{mn}{L}\sum_{k=1}^{L}(\bar{Y}_k^F - \bar{Y}_T)^2 \quad \text{... (3.5)}$$

m represents the number of experiments and n is the number of replications, $\bar{Y}_k^F$ is the average value of bio-oil yield of a certain factor in the kth level, $\bar{Y}_T$is the grand mean of all measurement values and expressed as

$$\bar{Y}_T = \sum_{j=1}^{m}(\sum_{i=1}^{n} Y_i)_j/mn \quad \text{...(3.6)}$$

In Equation (3), DOF_F is the degrees of freedom of factors, V_{er} is the variance of error which is given by

$$V_{Er} = \frac{SS_T - \sum_{F=A}^{D} SS_F}{m(n-1)} \quad \text{...(3.7)}$$

SST is the total sum of squares and expressed as

$$SS_T = \sum_{j=1}^{m}(\sum_{i=1}^{n} Y_i^2)_j - mn(\bar{Y}_T^2) \quad \text{...(3.8)}$$

3.2.11 Gas characterisation

Non-condensable gases were identified using an Agilent 6890N Network gas chromatography system. Samples for the analysis were collected from the outlet pipe at the

end of 4th scrubber (with glass balls) using a 200 ml plastic syringe when the production of fuel gas was constant. Thermal conductivity detector (TCD) heated up to a temperature of 180 °C was used to identify CO, CO_2, H_2 and N_2 with Helium as the carrier gas. At the second stage, a flame ionization detector (FID) heated up to a temperature of 70°C was used to quantify CH_4 and other hydrocarbons. Higher heating value of product gas was calculated according to the procedure described by **Ferreira *et al.* (2015).**

3.3 Design of Biochar Production Unit

The second objective of this work was to design a horizontal drum type biochar production unit for conversion of pine needle (*Pinus roxburgii*) to biochar and gas products. A horizontal charring kiln was designed and developed by Central Institute of Agricultural Engineering, Bhopal for conversion of crop waste to charcoal. This unit was studied closely for its operation and efficiency. In operation this kiln is loaded with loose crop wastes. A small fire is started and biomass loading is continued until it is full. After that it is closed and kept for charring process to complete. The disadvantages with this unit are that the operator has to face lot of smokes while filling and the gas product can not be utilized. Further, the conversion is always not complete. The drawback in this design was the improper distribution of air for initial burning. Keeping this view the horizontal biochar production unit has been designed.

The biochar production unit comprises an insulated pyrolysis chamber supported by two circular beams in both sides, an opening with lid at the centre of the horizontal plane of the pyrolysis chamber, three air supply pipes, a circular rotating handle, a gas outlet and chimney and a mounting frame. The unit with its all components is depicted in Figs. 3.3 to 3.6. The different components of the biochar production unit are described below:

3.3.1 Pyrolysis chamber

The target capacity (W) of the biochar production unit was 100 kg per batch. Average bulk density (ρ) of loose pine needle was found as 83 kg m^{-3}. So for 100 kg needles, the pyrolysis chamber volume (V) was calculated using the Eqn. (3.9) and was found to be 1.2 m^3.

$$V = \frac{W}{\rho} \qquad \ldots (3.9)$$

The length to diameter ratio for pressurized vessel is mostly 1.5 (**Couper *et al.*, 2009**). Considering this ratio, the diameter of the pyrolysis chamber was calculated using Eqn. (3.10) and was found as 1.0 m and length as 1.5 m.

$$D = \sqrt[3]{\frac{4V}{\pi(\frac{L}{D})}} \quad \ldots (3.10)$$

The pyrolysis chamber was made from heat treated mild steel sheet of 12 gauge thickness. The cylinder was closed from both sides by same mild steel sheet. At the centre of both sides of the chamber a circular flange (part 2 in Fig. 3.3) was welded to provide more support to the support beams.

Total weight of the pyrolysis chamber including the insulation, outer cover and biomass inside was estimated as 220 kg. Assuming half of this load to be carried out by each circular beam the bending moment (Eqn. 3.11) was 431.64 Nm.

$$M = Wl \quad \ldots (3.11)$$

where, M is bending moment, l is the length (it was 40 cm) and W is the load at each end. Bending strength of circular hollow section is given by Eqn. (3.12) as follows:

$$\sigma_m = \frac{M}{Z} \quad \ldots (3.12)$$

where, Z is section modulus and given by the equation:

$$Z = \frac{\pi(d_2^4 - d_1^4)}{32 d_2} \quad \ldots (3.13)$$

Selected circular hollow beams had an outer diameter of 80 mm and inner diameter of 70 mm and considering bending strength of mild steel as 150 MPa, allowable bending moment to the circular beam was calculated to be 3118.5 Nm which was sufficiently higher than required bending moment. Circular beams were fixed with the flange at one end and mounted inside bushes at other end.

The unit had a rectangular opening at the centre of horizontal plane of 450 mm × 300 mm for filling of biomass and decanting of biochar. The opening was provided with a neck of 100 mm which was made of 8 mm thick mild steel flat. At the top of the neck, a 60 mm wide rectangular flange had been provided. The flange had 8 bolts (size: 10 mm) fixed

to close the opening with a lid of same dimension. The mild steel chamber was insulated with 50 mm thick ceramic blanket (heat resistant up to 1600°C, density 64 kg m^{-3}) to prevent loss of heat during the pyrolysis process. The ceramic blanket was covered with a galvanized iron sheet of 0.5 mm thickness.

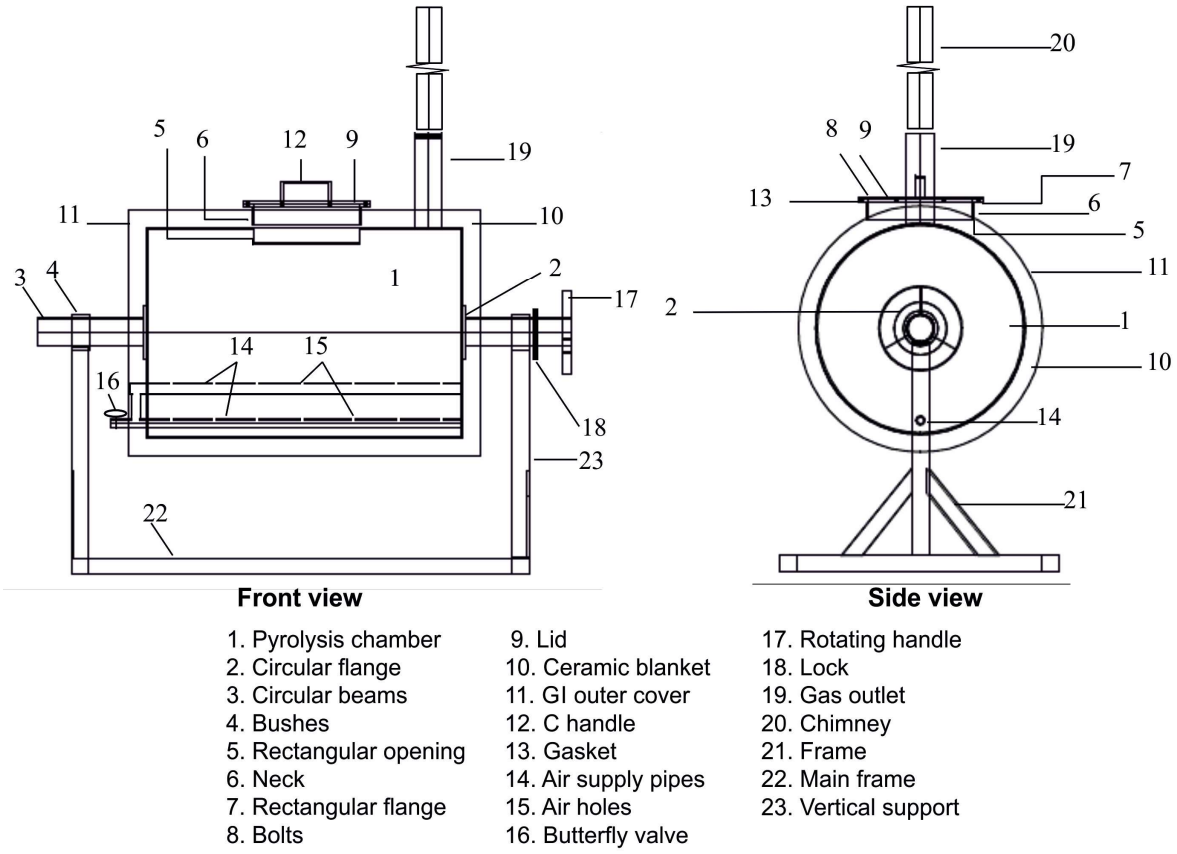

Fig. 3.3 Front View and Side View of Biochar Production Unit

3.3.2 Lid of the opening

The lid of the opening was of same dimension (570 mm × 420 mm) as that of the rectangular flange over the neck and could be fixed over the flange by nuts and bolts. It was made from mild steel sheet of 8 mm thickness. The lid was provided with a 'C' shape handle. Between the flange and the lid, an asbestos gasket had been provided to make the lid air tight at the time of pyrolysis.

3.3.3 Air supply pipes

Three air supply pipes had been provided to supply air during initial burning of material to produce sufficient heat for the pyrolysis of the remaining biomass material. The

pipes were of same length of that of pyrolysis reactor and made of mild steel. Ten equidistant holes had been provided on each pipe for evenly distribution of air inside the pyrolysis chamber. The pipes have been placed at the bottom and two sides at 300 mm distance from the centre and 300 mm above the bottom line of the reactor. At the entry of the central pipe an air flow control valve (butterfly valve of diameter 61.5 mm) has been attached and other ends of all three pipes are completely closed. The air flow control valve is connected with air hose which is connected with the air blower at the entrance. The arrangement of the pipes is shown in Fig. 3.6.

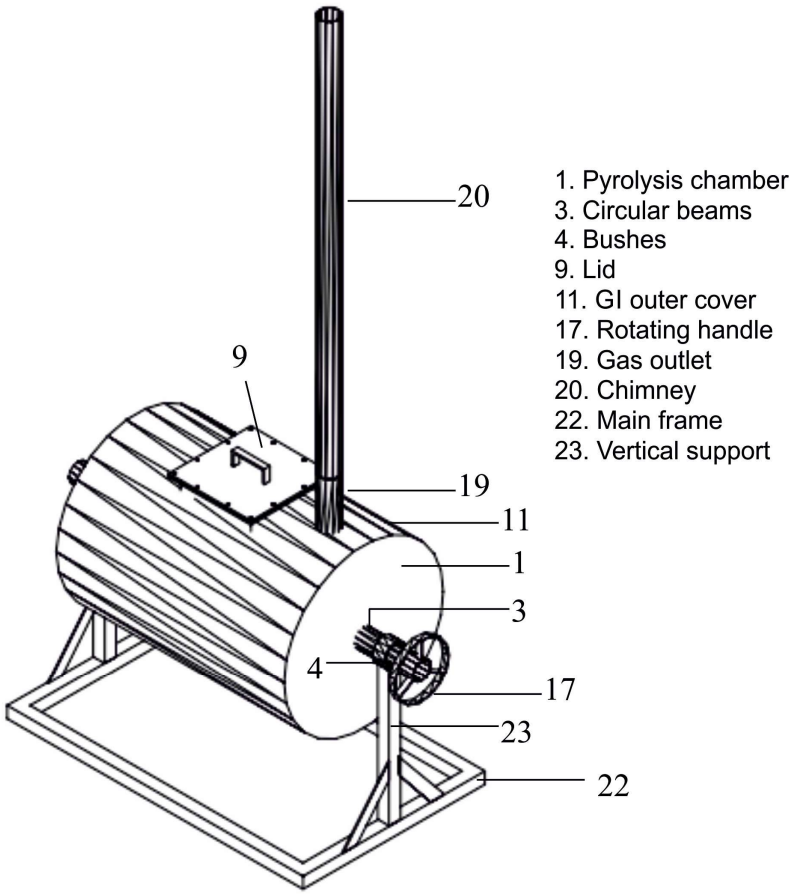

Fig. 3.4 S-E Isometric View of Biochar Production Unit

Inside diameter of blower outlet pipe was 62 mm. Same diameter was kept for the main air supply pipe. The internal resistance should be as low as possible and total cross sectional area of all distributors should be kept constant to reduce loss in air flow for a centrifugal pump (**Couper *et al*., 2009**). Thus, sizes of three air supply pipes and holes

were calculated based on the Eqn. (3.14) and were found to be 36 mm and 11.4 mm, respectively.

$$A_m = A_1 + A_2 + A_3 = 3A_1 \quad \ldots (3.14)$$

$$A_1 = 10A_h \quad \ldots (3.15)$$

where, A_m is the cross sectional area of main supply pipe, A_1, A_2, A_3 are cross sectional area of lateral air supply pipes and are equal, and A_h is the cross sectional area of holes. To keep this size in round figure and ease of manufacturing, pipe size was selected as 38 mm as available in market with wall thickness of 4 mm and hole size as 11 mm.

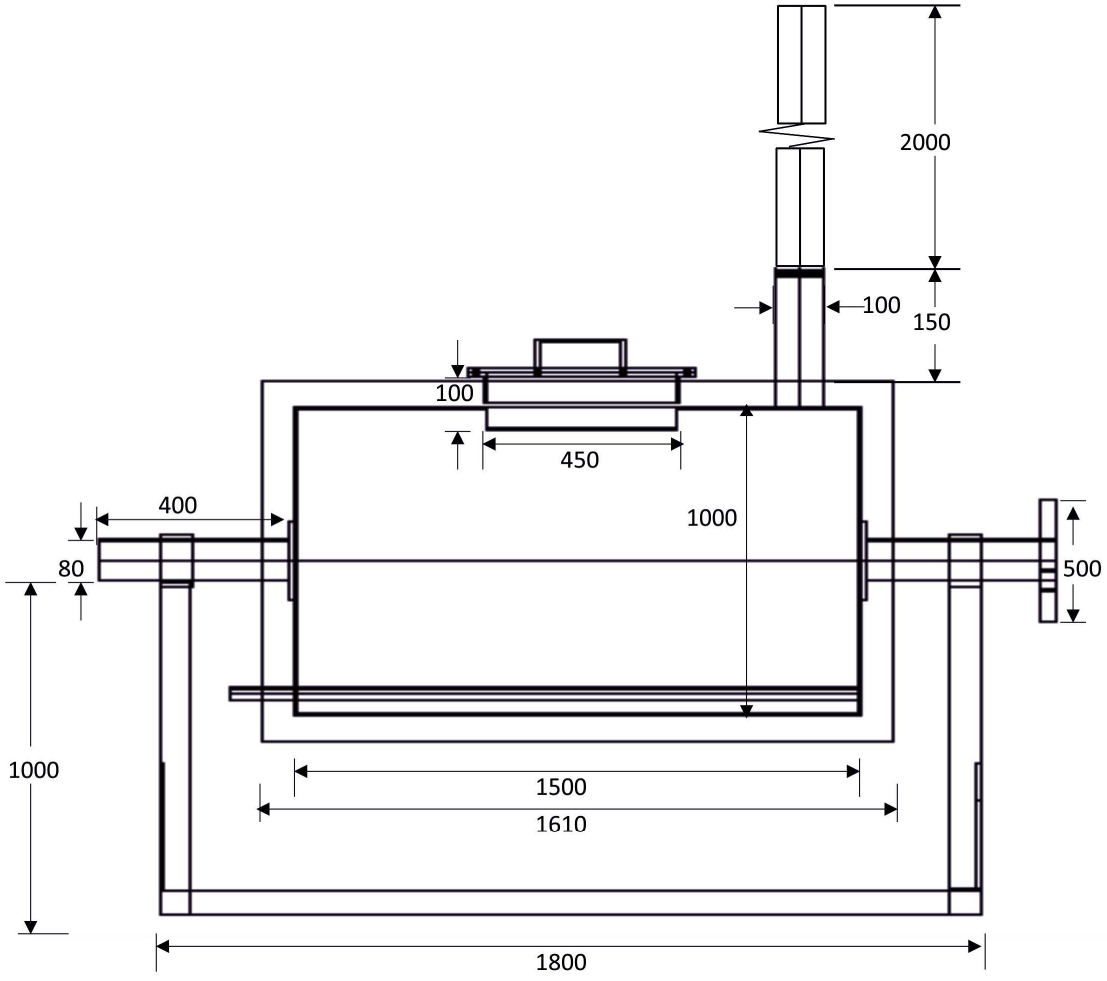

Fig. 3.5 Front View of Biochar Production Unit with Dimensions

3.3.4 Rotating handle

At the left side of the pyrolysis chamber a rotary handle of 0.5 m diameter had been fixed at the end of circular beam to rotate the pyrolysis reactor for filling of biomass and decanting of biochar from the reactor. It was also used for occasional rotating of reactor during the pyrolysis process to spread the heat uniformly so that all the biomass inside the reactor was converted to biochar evenly. The handle was made of mild steel flat and wrapped in cotton rope for grip and insulation. A locking arrangement was also provided to stop the reactor from rotating during filling and pyrolysis process.

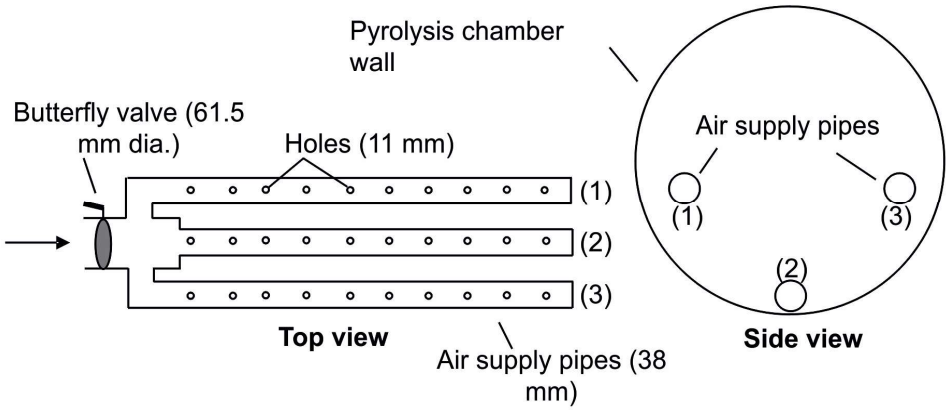

Fig. 3.6 Arrangements of Air Supply Pipes Inside the Pyrolysis Chamber

3.3.5 Gas outlet

The gas outlet had been provided at the top of left side of the pyrolysis reactor to allow escape of smoke of initial burning from the reactor and to burn flue gas. The outlet was made of mild steel pipe of 100 mm diameter, 4 mm thickness and welded with the reactor. The top end was threaded so that it can be closed using a threaded lid once the burning is complete. The heat produced during the initial burning was needed to conserve for pyrolysis of remaining biomass which necessitated closing of the gas outlet once the initial burning period was over.

3.3.6 Chimney

A two meter long chimney had been provided to drive away the smoke formed during initial burning. It was of the same diameter as that of the gas outlet and closely fit upon it. It was provided with long handles for easy handling during the pyrolysis process.

3.3.7 Mounting frame

Frame was the main support for the pyrolysis reactor. It was made of mild steel angle iron of 50 mm × 50 mm size. The base was of rectangular shape with size of 1.8 m × 1.2 m. In each side 1.0 m long vertical support had been provided and at the top of it a semicircular bush had been welded to put circular beam of the pyrolysis reactor.

3.3.8 Air blower

A centrifugal air blower with a motor of 700 watts and air blowing capacity of 120 $m^3\ h^{-1}$ had been provided with the unit to supply air for initial burning to generate reaction heat for pyrolysis. Outlet of the blower was connected with an air hose which was further connected to the main supply pipe at the other end.

Plate 3.4 Biochar Production Unit (64 kg per batch)

3.3.9 Testing of the biochar production unit

The biochar production unit was placed at an open area on a farm ground and the pyrolysis chamber was rotated to keep the door at the top. Sundried pine needles (*P. roxburgii*) with required moisture content were fed to the reactor and filed up to required capacity as per the experiment. Air blower was attached with the air supply pipe using flexible air hose. The blower was switched on and required air flow rate was maintained. A fire was started at the top of the biomass surface. Once the fire was sufficient, the opening was closed by the lid and made airtight by tightening the bolts fixed around the lid. The

product gas was ignited. After every twenty minutes, the reactor unit was rotated 3 to 4 turns to spread the reaction heat evenly. The temperature inside the reactor was measured using a 'K' type thermocouple. After required time of run, air flow was stopped and gas outlet was sealed with threaded cap. The unit was left to cool down for two hours. After that, the reactor was turned down to place the door at bottom and biochar was decanted through the door out of the reactor and collected in a polyethylene bag.

Charring process is greatly affected by the air flow rate, burning time and moisture content of the biomass. Results of some initial runs showed that filling ratio (% volume of reactor filled) greatly affected the charring quality which might be due to the space availability for redistribution of materials while rotating the drum. Therefore, in this experiment these four factors were varied as presented in Table 3.3. Burning time or gasification period was varied from 60 to 120 min to find out the optimum time required for complete charring of the biomass. Although the pyrolysis chamber was designed for a target capacity of 100 kg pine needles, in actual 64 kg of needles with 18% moisture could be filled at 100% capacity. So, in other loading biomass was filled accordingly. Moisture content of the pine needles stored at different conditions varied from 12 to 24%. The fresh needles contained 24% moisture whereas, the needles stored for a period of 4 months in shade contained 18% moisture. Moisture content of pine needles reduced to 12% when sundried for 2 to 3 days. Air-fuel ratio in gasifiers has been reported to be varied from 1.5 to 2.1 $Nm^3\ kg^{-1}$ (**Dogru *et al.*, 2002**). In this study, air-fuel ratio was varied from 1.05 to 1.95 $Nm^3\ kg^{-1}$.

Table 3.3 Variables and their Levels of Charring Experiment

Experimental Runs	Burning time (min)	Loading (%)	Moisture content (%wb)	Air flow rate ($m^3\ h^{-1}$)
1	60	60	12	40
2	90	60	12	40
3	120	60	12	40
4	120	100	12	40
5	120	80	12	40
6	120	80	24	40
7	120	80	18	40
8	120	80	12	30
9	120	80	12	50

3.3.10 Characterisation of biochar and product gas from Biochar Production Unit

Biochar of the experimental run which had maximum productivity was characterized following the same procedures described in Section 3.1. Non-condensable gases from the outlet of biochar production unit were identified using a Nucon 5700 Gas Chromatograph (NUCON ENGINEERS, New Delhi, India). Samples for the analysis were collected from the outlet pipe using a 20 ml plastic syringe at four different times. Thermal conductivity detector (TCD) at 180°C temperature with a Porapak Q column was used to quantify N_2, CH_4, CO and CO_2 with Hydrogen as the carrier gas. Oven and injector temperature were kept 50 and 120°C, respectively. Hydrogen was detected using a molecular sieve column connected with TCD at 50°C using nitrogen as carrier gas. Higher heating value of product gas was calculated according to the procedure described by **Ferreira *et al*. (2015).**

3.4 Energy Balance

Energy balance was carried out using laws of conservation of energy which states that total input energy into a control volume must be equal to the total output energy from the control volume (**Mahmood *et al*., 2016**). In all the experiments, this method of energy balance has been followed.

3.4.1 Energy balance in batch experiments

The energy balance system of batch pyrolysis experiments has been illustrated in Fig. 3.7. The dotted lines show the system boundary. Energy inputs into the control volume are chemical energy of pine needles, electrical energy for grinding and electrical energy for pyrolysis. The energy outputs from the control volume are bio-oil energy, biochar energy, syn gas energy and energy loss. Heat loss is difficult to estimate and therefore, it estimated as the energy required for balancing energy input and output. As per the laws of conversion of energy at equilibrium input energy must be equal to the output energy of the system and can be expressed as:

$$Q_b + Q_{eg} + Q_{ep} = Q_o + Q_c + Q_g + Q_l \quad \ldots (3.16)$$

where, Q_b = chemical energy of pine needles,

Q_{eg} = electrical energy for grinding,

Q_{ep} = electrical energy for pyrolysis,

Q_o = bio-oil energy,

Q_c = biochar energy,

Q_g = syn gas energy and

Q_l = energy loss.

Q_b, Q_o, and Q_c were evaluated in terms of HHV which had been determined by bomb calorimeter. Q_{eg} and Q_{ep} were evaluated in terms of electrical power rating of the grinder and the heater, respectively. Q_g was the considered as the HHV of the syn gas which was estimated using the method described by **Ferreira *et al.* (2015).**

After the calculation of energy components, the efficiency of the conversion process was estimated using Eqn. 3.17 as follows:

$$Energy\ Efficiency\ (EE) = \frac{Heating\ Value\ of\ Products}{Total\ Energy\ Input} \times 100\% \quad \ldots (3.17)$$

However, the EE (energy efficiency) defined above does not really reflect the usability of the products because total input energy considers the energy of the pine needles, which has very low usability as a direct fuel source. Therefore, a new ratio "Return on the energy invested" was defined which quantified the useful energy obtained from the system to the useful energy invested in the process (**Tekin *et al.*, 2014**).

$$Return\ on\ Energy\ Invested\ (REI) = \frac{\text{Total Useable Energy Output}}{Total\ Useable\ Energy\ Input} \times 100\% \quad \ldots (3.18)$$

where, the total useful energy input is $Q_{eg} + Q_{ep}$ and the total useful energy output is $Q_o + Q_c + Q_g$. In this ratio, only usable form of energy that had been used to obtain the usable form of energy products was considered. The energy of pine needles was considered unusable and excluded from the total useful energy input (**Mahmood *et al.*, 2016**).

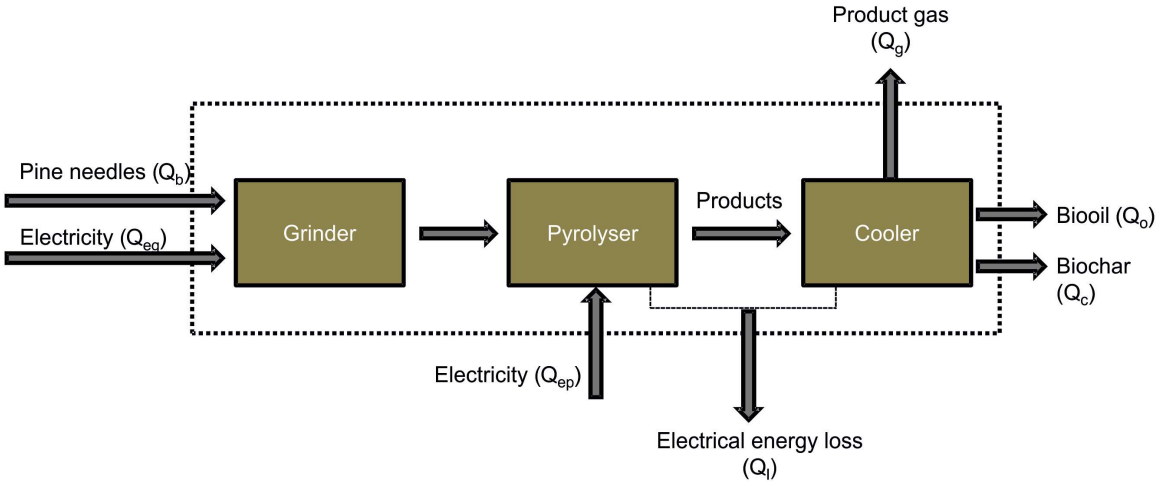

Fig. 3.7 Energy Balance System for Batch Pyrolysis of Pine Needles.

3.4.2 Energy balance in continuous pyrolysis experiments

In continuous pyrolysis experiments, control volume was same as that of batch experiments. Only difference observed was the electrical energy input for driving the screw conveyor and the feeder unit. Thus for continuous experiments, Q_{ep} can be expressed as:

$$Q_{ep} = Q_{er} + Q_{es} + Q_{ef} \quad \ldots(3.19)$$

where,

Q_{er} = electrical energy input for reactor heating,

Q_{es} = electrical energy input for rotating the screw conveyor and

Q_{ef} = electrical energy input for feeder unit.

3.4.3 Energy balance of the biochar production unit

In the process of biochar production using the rotating drum type biochar production unit, only electrical energy requirement was to run the blower unit (Fig. 3.8). Oil from the condensate was not recovered due to excess fraction of water. Major energy output was the product gas and biochar. Thus the energy balance equation becomes:

$$Q_b + Q_{bl} = Q_c + Q_g + Q_l \quad \ldots (3.20)$$

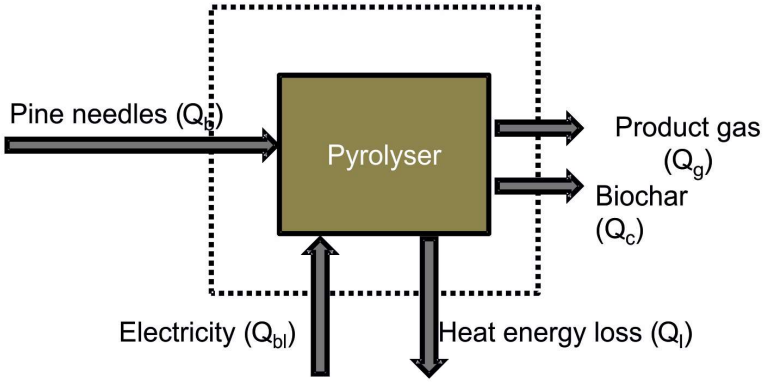

Fig. 3.8 Energy Balance System for Biochar Production Unit

Chapter – 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

Experiments were conducted to convert pine needles into bio-oil, biochar and product gas through pyrolysis as an alternate way to use pine needles as renewable energy source and to reduce forest fire. Process parameters such as pyrolysis temperature, gas flow rate, vapour cooling temperature, heating rate, holding time were optimized by employing central composite design (CCD) in Response Surface Methodology (RSM) for the batch process. Continuous pyrolysis experiments were conducted in a screw reactor. Process parameters were optimized by Taguchi's L_9 Orthogonal Array. A batch type biochar production unit was also designed and developed to convert pine needles to biochar in bulk. Chemical characterization of bio-oil was conducted using Fourier Transform Infrared (FTIR) spectroscopy and gas chromatographic/mass spectroscopy (GC/MS). Fuel properties of bio-oil and biochar were determined using ASTM standard methods. Product gas composition was determined using gas chromatography. This chapter presents the results of different experiments.

4.1. Properties of Pine Needle Biomass

The results of proximate, ultimate and compositional analysis of *Pinus roxburghii* and *Pinus cembra* pine needle biomasses are presented in Table 4.1. Detail results of each replication have been presented in Tables A-1 to A-3. Pine needles of *P. roxburghii* were collected from Bhowali, Nanintal, Uttarakhand, India and that of *P. cembra* from Lozorno, Bratislava, Slovakia. Collected pine needles from both sources were sundried before conducting experiments and found to have moisture content of 7.78 and 9.13%, respectively of *P. roxburghii* and *P. cembra* needles. It indicates that moisture content in both pine needles was reduced to <10 wt.% after drying which was suitable for grinding. Volatiles, ash and fixed carbon content were found to be 71.58, 2.08 and 26.34% and 71.71, 8.06, 19.42%, respectively. The observed results therefore indicate that *P. roxburghii* pine needle has very low ash, high volatile and high fixed carbon contents whereas *P. Cembra* pine needle has high ash, high volatile and low fixed carbon contents. **Chutia *et al.* (2013)** opined that biomass which contains low ash and high volatile is a suitable material for thermochemical conversion. Further, a high ash biomass is not advantageous to obtain a high-quality bio-oil as reported by **Luo *et al.*, (2004)** because some elements in ash negatively affect pyrolysis products distribution. Therefore both pine

needles were found suitable material for pyrolysis. However, *P. Cembra* pine needles had higher ash content which may affect the bio-oil yield.

Table 4.1 Properties of Pine Needles

Properties	***Pinus roxburghii***	***Pinus cembra***
Water content (% wb)	7.78	9.13
Volatile matter (% db)	71.58	71.71
Ash content (% db)	2.08	8.06
Fixed carbon (% db)	26.34	19.42
Extractives (% db)	17.45	22.42
Cellulose (% db)	27.17	24.51
Hemicellulose (% db)	24.15	19.09
Lignin (% db)	29.15	25.91
Elemental analysis (wt %)		
C	44.99	49.57
H	5.46	7.2
N	0.99	1.05
S	Not traceable	0.10
O	48.55	34.12
H/C	1.46	1.74
O/C	0.81	0.52
Empirical formula	$CH_{1.46}N_{0.02}O_{0.81}$	$CH_{1.74}N_{0.04}O_{0.52}$
HHV (MJ kg^{-1})	17.67	20.42

Extractives content of *P. roxburghii* and *P. cembra* pine needles were found to be 17.45 and 22.42%, respectively. Extractives mainly include fats, waxes, proteins, phenolics, simple sugars, gums, resins, terpenes, starches, glycosides, saponins, and essential oils as reported by **Mohan *et al.* (2006)**. Extractives also reduce the overall yield of bio-oil and also inhibit the formation of levoglucosan which is an important constituent of bio-oil (**Garcìa-Pérez *et al.*, 2007**). It is therefore evident that bio-oil from *P. cembra* needle may content higher amount of terpenes and essential oils. Cellulose, hemicelluloses and lignin content were found as 27.17, 24.15, 29.15% and 24.51, 19.09, 25.91, respectively for *P. roxburghii* and *P. cembra* needles. Thus it can be noted that the higher amount of lignin was present in both pine needles compared to cellulose and hemicellulose. Woody biomass are also characterised as high lignin biomass and considered good for high pressure briquetting and bio-oil production. **Mohan *et al.* (2006**)

reported that the typical range of cellulose, hemicelluloses and lignin in biomass varied from 40 – 50 %, 25 – 35% and 23 – 33%, respectively. **Ibrahim *et al.* (2005**) showed that lignin creates strong carbon-carbon bonds with other polysaccharides which hinders the pyrolysis reactions within the temperature range of 300 – 500 °C. Hence, higher lignin content leads to lower bio-oil yield at low temperature. This suggests that both pine needles may require higher temperature for higher bio-oil yield.

Results of elemental analysis presented in Table 4.1 also show that carbon, hydrogen, nitrogen and oxygen contents were 44.99, 5.46, 0.99, 48.55% and 49.57, 7.2, 1.05, 34.12%, respectively of *P. roxburghii* and *P. cembra* needles. This indicates that *P. cembra* needles have low oxygen content which is due to higher ash content in these needles indicating presence of higher amount of inorganic matters. These values are comparable with other biomass available from various sources reported by **Stolarski *et al.* (2013**). The empirical formula of pine needle biomass was found to be $CH_{1.46}N_{0.02}O_{0.81}$ and $CH_{1.74}N_{0.04}O_{0.52}$ for *P. roxburghii* and *P. cembra* which are typical of biomass. HHV of pine needle was found to be 17.67 and 20.42 MJ kg^{-1}, respectively for *P. roxburghii* and *P. cembra* which were higher as compared to HHV of paddy straw (14.7 MJ kg^{-1}) as found by **Torri *et al.* (2016**) and other biomass reported by **Mohan *et al.* (2006**).

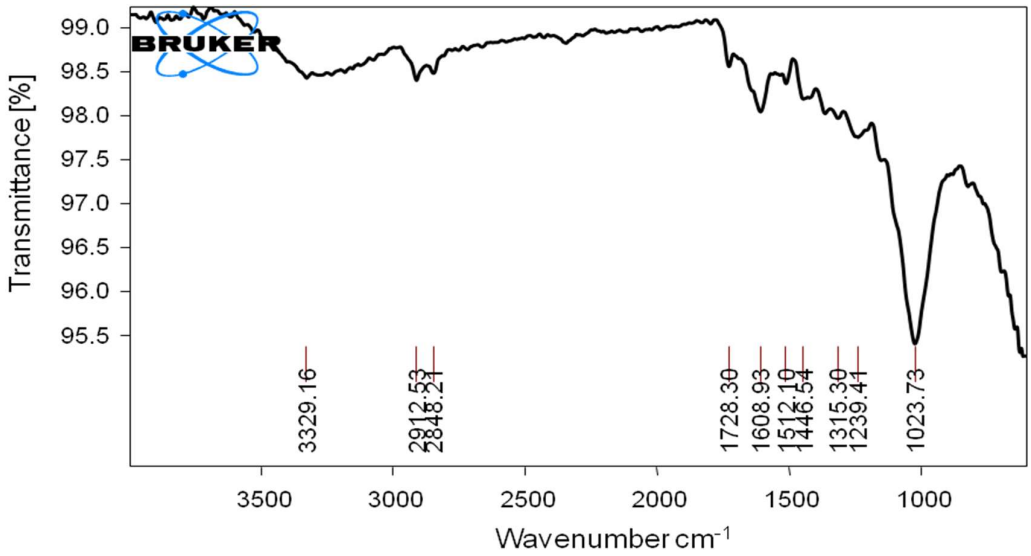

Fig. 4.1 FTIR Curve of *P. roxburghii* Pine Needle

The FTIR analysis of *P. roxburghii* pine needle biomass was carried out between 4000 and 600 cm^{-1} wavenumber and the spectrum is shown in Fig. 4.1. It shows the presence of different chemical compounds. The broad peak observed between 3400 –3200

cm^{-1} is associated with –OH stretching in hydroxyl groups originating from cellulose. The peaks at 2912 and 2848 cm^{-1} were due to CH stretching indicating presence of methylene groups as proposed by **Stark and Matuana** (**2007**). Peaks at 1728 and 1608, 1239 cm^{-1} provide evidence of aromatic combination bands and aromatic ring stretch, respectively. The C–O of syringyl ring of lignin was observed at peak of 1315 cm^{-1}. A strong peak at 1023 cm^{-1} was observed as a result of C–O stretching in cellulose and C–O deformation in lignin. Similar findings were reported by **Pandey (1999), Coates (2001**) and **Stark and Matuana (2007)** with different biomass.

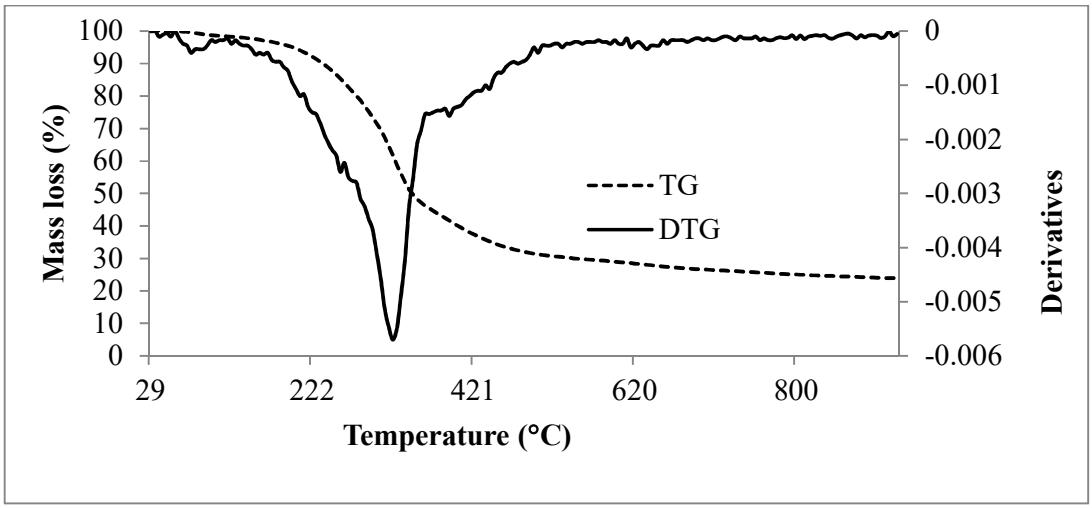

Fig. 4.2 Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) Curves of Pine Needles at 10 °C min^{-1} Heating Rate

The thermogravimetric analysis (TGA) curve of *P. cembra* needles is shwon in Fig. 4.2 and raw data are prrsented in Table B-1. It gives the decomposition behaviour of biomass components. The TG curve of pine needle shows three distinct region of thermal degradation: in the first region up to temperature of 200°C, most of the moisture and extractives are volatilized; in the second region between 207 to 351°C, volatile substances are released; in the third region beyond 351°C char is produced. Similar findings had been reproted by **Kercher and Nagle (2001**) for different biomass. The DTG curve in Fig. 4.2 shows two distinct peaks at the main region of volatilization between 202 to 361 °C. The shoulder peak at the left side of the main peak corresponds to the degradation of hemicelluloses and the main peak at 321 °C corresponds to degradation of celluloses. Degradation of lignin continues to higher temperature. Similar trends of thermal degradation of biomass have been found by **Kim (2015); Saikia *et al.* (2015)** and **Ferreira**

et al. **(2015**). As most of the weight loss of pine needle biomass took place below temperature of 500°C, it was selected as the central value of pyrolysis in the continuous screw pyrolysis.

4.2 Batch Pyrolysis

Batch pyrolysis was conducted in a stainless steel tubular reactor using CO_2 as sweep gas at Department of Farm Machinery and Power Engineering, GBPUA&T, Pantnagar, India.

4.2.1 Screening of significant factors affecting bio-oil yield

Five factors which would affect the bio-oil yield were pyrolysis temperature (A), gas flow rate (B), vapour cooling temperature (C), heating rate (D) and holding time (E). Effect of these factors on bio-oil yield was studied by fractional factorial experiments. The details of this design are presented in Section 3.1.10 and in Table A-4. The fractional factorial design consisted of 16 (2^{5-1}) factorial runs and 4 replicates of the central point making total 20 runs as presented in Table 3.1. Fig. 4.3 shows the Half-Normal plot of bio-oil yield in fractional factorial design. It can be observed that the factors A, B, C and D were away from the straight line which indicated less noise. Analysis of variance (ANOVA) of the experiment is presented in Table A-5. It showed that among the five factors selected, four factors were found significant. Holding time was found insignificant with 'p-value' of 0.54. This may be due to the overall slow heating rate. Pyrolysis temperature was the most significant factor for bio-oil production having an F-value of 221.54 followed by vapour cooling temperature (F-value of 195.50), heating rate (F-value of 152.73) and gas flow rate (F-value of 12.37). Curvature test was found significant which showed that optimization could be carried out. The model was found fit as Lack of fit test was not significant.

4.2.2 Bio-oil yield from *P. roxburghii* pine needles

After screening of four significant parameters, main experiment was carried out according to the CCD of RSM. The range of experimental variables and their coded values are presented in Table 4.2. Total number of experimental run for four variables, using CCD, was found to be 30 which included 16 factorial points, 8 axial points and 6 central point replications.

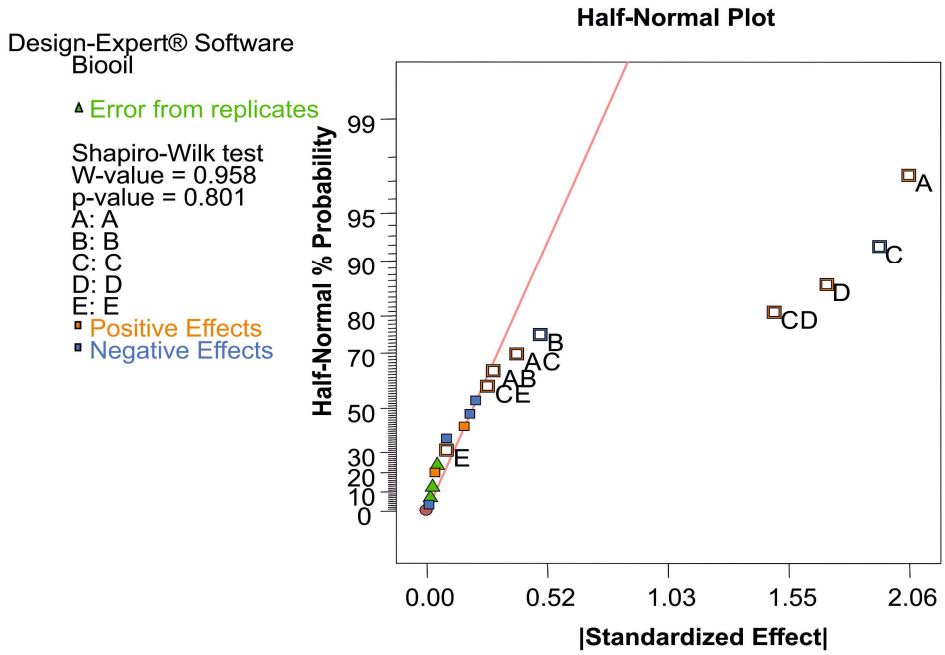

Fig. 4.3 Half-Normal Plot of Bio-oil Yield in Fractional Factorial Experiments

Isa *et al.* (2011) and **Kim (2015)** reported maximum bio-oil yield for various biomass near 500ºC pyrolysis temperature and 0 – 8ºC cooling temperature. In this experiment therefore, the central values were kept as 500ºC of pyrolysis temperature, 2 l min^{-1} of gas flow rate, 10ºC of cooling temperature and 30ºC min^{-1} of heating rate. Holding time of 20 min was kept constant for all experimental runs. CO_2 was used as sweep gas for this experiment because Boudouard reaction ($C+CO_2 \leftrightarrow 2CO$) takes place at temperatures higher than 720°C. Also considering its low cost and ease of availability compared to nitrogen, finding the way of using CO_2 as a reaction medium for pyrolysis experiments at lower than 720°C will be a desirable feature in the field of bio-energy. **Lee *et al.* (2017)** and **Valdés and Chejne (2017)** reported that decomposition of some compounds happened earlier under CO_2 atmosphere than under N_2 atmosphere and char produced under CO_2 atmosphere had larger surface area and better combustion properties.

Bio-oil yield of main pyrolysis experimental runs is presented in Table 4.2. It is clear from the table that bio-oil yield varied from 20.5 to 26.7 wt.% of *P. roxburghii* pine needle biomass. Highest yield was found in experimental runs 10, 28 and 30. **Uzun *et al.* (2010)** observed bio-oil yield of 29.62% at 500°C from tea waste which had a volatile content of 70.29%. **Bordoloi *et al.* (2015**) found maximum bio-oil yield of 29.6% and 28.5% at temperature of 550°C respectively from *Mesua ferrea* seed cover having 76.83%

volatiles and *Pongamia glabra* seed cover having 74.58% volatiles. Comparing these values this can be concluded that the batch pyrolysis of *P. roxburghii* needles was satisfactory in terms of bio-oil yield.

Table 4.2 Design Matrix using CCD and Bio-oil Yield

Experimental run	A. Pyrolysis Temp. (°C)	B. CO_2 flow ($l\ min^{-1}$)	C. Cooling temp. (°C)	D. Heating rate ($°C\ min^{-1}$)	Bio-oil yield (%)
1	450 (-1)*	1.5 (-1)	5 (-1)	20 (-1)	24.8
2	550 (+1)	1.5 (-1)	5 (-1)	20 (-1)	26.3
3	450 (-1)	2.5 (+1)	5 (-1)	20 (-1)	24.5
4	550 (+1)	2.5 (+1)	5 (-1)	20 (-1)	25.9
5	450 (-1)	1.5 (-1)	15 (+1)	20 (-1)	20.8
6	550 (+1)	1.5 (-1)	15 (+1)	20 (-1)	23.3
7	450 (-1)	2.5 (+1)	15 (+1)	20 (-1)	20.5
8	550 (+1)	2.5 (+1)	15 (+1)	20 (-1)	23.2
9	450 (-1)	1.5 (-1)	5 (-1)	40 (+1)	25.1
10	550 (+1)	1.5 (-1)	5 (-1)	40 (+1)	26.7
11	450 (-1)	2.5 (+1)	5 (-1)	40 (+1)	24.2
12	550 (+1)	2.5 (+1)	5 (-1)	40 (+1)	26.4
13	450 (-1)	1.5 (-1)	15 (+1)	40 (+1)	24.8
14	550 (+1)	1.5 (-1)	15 (+1)	40 (+1)	26.3
15	450 (-1)	2.5 (+1)	15 (+1)	40 (+1)	23.2
16	550 (+1)	2.5 (+1)	15 (+1)	40 (+1)	26.3
17	400 (-2)	2.0 (0)	10 (0)	30 (0)	21.8
18	600 (+2)	2.0 (0)	10 (0)	30 (0)	25.9
19	500 (0)	1.0 (-2)	10 (0)	30 (0)	24.8
20	500 (0)	3.0 (+2)	10 (0)	30 (0)	23.9
21	500 (0)	2.0 (0)	0 (-2)	30 (0)	26.5
22	500 (0)	2.0 (0)	20 (+2)	30 (0)	23.5
23	500 (0)	2.0 (0)	10 (0)	10 (-2)	23.9
24	500 (0)	2.0 (0)	10 (0)	50 (+2)	26.5
25	500 (0)	2.0 (0)	10 (0)	30 (0)	26.2
26	500 (0)	2.0 (0)	10 (0)	30 (0)	26.1
27	500 (0)	2.0 (0)	10 (0)	30 (0)	26.5
28	500 (0)	2.0 (0)	10 (0)	30 (0)	26.7
29	500 (0)	2.0 (0)	10 (0)	30 (0)	26.3
30	500 (0)	2.0 (0)	10 (0)	30 (0)	26.7

*Values in parenthesis indicate the coded values of RSM

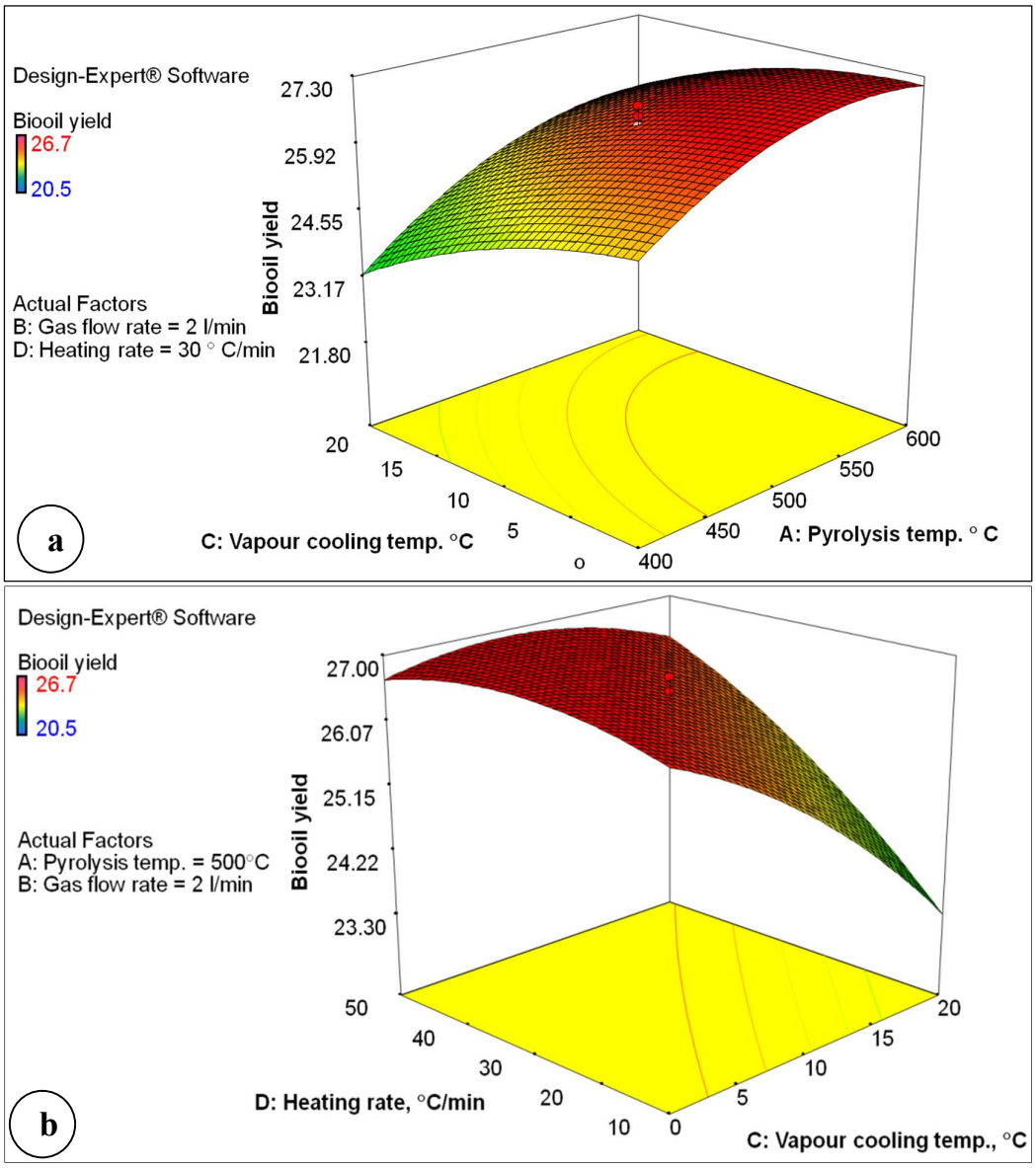

Fig. 4.4 a. Interaction Effect of Pyrolysis Temperature (A) and Vapour Cooling Temperature (C) and b. Vapour Cooling Temperature and Heating Rate (D) on Bio-oil Yield

4.2.3 Effects of pyrolysis parameters on bio-oil yield

Effects of four pyrolysis parameters on bio-oil yield from *P. roxburghii* pine needle have been depicted in Fig. 4.4. It shows that bio-oil yield increased initially with increasing temperature but reduced at higher temperature after 550°C. Vapour cooling temperature and heating rate were found very important for higher recovery of oil from pine needle. Bio-oil yield increased with increasing heating rate and decreasing vapour cooling

temperature. Therefore, it is evident that higher yield of bio-oil from pine needles can be achieved with a temperature near 550°C at high heating rate and low vapour cooling temperature. **Mohan *et al.* (2006)** in their extensive review work on bio-oil and its properties have sited similar findings. The vapour should be immediately cooled down to ambient to stop secondary reactions as suggested by **Beis *et al.* (2002**). This study reveals that very low vapour cooling temperature is not necessary for higher liquid recovery. Higher heating rate always gives higher liquid recovery because heat transfer rate to particle increases. But very high heating rate did not give significant higher yield as reported by **Mazaheri *et al.* (2010)** and **Bordoloi *et al.* (2015**).

Analysis of variance (ANOVA) of CCD was also conducted for the factors affecting bio-oil yield which is presented in Table A-6. The yield was greatly affected by the main factors and interactions of AC and CD as other interactions were found insignificant. Quadratic model was suggested with R^2 value of 0.984 which indicated that 98.4% variation in bio-oil yield was due to the experimental variables. Model test was also found significant. In ANOVA table, p-value and F-value indicate the significance of each term at a specified level of confidence. **Mazaheri *et al.* (2010)** reported that smaller p-value and higher F-value indicate higher significance. Lack of fit for quadratic model was found not significant with an F-value of 1.68 showing that quadratic model was fit (Table A-7) for the results obtained in experimental runs.

4.2.4 Prediction model

Regression analysis was conducted to develop a model for predicting bio-oil yield from pyrolysis parameters. The coded values were used for the prediction model which is expressed by the following equation:

$$\text{Bio-oil yield (wt.\%)} = 26.42 + 1.029A - 0.237B - 0.895C + 0.787D + 0.144AB + 0.193AC + 0.019AD - 0.006BC - 0.106BD + 0.744CD - 0.655A^2 - 0.530B^2 - 0.368C - 0.318D^2 \quad \ldots (4.1)$$

Where, *A, B, C* and *D* are the coded values of pyrolysis temperature, CO_2 gas flow rate, vapour cooling temperature and heating rate, respectively.

The data of actual experiment and predicted by the above model were plotted and shown in Fig. 4.5. It shows that data points of actual values of bio-oil yield obtained by experimental runs and predicted values obtained from quadratic model were near to straight line. It indicates good fit of the model and demonstrates that the model covers the experimental range of variables sufficiently.

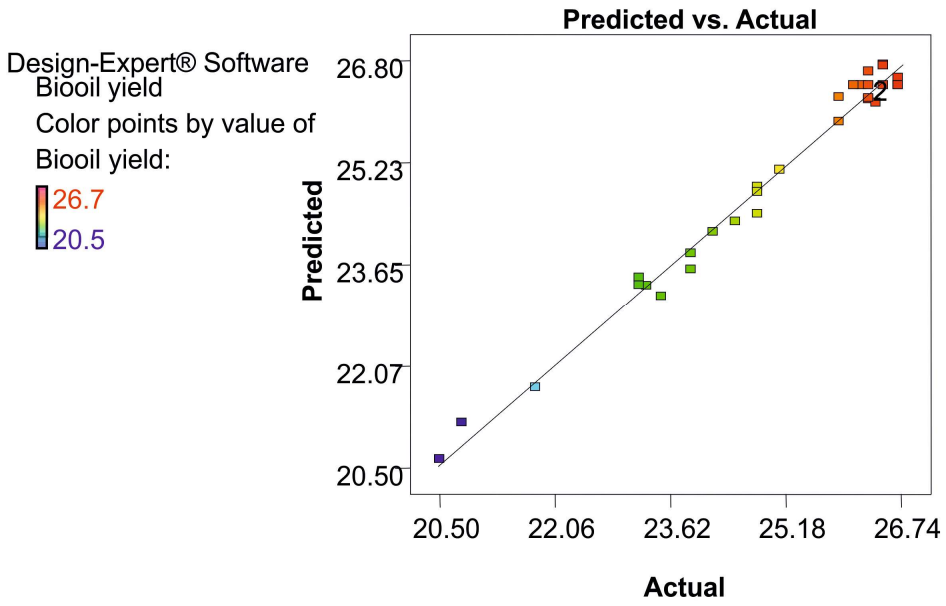

Fig. 4.5 Plot of Model Predicted Value against Actual Value of Bio-oil Yield

4.2.5 Optimization of bio-oil yield

Process optimization for batch experiments was conducted using the Design Expert software to find out the optimum condition for maximum bio-oil yield. The upper and lower limits of each variable and their responses predicted by the model based on surface and contour plots were provided. Constraints of each variable are presented in Table 4.3. The possible solutions for optimum conditions for maximum bio-oil yield suggested by the Design Expert software are presented in Table 4.4. It shows that there are three solutions with a desirability of 0.986 for same bio-oil yield. The conditions in all solutions are almost similar. The solution number 1 (pyrolysis temperature of 547°C, CO_2 gas flow rate of 1.85 l min^{-1}, vapour cooling temperature of 15°C and heating rate of 50°C min^{-1}) was selected as optimum. Confirmation tests were conducted with these optimum values and found average bio-oil yield of 27.3%. This shows that the yield obtained at optimal condition was in good agreement with the predicted value by the model. Bio-oil yield can be further improved by smaller particle size but it may incur higher energy expenditure in grinding the biomass as suggested by **Isa *et al.* (2011**).

Table 4.3 Constraints of Each Variable for Optimization of Bio-oil Yield

Name of variable	Goal	Lower Limit	Upper Limit
Pyrolysis temperature (°C)	Is in range	- 2	2
Gas flow rate (l min^{-1})	Is in range	- 2	2
Vapour cooling temperature (°C)	Is in range	- 2	2
Heating rate (°C min^{-1})	Is in range	- 2	2
Biooil yield (%)	Maximize	20.5	27.6

Table 4.4 Optimal Conditions for Maximal Bio-oil Yield

No.	Pyrolysis temperature (°C)	Gas flow rate (l min^{-1})	Vapour cooling temperature (°C)	Heating rate (°C min^{-1})	Bio-oil yield (%)	Desirability
1	547.0	1.85	15.25	50	27.6	0.986
2	547.0	1.84	15.25	50	27.6	0.986
3	546.5	1.84	15.25	50	27.6	0.986

4.3 Continuous Pyrolysis

Continuous pyrolysis experiments were conducted in a stainless steel screw pyrolysis reactor using N_2 as sweep gas at Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, Slovakia.

4.3.1 Products yield from *P. cembra* pine needles

Yields of bio-oil, aqueous phase of oil, biochar and product gas of nine experimental runs with *Pinus cembra* needles are presented in Table 4.5 and detail data are presented in Table B-2. It can be observed that highest bio-oil yield of 28.1% was obtained in Treatment 5 where pyrolysis temperature was 500°C, particle size was 1.25 – 2 mm, residence time was 8 min and N_2 flow was 30 l h^{-1}. The water content in bio-oil at this condition was 18.6%, charcoal yield was 31.7% and product gas yield was 21.6%. **Ferreira *et al.* (2015)** found a bio-oil yield of 23.9% and char yield of 24.9% from medium density fibre board at 450°C pyrolysis temperature and 15 min residence time with a twin screw pyrolyzer. It is also evident in Table 4.5 that at higher temperature char yield was lower and gas yield was higher and at lower temperature it was vice versa. Similar trend was also observed by **Kim *et al.* (2015)**.

Table 4.5 Product Yields and S/N Ratios of Bio-oil Yield at Different Treatments

Treatment	Bio-oil yield (%)	Aqueous phase (%)	Char (%)	Syn Gas (%)	S/N of Bio-oil yield
T_1	20.7	12.5	38.9	27.9	26.27
T_2	22.5	19.1	30.3	28.1	27.05
T_3	16.6	25.4	33.7	24.3	24.41
T_4	25.4	16.6	27.7	30.3	28.10
T_5	28.1	18.6	31.7	21.6	28.97
T_6	26.3	18.3	29.8	25.6	28.40
T_7	18.2	18.0	23.7	40.0	25.19
T_8	23.2	16.5	26.8	33.5	27.31
T_9	21.4	18.7	22.3	37.5	26.62

4.3.2 Effect of pyrolysis parameters on bio-oil yield

Using the bio-oil yield data in Eqn. 3.2, the S/N ratios for bio-oil yield have been calculated. Subsequently, analysis of mean has been carried out using Eqn. 3.3 and presented in Table B-3. Analysis of mean helps to find out the effect of different levels of each factor on output response. The average S/N ratios of bio-oil yield in different levels of four factors under study have been graphically presented in Fig. 4.6. It shows that bio-oil yield was highest at temperature of 500 °C and reduced at both higher and lower temperatures. Bio-oil yield was low at low temperature due to limited conversion of volatiles resulting higher char yield. **Pütün (2010)** concluded that at high temperature, secondary decomposition reaction of the liquid fraction of volatiles took place resulting reduced bio-oil yield and increased incondensable gases.

Particle size controls the rate of heat transfer from reactor to the biomass and is an important parameter in biomass pyrolysis. As seen in Fig. 4.6, bio-oil yield was higher in medium particle size of 1.25 – 2 mm size range in the current reactor configuration. Higher bio-oil yield with smaller particle reported by **Kim (2015**) was attributed to high heat transfer rate. Lower bio-oil yield in small particle size (<1.25 mm) might be due to the overheating of small biomass particle leading to more yield of non-condensable gases as per the findings of **Heo *et al.* (2010**). With 2 – 3 mm particle size, lower yield of bio-oil was observed which was due to slower heating rate of biomass particles caused by lower absorption of heat during pyrolysis as reported by **Sirijanusorn *et al.* (2013**).

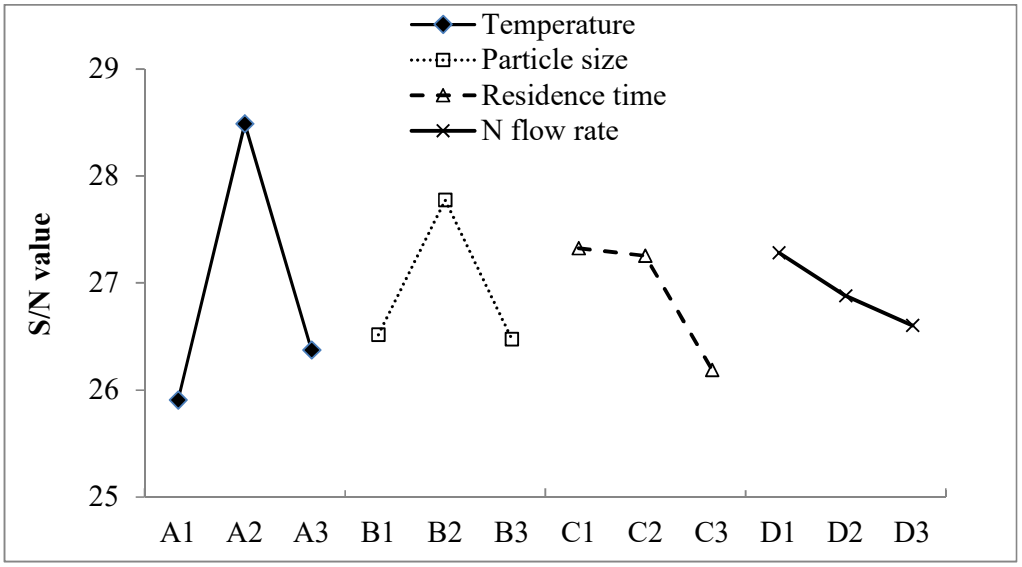

Fig. 4.6 S/N Ratio Response of Different Factors on Bio-oil Yield (A1, A2 A3 indicate temperatures of 400°C, 500°C and 600°C, B1, B2, B3 indicate particle sizes of <1.25 mm, 1.25–2.0 mm and 2.0–3.0 mm, C1, C2, C3 indicate residence time of 15 min, 10 min and 5 min and D1, D2, D3 indicate N_2 flow rate of 30, 45 and 60 lph, respectively).

Fig. 4.6 also shows the effect of solid residence time and N_2 flow. It is evident from Fig. 4.6 that with decreasing residence time bio-oil yield also decreased. Thus, highest yield of bio-oil was observed at 15 min residence time. At higher pyrolysis temperature, bio-oil yield was higher with higher residence time and opposite was the case with higher pyrolysis temperature as seen in Table 4.5. This could be due to higher heat transfer rate in higher temperature where less time was required for absorption of heat by the biomass particles and at lower temperature more time was needed. N_2 flow was found to have minor effect on bio-oil yield. With increasing flow, bio-oil yield decreased but the difference was insignificant. Low yield at higher flow might be due to insufficient quenching of pyrolysis vapours.

Effect of four factors, A (Pyrolysis temperature), B (Particle size), C (Residence time) and D (N_2 flow) was determined by Analysis of variance which was carried out using Eqns. 3.4 to 3.8 to explore the contribution of each factor on bio-oil yield. Calculated values of SS_F and ρ_F are presented in Table 4.6. According to their magnitude, highest contribution was of pyrolysis temperature (67.18%) followed by particle size (17.08%), residence time (9.03%) and N_2 flow rate (3.37%). Pyrolysis temperature and particle size mostly affected the bio-oil yield in present experimental conditions. Results in the same line were reported by **Kelkar *et al.* (2015)** with spent coffee grounds.

Table 4.6 SS_F and ρ_f of Experimental Factors

Factor	SS_F	ρ_f (%)
A	233.34	67.18
B	59.98	17.08
C	32.13	9.03
D	12.56	3.37

4.3.3 Determination of optimum conditions

Fig. 4.6 shows that maximum of average S/N ratios of factor A (Pyrolysis temperature), B (Particle size), C (Residence time) and D (N_2 flow) among three levels were 28.49, 27.78, 27.33 and 27.28, respectively. Therefore, the optimum conditions for maximum bio-oil yield from pine needles were 500°C of pyrolysis temperature, 1.25 – 2 mm particle size, 15 min of residence time and 30 l h^{-1} of N_2 flow. Results of confirmation runs under the optimum conditions are presented in Table 4.7. It shows that the average bio-oil yield was 28.98% (S/N ratio of 29.24) which was very close to Treatment 5. It is worth noting that the difference between optimum condition and test run 5 is only the residence time. Neglecting the minute yield differences between two operating conditions, treatment 5 can be adopted owing to the fact that process is much faster with less residence time which would also reduce the energy requirement for pyrolysis.

Table 4.7 Bio-oil Yield and S/N Ratio in Treatment 5 and Optimum Conditions

Treatment	Temperature (°C)	Particle size (mm)	Residence time (min)	N flow (l h^{-1})	Y1	Y2	Y3	S/N
T_5	500	1.25 - 2.0	5	30	28.2	27.8	28.3	28.97
Optimum	500	1.25 - 2.0	15	30	28.8	28.6	29.6	29.24

4.4 Evaluation of Biochar Production Unit

A batch type biochar production unit was designed and developed at Department of Farm Machinery and Power Engineering, GBPUA&T, Pantnagar, India for conversion *P. roxburghii* needles into biochar.

4.4.1 Optimum conditions for maximum biochar yield

Results of the nine experimental runs with biochar production unit have been summarized in Table 4.8. It was observed that in most of the runs charring was incomplete. Firstly, gasification time was varied keeping the other variables constant. In the conditions

of Run 1, charring was not complete and air-fuel ratio was calculated to be 1.04 which was quite low as compared to typical air-fuel ratio (1.6:1) for biomass gasification reported by **Dogru *et al.* (2002**). When gasification time was increased to 90 min, with 60% filling, 12% moisture and 40 m^3 h^{-1} air flow rate (Run 2), charring efficiency was observed as 26.64%. Further increase in gasification time, decreased the biochar yield by 2.44% in Run 3 which might be due to complete burning of some biomass with excess air. To find the optimum loading of the pyrolysis chamber, filling was increased to 100%, but at this condition charring was incomplete (Run 4). At Run 5, with 80% filling, conversion efficiency was found to be 28.88%. Fresh pine needles contained about 24% moisture. Therefore, Run 6 was conducted with fresh pine needles but there was incomplete charring. Tests were then continued with partially dried pine needles (18% moisture) and conversion efficiency was 25.92% in Run 7. With lesser air-fuel ratio at Run 8, again incomplete charring was observed. Finally in Run 9, with excess air-fuel ratio, charring efficiency was quite low. Thus from these results it can be concluded that higher gasification time (120 min), 80% filling, sun dried needles (12% moisture) and an air-fuel ratio of 1.57 (air flow rate of 40 m^3 h^{-1}) was optimum (Run 5) for the current reactor configuration.

Table 4.8 Biochar Yield from Biochar Production Unit

Experimental Runs	Burning time, min	Filling (%)	Moisture content (% wb)	Air flow rate (m^3 h^{-1})	Biochar yield (%)
1	60	60	12	40	Incomplete charring
2	90	60	12	40	26.64
3	120	60	12	40	24.20
4	120	100	12	40	Incomplete charring
5	120	80	12	40	28.88
6	120	80	24	40	Incomplete charring
7	120	80	18	40	25.92
8	120	80	12	30	Incomplete charring
9	120	80	12	50	23.22

4.4.2 Temperature profile

Temperature profile of the charring process in Run 5 has been depicted in Fig. 4.7 and data are presented in Table C-1. It shows that there was a rapid temperature increase up to 10 min where rate of increase was 37 °C/min. After that there was a slow increase in

temperature up to 55 min where it reached 538 °C and then temperature was almost constant for rest of the period. Biochar has been produced within temperature range of 350 – 500 °C from different biomass. **Antal and Gronli (2003)** reported that the highest temperature during pyrolysis is critical in determining the yield and quality of biochar. **Demirbas (2004**) found that the yield of biochar decreased significantly with increasing pyrolysis temperature, especially after the temperature exceeded 480 °C. **Dai and Antal (1999)** reported that elevating the peak temperature, the yield and water sorption capacity of biochar decreased, whereas the carbon content increased. **Song and Guo (2012)** found that at low temperature biochar had negligible BET surface area and a low iodine number whereas, at higher temperature, the surface area, porosity, and iodine number of biochar were greater. In this experiment, it can be concluded that biochar was prepared at temperature of 550 °C and expected to be of good quality.

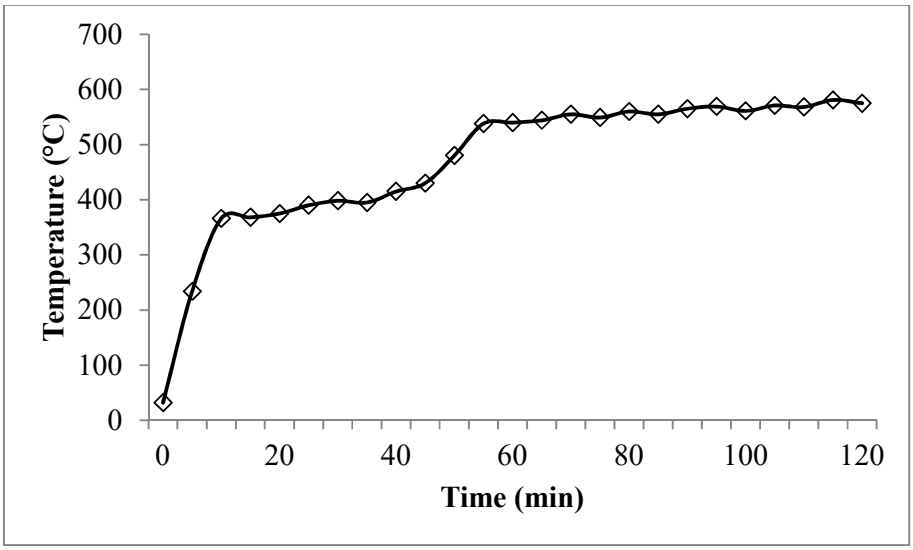

Fig. 4.7 Temperature Profile at Run 5

4.5 Properties of bio-oil

The properties such as density, pH, pour point, flash point, fire point, kinematic viscosity, high heating value and elemental composition were determined for bio-oil produced from both *Pinus roxburghii* and *Pinus cembra* needles.

4.5.1 Fuel properties

Fuel properties of pine needle bio-oil obtained at optimal condition of batch and continuous pyrolysis are presented in Table 4.9. Detail analysis data are presented in Table A-8 to A-9. It is evident from Table 4.9 that appearance of the bio-oil was dark brownish

with little transparency and strong odour. The density and pH of pine needle bio-oil derived by batch pyrolysis were 1105 kg m^{-3} and 4.60 and in continuous pyrolysis were 1055 kg m^{-3} and 4.05, respectively. Bio-oil of continuous pyrolysis was heavier than batch pyrolysis. The pH is considered one of the most important properties while considering bio-oil for fuel as it indicates the corrosiveness. **Mohamed *et al.* (2016**) reported that typical value of pH of bio-oil ranges from 2.5 to 4.5 which is due to presence of carboxylic compounds such as acetic and formic acids. In both processes, bio-oil was found heavier than water at 15°C and less acidic than bio-oil produced from other biomass as reported by **Özçimen and Ersoy-Meriçboyu (2010**). It was might be due to presence of lesser amounts of acidic compounds. However, density was higher and pH was lower than that of high speed diesel (HSD) of which density is 850 kg m^{-3} and pH 5.5 to 8.

Its pour point, flash point and fire point were found to be –2, 63°C and 68°C, respectively, which were higher than conventional HSD having these values of –40°C, 53°C and 58°C, respectively. Cloud point and acid value could not be judged due to dark colour. Kinematic viscosity is another important fuel property which defines its atomization characteristics. Its values at 40°C were 7.84 cSt and 11.5 cSt, respectively in batch and continuous pyrolysis. Bio-oil of continuous pyrolysis was thicker than batch pyrolysis due to higher density. However, these values were near to HSD (2 to 5 cSt) and much lower than furnace oil (160 cSt) which indicates that it can be used in compression ignition engines without any modification in injection system. High heating value was found to be 28.52 MJ kg^{-1} and 28.64 MJ kg^{-1}, respectively in batch and continuous pyrolysis. These values of HHV were almost 70% of HSD and much higher than its parent material, pine needles. Similar finding were reported by **Saikia *et al.* (2015**) in bio-oil prepared from *Arundo donax*.

Elemental analysis of pine needle bio-oil showed that the carbon, hydrogen, nitrogen and oxygen content were 69.44, 7.82, 1.44, and 21.31% in batch pyrolysis and 63.78, 9.69, 1.63 and 24.8% in continuous pyrolysis, respectively. Carbon content in batch pyrolysis bio-oil was higher than continuous pyrolysis bio-oil but hydrogen, nitrogen and oxygen contents were higher in continuous pyrolysis bio-oil. Overall, in both processes oxygen content reduced in bio-oil as compared to feedstock. **Bordoloi *et al.* (2015**) concluded that the decrease in the oxygen contents of the bio-oil was favourable since high oxygen content was not conducive for production of transportation fuel. Further, higher amount of hydrogen content indicates presence of higher amount of hydrocarbons in bio-

oil. Based on these findings, it can be concluded that continuous pyrolysis bio-oil was better than batch pyrolysis bio-oil as it had higher H/C ratio. Empirical formulae of both bio-oil were typical of biomass pyrolysis oil but continuous pyrolysis bio-oil was more close to HSD of which empirical formula is $C_{12}H_{24}$.

Table 4.9 Properties of Pine Needle Bio-oil

Properties	Standard test methods	Batch pyrolysis	Continuous pyrolysis	HSD
Appearance	-	Dark brownish	Dark brownish	
Density, 15°C (kg m^{-3})	ASTM D1217-15	1105	1055.2	850
pH	pH meter	4.60	4.05	5.5–8.0
Pour point (°C)	ASTM D5853-05	(-)2	-	–40 to –1
Cloud point (°C)	ASTM D2500	Not visible	-	-
Flash point (°C)	ASTM D93	63	-	53
Fire point (°C)	ASTM D93	68	-	58
Kinematic viscosity (cSt)	Redwood viscometer	7.84	11.5	2–5
Acid value	ASTM D974	Colour change was not visible	-	0.5
C residue, %	ASTM D189	16.13	-	0.1
HHV, MJ kg^{-1}	ASTM D 240	28.52	28.64	45.14
Elemental analysis (wt %)				
C		69.44	63.78	90.0
H		7.82	9.69	9.50
N		1.44	1.63	0.06
O		21.31	24.8	0.3
H/C		1.35	1.82	-
O/C		0.23	0.29	-
Empirical formula		$CH_{1.35}N_{0.017}O_{0.23}$	$CH_{1.82}N_{0.04}O_{0.29}$	

Fuel properties of bio-oil showed it as a promising fuel for internal combustion engines and boilers as it has many properties close to HSD and furnace oil. It can be used in IC engines after blending with lighter fuels to reduce its viscosity and density. It can be

directly used in furnaces as its major properties are very close to furnace oil. Upgradation of pine needle bio-oil by emulsification and esterification to high grade transportation fuel is also possible as opined by **Jiang and Ellis (2010**). The disadvantage with bio-oil is its storability. Studies conducted by **Garcia-Perez et al. (2006)** showed that the main macroscopic difference observed between the oils investigated is the tendency to form a separate "aqueous phase" after 96 h of aging. The amount of aqueous phase formed was around 20 mass % after 168 h of aging.

4.5.2 Chemical properties

4.5.2.1 FTIR analysis

The functional groups and organic compounds present in bio-oil were identified by FTIR and GC/MS analysis, respectively. FTIR spectra of pine needle (*Pinus roxburghii*) bio-oil from batch pyrolysis, shown in Fig. 4.8, were recorded in the transmission mode between wave number from 4000 to 600 cm^{-1}. It shows a wide variety of functional groups present in pine needle bio-oil. The presence of alkanes was indicated by the C–H stretching vibrations between 2855 and 2926 cm^{-1} and C–H deformation vibrations between 1362 and 1462 cm^{-1}. The peak at 1514.26 cm^{-1} provides the evidence of C=C bond of alkene. The presence of peak at 1606 cm^{-1} indicates a C=C stretching vibration caused by aromatics present in the bio-oil. The chemical compound groups in specific wave number were decided based on report of **Coates (2000**). The C=O stretching vibrations observed at 1707.07 cm^{-1} indicated the presence of ketones, aldehydes and quinones. Medium C–O stretching vibrations for carboxylic acids and their derivatives are indicated by the region between 1210 and 1320 cm^{-1}. Presence of amines was indicated by the C–N stretching vibration between 1034 and 1111 cm^{-1} and C–O groups that show the alcohol structure of OH groups can be seen between 1000 and 1100 cm^{-1}. The region between 700 and 900 cm^{-1} contains various bands related to the aromatic, out of plane C–H bending.

4.5.2.2 GC/MS analysis

The chemical compounds in pine needle (*Pinus roxburghii*) bio-oil from batch pyrolysis were identified by GC/MS analyses. Organic compounds were matched by using standard chromatographic data available from NIST 14.L spectrum library. Total 38 chemical compounds were identified. The concentrations of these compounds are shown in Table A-10 and the peaks observed are shown in Fig. A-1. Similarly, chemical compounds identified by GC/MS analyses of pine needle (*Pinus cembra*) bio-oil from continuous

pyrolysis are presented in Table B-4. Total 46 chemical compounds were identified and peaks are shown in Fig. B-1. The compounds identified were from nine major organic groups and their total concentrations have been presented in Table 4.10. It is clear from Table A-10 and Table B-4 that the compounds identified were mostly oxygenated hydrocarbons and their distribution was observed in the range of C_5–C_{24} chain structure. It can be seen from Table 4.10 that compounds in bio-oil from batch pyrolysis are mainly composed of phenols (50.30%) followed by ketones (21.15%), alcohols (5.35%), alkanes (5.33%), sesquiterpene (3.66%), PAH (3.50%) and organic acids (3.26%) and in continuous pyrolysis major compounds were phenols (26.09%) followed by polycyclic aromatic hydrocarbons or PAH (20.98%), organic acids (15.15%), sesquiterpene (9.39%), alkene (9.11%), ketones (5.56%) and alcohol (4.85%). Both bio-oils were rich in phenolic compounds. Ketones were higher in amount in batch pyrolysis bio-oil. Continuous pyrolysis bio-oil contained more PAH, organic acids and sesquiterpene. This was may be due to lower residence time in continuous pyrolysis and better heat transfer rate from reactor wall to biomass particles. **Mohan *et al.* (2006)** reported that bio-oils are complex mixtures of different organic compounds from wide variety of chemical groups. Synthesis of different chemical groups and their relative percentage in the bio-oil mixture is dependent on the process conditions and the properties of the parent material.

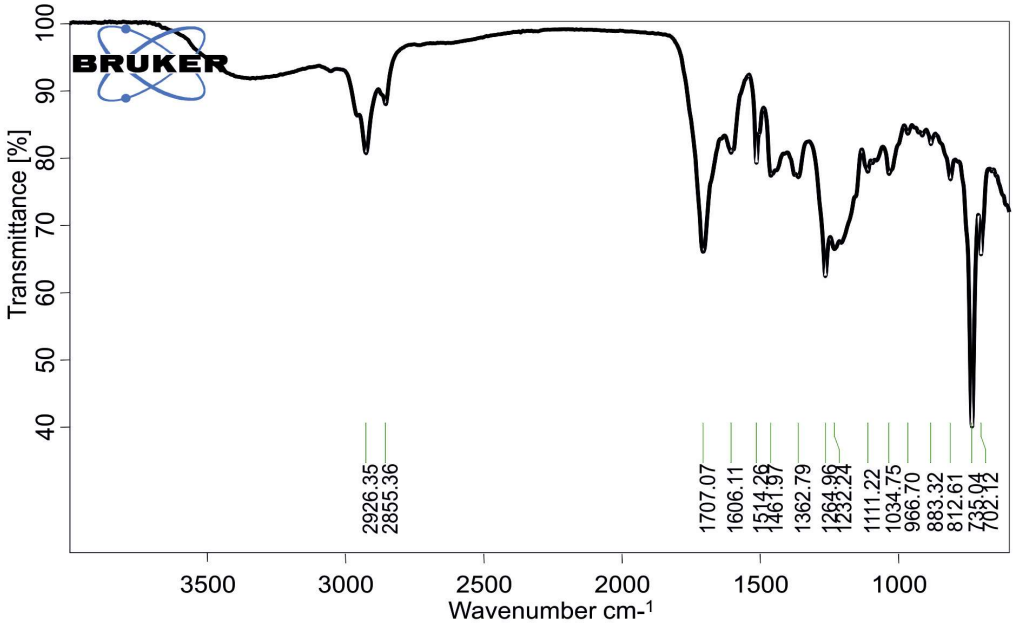

Fig. 4.8 FTIR Spectra of Pine Needle (*Pinus Roxburghii*) Bio-oil in Transmission Mode between Wavenumber of 4000 – 600 cm $^{-1}$

About 50% of the bio-oil from batch pyrolysis was of phenolic group which might be related to slower heating rates, which allows the increase of secondary reactions and, consequently, the production of oxygenated compounds of lower molecular weight as suggested by **Torry *et al.* (2016**). Similar results were found by **Yang *et al.*, (2014)** in the bio-oil of pine wood and barley straw which contained about 67% phenolic compounds. Acid content was low as compared to eucalyptus wood bio-oil found by **Chang *et al.* (2013**). There was a balance between yield of PAHs and Phenols in pine needle bio-oil from continuous pyrolysis at 500°C. **Heo *et al.* (2010**) showed that at higher temperature yield of PAHs was higher whereas, at lower temperature yield of phenolic compounds were higher.

Table 4.10 Quantitative Analysis of Main Compounds in Pine Needle Bio-Oil by GC/MS

Chemical group	Area (%)	
	Batch pyrolysis (*Pinus roxburghii*)	Continuous pyrolysis (*Pinus cembra*)
Acid	3.26	15.15
Alcohol	5.35	4.85
Aldehyde	2.15	2.01
Alkane	5.33	2.02
Alkene	3.16	9.11
Ketone	21.15	5.56
PAH	3.50	20.98
Phenol	50.30	26.09
Sesquiterpene	3.66	9.39
Others	2.14	4.84

Extraction of phenol from pine needle bio-oil could be economical in point of view of industrial use. Compound similar to ethisolide which is valuable and rare was also detected in pine needle bio-oil. Chemical profile of pine needle bio-oil suggests that it could be a good source for phenolic and other organic compounds. Amount of sesquiterpenes detected was 9.39% which are mostly found in essential oils. Extraction of these compounds might fetch higher value of bio-oil.

4.6 Properties of biochar

Properties of pine needle biochar prepared at optimum conditions of batch, continuous pyrolysis and with biochar production unit are presented in Table 4.11. Recovery of biochar at optimum conditions of batch, continuous pyrolysis and biochar production unit was 31.25%, 31.23% and 28.88%, respectively. Its water content was

found 4.84%, 2.6% and 5.06%, respectively in batch, continuous pyrolysis and biochar unit, respectively. Water content was quite low in biochar from all three processes as far as its fuel use is concerned. The pHs of biochar from three processes were 8.48, 6.91 and 9.92, respectively. The typical pH values in biochars range from 8 – 9. It is evident that pH of biochar from biochar production unit was highest among three. It was may be due to higher amount of inorganic compounds produced after complete burning of biomass as oxygen was added in this process. However, all biochars had pH in alkaline range which makes it a suitable material as soil amendment for amelioration of acid soil as suggested by **Mandal *et al.* (2013).**

Table 4.11 Properties of Pine Needle Biochar at Optimum Conditions

Properties	**Batch pyrolysis** (*Pinus roxburghii*)	**Continuous pyrolysis** (*Pinus cembra*)	**Biochar production unit** (*Pinus roxburghii*)
Recovery (%)	31.25	31.23	28.88
Water content (% wb)	4.84	2.60	5.06
pH	8.48	6.91	9.92
Volatile matter (%)	37.09	39.42	42.14
Fixed carbon (%)	55.27	46.64	50.64
Ash content (%)	7.64	11.34	7.22
Elemental analysis (wt %)			
C	69.54	71.87	66.8
H	4.24	3.88	2.41
N	1.38	1.75	1.55
O	24.84	11.16	22.02
H/C	0.73	0.65	0.433
O/C	0.27	0.17	0.247
Empirical formula	$CH_{0.73}N_{0.017}O_{0.27}$	$CH_{0.65}N_{0.04}O_{0.17}$	$CH_{0.43}N_{0.02}O_{0.25}$
HHV (MJ kg^{-1})	28.62	28.10	29.15
Surface area (m^2 g^{-1})	-	15.59	-

Volatile matter contents in three biochar were determined as 37.09%, 39.42% and 42.14%, respectively, whereas, fixed carbon and ash contents were 55.27%, 46.64%, 50.64% and 7.64%, 11.34%, 7.22%, respectively. Highest fixed carbon content and lowest volatile matter in biochar of batch pyrolysis were due to the fact that pyrolysis was carried out for longer period during which volatiles were removed from the biochar. Higher

volatile is not desired in biochar as a soil amendment as it indicates presence of more organic compounds but desirable as fuel. However, volatile matter in all three biochar was lower as compared to volatile matter content of various biomasses reported by **Özçimen and Ersoy-Meriçboyu (2010**). High carbon content in all three biochars makes them suitable for soil carbon sequestration because higher amount of carbon can be sequestered in soil for a very long time if used for soil amendment as per the research findings of **Lal (2009)** and **Mandal *et al.* (2015). Lehmann *et al.* (2007a**) suggested that biochar with high fixed carbon can be used as soil amendment for carbon sequestration because the carbon present in biochar is recalcitrant in nature and can remain in soil for thousands of years. The high ash content in continuous pyrolysis biochar indicated presence of higher amount of essential plant nutrients which are favoured for improving soil productivity and increasing crop yield. Thus pine needle biochar could be used as a balanced fertilizer for plants and crops according to the report of **Mullen *et al.* (2010)** and **Mohamed *et al.* (2016**). Lower moisture and volatile matters with higher carbon content than its parent material indicate that biochar produced from pine needle has better fuel values than pine needle biomass.

Elemental analysis showed 69.54%, 71.87%, 66.8% carbon, 4.24%, 3.88%, 2.41% hydrogen and 1.38%, 1.75%, 1.55% nitrogen in biochars of batch, continuous pyrolysis and biochar unit, respectively. Oxygen content was found to be 24.84%, 11.16% and 22.02%, respectively in three biochars. No sulphur was traced in pine needle biochar. Low nitrogen content would lead to low NO_x emission during combustion proving it to be good charcoal fuel. These values are in good agreement with other biochars produced from different biomass reported by **Özçimen and Ersoy-Meriçboyu (2010**). Empirical formulae were determined as $CH_{0.73}N_{0.017}O_{0.27}$, $CH_{0.65}N_{0.04}O_{0.17}$ and $CH_{0.43}N_{0.02}O_{0.25}$ for three biochars from three reactors respectively.

High heating values of biochar was found as 28.62, 28.10 and 29.15 MJ kg^{-1}, respectively in batch, continuous pyrolysis and biochar unit. In relation to energy use of biochar in replacement of coal, it was comparable to that of fossil coal (i.e., 28.0–32.0 MJ kg^{-1}) according to **Tsai *et al.* (2012**). Biochar from drum type production unit had highest heating value although the difference was not much. These values of high heating value were comparable to biochar from pine wood biochar reported by **Das *et al.* (2008)**.

Surface area of pine needle biochar from continuous pyrolysis was found to be 15.59 m^2 g^{-1}. **Fabbri *et al.* (2012)** reported that biochar surface area varied in a wide range depending on the process condition and raw materials. Hence, a comparison is difficult. However, this surface area was higher than biochar surface area of various biomass reported by **Özçimen and Ersoy-Meriçboyu (2010)**.

Biochar has been envisaged as solid renewable fuel and a medium for soil-carbon sequestration. So, its properties should be relevant to its uses. Low ash and higher calorific value are desirable as fuel whereas, higher fixed carbon and pH are required for soil carbon sequestration. Pine needle biochar has qualified for both uses. Results of elemental analysis resemble the typical values for biochar. Biochar prepared with the drum type biochar production unit had better properties in many aspects than the biochar produced with batch type pyrolysis reactor. Its pH value, fixed carbon and HHV were higher and volatile matter was lower. Lower amount of oxygen and hydrogen also indicates the absence of organic compounds which makes it more suitable for soil amendment suggested by **Lehmann (2007b)**.

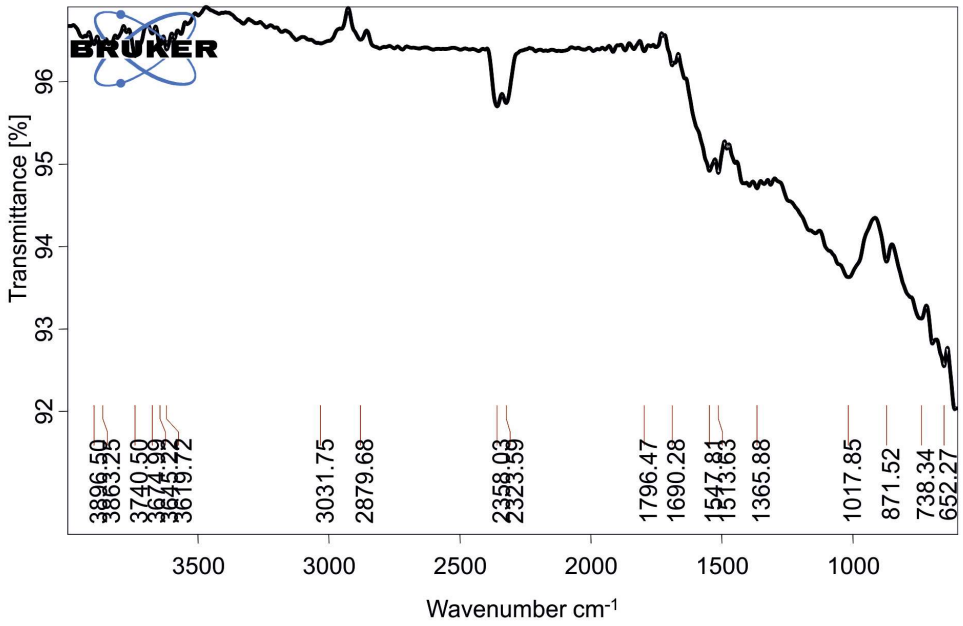

Fig. 4.9 FTIR Curve of Pine Needle (*Pinus roxburgii*) Biochar in Batch Experiment

FTIR spectra of pine needle biochar from batch pyrolysis are shown in Fig. 4.9 and spectra of biochar from drum unit are shown in Fig. 4.10. A number of peaks were observed in both spectra. There were similar peaks observed in both biochars. The aliphatic C–H stretching was observed between peaks 2950–2850 cm^{-1}. A small peak at

3036 cm^{-1} was due to alkene C–H stretching. Peaks at 3031 and 2879 cm^{-1} were due to vinyl and methyl C–H stretching, respectively. The strong peaks at 2362 cm^{-1} and at 2358 cm^{-1} were related to the adsorption peak of CO_2 in biochar which was also found by **Shu *et al.* (2008**). Several peaks between 2000 and 1660 cm^{-1} are assigned to aromatic combination bands. Peak at 1799 cm^{-1} was due to acid halides (C=O), at 1645 cm^{-1} due to C=C alkane stretching, at 1514 cm^{-1} for aliphatic nitro compounds and at 1448 cm^{-1} due to alkane C–H bending in both biochars. Peaks between 1400 and 1000 cm^{-1} were due to carboxylic acid, phenol, ester, aliphatic ether and alcohol, respectively. Peaks between 900 and 700 cm^{-1} were due to aromatic out of plane C–H bending as reported by **Bordoloi *et al.* (2015**). Peak at 665 cm^{-1} was due to alkyne C–H bends. Presence of organic compound groups in biochar made with biochar unit was at par with the biochar prepared at 500°C with the batch pyrolysis unit at controlled conditions except presence of some more aromatic group of compounds. This might be due the fact that in controlled condition CO_2 was used to drive away all the compounds formed during pyrolysis whereas, in Biochar unit it was totally closed. In the later case, compounds formed inside deposited on biochar surface.

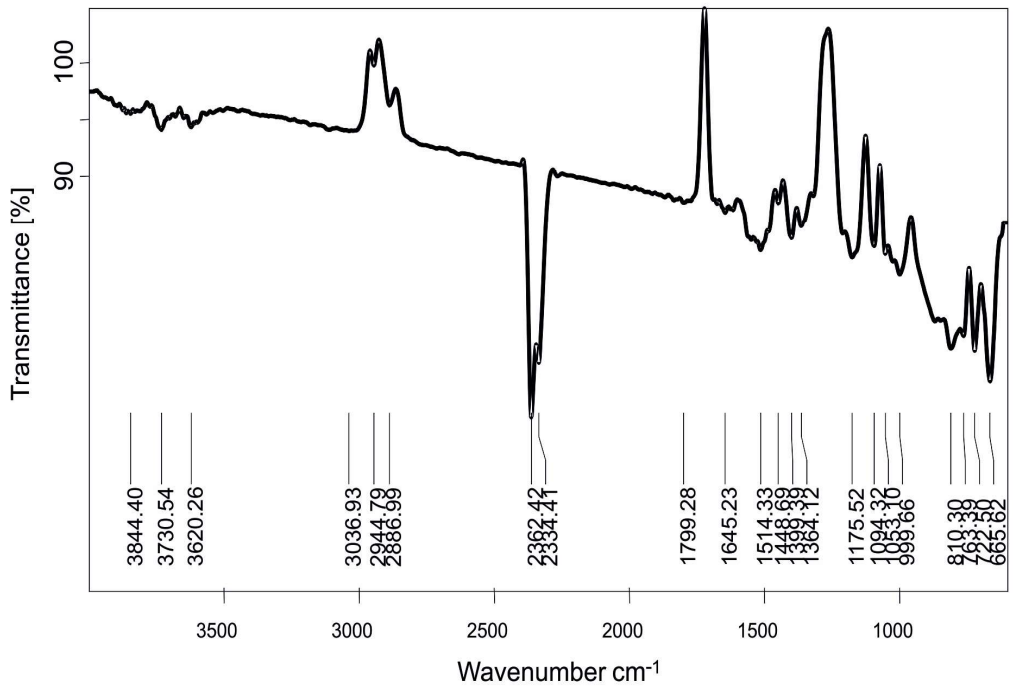

Fig. 4.10 FTIR Spectrum of Pine Needle Biochar made with Biochar Production Unit

4.7 Properties of Product Gas

4.7.1 Composition of Product gas

The product gas composition is typically 40–50% N_2, 15–20% H_2, 10–15% CO, 10–15% CO_2 and 3–5% CH_4, 1–2% other hydrocarbons with a net calorific value of 4–6 MJ Nm^{-3} (1000 to 1500 Kcal Nm^{-3}). Permanent gases formed during pyrolysis are the source of heat and can be used industrially. Composition of product gas during continuous pyrolysis of pine needles at optimum conditions (500°C, 1.25 – 2 mm particle size, 15 min residence time and 30 l h^{-1} gas flow rate) is presented in Table 4.12 and composition of product gas from biochar production unit at different time interval has been shown in Fig. 4.11 and data are presented in Table C-2. It is evident from the Table 4.12 that product gas from continuous pyrolysis contained 12% CO_2, 15.89% CO, 5.33% H_2, 56.41% N_2, 9.22% CH_4 and 1.15% C_2H_4, whereas, average composition of product gas from biochar production unit was 12.1% CO_2, 10.46% CO, 6.79% H_2, 65.67% N_2, 3.89% CH_4 and 1.06% C_2H_4. There was not much difference in composition of product gas from two experimental units except percentage of CH_4 which was higher in continuous pyrolysis product gas. It was may be due to better heat transfer mechanism from reactor surface to biomass particles during pyrolysis.

Higher amount of carbon oxides in both reactors were produced because the main constituents of biomass (cellulose, hemicelluloses and lignin) are rich in oxygen content as opined by **Duman *et al.* (2011)**. The composition of pine needle product gas was similar to typical range of pyrolysis gases from biomass as reported by **Bridgwater and Peacocke (2000**) and **McKendry (2002**). Nitrogen was major part of the product gas as it was used as carrier gas in the continuous pyrolysis experiment and air was used for biochar production unit.

Table 4.12 Composition of Product Gas from Continuous Pyrolysis at Optimal Conditions

Gases	CO_2	CO	H_2	N_2	CH_4	C_2H_4	Product gas
% by Vol	12.0	15.89	5.33	56.41	9.22	1.15	100
Molar fraction	0.12	0.159	0.053	0.564	0.092	0.0115	1.0
HHV (MJ m^{-3})	0	11.7	12	0	37	63	6.63

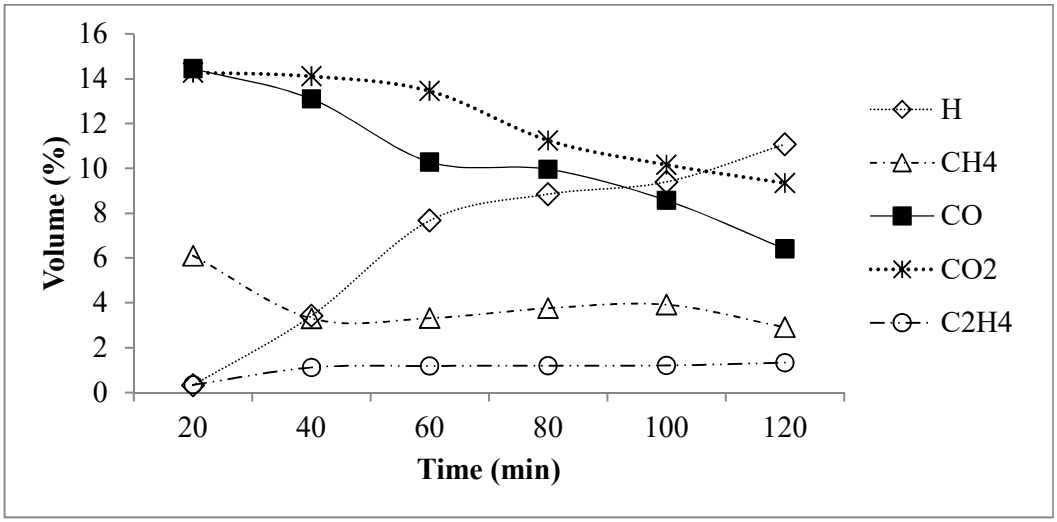

Fig. 4.11 Composition of Product Gas from Biochar Production Unit

The trend in composition of product gas from biochar production unit with time is shown in Fig 4.11. It shows that initially fraction of CO, CO_2 and CH_4 was higher which gradually decreased with time, whereas, fraction of H_2 increased over period of gasification. Production of C_2H_4 was almost constant throughout the period. Similar trend has been reported by **Kirubakaran *et al.* (2009**). The composition suggests that it can be effectively used in IC engines for whole period of burning.

4.7.2 Higher heating value of product gas

HHV of product gas from continuous pyrolysis calculated at 20°C and 101.325 kPa reference pressure has been presented in Table 4.12 and found to be 6.63 MJ Nm^{-3}. HHV of product gas from biochar production unit at different time interval is shown in Fig. 4.12. Although there was much variation in the composition with time, HHV was almost constant at 4.16 MJ Nm^{-3}. Therefore, it is evident from the result that HHV of product gas from continuous reactor was higher than the biochar production unit. It was due to the fact that in the continuous reactor pyrolysis vapour was cooled down to separate the liquid products and moisture present which reduce the HHV of product gas. Also, the amount of combustible gases like CO and CH_4 was higher in continuous pyrolysis gas. However, the value of HHV of product gas from both reactors was lesser in compared to values presented by **Stals *et al.* (2010)** and **Ferreira *et al.* (2015**) due to higher amounts of N_2 and CO_2. Gas yield can be increased by increasing the pyrolysis temperature but with the expense of reduced bio-oil yield.

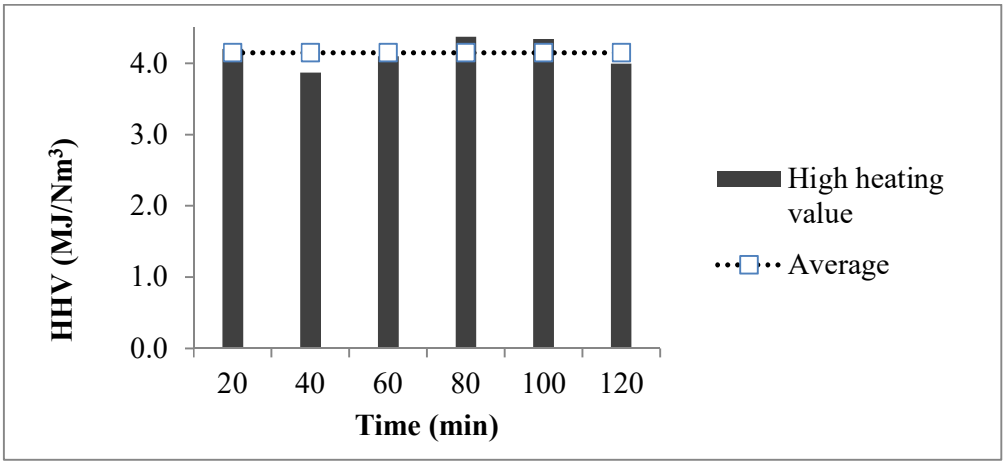

Fig. 4.12 Higher Heating Value of Product Gas at Different Time Intervals

4.8 Energy Balance of Pine Needle Conversion

Table 4.13 summarizes the energy balance results of pine needle conversion in three different routes. The sample size was 200 g for both pyrolysis experiments and 51 kg for biochar production unit. The energy streams were evaluated in terms of HHV values of the materials. Pine needles and electrical energy are the energy inputs and the bio-oil, biochar and product gases are the energy outputs. The biomass energy (Q_b) varied in two processes due the difference in high heating values of two different pine needle species. Energy input for grinding (Q_{eg}) was 0.87 MJ kg^{-1} and 0.72 MJ kg^{-1}, respectively for two species. Therefore, hammer mill consumed more energy than the cutting mill as the hammer mill was used for grinding of *Pinus roxburghii* needles and cutting mill was used for grinding of *Pinus cembra* needles. Pyrolysis energy input (Q_{ep}) was 7.2 MJ kg^{-1} for batch pyrolysis whereas, for continuous pyrolysis it was 1.31 MJ kg^{-1}. It was due the fact that in batch pyrolysis every time reactor had to be heated to the maximum temperature and again cooled down to reload fresh biomass. In this process a lot of energy was consumed and lost. For biochar production unit electrical energy consumption (Q_{bl}) was only 0.1 MJ kg^{-1}.

Energy output in terms of bio-oil (Q_o) was 7.7 MJ and 8.31 MJ for batch and continuous reactors, respectively. There was not much difference in these values because of almost equal HHV of both bio-oils and equal recovery rate. Product gas energy output (Q_g) were 3.21, 2.69 and 7.96 MJ, respectively for batch, continuous pyrolysis and biochar production unit. Higher output in biochar production unit was due to the higher gas output

compared to other two processes. Energy loss was highest in batch pyrolysis. Energy conversion efficiency was found to be 79.06%, 87.65% and 86.46%, respectively for three processes, continuous pyrolysis being the most energy efficient. It was due its continuous operation which rendered less energy loss. Return on energy invested (REI) was calculated as 2.52, 9.68 and 155.4, respectively in three processes. This value was calculated considering that biomass is freely available and its energy content should not be included in the energy input. Due to this fact REI value of biochar production unit was very high. The REI value of continuous pyrolysis process was higher than values found in other studies done using municipal waste by **Prawisudha *et al.* (2012**), which was around 4.0 and food waste by **Mahmood *et al.* (2016**).

Table 4.13 Energy Balance of Pine Needle Conversion for One Kg Biomass

Process	Energy input (MJ kg^{-1})				Energy output (MJ)			Loss (MJ)	EE (%)	REI
	Q_b	Q_{eg}	Q_{ep}	Q_{bl}	Q_c	Q_o	Q_g	Q_l		
Batch pyrolysis	17.67	0.87	7.20	0	9.44	7.70	3.21	5.39	79.06	2.52
Continuous pyrolysis	20.42	0.72	1.31	0	8.68	8.31	2.69	2.77	87.65	9.68
Biochar production	17.67	0	0	0.1	7.41	0	7.96	2.41	86.46	155.4

The quantitative results presented in Table 4.13 clearly indicate that the all three processes could be used to produce bio-oil, biochar and product gases to recover energy from pine needles. Among three processes, continuous pyrolysis process was most energy efficient. It was may be due to lesser heat loss in continuous process and recovery of all three products in good quality. REI calculations show that the three processes convert the pine needles into useful energy products, which have more energy compared to the energy used to run the process. An REI value of greater than one indicates that all three processes are energetically viable. Batch pyrolysis was found least efficient in terms of REI which may be attributed to the higher energy input during heating of the reactor for each run. REI value of biochar production was exceptionally high as only input energy in the process was the electrical energy input of the blower unit during initial burning. A detail exergy analysis may show some good comparison of this process with other processes.

4.9 Economics of Pine Needle Conversion

The economic analysis of pine needle conversion to bio-oil and biochar has been presented in Table 4.14. The costs of three experimental units were roughly estimated as Rs. 21000 for batch pyrolysis, Rs. 350000 for screw pyrolysis and Rs. 25000 for biochar production unit. Assuming the life of batch pyrolysis unit as 2000 experimental runs, cost for per kg of pine needle biomass pyrolysis will be Rs. 52.50. Similarly, cost in continuous pyrolysis unit was found to be Rs. 36.48 per kg of biomass with a life of 4000 h. For biochar production unit, this cost was found to be Rs. 0.50. Energy input cost was Rs. 13.32, 3.36 and 0.168 per kg biomass, respectively in three units assuming electricity cost of Rs. 6 per kWh. Thus including the manual handling cost, total input cost was found to be Rs. 104.32, Rs. 56.47 and Rs. 4.67 respectively in batch pyrolysis unit, continuous pyrolysis unit and biochar production unit. In this calculation, cost of product gas was not considered as it is mostly used in the process. Cost of bio-oil and biochar was considered equal due to their equal high heat value. Thus, cost of bio-oil and biochar in batch and continuous unit was Rs. 173.86 and Rs. 94.11, respectively. The high cost in both the units was due to their laboratory scale size which has very small capacity. Once scaled up, these costs can be reduced considerably. However, cost of biochar produced using the biochar production unit was quite low (Rs. 16.10).

4.14 Economic Analysis of Pine Needle Conversion

Parameters	**Batch pyrolysis**	**Continuous pyrolysis**	**Biochar production unit**
Cost of Inputs			
Cost of experimental setup (Rs.)	21000	350000	25000
Setup cost/kg biomass (Rs.)	52.50	36.48	0.50
Cost of pine needle collection (Rs. t^{-1})	1000	1000	1000
Energy input cost (Rs. kg^{-1})	13.32	3.36	0.168
Man power cost (Rs. kg^{-1})	37.50	15.63	3.00
Total input cost (Rs. kg^{-1})	104.32	56.47	4.67
Cost of outputs			
Biochar (Rs. kg^{-1})	173.86	94.11	16.10
Bio-oil (Rs. kg^{-1})	173.86	94.11	-

The experiments conducted to find out the suitability of pine needles as source of liquid, solid and gaseous bio-fuels was found successful in terms of product quality and energy balance. Bio-oil was produced from *Pinus roxburghii* needles with a recovery rate of 26.7 wt.% in batch pyrolysis experiment, whereas, in continuous experiments highest bio-oil yield of 28.98% was achieved from *Pinus cembra* needles at the optimum conditions. The optimum condition in batch pyrolysis was found at pyrolysis temperature of 547°C, 1.85 l min^{-1} gas flow rate, 15°C vapour cooling temperature and 50°C min^{-1} heating rate. In continuous pyrolysis the optimum conditions were pyrolysis temperature of 500°C, particle size of 1.25 – 2.0 mm, residence time of 15 min and N_2 gas flow rate of 30 l h^{-1}. Conversion efficiency of the biochar production unit with *Pinus roxburghii* needle as substrate was found to be 28.88% at 80% loading, 12% moisture and an air-fuel ratio of 1.57 (air flow rate of 40 m^3 h^{-1}). In this experiment, biochar was prepared at temperature of about 540°C. Bio-oil produced at optimum conditions of batch and continuous pyrolysis were found heavier than water and less acidic. Fuel properties like pour point, flash point, fire point, kinematic viscosity and HHV were comparable to HSD. Higher heating values of both bio-oils were 70% of HSD. They had less oxygen content than parent material. The GC/MS analysis showed that both bio-oils were rich in phenolic compounds. Biochars produced in all three processes had pH in alkaline range, low volatile matter and higher fixed carbon making it a suitable material for acid soil amelioration. HHV of product gas from screw pyrolysis was 6.63 MJ Nm^{-3} and from biochar production unit was 4.16 MJ Nm^{-3}. The quantitative results of energy analysis indicated that the all three processes could be used to produce bio-oil, biochar and product gases to recover energy from pine needles. Among three processes, continuous screw pyrolysis process was most energy efficient. The cost of bio-oil and biochar produced in batch and continuous pyrolysis unit was high due to their laboratory scale sizes.

Chapter – 5

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

Considering the threat of pine needles as fire hazard and its higher availability, the aim of the present study was to utilize pine needles through pyrolysis process to produce bio-oil, biochar and product gas, which otherwise would only be burnt to add pollution in environment. Pyrolysis of *Pinus roxburghii* needles was conducted using batch reactor and of *Pinus cembra* by a continuous reactor and their product characteristics were determined by standard methods. Batch pyrolysis of pine needles was carried out in a stainless steel tubular reactor using CO_2 as sweep gas. Continuous pyrolysis experiments were conducted in a screw reactor using N_2 as sweep gas. Optimization of pyrolysis process parameters such as pyrolysis temperature, gas flow rate, vapour cooling temperature, heating rate, and particle size was done using RSM for production of maximum bio-oil in batch experiments. Parameters studied in continuous pyrolysis were pyrolysis temperature, particle size, residence time and gas flow rate. Optimization in continuous pyrolysis was carried out using Taguchi's Orthogonal Array. Additionally a batch type biochar production unit was designed to convert pine needles in bulk to biochar and product gas. Its performance was evaluated by varying the time of burning, loading rate, moisture content of feed and air flow rate. Fuel and chemical properties of produced bio-oil, biochar and product gases at different experiments were determined using ASTM standard methods, FTIR, gas chromatography and GC/MS analysis. Energy balance exercise was also carried out for all three processes. On the basis of obtained results and their analytical interpretation following major conclusion were drawn:

- The experiments conducted to find out the suitability of pine needles as source of liquid, solid and gaseous bio-fuels was found successful in terms of product quality and energy balance.
- Needles of *Pinus roxburghii* had very low ash, high volatile and high fixed carbon contents whereas *Pinus cembra* needle had high ash, high volatile and low fixed carbon contents. Higher amount of lignin was present in both pine needles compared to cellulose and hemicellulose. Thus, both pine needles were found suitable material for pyrolysis.
- Bio-oil was produced from *Pinus roxburghii* needles with a recovery rate of 26.7 wt.% in batch pyrolysis experiment, whereas, in continuous experiments highest

bio-oil yield of 28.98% was achieved from *Pinus cembra* needles at the optimum conditions.

- In batch experiments bio-oil yield increased initially with increasing temperature but reduced at higher temperature after 550°C. Also, bio-oil yield increased with increasing heating rate and decreasing vapour cooling temperature.
- The adaptation of response surface methodology indicated the optimum condition for maximum bio-oil yield of 27.6 % in batch pyrolysis and was found at pyrolysis temperature of 547°C, 1.85 l min^{-1} gas flow rate, 15°C vapour cooling temperature and 50°C min^{-1} heating rate. The quadratic model of RSM in CCD was found fit to optimize the bio-oil yield and confirmation run showed bio-oil yield of 27.3% in the optimum condition.
- In continuous pyrolysis, bio-oil yield decreased with both increase and decrease in pyrolysis temperature. At higher temperature char yield was lower and gas yield was higher and at lower temperature it was vice versa. Bio-oil yield was higher in medium particle size of 1.25 – 2 mm size and higher residence time. N_2 flow was found to have minor effect on bio-oil yield in continuous pyrolysis. Highest contribution in bio-oil yield was of pyrolysis temperature (67.18%) followed by particle size (17.08%), residence time (9.03%) and N_2 flow rate (3.37%).
- The Taguchi Orthogonal Array was found effective in optimizing the process parameters of continuous pyrolysis experiments and the optimum conditions were pyrolysis temperature of 500°C, particle size of 1.25 – 2.0 mm, residence time of 15 min and N_2 gas flow rate of 30 l h^{-1}.
- Conversion efficiency of the biochar production unit with *Pinus roxburghii* needle as substrate was found to be 28.88% (biochar productivity) at 80% loading, 12% moisture and an air-fuel ratio of 1.57 (air flow rate of 40 m^3 h^{-1}). In this experiment, biochar was prepared at temperature of 538°C.

- Bio-oil produced at optimum conditions of batch and continuous pyrolysis were found heavier than water at 15°C and less acidic than bio-oil of other biomass. Fuel properties like pour point, flash point, fire point and kinematic viscosity were comparable to HSD. Higher heating values of both bio-oils were 70% of HSD. They had less oxygen content than parent material. The GC/MS analysis showed that both bio-oils were rich in phenolic compounds. Ketones were higher in amount in batch

pyrolysis bio-oil. Continuous pyrolysis bio-oil contained more PAH, organic acids and sesquiterpenes.

- Biochars produced in all three processes had pH in alkaline range and found suitable material as soil amendment for amelioration of acid soil. Volatile matter was lower and carbon content was higher in all three biochars as compared to biochars of various other biomasses. High heating values were comparable to biochar from pine wood biochar.
- Biochar prepared with the drum type biochar production unit had better properties in many aspects than the biochar produced with batch type pyrolysis reactor. It was prepared at temperature of 538°C and had good quality as soil amendment and fuel.
- Product gas from continuous pyrolysis contained 12% CO_2, 15.89% CO, 5.33% H_2, 56.41% N_2, 9.22% CH_4 and 1.15% C_2H_4, whereas, average composition of product gas from biochar production unit was 12.1% CO_2, 10.46% CO, 6.79% H_2, 65.67% N_2, 3.89% CH_4 and 1.06% C_2H_4. There was not much difference in composition of product gas from two experimental units except percentage of CH_4. HHV of product gas from continuous pyrolysis was 6.63 MJ Nm^{-3} and from biochar production unit was 4.16 MJ Nm^{-3}. Moisture present in product gas of biochar production unit reduced its HHV.
- The quantitative results of energy analysis indicated that the all three processes (Batch pyrolysis, continuous pyrolysis and biochar production unit) could be used to produce bio-oil, biochar and product gases to recover energy from pine needles. Among three processes, continuous pyrolysis process was most energy efficient.
- The economic analysis showed that cost of of bio-oil and biochar in batch and continuous unit was Rs. 173.86 and Rs. 94.11 per kg, respectively. The high cost in both the units was due to their laboratory scale size which has very small capacity. However, cost of biochar produced using the biochar production unit was quite low (Rs. 16.10).

The study shows that pine needles can effectively be used as bio-energy source. It can be converted to bio-oil, biochar and product gas by pyrolysis. In batch pyrolysis, 27.6% bio-oil, 31.2% biochar and 28% product gas can be produced at temperature of about 550°C, 2 l min^{-1} gas flow rate, 15°C vapour cooling temperature and 50°C min^{-1} heating rate. Whereas, in continuous pyrolysis with screw reactor, 29% bio-oil, 31.2% biochar and 21.5% product gas can be produced at pyrolysis temperature of 500°C, particle

size of 1.25 – 2.0 mm, residence time of 15 min and N_2 gas flow rate of 30 l h^{-1}. The developed biochar production unit can be used to convert pine needles to biochar with a conversion efficiency of 28.88% at 80% loading, 12% moisture content and 40 m^3 h^{-1}air flow rate. However, continuous pyrolysis was found most energy efficient among three processes. Cost of biochar and bio-oil was high in batch and continuous pyrolysis units but low in biochar production unit.

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APPENDICES

APPENDICES

Appendix A: Data related to batch experiments at GBPUA&T, Pantnagar

Table A-1 Proximate Analysis of Pine Needles (*Pinus roxburgii*)

Replications	Water content	Volatile matter	Ash content	Fixed carbon
1	7.67	71.27	2.13	26.60
2	7.6	73.12	2.11	24.78
3	8.06	70.35	2.00	27.66
Avg	7.78	71.58	2.08	26.34

Table A-2 Composition Analysis of Pine Needles (*Pinus roxburgii*)

Rep	1	2	3	avg	sd
Hemicellulose	24.85	22.81	24.79	24.15	1.160862
Lignin	29.02	27.42	31.02	29.153333	1.8037
Cellulose	26.8	29.6	25.1	27.166667	2.272297
Extractives	17.25	18.09	17.01	17.45	0.567098

Table A-3 Elemental Analysis of Pine Needles (*Pinus roxburgii*)

Elements	1	2	3	Average	SD
C	44.969	44.883	45.129	44.99367	0.124841
H	5.46	5.51	5.41	5.46	0.05
N	1.043	0.998	0.943	0.994667	0.050083
O	48.528	48.609	48.518	48.55167	0.049903

Table A-4 Design of Factorial Experiment

Run no.	Expt. Order	Block	Temp	Gas flow	Cooling temp	heating rate	holding time	Oil %
1	9	Block 1	-1	-1	-1	-1	1	24.8
2	13	Block 1	1	-1	-1	-1	-1	26.3
3	20	Block 1	-1	1	-1	-1	-1	24.5
4	18	Block 1	1	1	-1	-1	1	25.9
5	14	Block 1	-1	-1	1	-1	-1	20.8
6	5	Block 1	1	-1	1	-1	1	23.3
7	11	Block 1	-1	1	1	-1	1	20.5
8	16	Block 1	1	1	1	-1	-1	23.2
9	19	Block 1	-1	-1	-1	1	-1	25.1
10	7	Block 1	1	-1	-1	1	1	26.7
11	12	Block 1	-1	1	-1	1	1	24.2
12	3	Block 1	1	1	-1	1	-1	26.4
13	6	Block 1	-1	-1	1	1	1	24.8
14	4	Block 1	1	-1	1	1	-1	26.3
15	15	Block 1	-1	1	1	1	-1	23.2
16	2	Block 1	1	1	1	1	1	26.3
17	1	Block 1	0	0	0	0	0	26.2
18	17	Block 1	0	0	0	0	0	26.1
19	10	Block 1	0	0	0	0	0	26.5
20	8	Block 1	0	0	0	0	0	26.7

Table A-5 ANOVA for Selected Factorial Model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	54.800625	9	6.088958	79.27758	< 0.0001	significant
A-A	17.015625	1	17.01563	221.5416	< 0.0001	
B-B	0.950625	1	0.950625	12.37703	0.0065	
C-C	15.015625	1	15.01563	195.5018	< 0.0001	
D-D	11.730625	1	11.73063	152.7315	< 0.0001	
E-E	0.030625	1	0.030625	0.398734	0.5434	
AB	0.330625	1	0.330625	4.304702	0.0678	
AC	0.600625	1	0.600625	7.820072	0.0208	
CD	8.850625	1	8.850625	115.2342	< 0.0001	
CE	0.275625	1	0.275625	3.588608	0.0907	
Curvature	11.026125	1	11.02613	143.559	< 0.0001	significant
Residual	0.69125	9	0.076806			
Lack of Fit	0.46375	6	0.077292	1.019231	0.5381	not significant
Pure Error	0.2275	3	0.075833			
Cor Total	66.518	19				
Std. Dev.	0.277138152		R-Squared	0.987543		
Mean	24.89		Adj R-Squared	0.975086		
C.V. %	1.113451798		Pred R-Squared	0.944343		
PRESS	3.702222222		Adeq Precision	28.88856		

Table A-6 ANOVA for Response Surface Quadratic Model of Coded Values

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Comment
Model	89.977	14	6.427	67.376	< 0.0001	significant
A-A*	25.420	1	25.420	266.492	< 0.0001	significant
B-B	1.354	1	1.354	14.192	0.0019	significant
C-C	19.260	1	19.260	201.915	< 0.0001	significant
D-D	14.884	1	14.884	156.032	< 0.0001	significant
AB	0.331	1	0.331	3.466	0.0823	
AC	0.601	1	0.601	6.297	0.0241	significant
AD	0.006	1	0.006	0.059	0.8114	
BC	0.001	1	0.001	0.007	0.9366	
BD	0.181	1	0.181	1.894	0.1890	
CD	8.851	1	8.851	92.785	< 0.0001	significant
A^2	11.775	1	11.775	123.442	< 0.0001	significant
B^2	7.711	1	7.711	80.835	< 0.0001	significant
C^2	3.709	1	3.709	38.879	< 0.0001	significant
D^2	2.769	1	2.769	29.024	< 0.0001	significant
Residual	1.431	15	0.095			
Lack of Fit	1.103	10	0.110	1.679	0.2953	not significant
Pure Error	0.328	5	0.065			
Cor Total	91.408	29				
Std. Dev.	0.309		R-Squared	0.984		
Mean	24.920		Adj R-Squared	0.969		

*A, B, C, D represent the parameters pyrolysis temperature, CO_2 gas flow rate, vapour cooling temperature and heating rate

Table A-7 Data of RSM Lack of Fit Tests Experiment

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Linear	30.16133333	20	1.508067	22.96548	0.0013	
2FI	20.19258333	14	1.442327	21.96438	0.0015	
Quadratic	1.1025	10	0.11025	1.678934	0.2953	Suggested
Cubic	0.065833333	2	0.032917	0.501269	0.6333	Aliased
Pure Error	0.328333333	5	0.065667			

Table A-8 Properties of Bio-oil (*Pinus roxburgii*) from Batch Experiment

Rep	pH	Flash point, °C	Fire point, °C	Pour point, °C	Density, kg/m^3	CV, MJ/kg	C residue, %	Viscosity, cSt
1	4.61	63.00	66.00	-1.00	1.096	28.93	15.98	7.72
2	4.60	64.00	69.00	-3.00	1.110	28.10	16.25	8.07
3	4.60	64.00	68.00		1.110	28.54	16.15	7.72
Avg	4.60	63.67	67.67	-2.00	1.11	28.52	16.13	7.84
SD	0.005	0.577	1.52	1.41	0.0080	0.416	0.136	0.20

Table A-9 CHN Analysis of Bio-oil (*Pinus roxburgii*) from Batch Experiment

Replications	1	2	Average	SD
C	69	69.9	69.45	0.636396
H	7.81	7.83	7.82	0.014142
N	1.43	1.44	1.435	0.007071
O	21.6	20.9	21.25	0.494975

Table A-10 Quantitative Analysis of Main Compounds in Pine Needle Bio-0il (*Pinus roxburgii*) by GC/MS

Run Time (min)	Compound	Chemical formula	Chemical group	Concentration (wt.%)
3.36	Toluene	$C_7 H_8$	Alkene	1.43
3.76	Cyclopentanone	C_5H_8O	Ketone	1.25
4.64	2-Cyclopenten-1-One	C_6H_8O	Ketone	5.35
5.28	2-Furanmethanol	$C_5H_6O_2$	Furans	1.56
5.56	1-(Acetyloxy)- 2-propanone	$C_5H_8O_3$	Ketone	2.42
6.71	2-Methyl-2-cyclopenten-1-one	C_6H_8O	Ketone	2.19
6.92	1-(1H-Imidazol-4-YL)- Ethanone	$C_5H_6N_2O$	Ketone	1.68
8.82	4-Ethyldihydro-3-methylene-, [3aR-(3a.alpha.,4.beta.,6a.alpha.)]-Furo[3,4-b]furan-2,6(3H,4H)-dione	$C_9H_{10}O_4$	Ethisolide	3.89
9.92	Phenol		Phenol	8.82
11.40	3-Methylcyclopentane-1,2-dione	$C_6H_8O_2$	Ketone	4.30
11.80	2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	Ketone	1.88
13.02	2-Methyl-phenol	C_7H_8O	Phenol	4.00
14.08	4-Methyl-phenol	C_7H_8O	Phenol	4.70
14.17	2-Methoxyphenol	$C_7H_8O_2$	Phenol	7.68
14.89	Dioctyl disulfide	$C_{16}H_{34}S_2$	-	0.56
15.10	1-Propene	C_3H_6	Alkene	0.38
17.33	2,4-Xylenol	$C_8 H_{10} O$	Phenol	1.64
18.23	4-Ethyl-phenol	$C_8H_{10}O$	Phenol	1.54
18.96	Creosol	$C_8 H_{10} O_2$	Phenol	10.51
20.13	3,4,5-Trifluorobenzyl alcohol	$C_{12}H_{15}F_3O$	Alcohol	1.13
22.84	4-Ethyl-guaiacol	$C_9 H_{12} O_2$	Phenol	7.96
23.73	1-Dodecanol	$C_{12}H_{26}O$	Alcohol	2.41
24.13	Docosane	$C_{22}H_{46}$	Alkane	3.74
24.52	1-(4-Hydroxy-3-methylphenyl) ethanone	$C_9H_{10}O_2$	Ketone	1.33
26.77	Erythro (2R,3R)-3-(4-methoxyphenyl)-1,1-BIS(P-tolylthio)propane-2,3-diol	$C_{24}H_{26}O_3S_2$	-	1.03
28.13	1-Tetradecanol	$C_{14}H_{30}O$	Alcohol	0.72
29.10	(Z)-, beta-Farnesene	$C_{15} H_{24}$	Sesquiterpenes	2.05
30.41	4-Cyclopropyl-2-methoxyphenol	$C_{10}H_{12}O_2$	Phenol	2.48
33.56	Nonanoic acid	$C_{10}H_{20}O_2$	Acid	0.33
35.40	4-Methyl-pentanoic acid	$C_6H_{12}O_2$	Acid	1.52
35.74	1,4-Difluoro-2,3,5,6-tetramethyl-benzene	$C_{10}H_{12}F_2$	Phenol	0.97
36.27	3-Ethoxy-1-propyne	C_5H_8O	Alkyne	0.75
36.58	2,2-Dimethyl-3-Hexanone	$C_8H_{16}O$	Ketone	0.75
41.30	1-Undecanol	$C_{11}H_{24}O$	Alcohol	1.09
45.09	R(-)3,7-Dimethyl-1,6-octadiene	$C_{10}H_{18}$	Alkene	1.35
47.79	Gamma.-epoxy-elemene	$C_{15}H_{24}O$	Sesquiterpenes	1.61
47.92	2-Isopropyl-1,3-dimethyl-Cyclopentane	$C_{10}H_{20}$	Alkane	1.59
59.05	Dehydroabietic acid	$C_{21}H_{30}O_2$	Acid	1.41
	Total			**100 %**

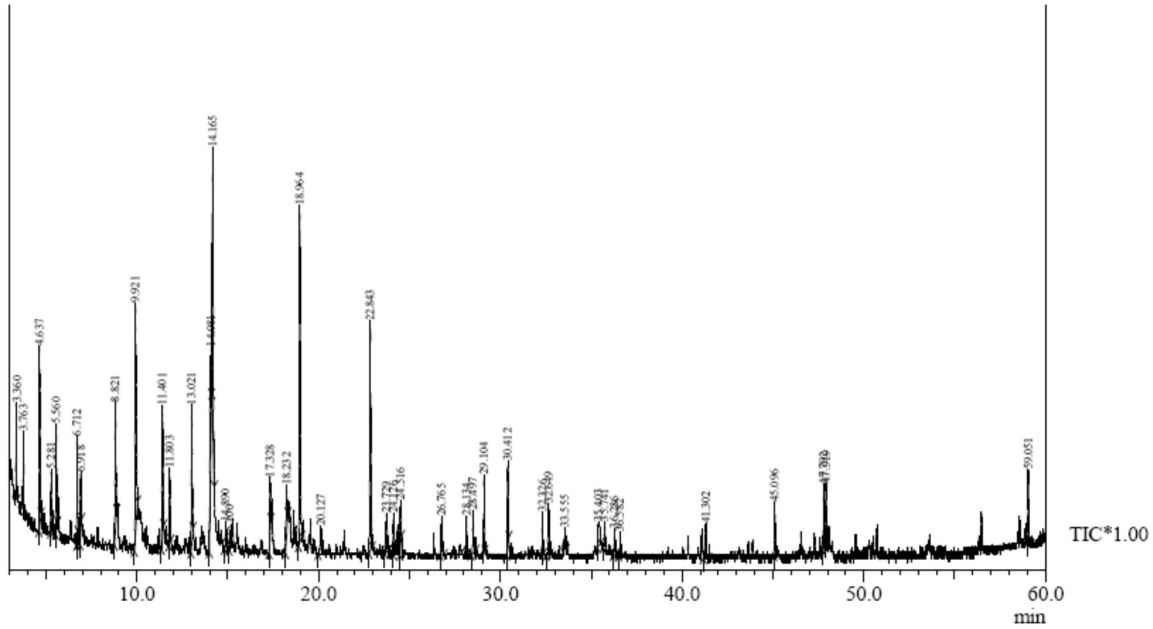

Fig. A-1 Peaks Observed in GC/MS Analyses of Pine Needle (*Pinus roxburgii*) Bio-oil

Appendix B: Data related to continuous experiments at STU, Bratislava, Slovakia

Table B-1 Raw Data from Thermogravimetric Analyser (TGA) of *Pinus cembra*

	mg	%
Sample		
wt	**11.7**	**100.00**
Ash wt	**0.73**	**6.26**
Moisture		**2.00**
Volatiles		**74.15**
Carbon	**2.79**	**17.60**

##Temp./°C	Time/min	DSC/(mW/mg)	Mass/%	Sensit./(dV/mW)	Segment	biomass	alpha	dV	dV/dT
28.759	0	4.75E-03	100	0.6455	1	11.7000	0	-0.0009	0.000133
28.593	1	4.85E-03	100.06838	0.64549	1	11.7080	-0.0009	-0.00022	3.33E-05
28.714	2	-1.09E-02	100.08547	0.6455	1	11.7100	-0.00112	0.000673	-1E-04
29.981	3	-2.72E-02	100.03419	0.64559	1	11.7040	-0.00045	0.000449	-6.7E-05
32.804	4	-5.45E-02	100	0.64577	1	11.7000	0	0.000224	-3.3E-05
37.171	5	-7.48E-02	99.98291	0.64603	1	11.6980	0.000224	0.000674	-0.0001
42.645	6	-9.64E-02	99.93162	0.64632	1	11.6920	0.000898	0	0
48.818	7	-0.12455	99.93162	0.64661	1	11.6920	0.000898	0.000898	-0.00013
55.198	8	-0.14688	99.86325	0.64686	1	11.6840	0.001796	0.001571	-0.00023
61.54	9	-0.16326	99.74359	0.64706	1	11.6700	0.003367	0.001796	-0.00027
67.704	10	-0.17471	99.60684	0.6472	1	11.6540	0.005163	0.002694	-0.0004
73.616	11	-0.1773	99.40171	0.64729	1	11.6300	0.007857	0.002245	-0.00033
79.278	12	-0.16248	99.23077	0.64734	1	11.6100	0.010102	0.002245	-0.00033
84.77	13	-0.13508	99.05983	0.64735	1	11.5900	0.012347	0.002245	-0.00033
90.181	14	-9.72E-02	98.88889	0.64733	1	11.5700	0.014591	0.001796	-0.00027
95.508	15	-6.86E-02	98.75214	0.64726	1	11.5540	0.016387	0.001122	-0.00017
100.789	16	-4.09E-02	98.66667	0.64717	1	11.5440	0.01751	0.001347	-0.0002
106.006	17	-2.28E-02	98.5641	0.64704	1	11.5320	0.018857	0.001122	-0.00017
111.166	18	-6.96E-03	98.47863	0.64688	1	11.5220	0.019979	0.001122	-0.00017
116.285	19	1.53E-02	98.39316	0.64669	1	11.5120	0.021102	0.000898	-0.00013
121.378	20	2.81E-02	98.32479	0.64647	1	11.5040	0.021999	0.001571	-0.00023
126.475	21	4.43E-02	98.20513	0.64621	1	11.4900	0.023571	0.001122	-0.00017
131.593	22	6.29E-02	98.11966	0.64592	1	11.4800	0.024693	0.001571	-0.00023
136.683	23	7.61E-02	98	0.64561	1	11.4660	0.026265	0.001796	-0.00027
141.776	24	9.34E-02	97.86325	0.64526	1	11.4500	0.028061	0.001796	-0.00027
146.845	25	0.1085	97.7265	0.64487	1	11.4340	0.029856	0.002245	-0.00033
151.904	26	0.12445	97.55556	0.64446	1	11.4140	0.032101	0.002918	-0.00043
156.965	27	0.14945	97.33333	0.64402	1	11.3880	0.03502	0.002694	-0.0004
161.976	28	0.16567	97.12821	0.64355	1	11.3640	0.037713	0.002918	-0.00043
166.995	29	0.18729	96.90598	0.64305	1	11.3380	0.040632	0.002694	-0.0004

172.016	30	0.20338	96.70085	0.64252	1	11.3140	0.043326	0.003592	-0.00053
177.046	31	0.22276	96.42735	0.64196	1	11.2820	0.046917	0.003816	-0.00057
182.065	32	0.24909	96.13675	0.64137	1	11.2480	0.050734	0.003816	-0.00057
187.053	33	0.2591	95.84615	0.64075	1	11.2140	0.05455	0.00449	-0.00067
192.058	34	0.28616	95.50427	0.6401	1	11.1740	0.059039	0.004939	-0.00073
197.073	35	0.30635	95.1282	0.63942	1	11.1300	0.063978	0.006286	-0.00093
202.074	36	0.32272	94.64957	0.63871	1	11.0740	0.070264	0.007184	-0.00107
207.057	37	0.34456	94.10256	0.63797	1	11.0100	0.077447	0.008081	-0.0012
212.036	38	0.36769	93.48718	0.63721	1	10.9380	0.085529	0.007857	-0.00117
217	39	0.38454	92.88889	0.63642	1	10.8680	0.093386	0.009428	-0.0014
221.994	40	0.41664	92.17094	0.63559	1	10.7840	0.102814	0.010102	-0.0015
226.966	41	0.44103	91.40171	0.63474	1	10.6940	0.112916	0.010326	-0.00153
231.959	42	0.4614	90.61538	0.63386	1	10.6020	0.123242	0.011449	-0.0017
236.936	43	0.48452	89.74359	0.63295	1	10.5000	0.134691	0.012796	-0.0019
241.888	44	0.51309	88.76923	0.63201	1	10.3860	0.147486	0.013918	-0.00207
246.859	45	0.5392	87.7094	0.63105	1	10.2620	0.161404	0.014816	-0.0022
251.814	46	0.56851	86.5812	0.63006	1	10.1300	0.17622	0.015489	-0.0023
256.787	47	0.59037	85.40171	0.62903	1	9.9920	0.19171	0.01751	-0.0026
261.762	48	0.62064	84.06838	0.62798	1	9.8360	0.20922	0.016387	-0.00243
266.708	49	0.64666	82.82051	0.62691	1	9.6900	0.225607	0.018183	-0.0027
271.665	50	0.67333	81.4359	0.62581	1	9.5280	0.24379	0.018632	-0.00277
276.625	51	0.70785	80.01709	0.62468	1	9.3620	0.262422	0.018857	-0.0028
281.601	52	0.73751	78.5812	0.62352	1	9.1940	0.281279	0.020877	-0.0031
286.558	53	0.77266	76.99145	0.62233	1	9.0080	0.302156	0.021775	-0.00323
291.529	54	0.81375	75.33333	0.62112	1	8.8140	0.323931	0.023346	-0.00347
296.463	55	0.84366	73.55556	0.61988	1	8.6060	0.347278	0.024693	-0.00367
301.449	56	0.88661	71.67521	0.61861	1	8.3860	0.371971	0.027612	-0.0041
306.436	57	0.93316	69.57265	0.61731	1	8.1400	0.399582	0.030754	-0.00457
311.39	58	0.95739	67.23077	0.616	1	7.8660	0.430337	0.034571	-0.00513
316.369	59	1.00723	64.59829	0.61465	1	7.5580	0.464907	0.036815	-0.00547
321.328	60	1.04914	61.79487	0.61328	1	7.2300	0.501723	0.038387	-0.0057
326.292	61	1.0818	58.87179	0.61188	1	6.8880	0.54011	0.03704	-0.0055
331.245	62	1.1263	56.05128	0.61046	1	6.5580	0.57715	0.032999	-0.0049
336.224	63	1.16004	53.53846	0.60901	1	6.2640	0.610149	0.02851	-0.00423
341.169	64	1.19182	51.36752	0.60754	1	6.0100	0.638658	0.021999	-0.00327
346.13	65	1.22306	49.69231	0.60604	1	5.8140	0.660658	0.018408	-0.00273
351.088	66	1.2503	48.2906	0.60452	1	5.6500	0.679066	0.014142	-0.0021
356.046	67	1.26951	47.21368	0.60297	1	5.5240	0.693208	0.012347	-0.00183
361.005	68	1.29278	46.2735	0.6014	1	5.4140	0.705555	0.010326	-0.00153
365.95	69	1.30795	45.48718	0.59981	1	5.3220	0.715881	0.010326	-0.00153
370.92	70	1.33003	44.70085	0.59819	1	5.2300	0.726208	0.010102	-0.0015
375.848	71	1.34886	43.93162	0.59656	1	5.1400	0.736309	0.009877	-0.00147
380.786	72	1.36643	43.17948	0.5949	1	5.0520	0.746187	0.009877	-0.00147
385.729	73	1.39317	42.42735	0.59322	1	4.9640	0.756064	0.009653	-0.00143

390.7	74	1.42014	41.69231	0.5915	1	4.8780	0.765717	0.010551	-0.00157
395.67	75	1.44114	40.88889	0.58976	1	4.7840	0.776267	0.009653	-0.00143
400.657	76	1.45667	40.15385	0.58799	1	4.6980	0.78592	0.009428	-0.0014
405.611	77	1.478	39.4359	0.58622	1	4.6140	0.795349	0.009204	-0.00137
410.593	78	1.50913	38.73504	0.58441	1	4.5320	0.804553	0.00853	-0.00127
415.529	79	1.53129	38.08547	0.58259	1	4.4560	0.813083	0.008082	-0.0012
420.508	80	1.55436	37.47008	0.58074	1	4.3840	0.821164	0.007632	-0.00113
425.466	81	1.59408	36.88889	0.57887	1	4.3160	0.828797	0.007408	-0.0011
430.446	82	1.62847	36.32478	0.57698	1	4.2500	0.836205	0.007408	-0.0011
435.427	83	1.65545	35.76068	0.57506	1	4.1840	0.843613	0.006735	-0.001
440.387	84	1.68856	35.24786	0.57313	1	4.1240	0.850347	0.007184	-0.00107
445.392	85	1.71207	34.70085	0.57116	1	4.0600	0.857531	0.005837	-0.00087
450.355	86	1.74286	34.25641	0.56919	1	4.0080	0.863367	0.005163	-0.00077
455.335	87	1.76993	33.86325	0.56719	1	3.9620	0.868531	0.005163	-0.00077
460.292	88	1.79064	33.47008	0.56518	1	3.9160	0.873694	0.00449	-0.00067
465.287	89	1.82517	33.12821	0.56314	1	3.8760	0.878183	0.004041	-0.0006
470.259	90	1.85091	32.82051	0.56108	1	3.8400	0.882224	0.003816	-0.00057
475.216	91	1.88995	32.52991	0.55902	1	3.8060	0.88604	0.004041	-0.0006
480.198	92	1.93886	32.22222	0.55692	1	3.7700	0.890081	0.003816	-0.00057
485.169	93	1.9983	31.93162	0.55481	1	3.7360	0.893897	0.003592	-0.00053
490.125	94	2.07959	31.65812	0.55269	1	3.7040	0.897489	0.002918	-0.00043
495.087	95	2.161	31.4359	0.55055	1	3.6780	0.900407	0.00202	-0.0003
500.063	96	2.2624	31.28205	0.54838	1	3.6600	0.902428	0.002694	-0.0004
505.033	97	2.34211	31.07692	0.5462	1	3.6360	0.905122	0.001796	-0.00027
509.991	98	2.39398	30.94017	0.54401	1	3.6200	0.906918	0.001796	-0.00027
514.983	99	2.42089	30.80342	0.54179	1	3.6040	0.908713	0.001796	-0.00027
519.979	100	2.42406	30.66666	0.53954	1	3.5880	0.910509	0.001571	-0.00023
524.948	101	2.42388	30.54701	0.5373	1	3.5740	0.912081	0.001571	-0.00023
529.941	102	2.4109	30.42735	0.53502	1	3.5600	0.913652	0.00202	-0.0003
534.934	103	2.38332	30.2735	0.53273	1	3.5420	0.915672	0.001571	-0.00023
539.895	104	2.3437	30.15385	0.53044	1	3.5280	0.917244	0.001571	-0.00023
544.899	105	2.3066	30.03419	0.52812	1	3.5140	0.918815	0.001347	-0.0002
549.874	106	2.27166	29.93163	0.52579	1	3.5020	0.920162	0.001347	-0.0002
554.882	107	2.24588	29.82906	0.52344	1	3.4900	0.921509	0.001571	-0.00023
559.857	108	2.22513	29.7094	0.52108	1	3.4760	0.92308	0.001347	-0.0002
564.834	109	2.20776	29.60684	0.51871	1	3.4640	0.924427	0.001347	-0.0002
569.83	110	2.20966	29.50427	0.51632	1	3.4520	0.925774	0.001347	-0.0002
574.804	111	2.20701	29.40171	0.51393	1	3.4400	0.927121	0.001122	-0.00017
579.78	112	2.2127	29.31624	0.51151	1	3.4300	0.928244	0.001347	-0.0002
584.735	113	2.2064	29.21368	0.5091	1	3.4180	0.92959	0.001347	-0.0002
589.711	114	2.19951	29.11111	0.50667	1	3.4060	0.930937	0.001571	-0.00023
594.668	115	2.20924	28.99145	0.50423	1	3.3920	0.932509	0.001122	-0.00017
599.662	116	2.22296	28.90598	0.50176	1	3.3820	0.933631	0.001571	-0.00023
604.631	117	2.22206	28.78632	0.49929	1	3.3680	0.935203	0.001571	-0.00023

609.62	118	2.21456	28.66666	0.4968	1	3.3540	0.936774	0.000898	-0.00013
614.61	119	2.22059	28.59829	0.49431	1	3.3460	0.937672	0.00202	-0.0003
619.606	120	2.21644	28.44445	0.49179	1	3.3280	0.939692	0.001572	-0.00023
624.573	121	2.21503	28.32478	0.48928	1	3.3140	0.941264	0.001347	-0.0002
629.555	122	2.22225	28.22222	0.48675	1	3.3020	0.942611	0.001796	-0.00027
634.552	123	2.22007	28.08547	0.4842	1	3.2860	0.944406	0.002245	-0.00033
639.55	124	2.2179	27.91453	0.48165	1	3.2660	0.946651	0.001796	-0.00027
644.545	125	2.22188	27.77778	0.47908	1	3.2500	0.948447	0.001796	-0.00027
649.574	126	2.22684	27.64102	0.47649	1	3.2340	0.950243	0.001796	-0.00027
654.621	127	2.24543	27.50427	0.47388	1	3.2180	0.952039	0.001122	-0.00017
659.656	128	2.24321	27.4188	0.47127	1	3.2080	0.953161	0.001571	-0.00023
664.695	129	2.23015	27.29914	0.46865	1	3.1940	0.954733	0.001122	-0.00017
669.738	130	2.22903	27.21368	0.46602	1	3.1840	0.955855	0.001123	-0.00017
674.775	131	2.21667	27.1282	0.46338	1	3.1740	0.956978	0.001122	-0.00017
679.773	132	2.2191	27.04273	0.46076	1	3.1640	0.9581	0.001122	-0.00017
684.79	133	2.20798	26.95726	0.45812	1	3.1540	0.959222	0.001347	-0.0002
689.773	134	2.20541	26.8547	0.45549	1	3.1420	0.960569	0.001122	-0.00017
694.76	135	2.19953	26.76923	0.45285	1	3.1320	0.961692	0.000898	-0.00013
699.76	136	2.1825	26.70085	0.4502	1	3.1240	0.96259	0.000898	-0.00013
704.734	137	2.17674	26.63248	0.44756	1	3.1160	0.963488	0.001122	-0.00017
709.717	138	2.16188	26.54701	0.4449	1	3.1060	0.96461	0.000898	-0.00013
714.706	139	2.15379	26.47863	0.44224	1	3.0980	0.965508	0.001122	-0.00017
719.693	140	2.14121	26.39316	0.43957	1	3.0880	0.96663	0.001122	-0.00017
724.683	141	2.13102	26.30769	0.4369	1	3.0780	0.967753	0.000898	-0.00013
729.669	142	2.17328	26.23932	0.43423	1	3.0700	0.968651	0.000674	-0.0001
734.658	143	2.15082	26.18803	0.43155	1	3.0640	0.969324	0.000673	-1E-04
739.64	144	2.14328	26.13675	0.42887	1	3.0580	0.969998	0.000898	-0.00013
744.641	145	2.12592	26.06837	0.42617	1	3.0500	0.970896	0.001122	-0.00017
749.627	146	2.11401	25.9829	0.42348	1	3.0400	0.972018	0.000673	-1E-04
754.611	147	2.09902	25.93163	0.42079	1	3.0340	0.972691	0.000898	-0.00013
759.623	148	2.07395	25.86325	0.41808	1	3.0260	0.973589	0.000898	-0.00013
764.615	149	2.06655	25.79487	0.41538	1	3.0180	0.974487	0.000898	-0.00013
769.621	150	2.04158	25.72649	0.41267	1	3.0100	0.975385	0.000673	-1E-04
774.616	151	2.0269	25.67521	0.40996	1	3.0040	0.976059	0.001122	-0.00017
779.615	152	1.98564	25.58974	0.40725	1	2.9940	0.977181	0.000898	-0.00013
784.619	153	1.9477	25.52136	0.40454	1	2.9860	0.978079	0.001122	-0.00017
789.632	154	1.91432	25.43589	0.40181	1	2.9760	0.979202	0.001122	-0.00017
794.619	155	1.87747	25.35042	0.39911	1	2.9660	0.980324	0.000898	-0.00013
799.616	156	1.85743	25.28205	0.39639	1	2.9580	0.981222	0.000758	-0.00011
800.261	157	1.06547	25.2243	0.39604	2	2.9512	0.98198	0.000879	-0.00013
800.3028	158	0.88542	25.1574	0.39602	2	2.9434	0.982859	0.000814	-0.00012
800.2906	159	0.81816	25.09545	0.39603	2	2.9362	0.983672	0.000513	-7.6E-05
800.2597	160	0.77996	25.05638	0.39604	2	2.9316	0.984185	0.000976	-0.00014
800.2287	161	0.76398	24.98204	0.39606	2	2.9229	0.985162	0.000535	-7.9E-05

800.199	162	0.74149	24.9413	0.39608	2	2.9181	0.985697	0.000973	-0.00014
800.1698	163	0.72411	24.86723	0.39609	2	2.9095	0.986669	0.000692	-0.0001
800.149	164	0.7118	24.81455	0.3961	2	2.9033	0.987361	0.00058	-8.6E-05
800.1225	165	0.70206	24.77038	0.39612	2	2.8981	0.987941	0.000506	-7.5E-05
800.0926	166	0.69593	24.73185	0.39613	2	2.8936	0.988447	0.000578	-8.6E-05
800.093	167	0.69729	24.68784	0.39613	2	2.8885	0.989025	0.0005	-7.4E-05
800.0723	168	0.67468	24.64975	0.39614	2	2.8840	0.989525	0.000827	-0.00012
800.0596	169	0.66888	24.5868	0.39615	2	2.8767	0.990352	0.000931	-0.00014
800.0582	170	0.66902	24.51593	0.39615	2	2.8684	0.991283	0.000678	-0.0001
800.0495	171	0.66542	24.4643	0.39616	2	2.8623	0.991961	0.000502	-7.5E-05
800.0545	172	0.67063	24.42607	0.39615	2	2.8579	0.992463	0.000357	-5.3E-05
800.0409	173	0.66747	24.39892	0.39616	2	2.8547	0.992819	0.000307	-4.6E-05
800.0303	174	0.6642	24.37552	0.39617	2	2.8519	0.993127	0.000562	-8.4E-05
800.0324	175	0.6552	24.33269	0.39617	2	2.8469	0.993689	0.000908	-0.00013
800.0242	176	0.65853	24.26352	0.39617	2	2.8388	0.994598	0.000508	-7.5E-05
800.023	177	0.66253	24.22487	0.39617	2	2.8343	0.995105	0.000768	-0.00011
800.0176	178	0.65291	24.16637	0.39617	2	2.8275	0.995873	0.000546	-8.1E-05
800.0108	179	0.66304	24.12482	0.39618	2	2.8226	0.996419	0.000488	-7.3E-05
800.0096	180	0.65167	24.08763	0.39618	2	2.8183	0.996907	0.000564	-8.4E-05
800.0095	181	0.65385	24.04466	0.39618	2	2.8132	0.997472	0.000849	-0.00013
800.0146	182	0.65246	23.98003	0.39618	2	2.8057	0.99832	0.000645	-9.6E-05
799.9852	183	0.65506	23.93089	0.39619	2	2.7999	0.998966	4.66E-05	-6.9E-06
799.9934	184	0.65506	23.92734	0.39619	2	2.7995	0.999012	0.000641	-9.5E-05
800.0037	185	0.66316	23.87852	0.39618	2	2.7938	0.999654	0.000346	-5.1E-05

Table B-2 Continuous Pyrolysis Experimental Data

Treatment	A	B	C	D	R1	R2	R3	R1	R2	R3	S/N
1	1	1	1	1	38.4	42.43	43.1	19.2	21.2	21.6	26.27
2	1	2	2	2	45.6	44.6	44.9	22.8	22.3	22.5	27.05
3	1	3	3	3	33.2	32.4	34.1	16.6	16.2	17.1	24.41
4	2	1	2	3	51.3	50.21	50.9	25.7	25.1	25.5	28.10
5	2	2	3	1	56.3	55.6	56.6	28.2	27.8	28.3	28.97
6	2	3	1	2	54.27	50.22	53.6	27.1	25.1	26.8	28.40
7	3	1	3	2	36.4	35.6	37.1	18.2	17.8	18.6	25.19
8	3	2	1	3	45.5	47.25	46.5	22.8	23.6	23.3	27.31
9	3	3	2	1	42.1	42.06	44.5	21.1	21.0	22.3	26.62

Table B-3 'M' Values of Experimental Data

	j=1	j=2	j=3	M
A1	26.26608	27.04896	24.4052	25.91
A2	28.09622	28.96824	28.39989	28.49
A3	25.18976	27.30976	26.61685	26.37
B1	26.26608	28.09622	25.18976	26.52
B2	27.04896	28.96824	27.30976	27.78
B3	24.4052	28.39989	26.61685	26.47
C1	26.26608	28.39989	27.30976	27.33
C2	27.04896	28.09622	26.61685	27.25
C3	24.4052	28.96824	25.18976	26.19
D1	26.26608	28.96824	26.61685	27.28
D2	27.04896	28.39989	25.18976	26.88
D3	24.4052	28.09622	27.30976	26.60

Table B-4 Main Compounds Identified by GC/MS in Pine Needle (*Pinus cembra*) Bio-oil Obtained in Continuous Pyrolysis

No.	RT (min)	Compound name	Chemical formula	Chemical group	Area (%)
1	2.285	Cyclopropane, 1,2-dimethyl-, cis-	C_5H_{10}	Alkane	0.55
2	2.754	Acetic acid	$C_2H_4O_2$	Acid	4.63
3	11.167	Phenol, 2-methoxy-	$C_7H_8O_2$	Phenol	3.89
4	12.239	Phenol, 3-ethyl-	$C_8H_{10}O$	Phenol	1.62
5	12.34	Creosol	$C_8H_{10}O_2$	Phenol	3.77
6	13.128	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	Phenol	2.74
7	13.211	Tridecane	$C_{13}H_{28}$	Alkane	0.95
8	13.446	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	Phenol	3.27
9	13.764	Eugenol	$C_{10}H_{12}O_2$	Phenol	1.89
10	13.915	1-Tetradecene	$C_{14}H_{28}$	Olefins	1.02
11	14.058	6,6-Dimethyl-10-methylene-1-oxa-spiro[4.5]decane	$C_{12}H_{20}O$	Phenol	1.75
12	14.242	Caryophyllene	$C_{15}H_{24}$	Sesquiterpene	1.36
13	14.443	Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	Phenol	2.03
14	14.502	3-(4-Isopropylphenyl)-2-methylpropionaldehyde	$C_{12}H_{16}O$	Monoterpenes	1.83
15	14.602	Naphthalene, 1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	$C_{15}H_{24}$	Sesquiterpene	2.18
16	14.703	Aromandendrene	$C_{15}H_{24}$	Terpene	2.62
17	14.862	Bicyclo[4.4.0]dec-1-ene, 2-isopropyl-5-methyl-9-methylene-	$C_{15}H_{24}$	Alkene	5.32
18	14.904	Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-, (1S-cis)-	$C_{15}H_{24}$	Alkene	3.79
19	15.013	3,7-Benzofurandiol, 2,3-dihydro-2,2-dimethyl-	$C_{10}H_{12}O_2$	Phenol	3.73
20	15.063	Naphthalene, 1,2-dihydro-3,5,8-trimethyl-	$C_{13}H_{16}$	PAH	1.74
21	15.306	1H-Cycloprop[e]azulen-7-ol, decahydro-1,1,7-trimethyl-4-methylene-, [1ar-(1a.alpha.,4a.alpha.,7.beta.,7a.beta., 7b.alpha.)]-	$C_{15}H_{24}O$	Sesquiterpene	1.67
22	15.658	1-Isopropyl-4,7-dimethyl-1,2,3,4,5,6-hexahydronaphthalene	$C_{15}H_{24}$	PAH	1.72
23	15.742	.alpha.-Cadinol	$C_{15}H_{26}O$	Sesquiterpene	1.83
24	16.194	E-9-Tetradecenoic acid	$C_{14}H_{26}O_2$	Acid	0.53
25	16.236	1-((1S,3aR,4R,7S,7aS)-4-Hydroxy-7-isopropyl-4-methyloctahydro-1H-inden-1-yl)ethanone	$C_{15}H_{26}O_2$	Kitone	1.37
26	16.613	9-Undecenol, 2,10-dimethyl-	$C_{13}H_{24}O$	Alcohol	0.63
27	16.839	Cyclohexanone, 2,2-dimethyl-5-(3-methyloxiranyl)-, [2.alpha.(R*),3.alpha.]-(.+-.)-	$C_{11}H_{18}O_2$	Kitone	0.69
28	17.015	7-Tetradecene	$C_{14}H_{28}$	Alkane	0.52
29	17.208	Z-1,6-Tridecadiene	$C_{13}H_{24}$	Alkyne	0.73
30	17.25	Oxacycloheptadecan-2-one	$C_{16}H_{30}O_2$	Kitone	2.81
31	17.585	1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-, [1S-(1.alpha.,4a.alpha.,10a.alpha.)]-	$C_{20}H_{28}O$	Aldehyde	1.54
32	17.677	1H-Indene, 2,3-dihydro-1,1-dimethyl-4-(3-methyl-3-butenyl)-	$C_{16}H_{22}$	PAH	1.91
33	17.878	Phenanthrene, 3,6-dimethyl-	$C_{16}H_{14}$	PAH	1.02
34	17.954	(E)-1-Phenyl-1,2-bis(4-methoxyphenyl)-1-propene	$C_{23}H_{22}O_2$	Phenol	6.24
35	18.054	Anthracene, 1,4-dimethoxy-	$C_{16}H_{14}O_2$	PAH	1.25
36	18.415	((1R,4S,5R)-1-Methyl-4-(prop-1-en-2-yl)spiro[4.5]dec-7-en-8-yl)methanol	$C_{15}H_{24}O$	Alcohol	3.3
37	18.515	Benzo(a)pyrene, 7,8-dihydro-	$C_{20}H_{14}O_2$	Pyrene	0.73
38	18.834	1-Phenanthrenecarboxaldehyde, 1,2,3,4,4a,9,10,10a-	$C_{20}H_{28}O$	Aldehyde	1.19

		octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-			
39	19.102	Dehydroabietic acid, methyl ester	$C_{21}H_{30}O_2$	Acid	4.18
40	19.236	1-Phenanthrenemethanol, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-	$C_{20}H_{30}O$	Alcohol	0.92
41	19.303	Retinol	$C_{20}H_{30}O$	Phenol	4.07
42	19.688	1-Naphthalenepentanoic acid, decahydro-5-(methoxycarbonyl)-.beta.,5,8a-trimethyl-2-methylene-, methyl ester, [1S-[1.alpha.(S*),4a.beta.,5.beta.,8a.alpha.]]-	$C_{15}H_{24}$	Sesquiterpene	2.35
43	19.898	Anthracene, 9-ethyl-9,10-dihydro-10-t-butyl-	$C_{20}H_{24}$	PAH	2.02
44	20.065	7-Oxodehydroabietic acid, methyl ester	$C_{21}H_{28}O_3$	Acid	1.5
45	21.063	Tricyclo[4.3.1.1(3,8)]undecane-1-carboxylic acid, methyl ester	$C_{12}H_{18}O_2$	Acid	0.4
46	22.705	Carvacrol	$C_{10}H_{14}O$	Phenol	3.09

Appendix-B

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File       :C:\msdchem\1\PROJECTS\Haidary\Sandip\biooil_DCM_500_02.D
Operator   : A.Haz
Acquired   : 19 Jun 2017  15:42     using AcqMethod HP5_MS_IDENTIFIKACIA.M
Instrument :   5975C
Sample Name: sample bio
Misc Info  : pyrolysis, 500, pine needles, DCM, 60mg/ml
Vial Number: 62
```

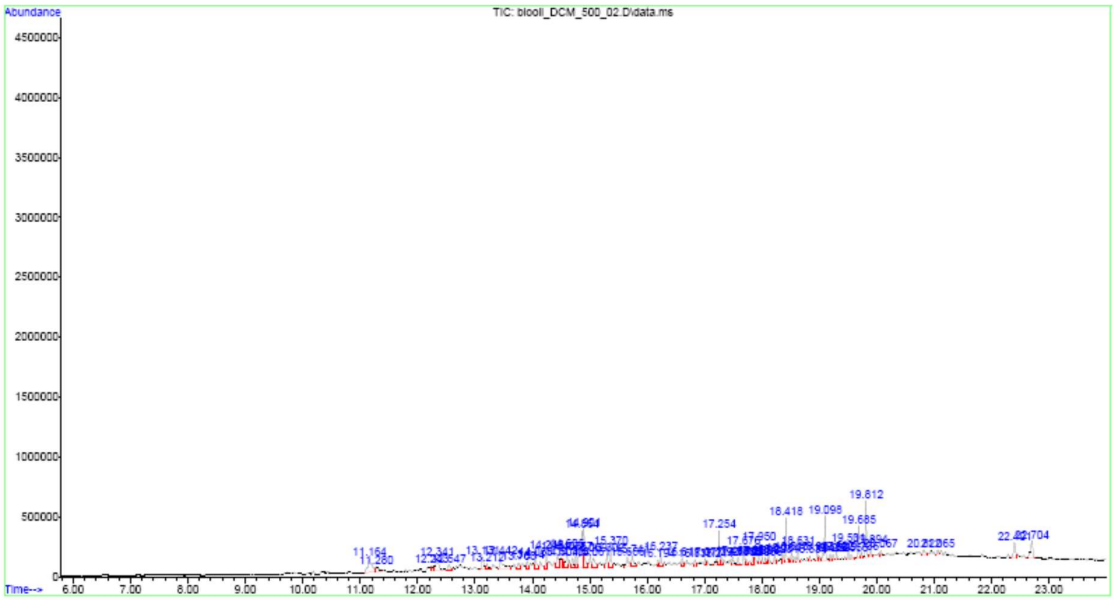

Fig. B-1 GC/MS Plot of Pine Needle (*Pinus cembra*) Bio-oil from Screw Pyrolysis

Appendix C: Data of Experiments with Biochar Production Unit

Table C-1 Temp Profile during Charring with Pine Needles (*Pinus roxburgii*) at Experimental Run 5

Time, min	Temp, °C
0	32
5	234
10	366
15	368
20	375
25	390
30	398
35	395
40	415
45	430
50	480
55	538
60	540
65	544
70	555
75	549
80	560
85	555
90	565
95	569
100	561
105	571
110	568
115	581
120	575

Table C-2 Gas Composition at Different Time Interval during Charring with Pine Needles (*Pinus roxburgii*) at Experimental Run 5

Time	H	N	CH4	CO	CO2	C2H4
20	0.32	64.50	6.11	14.45	14.28	0.34
40	3.42	64.95	3.31	13.10	14.11	1.12
60	7.67	64.05	3.32	10.29	13.45	1.18
80	8.85	64.90	3.76	9.96	11.25	1.19
100	9.40	66.74	3.92	8.57	10.16	1.21
120	11.08	68.90	2.91	6.40	9.34	1.33
Average	**6.79**	**65.67**	**3.89**	**10.46**	**12.10**	**1.06**

VITA

The author, Sandip Mandal was born on April 25, 1983 at Kushadwip in Bankura district of West Bengal State. He passed his Secondary School Examination in 1999 from West Bengal Board of Secondary Education and Higher Secondary School Examination in 2001 from West Bengal Council of Higher Secondary Education of West Bengal State. He earned his B. Tech. (Hons.) in Agricultural Engineering from Bidhan Chandra Krishi Viswavidyalaya, Nadia, West Bengal in July, 2005. He completed his M. Tech. in Agricultural Engineering with major in Farm Machinery and Power Engineering from G. B. Pant University of Agriculture and Technology, Pantnagar (Uttarakhand) in July, 2007. He secured 1st rank in ICAR-JRF (2005) and was recipient of Junior Research Fellowship during Post Graduate Studies. After that, he joined IIT, Kharagpur for PhD but left after six months. He then worked as Senior Research Fellow at Dept. of FMPE for eight months and left after being selected as Assistant Professor at CAET, AAU, Godhra, Gujarat. He worked there for one year and two months until 5 April, 2010. Then he began his career as Scientist (FMP) in Indian Council of Agricultural Research on 16 April, 2010. He joined ICAR Research Complex for NEH Region as a first posting and worked there for four years. After that he joined Central Institute of Agricultural Engineering in 2014. In July 2015, he took study leave and joined his Ph.D. at G. B. Pant University of Agriculture and Technology, Pantnagar (Uttarakhand). During his Ph.D. programme, he visited Slovakia, Czech Republic, Austria and Hungary as an International scholar at Slovak Technical University, Bratislava, Slovakia. He received Young Engineer Award from Institution of Engineers, Young Scientist Award from Indian Association of Hill Farming.

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Major	**: Farm Machinery and Power Engineering**		
Minor	**: Mechanical Engineering**		
Thesis Title	**: Optimization of Process Parameters for Conversion of Pine Needles to Bio-Oil, Biochar and Product Gas through Batch and Continuous Pyrolysis**		
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ABSTRACT

Experiments were conducted to convert pine needles into bio-oil, biochar and product gas through pyrolysis as an alternate way to use pine needles to reduce forest fire. Batch pyrolysis of pine needles was carried out in a stainless steel tubular reactor using CO_2 as sweep gas. Process parameters such as pyrolysis temperature, gas flow rate, vapour cooling temperature, heating rate, holding time were optimized by employing central composite design (CCD) in Response Surface Methodology (RSM) for the batch process. Continuous pyrolysis experiments were conducted in a screw reactor using N_2 as sweep gas. Process parameters were optimized by Taguchi's L_9 Orthogonal Array. A batch type biochar production unit was also designed and developed to convert pine needles to biochar in bulk. Chemical characterization of bio-oil was conducted using Fourier Transform Infrared (FTIR) spectroscopy and gas chromatographic/mass spectroscopy (GC/MS). Fuel properties of bio-oil and biochar were determined using ASTM standard methods. Product gas composition was determined using gas chromatography. Bio-oil was produced from pine needles with a recovery rate of 26.7 wt.% in batch pyrolysis experiment and 28.98% in screw pyrolysis. The adaptation of response surface methodology indicated the optimum conditions for maximum bio-oil yield at pyrolysis temperature of 547°C, 1.85 l min^{-1} gas flow rate, 15°C vapour cooling temperature and 50°C min^{-1} heating rate. The optimum conditions in screw pyrolysis experiments were pyrolysis temperature of 500°C, particle size of 1.25 – 2.0 mm, residence time of 15 min and N_2 gas flow rate of 30 l h^{-1}. Bio-oil produced at optimum condition had a high heating value of 28.52 MJ kg^{-1} and had less oxygen content than parent material. The GC/MS analysis showed presence of about 50% phenolic compounds and many other valuable compounds. Conversion efficiency of the biochar production unit with pine needle as substrate was found to be 28.88% at 80% loading, 12% moisture and air flow rate of 40 m^3 h^{-1}. Bio-char had a higher pH value and high heating value with suitability for both acid soil ameliorant and solid bio-fuel. The average composition of product gas was 6.8% H_2, 65.7% N_2, 3.9% CH_4, 10.46% CO, 12.1% CO_2 and 1.06% C_2H_4 with a high heating value of 4.16 MJ Nm^{-3}. The quantitative results of energy analysis indicated that the all three processes could be used to produce bio-oil, biochar and product gases to recover energy from pine needles. Among three processes, screw pyrolysis process was most energy efficient.

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शोध का शीर्षक	: पाइन के पत्ते का पाइरोलिसिस के माध्यम से जैव-तेल, बायोचार और उत्पाद गैस में रूपांतरण के लिए प्रक्रिया मापदंडों का अनुकूलन		
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सारांश

जंगल की आग को कम करने के लिए पाइन (चीढ़) के पत्ते का इस्तेमाल करने के वैकल्पिक मार्ग के रूप में पाइन के पत्ते का जैव-तेल, बायोचार और उत्पाद गैस में पाइरोलिसिस के माध्यम का प्रयोग किया गया। पाइन के पत्ते का बैच पाइरोलिसिस एक स्टेनलेस स्टील ट्यूबलर रिएक्टर में कार्बन डाइऑक्साइड का उपयोग स्वीप गैस के रूप में किया गया था। बैच प्रक्रिया के लिए रिस्पांस सर्फेस मेथोडोलॉजी (आरएसएम) में सेंट्रल कम्पोजिट डिज़ाइन (सीसीडी) को नियोजित करके पाइरोलिसिस तापमान, गैस प्रवाह दर, वाष्प ठंडा करने का तापमान, हीटिंग दर, प्रसंस्करण समय जैसे परिचालन मापदंडों को अनुकूलित किया गया था। सतत पाइरोलिसिस प्रयोगों को एक निरंतर रिएक्टर में आयोजित किया गया, जहाँ नाइट्रोजन को स्वीप गैस के रूप में उपयोग किया गया था। प्रक्रिया मापदंडों को टैगुची के एल-9 ऑर्थोगोनल अर्रे द्वारा अनुकूलित किया गया था। एक बैच प्रकार की बायोचार उत्पादन इकाई को भी डिजाइन किया गया था और थोक में पाइन के पत्ते को बायोचार में बदलने के लिए तैयार किया गया था। जैव तेल के रासायनिक लक्षण वर्णन फूरियर ट्रांसफ़ॉर्म इन्फ्रारेड (एफटीआईआर) स्पेक्ट्रोस्कोपी और गैस क्रोमैटोग्राफिक / मास स्पेक्ट्रोस्कोपी (जीसी / एमएस) के जरिए किया गया था। जैव-तेल और बायोचार के ईंधन गुणों को एएसटीएम मानक तरीकों का उपयोग कर निर्धारित किया गया था। गैस क्रोमैटोग्राफी का उपयोग करके उत्पाद गैस संरचना निर्धारित की गई थी। बैच पाइरोलिसिस प्रयोग में 26.7% की एक वसूली दर और स्क्रू पायरोलिसिस में 28.98% की जैव तेल का उत्पादन किया गया। प्रतिक्रिया सतह पद्धति का अनुकूलन 547° सेंटीग्रेड पायरोलिसिस तापमान, 1.85 ली प्रति मिन गैस प्रवाह दर, 15° सेंटीग्रेड वाष्प ठंडा तापमान और 50° सेंटीग्रेड प्रति मिन हीटिंग दर के पीयरोलिसिस तापमान पर अधिकतम जैव-तेल उपज के लिए इष्टतम स्थितियों को दर्शाता है। स्क्रू प्योरोलिसिस प्रयोगों में इष्टतम स्थितियों में 500° सी का पायरोलिसिस तापमान, 1.25 - 2.0 मिमी के कण आकार, 15 मिनट का निवास समय और 30 ली प्रति घंटा की नाइट्रोजन गैस प्रवाह दर थे। इष्टतम हालत में उत्पादित जैव-तेल में 28.52 मेगा जुल प्रति किग्रा के उच्च ताप मूल्य था और मूल सामग्री से कम ऑक्सीजन सामग्री थी। जीसी / एमएस विश्लेषण ने लगभग 50% फीनॉलिक यौगिकों और कई अन्य मूल्यवान यौगिकों की उपस्थिति दिखायी। सब्सट्रेट के रूप में पाइन के पत्ते के साथ बायोचार उत्पादन इकाई की रूपांतरण क्षमता 80% लोडिंग, 12% नमी और 40 घन मीटर प्रति घंटा की वायु प्रवाह दर पर 28.88% थी। बायोचार में उच्च पीएच मान और उच्च ताप मूल्य था, जो कि दोनों एसिड मिट्टी के सुधार और ठोस जैव-ईंधन के लिए उपयुक्त थे। उत्पाद गैस की औसत संरचना 6.8% हाइड्रोजन, 65.7% नाइट्रोजन, 3.9% मीथेन, 10.46% कार्बन मोनोऑक्साइड, 12.1% कार्बन डाइआक्साइड और 1.06% अन्य गैस थे। ऊर्जा विश्लेषण के मात्रात्मक परिणामों ने संकेत दिया कि सभी तीन प्रक्रियाएं पाइन के पत्ते से ऊर्जा प्राप्त करने के लिए जैव-तेल, बायोचार और उत्पाद गैसों के उत्पादन के लिए इस्तेमाल की जा सकती हैं। तीन प्रक्रियाओं में, स्क्रू पायरोलिसिस प्रक्रिया सबसे ऊर्जा कुशल थी।

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