MICROWAVE ASSISTED PYROLYSIS OF FOOD WASTE TO BIOCHAR AND BIOFUELS

Thesis

Submitted in partial fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

HUCHAPPA KADLIMATTI

(121159CH12P02)

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA

SURATHKAL, MANGALORE-575025

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DECLARATION
by the
Ph.D. Research Scholar

I hereby *declare* that the Research Thesis entitled **“Microwave assisted Pyrolysis of Food waste to Biochar and Biofuels”** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Chemical Engineering**, is a *bonafide report of the research work carried out by me*. The material contained in this **Research Thesis** has not been submitted to any University or Institution for the award of any degree.

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Register No. CH12P02

Department of Chemical Engineering

National Institute of Technology Karnataka, Surathkal

Place: NITK-Surathkal
Date: 31-12-2019

CERTIFICATE

This is to *certify* that the Research Thesis entitled **"Microwave assisted Pyrolysis of Food waste to Biochar and Biofuels"** submitted by **HUCHAPPA KADLIMATTI** (Register Number: **CH12P02**) as the record of the research work carried out by him, is *accepted as the Research Thesis submission* in partial fulfilment of the requirements for the award of degree of **Doctor of Philosophy**.

Research Guide(s)

Dr. Raj Mohan B. **Dr. Saidutta M.B.**

Chairman - DRPC

Dedicated to my late grand mother

Smt. Gangamma H. Kadlimatti

and

Late brother

Sri. Siddramappa M. Kadlimatti

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ABSTRACT

Mangalore is one of the fast growing cities of India and situated on the west coast of the Indian peninsula covering an area of 132.45 sq-km. The city is generating approximately around 312 tons of MSW per day of which 40% is the food waste (125 tons per day). At present this MSW is land filled leading to serious environmental and health problems. The given research thesis aims to (i) quantify and characterize the food waste generated in commercial and residential complexes of Mangalore city, (ii) pyrolysis of food waste with the assistance of microwave irradiation, optimization of the process parameters for better yields and (iii) characterization of the pyrolysis products using ASTM standard methods.

Preliminary pyrolysis experiments were carried out to decide about the operating ranges for the pyrolysis temperature, residence time and nitrogen flow rate. Based on the thermogravimetric analysis (TGA) and preliminary pyrolysis experiments, the operating ranges for the time, nitrogen flow rate and temperature to carry out pyrolysis experiments were 25 to 35 min., 40 to 60 mL min^{-1} and 350 to 450 ºC respectively to design the experiments by response surface methodology (RSM).

Pyrolysis yields of 30. 24 wt. % (bio-oil), 60.03 wt. % (biochar) and 9.73 wt. % (biogas) were obtained under the optimum pyrolysis conditions of 400 ºC temperature, 30 min. residence time and nitrogen flow rate of 50 mL min^{-1} respectively. The actual values of the operating parameters namely temperature, time and nitrogen flow rate and the responses for twenty experiments were used for the prediction of bio-oil, biochar and fixed carbon models. The regression models with 95% confidence level resulted in the high value of R^2 = 95.4% with R^2 adjusted = 91.2% indicated a very good or excellent fit of the data to the bio-oil model, high value of R^2 = 92.9% with R^2 adjusted = 86.4% indicated a very good or excellent fit of the data to the biochar model and high value of R^2 = 90.3% with R^2 adjusted = 81.60% indicated a very good or excellent fit of the data to the fixed carbon content model respectively. Bio-oil model was analyzed statistically by using experimental data and analysis of variance (ANNOVA). The linear terms such as temperature, time and nitrogen flow rate were having the positive effect to increase the bio-oil yield when these variables are increased, whereas, square terms were having negative effect and decreased the bio-oil yield. The predicted value of the bio-oil yield was 0.02 wt. % less than the experimental value. Main functional groups as detected by the Fourier transform infrared (FTIR) analysis are alcohols, alkenes, aromatic compounds, primary and secondary amines, carboxylic acid, esters and phenols. GC-MS analysis was carried out to find the major compounds present in the bio-oil. GC-MS analysis identified 11 major compounds out of more than 500 compounds those were present in the bio-oil. Compounds such as oxygenated and non-oxygenated compounds, nitrogenated compounds and other compounds such as phosphine, methyl-, propane, 2-fluoro-, (2-hydroxyethyl) trimethylsilyl methyl sulfide, and 1,3-bis(2-hydroxymethyl) urea were identified by the GC-MS analysis. Though the heating value of the bio-oil was 23.94 MJ kg^{-1} it cannot be used as a bio-fuel, as it contains more water as well as nitrogenated compounds. However, bio-oil obtained can be upgraded and blended with diesel to use as a fuel through further investigation.

Biochar and fixed carbon content model were analyzed statistically by using experimental data and ANNOVA. Linear and square terms were significant to effect biochar production followed by the fixed carbon content whereas the interaction terms were less significant parameters. The predicted value of the biochar was 0.05 wt. % less than experimental value, whereas, the fixed carbon content was 0.03 wt. % less than the experimental value. Biochar obtained under the minimum pyrolysis conditions of 400 ºC temperature, 30 min time and 50 mL min^{-1} of nitrogen flow rate at a power level of 450 W was used for characterization. Higher heating value (HHV) of the biochar was 33.35 MJ kg^{-1}. HHV as calculated by the bomb calorimeter (33.35 MJkg^{-1}) was higher than that of the Dulong formula (27.79 MJkg^{-1}) value as the latter did not include the dissociation effects. HHV of the biochar was more than that of the FWS due to reduction of some higher heating value hydrocarbons.

Keywords: Food waste, microwave pyrolysis, bio-oil, biochar, fixed carbon, optimization and response surface methodology.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AEC	Anion exchange capacity
ANNOVA	Analysis of variance
AP	Air potato
BC	Undigested bagasse biochar
BCSC	Black cumin seed cake
BET	Brunauer-Emmet-Teller
BGAB	Blue-green algae blooms
BOD	Biological oxygen demand
BP	Brazilian Pepper
CCD	Central composite design
CCRD	Central composite rotatable design
CEC	Cation exchange capacity
CF	Coconut fibers
CR	Cassava rhizome
CSBR	Conical spouted bed reactor
CSS	Cherry seeds shells
CV	Calorific value
CWS	Cherry seeds
CSS	Cherry seeds shells
DBC	Digested bagasse biochar
DDGS	Distillers dried grain with solubles
DFW	Digested food waste
DOE	Design of experiments

DPG	Date palm glaich
DPL	Date palm leaflets
DPR	Date palm rachis
DPW	Tunisian date palm wastes
DSTC	Digested sugar beet tailing biochar
DTA	Differential thermal analysis
DTG	Differential thermogravimetric
ECR	Exhausted coffee residue
EFB	Empty fruit bunch/bunches
EG	Ethylene glycol
EL	Eucalyptus leaves
EM	Electromagnetic
ERPC	Energy ratio of production to consumption
FTIR	Fourier transform infrared spectroscopy
FWP	Food waste particles
FWS	Food waste samples
GC	Gas chromatograph
GC-MS	Gas chromatography-mass spectrometry
GDP	Gross domestic product
HHV	Higher heating value
HPO	Hydropyrolysis oil
HTC	Hydrothermal carbonization
HVF	Hot vapor filtration
IR	Infrared

JCL	Jatropha curcas L
LDPE	Low-density polyethylene
LEMA	Lipid extracted microalgae
LHV	Lower heating value
LTP	Low temperature pyrolysis
MADL	Microwave-assisted direct liquefaction
MAP	Microwave assisted pyrolysis
MBM	Meat-and-bone-meal
MEP	Microwave-enhanced pyrolysis
MFSC	Mesua ferrea seed cover
MIP	Microwave induced pyrolysis
MPW	Municipal plastic waste
MSS	Municipal sewage sludge
MSW	Municipal solid waste
MW	Multimode microwave / Microwave
OPF	Oil palm fiber
OPFP	Oil palm fiber pellet
OPS	Oil palm shell
PC	Pig compost
PCG	Prairie cordgrass
PCR	Pyrolysis centrifuge reactor
PE	Polyethylene
PGSC	Pongamia glabra seed cover
PKO	Palm kernel shell oil

PKS	Palm kernel shell
RFW	Raw food waste
RH	Rice husks
RSM	Response surface methodology
SADPM	Separated solid fraction of anaerobically digested pig manure
SEM-EDS	Scanning electron microscopy – Energy dispersive spectroscopy
SPC	Safflower seed press cake
SRC	Short rotation coppice
SS	Sewage sludge
STC	Sugar beet tailing biochar
SWO	Sago wastes oil
TG	Thermogravimetric
TG/DTG	Thermogravimetric/differential thermogravimetric analyses
TGA	Thermal gravimetric analysis
THR	Total heat release
TPD	Tones per day
TPO	Temperature-programmed oxidation
VOC	Volatile organic carbon
WC	Wood chip / chips
WCO	Wood chips oil
WP	Wood pellets
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

The rising energy demands as a result of faster growth in the global population and never ending expansion of industries, development of commercial as well as new service sectors that have caused increased focus over greenhouse gas emissions and worldwide soil degradation. At the same time energy resources which are fulfilling our present day energy requirements are decreasing at an unimaginable manner. This has forced the human beings to search alternate sources of energy and suitable harnessing methodologies. Declining fossil fuel resources can be supplemented by harnessing energy from the biomass and it has been recognized as a global major renewable energy source. Major renewable energy source which has the potential to supplement fossil fuels is “biomass” and believed to supply 14% of world’s energy requirement as a fourth largest source. Carbohydrates are the major constituents of biomass and these are the elements of carbon, oxygen and hydrogen. Biomass is the potential renewable source of energy which has been believed to play an important role, on a global scale, in the future energy systems (Capunitan and Capareda, 2012; Özçimenand Karaosmanoglu, 2004; Abnisa et al. 2011; Azargohar et al. 2014; Demiral et al. 2012).In regard to this research and development of renewable energy sources has increased recently due to crisis in the supply of conventional fuels and enhanced release of greenhouse gas emissions due to burning of fossil fuels. The new sources of energy can be renewed within a short period of time and simultaneously reduce the burden of fossil fuel crisis. Moreover, these sources are environmentally cleaner sources of energy (Abnisa et al. 2011; Amutio et al. 2012; Bok et al. 2013; Demiral and Ayan 2011; Demirbas et al. 2006; Haykiri-Acma et al. 2006).

Energy self-sufficiency can be attained by adopting the thermochemical conversion of biomass which has been believed the most suitable path. This includes carbonization, liquefaction, gasification and combustion. Pyrolysis is one of the most popular thermal conversion processes among the different processes of energy production from biomass.

Pyrolysis is the process of heating the biomass in the pyrolytic reactor with limited supply of oxygen or absence of air to produce solid (char), liquid (bio-oil) or gaseous products (Inyang et al. 2010; Ozcimen and Karaosmanoglu, 2004).

1.1. Biowastes - An alternate source of energy

The various types of biomass resources available for conversion in to energy includes organic portion of municipal solid waste (MSW), dedicated energy crops, agricultural crop residues, forestry residues, wood waste, agricultural by-products, industrial wastewater sludge and manures. Biomass is the major sources of energy in the developing and developed countries contributing about 64% of the primary energy supply. The abundant quantity of lignocellulosic biomass available globally has proved it as a potential feedstock for biofuel production. Biomass mainly composed of lignin, hemicellulose, cellulose, and small amounts of extractives having an average elemental composition of $CH_{1.4}O_{0.6}$. The proportions and composition of these constituents vary with the type of biomass. The various characteristics such as volatiles, fixed carbon, calorific value, ash content, moisture content, oxygen, hydrogen, nitrogen and ratio of lignin to cellulose ratio are the deciding factors to select the particular type of biomass as a potential feed material for biofuel production (Ger'cel, 2002; Easterly and Burnham, 1996; Inyang et al. 2010; Dukua et al. 2011; Ahmad et al. 2012; Borges et al. 2014).

1.2. Scenario of biowaste generation

The two major problems faced by the waste sector are the availability and qualities of annual data. The data are lacking for many countries, data quality is variable, definitions are not uniform, and inter annual variability is often not well quantified (Bogner et al. 2007). Hence it is very difficult to calculate globally, the biowastes quantitatively and qualitatively.

Population growth, industrialization, urbanization and economic growth resulted in the significant increase of MSW generation has been recorded worldwide. MSW generation, in terms of kg/capita/day, has shown a positive correlation with economic development at world scale. Industrial growth is the cause for the migration of people from villages to urban centers increasing the urban population. Annual increase in the waste generation has been recorded in proportion to urbanization and rise in population. Tremendous increase in per capita generation of MSW has been recorded with social status and improved life style of population in urban centers (Sharholy et al. 2007). Disposal of MSW generated has become highly challenging every day and is a ‘critical issue’ with respect to availability of disposal land (Idris et al. 2004).

Total global share of the Indian population, as per 2011census, is 17.5% with a population of over 1.21 billion. Among the total population of 1.21 billion, Indian urban population is 377 million. Total percentage of urban population is around 31.16% as per provisional figures of Indian census 2011. Seasonal food habits, degree of commercial activities followed by the standard of living are the main factors affecting the MSW generation rate. Design of collection and disposal systems mainly depends upon the MSW generation rate and variation in quantity. At present Indian cities are experiencing eight-fold increase in the MSW generation rate compared to 1947 generation rate. (Sharholy et al. 2008).

MSW generation rate in Indian urban areas is more than that of the suburban cities. The per capita MSW generation rate ranges from 0.2 to 0.5 kg d^{-1}. Estimated per capita annual increase in MSW generation rate for Indian cities is from 1 to 1.33%. Compared to western countries, MSW differs greatly in India with respect to hazardous nature and composition. Main categories of MSW found are construction and demolition waste, street sweeping waste, commercial waste, institutional waste, industrial waste, sanitation waste rubbish and food waste (40%). MSW contains recyclables (paper, plastic, glass, metals, etc.), soiled waste (blood stained cotton, sanitary napkins, disposable syringes), toxic substances (paints, pesticides, used batteries, medicines), and compostable organic matter (fruit and vegetable peels, food waste). MSW composition is determined, on a wet basis, based on the generation sources. It is mainly composed of higher organic fraction (40–60%), fine earth and ash (30–40%), paper (3–6%) and metals, glass and plastic (each less than 1%). The lower calorific value ranges from 3349 to 4186kJkg^{-1} and C/N ratio ranges between 20 and30 (Kaushal et al. 2012).

1.3. Agro waste residues

Any human activity results in a residue known as waste. Agro waste is the residue generated by the agricultural activities. The various sources of agro wastes are crop wastes, plant residues, animal wastes etc. (Singh and Singh, 2012). Dukua et al. (2011) have reported that, around 500 million tons of agricultural residues have been generated annually on a global scale. The low ash content and high calorific values of the agro wastes indicates their use as feed stocks to produce biochar and biofuels.

Agricultural residues are believed to be the potential renewable energy resources to produce bio-gas from anaerobic digestion, bio-oil from pyrolysis, and bio-char from carbonization and slow pyrolysis processes. Among the various energy production processes using biowastes, pyrolysis is the most popular thermal conversion process. Agro wastes helps in reducing the total emissions per unit energy produced though the heating value is much lower than that of the coal. Hence the agro wastes are the lowest-cost option for reducing greenhouse gas emissions (Demirbas et al. 2006).

1.4. Forestry residues

Forest products industry residues can be classified into two main categories namely industrial byproducts, generated as a result of processing of pulpwood, plywood, timber, particleboard, and logging residues, generated from logging operations, e.g. from final fallings. Generally, less than 66% of the forest volume will be removed for further processing from the forest. Remaining quantity which is left on-site such as split firewood or fuel chips either burnt on-site or utilized as fuel. Nearly 28% of the tree becomes sawn wood after processing and the remainder will be treated as forest residues (Parikka, 2004).

1.5. Urban residues

Urban wastes which have been believed as the potential resources of energy can be classified into livestock and poultry wastes, MSW, sewage sludge and industrial waste water (Dukua et al. 2011).

Global population explosion and industrial growth followed by the migration of people from villages to cities all over the world resulted in the generation of thousands of tons MSW. The generation rate of MSW in the near future is further expected to increase significantly (Gidde et al. 2008).

Table 1.1. Urban populations of Asian countries and per capita MSW generation (Khajuria et al. 2010)

Country	**Urban population (% in total)**			**MSW generation per capita (kg d^{-1})**		
	2007	**2010**	**2030**	**2007**	**2010**	**2030**
India	12.28	17.35	32.43	0.75	0.79	0.97
Nepal	15.25	21.87	38.65	0.32	0.35	0.44
Pakistan	17.93	25.10	45.00	0.39	0.44	0.59
Bangladesh	18.03	25.37	44.45	0.67	0.73	0.98
Srilanka	12.27	17.35	32.43	0.56	0.59	0.73

Generally, the main constituents of the generated MSW are similar throughout the world but the proportions, density and quantity generated vary from nation to nation depending upon the culture, income level, life style, tradition and geographical locations (Khatib, 2011).In Asia, rapid urbanization has resulted in the economic growth dramatically, as a result of which the MSW generation rate has increased proportionately with the growth of urban population and is as shown in the Table 1.1 (Khajuria et al. 2010).

Increased population and gross domestic product (GDP)in India have resulted in the higher amounts of solid waste generated annually. Around 300 million tons of MSW is anticipated by 2047.Table 1.2 and Table 1.3 shows the population wise physical and chemical characteristics of MSW generated in Indian cities (Singh et al. 2011).

Table 1.2. Population wise physical characteristics of MSW generated in Indian cities (Singh et al. 2011)

Population range (million)	Biodegradable matter (Wt. %.)	Metal (Wt. %)	Inert material (Wt. %)	Paper (Wt. %)	Rubber, leather and synthetics (Wt. %)	Glass (Wt. %)
0.1–0.5	44.57	0.33	43.59	2.91	0.78	0.56
0.5–1.0	40.04	0.32	48.38	2.95	0.73	0.56
1.0–2.0	38.95	0.49	44.73	4.71	0.71	0.46
2.0–5.0	56.57	0.59	40.07	3.18	0.48	0.48
5.0 and above	30.84	0.80	53.90	6.43	0.28	0.94

Table 1.3. Population wise chemical characteristics of MSW generated in Indian cities (Singh et al. 2011).

Population range (million)	Nitrogen as total N	Phosphorus as P_2O_5	Potassium as K_2O	C/N ratio	Calorific value ($kcalkg^{-1}$)
0.1–0.5	0.71	0.63	0.83	30.94	1009.89
0.5–1.0	0.66	0.56	0.69	21.13	900.61
1.0–2.0	0.64	0.82	0.72	23.68	980.05
2.0–5.0	0.56	0.69	0.78	22.45	907.18
5.0 and above	0.56	0.52	0.52	30.11	800.70

1.5.1. Industrial waste water and sewage sludge

Sewage sludge is the residues generated as a result of treatment of waste water, released from various sources such as industries, street runoff, medical facilities, homes, business and shopping malls, at centralized wastewater treatment plants. This sewage sludge can be used assoil fertilizer as it contains nutrients and organic matter (Harrison et al. 2006). Since sewage contains nearly 75% of organic matter by weight, it can be a suitable feed stock for biofuel production after suitable pretreatment (Ronald et al. 2008).

1.5.2. Livestock and poultry residues

In the recent decades the poultry industry has become one of the fastest growing and largest agro-based industries all over the globe. This is because of the increased demand for poultry meat due to its low cholesterol content and universal acceptance by most of the societies. But at the same time the poultry industry is facing the problem of accumulation and disposal of large quantities waste generated as result of intensive production (Bolan et al. 2010).

The main constituents of poultry litter are the bedding material and manure such as sawdust, straw, wood shavings, shredded sugar cane, peanut hulls, and other dry absorbent low-cost organic materials. Since the conversion of poultry litter in to energy is free from carbon dioxide, the generation of power using animal biomass can be chosen as one of the better alternatives for the waste disposal problem (Perera et al. 2010). Careful management and exploitation of poultry residue can become a very good resource for heating, power generation and biofuel production though the ash content ranges from 15 to 20% (Dukua et al. 2011).

1.5.3. Food waste

Globally around 1.3 billion tons of food wasted every year which is believed to be 33.33% of the food produced for human consumption. It is wasted right from initial agricultural production level to final household consumption. The food which is wasted to a greater extent and simply thrown away in medium- and high-income countries is believed to be suitable for human consumption. But in lower income nations much less food is wasted at the consumer level where as the main wastage is experienced during the early as well as middle stages of the food supply chain.

Per capita food losses and waste at consumption and pre-consumption across the world is shown in the Fig. 1.1. The total per capita food production for consumption in Sub-Saharan Africa, South/Southeast Asia is 460 kgy^{-1}while in Europe and North-America is 900 kgy^{-1}. The total loss of food during harvesting for North-America and Europe region is 120-170 kgy^{-1} and South/Southeast Asia and Sub-Saharan Africa region is 280-300 kgy^{-1}.

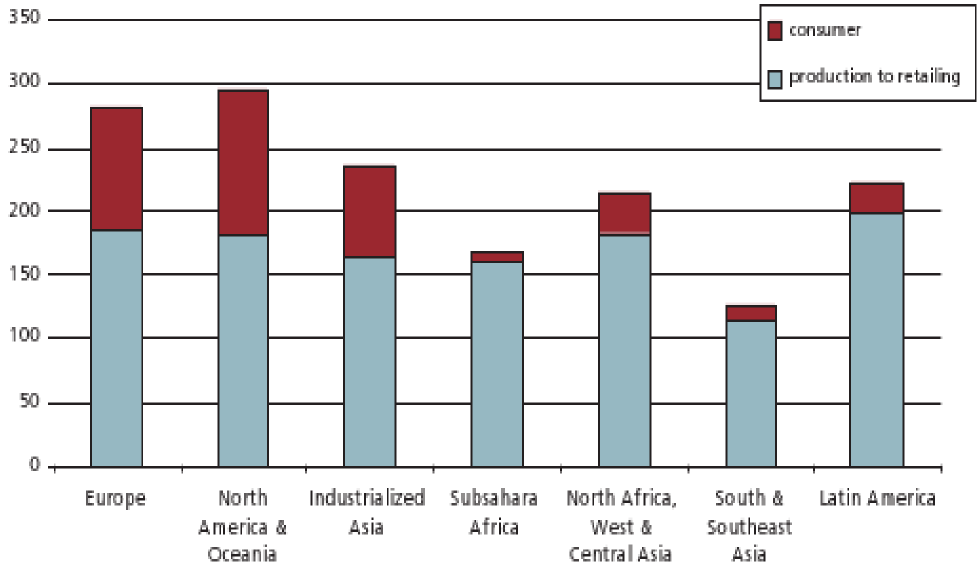


Fig.1.1. Per capita food losses and waste at consumption and pre-consumption stages across the world (Gustavsson et al. 2011)

The per capita food waste in North-America and Europe by consumers is about 95-115 kgy^{-1} whereas the quantity of food loss in South/Southeast Asia and sub-Saharan Africa is only 6-11 kgy^{-1}. Nearly 40% of the food losses occur in developing nations at post-harvest and processing levels, but the same quantity of food loss occurs in industrialized nations at retail and consumer levels (Gustavsson et al. 2011).

1.6. Waste disposal problems

Serious environmental degradation and health problems are being observed in many metropolitan cities of India due to direct disposal of more than 90% of MSW on land in an unscientific manner. This type of disposal has resulted in the leaching of heavy metals into the coastal waters and corrosive acids (leachate) in natural drinking water bodies. Presently cities like Delhi are facing shortage of lands for disposal of MSW.

Though the sanitary land filling is one of the most accepted methods in some of the metros, considering the energy values of MSW it is better to convert this MSW completely or part of it to produce biochar and biofuels by the pyrolysis process. The estimated generation of MSW and its potential for power generation is shown in Table 1.4. Food waste dumping in a landfill leads to environmental problems. Increased methane (CH_4) gas production by volume is being observed due to land filled waste. Decomposition of dumped food waste causes public annoyance due to bad odour in addition to attracting vermin, flies and forming germs.

Table 1.4. Estimated potential of MSW to energy (Singh et al. 2011)

Year	Projected MSW generation (TPD)	Potential for power generation (MWe)
2007	148,000	2550
2012	215,000	3650
2017	304,000	5200

Landfill leachate formation is another problem associated with the waste dumping sites that either doesn’t have liners or leakage through improper/breakage of liners. This liquid(leachate) is formed due to biological degradation of vegetative/food materials in the landfill and enters into the ground water thereby contaminating the ground water and increasing its biological oxygen demand (BOD) levels (Ahmed and Gupta, 2010). Environment friendly management of food waste is one of the present day requirements using suitable treatment technologies as it is a part of the MSW constituting about 40%. Food waste offers a potential feedstock for biomass pyrolysis to produce biofuels as it is having a higher energy content. Food waste pyrolysis helps to solve two major problems, reduction of landfill problems and helps to recover energy at the same time. Biochar and biofuels production from this biomass waste is of much importance due to its use for other applications and carbon sequestration (Singh et al. 2011).

1.7. Biomass conversion technologies

Tremendous research has been carried out across the globe to derive energy from biomass and especial convert the biological wastes into biofuels or value added products. This is mainly because of the concerns over greenhouse gas emissions and rising energy demands, as well as worldwide soil degradation due to dumping of waste in landfills. Thermal pyrolysis of biomass is one of the popular bioenergy conversion technologies as it produces biochar (charcoal) in addition to biofuels. The major difference between the alternate ways of converting biomass into energy via pyrolysis is that, a carbon-rich solid byproduct known as biochar is also produced along with the biofuels (Fig. 1.2).

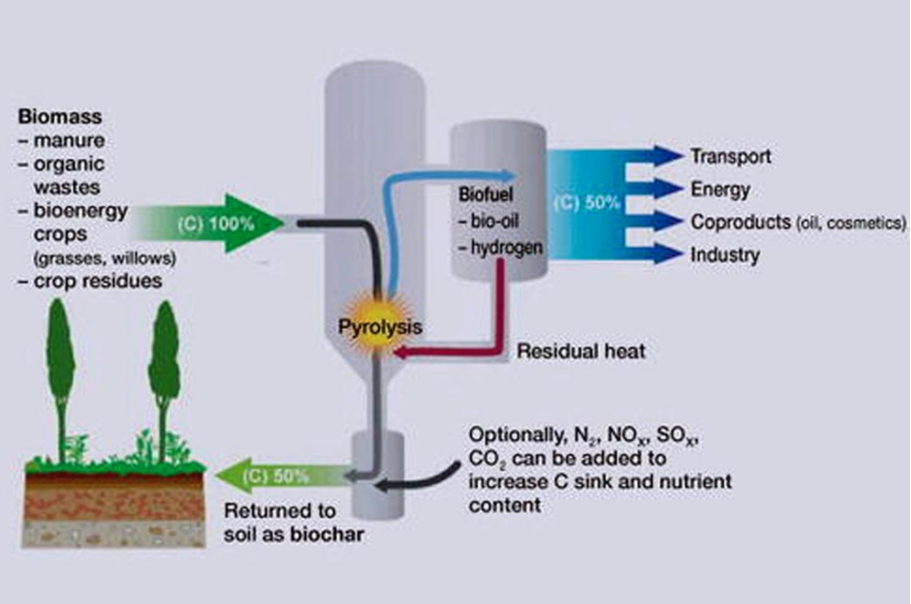


Fig.1.2. Concept of low-temperature pyrolysis to produce biofuels (Lehmann 2007)

In a low temperature pyrolysis, the biomass is heated up to 400 to 500°C under complete or partial absence of oxygen to produce biochar using a variety of reactor configurations. It is an exothermic process and releases gaseous components in addition to heat which can be captured to produce bio-oil, electricity, or powering cars or hydrogen for household use. One of the most important advantages of the biochar is the carbon sequestration via land applications. It is the subsequent storage and capture of carbon to prevent it from being released to the atmosphere. Hence the pyrolytic conversion of biomass into biochar and biofuels has attracted the government as well as greater attention from the general public.

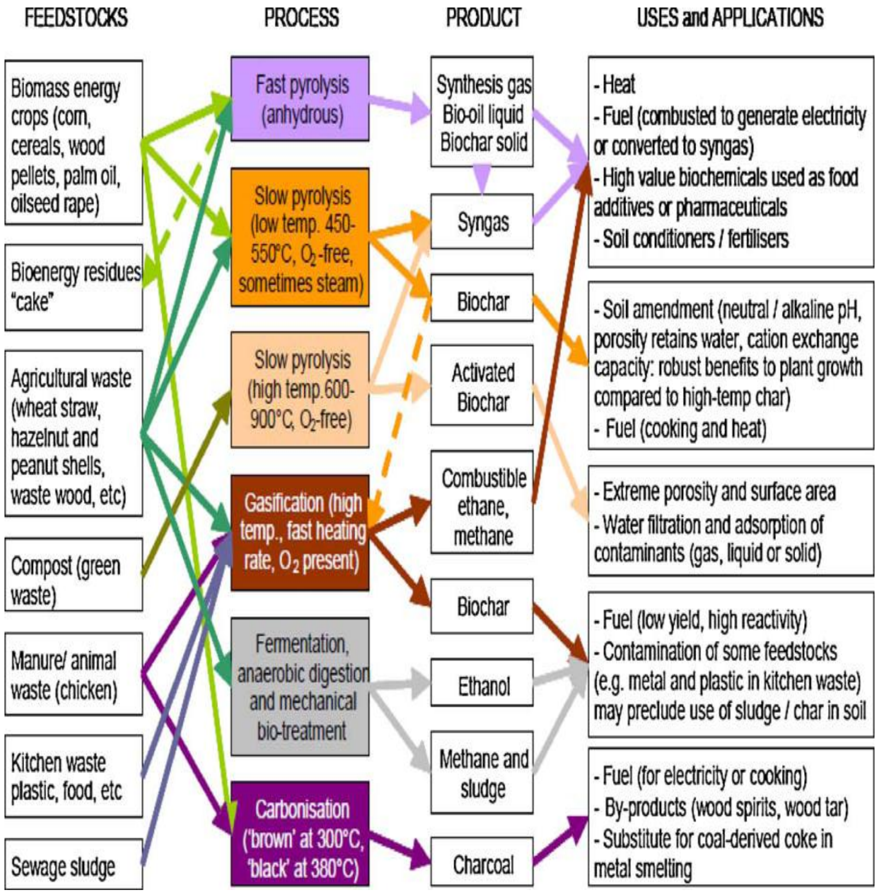


Fig.1.3. Summary of biomass conversion processes (Sohi et al. 2009)

Present day bioenergy systems involve both the processes of gasification and pyrolysis to produce synthesis gas (syngas), oil (bio-oil) and biochar (solid residue) by heating biomass under controlled conditions. Heat and power or both are produced by burning bio-oil and synthesis gas. The third product that is produced by pyrolysis is the carbon rich solid biochar. The characteristics of the biochar produced and its potential value to agriculture in terms of carbon sequestration as well as a fuel for heating applications greatly influenced by the pyrolysis. Though the process parameters like residence time and temperature are particularly very important, the interaction of the process parameters with the type of feed material will decide the nature of the product. These variables are the key parameters in deciding the physical, chemical, biological properties and limiting factors in the potential use of biochar products. Fig. 1.3 illustrates the summary of production processes, feed stocks, and products of different pyrolysis processes.

Table 1.5. Mode of pyrolysis and products of the processes (Sohi et al. 2009)

Mode	Condition	Liquid biofuel	Solid (Biochar)	Gas (Syngas)
Fast pyrolysis	Moderate temperature (~500 °C) Short vapour residence time (<2 s)	75% (25% Water)	12%	13%
Intermediate pyrolysis	Low-moderate temperature, Moderate hot vapour residence time	50% (50% water)	25%	25%
Slow pyrolysis	Low-moderate temperature, Long residence time	30% (70% water)	35%	35%
Gasification	Long residence time High temperature (>800 °C), Long vapour residence time	5% tar (5% water)	10%	85%

Many categories of pyrolysis processes are characterized, as shown in the Table 1.5, by a close balance between syngas, bio-oil and biochar. The exact ratio of pyrolysis products may vary between different types of plants used but can be optimized at a particular installation. Maximization of biochar production always decreases the energy content of liquid and gaseous fuels as the greenhouse gas mitigation strategies favor the maximum production of biochar (Lehmann, 2007; Sohi et al., 2009; Inyang et al. 2010).

1.8. Microwave assisted pyrolysis

An efficient thermo-chemical process to produce bio-char, bio-oil and syngas is the microwave assisted pyrolysis (MAP) because of its advantages over the conventional process. MAP is easy to control, provides uniform internal heating of biomass particles, higher biofuel yields without the agitation or fluidization, savings in the energy cost along with the reduction of harmful chemicals in the bio-oil. This method has been applied successfully to agricultural residues, wood, sewage sludge, sea weeds and any other waste biomass respectively (Lei et al. 2011; Du et al. 2011; Yin, 2012).

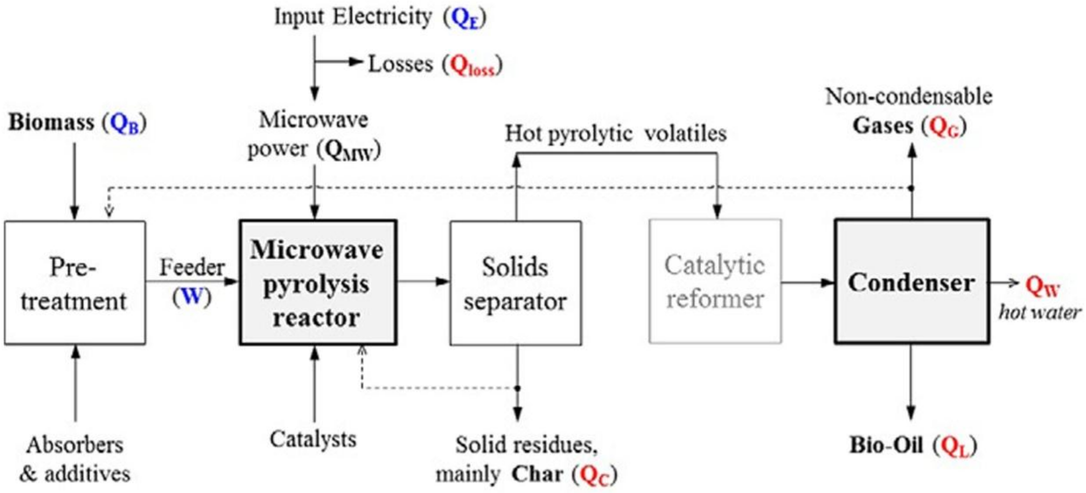


Fig.1.4. Schematic representation of the microwave assisted pyrolysis process (Yin, 2012)

Fig. 1.4 schematically represents the process of MAP with all the units. The catalytic reformer before the condenser for a preferred product is totally depending upon the requirement. Biochar produced by the process can be used as microwave absorber to recover the heat by radiation. Heat energy from the gaseous products can be used for feed stock drying.

1.8.1. Microwaves

Electromagnetic wave radiations with the wavelength range between 1µmand 1mm are popularly known as ‘‘microwaves’. The frequency range of microwaves is from 1to300 GHz (Fig. 1.5).

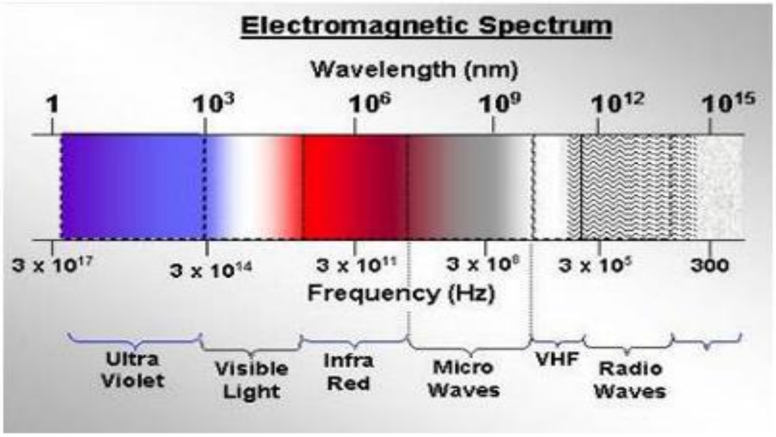


Fig.1.5. Electromagnetic Spectrum (Sharobem and Park, 2010)

Frequency range of microwaves is similar to radio waves and visible light of electromagnetic spectrum. Government agencies regulate the most of the microwave frequency band as it is used for radar and communication applications. Microwave frequencies allocated for exclusive scientific, medical and industrial use are 2.45, 5.85 GHz, 20.2-21.2 GHz and 915 MHz. Frequency range between 915MHz and 2.45GHz are having the prominent application at medical and industrial sectors for heating water. Commercial units are normally designed to operate between 915MHz and 2.45GHz.

Energy in the form of heat is transferred by radiation, convection and conduction from the surfaces of the material in conventional thermal processing. Contrary to this, microwave energy is transferred to the materials via molecular interaction with the electromagnetic field. Heat transfer occurs as a result of temperature gradients in the materials, whereas, the microwave heating is the conversion of electromagnetic energy in to thermal energy rather than heat transfer (Thostenson and Chou, 1999).

1.8.2. Microwave heating

Microwaves consist of electric and magnetic field components both perpendiculars to each other. Generally, there are three qualitative ways by which a material can be categorized with respect to its interaction with electric field component of the microwave: (i) absorbers, (ii) insulators, where microwaves pass through without any losses (transparent)(iii) conductors, where microwaves are reflected and cannot penetrate. Microwave heating is considered as dielectric heating as the materials absorb microwave radiation has dielectric properties and referred as dielectrics.

Materials are heated normally by a number of significant mechanisms when they are exposed to a microwave field. The mechanism of heating is based on the behavior of molecules of the material when exposed to the microwaves. The first mechanism is polarization- having either the electrons of individual atoms (electronic polarization) or the nuclei of the atoms themselves (atomic polarization) responds to an applied field and are displaced from their equilibrium position, which results to induced dipoles. This effect is more pronounced in molecules that have permanent dipoles from asymmetric charge distributions-like water. The second mechanism is interfacial polarization, which arises from a buildup of charge in contact areas of heterogeneous systems (heterogeneous being defined as multiple components that have different conductivities or dielectric constants). The third mechanism is via ionic conduction where some materials produce electric currents when subjected to electromagnetic (EM) fields. Localized friction or heating occurs due to movements aligned with the EM fields, as the atoms of the molecules of a given material undergo one of these phenomenon mentioned above.

The extent to which a material is heated depends on two parameters namely the dielectric constant ε' and dielectric loss factor ε'' when exposed to microwave radiation. The dielectric constant describes how effectively an electric field polarizes a material easily whereas the efficiency with which the electromagnetic radiation is converted into heat is usually measured by the loss factor. The ratio of dielectric loss factor to dielectric constant is the dielectric loss tangent or dissipation factor

$$\tan \delta = \varepsilon'' / \varepsilon' \quad (1.1)$$

The capacity of a material to absorb and convert electromagnetic energy into thermal energy at a given temperature and frequency is described by Eq. 1.1. Since microwave heating depends mainly on the characteristics of the workload, the sources of microwave radiation enable high temperatures and high rates of heating and show excellent efficiencies of conversion of electrical energy into heat (80–85%)when a material is suitable for this type of heating. Modern microwave heating equipment has a very high reliability and is highly competitive with other heating methods.

Dielectric power absorption (Eq. 1.2) is another term used to describe the heating of materials.

$$P=K\, f\, E^2 \acute{\varepsilon} \tan \delta \quad (1.2)$$

Where, P is the power dissipation in Wcm^{-3}, K is a constant equal to 55.61×10^{-14}, f is the applied frequency in Hz, E is the electric field strength inVcm^{-1}, $\acute{\varepsilon}$ is the dielectric constant, and $tan\delta$ is the dielectric loss tangent.

The terms $\acute{\varepsilon}$ and $\tan\delta$ are depending upon the sample temperature and operating frequency. Moisture content and physical state (solid or liquid) are also responsible for the variation of $\acute{\varepsilon}$ and $\tan\delta$ values. The electromagnetic field energy which is released as heat per unit volume is proportional to the frequency of the applied field, square of the field strength and dielectric loss factor. Hence it is clear from Eq.1.2 that, the influence of heat of the reaction upon heating rate is negligible. It is evident from Eq.1.2 that, the dielectric loss factor is a very important parameter in deciding whether given material can be possibly pyrolyzed or heated by microwave radiation. This quantity is directly proportional to the dielectric constant, which is a more common material property (Thostenson and Chou, 1999).

1.8.3. Microwave system

The main components of the microwave furnaces are the sources, the transmission lines, and the applicator (Fig. 1.6). The electromagnetic radiation is generated as a result of

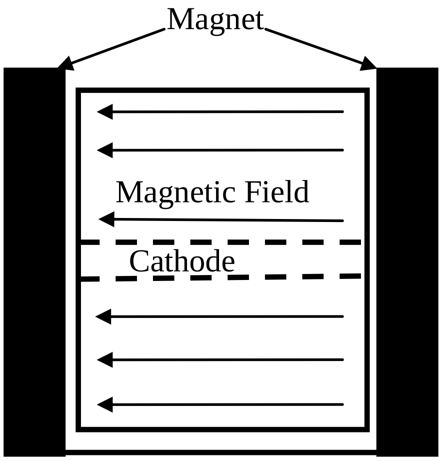


Fig.1.6. Schematic of magnetron microwave tube (Thostenson and Chou, 1999)

acceleration of charge by the source which in turn delivered to the applicator, where the microwaves are either reflected or absorbed. The most common microwave source is a magnetron which is a vacuum tube. In this vacuum tube the cathode (electrode) is heated due to a strong electric field produced by the potential difference between an anode (an electrode with high density of electrical charge) and cathode and results in the release of loosely bound valence electrons. The presence of electric field results in the acceleration of these released electrons towards the anode. The magnetic field, produced by using an external magnet perpendicular to the applied magnetic field and electric field results in the formation of a circumferential force on the electron.

This force is responsible for the spiral movement of electrons and thus swirling cloud of electrons is created. The oscillations in the electron cloud are observed due to the movement of swirling cloud of electrons through the resonant cavities and size of the cavities decides the frequency of oscillations. This electromagnetic energy is connected to the transmission lines through a waveguide launcher or coaxial line from one of the resonant cavities. Electromagnetic radiation with higher efficiency, around 80% for 2.45 GHz and 85% for 900 MHz is generated by the magnetron (Meredith, 1998).

1.9. Comparison between microwave and conventional heating

Thermal heating by conventional method is relatively inefficient compared to microwave heating due to lesser rate of heat transfer to the center of a material from the surface. Because of this the surface temperature is higher than that of the centre of the reaction vessel. But the use of microwave-transparent materials, such as quartz or borosilicate glass, in microwave heating process produces higher centre temperatures compared to the surface temperatures.

Table 1.6. Comparison between conventional and microwave assisted heating (Yin, 2012)

Microwave dielectric heating	Conventional thermal heating
Conversion of energy	Transfer of energy
In-core volumetric and uniform heating: the whole material heated simultaneously, energetic coupling at molecular level	Superficial heating: via convection/conduction
Rapid and efficient, e.g., methanol can be rapidly super-heated to above 100 °C; ionic liquids can gain temperature jumps of 200 °C within seconds	Slow, inefficient, limited by material thermal conductivity
Selective: rapid intense heating for polar substances while ineffective for a polar substances	Non-selective
Hot spots: an effect due to non-homogeneities of microwave field or dielectric properties within a material, resulting in local temperatures in the material being much higher than the temperature measured in the bulk	No hot spot
Dependent on material's properties	Less dependent
Precise and controlled heating: the energy input starts and stops immediately when the power is turned on or off, respectively	Less controllable

Relative comparison between the conventional heating and microwave assisted heating is very difficult though, the microwave assisted pyrolysis results in the higher yields due to thermal effects. Relative comparison between the conventional and microwave assisted heating is presented in Table 1.6 (Yin, 2012).

1.10. Cost benefits of biomass conversion

The economic analysis of biofuel production is based on the total cost of production and potential benefits in development, implementation and management of biofuel production systems.

Table 1.7. Summary of benefits and costs associated with the pyrolysis systems (Shackley et al. 2011)

Total costs: Cost of producing, delivering and application of biofuel			**Total benefits: Value of biofuel**			
Biofuel production	**Transportation & storage**	**Application Equipment**	**Energy production**	**Agricultural gains**	**Carbon storage**	**Diffuse pollution abatement**
Labour Capital costs Feed stock Transport Utilities Gate fee Maintenance & operation	Labour Equipment New covered storage facilities	Labour Monitoring, verification & reporting	Heat value Electricity value	Reduced fertilizer Water retention Soil workability Yield gain Quality	Carbon abatement	Reduced nitraterun off

The relevant information on the theses costs and benefits are currently not available on a global scale as the competent design technologies and management systems have not been developed. The biofuel production systems have become unsuccessful on a commercial term despite the considerable investments have been made towards their development. Further the cost benefits to agriculture sector with the application of biochar to the soil are not yet understood completely on a global scale. However, many studies have attempted the potential cost benefits of biochar production in terms of increased crop yield, increased soil organic carbon, cost savings of fertilizers and decreased emissions of carbon dioxide (CO_2) and nitrogen oxide (N_2O). Table 1.7 shows the summary of costs and benefits associated with the pyrolysis systems (Shackley et al. 2011).

1.11. Need for the study

Mangalore is one of the important cosmopolitan cities of Indian peninsular state Karnataka and situated on the west coast of Karnataka covering an area of 132.45 sq-km. Mangalore port city is located at 12°-52'N latitude and 74°-49'E longitude. The current population of Mangalore city is around 6,23,483 (4,99,487 as per 2011 census). Mangalore is known for its fast growing industries, educational institutions, restaurants and attracts the people from all over the globe. Working couples, moderate to high level income groups and overtime working hours with modern life style. Ready to eat foods like packaged foods, fast food meals and frozen foods have penetrated into the culture of Mangaloreans as a result of globalization. Packaged food items attract the student community/younger generation along with all age groups who seek variety and tasty food on daily basis. The food waste contributes 40% (125 tons per day) of the solid waste generated in Mangalore city, on daily basis of a total MSW around 312 tons. At present this MSW is land filled and is not being used as a source of energy. Thus the MSW generated in Mangalore city need to be managed in an eco-friendly manner as it contains, on an average, 40 % of organic waste that is unhygienic and undergoes fast degradation process. This food waste is having potential of conversion in to value added products like bio-fuels through suitable thermal processes and can substitute for the declining fossil fuels. Food waste offers a potential feedstock for biomass pyrolysis to produce bio-fuels as it is having a higher energy content. Two major problems can be solved by food waste pyrolysis, namely recovery of energy and reduction of landfill problems. Production of biofuels such as biochar, bio-oil and biogas from this biomass waste is of importance due to carbon sequestration through carbon neutral cycle and other applications.

CHAPTER 2

LITERATURE REVIEW

Conversions of biowastes into value-added products through suitable thermal processes are abundant in the literature. Literature citations on the pyrolysis of various types of biomass resources such as agricultural crop residues and by-products, see weeds, forestry residues, wood waste, organic portion of MSW, industrial wastewater sludge, livestock and poultry manures as well as food waste by conventional pyrolysis, conventional co-pyrolysis, microwave assisted pyrolysis, microwave assisted co-pyrolysis, catalytic pyrolysis, comparative and optimization studies are critically reviewed and reported in the following paragraphs.

2.1. Pyrolysis

Basic methods available to convert biomass into value added products such as biochar, bio-oil and biogas are pyrolysis, gasification and direct combustion. Among the three methods mentioned above, pyrolysis plays a major role in converting biomass which is one of the fourth largest energy resources and constitutes 14% of the world primary energy resources. In the pyrolysis process biomass is heated under an inert atmosphere using moderate temperature between 400 and 600 ºC to cause thermal decomposition that result in the non-condensable gases, condensable gases and solid residue (biochar). Bio-oil is obtained upon cooling of the condensable gases (Yin, 2012). Heat energy required for the pyrolysis process is supplied by the combustion of conventional fuels or by electrical energy. This process is popularly known as “Conventional Pyrolysis”.

Effects operating parameters such as temperature, heating rate and nitrogen flow rate on the pyrolysis of sunflower (*Helianthus annus L.*)-oil cake in a fixed bed tubular reactor was reported by Ger'cel (2002). Pyrolysis temperature 550 ºC resulted in the bio-oil yield of 48.69 wt. %. The heating and inert gas flow rates were 5 ºC min^{-1} and 100 cm^3min^{-1} respectively. The final pyrolysis temperature of 700 ºC with the nitrogen flow rate of 400 cm^3min^{-1} resulted in the overall conversion of 75.8 wt. %. The aliphatic, aromatic hydrocarbons were the main contents of the bio-oil. The heating value of the bio-oil was 32.15 MJkg^{-1}.

Sensoz, (2003) has investigated experimentally the effect of heating rate on the pyrolysis of pine bark (*Pinus brutia Ten.*) using externally heated fixed-bed reactor. Pyrolysis experiment was performed in the temperature range from 300 to 500 °C with heating rates between 7 and 40 °Cmin^{-1}. Maximum bio-oil yield of 33.25 wt. % was obtained at a temperature of 450 °C with a heating rate of 40 °Cmin^{-1}. The oxygenated components were the main contents of the bio-oil with very small fraction of hydrocarbons. Calorific value of the bio-oil was 31.03MJkg^{-1}. Increase in the operating temperature from 300 to 500 °C was the key parameter to increase the gas yield from 11.06 to 23.45 wt. %, the bio-oil yield from 30.91 to 32.79 wt. % (heating rate: 40 °C min^{-1}) and 29.68 to 30.97 wt. % (heating rate: 7°C min^{-1}), while the char yield decreased from 54.31 to 41.57 wt. % (heating rate: 40 °C min^{-1}) and 59.26 to 45.58 wt. % (heating rate: 7 °C min^{-1}).

The yields of bio-oil, biochar and biogas produced by the pyrolysis of rapeseed cake in a fixed bed reactor at a temperature of500 ºC with a heating rate of 7 ºC min^{-1}were 59.7%, 27.4% and 12.8% with a conversion efficiency of 72.6%. The flow of nitrogen was between 50 and 300 cm^{3}min^{-1}. Carbon rich bio-oil and biochar were obtained due to increased amount of fixed carbon. Lower amounts of volatile matter than rapeseed cake were noticed with high heating values of 36.4 and 25.3 MJkg^{-1}. Biochar produced was pollution-free fuel with rich energy content. Relatively pollution free green colour bio-oil was obtained by the process (Ozcimen and Karaosmanoglu, 2004).

The effect of heating rate on the pyrolysis yields of rapeseed by applying thermogravimetric analysis technique was analyzed by Haykiri-Acma et al. (2006). The experiments were conducted using an alumina crucible up to 1273 K with heating rates of 5, 10, 20, 30, 40 and 50 Kmin^{-1} at 40 cm^{3}min^{-1}of nitrogen flow. The lower heating rates resulted in the lesser yield of biochar due to resistance of biomass particles for heat transfer whereas the higher heating rates resulted in the higher conversion rates. The final pyrolysis temperatures as well as the activation energy values were affected by the variation in the heating rates.

Senso¨z et al. (2006) have investigated the effects of pyrolysis temperature, heating rate, particle size and sweep gas flow rates on the product yield. Pyrolysis of olive bagasse (*Olea europea L.*) was carried out in a fixed-bed reactor at an operating temperature range between 350 and 550 °C with heating rates of 10 and 50 °C min^{-1}. Increase in the operating temperature from 350 °C to 550 °C resulted in the increased bio-oil yield from 27.8% to 30.7% for the heating rate of 10 °C min$^{-1.}$ Biochar yield decreased from 35.3% to 30.6% due to increased heating rate of 50 °C min^{-1}. Gas yield increased from 9.0% at 350 °C to 14.0% at 550 °C for the heating rate of 10 °C min^{-1}, while for the heating rate of 50 °C min^{-1} it was from 14.8–18.0%. Particles size between 0.425–0.60 mm resulted in the maximum bio-oil yield of 34.4% and char yield of 30.9% at 500 °C with a heating rate of 10 °C min^{-1}. Nitrogen gas flow rate of 150 cm^{3}min^{-1} resulted in the increased bio-oil yield of 37.7 wt. % compared to the yield of 34.4% without the flow of sweep gas and same gas flow resulted in the char and gas yield of 31.7% and 5.8%, respectively. The heating values of the bio-oil and char were 31.8 MJkg^{-1}and 24.8 MJkg^{-1}respectively.

Apaydin-Varol et al. (2007) reported the slow pyrolysis of pistachio shell using a fixed-bed reactor at atmospheric pressure in the temperature range between 300 and 700 ºC with a heating rate of 7 ºCmin^{-1}. Bio-oil yield of 20.5% was obtained in the temperature range from 500 to 550 ºC. Increase in the pyrolysis temperature from 300 to 700 ºC resulted in the decrease of biochar yield by an amount of approximately equal to 21%, while the gas yield increased with the increase in temperature. Characterization of the bio-fuels exhibited the similar characteristics as that of conventional fuels.

Tsai et al. (2007) have carried out experimental investigations on the optimum conditions to obtain the maximum bio-oil yield of 40% by the fast pyrolysis of rice husk in a fix-bed induction heating system. Increased pyrolysis temperature (above 500 °C), heating rate (above 200 °Cmin^{-1}), residence time (above 2 min.) with decreased condensation temperature (less than −10 °C) and particle size (less than 0.50 mm) were responsible for the maximum bio-oil yield. Inert gas flow was not having any significant effect on the bio-oil yield. The pH and heating value of the bio-oil were reduced due to the presence of carbonyl groups and/or oxygen content. Biochar yield of 84.22% was obtained at a pyrolysis temperature of 400 °C and yield decreased with the increase in temperature.

Ji-lu et al. (2008) have reported the pyrolysis of cotton stalk in a fluidized bed reactor. Optimum temperature ranges to obtain the maximum bio-oil yield (55 wt. % at 530 ºC), bio-gas (30 wt. %at 530 ºC) and biochar (30 wt. %at 480 ºC) was between 480 and 530 ºC. Homogeneous emulsions were obtained by mixing bio-oil and emulsifier with diesel in different proportions. Corrosive nature of the bio-oil was very low towards copper and stainless steel.

Senso¨z andAngın (2008) have carried out experimental studies on the structural characterization of bio-oil. Bio-oil obtained by the pyrolysis of safflower seed press cake (SPC) at the heating rates of 10, 30 and 50 ºC min^{-1} with an operating temperature of 500 ºC was dominated by oxygenated and polar fractions as well as little quantities of aliphatic hydrocarbons. The hydrogen to carbon (H/C) and oxygen to carbon (O/C) molar ratios of the bio-oil were in the range of 1.13 to 1.55 and 0.22 to 0.33 with the calorific value ranging between 36 and 37 $MJkg^{-1}$. Presence of carboxyl, carbonyl and methoxy groups in the bio-oil was the reason for the increased oxygen content.

Fast pyrolysis of nut shells of *Jatropha curcas L* (JCL) plant was investigated experimentally by Manurung et al. (2009). Pyrolysis experiments were conducted on a continuous basis using a bench scale rotating cone flash pyrolysis reactor, with a biomass feed rate of 2.27 kg h^{-1} at 480 ºC for 80 min. maintaining the atmospheric pressure within the reactor. Pyrolysis yields of bio-oil, char and gases were 50 wt. %, 23 wt. % and 17 wt. % respectively and the remainder was ash.

Griffin (2011) investigated the effects of fire retardants on the pyrolysis of sugar cane baggase. Increase in biochar mass production was observed from 16% up to 41% during the pyrolysis of sugar cane baggase treated with the aqueous solutions of 0.1–0.5 M fire retardants (ammonium sulphate, boric acid and borax) by thermal gravimetric analysis (TGA) and cone calorimetry compared to untreated bagasse. Treatment of bagasse with fire retardants decreased the total heat release (THR) during combustion (41% reduction).

Char production rate and heat release rates were not affected by the combination of fire retardants.

Relation between fast pyrolysis of wheat straw and the short-term degradability of biochar in soil using a fast pyrolysis centrifuge reactor (PCR) under different reactor operating temperatures was investigated by Bruun et al. (2011). Pyrolysis experiments were carried out in a centrifuge reactor with a heating rate between 250 and 1000 °C $s^{-1}$with a feed rate of 23 g min^{-1}. The outputs of biochar, bio-oil and syngas as well as the stability of the biochar produced were varied significantly depending upon the reactor temperature. Fast pyrolysis temperature (475 to 575 ºC) resulted in the incomplete conversion of biomass (unconverted cellulosic and hemicellulosic fractions) and was matched with the short-term biochar degradation in soil.

Abnisa et al. (2011) have investigated the effects of pyrolysis conditions and particle size on the yield of bio-oil. Pyrolysis of palm shells was performed in a fluidized-bed reactor. Pyrolysis operating conditions such as 500 ºC temperature, nitrogen flow of 2 $Lmin^{-1}$ and 60 min. reaction time were responsible for the bio-oil yield of 47.3 wt. %. The sizes of the palm shells used for the pyrolysis were in the range of 1.7 to 2 mm. The main contents of the bio-oil were organic compounds of carbons (C_3, C_5, C_6, C_7, C_8 and C_9), 53 wt. % of water, low pH value of 2.5 and71.40 wt. % of oxygen content.

Sen and Kar (2011) have reported the effects of operating conditions as well particle size on the yields of pyrolysis. Pyrolysis of black cumin seed cake (BCSC) in a fixed bed reactor at an operating condition of 450 ºC, heating rate of 35 ºC min^{-1}, particle size > 850 µm and nitrogen flow rate of 0.200 $Lmin^{-1}$resulted in the higher bio-oil yield of 44.37% by weight. The calorific value of the bio-oil obtained was 38.48 $MJkg^{-1}$. Density and viscosity of the oil were 970.25 kg $m^{-3}$and 63.42 mm^2s^{-1} respectively. The results of the Fourier transform infra-red and gas chromatography-mass spectrometry (FT-IR and GC-MS) revealed the presence of alkanes and alkenes in the aliphatic sub fraction bio-oil along with paraffinic and olefinic hydrocarbons.

Chen et al. (2011) have investigated experimentally the effect of filtration on the characteristics of bio-oil. Filtration of pyrolysis vapor by hot vapor filtration (HVF) to filter the solid particles and bio-char resulted in the decrease of bio-oil yield from 41.7% to 39.5% by weight. Fast pyrolysis of the rice husk was carried out in bench-scale fluidized-bed reactor at a feed rate of 1–5 kgh^{-1}. Bio-oil with higher water content (75.09% by weight), higher pH value (2.84 to 4.40), lower alkali metal content and decreased weight of the chemical compounds were the effects of the hot vapor filtration. The alkali metal content of the biochar was high compared to bio-oil. High oxygen content of the bio-oil resulted in the lower energy density of 23.86 MJkg^{-1}.

Demiral and Ayan (2011) have reported the effects pyrolysis operating parameters such as temperature (350 - 600 ºC), heating rate (10 - 50 ºC min^{-1}) and nitrogen flow rate (50 - 200 cm^{3}min^{-1}) on the pyrolysis of grape bagasse. Pyrolysis was carried out in a fixed bed stainless steel reactor. Process parameters such as temperature of 550 ºC, heating rate of 50 ºC min^{-1} and inert gas flow rate of 100 cm^{3}min^{-1} resulted in the bio-oil yield of 27.60%. Aliphatic and aromatic hydrocarbons were the main contents of the bio-oil. The heating value of the bio-oil was 32.95 MJkg^{-1}.

Bio-oil and biochar yields produced by the pyrolysis (heating rate of 10 ºCmin^{-1} up to a maximum temperature of 500 ºC) of unicellular marine diatom *Tetraselmis chui* in a fixed bed infrared pyrolysis reactor were 24–43wt. % and 34–63wt. % with the higher heating values (HHV) of28 MJkg^{-1} and 14.5 MJkg^{-1} respectively. Insulation for the heating element was provided by argon (Ar-flow rate - 5 mL min^{-1}) while the helium with a flow rate of 50 mL min^{-1} was used to create an inert atmosphere. The main components of the bio-oil were fatty acids, alkanes, alkenes, amides, aldehydes, terpenes, pyrrolidinines, phytol and phenols. Biochar exhibited high cation exchange capacity (CEC), large concentration of N, and a low C: N ratio, stabilized carbon of 9 wt. % (Grierson et al. 2011).

Melligan et al. (2011) have studied experimentally the effects of temperature, retention time and operating pressure on the pyrolysis of *miscanthus xgiganteus* using fixed bed reactor. Properties of bio-oil and biochar were dependent upon the temperature (from ambient to 550 ºC), gas flow rate (13 ºCmin^{-1}), retention time (25 min) and pressure (from atmospheric to 26 bars) within the reactor. Major contents of the bio-oil identified were water, phenol, and phenol derivatives. Biochars obtained at the higher pressures were having higher carbon content with extended fused aromatic structures and thermally stable. The operating pressure was not having any effect on the quantity of the biochar produced by slow pyrolysis.

Biochar yield produced by the pyrolysis of waste water sludge was decreased with increase in temperature from 300 ºC (72.3%) to 700 ºC (52.4%). Pyrolysis was carried out in a fixed bed horizontal tubular reactor with a heating rate of 10 °Cmin^{-1} by purging nitrogen at the rate of 50 Lmin^{-1}.Feed rate of the sludge was in the range from 264-273 g. Acidic biochar was produced at lower temperature (300 ºC and 400 ºC) with decreased concentration of nitrogen whereas the higher temperature (700 ºC) resulted in the alkaline biochar with increased concentration of micronutrients (Ca, Fe, Mg, S, Cu and Zn) suitable for soil application including carbon sequestration. The concentrations of the trace metals (such as N, P, and K) were varied with temperature and responsible for the enrichment of the biochar (Hossain et al. 2011).

Chen et al. (2012) have investigated the effect of temperature on the pyrolysis of cotton stalk. Pyrolysis temperature was the key parameter to obtain higher calorific value (~28 MJkg^{-1}) and higher surface area (>200 m^{2}g^{-1}) biochar produced by the pyrolysis of cotton stalk in a fixed bed reactor. Increased temperature resulted in the higher ash content (8.42% at 550 ºC) compared to the char produced at low temperature (3.65% at 250 ºC). The biogas obtained was having a calorific value in the range from 8–10 MJm^{-3} at higher operating temperatures (550 and 750 ºC).

Tushar et al. (2012) have reported the effects of process parameters on the pyrolysis of flax straw. Pyrolysis temperature (300 and 500 ºC) and residence time (15 to 60 min) influenced the physicochemical as well as yield of biochar produced by the isothermal pyrolysis of flax straw. Experiments were carried out in a muffle furnace by purging nitrogen at 200 mLmin^{-1}. Increased temperature and residence time resulted in the lesser yield of biochar but the porosity and graphitization were increased with the similar reactor conditions. Presence of amorphous filamentous carbon and crystalline graphitic carbon were evidenced by X-ray diffraction (XRD) and temperature-programmed oxidation (TPO) techniques. Biochar produced at a lower temperature was more reactive (combustion kinetics and reactivity analyzed by thermogravimetric analysis) than the char produced at higher temperature.

Kim et al. (2012) have investigated experimentally the effect of temperature on the physicochemical properties and structure of biochar produced by the pyrolysis of pitch pine (*Pinus rigida*). Pyrolysis was performed using a fluidized bed reactor at different pyrolysis temperatures of 300, 400 and 500 ºC respectively. Increase in reactor temperature (from 300 ºC to 500 ºC) resulted in the decrease of biochar yield from 60.7% to 14.4%. Analysis of the experimental results revealed that the biochar obtained at 400and 500 ºC was composed of highly ordered aromatic carbon structure.

Sait et al. (2012) have reported the pyrolysis possibility of Saudi Arabian date palm biomass. Biochar yield of ~40 wt. % was observed by the pyrolysis of date palm biomass at pyrolysis temperature of 500 ºC. Experiments were conducted in an environment of nitrogen with flow rate of 50 $\mathrm{mLmin^{-1}}$ and the samples were subjected to a constant heating rate of 20 $\mathrm{ºCmin^{-1}}$. The maximum conversion and reaction was found between the temperature range of 200ºC and 450 ºC. Similar pyrolysis and combustion characteristics were exhibited by the seed and leaf. Leaf stem was not suitable for thermo-chemical conversion due to higher moisture content.

Capunitan and Capareda (2012) have carried out experimental studies on the production potential of bio-fuels by the pyrolysis of corn stover. Pyrolysis was carried out in a pressurized batch reactor at different operating temperatures. Increased gas yield with reduced char yield was observed with increase in the reaction temperature. Maximum biochar (37.3 wt. %) and bio-liquid (31.4 wt. %) yields were obtained at a temperature of 400 ºC. The gas yield ((21.2 wt. %) was maximum at 600 ºC. The major components of the bio-oil (analyses of FTIR and GC–MS) were phenolic, aromatic and aliphatic compounds. The gas energy content was ranging between 10.1 and 21.7 $\mathrm{MJm^{-3}}$ with the gas constituents like methane, hydrogen and carbon dioxide.

Effects of pyrolysis temperature, reaction time and sweeping gas (N_2) flow rate on product yields were investigated experimentally by Açıkalın et al. (2012). Pyrolysis of pistachio shell was carried out in a fixed bed reactor in the temperature range from 350 to 650 ºC, reaction time from 10 to 50 min and nitrogen flow rate from 50 to 450 mL min^{-1} respectively. Maximum bio-oil yield of 53.36% was obtained at an operating temperature of 500 ºC, residence time of 30 min and nitrogen flow rate of 150 mL min^{-1}. Bio-oil obtained was highly oxygenated complex mixture with a heating value of 4645 kcalkg^{-1}. Energy content of the biochar produced at lower pyrolysis temperature was higher than that of subbituminous coal.

Demiral et al. (2012) have reported the effects operating parameters such as temperature (400 - 550 ºC), heating rate (7 - 40 ºC min^{-1}) and nitrogen flow rate (50 - 200 $\mathrm{cm}^3\mathrm{min}^{-1}$) on the pyrolysis of corncob. Pyrolysis was performed in a fixed bed reactor. Pyrolysis process temperature of 500 ºC, heating rate of 40 ºC min^{-1} and inert gas flow rate of 100 $\mathrm{cm}^3\mathrm{min}^{-1}$ were the causes for bio-oil yield of 26.44 wt.%. Oxygenated species such as carboxyl and carbonyl groups, aromatic and aliphatic hydrocarbons were the main contents of the bio-oil. Bio-oil was having a heating value of 26.22 MJkg^{-1}.

Suttibak et al. (2012) have studied experimentally the fast pyrolysis of cassava rhizome (CR), in a fluidized-bed fast pyrolysis reactor unit incorporated with a hot vapour filter. Maximum bio-oil yield of 63.23 wt. % on dry biomass basis was obtained at the optimum pyrolysis temperature of 472°C. Main contents of the bio-oil were water (18 wt. %), solids (0.8 wt. %) and ash (<0.01 wt. %) respectively. Higher heating value (HHV) of the bio-oil was 26.9 MJkg^{-1} with a pH value of 3.1and density 1.1 gmL^{-1}.

Maximum bio-oil yield of 75 wt. % was obtained by the flash pyrolysis of pinewood sawdust at a temperature of 500 ºC using a pilot plant provided with a conical spouted bed reactor (operating temperature range-400–600 ºC). Gas yield was very (less than 8 wt. % below 500 °C and increased to 20 wt. % at 600 ºC) low with low heating values at lower temperatures. Gas fraction was mainly composed of hydrogen, C_2–C_4 hydrocarbons, methane, carbon monoxide and carbon dioxide. Major constituents of the bio-oil were guaiacols (at low temperatures), phenols and catechols (at high temperature).

Biochar yield decreased from 22 wt. % at 400 °C to 15 wt. % at 600 °C. Higher heating values of the chars were obtained at 500 ºC (30.49 MJkg^{-1}) and 600 ºC (39.9 MJ kg^{-1}) compared to the solid fuels (29 MJ kg^{-1} -soft coal and 20 MJ kg^{-1}-lignite). Biochar quality and surface properties were improved due to the release of volatiles at higher temperature forming narrow pores (Amutio et al.2012).

Muradov et al. (2012) have reported the effects of temperature and inert gas flow rate on the pyrolysis of *Lemna minor*, a fast-growing aquatic biomass (duckweed) using tubular reactor (Thermolyne). Biochar yield increased from 50 - 52% at lower operating temperature (400 ºC) while the yield deceased between 44 and 47% due to increase in the temperature from 500-600 ºC with a constant argon flow rate of 60 cm^{3}min^{-1}. The pore structure (textural characteristics and Brunauer-Emmet-Teller(BET) surface area) development of the biochar was not affected by the reactor conditions such as temperature (400-700 ºC) and sweep gas flow rate (Ar gas flow of 36-150 cm^{3}min^{-1}). An inert (helium) and oxidative (air) mediums were used to analyze the differences in the patterns of thermogravimetric/differential thermogravimetric (TG/DTG) of *L. minor* and different bio-char samples.

Angin, (2013) has carried experimental studies to investigate the effects of pyrolysis temperature and heating rate on physicochemical, morphological properties and yield of biochar obtained from the safflower seed press cake (SPC). Biochar obtained at a temperature of 600 °C was having higher fixed carbon content (80.70%), percentage carbon (73.75%), higher heating value (30.27 MJkg^{-1}) and low volatile matter content (9.80%)compared with original SPC. However, the surface areas of the biochar were between 1.89 and 4.23 m^{2}g^{-1} with predominant aromatic compounds. Chemical activation of biochar with zinc chloride resulted in the activated carbon having the carbon content of 76.29%. Yield of activated carbons were dependent upon the impregnation ratio and pyrolysis temperature.

Pyrolysis of sweet sorghum bagasse in a fluidized bed reactor at a temperature of 500 ºC (feed rate of 1–5 kgh^{-1}) resulted in the carbon rich biochar, high content of potassium (K) and very good pore structure. Cyclone, fractional condensers and electrostatic precipitators were used to separate the biochar and bio-liquid. Water and chemical compounds from the bio-oil were separated due to annulations of bio-oil composition using fractional condensers. Water content of the bio-oil was in the range of 15–30 wt. %. The higher heating values of the biochar and bio-oils were 23.11 and 22.76 $MJkg^{-1}$ respectively (Yin et al. 2013).

Kader et al. (2013) investigated experimentally the pyrolysis of tamarind seed in an electrically heated fixed bed reactor. Bio-oil yield of 45 wt. % (feed size - 3200 μm diameter) was obtained at an operating temperature of 400°C for 30 min. with a nitrogen gas flow rate of 6 L min^{-1}. Pyrolysis temperature of 550 °C resulted in the gas yield of 27wt% (feed size - 3200 μm diameter). Reduction in the biochar yield was observed in the temperature range between 300 and 500 °C for the feed size of 3200 μm diameter, while the feed size of 800 μm diameter and 400 °C resulted in the char yield of 44wt. %.

Nayan et al. (2013) have carried out the experimental studies to produce bio-oil by the pyrolysis of neem seeds (*Azadirachta Indica*). Pyrolysis was carried out in a semi-batch reactor in the temperature range from 400–500 ºC at a heating rate of 20 $ºCmin^{-1}$. Bio-oil yield of 38 wt. % was obtained at the temperature of 475 ºC with a calorific value of $32.3MJkg^{-1}$. The main contents of the bio-oil were pentadecane, heptadecane, stearic acid methyl ester, octadecanenitrile, 9-octadecenoic acid methyl ester, oleanitrile,9-octadecenamide and e-11- hexadecenal and. Biochar yield of 47 wt. % was obtained at 400 ºC with a high calorific value of 7100 $kcalkg^{-1}$.

Biochar produced by the pyrolysis of exhausted coffee residue (ECR), was having higher calorific value of 31.9 $MJkg^{-1}$ compared to that of coal (28.0–32.0 $MJkg^{-1}$). Pyrolysis of ECR was carried out in a fixed-bed reactor at the pyrolysis temperature range from 673 to 973 K with a heating rate of 10 $Kmin^{-1}$. Nitrogen flow rate was 500 cm^3min^{-1}. Biochar yield was in the range between 25 and 45% depending upon the operating temperature. The contents of the biochar were carbon >80%, fixed carbon>60% and nitrogen about 5% (Tsai et al. 2013).

Abnisa et al. (2013) have reported the variations in the yields of bio-oil (16.58–43.50 wt. %) and biochar (28.63–36.75 wt. %) due to variations in the cellulose, hemicellulose, lignin, volatiles, fixed carbon, and ash contents of the oil palm tree residues. Pyrolysis of the palm oil residues were carried out in a fixed-bed reactor at a temperature of 500 °C maintaining a nitrogen flow rate of 2 $\mathrm{Lmin^{-1}}$ with a reaction time of 60 min. High energy density biochar (23.32 $\mathrm{MJkg^{-1}}$) was resulted from the palm leaf sample whereas a frond sample resulted in the high energy density bio-oil (15.41 $\mathrm{MJkg^{-1}}$). Bottom layer of the bio-oil showed the higher HHV (14.83–25.03 $\mathrm{MJkg^{-1}}$) compared to HHV (9.52$\mathrm{MJkg^{-1}}$ to 15.41 $\mathrm{MJkg^{-1}}$) of upper layer.

Wang et al. (2013) have studied experimentally the fast pyrolysis of residue remained after the extraction of lipid from a microalga (*Chlorella vulgaris*) using a fluidized bed reactor. Bio-oil, biochar, and gas yields of 53, 31, and 10 wt. % were obtained at a temperature of 500 ºC (feed rate - 100 g $\mathrm{h^{-1}}$). Main constituents of the bio-oil were amides, amines, aromatics and straight-chain hydrocarbons, carboxylic acids, fatty acids, phenols, as well as other organic compounds. Protein content of the fed stock was responsible for the higher nitrogen content (12.8 wt. %) in the bio-oil. The total energy recovery from the microalgae residue was around 94%.

Harman-Ware et al. (2013) have reported the fast pyrolysis of dried, ground *Scenedesmus sp.* in an isothermal spouted bed reactor and a dynamic pyrolysis-GC/MS unit. Pyrolysis temperature of 480 ºC (1 bar) with a vapour residence time of 2 s resulted in the crude oil to char ratio of 3.76 by weight. Main contents of the oil were various hydrocarbons as well as oxygenated and nitrogenous species, such as indoles, fatty acids and amides. Contents of the oxygen and nitrogen as identified by the elemental analysis were 27.6 wt. % and 8.6 wt. % respectively. Higher protein content of the algae was responsible for the increased nitrogen content of the oil. The calorific value of the bio-oil was 18.4 $\mathrm{MJkg^{-1}}$. Small amounts of carbohydrate pyrolysates were observed in bio-oil produced by the spouted bed reactor.

Degradation of the algae (*Spirulina Sp.*) by the slow pyrolysis process in a fixed bed reactor under oxygen limited condition was occurred at a temperature of 322 °C, less than that of biomass degradation temperature. Pyrolysis was carried out by purging nitrogen at the rate of 30 mLmin^{-1}with a heating rate of 8 °Cmin^{-1} for 60 min. Maximum yields of bio-oil (46 wt.%), biochar (32 wt.%) and bio-oil (27 wt.%) were observed at the temperatures of 550 500 and 600 °C respectively. Bio-oil was mainly composed of heptadecane, toluene, ethylbenzene, and indole. The saturated functional hydrocarbon groups of the bio-oil were comparable with the conventional fuels like heavy naphtha, kerosene and diesel oil with a higher oxygen and water content. The higher heating value (HVV) of the bio-oil was 21.68 MJkg^{-1} and higher than that of the wood. The components of the biochar were similar to the components of the biochar produced by using other types of algae except carbon content (Chaiwong et al. 2013).

Hu et al. (2013) have carried out experimental studies on the fast pyrolysis of microalgae (*Chlorella vulgaris*) using quartz tube reactor. Biofuel yield of 91.09 wt. % was obtained at pyrolysis temperature of 900 °C. Pyrolysis temperature in the range between 800 and 900 °C resulted in the increased syngas ($CO + H_2$) production. Solid residue yield decreased from 30.00to 8.91% wt. % due to increase in pyrolysis temperature from 500 to 900 °C. Heating value of the syngas was 29116 ppmv kJL^{-1}at 800 °C.

Hu et al. (2013) have reported the effects of sweep gas flow rate, pyrolysis temperature and particle size on the product yield and bio-oil properties produced by the pyrolysis of blue-green algae blooms (BGAB). Pyrolysis was performed in a fixed-bed reactor at the temperature range from 300 °C to 700 °C, particle size between 0.25 and 2.5 mm and nitrogen gas flow rate from 50 mLmin^{-1}to 400 mLmin^{-1}. Sweep gas flow rate of 100 mLmin^{-1}, particle size below 0.25 mm and pyrolysis temperature of 500 °C were responsible for the maximum bio-oil yield of 54.97wt. %. Higher heating value of the bio-oil was 31.9 MJkg^{-1}.

Carbon, hydrogen and oxygen contents of the bio-oil produced by the pyrolysis of microalgae (*Nannochloropsis oculata)* were 76wt. %, 11wt. % and 7 wt. % respectively. Pyrolysis was carried out by using pressurized fixed-bed batch-type reactor at a pressure of 100 psi in the temperature range between 400 and 600 °C with a heating rate of 5 °Cmin^{-1}under oxygen limited conditions. Higher heating value (HHV) of the bio-oil was

38 MJkg^{-1}. Main constituents of the bio-oil were saturated and unsaturated aliphatics and aromatics ranging from C_8 to C_{21}. Yield of biochar at a temperature of 400 °C was 52wt. %with a HHV of 27 MJkg^{-1}. Higher operating temperature of 600 °C resulted in the gas yield of 15wt. % with a HHV of 27 MJm^{-3}. Mass and energy conversion efficiencies were 76% and 68% respectively (Maguyon and Capareda 2013).

Mourant et al. (2013) have studied experimentally the effect of operating temperature on the properties of bio-oils obtained by the fast pyrolysis of mallee bark (a type of eucalypt grown for soil amendment in Western Australia) using fluidized- bed reactor. An increase in the pyrolysis temperature from 300 ºC to 580 ºC with a feed rate of 0.7 kg h^{-1} resulted in the decrease of biochar yield from 63 wt. % to 30 wt. %. Maximum bio-oil yield (43 wt. % dry bark) was obtained at a pyrolysis temperature of 450 ºC. Different phases of bio-oil (paste floating on the surface of the bio-oil produced between 300 and 400 ºC and under the liquid at higher temperatures) were experienced depending upon the temperature. Variations in the concentration of aromatic compounds were identified depending upon the phase of the bio-oil.

Amutio et al. (2013) have reported the flash pyrolysis of forest shrub wastes using conical spouted bed reactor. Biochar, bio-oil and gas yields produced by the pyrolysis of bushes such as *Cytisus multiflorus*, *Spartium junceum*, *Acacia dealbata* and *Pterospartum tridentatum* at an operating temperature of 500 ºC were in the range from 16 - 23 wt. %, 75 - 80 wt. % and 4 - 5 wt. % respectively. Main contents of the bio-oil were acids and furans, phenols, ketones, water (34-40 wt. %)as well as lower contents of alcohols, saccharides and aldehydes. Biochars obtained by the combination of the shrubs were having the higher carbon content (71.0 - 83.8 wt. %), high caloric values (24.8 - 31.2 MJ kg^{-1}) with negligible sulfur content and lower ash contents (2.4 - 5.8wt. %).

Increase in the pyrolysis temperature resulted in the higher surface area and reduced pore size of a biochar produced by the flash and conventional pyrolysis of grape seeds. Pyrolysis was carried out by using sandwich type electrical furnace at a temperature range from 300-1000 ºC with a heating rate of 10 ºC min^{-1}. Pore sizes in the range of 0.4 to 1.1 nm, surface area of 500 m^{2}g^{-1} and micropore volume of 0.2 cm^{3}g^{-1} were observed between the temperature range 700 and 800 ºC. The results of the experiment revealed that, the biochars can become one of the suitable raw materials for the production of activated carbon due to low sulfur (less than 0.15%) and ash contents (Jimenez-Cordero et al. 2013).

Duan et al. (2013) have investigated experimentally the non-catalytic hydropyrolysis of microalgae (*Chlorella pyrenoidosa)*. Pyrolysis was performed using stainless-steel batch reactor. Energy recovery of about 85% was observed in the form of hydropyrolysis oil (HPO) in the temperature range between 150 and 450 °C, operating time between 5 and 120 min. and initial hydrogen pressure between 1 atm and 8 MPa. Main contents of the HPO at moderate temperatures were amides, amines, aromatics and straight-chain hydrocarbons, carboxylic acids and nitriles. The nonreactive gases detected were CH_4, CO_2, CO and H_2. Hydrogen pressure from 1 atm to 3 MPa resulted in the HPO yield of 53.2 wt. %, char yield of 12.3 wt. % and gas yield of 15.2 wt.% at an operating temperature of 310 °C with a reaction time of 60 min.

Cascarosa et al. (2013) have reported the pyrolysis and gasification of meat-and-bone-meal (MBM) using fluidized bed reactor. Heating value of the bio-oil produced by the pyrolysis of MBM at 500 °C was 36.4 $MJkg^{-1}$with a feed rate of 18 kgh^{-1}. Higher bio-oil yield was observed (35% w/w) compared to bio-gas and biochar (25% w/w). Bio-gas (48% w/w) and solid chars (38% w/w) were the main products of gasification process.

Alvarez et al. (2014) have investigated the fast pyrolysis of rice husk using a bench-scale conical spouted bed reactor (CSBR) in the temperature range between 400 and 600 ºC. Higher mass capacity, increased heat transfers and reduced residence time of CSBR resulted in the maximum bio-oil yield of 70 wt. % and char yield of 26 wt. %at the pyrolysis temperature of 450 ºC with continuous removal of char. Bio-oil yield was decreased due to increase in the gas yield from 1 to 9 wt. % as a result of increase in the pyrolysis temperature.

Singh et al. (2014) have carried out an experimental study on the pyrolysis of Sal seed (*Shorea Robusta*) using a semi batch reactor in the temperature range from 400 to 625 °C with a heating rate of 20 °Cmin^{-1}. Higher bio-oil yield of 52.8 wt. % was obtained at the operating temperature of 600 °C. Bio-oil contained around 32 types of compounds having carbon chain length in the range of C_6–C_{20}. The properties of the bio-oils were similar to that of the petroleum products. Solid residue of the process was having higher calorific value and larger pore diameters.

2.1.1. Co-pyrolysis

Over the past few years some studies have been under taken to produce biofuels through pyrolysis or gasification of blended biomass feed stocks. This method is known as "co-pyrolysis". Literature citations on the conventional co-pyrolysis of biomass feed stocks are reviewed critically and presented in the following paragraphs.

Pyrolysis of rice husk saw dust and their mixtures were investigated experimentally by Zheng et al. (2006). Pyrolysis experiments were carried out in a fluidized bed reactor in a temperature range from 420 to 540 °C with nitrogen as a carrier gas for rice husks or saw dust with sand. Liquid fuel yields of 56%, 61% and 60% were obtained at 465, 490 and 475 °C for rice husks, sawdust and their mixture respectively. The liquid fuel, as identified by GC–MS analysis, was a complicated organic compound containing water, acids and heterocyclic substances. Lower heating values of the liquid fuels were 17.42 (Rice husk), 18.2 (Saw dust) and 17.4 MJkg^{-1} (mixtures of rice husk and saw dust) respectively.

Delgado et al. (2013) have reported the effects of blending ratios of corn straw and crude glycerol on the pyrolysis yields. Pyrolysis of corn straw mixed with the crude glycerol (byproduct from biodiesel industry) at a temperature of 550 ºC with a heating rate of 30 ºCmin^{-1} resulted in the higher yield of bio-oil (39 wt.%) compared to the yield of bio-oil obtained by the pyrolysis of crude glycerol (23 wt.%). Biochar and bio-oil production were affected by the blending ratios of corn straw and crude glycerol. The biogas produced by the blending ratio of 1:1 was rich in light hydrocarbons (due to presence of glycerol) along with a very good H_2, CO and CH_4 (due to presence of corn straw) concentration. The calorific vale of the biochar was increased from 24.84 (ratio-1:1) to

27.64 MJ kg^{-1} (ratio-1:3) due to increase in the corn straw ratio. Increase in the glycerol concentration resulted in the decrease of biochar yield with high ash content. Higher percentage of carbonaceous residue was observed as a result of impurities in the crude glycerol.

Ding and Jiang, (2013) have studied experimentally the co-pyrolysis of agricultural residues and sludge using vertical fixed-bed reactor. Decreased bio-oil yield was observed due to increase of sludge content from 0% to 100%. Co-pyrolysis was carried out at a temperature of 450 °C by maintaining the nitrogen flow rate of 400 mLmin^{-1}for first20 min. and maintained at 160 mLmin^{-1} throughout the experiments. Bio-oil yield decreased from 58.8 to 19.4 wt. % with the addition of saw dust and 43.0 to 19.4 wt. % for rice husk respectively due to chemical composition of the sawdust and rice husk.

Pyrolysis of cherry pulp was investigated experimentally by Pehlivan et al. (2017) to obtain biochar. Pyrolysis was carried out in fixed bed tubular reactor at the operating temperatures of 400,500,550, 600 and 700 ºC with heating rates of 10, 100 and 200 ºCmin^{-1} respectively. Increased pyrolysis temperature and heating rate resulted in the decreased biochar yield. Maximum biochar yield of 31.25 wt. % was obtained at the pyrolysis temperature of 400 ºC with a heating rate of 10 ºCmin^{-1} at 100 cm^{3}min^{-1} of nitrogen flow rate. Higher heating value of (HHV) the biochar was 34.56 MJ kg^{-1} at the pyrolysis temperature of 700 ºC.

2.1.2. Comparative studies

In recent years' attention has been paid towards the comparative studies on pyrolysis of various biowastes and characteristics of pyrolysis products. Literature citations on the comparative studies using conventional pyrolysis are reviewed critically and presented in the following paragraphs.

Pyrolysis of three agricultural wastes namely corncob, straw and oreganum stalks at 500 °C in a fluidized bed reactor resulted in the bio-oil yields in the range from 35 to 41%, gas yields from 30 to 39 %, and char yield from 20 to 23% respectively. The aqueous fraction of the bio-oil was around 6% for all the feed stocks. Water soluble fraction of the bio-oil for corncob was 68%, whereas for the straw and oreganum stalks it was around 52%. Main contents of the water soluble fraction of the bio-oil were mainly acetic acid, mainly acetone, carboxylic acids, non-aromatic ketones, phenols and methanol. Higher heating values of the biochars were in the range between 4600 and 6000 kcalkg^{-1} with lower sulphur content (Yanik et al. 2007).

Inyang et al. (2010) have reported the effects of anaerobically digested sugarcane baggase and fresh baggase on biochar production. Pyrolysis of the digested residue and fresh baggase was performed in a bench scale tubular pyrolysis reactor at 600 °C with a heating rate of 10 °Cmin^{-1} in an environment of nitrogen for 1.5 h. The similar rates of biochar production from the digested residue (18% by weight) and the raw bagasse (23%) were observed with different physicochemical properties. Higher pH, surface area, cation exchange capacity (CEC), anion exchange capacity (AEC), hydrophobicity and more negative surface charge were noticed with the digested bagasse biochar (DBC) compared to undigested bagasse biochar (BC).

O¨zçimen and Ersoy-Meriçboyu (2010) have investigated the carbonization and characterization of various biomass feed stock materials. Biochars produced by the pyrolysis of apricot stone, hazelnut shell, grape seed and chestnut shell were relatively pollution-free, carbon rich, high heating value potential solid biofuels and capable of replacing conventional fossil fuels. The highest gross calorific values for biochar and bio-oil were 30.76 MJkg^{-1} for apricot stone biochar and 29.76 MJkg^{-1} for grapeseed bio-oil and proved as environmentally friendly green biofuel candidates. Brunauer-Emmet-Teller(BET) surface area, porosity and total pore volume of the above mentioned biochars were higher in comparison with biochar samples except chestnut shell. The porosity of biomass and biochar samples were ranging between 0.024–0.276 (%) and 0.113–0.170 (%), respectively. The BET surface areas of biomass and biochar samples were ranging between 5.8421–10.5881 (m^{2}g^{-1}) and 0.6717–14.6836 (m^{2}g^{-1}) respectively.

Ahmed and Gupta, (2010) have carried out an experimental investigation on pyrolysis and gasification of food waste with the assistance of steam at operating temperatures of 800 and 900 ºC. Results of the experiments showed that, the pyrolysis was less beneficial than gasification. Gasification resulted in the enhanced production of syngas, hydrogen and energy in comparison to pyrolysis. However, the time required for gasification was more as compared to pyrolysis. The time required for the gasification of food waste was more compared to the paper gasification at the same operating conditions. Catalytic effects were observed with the inorganic constituents of food char.

Agblevor et al. (2010) have reported the properties of biofuels produced the fast pyrolysis of poultry litters of broiler chicken and turkey houses and bedding materials in a fluidized bed reactor. Biochar and bio-oil yields produced by the fast pyrolysis (temperature range between 450 and 550 ºC, feed rate 200 g h^{-1}, residence time from 2-5 h and nitrogen flow rate 18 $Lmin^{-1}$) of poultry litters of broiler chicken and turkey houses were 27 wt.% to 40 wt. % and 36 wt. % to 50 wt. % respectively. Pyrolysis of bedding material resulted in the bio-oil yield of 63 wt. %. The source, age and bedding material (hard wood) content of the poultry litter were the key parameters in controlling the output from the reactor. Higher heating value of the bio-oil produced by the poultry litter was in the range between 26 $MJkg^{-1}$and 29 $MJkg^{-1}$ due to protein content of the litter while that produced by the bedding material was 24 $MJkg^{-1}$. Chemical analysis of the bio-oil revealed that the oil was having higher viscosity, nitrogen content from 4 wt. % to 8 wt. %, sulfur less than 1 wt. % and pH around 6. Biochar was mainly composed of potassium, phosphorous calcium, magnesium and higher ash content (24 to 54 wt. %)

Maddi et al. (2011) have studied experimentally the yields and composition of bio-oil, gas and biochar produced by the pyrolysis of algal and lignocellulosic feedstocks under the same pyrolytic reactor conditions (operating temperature - 550 ºC to 600 ºC; heating rate -30 $ºCmin^{-1}$; time - 20 min). Analysis of the products showed that the carbon to oxygen (C/O) and hydrogen to carbon (H/C) molar ratio, overall C, H and O-contentas well as calorific values were similar for algae and lignocellulosic materials though there was a major difference in component bio-polymers. The composition of the algal bio-oil was different in comparison to the algal biochar. Fuel value of the algal bio-oil was reduced as a result of protein degradation during pyrolysis due to the presence of N-compounds.

Cao et al. (2011) have studied experimentally the fast co-pyrolysis of sewage sludge (SS), pig compost (PC), and wood chip (WC). Bio-oil yields of 45.2%, 44.4%, and 39.7% were obtained by using internally circulating fluidized bed with feed rate of 1-1.5 kg h^{-1} at 500 °C using nitrogen as a fluidizing gas. Higher calorific value of bio-oil produced by the pyrolysis of PC (31.2 MJ kg^{-1}) compared to SS (rich in poly cyclic organonitrogen and aliphatic species) and WC (low H/C ratio and caloric value, high oxygen content) bio-oil was due to high carbon content and low oxygen content. Similar chemical composition between SS and PC was detected with organonitrogen species.

Effects of pyrolysis reactor type (Slow or fast) and temperature on the pyrolysis yields were reported by Duman et al. (2011). Pyrolysis of cherry seeds (CWS) and cherry seeds shells (CSS) was carried out in fixed-bed and fluidized bed reactors at different operating temperatures. Maximum bio-oil yield of 44 wt. % was obtained at the pyrolysis temperature of 500 °C for both CWS and CSS with fast pyrolysis compared to 21 (CWS) and 15 wt. % (CSS) at 500 °C with slow pyrolysis.

Maximum bio-oil yields of 62 wt. % and 65 wt. % were obtained by the fast pyrolysis of cassava stalk and cassava rhizome. Pyrolysis of both the feed stocks was carried out in fluidized-bed reactor (temperature range from 440 to 540 °C) using a nitrogen flow rate between 1.3 and 2.3 g min^{-1}. Increased percentage of bio-oil yield was obtained in the temperature range between 475 and 510 °C. Quality of the cassava rhizome bio-oil was better compared to the cassava stalk bio-oil due to lower oxygen content (Pattiya, 2011).

Yao et al. (2011) have studied experimentally the comparative analysis of biochars produced by the pyrolysis of anaerobically digested and undigested sugar beet tailings. Yields of biochars obtained from anaerobically digested and undigested sugar beet tailings through bench scale slow-pyrolysis at 600 ºC were 45.5% and 36.3% of initial dry weight respectively. Digested sugar beet tailing biochar (DSTC) was having same pH and surface functional groups, but higher surface area with less negative charge compared to raw sugar beet tailing biochar (STC). An analysis of SEM-EDS and XRD revealed the presence of colloidal and nano-sized periclase (MgO) on the surface of DSTC.

Volli and Singh (2012) have investigated the variations in the pyrolysis yields of de-oiled cakes. The bio-liquid yields produced by the pyrolysis of sesame (*Sesamum indicum*), mustard (*Brassica napus*) and neem (*Azadirachta indica*) de-oiled cakes at a heating rate of 25 ºCmin^{-1} were increased from 18.6%, 23.4%and 17.9% to58.5% (CV-25.5MJkg^{-1}), 53.2% (CV-25.1 MJkg^{-1}) and 40.2% (CV-30 MJkg^{-1}) by weight due to increase in pyrolysis temperature from 300 ºC to 400 ºC. Biochar yields were decreased from 53.4%, 60.1% and 60.6% to 26.4%, 24.9% and 36.5% by weight respectively for the same feed stocks and temperature range due to higher primary decomposition. Biochar showed very good adsorption characteristics due to presence of heterogeneous pores.

Shah et al. (2012) have investigated the effects of feed stock storage on the pyrolysis yields. Biomass storage conditions were responsible for the difference in the yields of bio-oil, biochar and biogas produced by the fast pyrolysis of corn stover and cobs stored inside a metal building or wrapped inside a plastic anaerobically. Lesser bio-oil yield (45wt.%) for the single pass corn stover stored inside a building was obtained in comparison to the single pass corn stover wrapped inside a plastic (55wt.%). Similar results were experienced with the non-condensable gases. But the biochar yield (36.1wt. %) was higher for the stored corn stover in comparison to the wrapped stover (25.5 wt. %). Bio-oils generated from the ensiled single-pass cobs were more acidic than that of the bio-oils generated from the wrapped single-pass stover.

Effect of pyrolysis temperature on the fuel characteristics, the combustion profile, and the kinetic study was reported by Park and Jang, (2012). Pyrolysis of rice husks (RH), wood chips (WC) and wood pellets (WP) were carried out in an air tight crucible in the temperature range from 300 to 500 °C and then placed in an electric furnace to complete the process. Increase in the pyrolysis temperature resulted in the increased calorific value from 4725 kcal kg^{-1} at 400 °C to 4948 kcal kg^{-1} at 500 °C for RH, 7430 kcal kg^{-1} at 400 °C to 7953 kcal kg^{-1} at 500 °C for WC and 7368 kcal kg^{-1} at 400 °C to 7997 kcal kg^{-1} at

500 °C for WP respectively. The energy yields of the samples prepared at 400 °C and at 500 °C were from 50.07- 58.97% and 35.57 to 47.12% respectively.

Zhou et al. (2012) have investigated the effect of sulfuric acid on the properties of bio-oils produced by the pyrolysis of Douglas fir wood chips using auger and fluidized bed reactors. Water and biochar yields were increased due to the impregnation of sulfuric acid (concentration between 0 and 0.6 mass %) to the feed stock (500 ºC). At the same time bio-oil yield was decreased due to the presence of sulfuric acid. Yields of gas, bio-oil and char were comparable for both the reactors. Lower heating rates were responsible for the higher yield of water in the auger reactor. Reduction in the yields of acetic acid, acetol and lignin derived compounds (lignin oligomers and guaiacols) were identified due to the dehydration of cellulose in the presence of sulfuric acid.

Biochars produced by using different feed stocks such as pine wood (Pine),oak wood (Oak), bull manure with sawdust (Bull Manure), hazelnut shells (Hazelnut),dairy manure with rice hulls (Dairy Manure),corn stover (Corn), and poultry manure with sawdust (Poultry Manure) were having fixed carbon from 0% to 77.4% (w/w), volatile matter from 13.2% to 70.0%andash contents from 0.4% to 88.2%.Higher pyrolysis temperature (600 ºC) was responsible for the increase of fixed carbon depending on type of feedstock used for low-ash biochars whereas fixed carbon content decreased for the biochars having ash content more than 20%(Enders et al. 2012).

Cantrell et al. (2012) have reported the effects of pyrolysis temperature and manure source on the physicochemical characteristics of the biochars produced by using Lindburg electric box furnace. Pyrolysis temperature and manure source were responsible for the similarities and variations in physicochemical characteristics of the alkaline biochars produced by the pyrolysis of poultry litter and turkey litter, paved-feedlot manure, swine separated-solids, dairy manure at 350 ºC and 700 ºC. Results of the Fourier transform infrared spectroscopy (FTIR) revealed the similarities for (i) feedlot and dairy biochars and (ii) turkey and poultry, but differed for swine biochars. Dairy biochars were having higher contents of volatile matter, C and energy with low ash, N, and S contents. Greater contents of P, N, and S were observed for swine biochars with lowest pH and EC values whereas the poultry litter biochars demonstrated the higher EC values. Maximum biochar mass recovery was observed for turkey litter biochars (high ash content) compared to feedlot biochars

Kim et al. (2013) have studied experimentally the physicochemical properties of bio-oils and biochars produced by the pyrolysis of woody biomasses using fluidized bed reactor. The yields of bio-oil and biochar produced by the fast pyrolysis of two hard woods (oak and eucalyptus) and two soft woods (pitch pine and Japanese cedar) at a temperature of 500 ºC (residence time of volatiles 1.9 sec) were 62-68% and 11-14% based on dry weight of feedstock respectively. Similar physical properties such as such as pH (1.7-2.4), water content (20% - 26%), and heating value (15.5-19 MJkg^{-1}) were experienced with the bio-oils irrespective of the type of feedstock. Higher carbon content of the softwood was responsible for the higher calorific value of the bio-oil in comparison to hardwood.

Liu and Balasubramanian, (2014) have carried out the comparative evaluation of low temperature pyrolysis (LTP) and hydrothermal carbonization (HTC) of coconut fibers (CF) and eucalyptus leaves (EL). Pyrolysis of CF and EL carried out using a horizontal fixed-bed quartz reactor at a temperature of 250 °C for 20 min. with a heating rate of 20 °Cmin^{-1} resulted in the higher yields of biochars (CF-PY-69.2% and EL-PY-72.2%) compared to biochars produced by HTC in a Parr autoclave reactor (USA). Higher energy density was observed with the biochars produced by HTC, while the higher energy yields with LTP biochar. Increased thermal efficiency and reduced pollutant emissions were evidenced by the HTC biochars compared to LTP biochars due to higher combustion temperature range and sudden decrease of residue. Pre-treatment of biomass feedstocks by HTC resulted in the biochars with better fuel qualities compared to LTP biochars.

Lee et al. (2013) have carried out the comparative analysis of biochar characteristics produced by the pyrolysis of umbrella tree, cocopeat, palm kernel shell (PKS), paddy straw and sugarcane bagasse using bench-scale fixed bed reactor. Pyrolysis was carried out at 500 °C with a heating rate of 10 °Cmin^{-1} for 1 h. Biochar yields from the wood stem, bagasse and paddy straw were in the range from 24 to 28 wt. % whereas, the yield from cocopeat was 46 wt. %. Carbon content of the biochars was increased from 84to 89 wt. % compared to original carbon content of the biomass (43–63%).

Liao et al. (2013) have compared experimentally, the product yields of Brazilian Pepper (BP) and Air Potato (AP) with the feedstock materials (traditional) like energy cane and water oak. Biochar and bioenergy yields produced by the pyrolysis of BP and AP at three pyrolysis temperatures (300, 450, and 600 ºC) at a heating rate of 20 ºCmin^{-1}(feedstock masses10, 15, 20, and 25 g) were similar in comparison to the yields of the traditional feedstock materials. Increased production of biochar and bioenergy was observed at the lower temperature due to increase in the feedstock weight with minimum feedstock residence time. Increase in the pyrolysis temperature from 300 to 600 ºC resulted in the reduction of biochar production by 50% along with the increased bio-oil production rate (2% for AP at 300 ºC to 42% for BP at 450 ºC).

Effects of reactor configuration and operating temperature on the fast pyrolysis of *Miscanthus sinensis* were reported by Bok et al. (2013). Pyrolysis was carried out in two types of reactors namely rectangular and cylindrical fluidized beds, in the temperature range between 400 and 550 °C. Increase in the pyrolysis temperature (550 °C) resulted in the quicker decrease in the bio-oil yield with rectangular reactor compared to cylindrical reactor. Bio-oil yield of 48.9 wt. % was obtained at 500 °C using rectangular reactor whereas the bio-oil yield of 50.01 wt. % was produced at 450 °C with cylindrical reactor. Bio-oil obtained from the rectangular reactor showed the lower sugar content (2.11 to 9.35 wt. %) compared to the sugar contents of the bio-oil produced with cylindrical reactor (7.93 to 10.79 wt. %). Main chemical contents of the bio-oil were non-aromatic ketones, furans, sugars, lignin derived phenols, guaiacols and syringols and varied with the type of reactors and pyrolysis temperatures.

Troy et al. (2013) have investigated experimentally the effects of addition of saw dust on the pyrolysis yields of separated solid fraction of an aerobically digested pig manure (SADPM). Addition of saw dust resulted in the enhanced yield of bio-liquid and decreased yield of biochar in comparison to the yields without the addition of saw dust. Pyrolysis of the pig manure and mixtures (4:1w/w and 3:2w/w) was carried out in a laboratory scale reactor (purged with nitrogen at 50 cm^3min^{-1}) at 600 ºC with a residence time of 15 min (50 g feed stock in each run). Higher heating values (HHV) of biochar and gases were increased with the addition of saw dust compared to the HHV of bio-liquid. Addition of saw dust also resulted in the biochar with decreased nutrient concentrations. Composting of the feed stocks prior to pyrolysis was responsible for the increased bio-liquid yield and decreased yield of biochar. Addition of saw dust to SADPM increased the HHV of bio-liquid compared to the HHV of biochar. Net energy yield was increased with the addition of saw dust to the undigested and digested pig manure.

Wnetrzak et al. (2013) have studied experimentally the effects of chemical pretreatment of feed stocks prior to the pyrolysis. Chemically pre-treated pig manure resulted in an overall energy loss of 595.9 MJt^{-1}compared to the energy values of anaerobically digested and untreated feed stock due to loss of solid fractions as a result of pretreatment. Pyrolysis of both the feed stocks were conducted in a fixed bed reactor at two different temperatures 400 and 600 ºC with a heating rate of 20 $ºCmin^{-1}$ and residence time of 30 min. The behavior and properties of both the samples were similar during the thermogravimetric analysis. Lesser energy values were identified for the anaerobically digested (351.7 MJt^{-1}) and un-pretreated (817.3 MJt^{-1}) feed stocks compared to the energy value of beech wood (8935 MJt^{-1}) due to the higher mineral content of the pig manure.

Maximum bio-oil yields of 29.6 wt. % and 28.5 wt. % were obtained by the pyrolysis of *Pongamia glabra* seed cover (PGSC) and *Mesua ferrea* seed cover (MFSC) at 550 °C maintaining the heating rate of 40 $°Cmin^{-1}$. Pyrolysis was performed in a fixed bed reactor in the temperature range between 350 and 650 °C. Higher calorific value of 32.63 $MJkg^{-1}$ was observed with MFSC bio-oil (Bordoloi et al. 2015).

Effect of pyrolysis temperature on the physicochemical characteristics of the biochars produced by the fast pyrolysis of Canadian waste biomass such as forest residue (sawdust), agricultural waste (wheat straw and flax straw) and animal manure (poultry litter) was studied experimentally by Azargohar et al. (2014). Pyrolysis experiments were conducted by using a mobile pyrolysis unit in the temperature range from 400 to 550 °C.

Increased pyrolysis temperature resulted in the development of aromatic structure in biochar samples. Biochars produced by the poultry litter were having higher ash content compared with the other biochars.

Effect of sand addition to the packed bed pyrolysis reactor on the yields of pyrolysis process was reported by Sarkar et al. (2015). Biogas yield of 210 mL g^{-1} was obtained by sand addition at an operating temperature of 600°C (2 h operation) using lipid extracted microalgae (LEMA) as a feedstock whereas, freshly harvested microalgae without sand addition resulted in the biogas yield of 420 mL g^{-1} at an operating temperature of 800 °C (3 h operation). Sand addition also resulted in the increased production of hydrogen gas with decreased production of carbon dioxide.

Energy potential assessment of raw food waste (RFW) and digested food waste (DFW) were investigated experimentally by Opatokun et al. (2015). Pyrolysis of RFW and DFW was carried out in a tubular reactor for four hours at the heating rate of 10 °C min^{-1} using Ar as a carrier gas at the rate of 1000 mL min^{-1}. Pyrolysis energy distribution of RFW and DFW (in terms of gas, char and bio-oil) was 15.7 $MJkg^{-1}$ and 17.2 $MJkg^{-1}$ respectively. Energy rich solid fuel was obtained at a temperature of 500°C.

Mahmood et al. (2016) have reported the hydrothermal oxidation of food waste with and without enzymatic pre-treatment to produce hydrochar and bio-oil. Hydrothermal oxidation was carried out in pressure batch reactor (7, 21 and 36 bars) at different temperatures (150°C, 250°C and 350°C) with a residence time of 20 min. High quality hydrochar was produced with the increase in the process temperature. Decreased bio-oil yield and quality hydrochar was observed with the enzyme treatment. Efficiency of the process was decreased with the increased process temperature. Enzyme pre-treatment resulted in the increased cost of the biofuels.

Effects of biomass pattern, temperature and carrier gas on the pyrolysis of oil palm fibre (OPF) and oil palm fibre pellet (OPFP) were investigated experimentally by Chen and Lin, (2016). Pyrolysis of OPF and OPFP was carried out in tubular furnace with N_2 and CO_2 atmosphere at three reaction temperatures of 400, 450, and 500°C with a reaction time of 30 min. Pyrolysis of OPFP with CO2 as a carrier gas resulted in the higher liquid yield compared to OPF pyrolysis with N_2 atmosphere. Components of the bio-oils from OPF and OPFP were not affected by the biomass pattern and carrier gas atmosphere. Higher heating value (HHV) of the biochar was found to vary between18.90MJ kg^{-1} and 21.32 MJ kg^{-1}.

Bensidhom et al. (2018) have investigated the pyrolysis of Date Palm Rachis (DPR), Date Palm Leaflets (DPL), Tunisian date Palm Wastes (DPW), Date Palm Glaich (DPG) and Empty Fruit Bunches (EFB). Pyrolysis was carried out in a fixed bed reactor at an operating temperature of 500 °C with a heating rate of 15 $°Cmin^{-1}$. Maximum bio-oil yield of 25.99 wt. % was obtained with EFB while biochar yield of 36.66 wt. % was produced with DPL. Highest syngas fraction of 46.31 wt. % was obtained with DPL compared to other feed stock materials. Moderate amounts of hydrogen and carbon were present in the bio-oil where as significant proportions of methane and hydrogen were present in the syngas.

Leng et al. (2018) have studied experimentally the co-liquefaction of and lignocellulosic biomass and municipal sewage sludge (MSS). Liquefaction was carried out in an airtight autoclave at 300 ºC using different mixing ratios of rice straw or wood sawdust and MSS. Increased bio-oil yield from 22.74% (MSS) or 23.67% (rice straw) to 32.45% was obtained by the liquefaction of rice straw/MSS (4/4, wt). Yield of bio-oil produced by wood sawdust mixtures/MSS (6/2, wt) was comparable with MSS/wood dust. Esters and phenols were the main contents of the bio-oil. Compared to bio-oils obtained from individual feedstock lower boiling points (degradation temperatures) were observed with the bio-oils produced from MSS/biomass mixtures.

2.1.3. Catalytic pyrolysis

Pyrolysis product yield enhancement and upgradation of biofuel properties are the present day requirements. This has been achieved through the use of catalysts and this process is popularly known as “catalytic pyrolysis”. Literature citations on the catalytic pyrolysis of different biomass feed stocks is reviewed critically and presented in the following paragraphs.

Smets et al. (2013) have reported the slow pyrolysis of rapeseed cake in a horizontal tubular quartz reactor at atmospheric pressure and temperature range between 150 and 550 °C for 20 min in presence of few catalysts. A maximum liquid yield of 44.9 wt. % was obtained using ZSM-5 zeolite (HZSM-5) as catalyst. Reduced water and organic compounds were observed in the oil due to the presence of catalysts. Organic compounds about 34.06 wt.% were obtained in the non-catalytic experiments compared to the catalytic experiments (Na_2CO_3 -27.10 wt. %, HZSM-5-26.43wt. % and γ-Al_2O_3 -21.64 wt. %). Calorific value of the bio-oil obtained by using Na_2CO_3as catalyst was 36.8 $MJkg^{-1}$. An effective deoxygenation of about 14.0 wt. %was identified with HZSM-5. Ex-bed HZSM-5 and in bed Na_2CO_3 were proved as better performing catalysts among the three used for the pyrolysis process.

Effects of addition of metal salts and metal oxides to the algae (*Gulfweed*) and microwave power on the pyrolysis products were examined experimentally by Longjun et al. (2013). Increase in the microwave power from 750W to 2250 W resulted in the increase of gas yield by 39.45% and decrease of solid residue by 22.05%. Decreased yields of solid residue (14.35%) and bio-oil (11.04%) were observed due to addition of 5% of copper oxide (CuO) and magnesium oxide (MgO) on mass basis to the feed stock.
Addition of magnesium chloride ($MgCl_2$), zinc chloride ($ZnCl_2$) and NaH_2PO_3 (5% on mass basis) to the algae resulted in the increased yield of solid residue by 3.98%,1.13% and 2.31%, and bio-oil yield by 6.3%, 16.92% and 0.71%, respectively. The final temperature up to 756.27 °C was observed with 5% addition of CuO, while 5% addition of calcium oxide (CaO) resulted in the reduction of final temperature around 10.63%. Electrical energy consumption was decreased by 40.76% due to addition of MgO.

Miskolczi et al. (2013) have studied experimentally the pyrolysis of municipal plastic waste (MPW) and municipal solid waste (MSW) using catalysts. Pyrolysis of MSW in a laboratory scale batch reactor at 500 °C with Ni-Mo-catalyst resulted in the biochar with highest BET surface area (39.1 m^2g^{-1}) with average pore diameter of 0.6 nm. Viscosity of oil produced by the pyrolysis of MPW was higher compared to MSW oil at all the temperatures studied and decreased due to β-zeolite and MoO_3 catalysts. The contaminants of the pyrolytic oils such as potassium (K), sulphur (S), phosphorous (P), chlorine (Cl) and bromine (Br) were decreased by the use of catalysts.

Aysu and Küçük, (2014) have investigated experimentally the effects of operating parameters such as particle size, catalyst and ratio of catalyst, temperature and sweep gas flow rate on the yields of pyrolysis. Pyrolysis of giant fennel (*Ferula orientalisL.*) stalk was carried out in a fixed-bed tubular reactor in the temperature range between 350 and 600 °C with different heating rates of 15, 30 and 50 °$Cmin^{-1}$ respectively. Particle size between 0.224 and 0.150 mm, 15% zinc oxide (ZnO) catalyst, operating temperature 500 °C with a heating rate of 50 °$Cmin^{-1}$ and 100 cm^3min^{-1} of nitrogen together resulted in the maximum liquid yield of 45.22%. Main constituents of the bio-oil were water, aromatic, oxygenated and nitrogenated organic compounds. ZnO was the more effective catalyst to produce bio-oil compared to aluminium oxide.

Production of olefinic and aromatic hydrocarbons and nutrient-rich biochar by ex-situ catalytic pyrolysis using HZSM-5 catalyst was reported by Wang et al. (2017). Sewage sludge pyrolysis was carried out in a tandem micro-reactor system using helium as a carrier gas at optimal pyrolysis temperature of 500 ºC. Nitrogen content of the sludge was contained in the char and released as ammonia (31.80%). Olefin and aromatic yields of 24.41% and 19.13% were obtained at pyrolysis temperature of 500 ºC and catalyst temperature 600 ºC respectively.

2.2. Hydrothermal carbonization

Hydrothermal carbonization is the hydro-thermal conversion process to treat discarded biomass. This is a low temperature thermal treatment process to biofuels. Literature citations on the hydrothermal carbonization of different biomass feed stocks are reviewed critically and presented in the following paragraphs.

Biochars produced by the hydrothermal carbonization of feed stocks such as coconut fiber and dead eucalyptus leaves were having better fuel qualities compared to the untreated feedstock. Hydrothermal carbonization was performed by using a laboratory scale semi-batch 500-ml Parr autoclave reactor at temperatures between 150 and 375 ºC and residence time of 30 min. Decreased volatile matter/ (volatile matter + fixed carbon) ratio, increased carbon content, higher hydrophobicity and lower ash content were observed through the chemical analysis of biochar produced by the pretreated feedstock. The aromatic characteristics of the biochars were increased with the increasing temperature. The fragments of lignin and decomposition intermediates were present in the biochar even after the supercritical water treatment (Liu et al. 2013).

Kaushik et al. (2014) have investigated the hydrothermal carbonization of food waste with and without pretreatment. Pre-treated food waste with an enzyme ratio of 1:2:1 (carbohydrase: protease: lipase) resulted in the increased carbon content from 43.7% to 65.4% and calorific values from 17.4 to 26.9 $MJkg^{-1}$ by hydrothermal carbonization compared with the untreated food waste. Hydrothermal carbonization was performed in a stirred pressure batch reactor at the pyrolysis temperature between 150 and 350 °C with a constant reaction time of 20 min maintaining the operating pressures of 7, 21 and 36 bars respectively. Diverse surface functional groups and carbonaceous microspheres with low concentrations of inorganic elements were observed due to pretreatment, but no significant change was noticed in the yield of bio-oil with and without pretreatment.

Parshetti et al. (2014) have reported the hydrothermal carbonization of urban food waste to produce biochars for adsorption studies. Hydrothermal carbonization was carried out in a 500 mL Parr stirred pressure batch reactor in the temperature range between 180 and 350 °C in the presence of water under autogenous pressures with a constant residence time of 20 min. Hydrochar produced at the lower operating temperature (250 °C) to adsorb Rhodamine 6G dyes and Acridine Orange from the textile waste water was more efficient compared to hydrochar produced at 350 °C.

2.3. Oxidative pyrolysis

Pyrolysis process is normally carried out under the inert atmosphere. In the following study pyrolysis has been carried out by using atmospheric air as a carrier gas and this process is commonly termed as “oxidative pyrolysis”.

Biochar and bio-oil yields produced by the oxidative pyrolysis of sugar cane straw in a fluidized bed reactor with a feeding rate of 200 kg h^{-1} were 48.2 wt. % and 35.5 wt. % respectively. Maximum bio-oil yield was obtained at an operating temperature of 470 ºC with equivalence ratio (ratio of flow rate of air used to the stoichiometric flow rate required for the complete fuel combustion) of 0.14. Heating value of the bio-oil was 22.95 $MJkg^{-1}$ with low water content and oxygen content of 38.48 wt. % on dry basis. Presence of acid organic compounds was responsible for the variation of pH value of the bio-oil (3.14 to 3.57). Higher heating value of 13.54 MJ kg^{-1}, high fixed carbon and volatile matter content were the characteristics of the biochar obtained (Mesa-Pérez et al. 2013).

2.4. Torrefaction

Torrefaction is the slow pyrolytic process to treat biowastes and normally carried out between the temperature range 250 ºC and 350 ºC to produce biofuels. Literature citations on the torrefaction of biomass feed stocks are reviewed critically and presented in the following paragraphs

Vakalis et al. (2017) have reported the torrefaction, carbonization and high temperature pyrolysis of household biowaste. Torrefaction (260 ºC for 30 min), carbonization (550 ºC for 10 min) and high temperature pyrolysis (860 ºC for 10 min) were performed using bench scale tubular (quartz) pyrolysis reactor. Energy dense fuel (24.09 MJ kg^{-1}) was obtained by torrefaction compared to carbonation that produced graphite like material with high yield.

Correia et al. (2017) have studied experimentally the low-temperature carbonization and impact of torrefaction on the properties of biochars produced by the thermal conversion of *Arundo donax L.* and *Phoenix canariensis*. Carbonization was carried out by using muffle furnace at the temperature range between 200 ºC and 350 ºC under oxygen limited conditions for time periods from 15 to 90 min. Biochar composition, mass and energy yields were strongly dependent on the temperature. Heating value, ash content and fixed carbon content of the biochars were increased due to torrefaction while moisture, volatile matter, O/C and H/C ratios were decreased. Improved grindability of the biochar was observed for the temperature 250 ºC and above.

Torrefaction of food waste to enhance the energy density, calorific value and carbon content compared to untreated food waste was investigated experimentally by Rago et al. (2018). Torrefaction was carried out in a stainless steel cylindrical laboratory scale reactor from 225 ºC to 300ºC using preheated muffle furnace for 1 h and 3 h with a heating rate of 15 $^{\circ}\mathrm{Cmin}^{-1}$. Energy value of the torrefied food waste above 275 ºC (1 h and 3 h) was energetically efficient to that of the coal whereas, the torrefaction at 300 ºC for 3 h was inefficient.

2.5. Microwave assisted pyrolysis

Energy efficient pyrolysis processes, with higher yields as well as better quality bio-fuels, are the present day requirements. In this regard an efficient thermo-chemical process to produce bio-oil, bio-char and syngas is the MAP (Yin, 2012). Literature citations on the microwave assisted pyrolysis are presented in the following paragraphs.

Product yield and compositions of microwave assisted pyrolysis of rice straw were dependent upon the microwave power and size of the feed stock. Pyrolysis was carried out in a quartz tube using single mode microwave oven with a frequency of 2.45 GHz. Increased reduction in the fixed carbon content of the biomass was observed in the microwave power range between 400 and 500W. The main contents of the gaseous products were hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) respectively. Among the various gaseous products hydrogen gas concentration by volume was in the range from 50.67% to 55%. The variation in the production rate of hydrogen gas was observed due to the generation of hot spots as a result of microwave heating. Bio-oil yield was not affected by the increase in the microwave power and remained constant at 55 wt. % except for 150 W. Major components of the bio-liquid were alkanes, polars, and low-ringed polycyclic aromatic hydrocarbons (PAH) and highly oxygenated. Solid residues with higher calorific value from 18.51 to 19.66 MJkg^{-1}were obtained for the microwave power range from 200 to 350 W. Increased gaseous products, kinetic parameters and decreased H/C and O/C atomic ratios for solid residues were evidenced as a result of increased microwave power. Nearly 60 % of the energy available with the feed stock was converted into useful biofuel (Huang et al. 2008; Huang et al. 2010; Huang et al. 2013).

Salema and Ani (2011) have reported the effect of biomass to microwave absorber on the pyrolysis products of oil palm biomass. Products of microwave assisted pyrolysis such as bio-oil, char and gas produced by using shell and fibers of palm were dependent upon the ratio of biomass to microwave absorber. The main contents of the bio-oil were phenols, ketones, aldehydes and carboxylic acids. The pH of the bio-oil was in the range between 2.7 and 3.0. Surface image analysis of the biochar produced by the conventional pyrolysis revealed the presence of large and deep cracks due to overheating of the surface compared to the char produced by the assistance of microwaves. Salema and Ani (2012) also investigated the pyrolysis of oil EFB in a multimode microwave (MW) system. Temperature profiles of EFB were affected by the ratio of biomass to MW absorber along with the products of pyrolysis (5–21 wt. % bio-oil, 48–80 wt. % char and 14–31 wt. % gas). Addition of 25% of biochar (MW absorber) to the EFB resulted in the bio-oil yield of 21 wt. %. Nearly 60–70% of area, as identified by the GC–MS and FT-IR analysis, was occupied by the phenolic compounds. The heating value of the biochar was 25 MJ kg^{-1}. Plasma arc was observed in the absence of MW absorber due to residual palm oil in the EFB biomass.

Du et al. (2011) have carried out an experimental study on microwave assisted pyrolysis (MAP) of microalgae (*Chlorella sp.*). Microwave power of 750 W yielded a maximum bio-oil yield of 28.6%. The main contents of the bio-oil, as identified by the gas chromatograph-mass spectroscopy (GC-MS), were long chain fatty acids, aromatic hydrocarbons, and nitrogenated compounds. Aromatic and aliphatic hydrocarbons accounted for about 22.18% of the total GC–MS spectrum area (ion chromatogram) with low oxygen content. The higher heating value (HHV), density and viscosity of the oil were 30.7 MJkg^{-1}, 0.98 kgL^{-1} and 61.2 cSt respectively.

Bio-oil yield of 49.8 wt. % with some of the desirable properties like high calorific value of 35.0 MJkg^{-1}, low density of 929 kgm^{-3}, 29.5 wt. % of monoaromatics and negligible quantities of poly aromatic hydrocarbons (PAHs) were obtained by the microwave assisted pyrolysis of sewage sludge at an operating power of 400W (residence time - 6 min). Pyrolysis was carried out in a microwave oven having a magnetron of 2450 MHz and graphite as a microwave absorber. Optimum power range to produce bio-oil was in the range between 400 and 600 W. Gas formation was observed in the power range from 600–800W and further increase in the power above 800 W resulted in the favored conversion of solids into gases. Certain elements like sulfur and nitrogen were detected in the bio-oil at the power range from 600-800 W and retained in the solid residues at 1000 W (Tian et al. 2011).

Wang et al. (2012) have carried out the experimental studies on the occurrences of exothermic reactions during the microwave assisted pyrolysis of corn stover in the temperature range from 188.4–224.0 ºC and 367.0–387.0 ºC by alternate heating methods. These reactions were capable of sustaining the pyrolysis reactions in the absence of external heat sources and indicated that, the microwave-assisted pyrolysis (MAP) is a highly energy saving process. Increased heating efficiency of the solid chars was observed because of the absorption of the microwaves.

Zhao et al. (2012) have reported the microwave assisted pyrolysis (MAP) of wheat straw using a modified 3000 W, 2.45 GHz domestic microwave oven. MAP resulted in the increase of gaseous products yield from 17.69 wt. % to 22.27 wt. %, combustible gas to total gas products ratio from 67.21 vol. % to 77.14 vol. % and increase in the number of uniform pores due to increase in the temperature from 400 °C to 600 °C with reduced pore sizes (282.16 nm at 400 °C to 46.64 nm 600 °C). Surface area and pore volume of the resulting coke (char) was increased from 0.89 m^2g^{-1}at 400 °C to 9.81 m^2g^{-1} at 600 °C and 0.006 cm^3g^{-1} at 400 °C to 0.012 cm^3g^{-1} at 600 °C respectively. Higher concentration of the syngas was detected in the gaseous products with lower concentrations of CO_2 and CH_4.

Effects of stirrer speed and microwave (MW) absorber percentage on the product yield, the properties of the products and temperature profile were investigated by Abubakar et al. (2013). Pyrolysis of oil palm shell (OPS) was conducted in a modified domestic MW system with maximum power of 800W and 2.45 GHz frequency at an operating temperature between 450 and 550 °C. Stirrer speed of 50 rpm and 25% MW absorber resulted in the maximum bio-oil yield of 28 wt. % while the maximum biochar (41wt. %) and biogas yields (47 wt. %) were obtained at 150 rpm with 25% MW absorber and 100 rpm with 50%MW absorber respectively. The calorific value of the biochar was 29.5 MJ kg^{-1} at 100 rpm stirrer speed and 50% MW absorber. Bio-oil obtained was rich in phenol.

Beneroso et al. (2013) have reported the microwave induced pyrolysis (MIP) of the extraction residue of microalga *Scenedesmus almeriensis*. Higher syngas concentration of 94 vol. % was obtained at a temperature of 800 ºC. Biochar produced by the pyrolysis of the sample at 800 ºC was used as a microwave absorber (sample proportion 30:70 wt. %) to attain higher operating temperatures due to poor microwave absorption characteristics of the microalga. The pyrolysis of the microalga at 400 ºC resulted in the gas having the highest hydrogen to carbon monoxide ratio (H_2/CO) of 2.3. Throughout the pyrolysis experiments the helium flow rate was 20 $mLmin^{-1}$.

Pyrolysis of multilayer packaging beverage composed of paper, polyethylene (PE), and aluminum (Al) with and without using microwave absorbers was investigated experimentally by Undri et al. (2014). Experiment was carried out using 1000 cm^3 borosilicate Erlenmeyer flask inside the microwave oven at a microwave power of 3 kW with a frequency of 2.45 GHz. Main constituents of the bio-oil were water, alcohols, aldehydes, acids, and anhydrosugars depending upon the pyrolysis conditions. Aromatics content in the bio-oil was increased due to the presence of carbon as microwave absorber.

Effect of well mixed carbon bed on thermal cracking of waste palm oil by pyrolysis was studied experimentally by Lam et al. (2016). Bio-fuel obtained by the microwave assisted pyrolysis of waste palm oil was free from sulphur, carboxylic acid, triglycerides and low oxygen content with a calorific value close to that of diesel fuel. Rapid heating rate of 18 ºC min^{-1} was provided by the carbon bed at an operating temperature of 450 ºC with residence time less than 25 min.

Zhang et al. (2016) have reported the effects of microwave power, microwave absorber, particle size, catalyst and different pyrolysis atmospheres on microwave-enhanced pyrolysis (MEP) of natural algae. Pyrolysis of algae was performed in a microwave oven at 723 K under the different atmospheres of nitrogen, 10% hydrogen to argon (H_2/Ar) and CO_2. Among the three atmospheres investigated CO_2 atmosphere resulted in the maximum bio-oil yield of 54.3% compared to nitrogen (49.1%) and 10% H_2/Ar (51.7 %,) respectively. Bio-oil was mainly composed of hydrocarbons under 10% H_2/Ar atmosphere and carboxylic acids under CO_2 atmosphere. Higher heating value (HHV) of bio-oil under 10% H_2/Ar was 34.24 MJ kg^{-1}.

Bartoli et al. (2016) have carried out an experimental investigation on the microwave assisted pyrolysis of short rotation coppice (SRC) of poplar clones. Bio-oil yield of 32.0 % with lower water content of 17.5% was obtained by the pyrolysis of stump-roots and leaves of poplar clones at an operating temperature of 702 K. Bio-oil was mainly composed of acetic and formic acids, acetic anhydride, furanes and various phenols. Higher acetic acid concentration (543.3 mg mL^{-1}) was observed with bio-oil.

Microwave assisted pyrolysis of corn stalk biomass briquettes resulted in the bio-oil, biochar and gas yields of 19.6%, 41.1%, and 54.0% respectively. Pyrolysis of corn stalk biomass briquettes was carried out in a developed microwave reactor using 3 kW power generators at 2.45 GHz frequency. Heating value of the biochar was 32 MJ kg^{-1} while that of the bio-oil was 2.47 MJ kg^{-1}. Bio-oil produced was not suitable for energy applications as well as chemical production (Salema et al. 2017).

2.5.1. Co-pyrolysis

In the recent years some studies have been under taken to produce biofuels through pyrolysis or gasification of blended biomass feed stocks using microwaves. This method is known as “microwave assisted co-pyrolysis”. Literature citations on the microwave assisted co-pyrolysis of biomass feed stocks are reviewed critically and presented in the following paragraphs.

Effects of microalgae to scum ratio, catalyst to feed ratio, co-pyrolysis temperature on bio-oil yield and composition were investigated experimentally by Xie et al. (2015). Fast microwave assisted co-pyrolysis of scum and a microalga was carried out in the temperature from 450 to 650 °C usinGHzSM-5 as catalyst. Bio-oil yield of 22 wt. % was obtained at the pyrolysis temperature of 550 °C. Increase in the catalyst to feed ratio from 1:1 to 2:1 resulted in the increased production of aromatic hydrocarbons in the bio-oil.

Wang et al. (2017) have reported the microwave assisted co-pyrolysis of used waste tires and bamboo saw-dusts with HZSM-5 as the catalyst. Bio-oil yield of 30.23 % was obtained at 550 °Cwith lower proportions of polycyclic aromatic hydrocarbons. Waste tire to bamboo saw-dust of 1:1 resulted in the maximum proportions of polycyclic aromatic hydrocarbons (PAH). Bio-oil yield of 44.70 % was attained at the pyrolysis temperature of 550 °C with catalyst to feed ratio of 3:10.

Dai et al. (2017) have investigated the effects of catalyst to feed ratio, soap stock to tire ratio and co-pyrolysis temperature on the pyrolysis yields and their chemical composition. Microwave assisted catalytic fast co-pyrolysis of waste tire and soap stock was carried out at an operating temperature of 550°C. Addition of HZSM-5 catalyst resulted in the decrease of bio-oil yield from 42% to 38.86% with the increase of aromatic compounds. Presence of waste tire was responsible for the increase of aromatic compounds.

Effects of addition of catalysts (HZSM-5 and MgO) on microwave assisted fast co-pyrolysis of low-density polyethylene (LDPE) and lignin were studied experimentally by Fan et al. (2017). Maximum bio-oil yield of 32 wt. % was obtained at the pyrolysis temperature of 500 ºC. Lignin to LDPE ratio of 1:2 resulted in the complete removal of methoxyl group in the phenols along with the increased aromatics in the bio-oil. Increased HZSM-5 to MgO ratio resulted in the increased aromatics and decreased alkylated phenols in the bio-oil.

Effects of straw stalk to soapstock ratio, catalyst to feed ratio and pyrolysis temperature on bio-oil yield were investigated by Zhou et al. (2017). Fast catalytic pyrolysis using microwave irradiation was carried out using microwave oven (800 W) under the vacuum atmosphere of 100 mm of mercury (Hg). Maximum bio-oil yield of 43.00 wt. % with increased proportion of aromatic hydrocarbons and aliphatic compounds was obtained at 550 ºC with a straw stalk to soapstock ratio of 1:1 to 1:2. Improved quality bio-oil with decreased yield was experienced under the influence of HZSM-5 catalyst.

2.5.2. Comparative studies

In recent years' attention has been paid towards the comparative studies on microwave assisted pyrolysis of various biowastes and characteristics of pyrolysis products. Literature citations on the comparative studies on microwave assisted pyrolysis with conventional pyrolysis as well as different biomass feed stocks are reviewed critically and presented in the following paragraphs.

Effects of multimode and single mode microwave oven with char and graphite as microwave absorbers on the pyrolysis of sewage sludge were reported by Domı´nguez et al. (2005). Cracking and dehydrogenation reactions were experienced with the multimode microwave oven compared to single mode oven, in spite of similar compositions of bio-oils. Higher proportion of 1-alkenes than n- alkanes, an increase in the proportion of monoaromatics and increased cracking in the large aliphatic chains were observed with graphite as a microwave absorber than the char. Bio-oils obtained were free from harmful compounds such as heavy PAHs and more aliphatic and oxygenated at an operating temperature of 1000 °C.

Domı´nguez et al. (2006) have investigated experimentally the effect of high temperature (above 1000 °C) on pyrolysis of sewage sludge using electrical and microwave heating. Microwave pyrolysis resulted in the resulted in the hydrogen (H_2) gas yield of 38% and syngas yield (H_2 + CO) of 66% as a result of multimode heating with char as absorber. Increased yields were observed with microwave pyrolysis compared to the electrical heating. Main contents of the bio-oil produced by the microwave heating were carboxylic or amide groups, ester, while the high proportion of esters and nitriles, aromatic hydrogen and aliphatic hydrogen were the contents identified due to electrical heating. Gas obtained by the electrical oven was rich in hydrocarbons (25%) with better calorific value in comparison to 6–11% of hydrocarbons by microwave heating.

Comparative study on the pyrolysis of biomass wastes (glycerol, coffee hulls and sewage sludges) was performed experimentally by Fernández and Menéndez, (2011). Higher gas yield with increased syngas content was observed with the microwave heating compared to conventional pyrolysis. Hot spot phenomenon, the unique feature of microwave heating, resulted in the desired effects with the increase in the pyrolysis temperature. Lower pyrolysis time and energy consumption were noticed with the microwave heating compared to conventional heating.

Shuttleworth et al. (2012) have investigated the differences between the microwave assisted pyrolysis (MAP)and conventional pyrolysis using different biomass feed stock materials. Main contents of the gaseous products obtained by the MAP of various biomass feed stocks such as reed canary grass, wheat straw, pelletized bracken, pelletized softwood, barley dust, waste office paper and macro algae were CO_2 (50%−70%), CH_4 (15%−20%), CO (5%−10%) and other volatiles including hydrocarbons, acids and aldehydes (<5%). The MAP was carried out with the considerable reduction in the temperature range between 120 and180 ºC (conventional pyrolysis-250−380 ºC) with a nitrogen flow of 100 cm^3min^{-1} at a heating rate of 10 $ºCmin^{-1}$.

Aziz et al. (2013) have reported the characteristics of bio-oils produced by the pyrolysis of wood chips, sago wastes and palm kernel shell. Pyrolysis was performed in the temperature range from 250°C to 390 °C using a modified household microwave oven.

Nitrogen flow rate of 500 mL min^{-1} with different heating times (3 min, 5 min, and 7 min for PK and WC, and 2, 3 and 4 min for SW) resulted in the higher calorific values (PKO-27.19 MJ kg^{-1}, WCO-25.99 MJkg^{-1}and SWO-21.99 MJ kg^{-1}). Functional groups dominated in the bio-oils as identified by the Fourier transform infrared (FTIR) spectroscopy were phenol, alcohols, ketones, aldehydes and carboxylic acids. The gas chromatograph (GC) and mass spectroscopy revealed the presence of phenolic compounds and high value hydrocarbons such as monoaromatic hydrocarbons. Carcinogenic polyaromatic hydrocarbons (PAH) were absent in the bio-oils due to high oxygen content.

Microwave assisted pyrolysis of cellulose, using closed and open microwave setups, was experimentally investigated by Shra'ah and Helleur (2014) at a lower temperature range from 200 °C to 280 °C. Pyrolysis of amorphous cellulose at 260°C using an open system resulted in the bio-oil yield of 45%. Bio-oil yields of 52% and 47% were obtained by adding water to the amorphous and crystalline celluloses. Increased gaseous products were observed by adding activated carbon to the feed stocks. Variations in the chemical nature and dependence on the feed stocks were observed with the open and closed pyrolysis processes.

Ferrera-Lorenzo et al. (2014) have carried out the comparative analysis of biochars produced by the pyrolysis of microalgae industrial solid waste (algae meal) using microwave furnace and electrical conventional furnace. Biochars were similar in properties as a solid bio-fuel. The operating conditions were similar for both the processes (Temperature - 750 °C, Residence time - 60 min, and Nitrogen flow rate - 60 mL min^{-1}). Microwave pyrolysis resulted in the higher percentage of syngas ((74.91%) compared to the fraction of syngas obtained with conventional furnace. Bio-oil having higher heating value of 27.54 MJ kg^{-1} was produced by the microwave pyrolysis. Greater numbers of phenolic, pyrrole and alkane compounds were found in the bio-oils produced by the conventional pyrolysis in comparison to the benzene and pyridine compounds by microwave pyrolysis.

Microwave assisted fast pyrolysis of leaves, stems and rhizomes of *Arundo donax* and relevance of these organs on pyrolysis yields with carbon as microwave absorber under different conditions was reported by Bartoli et al. (2016). Rhizomes and leaves were responsible for the increased biochar yield whereas the stem was the cause for higher bio-oil yield. Biochar, bio-oil and biogas yields were 62.9%, 40.9% and 4.6%respectively. Higher amounts of aromatics, acetic acid, furanes and levoglucosan (47.6 g L^{-1}) were the main contents of the bio-oil. Caloric value of the biochar was 30.8 $MJkg^{-1}$.

Microwave assisted pyrolysis (MAP) of three marine biomasses such as microalgae-spirulina, chlorella and macroalgae-porphyra was investigated by Hong et al. (2017). Pyrolysis was carried out in a laboratory-scale multimode-microwave cavity at three different temperatures (400, 550 and 700 °C). Higher fraction of syngas (87.1 wt. % and 73.3 vol. %) was obtained by the pyrolysis of porphyra. Protein rich microalgae (spirulina and chlorella) was found to be the suitable biomass to produce bio-oil compared to porphyra due to lesser content of polycyclic aromatic hydrocarbons (PAH). High carbohydrate content (47.7 wt. %) of porphyra resulted in the H_2 + CO rich gas (85.6–87.1 wt. %).

2.5.3. Catalytic pyrolysis

Pyrolysis product yield enhancement and upgradation of biofuel properties using microwave irradiation are the present day requirements. This has been achieved through the use of catalysts and this process is popularly known as “microwave assisted catalytic pyrolysis”. Literature citations on the microwave assisted pyrolysis with the assistance of catalysts are reviewed critically and presented in the following paragraphs.

Hu et al. (2012) have studied experimentally the effects of catalysts on the microwave assisted pyrolysis of *Chlorella vulgaris*. Maximum bio-fuel yield of 87.47% was obtained by using activated carbon (5%) as a catalyst. Bio-oil and gas yields were 35.83 wt. % and 52.37 wt. % using microwave power levels of 1500 W and 2250 W respectively. The optimum power level to obtain the bio-fuel product was 2250 W. Nitrogen was used as an inert carrier (300 mL min^{-1}) gas during the experiment to maintain oxygen limited condition.

Effects of liquefaction temperature, liquefaction time, microwave power, solvent-to-feedstock ratio, catalyst content and moisture content on bio-oil yield produced by the microwave-assisted direct liquefaction (MADL) of algae (*Ulva prolifera)* were investigated experimentally by Zhuang et al. (2012). Microwave power of 600 W, liquefaction time of 30 min., liquefaction temperature of 180 °C, 6% of sulphuric acid catalyst (H_2SO4) and solvent-to-feedstock ratio of 16:1 resulted in the maximum bio-oil yield of 84.81 ± 0.13%. Bio-oil was mainly composed of water, long-chain fatty acids (C_{13} to C_{18}), benzene carboxylic acid, fatty acid methyl esters and diethyl phthalate. Heating value of the bio-oil was 15.05 MJ kg^{-1}.

Kuan et al. (2013) have reported the effects of catalysts on the pyrolysis product yields. Addition of metal oxide catalysts resulted in the increase of mass reduction ratio (from 81.3% to 82.7–86.9 %.) and reaction rate of microwave assisted pyrolysis of sugarcane bagasse, though the maximum temperature was decreased. The process was carried out in an oxygen limited atmosphere (50 mL min^{-1}) for period of 30 min. with microwave power level of 500 W. Hydrogen gas (H_2) and liquid productions were increased due to the presence of nickel oxide (NiO) or calcium oxide (CaO) (from 23 to NiO-32 and NiO-24 wt%), while the higher gas production was observed with CaO or MgO (from 58 to CaO - 62, and MgO-65 wt.%). Compositions of the gaseous products were affected by the self-gasification and interactions between the gaseous molecules formed during the early pyrolysis stage. Calorific values of the solid residues were decreased slightly from 24.38 MJ kg^{-1} to 22.84–23.94 MJ kg^{-1} under the influence of catalysts.

Huang et al. (2013) have investigated the effects of catalysts on the characteristics of pyrolysis yields under different atmospheric conditions. Reaction performance of Microwave assisted pyrolysis (MAP) of corn stover under N_2 atmosphere (500 W and 30 min. time) was more suitable compared to CO_2 atmosphere due to increased absorption of heat by the CO_2 molecules. Reduced calorific values of the solid residues, decreased toxicity of liquid products due to reduced formation of PAHs, more liquid products, decreased gaseous products, increased temperature and mass reduction ratio were observed due to the presence of metal-oxide catalysts. Gaseous products identified were CO_2 under CO_2 atmosphere and CO under N_2 atmosphere. The calorific values of the solid residues were higher (26.32 and 25.07 MJ kg^{-1} under N_2 and CO_2 atmospheres) compared to the as-received corn stover (18.20 MJ kg^{-1}) in the absence of catalysts.

Liu et al. (2014) have studied experimentally the effects of addition of metal salts on microwave assisted pyrolysis of food waste. Addition of 5% (mass basis) metal oxides (Manganese oxide-MnO_2, Magnesium oxide-MgO and Iron oxide-Fe_2O_3) and chloride salts (Sodium chloride-NaCl and Copper chloride-$CuCl_2$) resulted in the decreased yield of bio-oil and increased yield of gas. Catalysts such as MgO and MnO_2were responsible for the lower heating value (LHV) of the biochars and increased pH values of the lower layer bio-oils, but the effects of catalysts $CuCl_2$ and NaCl were exactly opposite. The optimum microwave power for pyrolysis process was 400 W. The optimum energy ratio of production to consumption (ERPC) of 0.91 was evidenced with the use of $CuCl_2$. Negative effects were observed with the addition of CuO, CaO and $MgCl_2$.

Addition of multiple microwave absorbers (also used as a catalyst) resulted in the improved microwave absorption as well better quality bio-oil and biochar compared to the use of single catalyst. Biomass sample (switch grass) containing a mixture of 10 wt.% K_3PO_4 (Potassium Phosphate Tribasic, reagent grade, ≥98%)and 10 wt.% bentonite reached a temperature of 400 °C in 2.8 min. with microwave heating compared to 28.8 min. with conventional heating. Water content of the bio-oil was decreased from 22.7 to15.0 wt. % compared to switch grass mixed with 20 wt. % silicon carbide (Mohamed et al. 2016).

Zhang et al. (2017) have reported the effect of modified ZSM-5 zeolite catalyst during microwave-assisted fast pyrolysis of spent edible mushroom substrate. Pyrolysis experiments were carried out using three modified catalysts (SiO_2-ZSM-5, EDTA-ZSM-5, and PC-ZSM-5) and original ZSM-5. All the experiments were carried out in a microwave oven (750 W) at 500 ºC in a vacuum atmosphere of 250 mm of Hg with a residence time of 45 min. Modified catalyst (SiO_2-ZSM-5) was responsible for the maximum bio-oil yield (16.0%) with reduced coke (2.20%) yield.

Dai et al. (2017) have studied experimentally the effects of pyrolysis temperature and catalyst on the yields of bio-oil and biochar produced by the microwave-assisted co-catalytic fast pyrolysis of soap stock. Addition of bentonite resulted in the increased bio-oil yield with reduced water content at the optimum pyrolysis temperature of 550 ºC. Compared to non-catalytic process, increased percentages of hydrocarbons (17.07 wt. %) were observed with the co-catalytic process. Addition of catalyst (bentonite and HZSM-5) resulted in the reduced oxygenated compounds up to 15.84 wt. % and nitrogenous compounds were eliminated completely in the bio-oil.

2.6. Pyrolysis process optimization

Literature citations for optimizing the process parameters either by conventional or microwave assisted pyrolysis using different statistical tools are reviewed critically and presented in the following paragraphs.

Özçimen and Ersoy-Meriçboyu, (2008) have reported the statistical evaluation of biochar produced by the pyrolysis of grapeseed and chestnut shell using fixed bed reactor. The regression equation obtained with a high determination coefficient based on the statistical design technique was able to determine biochar yield without doing experiments in the investigated parameter range. Pyrolysis temperature was the strongest parameter in comparison to nitrogen gas flow rate (0 and 1000 $cm^3 min^{-1}$) and heating rate (5 and 20 $Kmin^{-1}$) on the yields of biochar produced by the particles having the size of 0.657 mm and 0.377 mm as feed stocks. Increase in heating rate, temperature and sweep gas flow rates were responsible for the decrease of biochar yield. Maximum biochar yields were obtained at the temperature of 723 K, heating rate 5 K min^{-1} and gas flow rate of zero $cm^3 min^{-1}$for grapeseed (52.98%) and chestnut shell (58.8%)samples respectively.

Azargohar and Dalai, (2008) have developed the statistical model to study the effects of steam and potassium hydroxide (KOH) for activation of biochar using central composite design (CCD). Biochar was produced by the fast pyrolysis of white wood (spruce) using fixed bed inconel tubular reactor. Quadratic models (Design expert software) were used to decide the optimum operating conditions to produce physically and chemically activated carbons with large surface area and product yield. The optimum BET surface area and product yield, as predicted by the model, were 643 $m^2 g^{-1}$ and 56.9 wt. % for physical activation process and 783 $m^2 g^{-1}$ and 75.3 wt. % for chemical activation process respectively. Average pore diameters of the activated carbons were 13–26 Å (steam activation) and 13–15 Å (KOH activation) respectively.

Effects of reactor conditions, such as and power input, time and temperature on microwave assisted pyrolysis of distillers dried grain with solubles (DDGS) were studied experimentally by Lei et al. (2011). Effects of these variables on the yields of biochar, bio-oil and syngas yield were carried out by using response surface methodology (RSM) to establish the prediction models. Bio-oil recovery was 26.5–50.3 wt. % and biochar yield was 23.5–62.2wt. % based on the pyrolysis conditions. Bio-oil having the higher heating value about 28 MJ kg^{-1} (66.7% of the heating value of gasoline) was found at a temperature of 650 ºC with a retention time of 8 min. Useful chemical compounds of the bio-oil like aliphatic and aromatic hydrocarbons were reported through GC-MS analysis.

Abnisa et al. (2011) have investigated the effects of process parameters such as reaction time, feed-stock particle size, temperature and N_2 flow rate, on the pyrolysis of palm shell by using response surface methodology (RSM). Optimum bio-oil yield of 46.4 wt. % was obtained by the pyrolysis of palm shell waste in a stainless steel tubular reactor. Operating temperature of 500 ºC, N_2 flow rate of 2 L min^{-1}, particle size of 2 mm and reaction time of 60 min. were the optimum conditions. The most significant factor was the nitrogen flow rate. Bio-oil was having a low pH value of 2.5, high-water content about 53 wt. % and high oxygen content of 71.40 wt. %.

Brown and Brown, (2012) have studied experimentally the process optimization of an auger pyrolyzer. Regression models for bio-oil and char yield using surface response methodology was used to optimize the pyrolysis of red oak biomass. Maximum bio-oil yield (73 wt. %.) and minimum char yields were obtained by using one kg h^{-1} auger reactor utilizing mechanical mixing of steel shot heat carrier. Optimum pyrolysis conditions to obtain the maximum bio-oil and minimum char yields were 3.5 standard Lmin^{-1} (sweep gas), 600 ºC (heat carrier temperature) and 63 rpm (auger speed) respectively. Increase in the auger speed increased the bio-oil yield between the temperature range of 525 and 550 ºC and decreased the yield of biochar.

Effects of reaction time and temperature on the yields of bio-oil, char and syngas were investigated by Ren et al. (2012) using a central composite design (CCD) and response surface analysis. Maximum bio-oil yield of 57.8 wt. % was obtained by the microwave pyrolysis of Douglas fir sawdust pellet at an operating temperature of 471ºC and residence time of 15 min. Yields of the syngas and biochar were in the range from 7.9 to 5.0 wt. % and 31.2 to 60.7 wt. % respectively. Main contents of the bio-oil were ketones/aldehydes, furans, guaiacols, organic acids and phenols. Syngas contained mainly short chain hydrocarbons accounting for 70% (v/v) of the total gas, methane and carbon monoxide.

Liu et al. (2013) have reported the optimization of the operating parameters such as temperature, catalyst content and solvent-to-feedstock ratio using response surface methodology (RSM) based on central composite rotatable design (CCRD). Microwave assisted direct liquefaction (MADL) of Ulva prolifera was carried out in ethylene glycol (EG) using sulfuric acid (H_2SO_4) as catalyst. Solvent-to-feedstock ratio of 18.87:1 and 4.93% sulfuric acid, microwave power of 600 W, temperature of 165 °C and 30 min. residence time resulted in the maximum liquefaction yield of 93.17%. The main contents of the bio-oil were fatty acid methyl ester with a long chain from C_{16} to C_{20}, alkenes and phthalic acid esters.

Optimum conditions required for the pyrolysis of palm kernel shell (PKS) using microwave-assisted pyrolysis system were analyzed statistically by Jamaluddin et al. (2013) using response surface methodology (RSM) based on central composite rotatable design (CCRD) for three operating variables (sample mass, reaction time, and nitrogen gas flow rate). Pyrolysis of PKS was carried out in a microwave oven with maximum power of 300 W at frequency of 2450 MHz. Calorific value of 29.9 MJ kg^{-1}, fixed carbon content of 59.8 wt. %,volatile matters content of 36.4 wt. % and char yield of 40.0 wt. %

were predicted for a reaction time of 31.5 min, sample mass of 30 g and nitrogen gas flow rate of 100 mL min^{-1} respectively.

Ngo et al. (2013) have developed a mathematical model to maximize the bio-oil yield by the fast pyrolysis of palm kernel cake by using fluidized bed reactor. Effects of feedstock feed rate (160–300 g h^{-1}), biomass particle size (300–600 µm), pyrolysis temperature (400–500 ºC), and residence time (0.6–0.9 s) were analyzed by the central composite rotatable design (CCRD). Bio-oil yield of 49.5 wt. % was obtained at a pyrolysis temperature of 500 ºC, a feed rate of 225 g h^{-1} and residence time of 0.6 s using particle size of 600 µm. Reduced heating value of the bio-oil (13.9 MJ kg^{-1}) was observed due to increased content of the oxygen.

Effects of microwave assisted pyrolysis temperature and time on the yields of bio-oil, biochar and syngas were investigated experimentally by Zhou et al. (2013). Pyrolysis of prairie cordgrass (PCG) was carried in the temperature range from 529 °C to 671 °C and residence time between 5.9 and 20.1 min. Maximum bio-oil yield of 33.1 wt. % was obtained at 650 °C and residence time of 18 min. Experimental results were verified by using surface response methodology (RSM). Bio-oil was mainly composed of aromatic and aliphatic hydrocarbons.

Borges et al. (2014) have carried out the comparative analysis of optimum conditions to produce bio-oils using central composite design. Pyrolysis temperature of 480 °C, 50 grit silicon carbide as microwave absorbent and 2 gmin^{-1} of biomass feeding were the optimum pyrolysis conditions to produce a maximum bio-oil yield of 65 wt. % by the fast microwave assisted pyrolysis of wood sawdust using a bench scale microwave oven. Bio-oil yield of 64 wt. % was obtained in the temperature range between 490 °C and 560 °C with the biomass particle sizes from 0.9 mm to 1.9 mm by maintaining vacuum degree lower than 100 mm of mercury with the corn stover as a feedstock. Analysis of the statistical model showed that the pyrolysis temperature and microwave absorbent were having the significant effect for wood sawdust, whereas the particle size and vacuum degree were significant for the corn stover.

Mushtaq et al. (2015) have reported the effects of microwave power (W), N_2 flow rate and coconut activated carbon loading (wt. %)on bio-oil yield, its composition and heating profile produced by the microwave assisted pyrolysis of oil palm shell using response surface methodology. Percentage of phenol and 1,1-dimethyl hydrazine were in the range from 32.24 to 58.09% and 10.54 to 21.20% respectively. Nitrogen flow rate was having the highest effect on the bio-oil yield.

Effects of pyrolysis parameters such as temperature, microwave power and nitrogen gas (N_2) flow rate on microwave assisted pyrolysis oil palm fiber (OPF) were investigated using response surface methodology (RSM) based on central composite design (CCD) by Hossain et al. (2017). An error of 10 % was observed between the actual and predicted values for hydrogen and biochar yield. Hydrogen and biochar yields were optimized at the temperature of 450 ºC, microwave power of 400W and nitrogen flow rate of 955.25cm^3 min^{-1}. Higher percentage of carbon (60 wt. %) was observed in the biochar obtained at optimized conditions.

SCOPE AND OBJECTIVES OF THE STUDY

Municipal solid waste (MSW) contains on an average 40% food waste and needs to be managed in an environment friendly manner. Around 1.3 billion tons of food is wasted globally every year though it is suitable for human consumption. Food waste contains high moisture content and decays easily under atmospheric conditions making its management as a challenging task. The different methods used, at present worldwide, to dispose the food waste are land filling, ocean dumping, incineration, composting, hydrothermal carbonization and torrefaction. The traditional method used to dispose food waste is the landfilling, which is the critical issue in connection with the availability of land. Land filled food waste causes health and environmental related problems such as bad odour, leachate generation within the landfills, methane gas production as well as emission of greenhouse gases. Methane gas generated leads to fire hazards. Leachate generated within the landfills can contaminate the nearby soil as well as ground water. Further this contaminated water can increase the biological oxygen demand (BOD) by microorganisms.

Ocean dumping of food waste results in the breaking of marine food chain system and affects the marine biodiversity seriously. High moisture content of the food waste results in the release of dioxins when it is incinerated with other organic matter. Composting of food waste is the cause for secondary environmental pollution due to release of leachate, ammonia and greenhouse gases. Hydrothermal carbonization is the recent technology to recover the energy from the food waste in the form of hydro-char and bio-oil which requires enzymatic pre-treatment. The disadvantages associated with hydrothermal carbonization are the requirement of high pressure within the reactor and overnight drying of hydro-char. Torrefaction is the thermochemical conversion process in which the food waste is heated under the influence of inert atmosphere to produce biochar and bio-oil. The disadvantage of torrefaction process is the requirement of longer process time. Hence conversion of food waste into value added products, through suitable thermal treatment processes, eliminates disposal problems by recovering energy in the form of liquid, solid and gas. The food waste contains high energy and is a promising feed stock for pyrolysis process.

Conversion of biowastes into value-added products such as biochar, bio-oil and biogas has attracted tremendous research interest globally. This is mainly because of the rising energy demands due to the rapid growth in the world's population and day to day development of new service, commercial and industrial sectors that have caused increased concerns over greenhouse gas emissions, as well as worldwide soil degradation. At the same time energy resources which are fulfilling our present day energy requirements are decreasing at an unimaginable manner. This has forced the human beings to search alternate sources of energy and suitable harnessing methodologies.

Pyrolysis is one of the suitable technologies to produce biofuels from biomass. The major difference between the pyrolysis and the alternative ways of converting biomass to energy is that, the pyrolysis of biomass produces a carbon-rich solid by product known as biochar. In a low temperature pyrolysis, the biomass is heated between 400 and 500 °C under complete or partial absence of oxygen to produce biofuels using a variety of different reactor configurations. Different categories of pyrolysis processes are characterized by a close balance between biochar, bio-oil and syngas. The exact ratio of these products may vary between different types of plants used but can be optimized at a particular installation. Maximizing the production of biochar is always at the expense of energy in the liquid or gaseous form, as the greenhouse gas mitigation strategy favours the maximum biochar production.

Energy efficient pyrolysis processes, with higher yields as well as better quality bio-fuels, are the present day requirements. An efficient thermochemical process to produce bio-oil, syngas and biochar is the microwave assisted pyrolysis (MAP) because of its advantages over conventional processes. The advantages of MAP are uniform internal heating of biomass particles, ease of control without the requirement of agitation or fluidization, harmful chemical reduction in the bio-oil and savings in energy cost. This method has been successfully applied to various agricultural residues, wood, sewage sludge, sea weeds and other biomass feed stocks to produce biofuels. Microwave assisted pyrolysis of food waste is appearing to be less studied, but is a promising technology to solve the major problems of food waste disposal and recovering the energy in the form of biochar, bio-oil and biogas.

Mangalore is one of the important cities of Indian peninsula situated on the west coast. The land area covered by Mangalore city is around 132.45 sq.km located at 12°-52’N latitude and 74°-49’E longitude. Mangalore city, on an average, generates approximately 312 tons of municipal solid waste (MSW) per day with a population of 6,23,481. The total share of the food waste among this MSW is 125 tons per day (40%) along with plastics, paper, ceramics, glass, wood, metals etc. This MSW is land filled presently in Mangalore, neigh in India, leading to serious social and environmental issues and not thought as an energy source. The current research work is aimed at utilization of the advantages of microwave heating in pyrolysis reaction towards the following objectives

- To quantify and characterize the food waste generated in commercial and residential complexes of Mangalore city.
- To carry out the pyrolysis of food waste with the assistance of microwave irradiation and characterize the products.
- To optimize the operating variables for better yield of the desirable products.

CHAPTER 3

MATERIALS AND METHODS

In order to meet the aims and objectives of the present research work, a detailed experimental procedure was designed and is presented in the following sections.

3.1. Sample collection and preparation

Food waste samples (FWS) were collected from the different locations of Mangalore city and their sources, technical names are given in table 3.1. The individual FWS were mixed thoroughly and placed in an electric oven (Polar industrial corporation Bombay) for 24 hat 105ºC to minimize the moisture content of the samples. The dried samples were further pulverized to pass through an American Society for Testing and Materials (ASTM)-40 standard meshes and sieved to the size of diameter 0.420 mm. These food waste particles (FWP) were used for characterization of FWS.

Table 3.1. Food waste collection sources and technical names

Sl. No	Source	Type of food waste	Technical name
1	PG hostel block National Institute of Technology Karnataka Surathkal	Vegetarian	FWS-1
2	Fourth hostel block National Institute of Technology Karnataka Surathkal	Vegetarian	FWS-2
3	Hotel Ocean Pearl, Mangalore	Vegetarian	FWS-3
4	Hotel Sadanand Surathkal	Vegetarian	FWS-4
5	Homogeneous random mixture of FWS-1 to FWS-4		FWSMX
6	Hotel Sadanand Surathkal	Homogeneous random mixture of vegetarian food and meat	FWSVNV-1
7	Hotel Suraj International Surathkal	Meat	FWSNV-2
8	Homogeneous random mixture of FWSVNV-1 and FWSNV-2		FWSNVMX

3.1.1. Particle size analysis

Vegetarian as well non-vegetarian FWS collected from the different parts of the Mangalore city were mixed randomly and placed in an electric oven for 24 h to minimize the moisture content of the samples by maintaining the temperature at 105 ºC. The dried samples were removed from the oven and pulverized to pass through an ASTM-18 standard mesh to have particle size less than 1 mm (ASTM standard). Screen analysis was carried out by using sieve shacking machine available at National Institute of Technology, Karnataka Surathkal.

Screen analysis was carried out by placing a sample on the ASTM-18 standard sieve having the openings of less than 1 mm, below this screen remaining screens (ASTM-20 to ASTM-60) were arranged one below the other in the order of decreasing sizes. The stack of screens with the known quantity of sample on the top of ASTM-18 screen was shaked for a period of 30 min. using sieve shaking machine. The FWP collected on each screens were removed and weighed. Resulting FWP were used for pyrolysis experiments (Badger and Banchero, 1997).

3.2. Physicochemical characterization of food waste

Physicochemical properties of the food waste to be known are moisture content, ash content, volatile matter content, fixed carbon content and chemical composition. Since there is hardly any standard protocol to determine the properties of food waste by ASTM or any other societies, the protocol of solid fuels (coal and coke) has been modified to analyze the physicochemical properties of the food waste. The modifications are made to address large quantities of volatiles present in food waste as per the suggestions of Ebeling and Jenkins (1985).

3.2.1. Proximate Analysis

Proximate analysis of the food waste was carried as per ASTM standard method (D-3172-73 through D-3174-82 and D-3175-82 Anon., 1993). The moisture content of the sample was determined according to ASTM standard method (D-3172-73 Anon., 1993) by placing one gram of sample in silica crucible. The crucible was then placed in a muffle furnace (Bionics-BST/MF/1450, India) for 1 h by maintaining the temperature at 105 ºC. The difference in weight of the sample was the moisture content. After determining the moisture content, the sample was heated in a muffle furnace at 600 ºC till it was turned in to ash. The ash content of the sample was represented by the residue in the crucible. This procedure was repeated for all the samples. Percentage volatiles was determined by placing one gram of sample in a crucible with a cover and heated in a muffle furnace at 450 ºC for 12 min. The temperature and heating time were selected based on the repeated trials. After the heating, the crucible was removed from the furnace and placed in desiccators. The difference in weight was the percentage volatiles. Finally, the fixed carbon content was obtained by subtracting the percentage moisture, percentage ash and percentage volatile matter from 100%. This procedure was repeated for all the samples by performing at least four trials.

3.2.2. Ultimate Analysis

Ultimate analysis was performed by using the oven dried FWS having the diameter less than 0.420mm to determine the percentages of carbon, hydrogen, nitrogen and oxygen. The percentages of carbon, hydrogen, nitrogen and oxygen were determined by using Thermo Finnigan Flash CHNS analyzer (Thermo Finnigan- EA 1112, Italy) available at Indian Institute of Science Bangalore, India. The ash content was determined in the proximate analysis by following the standard ASTM procedure. The percentage of oxygen was determined by subtracting the sum of carbon, hydrogen, nitrogen, oxygen and ash from 100% which is the standard procedure to determine the percentage of oxygen from the literature.

3.3. Thermochemical characterization of food waste

Thermochemical properties of the food waste to be known are heating values and thermal degradation behavior. Physicochemical and thermochemical properties are essential to select the operating parameters such as pyrolysis temperature, residence time, inert gas flow rate and microwave power level. These properties also help to understand the food waste degradation rate and bio-fuel characteristics of the products of the microwave assisted pyrolysis (MAP).

3.3.1. Heating values

Higher heating values of the FWS were determined as per ASTM-D-2015-17 standard procedure by using the bomb calorimeter (Advance Research Instruments Company - 28018, New-Delhi, India). Known quantities of dried FWS were burned in the bomb calorimeter under the presence of oxygen by maintaining the pressure between 10 and 15 kg cm^{-2}. Higher heating values of the samples were determined by increasing the heat capacity of the system and the temperature of the water bath

Heating values were also calculated by using the elemental analysis results. Generally heating values are reported as higher heating values (HHV - gross) and lower heating values (LHV - net), respectively. The difference between HHV and LHV is equal to the heat of vaporization of water formed by combustion of the fuel. The HHV of FWS were obtained by Dulong equation as given in Eq. 3.1and the LHV were calculated by the Eq. 3.2 proposed by Oasmaa (Abnisa et al. 2011).

$$\text{HHV}\left(\text{MJ kg}^{-1}\right) = \frac{338.2\times\text{C}+1442.8\times\left(\text{H-}\frac{\text{O}}{8}\right)}{1000} \tag{3.1}$$

$$\text{LHV}\left(\text{MJ kg}^{-1}\right) = \text{HHV-}(0.218\times\text{H}) \tag{3.2}$$

3.3.2. Thermal degradation studies

Thermogravimetric analysis (TGA) is one of the most commonly adopted techniques for the investigation of thermal degradation during the pyrolysis of solid raw materials such as coal, biomass, and plastic. Thermal behavior of the carbonaceous material by TGA is measured as a function of temperature and time to predict the weight loss of the sample. Semi quantitative understanding of thermal degradation processes occurring during thermochemical conversion under various atmospheres is provided by TGA.

The thermal degradation (pyrolysis and gasification) of the FWS were studied using the thermogravitic and differential analysis techniques. The thermal decomposition of each of the FWS was carried out by using Exstar thermoanalyser 6000 series (TG / DTA 6300) available at the Department of Chemical Engineering, N.I.T.K. Surathkal. The samples were prepared by drying and carefully pulverized to pass through an ASTM-40 standard mesh. The resulting fractions of FWS were having the size of 0.420 mm, so as obtain homogeneous material properties. A sample size of 12 mg or less was used for each experimental run.

3.3.3. Thermal degradation behavior by thermogravimetric analysis

Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) techniques have been used in literature to obtain the information about the thermal degradation (pyrolysis) of different kinds of biomass materials. FWS were subjected to TG, DTG and DTA to draw information regarding thermal degradation characteristics. Experiments were performed at the heating rate of 10 $^{\circ}$Cmin^{-1} under an inert atmosphere by maintaining the nitrogen flow rate at 50 mL min^{-1}. Thermograms, degradation rates and temperature differences were obtained due to endothermic and/or exothermic reactions such as dehydration, decomposition (pyrolysis) or other chemical reactions. The tests were conducted from the ambient temperature to a final temperature of > 600 ºC. At present higher heating rates were not considered.

3.4. Microwave assisted pyrolysis of FWS

The schematic arrangement of the microwave assisted pyrolysis system with the control panel is shown in the Fig. 3.1. Pictorial representation and inner view of the microwave reactor are shown in the Fig. 3.2 and Fig. 3.3. This reactor is facilitated with a single magnetron (150 to 750 W) with the maximum power rating of 750 W for low temperature applications and double magnetron (300 to 1500 W) for high temperature applications with the maximum power rating of 1500 W at a frequency of 2450 MHz. The reactor is incorporated with (i) microwave cavity (ii) nitrogen supply tube (iii) K

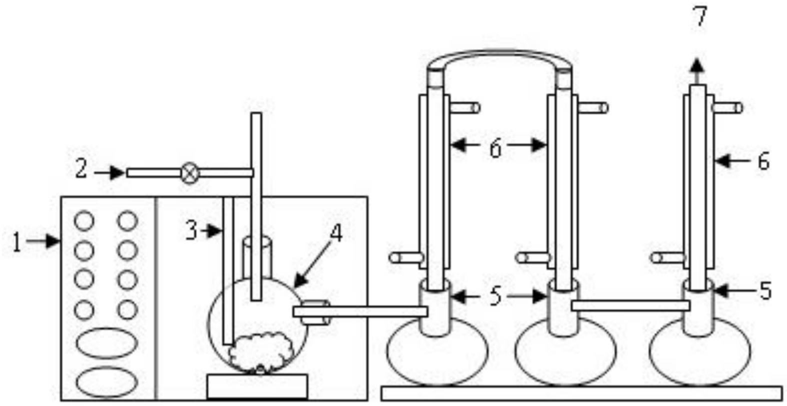


Fig.3.1. Schematic diagram of microwave assisted pyrolysis system: (1) microwave cavity with control panel; (2) nitrogen supply; (3) thermocouple; (4) quartz flask with food waste; (5) bio-oil collector; (6) condenser; (7) gas sampling

Fig. 3.2. Pictorial representation of the microwave reactor

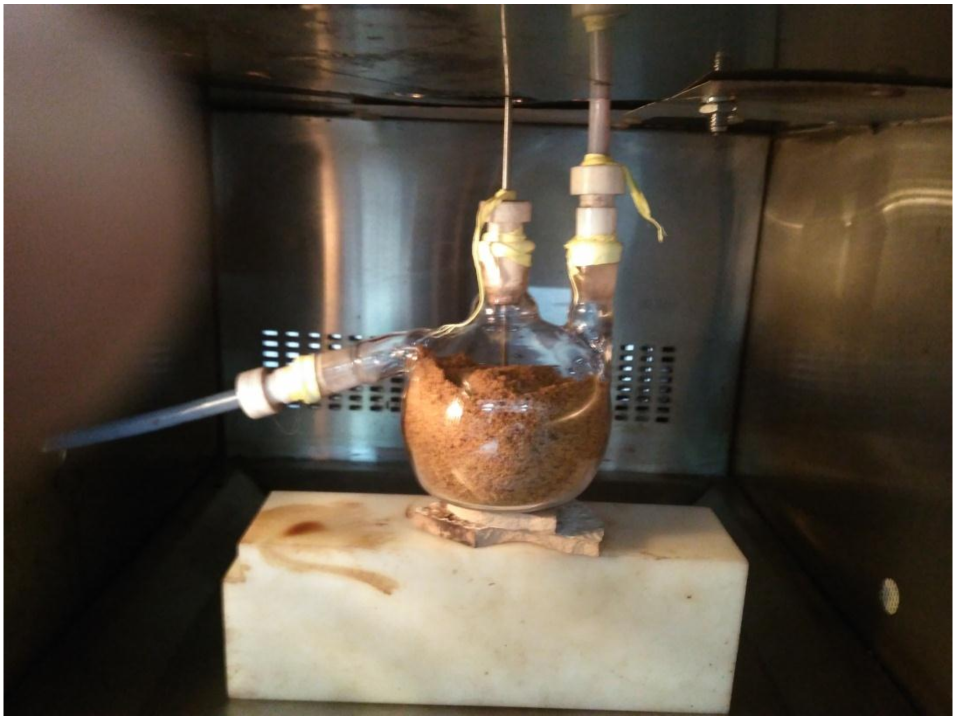


Fig. 3.3. Three neck quartz flask with FWP

type thermocouple (iv) quartz flask to feed the food waste (v) three condensers (vi) three bio-oil collectors and (vii) different power levels as fixed by the manufacturer.

Pyrolysis of FWP was carried out in a microwave reactor designed and supplied by Raga's scientific microwave synthesis system, Pune, India. FWP weighing 100 g were (size less than 1 mm) fed in to the quartz flask of capacity 250 mL by a hopper and placed exactly in the path of microwaves. Nitrogen gas was purged in to the quartz flask at 25 mL min^{-1} for 15 min. prior to the experiment to maintain an inert atmosphere and this inert atmosphere was maintained throughout the process with the varying flow rates and time depending upon the experimental requirements. FWP were subjected to microwave heating and the reactor temperature was raised by the microwaves till the preset reaction temperature was reached. K-type thermocouple was used to maintain and monitor the required temperature throughout the process. Pyrolysis resulted in the volatilization of the products and exits the microwave system. Condensable vapours due to microwave assisted degradation of FWP were condensed into the respective condensers by circulating the cooling water at 27 ºC and gas fraction was allowed to pass through the vent. The solid and liquid yields were calculated by respective weight fractions and gas fraction was calculated by difference. The entire process was conceived to operate at the pressure slightly above the atmospheric pressure and adequate care was taken while handling of the microwave oven chamber and all other associated internals so as to avoid direct contact with them.

3.5. Design of experiments

Design of experiments (DOE) provides a method to investigate the effects of multiple variables on an output variable (response). These experiments consist of a series of runs, or tests, in which purposeful changes are made to input variables or factors to maximize the product yields and data are collected at each run.

Evaluation of the operating variables for better performance (maximum yield) without the increase of process temperature is an important task in the pyrolysis process. This is usually carried out by the response surface methodology (RSM) introduced by Box and Wilson in the year 1951. RSM is a regression method of evaluating the correlation between operating variables and one or more response (output). Standard RSM design based on central composite design (CCD) will be used to study the effect of operating parameters on the yield. The experiments will be conducted with one response in CCD, which is either a yield of a biochar or bio-oil or biogas. The temperature, inert gas flow rate, reaction time and power input will be chosen as factors and each considered at five levels namely; −1, +1, 0, −α and +α. The alpha value depends on a number of factors in the factorial part of design. The values of alpha in CCD will be determined by the following equation (Box and Wilson, 1951).

$$\alpha=(2^n)^{1/4} \tag{3.3}$$

One of the advantages of using CCD is the model able to establish with only a minimum number of experiments and widely used for fitting a second-order model. Hence the CCD will be employed in this study for the prediction and verification of model equation.

Among some important steps of the optimization process, the first step is to determine a mathematical relationship between the response and the factors. This relationship is given by the following equation

$$Y=f(X_1,X_2,X_3,\ldots\ldots\ldots\ldots X_n) \tag{3.4}$$

Where Y is the response, f is the unknown function of response, X_1, X_2, $X_3,\ldots..,X_n$ are called as factors and n is the number of the independent factors. To find the suitable a suitable approximation for the true functional relationship between independent factors and the response surface, it is assumed that the independent factors are continuous and controllable by experiments with negligible errors (Sahu et al. 2010).

Estimation of coefficients in a mathematical model and prediction of response is carried out in the second step. Generally, a quadratic equation or second order model is used for predicting the model and written as given below

$$Y=\beta_o+\sum_{i=1}^{n}\beta_i\times X_i+\sum_{i=1}^{n}\beta_{ii}\times X_{ii}^2+\sum_{i=1}^{n}\sum_{j>1}^{n}\beta_{ij}\times X_iX_j \tag{3.5}$$

Where Y is the predicted response, β_o, β_i, β_{ii} and β_{ij} are regression coefficients for the constant, linear, quadratic and interaction coefficients respectively. X_i and X_j are the coded independent factors.

The last step is checking the adequacy of the model. One of the methods to achieve this aim is testing of the lack-of-fit. The lack-of-fit is a measure of a model failure in representing data in the experimental domain (Montgomery, 2000).

Twenty experiments were conducted (for three parameters) to support the RSM data in CCD. The numbers of experiments are decided by using the following equation

$$N=2^n+2n+n_c \tag{3.6}$$

Where N is the total number of experiments, n is the number of variables and n_c is the number of experimental trials that can be repeated (replicate trials). The total number of experiments includes the standard 2^n factorial with its origin at the center, $2n$ points fixed axially at a distance α from the center to generate the quadratic terms, and repeated (replicate) tests at the center (Sahu et al. 2009).

3.6. Characterization of pyrolysis products

Characterization of pyrolysis products such as biochar and bio-oil were carried out by using ASTM standard methods. The detailed procedure of characterization is presented in the following paragraphs.

3.6.1. Proximate analysis

Proximate analyses of biochar and bio-oil were carried out as per ASTM standard method on dry basis (D-3172-73 through D-3174-82 and D-3175-82 Anon., 1993). The moisture content of the samples was determined according to ASTM standard method (D-3172-73 Anon., 1993) by placing one gram of sample in silica crucible. The crucible was then placed in a muffle furnace for 1 h by maintaining the temperature at 105 ºC. The difference in weight of the sample is the moisture content. After determining the moisture content, the sample was heated in a muffle furnace at 600 ºC till it was turned in to ash. The ash content of the sample was represented by the residue in the crucible. This procedure was repeated for all the samples. To determine the percentage volatiles one gram of sample was placed in a crucible and covered with a lid and this was heated in a muffle furnace at 450 ºC for 12 min. After the heating, the crucible was removed from the furnace and placed in desiccators. The difference in weight was the percentage volatiles. Finally, the fixed carbon content was obtained by subtracting the percentage moisture, percentage ash and percentage volatile matter from 100%. This procedure was repeated for all the biochar samples by performing at least four trials.

3.6.2. Ultimate analysis

The ultimate analyses of biochar and bio-oil were performed by using oven dried samples to determine the percentages of carbon, hydrogen, nitrogen and oxygen. The percentages of carbon, hydrogen, nitrogen and oxygen were determined by using Thermo Finnigan Flash CHNS analyzer available at Indian Institute of Science Bangalore, India. The ash content was determined in the proximate analysis by following the standard ASTM procedure. The percentage of oxygen was determined by subtracting the sum of carbon, hydrogen, nitrogen, oxygen and ash from 100%, which is the standard procedure to determine the percentage of oxygen from the literature.

3.6.3. Heating values

Higher heating values of the biochar and bio-oil were determined as per ASTM-D-2015-17 standard procedure by using bomb calorimeter. Known quantities of biochar and bio-oil samples were burned in the bomb calorimeter under the presence of oxygen by maintaining the pressure between 10 and 15 kg cm^{-2}. Higher heating values of the samples were determined by increasing the heat capacity of the system and the temperature of the water bath.

Heating values were also calculated by using the elemental analysis results. Generally heating values are reported as higher heating values (HHV - gross) and lower heating values (LHV - net), respectively. The difference between HHV and LHV is equal to the heat of vaporization of water formed by combustion of the fuel. The higher and lower heating values of biochar and bio-oil samples were obtained by using Dulong and Oasmaa equations given in section 3.3.1.

3.7. Characterization of bio-oil

Bio-oil obtained under the optimized condition was used for the analysis. Digital pH meter (Equiptronics-EQ-610, India) available at National Institute of Technology, Karnataka Surathkal was used to know the corrosive property of the bio-oil at room temperature. The water content of the bio-oil was measured by using a Carlfischer-819 Coulometer (Metrohm Switzerland) available at National Institute of Technology, Karnataka Surathkal. Approximately 7-9 mg of bio-oil was injected in to the flask through titration cell. Instrument beeps one time after the completion of titration and water content of the bio-oil was displayed in parts per million (ppm) on the display panel.

Density of the bio-oil was calculated by specific gravity method. The following equation at room temperature (30 ºC) was used to calculate the density of bio-oil

$$\text{Density of Bio-oil} = \rho_{oil} = \frac{W_2 - W_1}{W_3 - W_1} \text{ x } C \tag{3.7}$$

Where W_1 = Weight of the empty specific gravity bottle in grams

W_2= Weight of the specific gravity bottle with water in grams

W_3= Weight of the specific gravity bottle with oil in grams

C = Density of water at 30 ºC = 995.647 kg m^{-3}

Viscosity of the bio-oils was calculated as per ASTM standard methods D 445 and D2515by using Cannon-Fenske viscometer at room temperature (30 ºC). Known quantity of bio-oil was filled up to the upper mark of the bulb of Cannon-Fenske viscometer having a tube number of 100 with the help of air bulb. Air bulb was removed after 5 min. and the oil starts flowing towards the bottom mark of the bulb. Time required to reach from upper mark to the bottom mark was recorded and the viscosity of the bio-oil was calculated by multiplying the time recorded by the standard factor of the bulb of the viscometer, that is, 0.0095 (Personal communication, Chemistry Department, NITK, Surathkal).

3.7.1. FT-IR analysis of bio-oil

FT-IR spectra of bio-oil derived from the microwave assisted pyrolysis of FWP was carried out by using a FT-IR analyzer (Bruker Alpha-400, Germany) available at National Institute of Technology, Karnataka Surathkal, India. FT-IR was equipped with silicon carbide as infrared (IR) source. A thin total reflectance accessory with a zinc selenide (ZnSe) crustal was used for the data collection. The sample under the study was recorded with 16 scans with sample resolution of 4 cm^{-1}. The IR spectra provide information about the functional groups present in the bio-oil.

3.7.2. GC-MS analysis of bio-oil

Gas chromatograph- mass spectrometry (GC-MS) analysis of bio-oil was carried out at Sophisticated Instrument Analysis Facility (SAIF), Indian Institute of Technology Bombay, Powai, Mumbai (Jeol-JMS-T100GCV, AccuTopGCV, Japan). GC-MS was equipped with standard non-polar capillary column of length 60 m and diameter 0.25 mm using nitrogen as a carrier gas. The GC oven temperature was raised to 200 ºC from the initial temperature of 20 ºC with a heating rate of 5 K min^{-1}. The sample injection size was 1 µL and total time of the analysis was around 30 min. The bio-oil obtained was not subjected to any pretreatment prior to the analysis.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter FWS collection, particle size analysis, physicochemical and thermochemical characterization, thermal degradation studies of FWS, preliminary pyrolysis of FWP, optimization of pyrolysis products by response surface methodology and their characterization have been presented and discussed in the following sections.

4.1. Particle size analysis

Pulverized FWP are normally specified according to their size or screen analysis. Screen analysis of the FWS is as shown in the Table 4.1. First and second column are the ASTM sieve numbers with their screen openings in microns. Arithmetic mean of the screen openings is shown in the third column. Quantity of the food waste fractions retained on each screens is given in the fourth column and weight percentage retained is shown in the fifth column. Sixth column shows the cumulative percentage of weight percentage retained on the screens (Badger and Banchero, 1997). Quantity of pulverized FWP retained on each screens was less than 10 grams and hence particles having size between 250 and 1003 microns are used for the pyrolysis process. Cumulative size distribution of pulverized FWP is shown in the Fig. 4.1.

Table 4.1: Size analysis of pulverized FWP

ASTM Screen	Screen openings in microns	Average particle size in microns	Quantity retained on the screen in grams	Weight percentage retained	Cumulative percentage
18	1003		45.16	44.95	44.95
20	850	926.50	8.82	8.78	53.73
25	710	780.00	8.11	8.08	61.81
30	600	655.00	9.04	9.00	70.81
35	500	550.00	9.62	9.58	80.39
40	420	460.00	9.51	9.47	89.86
45	355	387.50	6.58	6.54	96.40
50	300	327.50	3.03	3.01	99.41
60	250	275.00	0.6	0.59	100.00
			Total	100	

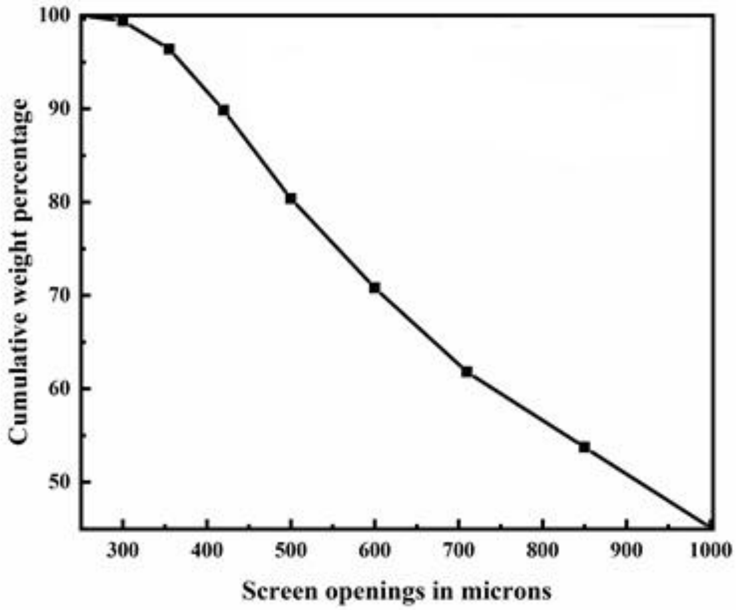


Fig. 4.1: Cumulative size distribution of FWP

4.2. Physicochemical properties of food waste

Physicochemical characterizations of FWS were carried out as per ASTM standard methods and are presented in the following sections.

4.2.1. Proximate analysis

The results of the proximate analysis of the FWS are shown in the Table 4.2 and 4.3. The average values of the volatiles, fixed carbon, ash and moisture content of the vegetarian FWS are in the range from 71.17% (for FWS -4) to 72.33% (for FWS-2), 10.72% (for FWS-3) to 16.52% (for FWS-4), 3.09% (for FWS-4) to 8.50% (for FWS-3) and 9.13% (for FWS-1) to 9.22% (for FWS-4) respectively. The average values of the volatiles, fixed carbon, ash and moisture content of the randomly mixed vegetarian FWS (Random mixture of FWS-1 to FWS-4) are 71.58%, 13.01%, 6.21% and 9.20% respectively. The average values of the volatiles, fixed carbon, ash and moisture content of the mixed vegetarian and non-vegetarian FWS (FWSVNV-1) are 71.12%, 13.63%, 6.73% and 8.52% respectively. The average values of the volatiles, fixed carbon, ash and moisture content of the non-vegetarian FWS are 69.45%, 14.83%, 9.30% and 7.42% respectively.

Table 4.2: Proximate analysis of vegetarian FWS (Percentage dry basis)

Vegetarian food waste sample	Volatile matter (Wt. %)	Fixed carbon (Wt. %)	Moisture (Wt. %)	Ash (Wt. %)
FWS-1	71.90	12.69	9.13	6.28
FWS-2	72.33	12.86	9.16	5.65
FWS-3	71.60	10.72	9.18	8.50
FWS-4	71.17	16.52	9.22	3.09
Avg. of 1 to 4	**71.75**	**13.19**	**9.17**	**5.88**
FWSMX	**71.58**	**13.01**	**9.20**	**6.21**

Table 4.3: Proximate analysis of non-vegetarian FWS (Percentage dry basis)

Vegetarian and non-vegetarian food waste sample	Volatile matter (Wt. %)	Fixed carbon (Wt. %)	Moisture (Wt. %)	Ash (Wt. %)
FWSVNV-1	71.12	13.63	8.52	6.73
FWNVS-2	68.45	14.83	7.42	9.30
Avg. of 1 to 2	**69.80**	**14.24**	**7.97**	**8.01**
FWSVNVMX	**70.12**	**14.88**	**7.60**	**7.40**

The average values of the volatiles, fixed carbon, ash and moisture content of the randomly mixed FWS (random mixture of FWSVNV-1 and FWSNV-2) are 70.12%, 14.88%, 7.40 and 7.60 % respectively. It is seen that the average values of the randomly mixed FWS are very close to that of the average values of the individual FWS. Hence the food waste which is separated and collected from the municipal solid waste (MSW) can be used for producing bio-fuels. Since the food waste contains considerable amount of volatile matter it is suitable for bio-oil and biogas production. Ash is the undesirable part of the biomass as well as fuels derived from it. The ash content of the non-vegetarian food waste is 9.30% compared to random mixture of vegetarian food waste which is having the ash content of 6.21%. Increased percentage of ash is due to increased percentage of non-combustible matter as well as bone content of the non-vegetarian food waste. Fixed carbon content of the random mixture of FWS are very close to that of the average values of the individual FWS. Presence of bones and muscle matter resulted in the reduced moisture content of 7.97% for non-vegetarian food waste compared to the moisture content of 9.17% for vegetarian food waste (Huff-Lonergan and Lonergan, 2005).

4.2.2. Ultimate analysis

The results of the ultimate analyses of the FWS are presented in the Table 4.4 and 4.5. The major elemental compositions of the FWS are carbon, hydrogen, nitrogen and oxygen. For the vegetarian FWS, the weight fraction of the carbon is in the range from 46.28% (for FWS-3) to 48.24% (for FWS-4), hydrogen is in the range between 7.32 (for FWS-3) and 7.47% (for FWS-4), oxygen varied from 35.36% (FWS-3) to 38.79% (for FWS-4) and nitrogen is in the range from 2.41% (for FWS-4) to 2.54% (for FWS-3). The average values of elemental compositions of the FWS-1 to FWS-4 are very close to that of the random mixture of FWS (FWSMX).

The weight fractions of the carbon, hydrogen, nitrogen and oxygen for the non-vegetarian FWS (FWSVNV-1 to FWSNV-2) as well as randomly mixed (FWSVNVMX) samples are similar to those of the vegetarian FWS. This clearly indicates that the random mixture of vegetarian and non-vegetarian food waste is suitable for bio-fuel production rather than the food waste collected from the particular location.

Table 4.4: Ultimate analysis of vegetarian FWS (Percentage dry basis)

Vegetarian food waste sample	Carbon (Wt. %)	Hydrogen (Wt. %)	Nitrogen (Wt. %)	Oxygen (by difference)	Ash (Wt. %)
FWS-1	47.26	7.39	2.47	36.63	6.25
FWS-2	47.75	7.43	2.44	36.73	5.65
FWS-3	46.28	7.32	2.54	35.36	8.50
FWS-4	48.24	7.47	2.41	38.79	3.09
Avg. of 1 to 4	**47.38**	**7.40**	**2.46**	**36.87**	**5.87**
FWSMX	**47.21**	**7.22**	**2.45**	**36.92**	**6.20**

Table 4.5: Ultimate analysis of non-vegetarian FWS (Percentage dry basis)

Vegetarian and non-vegetarian food waste sample	Carbon (Wt. %)	Hydrogen (Wt. %)	Nitrogen (Wt. %)	Oxygen(by difference)	Ash (Wt. %)
FWSVNV-1	46.47	7.12	2.74	36.95	6.72
FWNVS-2	44.29	6.78	3.70	35.96	9.27
Avg. of 1 to 2	**45.38**	**6.95**	**3.22**	**36.45**	**7.99**
FWSVNVMX	**46.70**	**7.28**	**2.98**	**35.64**	**7.40**

The low content of the nitrogen is one of the desirable properties to produce environmental friendly bio-fuels. From the ultimate analysis, it can be concluded that, though the food waste (biomass) exists in different physical forms, chemically they are similar to each other. This is in contrast to the structures of the different types of coals which are physically same, but differ chemically to the greater extent (Gangavati et al. 2002).

4.3. Thermochemical properties of food waste

4.3.1. Heating values

Higher and lower heating values were calculated by using the Eq. 3.1and 3.2 and experimentally by using bomb calorimeter are given in the Tables 4.6 and 4.7. It is seen from the tables that, the HHV for the non-vegetarian FWS as calculated by the Dulong formula are in the range from 19.84 MJ kg^{-1} (FWS-3) to 20.24 MJ kg^{-1} (FWS-2) and the HHV of the randomly mixed food waste sample (FWSMX) is 20.10 MJ kg^{-1}. But the HHV as calculated by the bomb calorimeter for the vegetarian and non-vegetarian FWS are higher than that of the Dulong formula values as the latter did not include the dissociation effects. HHV of the FWSVNV-1 is higher than that of the FWSVNV-2 and the HHV of the random mixture (FWSVNVMX) is higher than that of the average values of the FWSVNV-1 and FWSVNV-2. Hence the food waste is an important potential source of energy as it contains the energy values more than half of the energy value (≈ 20 $MJkg^{-1}$) of the coal available in India (Gangavati et.al 2002).

Table 4.6: Higher and lower heating values of vegetarian FWS

Vegetarian food waste sample	Higher heating values by Dulong formula (HHV-MJ kg^{-1})	Lower heating values by Oasmaa formula (LHV- MJ kg^{-1})	Higher heating values by Bomb calorimeter (HHV- MJ kg^{-1})
FWS-1	20.04	18.43	23.46
FWS-2	20.24	18.62	22.79
FWS-3	19.84	18.24	22.75
FWS-4	20.09	18.47	23.33
Avg. of 1 to 4	**20.10**	**18.44**	**23.08**
FWSMX	**19.72**	**18.15**	**23.54**

Table 4.7: Higher and lower heating values of non-vegetarian FWS

Vegetarian food waste sample	Higher heating values by Dulong formula (HHV- MJ kg^{-1})	Lower heating values by Oasmaa formula(LHV- MJ kg^{-1})	Higher heating values by Bomb calorimeter (HHV- MJ kg^{-1})
FWSVNV-1	19.32	17.77	23.40
FWSVNV-2	18.27	16.79	23.48
Avg. of 1 to 2	**18.79**	**17.28**	**23.44**
FWSVNVMX	**19.87**	**18.28**	**22.94**

4.3.2. Thermal degradation characteristics

Thermogravimetric analysis (TGA) data for FWS-1 to FWS-4, FWSMX, FWSVNV-1, FWSNV-2 and FWSNVMX are shown in the Fig. 4.2 to Fig. 4.9. The entire thermal degradation process is divided into moisture evaporation, rapid thermal degradation, slow thermal degradation and ash (residue) zones respectively. The DTA peak area tells about the enthalpy change during the thermal degradation process. It is found that the dehydration of the sample is an endothermic process, while pyrolysis is exothermic in nature.

Dual DTA peaks were observed for all the samples indicating the thermal degradation process with the release and absorption of heat in the second and third zones respectively. In the first zone minor weight loss was observed for all the FWS with the release of

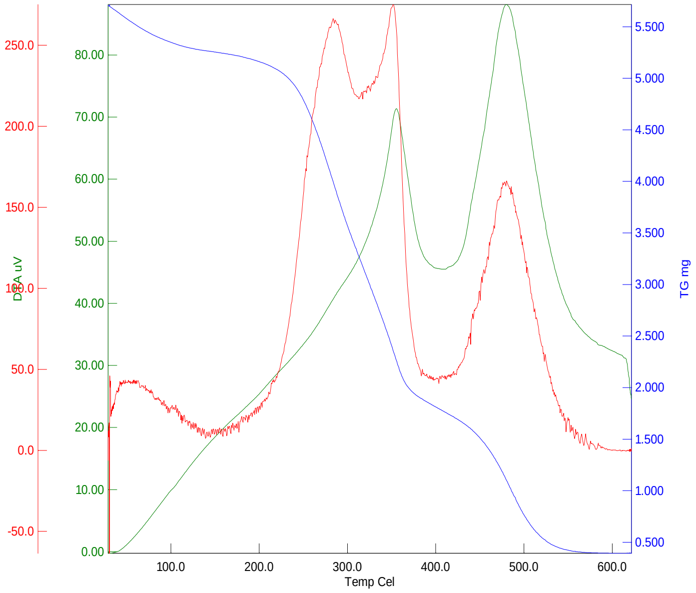


Fig.4.2: Thermogravimetric and differential thermal analysis of FWS-1

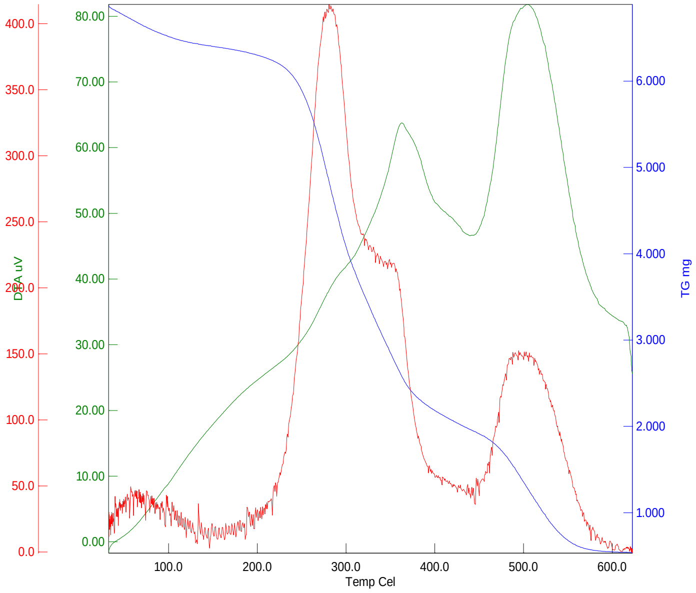


Fig.4.3: Thermogravimetric and differential thermal analysis of FWS-2

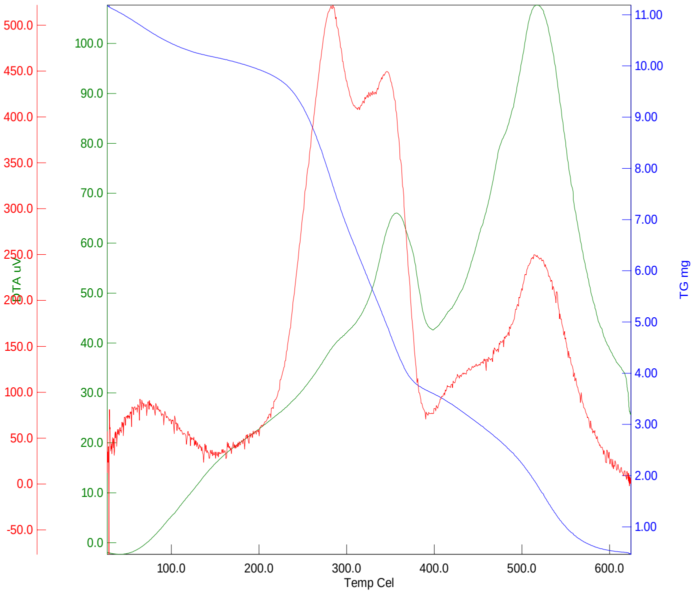


Fig.4.4: Thermogravimetric and differential thermal analysis of FWS-3

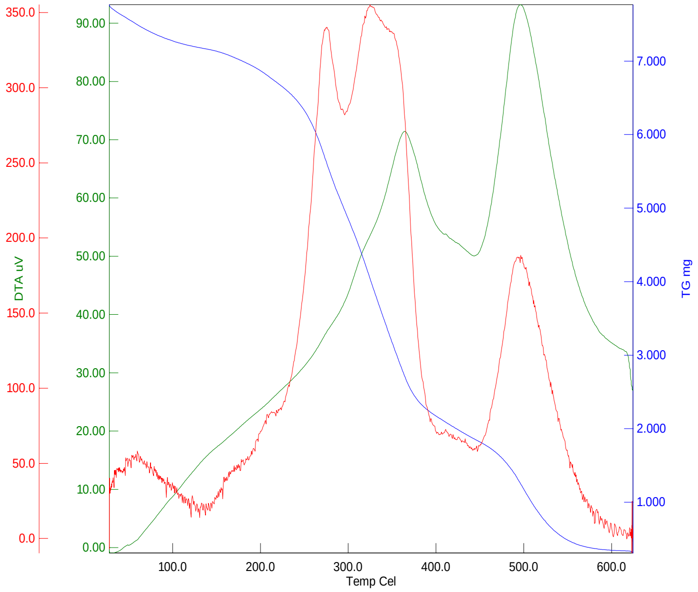


Fig.4.5: Thermogravimetric and differential thermal analysis of FWS-4

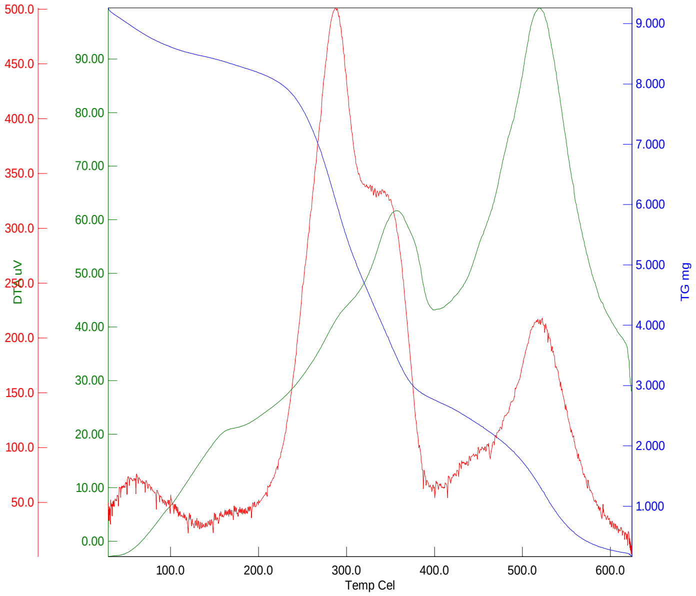


Fig.4.6: Thermogravimetric and differential thermal analysis of FWSMX

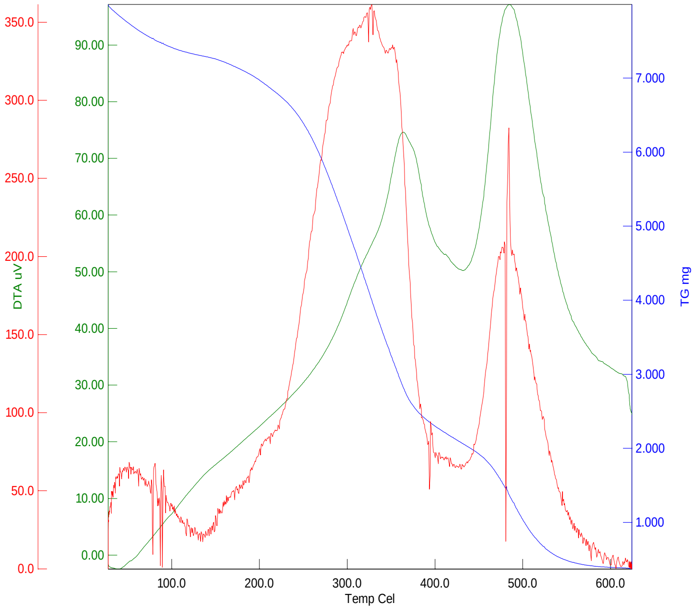


Fig.4.7: Thermogravimetric and differential thermal analysis of FWSVNV-1

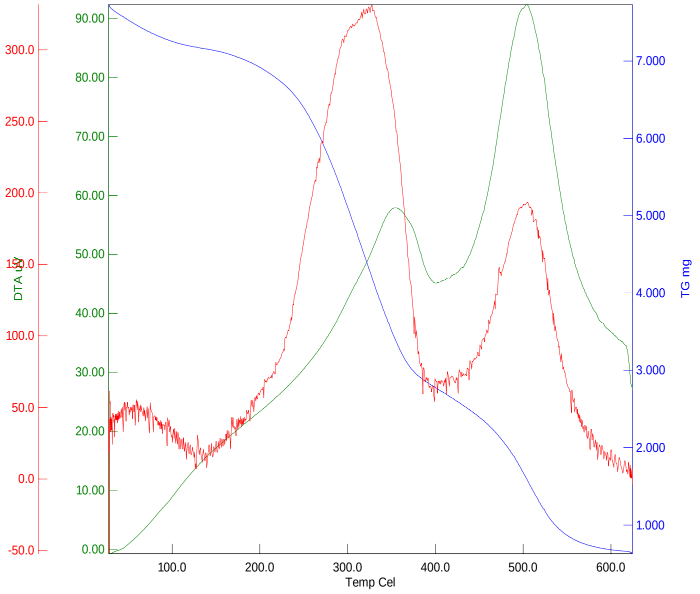


Fig.4.8: Thermogravimetric and differential thermal analysis of FWSNV-2

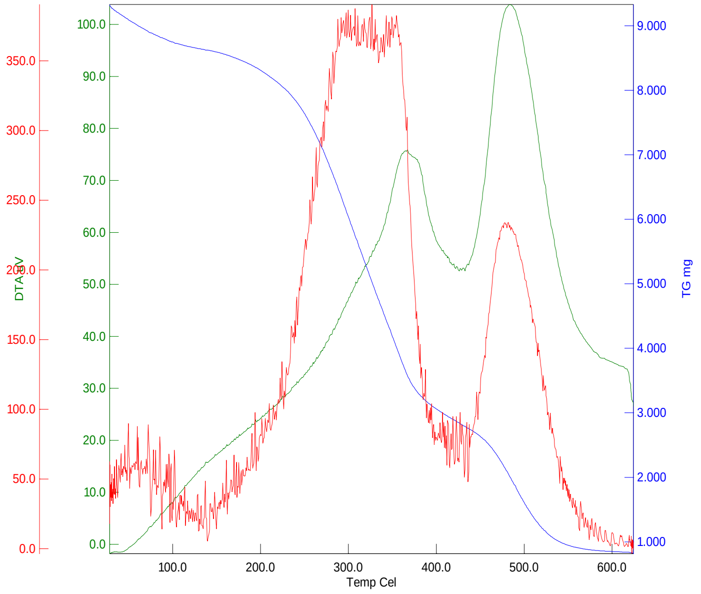


Fig.4.9: Thermogravimetric and differential thermal analysis of FWSNVMX

Table 4.8 (a): Thermal degradation in the First Zone (Nitrogen flow rate: 50 mL min^{-1})

Food waste sample	Heating rate (°Cmin^{-1})	Moisture removed (%)	Degradation temperature (°C)			Total degradation (%)	Degradation rate (µg min^{-1})	
			Initial	Final	Max.		Avg.	Max.
FWS-1	10	7.92	150	200	200	1.77	19.66	27.25
FWS-2	10	7.09	150	200	200	1.60	23.67	32.74
FWS-3	10	9.19	150	200	200	2.35	43.10	54.78
FWS-4	10	8.16	150	200	200	3.70	49.79	71.16
FWSMX	**10**	**9.21**	**150**	**200**	**200**	**2.72**	**45.39**	**50.55**
FWSVNV-1	10	8.21	120	200	200	4.99	51.85	76.56
FWSNV-2	10	6.96	120	200	200	3.84	42.42	60.52
FWSNVMX	**10**	**7.94**	**150**	**200**	**200**	**3.32**	**49.11**	**80.24**

Table 4.8 (b): Thermal degradation in the Second Zone (Nitrogen flow rate: 50 mL min^{-1})

Food waste sample	Degradation temperature (°C)				Total degradation (%)	Degradation rate (µg min^{-1})		
	Initial	Final	Max.	Peak degradation temperature		Avg.	Max.	Peak
FWS-1	200	380	380	351	61.80	39.92	52.59	275.48
FWS-2	200	380	380	280	61.90	61.38	90.00	414.56
FWS-3	200	380	380	285	60.50	83.90	113.03	523.77
FWS-4	200	380	380	325	63.04	100.35	129.53	355.54
FWSMX	**200**	**380**	**380**	**288**	**62.44**	**83.54**	**116.53**	**501.89**
FWSVNV-1	200	380	380	328	60.93	97.67	118.78	361.28
FWSNV-2	200	380	380	327	55.41	74.76	88.99	331.94
FWSNVMX	**200**	**380**	**380**	**308**	**58.37**	**114.05**	**147.85**	**391.46**

Table 4.8 (c): Thermal degradation in the Third Zone (Nitrogen flow rate: 50 mL min^{-1})

Food waste sample	Degradation temperature (ºC)				Total degradation (%)	Degradation rate (μg min^{-1})		
	Initial	Final	Max.	Peak degradation temperature		Ave.	Max.	Peak
FWS-1	380	500	500	479	21.80	87.50	22.37	167.45
FWS-2	380	500	500	500	15.27	117.30	44.59	144.59
FWS-3	380	514	514	514	18.46	181.53	50.03	250.03
FWS-4	380	500	500	498	16.73	156.03	82.52	188.22
FWSMX	**380**	**521**	**521**	**521**	**19.39**	**163.92**	**11.34**	**211.34**
FWSVNV-1	380	500	500	484	19.92	143.32	67.85	283.92
FWSNV-2	380	503	503	503	18.30	140.56	92.12	192.12
FWSNVMX	**380**	**500**	**500**	**481**	**19.54**	**172.46**	**97.06**	**235.60**

Table 4.8 (d): Thermal degradation in the Fourth Zone (Nitrogen flow rate: 50 mL min^{-1})

Food waste samples	Degradation temperature (ºC)		Total degradation (%)	Degradation rate (μg min^{-1})	Residue (%)
	Initial	Final		Average	
FWS-1	500	580	7.08	62.44	7.55 (580 ºC)
FWS-2	500	580	12.42	80.24	8.81(580 ºC)
FWS-3	514	624	14.08	122.92	4.61(624 ºC)
FWS-4	500	624	12.13	92.87	4.40(624 ºC)
FWSMX	**521**	**624**	**13.36**	**108.77**	**2.09(624 ºC)**
FWSVNV-1	500	600	08.80	85.04	5.36(600 ºC)
FWSNV-2	503	624	13.57	99.17	8.88(624 ºC)
FWSNVMX	**500**	**624**	**09.18**	**100.05**	**9.59(624 ºC)**

moisture until 150 °C. Percentage degradation in this zone varied from 1.60% (FWS-2) to 4.99% (FWSVNV-1), whereas the maximum degradation rate varied between27.254 (FWS-1) and 80.244 (FWSNVMX) µg min^{-1} respectively. The second stage of weight loss, as is evident from the both the TG and DTG curves, could be due to rapid loss of light volatiles. This stage is seen to exist between 200 and 380 °C and may be called as initial thermal degradation stage. Higher percentage degradation was observed from 55.41% (FWSNV-2) to 63.03% (FWS-4). Peak degradation temperature varied from 280 °C (FWS-2) to 351 °C (FWS-1) with the degradation rates of 414.5664 (FWS-2) and 275.4824 (FWS-1) µgmin^{-1} respectively.

The third zone of degradation is observed from 380 °C to 500 °C which extends up to 521 °C (FWSMX). Slow pyrolysis resulted in the lower percentage degradation from 15.17% (FWS-2) to 21.80% (FWS-1) with peak degradation rates of 283.9219 (FWSVNV-1) and 144.598 (FWS-2) µgmin^{-1}respectively. Finally, the fourth zone, which is the ash zone, exists between 500 and 624 °C. Average degradation rate was found to vary between 62.446 (FWS-1) and 122.923 (FWS-3) µg min^{-1} respectively. FWSNVMX remained with higher residue of 9.59% at 624 °C in comparison to other FWS used in this study. Thermal degradation characteristics as deduced from these figures are presented in the Tables 4.8 (a) to 4.8 (d).

4.4. Preliminary pyrolysis experiments

Preliminary pyrolysis experiments were carried out by using pulverized FWP with a particle size less than 1 mm. Experiments were carried out at different time intervals of 10, 20, 25, 30 and 35 min. at a fixed temperature of 400 ºC and microwave power of 450 W to decide about the time required to complete the pyrolysis. Pyrolysis temperature of 400 ºC was selected based on the thermogrvimetric study of pulverized FWP. The reactor was fed with a 100 g of pulverized FWP by a hopper into the quartz cavity (250 mL) of the microwave system. Inert atmosphere was maintained within the reactor by purging nitrogen gas at 100 mL min^{-1}. The reactor temperature was raised at a pre-determined controlled rate with the help of microwave heating (450 W) till the stipulated reaction temperature of 400 ºC was reached and maintained till the biochar,

Table 4.9: Pyrolysis yields at a temperature of 400 ºC, nitrogen flow of 100 mLmin^{-1} and 450 W power

Time (min)	Biochar yield (Wt. %)	Bio-oil yield (Wt. %)	Biogas yield (Wt. %)
10	82.87	12.97	4.16
20	69.82	22.91	7.27
25	69.22	23.50	7.28
30	68.03	23.91	8.06
35	67.94	23.92	8.14

Table 4.10: Pyrolysis yields at a temperature of 400 ºC, time 30 min. and 450 W power

Nitrogen flow rate (mLmin^{-1})	Biochar yield (Wt. %)	Bio-oil yield (Wt. %)	Biogas yield (Wt. %)
25	70.57	22.23	7.20
50	59.50	30.24	10.26
75	63.66	26.45	9.89
100	68.03	23.91	8.06

bio-oil and other gaseous products are obtained. Pyrolysis resulted in the volatilization of the products and exits the microwave system.

Vapours resulting due degradation of FWP were condensed into the respective condensers by circulating the cooling water at a temperature of 27 ºC and gas fractions were allowed to pass through the vent. Similar experiments were repeated with the cooling water available at 5 ºC to verify the effect of cooling water temperature on condensation of vapours and there was no difference in the yield of bio-oil. The results of the pyrolysis experiments are tabulated in the Table 4.9. Variation of pyrolysis products such as biochar, bio-oil and biogas with time is shown in the Fig. 4.10. Similar pyrolysis experiments were carried out at different nitrogen flow rates of 25, 50, 75 and 100 mLmin^{-1}at a fixed temperature of 400 ºC, 450 W microwave power and 30 min. residence time to decide about the nitrogen flow rate that will result in an increased bio-oil yield. Results of the pyrolysis process are tabulated in the Table 4.10

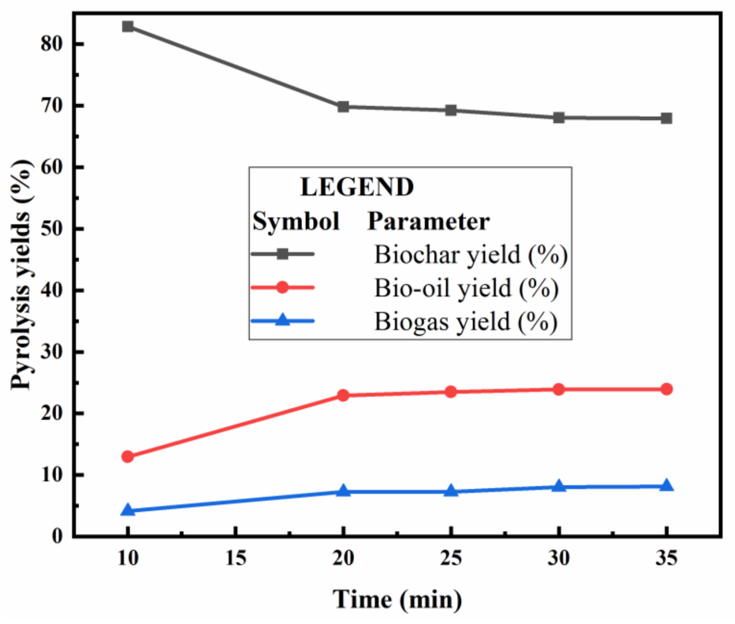


Fig. 4.10: Variation of pyrolysis yields with residence time

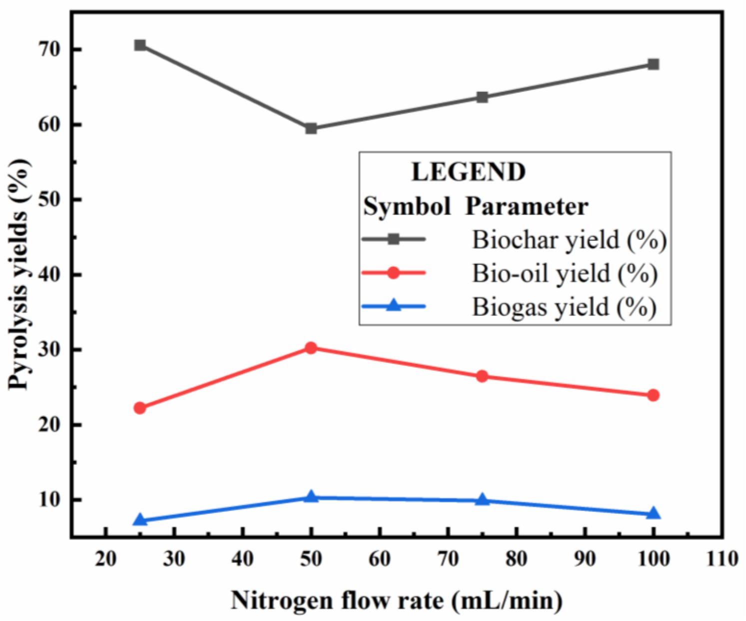


Fig. 4.11: Variation of pyrolysis yields with nitrogen flow rate

Variation of pyrolysis products such as biochar, bio-oil and biogas with nitrogen flow rate are shown in the Fig. 4.11. Based on the preliminary pyrolysis experiments carried out it can be inferred that, the biochar, bio-oil and biogas yields were very close to each other at the time intervals of 30 and 35 min. respectively. Therefore, the maximum time required to complete the pyrolysis of FWP was taken to be 30 min. Heating rate and final pyrolysis temperature were affected by the nitrogen flow rate. Increase in the nitrogen flow rate resulted in the decreased biomass heating rate and pyrolysis temperature of upper layer due to heat carrying capacity of the nitrogen. Mushtaq et al. (2015) reported that, an increase in the nitrogen flow rate reduces the final pyrolysis reaction temperature as the heat carried by the carrier gas is more than that of the heat released by the surface carbon solids of the upper biomass layer. Heat generated by the upper carbon particles, bottom layer FWP and heat carried with nitrogen reached equilibrium at 50 mLmin^{-1} and resulted in the maximum bio-oil yield with decreased char yield and increased gas yield.

Based on the preliminary pyrolysis experiments and TGA studies, the operating ranges for the time, nitrogen flow rate and temperature to carry out pyrolysis experiments by response surface methodology (RSM) were selected and shown in the Table 4.11.

Table 4.11: Operating ranges for time, nitrogen flow rate and temperature to design experiments

Parameter	Minimum	Middle	Maximum
Time (min.)	25	30	35
Nitrogen flow rate (mL min^{-1})	40	50	60
Temperature(°C)	350	400	450

4.5. Temperature profiles

Temperature profiles under different microwave powers, as recorded by the K-type thermocouple, are presented in Fig.4.12. Under all microwave powers the sample was 100 gand particle size was less than 1 mm. The temperature profiles as shown in Fig.4.12indicated that after ten min. in to the pyrolysis process the temperature in the pyrolysis chamber was more or less constant and increasing with increasing microwave power levels of 150, 225, 300, 375and 450 W respectively. Slight pyrolysis of the sample was observed at the microwave power of 150 W and the maximum temperature reached was 146 °C. Faster increase in the temperature was observed after the microwave power of 225 W. Temperature profiles also showed that, the microwave absorber was not necessary to increase the temperature as the food waste itself acted as a good dielectric material (Meredith, 1998).

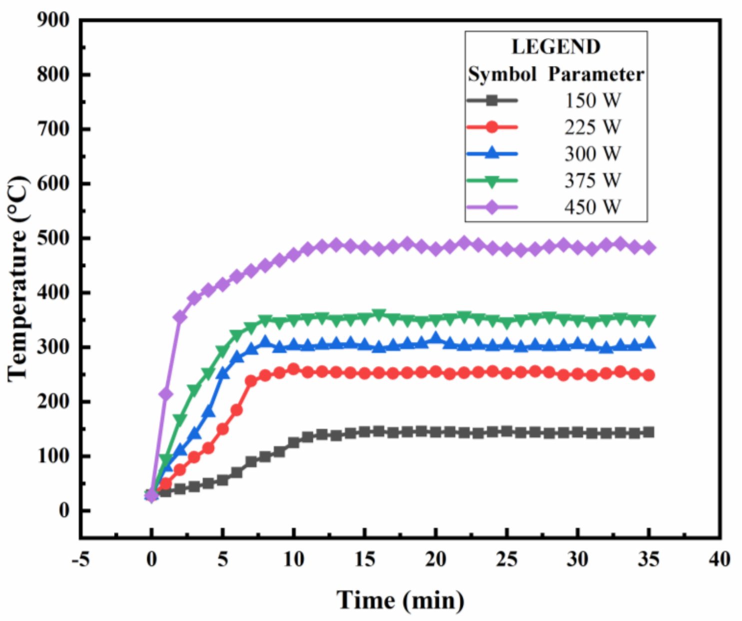


Fig.4.12: Temperature profiles under different microwave powers

Biochar which was produced during the initial stages of reaction promoted further reaction by absorbing the microwaves. Char produced during the pyrolysis reaction has a very good dielectric property and is commonly used as a microwave receptor (Domı´nguez et al. 2006). During the early stages of reaction (first two min.) the temperature was less than 100 °C and was used to heat the FWP. Increase in the temperature at this stage was also due to the presence of moisture in the feed stock which is very good microwave absorber. Microwaves absorbed by the moisture leads to the friction within the molecules resulting in an increase of temperature. Evaporation of the water and formation of volatiles resulted in the stable temperature profiles as the volatiles do not absorb the microwaves (Salemaand Ani,2011; Longjun et al. 2013). Stable temperature profiles were observed after 8-10 min. due to balance between the heat release and heat loss rates. During this time period an effective heating of the FWP was observed resulting in an effective temperature rise and formation of the char. Increase in the microwave power resulted in the higher pyrolysis temperature, as the char formed was a very good microwave absorber. This heating behavior was similar to the wok reported by Huang et al. (2010), Du et al. (2011), and Hu et al. (2012) with other biomass feed stocks. Higher microwave power of 450 W was used in our system to achieve the temperature above 450 °C. This was mainly due to the use of larger quantity of feed stock, characteristics of the experimental device and insulation method adopted (Huang et al. 2010; Du et al. 2011). FWP slowly turned in to ash as the pyrolysis temperature crossed 500 °C and completely turned in to ash at 600 °C. Hence the pyrolysis above 500 °C was not carried out in our study. Table 4.12 shows the final temperatures and heating rate under different microwave powers. Increase in the pyrolysis temperature was not observed during the first min. and an effective heating of the FWP was observed at around 10 minute after the start of heating. Input microwave energy was responsible for the increase in temperature and heating rate.

Table 4.12: Final temperatures and heating rate under different microwave powers

Microwave power (W)	150 W	225 W	300 W	375 W	450 W
Temperature (°C)	140±6	250±10	300±15	350±18	470±20
Heating rate [a] (°Cmin^{-1})	11	30	45	64	98
[a]Calculated from the slope of linear regression of temperatures from first to fifth min.					

Maximum temperature attained and the heating rates were increased depending upon an increase in the microwave power level which in turn resulted in the decreased time to complete pyrolysis. Microwave reactor type as well as type of feed stock was also responsible for the microwave heating. Increase in the microwave power enhanced the heating rate and final temperature. Heating rate was calculated from the linear regression of temperature from first to fifth min (Huang et al. 2013).

4.6. Pyrolysis yields

Three operating parameters namely pyrolysis temperature (A), residence time (B) and nitrogen flow rate (C) were investigated to study the effect of these parameters on bio-oil, biochar and biogas production. All the above three parameters were selected because of their effect on the biofuels (Bridgwater, 2011). Pyrolysis experiments were carried out at different microwave power levels of 150, 225, 300, 375 and 450 W respectively. Pyrolysis product yields such as biochar, bio-oil and biogas at different microwave powers are shown in the Table 4.13. Pyrolysis product yields, at a microwave power of 150 W, were not considered as the temperature attained at this power was below 150 ºC which was not sufficient to pyrolyze the FWP. It can be seen from Table 4.13 that, the lower microwave power (225 W) resulted in the lower heating rate and increased production of solid char compared to bio-oil and biogas. Increase in the heating rate as well pyrolysis temperature was observed when the microwave power was increased from 225 W to 450 W. Enhanced microwave heating resulted in the decrease of char yield and an increase in the oil yield as well as gas yield over the range of microwave power levels studied. Increase in the microwave power enhances the microwave absorption capacity of the FWP and results in the higher pyrolysis temperature. This temperature was responsible for the decomposition of macromolecules of FWP in to micro molecules resulting in the decreased char yield. This trend was similar to the other studies reported in the literature using different types of biomass feed stocks (Jamaluddin et al. 2013; Longjun et al. 2013).

Maximum pyrolysis temperature achieved with a microwave power of 225 W, time 30 min. and nitrogen flow of 50 mLmin^{-1} was 250 °C which resulted in the char yield of 92.40 wt. %, oil yield of 4.88 wt. % and gas yield of 2.72 wt. %. Similar trend was observed with the microwave power levels of 300,375and 450 W respectively. Char yield of 89.66 wt. %, oil yield of 6.97 wt. % and gas yield of 3.37 wt. % were obtained at the pyrolysis temperature of 300 °C, power level 300 W, residence time of 30 min. with a nitrogen flow rate of 50 mL min^{-1}. Maximum bio-oil yield of 30.24 wt. % was obtained at a power level of 450 W with a residence time of 30 min. and nitrogen flow rate 50 mL

min^{-1} due to complete pyrolysis of FWP at the pyrolysis temperature of 400 °C. Heating rate and final pyrolysis temperature were affected by the nitrogen flow rate. Increase in the nitrogen flow rate resulted in the decreased biomass heating rate and pyrolysis temperature of upper layer due to heat carrying capacity of the nitrogen. Nitrogen flow rate of 50 $mLmin^{-1}$ resulted in the increased bio-oil and biogas yields due to equilibrium between the heat release rate by the carbon particles and heat carried by the nitrogen flow at the microwave power level of 450 W (Mushtaq et al. 2015).

Similar trend was not observed at the microwave power of 375 W that resulted in the pyrolysis temperature of 300 °C with a bio-oil yield of just 14.02 wt. %. This could be due to the non-equilibrium between the heat release rate by the carbon particles and heat carried by the nitrogen flow due lower microwave power as well as lower pyrolysis temperature. Reduced gas yield at the lower microwave power as well pyrolysis temperature was observed due to lower volatile release rate as well as reduced gasification reactions (Zhao et al. 2012). Decreased bio-oil yield and increased gas yield was evidenced after 400 °C due to secondary cracking of oil vapours into noncondensable gases. The variations observed were mainly due to the feed stock and characteristics of the microwave system adopted (Du et al. 2011; Wang et al. 2017).

4.7. Optimization by response surface methodology

Three operating parameters namely pyrolysis temperature (A), residence time (B) and nitrogen flow rate (C) were investigated to study the effect of these parameters on bio-oil, biochar and biogas production by using RSM. All the above three parameters were selected because of their effect in maximizing the biofuels yield (Bridgwater, 2011). The number of experiments was calculated by using Eq.3.6 (Abnisa et al. 2011).CCD consists of eight factorial, six axial and six central points resulting in a total of 20 experiments. Operating ranges for the temperature, time and nitrogen flow rate were selected based on the preliminary experiments. Each of the operating parameter was varied over the five levels namely the high level (+1), low level (-1), centre point or coded level (0) and corresponding to a value of $\pm\alpha = 1.\ 68179$. Values of α were calculated by using Eq.3.3. The centre points or the coded levels were used to measure the experimental error as well

Table 4.13: Pyrolysis product yields at different microwave powers and operating parameters

Power (W)	Operating Parameters			Biochar (Wt. %)	Bio-oil (Wt. %)	Biogas (Wt. %)
	Temperature (°C)	Time (min.)	Flow rate (mL min^{-1})			
225	200	25	40	94.54	3.51	1.95
		25	60	95.72	2.53	1.75
		35	40	93.64	3.72	2.64
		35	60	95.62	2.58	1.80
	250	30	50	92.40	4.88	2.72
300	250	25	40	91.64	5.48	2.88
		25	60	92.73	4.59	2.68
		35	40	90.92	5.89	3.19
		35	60	92.63	4.65	2.72
	300	30	50	89.66	6.97	3.37
375	250	25	40	88.03	8.47	3.50
		25	60	89.42	7.34	3.24
		35	40	87.19	9.11	3.70
		35	60	89.12	7.40	3.48
	300	30	50	81.47	14.02	4.51
	350	25	40	75.28	17.73	6.99
		25	60	77.84	16.59	5.57
		35	40	74.80	18.16	7.04
		35	60	76.87	17.55	5.58
450	350	25	40	70.89	21.67	7.44
		25	60	73.54	19.51	6.95
		35	40	69.49	22.44	8.07
		35	60	71.43	21.56	7.01
	400	30	50	60.03	30.24	9.73
	400	39	50	60.40	29.92	9.68
	400	30	34	60.40	29.92	9.68
	400	22	50	72.36	18.66	8.98
	400	30	67	70.55	20.03	9.42
	450	25	40	62.46	22.69	14.85
		25	60	64.52	21.14	14.34
		35	40	61.59	22.91	15.50
		35	60	63.82	21.54	14.64

as lack of fit, whereas, the axial points were used to estimate the curvature of the model. The data obtained from the experimental runs was analyzed by using CCD consisting of20 experiments, which in turn used to optimize the pyrolysis process (Brown and

Brown, 2012; Jamaluddin et al. 2013; Liu et al. 2013). Twenty experiments were designed based on the operating ranges as shown in the Table 4.11 using Minitab software (Version 14; Minitab Ltd. Coventry CV 32TE, UK). Pyrolysis experiments were carried out at different power levels of 225, 300, 375 and 450 W respectively. Pyrolysis product yields such as biochar, bio-oil and biogas based on the design of experiments are shown in the Table 4.13.

4.7.1. Statistical analysis of bio-oil model

The actual values of the operating parameters namely temperature, time and nitrogen flow rate and the response, which is the bio-oil, yield, for twenty experiments were used for the prediction of bio-oil model. The regression model with 95% confidence level resulted in the high value of R^2 = 95.4 % with R^2 adjusted = 91.2 % indicated a very good or excellent fit of the data to the model. Similar results were observed with the other biomass feed stock materials (Abnisa et al. 2011; Brownand Brown,2012; Jamaluddin et al. 2013; Liu et al. 2013).

Second order model was used to approximate the true response due to parabolic curvature in the response surface as shown from Fig. 4.17 to Fig. 4.19. All the terms of the first order model, quadratic terms as well as cross product terms were included in the second order model (Bradely, 2007). The basic approach to fit the collected experimental data with the empirical model is the regression analysis. The response (bio-oil yield) and variables involved were fitted to each other by multiple regressions in this study (Montgomery, 2000). The final bio-oil model in terms of the coded values is given by Eq. 4.1

$$Y_{BOY}=30.2228 +1.1236A +1.2623B +0.1399C-3.0806A^2-1.6911B^2-3.6428C^2 -0.0825AB +0.4850AC +0.6125BC \quad (4.1)$$

Where Y_{BOY} is the bio-oil yield (wt. %), A is the temperature (ºC), B is the time (min) and C is the nitrogen flow rate (mL min^{-1}). It is evident from the equation 4.1that, a total of five main factors of the CCD design were significant with a positive value increasing

Table 4.14: Central composite design matrix for bio-oil optimization

Run order	Std. order	Coded factors			Actual factors			Actual yield (Wt. %)	Predicted yield (Wt. %)
					Temperature (^{o}C)-A	Time (min.)-B	Nitrogen flow rate (mL min^{-1})-C		
1	7	-1.00	1.00	1.00	350	35	60	21.86	22.29
2	13	0.00	0.00	-1.68	400	30	34	18.89	19.68
3	10	1.68	0.00	0.00	484	30	50	24.98	23.39
4	16	0.00	0.00	0.00	400	30	50	30.24	30.22
5	19	0.00	0.00	0.00	400	30	50	30.22	30.22
6	8	1.00	1.00	1.00	450	35	60	23.99	25.34
7	6	1.00	-1.00	1.00	450	25	60	21.14	21.76
8	2	1.00	-1.00	-1.00	450	25	40	22.19	21.74
9	1	-1.00	-1.00	-1.00	350	25	40	21.67	20.29
10	9	-1.68	0.00	0.00	316	30	50	18.02	19.62
11	12	0.00	1.68	0.00	400	39	50	28.92	27.56
12	17	0.00	0.00	0.00	400	30	50	30.23	30.22
13	11	0.00	-1.68	0.00	400	22	50	21.94	23.31
14	3	-1.00	1.00	-1.00	350	35	40	22.40	21.76
15	14	0.00	0.00	1.68	400	30	67	20.93	20.15
16	18	0.00	0.00	0.00	400	30	50	30.21	30.22
17	5	-1.00	-1.00	1.00	350	25	60	19.51	18.38
18	4	1.00	1.00	-1.00	450	35	40	21.76	22.87
19	15	0.00	0.00	0.00	400	30	50	30.24	30.22
20	20	0.00	0.00	0.00	400	30	50	30.20	30.22

the bio-oil yield, whereas, three other factors with a negative value were responsible for the decrease in the bio-oil yield. All the three parameters of the bio-oil model namely temperature, time and nitrogen flow rates along with the two interaction terms were having positive effect on the bio-oil yield whereas three square terms along with the one interaction term were having negative effect on the bio-oil yield. This indicated that, there exists an interactive relationship between the variables involved in the process. Hence the use of experimental design (CCD) was justified by identifying the parameters that were responsible for the yield of bio-oil. The relationship between the predicted bio-oil yields using equation 4.1and the experimental values is shown in Fig. 4.13. It is evident from the Fig. 4.13 that, the experimental values were very close to that of the predicted values. Central composite design matrix for process optimization is shown in Table 4.14.

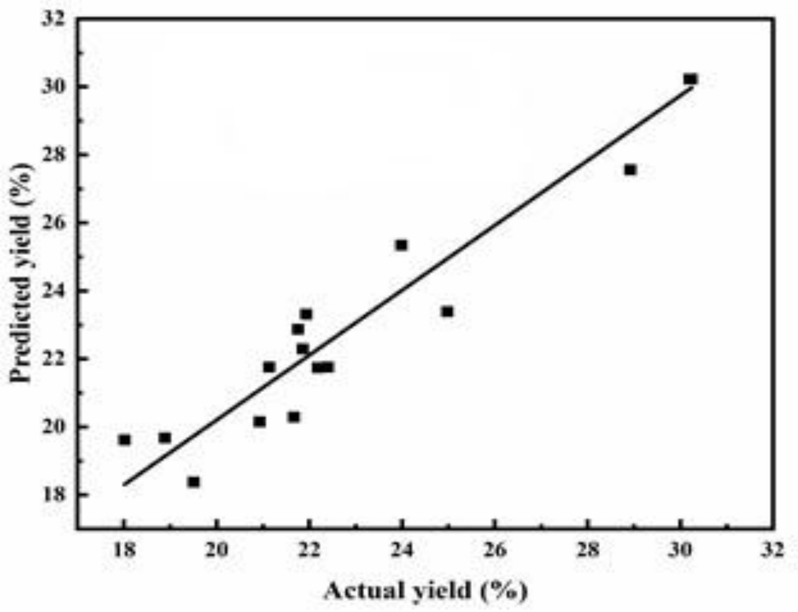


Fig. 4.13: Comparison between actual and predicted yields of bio-oil

The estimated regression coefficients and analysis of variance (ANNOVA) for bio-oil yield are presented in the Table 4.15 and Table 4.16. It is evident from the table of

Regression coefficients that, both the temperature and time were having the similar effect on the bio-oil yield with a model T value of 3.142 and 3.530 respectively. The effect of nitrogen flow rate is less significant with a higher value of P (0.704) as it was used as a carrier gas. The response surface quadratic model was checked statistically by F-tests and ANNOVA.

Table 4.15: Estimated regression coefficients for bio-oil yield (%)

Term	Coefficient	SE Coefficient	T	P	Remarks
Constant	30.23	0.54	56.07	0.000	Significant
Temperature (ºC)	1.12	0.35	3.14	0.010	Significant
Time (min)	1.26	0.35	3.53	0.005	Significant
Nitrogen flow rate (mL min^{-1})	0.14	0.35	0.39	0.704	
Temperature (ºC) × Temperature (ºC)	-3.08	0.34	-8.85	0.000	Significant
Time (min) × Time (min)	-1.69	0.34	-4.85	0.001	Significant
Nitrogen flow rate (mL min^{-1}) × Nitrogen flow rate (mL min^{-1})	-3.64	0.34	-10.46	0.000	Significant
Temperature (ºC) × Time (min)	-0.08	0.46	-0.17	0.863	
Temperature (ºC) × Nitrogen flow rate (mL min^{-1})	0.48	0.46	1.04	0.324	
Time (min) × Nitrogen flow rate (mL min^{-1})	0.61	0.46	1.31	0.219	
S = 1.322 R-Sq = 95.4% R-Sq (adj.) = 91.2%					

Table 4.16: Analysis of variance for bio-oil yield (%)

Source	Degrees of freedom	Sequential sum of squares	Adj. SS	Adj. MS	F	P	Remarks
Regression	9	360.27	360.27	40.03	22.92	0.000	Significant
Linear	3	39.27	39.27	13.09	7.50	0.006	Significant
Square	3	316.06	316.06	105.35	60.33	0.000	Significant
Interaction	3	4.93	4.93	1.64	0.94	0.456	
Residual Error	10	17.46	17.46	1.74			
Lack of Fit	5	17.46	17.46	3.49	13097.31	0.000	Significant
Pure Error	5	0.001	0.001	0.00			
Total	**19**	**377.40**					

The model value of F (22.92) indicated that, the model is statistically valid and significant. Model F value for linear (7.50) and square (60.33) with lower values of P suggested that, the linear and square terms were significant. However, model value of F for interaction (0.94) with a higher value of P (0.456) indicated that, the interaction terms are not having significant effect on the bio-oil yield. Model F-value of lack-of –fit and the lower probability (P) values of the parameters involved suggested that, the model terms were significant.

4.7.2. Effect of process parameters on bio-oil yield

The effect of operating parameters namely temperature, time and nitrogen flow rate on the bio-oil yield were found by using RSM. Effects these operating parameters were represented in the form of three dimensional plots from Fig. 4.14. to Fig. 4.16. Two dimensional contour plots for nitrogen flow rate vs. temperature with a hold value of time 30 min., time vs. temperature with a hold value of nitrogen flow rate 50 mL min^{-1} and nitrogen flow rate vs. time with a hold value of temperature of 400 ºC are shown from Fig. 4.17 to Fig. 4.19 respectively. It is evident from the regression coefficients Table 4.15 that, both the temperature and time were considered as most significant parameters to effect bio-oil production due to model value of T (3.14 for temperature and 3.53 for time) with lower P values. Nitrogen flow rate was considered as less significant to effect pyrolysis process due to higher value of P, as it was used to provide an inert atmosphere for the pyrolysis process as well as carrier gas (Jamaluddin et al. 2013). The interaction effect of nitrogen with temperature and time was positive as observed from equation 4.1that has increased the bio-oil yield. This was evident from the response surface graph Fig. 4.14 and Fig. 4. 16.

Mushtaq et al. [2015] reported that, an increase in the nitrogen flow rate reduces the final pyrolysis reaction temperature as the heat carried by the carrier gas was more than that of the heat released by the surface carbon solids of the upper biomass layer. Heat generated by the upper carbon particles, bottom layer FWP and heat carried with nitrogen reached equilibrium at 50 mLmin^{-1} and resulted in the maximum bio-oil yield. Bio-oil yield was

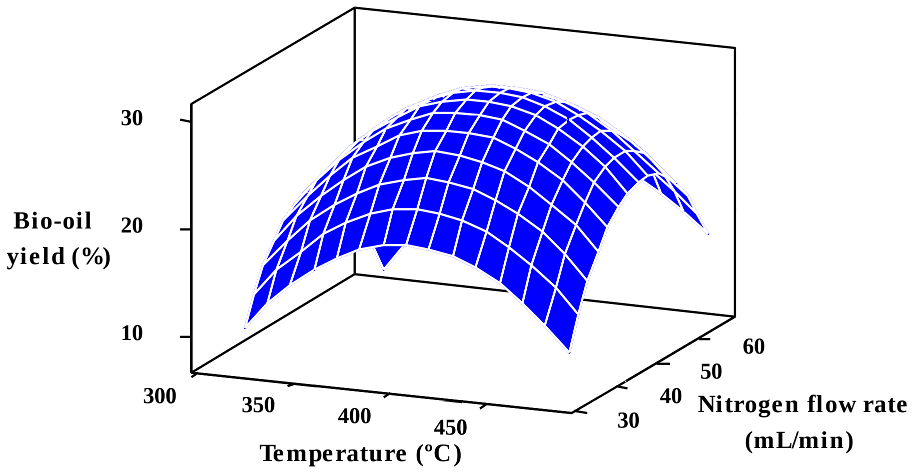


Fig. 4.14: Surface plot of bio-oil yield (%) vs. nitrogen flow rate (mLmin^{-1}) and temperature (°C) at 450 W

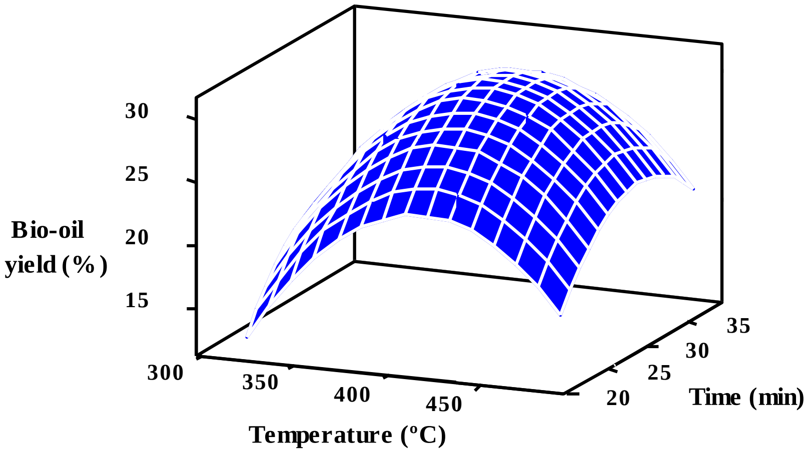


Fig. 4.15: Surface plot of bio-oil yield (%) vs. time (min) and temperature (°C) at 450 W

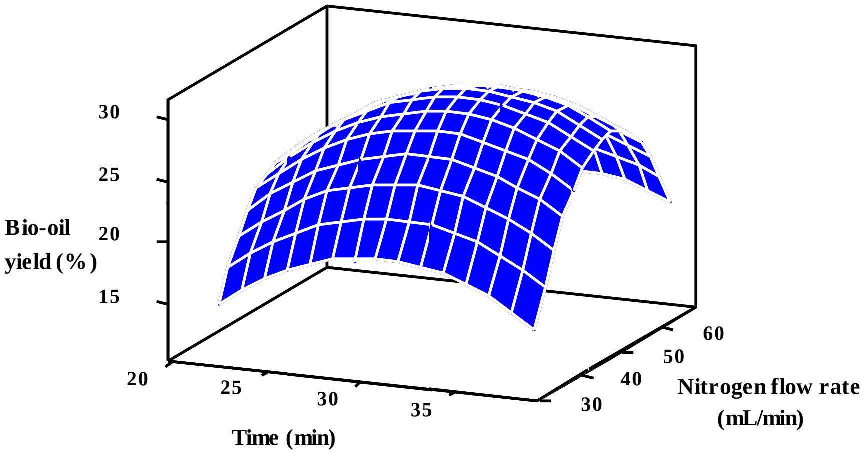


Fig. 4.16: Surface plot of Bio-oil yield (%) vs. Nitrogen flow rate (mLmin^{-1}) and Time (min) at 450 W

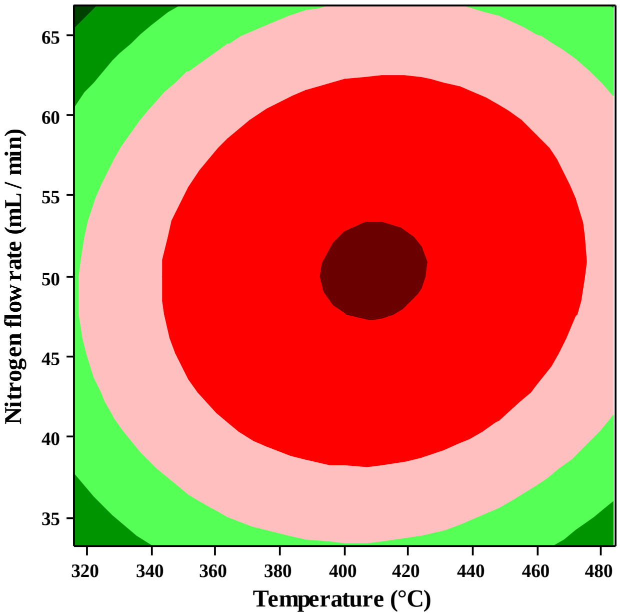


Fig. 4.17: Contour plot of bio-oil yield (%) vs. nitrogen flow rate (mLmin^{-1}) and temperature (°C) at 450 W

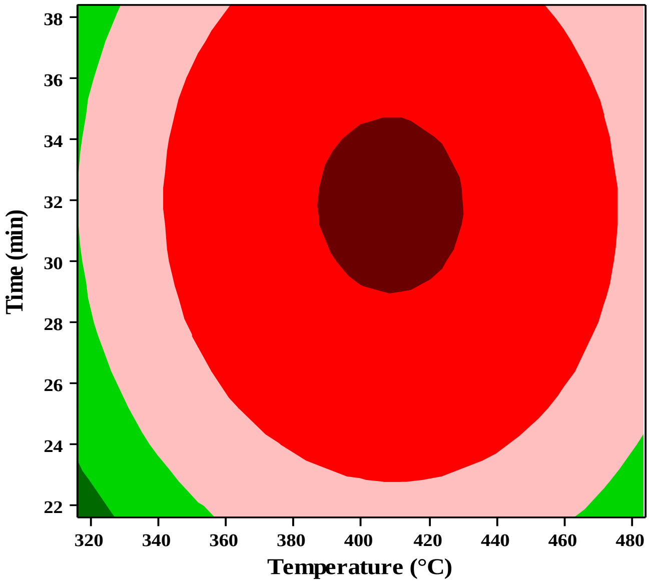


Fig. 4.18: Contour plot of bio-oil yield (%) vs. time (min) and temperature (ºC) at 450 W

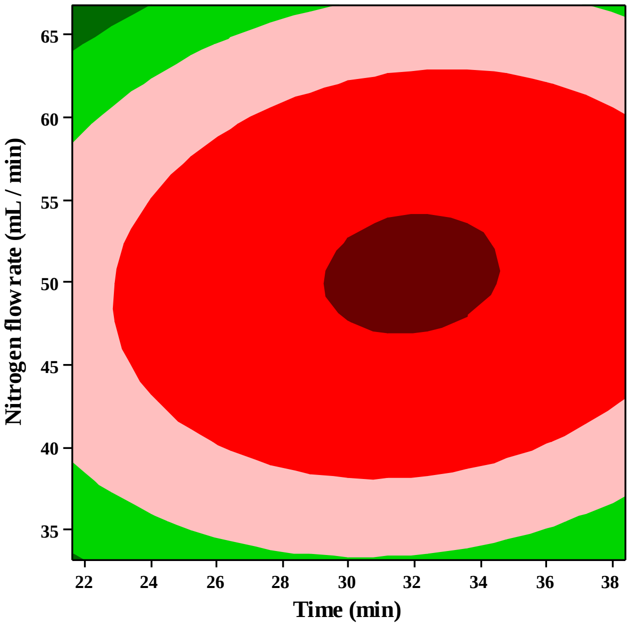


Fig. 4.19: Contour plot of bio-oil yield (%) vs. nitrogen flow rate (mLmin^{-1}) and Time (min) at 450 W

decreased beyond 50 mL min^{-1} nitrogen flow rate that has affected the optimum pyrolysis temperature (Huang et al. 2013). This effect is shown in the response surface and contour graphs (Fig. 4.14, Fig. 4.16, Fig. 4.17and Fig. 4.19). Among the variables investigated in this study, both temperature and time were having their effect to enhance the bio-oil yield (Fig. 4.15, Fig. 4.16, Fig. 4.18and Fig. 4.19).

Açıkalın et al. (2012) reported that, the bio-oil yield increases till optimum pyrolysis temperature and decreases beyond the optimum pyrolysis temperature due to secondary reactions thereby increasing the gas yield with increase in temperature. Increase in the reaction temperature (400 ºC) and time (30 min.) resulted in the removal of volatiles causing an increase in the bio-oil yield (30.24 wt. %) as the pyrolysis process was an endothermic process (Fig. 4.14to Fig. 4.19). Among the variables investigated in this study, both the temperature and time were having their effect on the bio-oil yield. On the other hand, an increase in the operating parameters beyond the optimum conditions resulted in the decrease of bio-oil yield and increase in the gas yield due to production of low molecular weight compounds, involving secondary cracking of vapours in to incondensable gases and faster pushing of the noncondensable gases due to increased flow of nitrogen gas, as it was used as a carrier gas (Fig. 4.14 and Fig. 4.16). Uniform heating of biomass sample from core to surface, which is the characteristics of microwaves, at 450 W resulted in the temperature required for the secondary cracking of vapours in to incondensable gases (Jamaluddin et al., 2013; Thostenson and Chou, 1999).

4.7.3. Statistical analysis of biochar model

The actual values of the operating parameters namely temperature, time and nitrogen flow rate and the response, which is the biochar yield, for twenty experiments were used for the prediction of biochar model. The regression model with 95% confidence level resulted in the high value of R^2 = 92.9 % with R^2 adjusted = 86.4 % indicated a very good or excellent fit of the data to the model. Similar results were observed with the other biomass feed stock materials (Brown and Brown,2012). Second order model was used approximate the true response due to parabolic curvature in the response surface as shown from Fig. 4.21 to 4.23. All the terms of the first order model, quadratic terms as well as cross product terms were included in the second order model (Bradely, 2007). The basic approach to fit the collected experimental data with the empirical model is the regression analysis. The response (biochar yield) and variables involved were fitted to each other by multiple regressions in this study (Montgomery, 2000). The final biochar model in terms of the coded values is given by Eq. 4.2

$$Y_{BC} = 60.0170 - 4.3518A - 1.8448B + 1.9002C + 2.5765A^2 + 2.3608B^2 + 2.0409C^2 + 0.2425AB - 0.0375AC - 0.0675BC \quad (4.2)$$

Where Y_{BC} is the biochar yield (%), A is the temperature (ºC), B is the time (min) and C is the nitrogen flow rate ($mLmin^{-1}$). It is evident from the equation 4.2that, a total of five main factors of the CCD design were significant with a positive value increasing the biochar yield, whereas, three other factors with a negative value were responsible for the decrease in the biochar yield. Among the parameters of the biochar model nitrogen flow rate and three square terms along with the one interaction term were having positive effect on the biochar yield, whereas, the operating temperature, residence time along with the two interaction terms were having negative effect on the biochar yield.

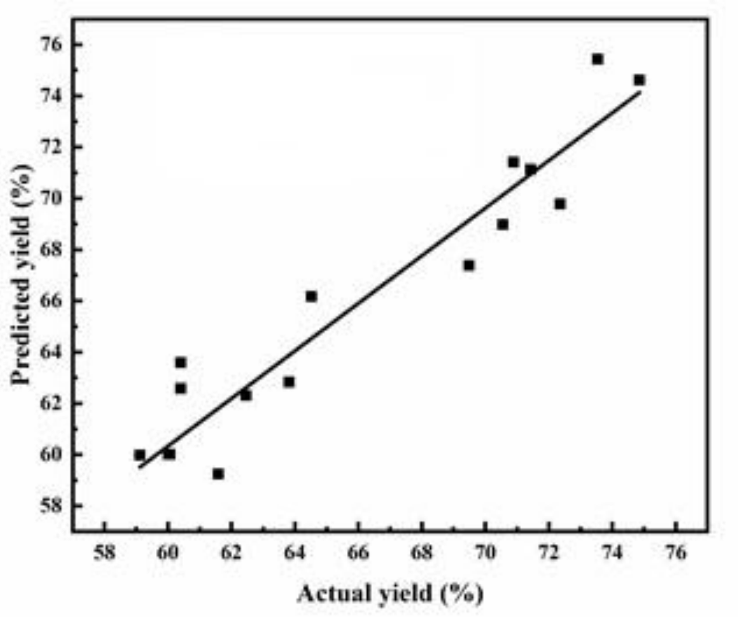


Fig. 4.20: Comparison between actual and predicted yields of biochar

Table 4.17: Central composite design matrix for biochar minimization

Run order	Std. order	Coded factors			Actual factors			Actual yield (Wt. %)	Predicted yield (Wt. %)
					Temperature (°C)-A	Time (min.)-B	Nitrogen flow rate (mL min^{-1})-C		
1	3	-1.00	1.00	-1.00	400	22	50	69.49	67.38
2	19	0.00	0.00	0.00	350	25	60	60.03	60.01
3	17	0.00	0.00	0.00	400	30	50	60.01	60.01
4	12	0.00	1.68	0.00	350	35	60	60.40	63.59
5	8	1.00	1.00	1.00	316	30	50	63.82	62.83
6	4	1.00	1.00	-1.00	484	30	50	61.59	59.24
7	9	-1.68	0.00	0.00	450	25	40	74.86	74.62
8	6	1.00	-1.00	1.00	400	30	50	64.52	66.17
9	10	1.68	0.00	0.00	450	35	40	59.12	59.98
10	2	1.00	-1.00	-1.00	450	35	60	62.46	62.31
11	5	-1.00	-1.00	1.00	400	30	50	73.54	75.43
12	20	0.00	0.00	0.00	400	38	50	60.05	60.01
13	18	0.00	0.00	0.00	350	35	40	60.04	60.01
14	7	-1.00	1.00	1.00	400	30	50	71.43	71.13
15	11	0.00	-1.68	0.00	450	25	60	72.36	69.79
16	14	0.00	0.00	1.68	400	30	50	70.55	68.98
17	15	0.00	0.00	0.00	400	30	33	60.06	60.01
18	13	0.00	0.00	-1.68	350	25	40	60.40	62.59
19	1	-1.00	-1.00	-1.00	400	30	50	70.89	71.42
20	16	0.00	0.00	0.00	400	30	67	60.02	60.01

The relationship between the predicted biochar yields using equation 4.2 and the experimental values is shown in Fig. 4.20. It is evident from the figure 4.20 that, the experimental values were very close to that of the predicted values. Central composite design matrix for process optimization is shown in Table 4.17.

The estimated regression coefficients and analysis of variance (ANNOVA) for biochar yield are presented in the Table 4.18 and Table 4.19. It is evident from the table of regression coefficients that, both the temperature and time were having the negative effect on the biochar yield with a model T value of -7.80 and -3.30 respectively. Nitrogen flow rate is having significant effect on the biochar yield with a lower P value of 0.007. The response surface quadratic model was checked statistically by F-tests and ANNOVA. The model value of F 14.46 indicated that, the model is statistically valid and significant. Model F value for linear (27.83) and square (15.51) suggested that, the linear and square terms were significant. However, model value of F for interaction (0.04) with a higher value of P (0.988) indicated that, the interaction terms were not having significant effects on the biochar yield. Model F-value of lack-of –fit and the lower probability (P) values of the parameters involved suggested that, the model terms were significant.

Table 4.18: Estimated regression coefficients for biochar yield (%)

Term	Coefficient	SE Coefficient	T	P	Remarks
Constant	60.17	0.84	71.42	0.000	Significant
Temperature (°C)	-4.35	0.55	-7.80	0.000	Significant
Time (min)	-1.84	0.55	-3.30	0.008	Significant
Nitrogen flow rate (mLmin^{-1})	1.90	0.55	3.40	0.007	Significant
Temperature (°C)× Temperature (°C)	2.57	0.54	4.74	0.001	Significant
Time (min) × Time (min)	2.36	0.54	4.35	0.001	Significant
Nitrogen flow rate (mL min^{-1}) × Nitrogen flow rate (mL min^{-1})	2.04	0.54	3.76	0.004	Significant
Temperature (°C) × Time (min)	0.24	0.72	0.33	0.746	
Temperature (°C) × Nitrogen flow rate (mL min^{-1})	-0.03	0.72	-0.05	0.960	
Time (min) × Nitrogen flow rate (mL min^{-1})	-0.06	0.72	-0.09	0.928	
S = 2.06 R-Sq = 92.90% R-Sq (adj.) = 84.40%					

Table 4.19: Analysis of variance for biochar yield (%)

Source	Degrees of freedom	Sequential sum of squares	Adj. SS	Adj. MS	F	P	Remarks
Regression	9	552.42	552.42	61.38	14.46	0.000	Significant
Linear	3	354.42	354.42	118.14	27.83	0.000	Significant
Square	3	197.48	197.48	65.82	15.51	0.000	Significant
Interaction	3	0.51	0.52	0.17	0.04	0.988	
Residual Error	10	42.45	42.45	4.24			
Lack of Fit	5	42.45	42.45	8.49	24257.96	0.000	Significant
Pure Error	5	0.002	0.002	0.00			
Total	**19**	**594.87**					

4.7.4. Effect of process parameters on biochar yield

The effect of operating parameters namely temperature, time and nitrogen flow rate on the biochar yield were found by using RSM. Effects these operating parameters are represented in the form of three dimensional plots Fig. 4.21 to Fig. 4.23. Two dimensional contour plots for nitrogen flow rate vs. time with a hold value of temperature of 400 ºC, nitrogen flow rate vs. temperature with a hold value of time 30 min. and time vs. temperature with a hold value of nitrogen flow rate 50 mL min^{-1} are shown from Fig. 4.24 to Fig. 4.26. It is evident from the regression coefficients Table 4.18 that, both the temperature and time were considered as most significant parameters to decrease biochar production due to model value of T (-7.80 for temperature and -3.30 for time) with lower values of P. Nitrogen flow rate was considered as significant parameter to effect pyrolysis process due to lower value of P.

It is evident from the Fig. 4.22 that, an increase in the nitrogen flow rate also resulted in the decrease in the char yield with an increase in the bio-oil yield, though the temperature was considered as most significant parameter to decrease char yield at a constant time of 30 min. This was in accordance with the increase of bio-oil yield with an increase in the nitrogen flow rate as discussed in the section 4.6.2(Brown and Brown,2012). Increase in the nitrogen flow rate beyond 50 mL min^{-1} resulted in the increase in the char yield there

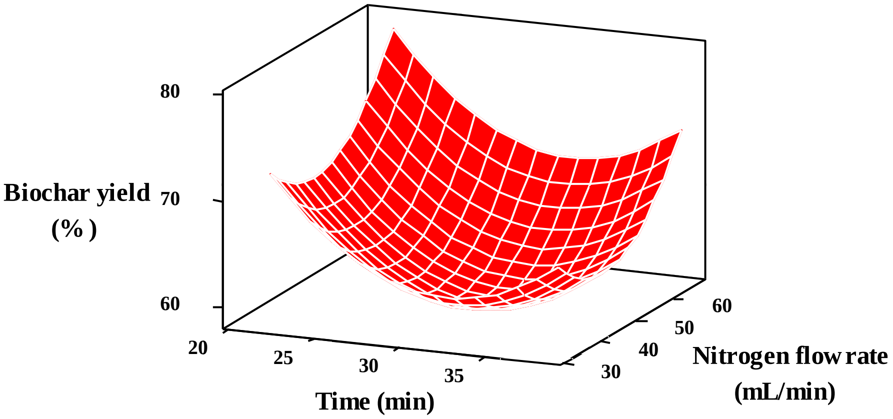


Fig. 4.21: Surface plot of biochar yield (%) vs. nitrogen flow rate, time at 400 ºC and 450 W

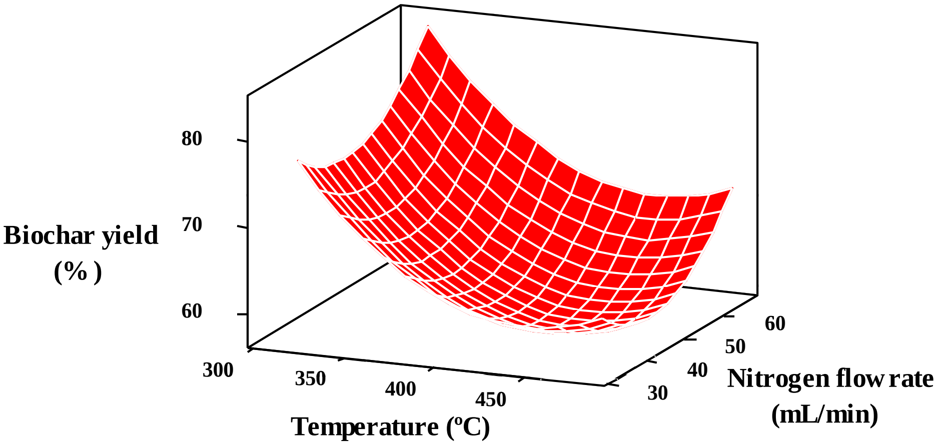


Fig. 4.22: Surface plot of biochar yield (%) vs. nitrogen flow rate, temperature at 30 min and 450 W

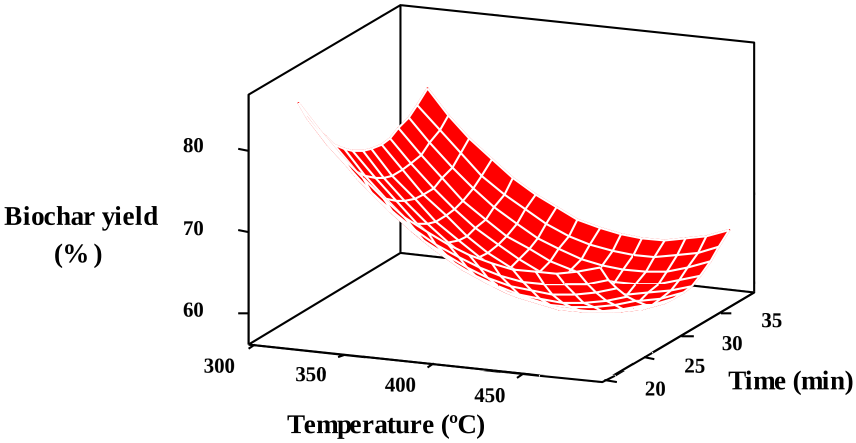


Fig. 4.23: Surface plot of biochar yield (%) vs. time, temperature at 50 mLmin^{-1} and 450 W

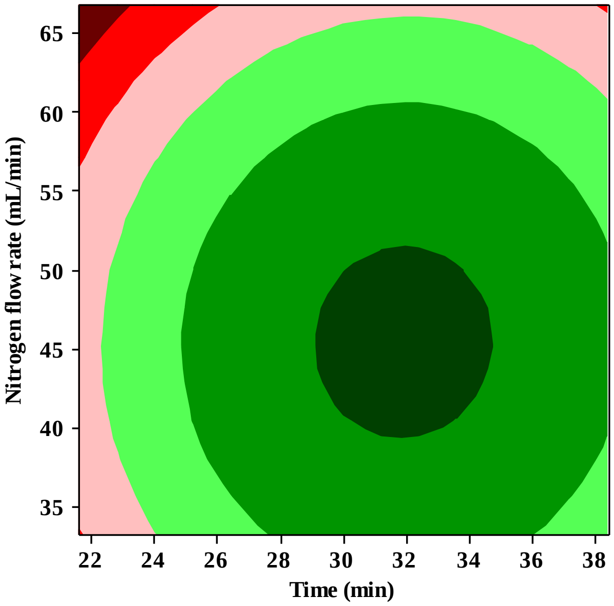


Fig. 4.24: Contour plot of biochar yield (%) vs. nitrogen flow rate, time at 400 °C and 450 W

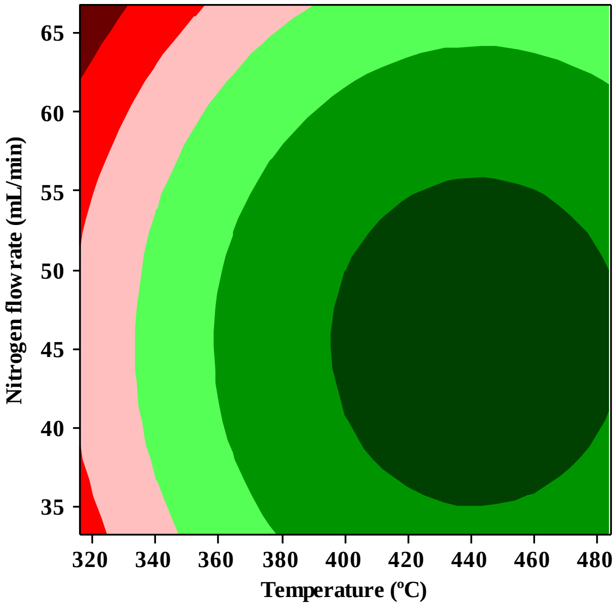


Fig. 4.25: Contour plot of biochar yield (%) vs. nitrogen flow rate, temperature at 30 min and 450 W

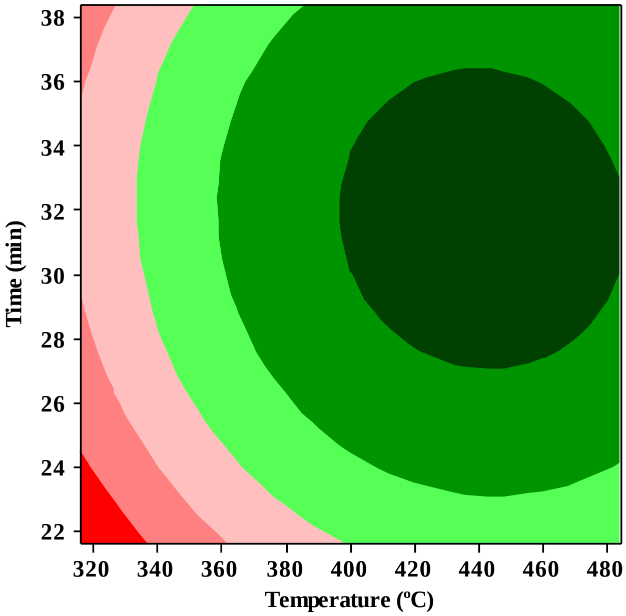


Fig. 4.26: Contour plot of biochar yield (%) vs. time, temperature at 50 mLmin^{-1} and 450 W

by decreasing the bio-oil yield. This could be due to the cooling effects of nitrogen associated with the condensation of vapours back in to the quartz flask. But, the interaction effect of nitrogen with temperature and time was negative, as observed from equation 4.2, which has decreased the biochar yield. This was evident from the response surface graph Fig. 4.21 and Fig. 4.23.

The interaction between the time and nitrogen flow rate with a hold value of temperature 400 ºC is shown in the Fig. 4.21, whereas, the interaction between the temperature and nitrogen flow rate with a hold value of time 30 min. is depicted in the Fig. 4.22. Interaction between the temperature and the time with a hold value of 50 $mLmin^{-1}$ is represented in the Fig. 4.23. It is evident from all the response graphs that, the mutual effects of lower temperature, time and nitrogen flow rate are favourable for increased char production as result of lower thermal cracking of FWP (Hossain et al. 2017). Similar results were observed with the other biomass feed stock materials (Zhang et al. 2009; Wang et al. 2009; Wang et al. 2015). Combined effects of higher temperature and time resulted in the release of more volatiles (Sensöz and Angın, 2008) but, the cooling effect caused by the increased nitrogen flow rate and condensation of vapours back in to the quartz flask resulted in the increased char yield. Hence it is evident from all the three response surface graphs that, the nitrogen flow rate of 50 $mLmin^{-1}$, temperature 400 ºC and time of 30 min. resulted in the maximum bio-oil yield of 30.24 wt. % and decreased better quality biochar yield of 60.03 wt% at a power level of 450 W.

4.7.5. Statistical analysis of fixed carbon content model

The actual values of the operating parameters namely temperature, time and nitrogen flow rate and the response, which is the fixed carbon content, for twenty experiments were used for the prediction of fixed carbon content model. The regression model with 95 % confidence level resulted in the high value of R^2 = 90.3 % with R^2 adjusted = 81.60 % indicated a very good or excellent fit of the data to the model. Similar results were observed with the other biomass feed stock materials (Brown and Brown,2012; Jamaluddin et al. 2013). Second order model was used approximate the true response due to parabolic curvature in the response surface as shown from Fig. 4.28 to Fig. 4.32. All the terms of the first order model, quadratic terms as well as cross product terms were included in the second order model (Bradely, 2007).

The basic approach to fit the collected experimental data with the empirical model is the regression analysis. The response (fixed carbon) and variables involved were fitted to each other by multiple regressions in this study (Montgomery, 2000). The final fixed carbon content model in terms of the coded values is given by Eq. 4.3

$$Y_{FC}=48.7219+3.0453A-0.0422B+1.4108C-2.1772A^2-0.1071B^2-1.9845C^2$$
$$+0.2800AB-1.3500AC+0.0400BC \quad (4.3)$$

Where Y_{FC} is the fixed carbon content (%), A is the temperature (ºC), B is the time (min) and C is the nitrogen flow rate ($mLmin^{-1}$). It is evident from the Eq. 4.3that, a total of four main factors of the CCD design were significant with a positive value increasing the fixed carbon content, whereas, five other factors with a negative value were responsible for the decrease in the fixed carbon content.

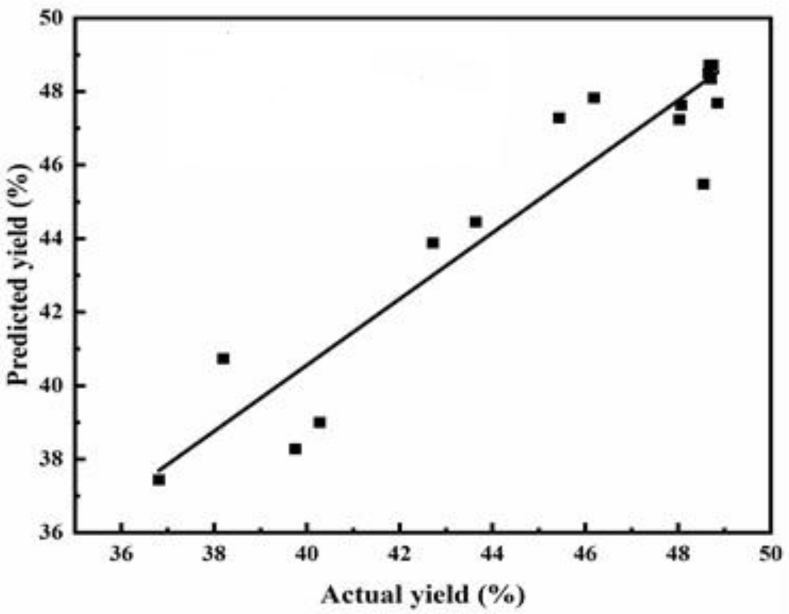


Fig 4.27:Comparison between the actual and predicted yields of fixed carbon content

Table 4.20: Central composite design matrix for fixed carbon content optimization

Run order	Std. order	Coded factors			Actual factors			Actual content (Wt. %)	Predicted content (Wt. %)
					Temperature(°C) -A	Time (min.)-B	Nitrogen flow rate (mL min^{-1})-C		
1	11	0.00	-1.68	0.00	400	22	50	48.66	48.49
2	5	-1.00	-1.00	1.00	350	25	60	43.64	44.45
3	19	0.00	0.00	0.00	400	30	50	48.71	48.72
4	7	-1.00	-1.00	1.00	350	35	60	42.72	43.88
5	9	-1.68	0.00	0.00	316	30	50	36.81	37.44
6	10	1.68	0.00	0.00	484	30	50	48.85	47.68
7	2	1.00	-1.00	-1.00	450	25	40	48.03	47.24
8	7	0.00	0.00	0.00	400	30	50	48.71	48.72
9	4	1.00	1.00	-1.00	450	35	40	48.07	47.63
10	8	1.00	1.00	1.00	450	35	60	46.19	47.83
11	15	0.00	0.00	0.00	400	30	50	48.69	48.72
12	12	0.00	1.68	0.00	400	38	50	48.71	48.34
13	3	-1.00	1.00	-1.00	350	35	40	39.75	38.28
14	16	0.00	0.00	0.00	400	30	50	48.68	48.72
15	6	1.00	-1.00	1.00	450	25	60	45.44	47.28
16	20	0.00	0.00	0.00	400	30	50	48.70	48.72
17	13	0.00	0.00	-1.68	400	30	33	38.20	40.73
18	1	-1.00	-1.00	-1.00	350	25	40	40.28	39.00
19	18	0.00	0.00	0.00	400	30	50	48.75	48.72
20	14	0.00	0.00	1.68	400	30	67	48.55	45.48

Among the parameters of the fixed carbon content model temperature, nitrogen flow rate and two interaction terms were having positive effect on the fixed carbon content whereas, the residence time, all the three square terms along with one interaction term were having negative effect on the fixed carbon content. This indicated that, there exists an interactive relationship between the variables involved in the process.

Hence the use of experimental design (CCD) was justified by identifying the parameters those were responsible for the yield of fixed carbon content. The relationship between the predicted fixed carbon content using Eq. 4.3 and the experimental values is shown in Fig 4.27. It is evident from the Fig. 4.27 that, the experimental values were very close to that of the predicted values. Central composite design matrix for process optimization is shown in Table 4.20.

The estimated regression coefficients and analysis of variance (ANNOVA) for fixed carbon content are presented in the Table 4.21 and Table 4.22. It is evident from the table of regressions coefficients that, both the temperature and nitrogen flow rate were having the positive effect on the fixed carbon content with a model T value of 6.448 and 2.987 respectively.

Table 4.21: Estimated regression coefficients for fixed carbon content (wt. %)

Term	Coefficient	SE Coefficient	T	P	Remarks
Constant	48.72	0.71	68.44	0.000	Significant
Temperature (ºC)	3.04	0.47	6.44	0.000	Significant
Time (min)	-0.04	0.47	-0.08	0.931	
Nitrogen flow rate (mL min^{-1})	1.41	0.47	2.98	0.014	Significant
Temperature (ºC) × Temperature (ºC)	-2.17	0.45	-4.73	0.001	Significant
Time (min) × Time (min)	-0.10	0.45	-0.23	0.820	
Nitrogen flow rate (mL min^{-1}) × Nitrogen flow rate (mL min^{-1})	-1.98	0.45	-4.31	0.002	Significant
Temperature (ºC) × Time (min)	0.28	0.61	0.45	0.660	
Temperature (ºC) × Nitrogen flow rate (mL min^{-1})	-1.35	0.61	-2.18	0.054	
Time (min) × Nitrogen flow rate (mL min^{-1})	0.04	0.61	0.06	0.950	
S = 1.745 R-Sq = 90.30% R-Sq (adj.) = 81.60%					

Table 4.22: Analysis of variance for fixed carbon content (wt. %)

Source	**Degrees of freedom**	**Sequential sum of squares**	**Adj. SS**	**Adj. MS**	**F**	**P**	**Remarks**
Regression	9	283.95	283.95	31.55	10.36	0.001	Significant
Linear	3	153.85	153.85	51.28	16.83	0.000	Significant
Square	3	114.88	114.88	38.29	12.57	0.001	Significant
Interaction	3	15.22	15.22	5.07	1.67	0.237	
Residual Error	10	30.46	30.46	3.04			
Lack of Fit	5	30.46	30.46	6.09	10384.56	0.000	Significant
Pure Error	5	0.003	0.003	0.006			
Total	**19**	**314.41**					

Nitrogen flow rate is having significant effect on the fixed carbon content with a lower P value of 0.014. The response surface quadratic model was checked statistically by F-tests and ANNOVA. The model value of F 10.36 indicated that, the model is statistically valid and significant. Model F value for linear (16.83) and square (12.57) suggested that, the linear and square terms were significant. However, model value of F for interaction (1.67) with a higher value of P (0.237) indicated that, the interaction terms were not having significant effect on the fixed carbon content. Model F-value of lack-of –fit and the lower probability (P) values of the parameters involved suggested that, the model terms were significant.

4.7.6. Effect of process parameters on fixed carbon content

The effect of operating parameters namely temperature, time and nitrogen flow rate on fixed carbon content were found by using RSM. Effects these operating parameters were represented in the form of three dimensional plots and represented from Fig. 4.28 to Fig. 4.30. Two dimensional contour plots for nitrogen flow rate vs. time with a hold value of temperature of 400 ºC, nitrogen flow rate vs. temperature with a hold value of time 30 min. and time vs. temperature with a hold value of nitrogen flow rate 50 mLmin^{-1} are shown in Fig. 4.31, Fig. 4.32 and Fig. 4.33 respectively. It is evident from the regression coefficients Table 4.21 that, both the temperature and nitrogen flow rate were considered

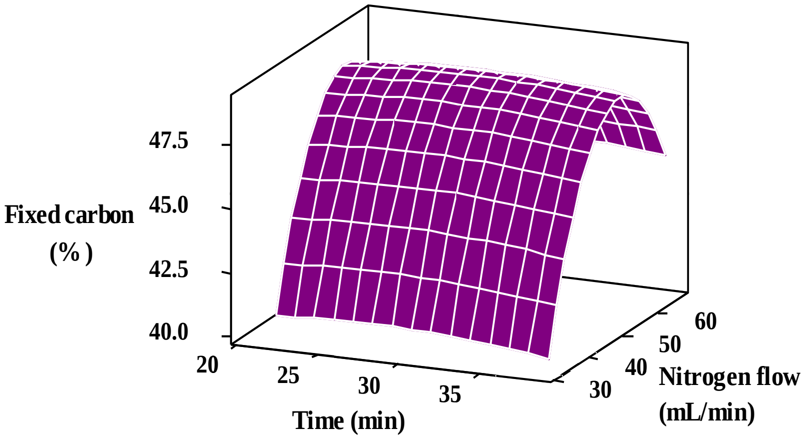


Fig. 4.28: Surface plot of fixed carbon content (%) vs. nitrogen flow rate, time at 400 ºC and 450 W

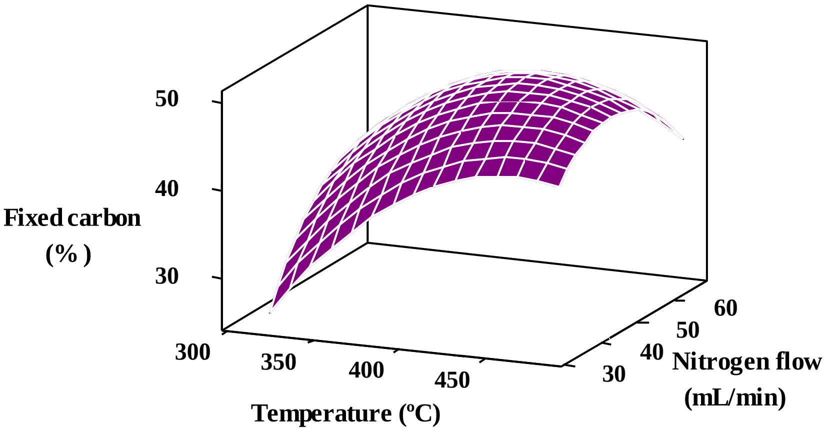


Fig. 4.29: Surface plot of fixed carbon content (%) vs. nitrogen flow rate, temperature at 30 min and 450 W

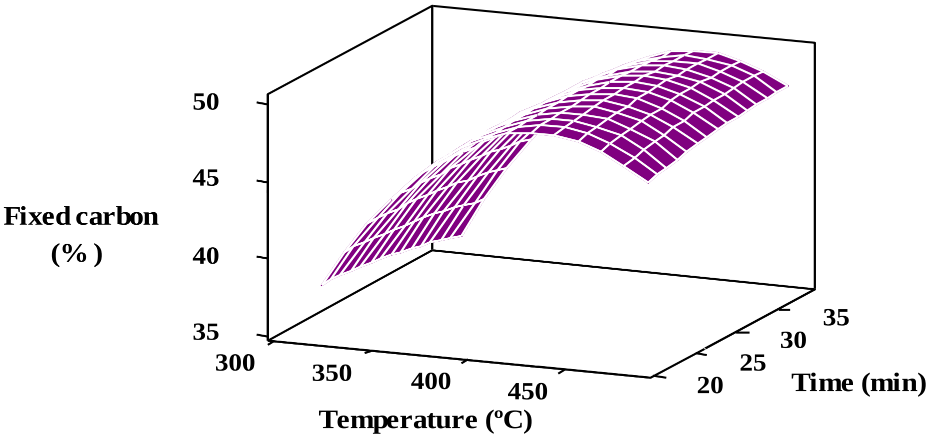


Fig. 4.30: Surface plot of fixed carbon content (%) vs. time, temperature at 50 mL min^{-1} and 450 W

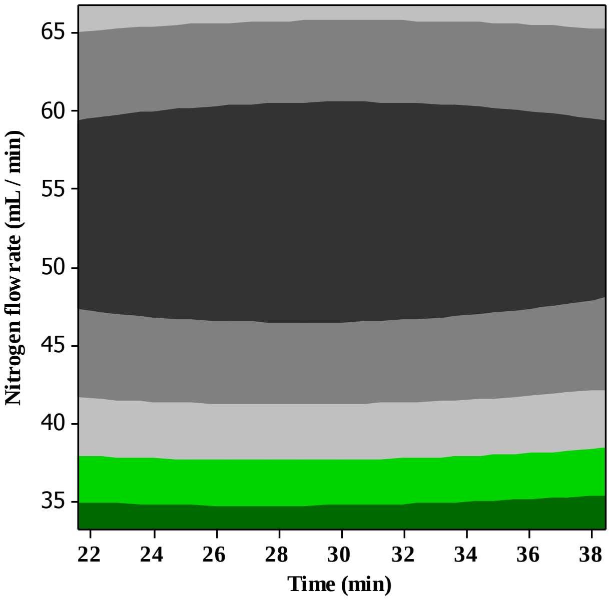


Fig. 4.31: Contour plot of fixed carbon content (%) vs. nitrogen flow rate, time at 400 ºC and 450 W

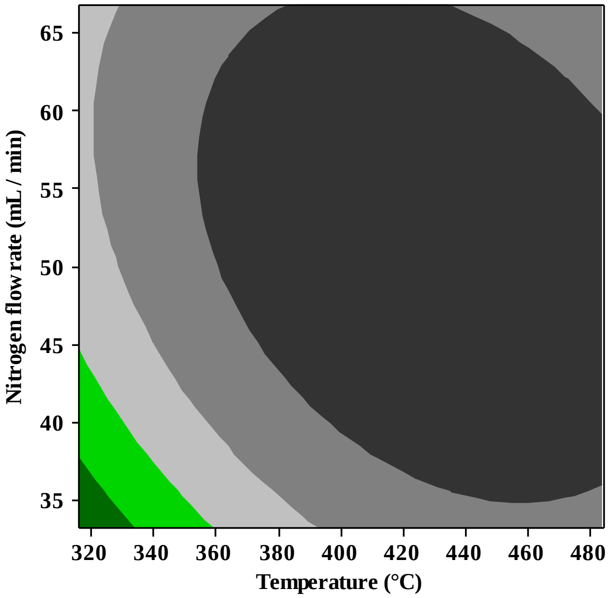


Fig. 4.32: Contour plot of fixed carbon content (%) vs. nitrogen flow rate, temperature at 30 min and 450 W.

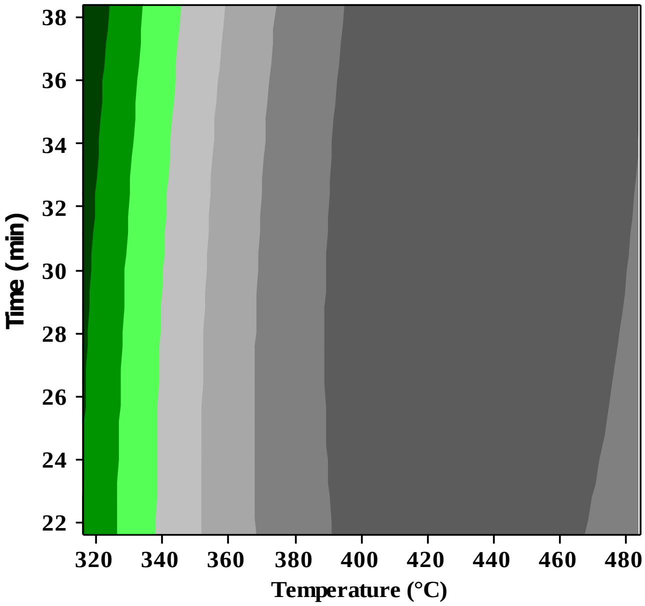


Fig. 4.33: Contour plot of fixed carbon content (%) vs. time, temperature at 50 mLmin^{-1} and 450 W

as most significant parameters to increase the fixed carbon content due to model value of T (6.44 for temperature and 2.98 for nitrogen flow rate) with lower values of P.

Temperature and nitrogen flow rate were considered as significant parameters to effect fixed carbon content due to lower value of P. It is evident from the Fig. 4.29 that, an increase in the nitrogen flow rate resulted in the increase in the fixed carbon content, though the temperature was considered as most significant parameter to increase fixed carbon content at a constant time of 30 min (Brown and Brown,2012).

Increase in the nitrogen flow rate beyond 50 mL min^{-1} resulted in the increase in the char yield and decrease in the fixed carbon content. This could be due to the cooling effects of nitrogen associated with the condensation of vapours back in to the quartz flask. But, the interaction effect of nitrogen flow rate with temperature was negative that decreased the fixed carbon content. Whereas, the interaction effect of nitrogen with time was positive that increased the fixed carbon content as observed from Eq. 4.3. This was evident from the response surface graph Fig. 4.28 and Fig. 4.30.

The interaction between the temperature and nitrogen flow rate with a hold value of time 30 min, the interaction between the time and nitrogen flow rate with a hold value of temperature 400 ºC and the between the temperature and the time with a hold value of 50 mLmin^{-1}are represented from Fig. 4.31 to Fig. 4.33 respectively. It is evident from the response graphs that, the mutual effects of lower temperature, time and nitrogen flow rate were favourable for increased char production with lower fixed carbon content as a result of lower thermal cracking of FWP (Hossain et al. 2017).

Increased fixed carbon content was observed due to saturation of aromatic rings, containing mainly carbon, due to combined effect of higher temperature and time which caused the release of more volatiles (Jamaluddin et al. 2013; Sensöz and Angın, 2008) but, the cooling effect caused by the increased nitrogen flow rate and condensation of vapours back in to the quartz flask resulted in the increased char yield. Hence it is evident from all the three response surface graphs that, the nitrogen flow rate of 50 mLmin^{-1}, temperature 400 ºC and time of 30 min. resulted in the maximum bio-oil yield of 30.24

wt. % and decreased biochar yield of 60.03 wt. % with a fixed carbon content of 48.71 wt. % at a power level of 450 W.

4.8. Characterization of biochar

Characterization of biochar was carried as per ASTM standard methods to know the physicochemical and thermo-chemical properties. Biochar samples obtained under the microwave power of 450 W were considered for characterization studies as the pyrolysis was incomplete under the microwave power levels of 225 W, 300 W and 375 W respectively. Analysis of biogas was not carried out due to its low weight percentage under the optimum pyrolysis conditions.

4.8.1. Proximate and ultimate analysis of biochar

Biochar samples collected at the end of each run under the microwave power of 450 W were analyzed through ASTM standard methods to evaluate the physicochemical and thermochemical properties. Proximate and ultimate analysis results are presented in the Table 4.23 and Table 4.24. Fixed carbon content and volatile organic carbons (VOC) in the biochar samples were affected by the operating parameters such as pyrolysis temperature, residence time of the sample and nitrogen flow rate. Very small variations in the moisture and ash contents of the biochar samples were observed throughout the pyrolysis process. Batch process and low temperature resulted in the large amount of volatile organic carbon (VOC) in the biochar as well as high yield of the biochar (Bartoli et al. 2016). Higher amount of VOC up to 68.26 wt. % was obtained at a pyrolysis temperature 250 °C using a microwave power of 375 W. Significant increase in the fixed carbon content from 23.93 to 55.91 wt. % was observed under different operating temperatures, residence time and nitrogen flow rate as well as microwave power levels. Lower temperature and nitrogen flow rate resulted in the decreased fixed carbon content due to condensation of volatiles back in to the quartz flask, whereas, increased temperature and nitrogen flow rate resulted in the increased fixed carbon content in the biochar samples. Ash content of all the biochar samples were very close to that of the

FWS. Moisture content of all the biochar samples were reduced from 2.69% to 0.82% depending upon the operating conditions.

Table 4.23: Proximate analysis of biochar samples obtained under the microwave power of 450 W

Power (W)	**Operating Parameters**			**Moisture**	**Volatiles**	**Ash**	**Fixed carbon**
	Temperature (°C)	**Time (min.)**	**Flow rate (mL min^{-1})**	**(Wt. %)**	**(Wt. %)**	**(Wt. %)**	**(Wt. %)**
450	350	25	40	1.12	51.70	6.90	40.28
		25	60	1.28	48.65	6.43	43.64
		35	40	1.10	52.10	7.08	39.75
		35	60	1.16	49.62	6.50	42.72
	400	30	50	1.05	44.01.	6.14	48.71
	400	39	50	1.05	44.01.	6.14	48.71
	400	30	34	1.08	54.52	6.20	38.20
	400	22	50	1.30	43.80	6.24	48.66
	400	30	67	1.32	42.99	7.14	48.55
	450	25	40	0.95	40.30	6.78	48.03
		25	60	0.84	37.94	6.66	45.44
		35	40	0.88	40.49	6.70	48.07
		35	60	0.86	38.45	6.88	46.19

Ultimate analysis of the biochar samples collected at the end of each test run were carried out at the Indian Institute of Science, Bengaluru, Karnataka, India. Ultimate analysis of the biochar samples are presented in the Table 4.24. It can be seen from the Table 4.24 that, there was a considerable increase in the carbon content of the biochar from 55.36 to 62.48 % compared with the variation of carbon content of the FWS (46.70 to 47.21 %). Small decrease in the hydrogen as well as nitrogen content was observed with all the biochar samples. Hydrogen content varied from 7.13 to 7.40 % compared to FWS (7.22 to 7.28%). Variation in the nitrogen content was observed from 1.87 to 2.80 % compared to FWS (2.45 to 2.98 %). Oxygen content was calculated by difference and varied from 20.09 to 27.31 % compared to FWS (35.64 to 36.92 %). Presence of nitrogen in the biochar plays an important role in retention of contaminants such as H_2S, CO_2 etc. (Ferrera-Lorenzo et al. 2014). Constant value of the nitrogen content in all the biochar

Table 4.24: Elemental compositions of biochar samples obtained under the microwave power of 450 W

Power (W)	Operating Parameters			Carbon	Hydrogen	Nitrogen	Oxygen (by difference)	Ash
	Temperature (°C)	Time (min.)	Flow rate (mL min^{-1})	(%)	(%)	(%)	(%)	(%)
450	350	25	40	56.73	7.27	2.40	26.70	6.90
		25	60	56.66	7.22	2.38	27.31	6.43
		35	40	56.58	7.31	2.42	26.61	7.08
		35	60	56.45	7.24	2.50	27.31	6.50
	400	30	50	62.48	7.283	2.80	21.29	6.14
	400	39	50	62.50	7.28	2.81	21.27	6.14
	400	30	34	56.89	7.25	2.37	27.29	6.20
	400	22	50	56.45	7.23	2.76	27.32	6.24
	400	30	67	62.56	7.18	2.79	20.33	7.14
	450	25	40	55.63	7.40	2.38	27.81	6.78
		25	60	55.56	7.38	2.38	28.02	6.66
		35	40	55.48	7.37	2.38	28.07	6.70
		35	60	55.36	7.36	2.38	28.02	6.88

samples favour the pyrolysis process. Increase in the carbon content was observed at the operating temperature of 400 ºC with the nitrogen flow rate of 50 mLmin^{-1}compared to other nitrogen flow rates at different pyrolysis temperatures. Small variations in the ash contents of the biochar samples were observed compared to FWS.

4.8.2. Heating values of biochar

HHV and LHV of the biochar samples collected at the end of each run were calculated by Dulong equation (Eq. 3.1) and Oasmaa equation (Eq. 3.2). Heating values were also determined experimentally by using bomb calorimeter and the results are presented in the Table 4.25.

Table 4.25: Heating values of biochar samples obtained under the microwave power of 450 W

Power (W)	**Operating Parameters**			**Higher heating values by Dulong formula**	**Lower heating values by Oasmaa formula**	**Higher heating values by Bomb calorimeter**
	Temperature (ºC)	**Time (min)**	**Flow rate (mL min^{-1})**	**(HHV- MJ kg^{-1})**	**(LHV- MJ kg^{-1})**	**(HHV-MJ kg^{-1})**
450	350	25	40	24.86	23.27	28.57
		25	60	24.65	23.08	28.34
		35	40	24.88	23.28	28.61
		35	60	24.61	23.03	28.30
	400	30	50	27.79	26.21	33.35
	400	39	50	27.80	26.21	33.36
	400	30	34	24.77	23.19	28.48
	400	22	50	24.59	23.01	28.27
	400	30	67	27.85	26.28	33.42
	450	25	40	24.47	22.86	28.14
		25	60	24.38	22.77	28.03
		35	40	24.33	22.72	27.97
		35	60	24.28	22.68	27.92

HHV as calculated by the bomb calorimeter were higher than that of the Dulong formula values as the latter did not include the dissociation effects. HHV were higher than that of the FWS as a result of reduction of low higher heating value hydrocarbons (Huang et al. 2013). It can be seen from the Table 4.25 that, the nitrogen flow rate of 50 mL min^{-1} resulted in the increased HHV of the biochar compared to the other flow rates. Pyrolysis temperature of 400 ºC and microwave power of 450 W resulted in the increased heating value of 33.35 MJ kg^{-1} at the nitrogen flow rate of 50 mL min^{-1}. This could be due to the loss of fixed carbon at the higher temperature and higher microwave power as well as equilibrium between the heat release rate by the carbon particles and heat carried by the nitrogen at 50 mL min^{-1} (Huang et al. 2013; Mushtaq et al. 2015). Increased pyrolysis temperature with nitrogen flow rate other than 50 mL min^{-1} resulted in the lower heating values. Biochar obtained at the pyrolysis temperature of 400 ºC at a nitrogen flow rate of 50 mL min^{-1} can be used for heating applications due to its higher heating value (Srinivasan, et al. 2015).

4.9. Characterization of bio-oil

Characterization of bio-oil was carried as per ASTM standard methods to know the physicochemical and thermo-chemical properties. Bio-oil samples obtained under the microwave power of 450 W was considered for characterization studies as the pyrolysis was incomplete under the microwave power levels of 225 W, 300 W and 375 W respectively.

4.9.1. Proximate and ultimate analysis of bio-oil.

Bio-oil samples collected at the end of each run under the microwave power of 450 W were analyzed through ASTM standard methods to evaluate the physicochemical and thermochemical properties. Proximate and ultimate analyses of the bio-oils are presented in the Table 4.26 and Table 4.27. Fixed carbon content and VOC in the bio-oil samples were affected by the operating parameters such as pyrolysis temperature, residence time of the sample and nitrogen flow rate. Higher moisture content was observed with all the

Table 4.26: Proximate analysis of bio-oil samples obtained under the microwave power of 450 W

Power (W)	Operating Parameters			Moisture	Volatiles	Fixed carbon
	Temperature (°C)	Time (min.)	Flow rate (mL min^{-1})	(Wt. %)	(Wt. %)	(Wt. %)
450	350	25	40	91.35	6.89	1.76
		25	60	89.44	8.58	1.98
		35	40	90.32	7.95	1.73
		35	60	91.12	7.35	1.53
	400	30	50	84.19	13.53	2.28
	400	39	50	84.20	13.55	2.45
	400	30	34	85.37	12.62	2.01
	400	22	50	85.28	12.35	2.37
	400	30	67	85.18	13.64	1.18
	450	25	40	83.87	14.01	2.12
		25	60	82.98	14.68	2.34
		35	40	83.23	14.12	2.65
		35	60	83.96	13.95	2.09

Table 4.27: Ultimate analysis of bio-oil samples obtained under the microwave power of 450 W

Power (W)	Operating Parameters			Carbon	Hydrogen	Nitrogen	Oxygen (by difference)
	Temperature (°C)	Time (min.)	Flow rate (mL min^{-1})	(%)	(%)	(%)	(%)
450	400	30	50	48.47	7.51	3.70	40.32
	400	39	50	48.57	7.52	3.71	40.20
	400	30	34	45.81	7.36	3.25	44.29
	400	22	50	47.38	7.21	3.19	42.22
	400	30	67	48.52	7.39	3.50	40.59
	450	25	40	45.48	7.22	3.20	44.10
		25	60	45.67	7.27	3.21	43.85
		35	40	45.39	7.20	3.18	44.23
		35	60	45.72	7.25	3.23	43.80

samples and this could be due to the absorption of moisture from the atmosphere as well as evaporation of some of the chemical compounds below 100 ºC. VOCs and fixed carbon content of the bio-oils were less than that of the biochar samples.

Ultimate analysis of the bio-oil samples collected at the end of each test run were carried out at the Indian Institute of Science, Bengaluru, Karnataka, India. Ultimate analysis of the bio-oil samples is presented in the Table 4.27. Elemental analysis of the bio-oil oil samples was carried out on dry basis. Known quantity of all the bio-oil samples were taken in a petry dishes and kept in the hot air oven for one hour by maintaining the temperature at 105 ºC. Nothing was left in the petry dish for the samples collected below 400 ºC. This could be due to more water content as well as highly volatile chemical compounds in the samples. Residue left in the petry dishes above 400 ºC was collected and analyzed for elemental composition. It can be seen from the Table 4.27 that, there is a small variation in the carbon content of the bio-oil from 45.39 to 48.87 % compared with the variation of carbon content of FWS (46.70 to 47.21 %). Small variations in the hydrogen and nitrogen contents were observed with all the bio-oils collected above 400ºC. Hydrogen content varied from 7.20 to 7.511 % compared to FWS (7.22 to 7.28%). Variation in the nitrogen content was observed from 3.18 to 3.70 % compared to FWS (2.45 to 2.98 %). Oxygen content was calculated by difference and varied from 40.319 to 44.23 % compared to FWS (35.64 to 36.92 %). Decrease in the oxygen content was due to the increase in the pyrolysis temperature that resulted in the loss of functional groups (Ferrera-Lorenzo et al. 2014).

4.9.2. Heating values of bio-oil

Bio-oils collected were light brown liquids and phase separation was not observed with the bio-oils during the storage at room temperature. Heating values of the bio-oils were calculated on dry basis. Known quantity of all the bio-oil samples were taken in a petry dishes and kept in the hot air oven for 1 h by maintaining the temperature at 105 ºC. Nothing was left in the petry dish for the samples collected below 400 ºC due to more water content as well as highly volatile chemical compounds in the samples. Residue left in the petry dishes for the samples collected above 400 ºC was used to calculate the heating values. HHV bio-oils were obtained by Dulong equation as given in Eq. 3.1 and LHV were calculated by using the Eq. 3.1 proposed by Oasmaa (Abnisa et al. 2011).

Table 4.28: Heating values of bio-oil samples obtained under the microwave power of 450 W

Power (W)	Operating Parameters			Higher heating values by Dulong formula	Lower heating values by Oasmaa formula	Higher heating values by Bomb calorimeter
	Temperature (°C)	Time (min.)	Flow rate (mL min^{-1})	(HHV-MJ kg^{-1})	(LHV- MJ kg^{-1})	(HHV- MJ kg^{-1})
450	400	30	50	19.95	18.32	23.94
	400	39	50	20.02	18.38	24.02
	400	30	34	18.12	16.52	21.74
	400	22	50	18.81	17.24	22.60
	400	30	67	19.75	18.14	23.69
	450	25	40	17.84	16.27	21.41
		25	60	18.02	16.44	21.62
		35	40	17.76	16.19	21.14
		35	60	18.02	16.44	21.62

Heating values were also determined experimentally by using bomb calorimeter and the results are presented in the Table 4.28. HHV as calculated by the bomb calorimeter were higher than that of the Dulong formula values as the latter did not include the dissociation effects. HHV, LHV and heating values of the bio-oils as determined by the bomb calorimeter were close to that of the FWS. This was mainly due to the loss of some higher heating value hydrocarbons in the FWS (Huang et al. 2013). Nitrogen flow rate of 50 mL min^{-1} resulted in the increased heating values compared with the other flow rates and pyrolysis temperatures. Compared to the heating value of gasoline (42 MJ kg^{-1}), the heating value of the bio-oil was around 24 MJ kg^{-1} at the nitrogen flow rate of 50 mL min^{-1} (Lei et al. 2011).

4.9.3. Physical properties of bio-oil

Physical properties of the bio-oils are depicted in the Table 4.29. The pH value of the bio-oil was calculated by using the digital pH meter available at the National Institute of Technology, Karnataka Surathkal, India. The pH value of the bio-oils was 4.5 irrespective of the range of operating parameters studied. The pH value of the bio-oils was in agreement with the literature reported values of most of the biomass feed stock materials used in the microwave assisted pyrolysis as well conventional pyrolysis. Acidic nature of the bio-oil makes its inability to compare with the Ph value of the commercially available diesel fuel (Aziz et al. 2013; Liu et al. 2014).

Table 4.29: Physical properties of bio-oil samples obtained under the microwave power of 450 W

Power (W)	Operating Parameters			pH	Density	Viscosity	Water content (Carl Fischer)
	Temperature (°C)	**Time (min.)**	**Flow rate (mL min^{-1})**		**(kg m^{-3})**	**(cSt)**	**(Wt. %)**
450	350	25	40	4.5	1022.69	0.47	27.53
		25	60	4.5	1027.99	0.49	31.73
		35	40	4.5	1022.92	0.51	35.79
		35	60	4.5	1028.99	0.53	37.63
	400	30	50	4.5	1046.36	1.16	50.12
	400	39	50	4.5	1046.48	1.16	50.52
	400	30	34	4.5	1040.90	0.79	42.78
	400	22	50	4.5	1045.24	0.81	37.87
	400	30	67	4.5	1046.61	0.83	47.63
	450	25	40	4.5	1030.36	0.84	45.32
		25	60	4.5	1032.88	0.87	46.20
		35	40	4.5	1030.45	0.86	45.65
		35	60	4.5	1032.97	0.87	46.75

Density of the bio-oils was affected by the operating parameters like temperature, residence time and nitrogen flow rate. Among the operating parameters, nitrogen flow rate of 50 mL min^{-1} resulted in the higher density of 1046 kg m^{-3} compared to other nitrogen flow rates at the operating power of 450 W. Densities of the bio-oils were similar to those obtained with other biomass feed stocks (Abnisa et al., 2011; Bartoli et al., 2016; Borges e al., 2014).

Viscosity of the bio-oils was calculated as per ASTM standard methods D 445 and D2515by using Cannon-Fenske viscometer at a room temperature of 30 ºC. Similar to the density of bio-oils, viscosity was also affected by the operating parameters of pyrolysis. Kinematic viscosity of 1.16 cSt was observed with the bio-oil obtained at an operating temperature of 400 ºC, time 30 min. nitrogen flow rate of 50 mL min^{-1} with a microwave of 450 W. Higher water content was responsible for the low viscosity of the bio-oils. Viscosity of bio-oils obtained was similar to the other biomass feed stocks reported in the literature (Salema and Ani, 2011).

Water content of the bio-oil was measured by using Carl-Fischer 899 Coulometer from Metrohm, available at National Institute of Technology, Karnataka Surathkal. Approximately 7-9 mg of bio-oil was injected in to the flask through titration cell. Instrument beeps one time after the completion of titration and water content of the bio-oil was displayed in parts per million (ppm) on the display panel. Variation in the bio-oil water content, as shown in Table 4.29, was observed with the operating parameters of the pyrolysis process. Water content of the bio-oils were similar to the other biomass feed stocks reported in the literature (Abnisa et al. 2011; Borges et al. 2014).

4.9.4. FT-IR analysis of bio-oil

FT-IR spectra of the bio-oil derived from microwave assisted pyrolysis of food waste was carried out by using a FT-IR analyzer (Brucker Alpha) available at National Institute of Technology, Karnataka Surathkal, India and presented in the Fig. 4.38. FT-IR spectra of the bio-oil contains two regions namely finger print region (unique patterns and difficult to assign all the absorption bands) between 1450 and 600 cm^{-1} and group frequency region (stretching of diatomic units) between 4000 and 1450 cm^{-1}. The O-H stretching vibrations between 3200 and 3500 cm^{-1} shows the presence of alcohols, phenols and is a very intense and broad band. The O-H bend of carboxylic acid was evidenced at 923.62 cm^{-1}(910 to 950 cm^{-1}).

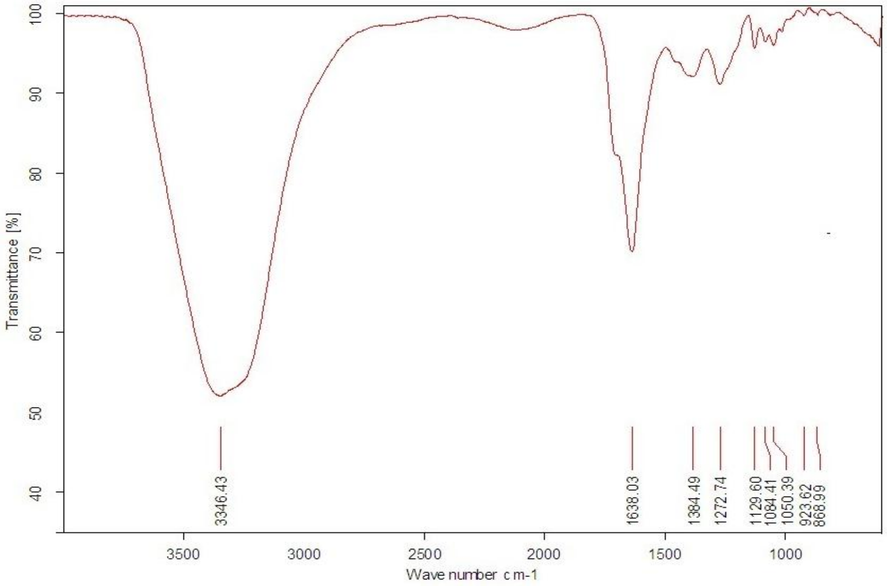


Fig. 4.34: FT-IR spectra of bio-oil derived from food waste at 450 W

The C-O stretch of alcohols was observed in the region from 1050 to 1260cm^{-1}. Three such regions of C-O stretches were observed at 1050.39 cm^{-1}, 1084.41 cm^{-1}, and 1129.60 cm^{-1}respectively. The C-O stretches of esters were observed between 1000 cm^{-1}and 1300 cm^{-1}. Four such regions of C-O stretches were observed at 1050.39 cm^{-1}, 1084.41 cm^{-1}, 1129.60 cm^{-1} and 1272.74 cm^{-1} respectively. The C-C stretching vibrations between1640 and 1680 cm^{-1}shows the presence of alkenes. Strongest bands of alkenes are belonging to the carbon – hydrogen bending vibrations of the =C–H group. These bands were observed in the fingerprint region from 650 to 1000 cm^{-1} and were observed at 868.99 cm^{-1}and 923.62 cm^{-1}. Week bands, commonly observed in most of the aromatic compounds, in the region from 1000 to 250 cm^{-1} are due to C-H in-plane bending. Out of plane or “oop” band that points out the difference between aromatics and organic compounds without an aromatic ring was noticed at 868.99 cm^{-1} which is normally observed between 675 cm^{-1} and 900 cm^{-1}. Similar to the other organic compounds a C-H methyl rock stretching vibration was observed at 1384.49 cm^{-1}. The N-H stretching vibrations between 3300 and 3400 cm^{-1} indicated the presence of weak secondary amines. The N-H bending vibration of primary amines was observed between 1580 cm^{-1} and 1650 cm^{-1}. The C-N stretches of aromatic amines (1272.74 cm^{-1}) were observed in the region from 1250 cm^{-1}to 1335 cm$^{-1,}$ whereas, aliphatic amines (1084.41 cm^{-1} and 1129.60 cm^{-1}) were observed in the region between 1020 cm^{-1} and 1250 cm^{-1} respectively. Another strong broad band representing the primary and secondary amines is N-H wag band (665 to 910 cm^{-1}) observed at 868.99 cm^{-1}. The N-O symmetric stretching vibration of nitroalkanes was observed at 1384.49 cm^{-1}which normally observed at 1365 cm^{-1}.

4.9.5. GC-MS analysis of bio-oil

Analysis of bio-oil using GC-MS was used find out the different types of chemical compounds present in the bio-oil based on the peaks area percentage (Ferrera-Lorenzo et al.,2014). Bio-oil with a maximum yield of 30.24 wt. % obtained at 400 ºC with a microwave power of 450 W, 30 min. operating time and nitrogen flow of 50 mLmin^{-1} was selected for GC-MS analysis.

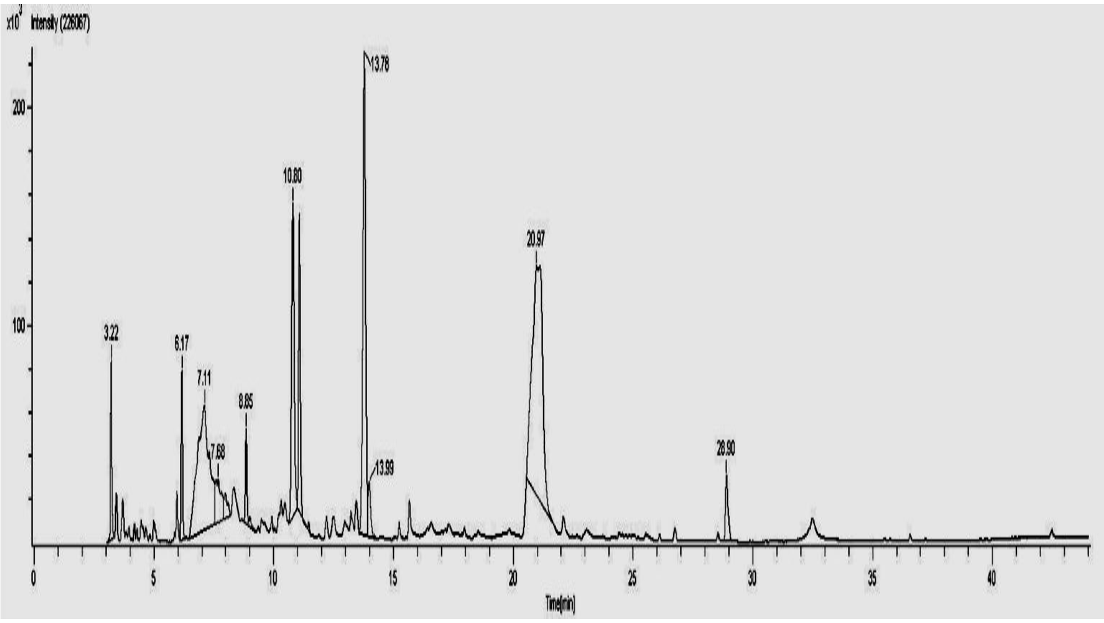
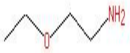
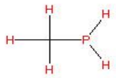
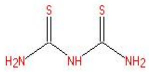
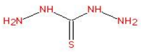
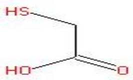
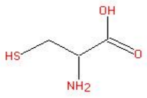
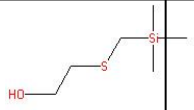
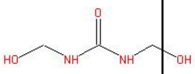


Fig. 4.35: GC-MS analysis of bio-oil obtained under a microwave power of 450 W

Table 4.30: Major identified chemical compounds of bio-oil by GC-MS

Sl. No	Retention time (min)	Chemical compounds	Molecular formula	Molecular weight	Structure	Area (%)
1	3.2	2-Pyrrolidinone	C_4H_7NO	85		7.63
2	6.18	2-Ethoxyethylamine	$C_4H_{11}NO$	89		18.75
3	7.10	Phosphine, methyl-	CH_5P	48		20.80
4	10.78	Propane, 2-fluoro-	C_3H_7F	62		9.27
5	11.07	Thioimidodicarbonic diamide	$C_2H_5N_3S_2$	135		5.58
6	12.20	Carbonothioicdihydrazide	CH_6N_4S	106		10.57
7	12.49	Ethanamine, 2-methoxy-	C_3H_9NO	75		9.37
8	13.79	Acetic acid, mercapto-	$C_2H_4O_2S$	92		7.79
9	14.00	L-Cysteine	$C_3H_7NO_2S$	121		5.05
10	28.91	(2-Hydroxyethyl) trimethylsilyl methyl sulfide	$C_6H_{16}OSSi$	164		3.03
11	32.5	1,3-Bis(2-Hydroxymethyl)urea	$C_3H_8N_2O_3$	120		2.15
Total area = 469.2						99.99

GC-MS analysis of bio-oil was carried out at the Sophisticated Instrument Analysis Facility (SAIF), Indian Institute of Technology Bombay, Powai, Mumbai (JMS-T100GCV). GC-MS analysis of bio-oil is shown in the Fig. 4.35.

Chemical compounds having molecular masses above 400 µ are normally not detected by the GC-MS analysis (Açıkalın et al. 2012). Large numbers of other chemical compounds were present in the bio-oil but, not identified by the GC-MS analysis due to their low peak areas (below 10%) compared to other chemical compounds (Abnisa et al., 2011). GC-MS analysis identified 11 major compounds out of more than 500 compounds those were present in the bio-oil. The major identified chemical compounds of the bio-oil along with their molecular formula, molecular weight, structure and peak area (%) are listed in the Table 4.30. Number of studies from the literature analyzed the bio-oil obtained by conventional pyrolysis as well as microwave assisted pyrolysis of various types of biomass feed stocks but the GC-MS analysis of food waste either by microwave assisted pyrolysis or conventional pyrolysis was rarely found in the literature (Abnisa et al. 2011; Du et al. 2011; Aziz et al. 2013; Ferrera-Lorenzo et al.2014).

Compounds such as oxygenated and non-oxygenated compounds, nitrogenated compounds and other compounds with phosphine, propane, sulfide and urea were identified by the GC-MS analysis. Identified chemical compounds were having the carbon distribution in the range between C and C_6 with molecular weight varying from 48 to 164. It can be seen from the Table4.30 that, the phosphine, methyl- was the compound with lower molecular weight of 48 with largest peak area of 97.6%, while (2-hydroxyethyl) trimethylsilyl methyl sulfide was having the higher molecular weight of 164 with the peak area of 14.2%. Among the identified compounds, the amines group was the largest compared to the other chemical compounds. Minimum peak area of 10.1% was observed with 1,3-bis(2-hydroxymethyl) urea with a retention time of 32.5 min. and molecular weight 120. Oxygenated compounds such as 2-pyrrolidinone, 2-ethoxyethylamine, ethanamine, 2-methoxy-, acetic acid, mercapto-, l-cysteine, (2-hydroxyethyl) trimethylsilyl methyl sulfide and 1,3-bis(2-hydroxymethyl)urea were dominant in the bio-oil compared to non-oxygenated compounds such as phosphine, methyl-, propane, 2-fluoro-, thioimidodicarbonicdiamide and carbonothioicdihydrazide. Bio-oil cannot be used as fuel due to presence of nitrogenous and sulpher compounds along with the more water content (50 wt %) and need to be upgraded before its use as a fuel. Presence of alcohols was detected in the FT-IR analysis, but not detected by the GC-MS analysis. This could be due to the thermal instability of the bio-oil (Abnisa et al., 2011) and storage of bio-oil till the GC-MS analysis. The sulpher which was not detected during the elemental analysis, probably due to the very low percentage, was detected by GC-MS analysis and appeared in the bio-oil as (2-hydroxyethyl) trimethylsilyl methyl sulfide with a peak area of 14.2%.

CHAPTER 5

CONCLUSIONS

In the current day scenario every country is regarded as a developed country based on its availability of energy resources, conversion of energy source in to useful form by cheaper methods, its per capita consumption and an environmental friendly management of wastes. The need for energy is increasing globally due to the rapid increase in the world's population and development of service, commercial and industrial sectors, while the current energy resources on the planet are decreasing. To avoid the 'energy blackmail', it has become mandatory for the developing countries to harness alternate energy resources and develop cheaper conversion technologies. In this regard biomass and biowastes have been recognized as a major world renewable energy source to supplement declining fossil fuel resources. Thermochemical conversion of biomass and biowastes is one of the most common and convenient routes for conversion into energy. This includes carbonization, liquefaction, gasification and combustion. Pyrolysis is the most popular thermal conversion process among the various processes of energy production from biomass.

Globally around 1.3 billion tons of food wasted per year which is believed to be one third of the food produced for human consumption. Mangalore is situated on the west coast of the Indian peninsula covering an area of 132.45 sq-km and one of the fast growing cities of India in the commercial, industrial as well educational sectors. The city is generating approximately around 312 tons of MSW per day of which 40% is the food waste (125 tons per day). At present this MSW is land filled and not thought as an energy source. The current research work revealed that, this land filled food waste caused serious environmental and health related problems. A detailed explanation and conclusion on the conversion of food waste generated in the Mangalore city in to biofuels with the assistance of microwaves has been mentioned in the following paragraphs.

Vegetarian as well as non-vegetarian FWS were collected periodically from the different parts of the Mangalore city like NITK campus hostels and hotels. This food waste represents the common food waste generated in the Mangalore city. The homogeneous mixture of FWS was dried in an oven for 24 h at 105 ºC. The dried samples were pulverized to pass through an ASTM-18 standard mesh to have pulverized FWP having size less than 1003 microns (1mm). Characterization of FWP was carried out as per ASTM standard methods to know proximate, ultimate and heating values of FWP. Characterization study revealed that, the characteristics of individual FWS were similar to that of the randomly mixed homogeneous FWS.

Pyrolysis of pulverized food waste particles (FWP) was carried out at different microwave power levels of 150, 225, 300, 375 and 450 W respectively. Pyrolysis of FWP using microwave power level of 450 W resulted in the above 450 ºC which was the required temperature to carry out the pyrolysis, as the complete pyrolysis of FWP was not possible below 400 ºC. Operating ranges for the pyrolysis temperature (350 to 450 ºC), residence time (25 to 35 min) and nitrogen flow rate (40 to 60 mL min^{-1}) to carry out the pyrolysis of FWP were determined by TGA and preliminary pyrolysis experiments at 450 W.

Optimum conditions to maximize or minimize the pyrolysis product yields were determined by conducting 20 experiments in order to validate RSM in central composite design (CCD). Combined effects of the operating variables namely pyrolysis temperature, residence time and nitrogen flow rate were resulted in the maximum bio-oil yield and minimum char yield at 450 W. The significant findings from the microwave assisted pyrolysis of food waste generated in the Mangalore city are as mentioned below.

- Characterization of the FWS revealed that, though the food waste (biomass) exists in different physical forms, chemically they are similar to each other.
- Maximum degradation of FWP, as per TGA analysis, was observed between 300 ºC and 500 ºC.
- The operating ranges to design the experiments by RSM were 350 to 450 ºC for temperature, 25 to 35 min. for residence time and 40 to 60 mL min^{-1} for nitrogen flow rate.

- Bio-oil yield of 30.24 wt. %, biochar yield of 60.03 wt. % and gas yield of 9.73 wt. % were obtained under the optimum pyrolysis conditions.
- The regression model with 95% confidence level resulted in the high value of R^2 = 95.4% with R^2 adjusted = 91.2% indicated a very good or excellent fit of the data to the bio-oil model.
- The regression model with high value of R^2 = 92.9% with R^2 adjusted = 86.4% indicated a very good or excellent fit of the data to the biochar model.
- The regression model with high value of R^2 = 90.3% with R^2 adjusted = 81.60% indicated a very good or excellent fit of the data to the fixed carbon content model.
- The predicted values of bio-oil, biochar and fixed carbon contents were 0.02 wt. %, 0.05 wt. % and 0.03 wt. % less than the experimental values respectively.
- Main functional groups as detected by the Fourier transform infrared (FTIR) analysis are alcohols, alkenes, aromatic compounds, primary and secondary amines, carboxylic acid, esters and phenols.
- Compounds such as oxygenated and non-oxygenated compounds, nitrogenated compounds and other compounds such as phosphine, methyl-, propane, 2-fluoro-, (2-hydroxyethyl) trimethylsilyl methyl sulfide, and 1,3-bis(2-hydroxymethyl) urea were identified by the GC-MS analysis.
- The sulfur which was not detected during the elemental analysis, probably due to the very low percentage, was detected by GC-MS analysis and appeared in the bio-oil as (2-hydroxyethyl) trimethylsilyl methyl sulfide.
- Bio-oil obtained in this study cannot be used as a bio-fuel, as it contains more water as well as nitrogenated compounds. However, bio-oil obtained can be upgraded and blended with diesel to use as a fuel through further investigation.
- HHV of the biochar as calculated by the bomb calorimeter (33.35 $MJkg^{-1}$) was higher than that of the Dulong formula (27.79 $MJkg^{-1}$) value as the latter did not include the dissociation effects.

- Characterization of gas fraction obtained in this study was not carried out due to its very low percentage.

LIMITATIONS AND SCOPE FOR FUTURE WORK

An efficient thermochemical process to produce bio-oil, syngas and bio-char is the MAP, which requires lesser time to dispose the biowastes compared to other pyrolysis methods. Pyrolysis of FWP was carried out at the laboratory conditions using a bench scale microwave reactor, which is one of the limitations of the current study. Moreover, size and quantity of the FWP used in each experimental run were less than 1 mm and 100 grams, due to small capacity of the quartz flask (250 mL) used. Hence, the future research work focusing on the following aspects may be under taken.

- Design and development of larger capacity microwave reactor to dispose the food waste (on as received basis as well as other biowastes also) on continuous basis.
- Effects of FWP size on pyrolysis products.
- Co-pyrolysis by blending food waste with other biowastes.
- Catalyst based pyrolysis to obtain enhanced biofuel yield.
- Basic chemistry of conversion of food waste in to biofuels.
- Effects of food waste chemical composition (such as lignocelluloses, starch, protein, lipids, fat, fiber etc.) on biofuels.
- Food waste biochar to remove contaminants by adsorption studies.
- Chemical reaction kinetics, exergy analysis and cost benefit analysis.
- Recovery of valuable chemicals from the bio-oil, as an example a variety of pharmaceutical drugs are derivatives of 2-pyrrolidinone, using suitable separation technology.

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LIST OF PUBLICATIONS:

1. Kadlimatti H.M., Raj Mohan B. and Saidutta M.B. “Physicochemical and thermochemical characterization of food waste – A potential biomass resource for biofuels”. Proceedings of the international conference on energy and environment: Global challenges (ICEE – 2018) held at National Institute of Technology Calicut during March 09 - 10. This paper was adjudged as “Best research paper” of the ICEE 2018.

2. Kadlimatti H.M., Raj Mohan B. and Saidutta M.B. “Bio-oil from Microwave assisted Pyrolysis of Food Waste-Optimization using Response Surface Methodology”. *Biomass and Bioenergy* (2019), 123, 25-33.

3. Kadlimatti H.M., Raj Mohan B. and Saidutta M.B. “Microwave assisted Pyrolysis of Food Waste-Optimization of Fixed Carbon content using Response Surface Methodology”. *Biofuels*, https://doi.org/10.1080/17597269.2019.1573609

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CERTIFICATE

This is to certify that ***Ms./Dr. KADLIMATTI H.M*** *from* ***Basaveshwar Engineering College, Bagalkot, Karnataka*** *have been awarded the* ***BEST PAPER AWARD*** *for the paper entitled* ***Physicochemical and Thermochemical Characterization of Food Waste- A Potential Biomass Resource for Biofuels*** *at the* ***"First International Conference on Energy & Environment: Global Challenges (ICEE 2018)"*** *NIT Calicut, Kerala, India during March 9 -10, 2018.*

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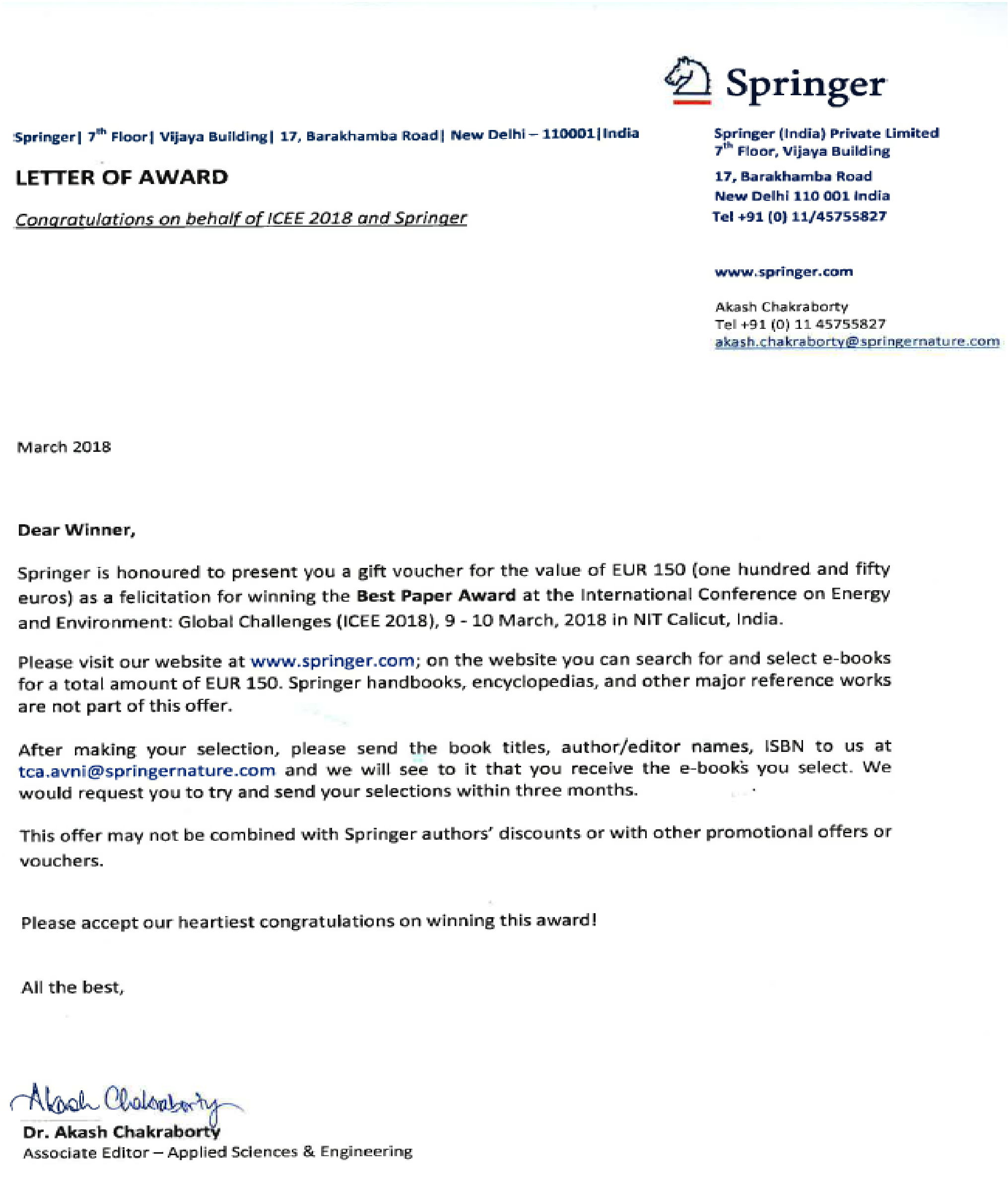

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Subjects Taught at Basaveshwar Engineering College (Autonomous), Bagalkot.

1. Heat and Mass transfer
2. Power Plant Engineering
3. Fluid Machinery
4. Applied Thermodynamics
5. Fluid mechanics
6. Elements of Mechanical Engineering

List of publications:

International Journal – 04, International Conferences –03, National conferences– 03

(A) International Journal (s)

1. **H. M. Kadlimatti,** Raj Mohan B. and Saidutta M.B. “Bio-oil from Microwave assisted Pyrolysis of Food Waste - Optimization using Response Surface Methodology. Biomass and Bioenergy, (2019), 123, 25-33.

2. **H. M. Kadlimatti,** Raj Mohan B. and Saidutta M.B. “Microwave assisted Pyrolysis of Food Waste - Optimization of Fixed carbon content using Response Surface Methodology. Biofuels https://doi.org/10.1080/17597269.2019.1573609.

3. **H. M. Kadlimatti**, Gavish Vastrad, Kiran B. Channi, Sangamesh P. Suliganvi and Vishal Sarikdar. “Safflower Seed Husk Reinforced Plastics (SRP)”. International Journal of Engineering Research in Mechanical and Civil Engineering, Vol 2. Issue 4, April 2017.

4. **H. M. Kadlimatti**, Gangamma S. and Varghese S.K. “generation of Monodisperse Aerosols through Condensation Nuclei control. Transaction of Wessex Institute of Technology, London, UK, on ‘Ecology and Environment’2007, 101,505-511.

(B) International Conference (s)

1.**H. M. Kadlimatti,** Raj Mohan B., and Saidutta M.B. “Physicochemical and Thermochemical Characterization of Food Waste-A Potential Biomass Resource for Biofuels”.Proceedings of the International Conference on “Energy and Environment: Global Challenges’, NIT Calicut, Kerala, 9-10 March 2018. \

2. **H. M. Kadlimatti**, Gavish Vastrad, Kiran B. Channi, Sangamesh P. Suliganvi and Vishal Sarikdar. “Safflower Seed Husk Reinforced Plastics (SRP)”. Proceedings of the International Conference on Advances in Mechanical Engineering Sciences, 21-22 April 2017, P.E.S. Engineering College Mandya, Karnataka, India.

3. **H. M. Kadlimatti,** Gangamma S and Varghese S.K. generation of Monodisperse Aerosols through Condensation Nuclei control. Proceedings of the 15th International

Conference on Modelling, Monitoring and Management of Air Pollution, 23-25 April 2007, Algarve, Portugal, Europe.

(C) National Conference (s)

1. **H. M. Kadlimatti,** Gangamma S and Varghese S.K. Flow Controlled Condensation Aerosols of Dioctylpathalate (DOP). Proceeding of the National Conference on Recent Advances in Mechanical and Materials Enginerring, 30-31 October 2014, Basavakalyan Engineering College, Basavakalyn, Karnataka,India.
2. **H. M. Kadlimatti,** Gangamma S and Varghese S.K. "Ärosol Generator". Proccedings of the National Conference on Environmental Conservation (NCEC-2006) 1-3 September 2006, BITS Pilani, Rajasthan, India.
3. **H. M. Kadlimatti,** Gangamma S and Varghese S.K. "Design and Testing of Condensation Aerosol Generator-Preliminary Results". Proceedings of the National Conference on Synergic Solutions for Sustainable Development, 28-30 December 2005, NITK Surathkal.

Awards:

1. Recipient of **First Rank** at M. Tech (Industrial Pollution Control) degree by Padmabhusan Dr. G. Madhavan Nair, Chairman, ISRO, Govt. of India at the 4th Convocation of NITK Surathkal held on 24-02-2007.
2. Appreciation letter from the Administrative officer B.V.V. Sangha Bagalkot on account of obtaining First Rank at M.Tech. degree
3. Certificate of Appreciation by Prof. Ashok Jhunjhunwala Chairman, QEEE Committee Indian Institute of Technology Madras, Chennai for being the part of QEEE programme, A MHRD initiative.
4. Certificate of Appreciation by B.E.C. Bagalkot for serving as a Resourceful facilitator during HRD training programme for First Year B.E. students.
5. Certificate of Appreciation as a tax payer in "Bronze" category in recognition of the contribution of taxes towards the building of India by Central Board of Taxes, Ministry of Finance, Government of India.

6. Recipient of “**Letter of Award**” by Dr. Akash Chakraborty, Associate Editor- Applied Sciences & Engineering, Springer (India) Pvt. Ltd. New-Delhi for winning “**Best Paper”** at the International Conference on “Energy and Environment: Global Challenges’ held at NIT Calicut, Kerala during 9-10 March 2018.

Awarded Research Paper(s):

1.Research paper titled “Physicochemical and Thermochemical Characterization of Food Waste-A Potential Biomass Resource for Biofuels” has been adjudged as “**Best Research Paper”** of the International Conference on “Energy and Environment: Global Challenges’ held at NIT Calicut, Kerala during 9-10 March 2018.

Awarded Projects (UG):

1. Project titled “Mechanical Behavior of Wood Plastic Composites” adjudged as **‘Outstanding Projects of the year 2016and selected for the Best Project Award**’ at the 39th series State level SPP at Vijayapur jointly organized by KSCST IISc Campus Bengaluru and BLDECET Vijayapur during 19-08-2016 to 20-08-2016.
2. Project titled “Mechanical Behavior of Wood Plastic Composites” awarded with the ‘**Third Prize’** at the 12th series Shrusti State level Project seminar cum exhibition held at CMR Institute of Technology Bangalore during 6-8 May 2016.

Administrative Responsibilities:

Sl. No.	Nature of work (Chairman, coordinator, member etc.)	Worked for (University, college, etc.)	Year
01	Director, B.E.C. Employees Co-Operative Credit Society	College	1999-2001
02	BEC Autonomous Member, Board of Examinations	Department	2007-2009
03	Coordinator, Department Library	Department	2008-2012
04	Department Coordinator, KSCST Projects	Department	2008
05	Coordinator, BEC Autonomous Valuation Centre	College	2009
06	Coordinator, BEC Autonomous Valuation Centre	College	2014
07	Board of Studies member (BOS)	Department	2018-

Declaration

I hereby declare that the above furnished information by me is true to the best of my knowledge and belief.

Date: 31-05-2019 Sd/-

Place: Surathkal (H.M.Kadlimatti)