A STUDY ON BIOCHAR FOR BIOENERGY AND COMPOSITE APPLICATIONS

A Thesis

Submitted to the University of Prince Edward Island

in Partial Fulfillment of the Requirements for the

Degree of Master of Science

in Sustainable Design Engineering

Faculty of Sustainable Design Engineering

Raj Kumar Dahal

Charlottetown, Prince Edward Island

August 2018

Abstract

This research focus on the production and characterization of the pyrolytic products (biochar, biooil and syngas) for potential bioenergy application, the application of biochar for treating wastewater and application of biochar in glassfibre reinforced polymer (GFRP) composites. The pyrolysis of crambe and meadowfoam oilcakes feedstocks was performed at 450 °C and 550 °C, at a heating rate of 10 °C/min with residence time of 30 mins. About 30-40 percent biochar, 40-50 percent biooil and remaining syngas were obtained. Lower biochar and higher biooil yields were seen when the pyrolysis temperature was increased. The energy value of biochar was in the range of 22-24 MJ/kg, that of biooil was above 35 MJ/kg. Carbon dioxide, Carbon monoxide, alkanes and alkenes were detected in syngas. The turbidity of the biochar treated wastewater was 50 NTU compared to its 1798 NTU initial measurement, and the foul smell was absent.

Biochar from pyrolysis of spruce pellets in a two-stage rotating drum pyrolyzer at 450 °C, 10 °C/min heating rate and 30 mins residence time was crushed to size below 53 µm. Glassfibre reinforced Polymer composites were prepared w/o biochar at 5 percent and 10 percent by weight of the resin. Samples were vacuum infused for curing. The flame test suggested that higher biochar concentration in the composites retarded the flame better. DMA tests showed increased in storage moduli thus stiffness of composites with higher biochar. Reduced loss factor i.e. lower damping was experienced in the same composites.

This signifies the importance of biochar in coal replacement, in wastewater treatment and in diversifying mechanical properties with better flame-retardant quality in composites. More importantly, it is bio-sourced and environmentally friendly.

Acknowledgements

I am indebted to my co-supervisors, Dr. Bishnu Acharya and Dr. Gobinda C. Saha, for having confidence in me to takeover and complete this work. Without their valuable time for guidance, encouragement and a continuous feedback, this scientific work would not have been possible.

I express my hearty appreciation to my committee members Dr. Aitazaz Farooque and Dr. Marya Ahmed for their feedbacks and recommendations. My special thanks go to Dr. Rabin Bissessur for providing working facility in the Chemistry department, lab supervisor Stephen Scully and my colleague Matthew Dunlop for their instruction and assistance in performing the tests.

I would like to show my gratitude to Charles Terrio and Andrew Townshend, Industry Research Assistants and Sandy Doucette, Lab Technician, at Faculty of Sustainable Design Engineering for their continued technical support and for their excellent fabrication work on my setup. I owe my gratitude to my friends Jesse Cameron and Ankita Shrestha for their help and support. At last but not the least, I am grateful to the faculties, friends and families who directly or indirectly have been my strength and support during this research work.

Finally, I acknowledge Nature Crops International for providing feedstock samples and NSERC for the funding support without which this would not have been possible.

Dedicated to

My Parents & Brother.

Table of contents

Abstract ii
Acknowledgements iii
Table of contents v
List of acronyms viii
List of figures xii
List of tables xiv
Chapter 1 1
Introduction 1
- **1.1 Motivation** 2
- **1.2 Objectives** 3
- **1.3 Novelty of this research** 4
- **1.4 Arrangement of thesis** 7

Chapter 2 9
Literature Review 9
- **2.1 Biomass** 9
- **2.2 Biomass as an energy source** 10
- **2.3 Biomass in composites application** 12
  - **2.3.1 Some research examples in composites** 13
  - **2.3.2 Hindrances and probable solutions in composites research** 14
- **2.4 Thermochemical conversion process** 15
  - **2.4.1 Torrefaction** 16
  - **2.4.2 Gasification** 17
  - **2.4.3 Hydrothermal carbonization** 18
  - **2.4.4 Pyrolysis** 19
- **2.5 Pyrolysis system used in this research** 28
- **2.6 Biomass feedstocks for pyrolysis** 28
- **2.7 Application of pyrolytic products** 30
  - **2.7.1 Biochar as an energy source** 31
  - **2.7.2 Biochar for soil amendment** 31
  - **2.7.3 Biochar as a carbon sink** 32
  - **2.7.4 Biochar as a potential filtering agent** 32
  - **2.7.5 Biochar in material applications** 33
  - **2.7.6 Biochar in concrete application** 34

2.7.7 Biochar in nanotube application 35

2.7.8 Biochar as a filler in polymer composites 36

2.8 Chemical and thermal behaviour of biochar-added composites 37

2.9 Morphology and flame retarding character of biochar-added composites 38

2.11 Application of biooil 40

2.12 Application of syngas 41

2.13 Summary 42

Chapter 3 43

Materials and Method 43

3.1 Materials and method for energy application study 43

3.1.1 Feedstock 43

3.1.2 Experimental method for pyrolysis 43

3.1.3 Analytical methods 44

3.2 Materials and method for biocomposite study 48

3.2.1 Feedstock 48

3.2.3 Blend preparation 49

3.2.4 Composites preparation 49

3.2.5 Characterization 51

Chapter 4 54

Results and Discussion 54

4.1 Products yield 54

4.2 Analysis of solid products 55

4.3 Analysis of liquid products 57

4.4 Analysis of gas 58

4.5 Thermal decomposition of oilcakes 59

4.6 Wastewater treatment: Biochar is a potential remedy 61

4.7 Scanning electron microscopy (SEM) analysis 62

4.8 Thermogravimetric analysis of the composites 64

4.9 Dynamic mechanical behaviour of the composites samples 65

4.9.1 Dynamic storage modulus (E’) 66

4.9.2 Loss modulus (E”) 68

4.9.3 Loss Factor (Tan δ) 69

4.10 Flame-retardant property of the composites 70

Chapter 5 72
Conclusions 72
Chapter 6 74
Future Works 74
References: 75
Appendices 83
  Appendix A: Some Physical and chemical properties of feedstocks 83
  Appendix B: Technical Data of Glassfibre 84
  Appendix C: Technical Data of Polymer 88
  Appendix D: Photographs of feedstocks 89
  Appendix E: Photographs of different lab setups used 91
  Appendix F: Photographs of pyrolytic products 93
  Appendix G: Photographs of Composites making process and accessories. 95
  Appendix H: Photographs of tests being performed 97
CURRICULUM VITAE 103

List of acronyms

Abbreviation	**Description**
AC10	Composites with 10 Percent Activated Charcoal
AC5	Composites with 5 Percent Activated Charcoal
Al_2O_3	Aluminum Oxide
ASTM	American Society for Testing Materials
BC10	Composites with 10 Percent Biochar
BC5	Composites with 5 Percent Biochar
BET	Brunauer Emmett Teller
BSE	Backscattered Electron
C	Carbon Composition
C:N	Ratio of Carbon is to Nitrogen
C_2H_4	Ethene Gas
C_2H_6	Ethane Gas
CEC	Cation Exchange Capacity
CH_4	Methane Gas
CO	Carbon Monoxide Gas

CO_2	Carbon Dioxide
DMA	Dynamic Mechanical Analysis
DTG	Differential Thermal Analysis
E’	Dynamic Storage Modulus or Flexural Modulus
E”	Loss Modulus
EIA	Energy Information Association
et al.	And others
FC	Fixed Carbon
GDP	Gross Domestic Product
GFRP	Glassfibre Reinforced Polymer Composites
GHG	Greenhouse Gases
GHV	Gross Heating Value
H	Hydrogen Composition
H_2	Hydrogen Gas
HHV	Higher Heating Value
ID	Identity
IPCC	Intergovernmental Panel on Climate Change

M	Moisture
MAPP	Maleic Anhydride grafted Polypropylene
Mg	Magnesium
N	Nitrogen Composition
N_2	Nitrogen Gas
NHV	Net Heating Value
NTU	Nephelometric Turbidity Units
O	Oxygen Composition
O_2	Oxygen Gas
OECD	Organization for Economic Cooperation and Development
P	Phosphorus
PHRR	Peak Heat Release Rate
PLA	Poly Lactic Acid
PP	Poly Propylene
R+GF	Resin and Glassfibre
Rpm	Revolution Per Minute
S	Sulphur

SD	Standard Deviation
SE	Secondary Electron
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TG	Thermogravimetric
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
TTI	Time to Ignition
UL	Underwriters Laboratories
UN	United Nations
US	United states
VM	Volatile Matter
WEC	World Energy Council
Wt.	Weight
δ	Phase Angle

List of figures

Figure 1.1 A brief research outline 2

Figure 1.2 Schematic diagram depicting circular bioeconomy 5

Figure 1.3 Flowchart indicating arrangement and presentation of thesis content 7

Figure 2.1 Global energy consumption scenario in 2013 10

Figure 2.2 Primary energy supply of biomass resources globally in 2013 10

Figure 2.3 World energy consumption by energy source (1990-2040) 11

Figure 2.4 Schematic diagram of torrefaction process 16

Figure 2.5 Schematic diagram of a downdraft gasifier 17

Figure 2.6 Schematic diagram of an autoclave reactor for hydrolysis of palm shell........ 18

Figure 2.7 System setup for pyrolysis process.. 19

Figure 2.8 Pyrolysis process and pyrolytic products flowchart 20

Figure 2.9 Bubbling fluidized bed & circulating fluidized bed reactors 27

Figure 3.1 Schematic diagram of double-stage pyrolysis working principle 48

Figure 3.2 Schematic diagram of the composite preparation technique 50

Figure 3.3 Specimen of GFRP without biochar (left), with 10% biochar (middle) & 5% biochar (right) 50

Figure 3.4 TA Q800 in action for three-point bending test (left) & schematic diagram of the three-point bending set-up (right) 51

Figure 3.5 Schematic of vertical burning test for 94V and 94VTM classifications 52

Figure 4.1 Van Krevelen diagram (H:C vs. O:C ratio) of the solid samples 56

Figure 4.2 TGA of crambe and meadowfoam under air and nitrogen 60

Figure 4.3 Solid concentration in water sample before and after biochar treatment 61

Figure 4.4 (a) SEM images of AC10 (100 µm, 50 µm, 20 µm and 10 µm respectively). 62

Figure 4.4 (b) SEM images of AC5 (100 µm, 50 µm, 20 µm and 10 µm respectively)... 62

Figure 4.4 (c) SEM images of BC5 (100 µm, 50 µm, 20 µm and 10 µm respectively)... 63

Figure 4.4 (d) SEM images of BC10 (100 µm, 50 µm, 20 µm and 10 µm respectively). 63

Figure 4.4 (e) SEM images of GFRP (100 µm, 50 µm, 20 µm and 10 µm respectively) 63

Figure 4.5 TGA thermal decomposition of the composites with temperature 66

Figure 4.6 TGA (DTG) results of various composites 66

Figure 4.7 Change in storage modulus of composites as a function of temperature 67

Figure 4.8 Change in loss modulus of composites as a function of temperature 68

Figure 4.9 Loss factor of various composites as a function of temperature 69

List of tables

Table 2.1 Classification of pyrolysis method 23

Table 2.2 Biomass feedstocks for bioenergy and biomaterials 28

Table 2.3 Composition used for composites preparation (a) 36

Table 2.4 Composition used for composites preparation (b) 37

Table 2.5 Summary of previous works in biocomposites 40

Table 3.1 Proximate and ultimate analysis of raw crambe and meadowfoam oilcakes ... 43

Table 3.2 Different samples with altered biochar compositions...................................... 50

Table 3.3 Criteria conditions for vertical burning tests 53

Table 4.1 Products yield from pyrolysis at 450 °C and 550 °C 54

Table 4.2 Analytical results of the solid products from oilcakes pyrolysis 55

Table 4.3 Ultimate analysis of biooils from pyrolysis of oilcakes in percentage 57

Table 4.4 Composition of gas collected from pyrolysis of oilcakes in percentage 59

Table 4.5 UL94 with 10 seconds flame exposure 71

Table 4.6 Modified UL94 test with 5 seconds flame exposure 71

Chapter 1

Introduction

Bioenergy contributes to 10% of the global energy supply (World Energy Council, World Energy Resources 2016) and biomass could be a major renewable resource for transition from fossil fuel to renewable future along with other renewable technologies like wind, solar and hydro [1]. Biomass can be processed to produce carbon rich energy dense solid fuel, which could replace coal. It can also be converted into biooil or gas for replacing petroleum resources for energy application [2]. Biomass comprises of all living and dead plants and animals found in land and water. Another benefit of biomass is its abundance availability around the globe unlike other non-renewable natural resources. Currently, raw and unprocessed biomasses like lumber, firewood, hay, sawdust, woodchips, bark, etc. are being used for space heating and power application. The processed plant products like ply, beams, wooden planks, etc. are used for material application. However, use of biomass as an option to reduce fossil fuel consumption and impact on our climate through various bioconversion processes for producing chemicals and materials has received greater attention in the last decade. The bioconversion processes include different thermo-chemical conversion process like pyrolysis, gasification and liquefaction where biological conversion process is digestion of biomass anaerobically to produce biogas or through fermentation process to produce alcohol in general. Thermochemical conversion process is a technique to convert biomass into energy dense products like briquette though briquetting, torrefied biomass through torrefaction, syngas through gasification and separate energy sources (solid-biochar, liquid-biooil and gaseous-syngas) through pyrolysis with the application of heat [3, 4]. The present study focuses on pyrolysis process for the conversion of biomass into pyrolytic products for bioenergy and material application. Biochar from pyrolysis has also been investigated as a possible wastewater treatment agent. The research work presented in this thesis investigates the pyrolysis of agricultural residue (meadowfoam and crambe oilcakes) at 450 °C and 550 °C and forestry waste (spruce pellet) at 450 °C. The research focuses on characteristics of pyrolytic products and their potential applications in the energy and biocomposites fields.

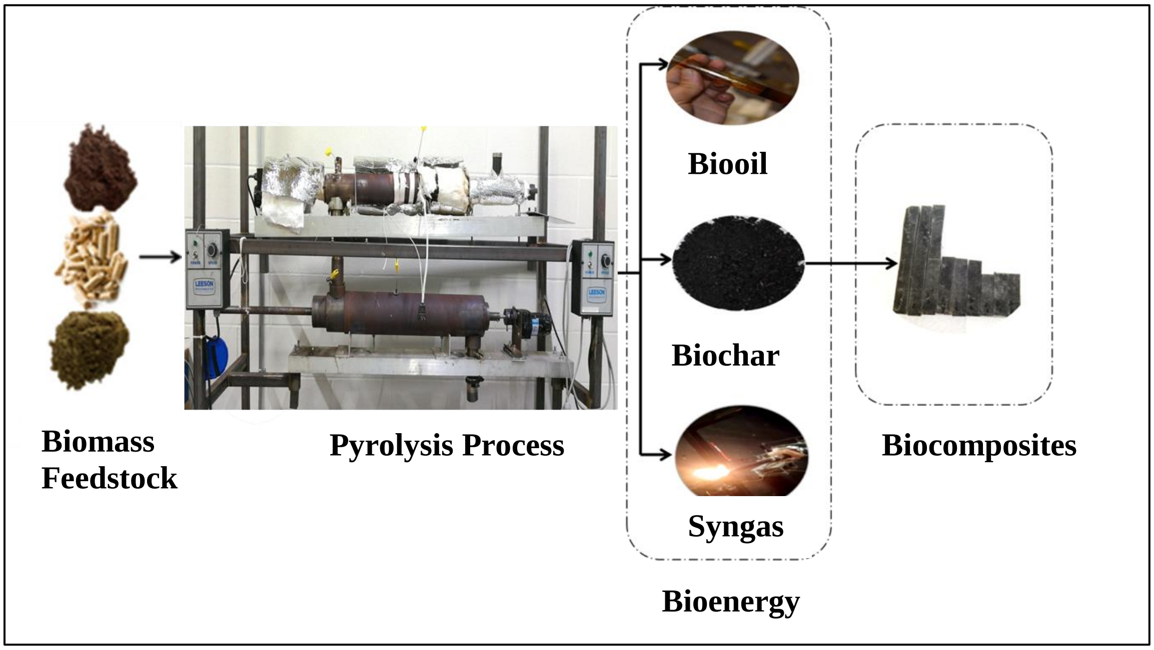


Figure 1.1: A brief research outline

1.1 Motivation

Fossil fuel in the form of natural gas, coal and oil is being extensively used for power generation and material production, emitting enormous amount of greenhouse gases impacting climate with many changes that the world today is experiencing today, such as frequent heat waves and infrequent rainfall, sea level rise and melting of icecaps. This rising global problem can only be solved by means of renewable energy sources like wind, solar and hydro. While these sources can not be ignored, there is hugely available biomass which can help address this problem to some extent. The energy potential of biomass to mitigate this problem is the motivation to study biomass to bioenergy.

Similarly, more than 30% polymer is produced worldwide annually for composites application and so is more than 53 million tons of additives fillers. These raw materials in composites world are fossil fuel sourced which could potentially be replaced with biomass sourced fillers in composites. The improved material properties including flexural strength, and stiffness and better flame-retardant property along with the ease of machinability will result in their stability in new composites material world through interlinkage, adaptation and producibility with better economic value. This is the motivation for second part of research work for studying biochar for biocomposite application.

1.2 Objectives

The main objective of the research is to investigate the pyrolysis of biomass and application of biochar for energy and composite application. The specific objectives are followings:

1) Examine the effect of operating parameter on the pyrolysis of oilcakes.
2) Investigate the application of biochar for energy and wastewater treatment.
3) Investigate the effect of biochar on the mechanical properties of composite material.
4) Examine the effect of biochar on the fire-retardant property of composite material.

1.3 Novelty of this research

Although there have been reports of many oilcakes used in pyrolysis system, crambe and meadowfoam oilcakes are the new feedstocks in thermochemical conversion world. Huge quantity of processed residues in oil industries generated as by-product after oil extraction from the seeds; also known as oilcake or meal; cause adverse environmental effects as these residues contain high concentration of fat, oil, grease, suspended solids, and dissolved solids [5]. Among many agro-processing wastes, Canada exports large amount of Oilcakes. Oilcakes with low glucosinolates like that from Canola seeds are widely used as feed for animals. However, crambe and meadowfoam oilcakes, with high glucosinolates, are unsuitable to be used as animal feed [6] as it breaks down in digestive systems and may cause liver and kidney damage with appetite depression. Thus, it is imperative to find solutions for appropriate management of oil cakes.

Circular bioeconomy (figure 1.2) is another novel idea this research carries. Agriculture and agri-food processing are major industry in the province of Prince Edward Island contributing 8.9% of the province’s total GDP with 2045 farm operators in 2012[7]. However, the agro-processing uses large amount of fresh water and generates equal amount of unwanted waste water. This has become a challenge to the management system. These wastes contain organic matter and nutrients, which if recovered could become a good soil fertilizer. Biochar from pyrolysis process utilizing waste biomass from another industry can be used to solve this problem.

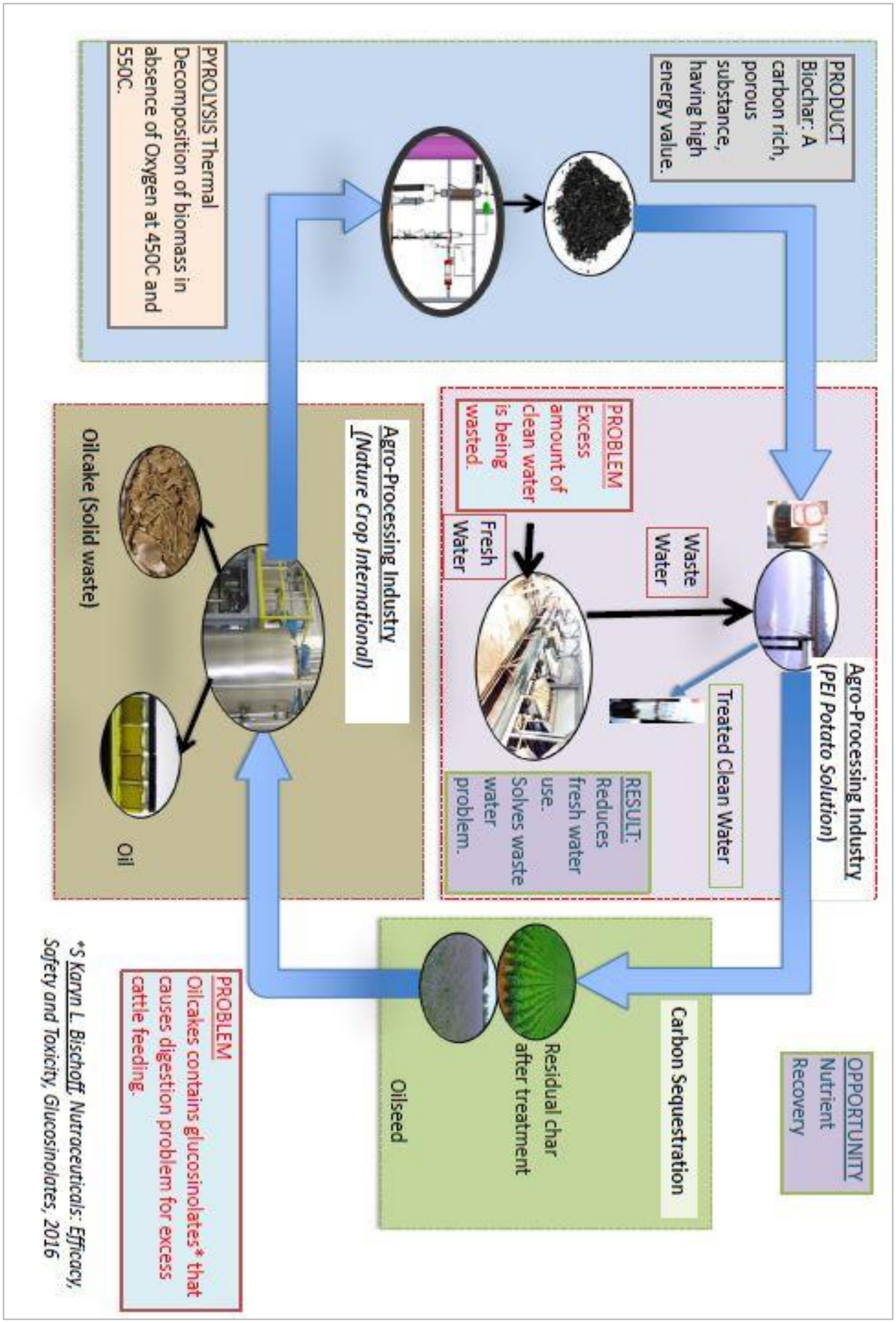


Figure 1.2: Schematic diagram depicting circular bioeconomy

The final novel idea this research possesses is on biocomposites. Among many fillers that are in use today, biochar is in the stage of infancy and possess a promising potential. Recent development in the use of biomass is its application in material. The strive for discovery and innovation of the newer and cheaper material along with the improved mechanical properties, better performance, machinability, ease of maintenance and abundant availability have kept the field of material science bustling. Due to the realization of the need for new alternative materials to replace existing fossil fuel-based products, the natural based materials are being promoted by the governmental and private organizations [8]. This is especially favorable when the raw material is a by-product of an industrial process and would otherwise be treated as waste. With cost factor and adverse nature of fossil fuel-based materials, the demand of bio-based material is increasing. The introduction of biocomposites materials has offered the best solution to this problem.

1.4 Arrangement of thesis

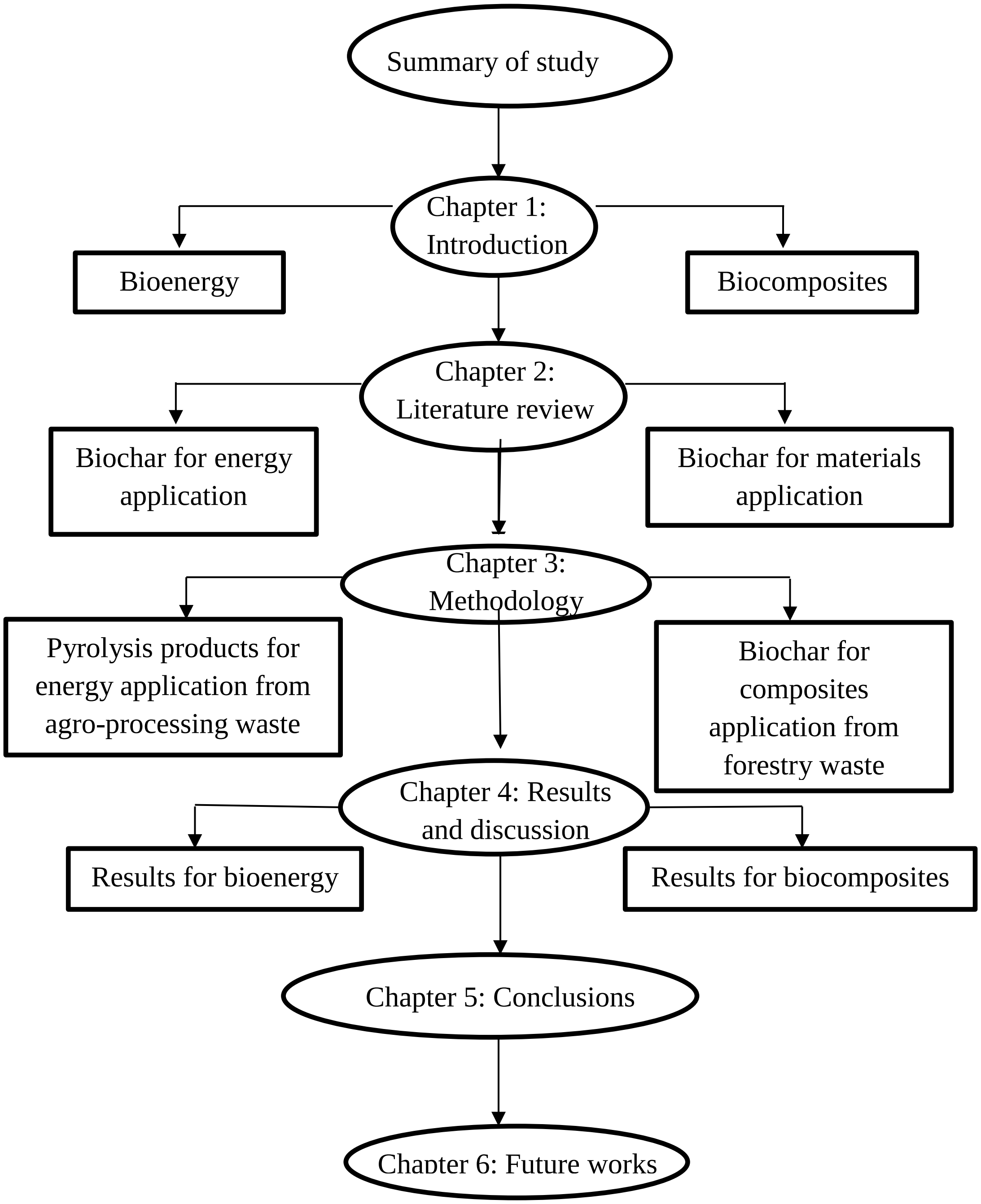


Figure 1.3: Flowchart indicating arrangement and presentation of thesis content

Chapter 2 discusses biomass and biowastes and their potentiality for replacing fossil fuel in energy application. A comprehensive review of pyrolysis process along with application of pyrolytic products in energy and composites application is discussed in the chapter. Chapter 3 discusses the methodology used for pyrolysis and the techniques used for characterization of the products. The detailed description of methods used to prepare glassfibre reinforced polymer GFRP) composite with biochar as filler material is discussed with the techniques used to study the morphology, mechanical and thermal properties of the resulting composite materials. The results from pyrolysis process, their energy values and use of biochar for wastewater treatment and composites application are discussed in chapter 4. The conclusions and future works are summed up in chapter 5 and 6 respectively. The flow of chapters and arrangements of thesis is presented in figure 1.3.

Chapter 2

Literature Review

This chapter reviews the concept of pyrolysis and use of pyrolytic products biochar for energy and biochar for composites applications and identifies the knowledge gap in these areas of research.

2.1 Biomass

Biomass is organic materials (from plants and animals) that includes agricultural products (like wood, grass, sawdust, hays, crops, etc.) and animal products (like bones, skin, fur, etc.). These along with discarded and inedible biomass are the waste biomass. Waste biomass includes forestry and agricultural residues, municipal solid waste, animal waste and energy crops [9, 10]. Forestry residues include biomass not harvested, logging residues, woodchips from branches and poor-quality stem wood and firewood. Agricultural residues represent the remains after crops harvesting and processing like woody chips, straw from cereal, hays, oilseed cakes. Agro-processing waste can be categorized into crops wastes and residues, fruit and vegetable residue, sugar, starch and confectionary industry residue, oil industry residue, grain and legumes by-product from distilleries, and breweries by-products. Animal wastes are farm slurry from pig and cattle farming, poultry litter slaughterhouse and fishery waste. Municipal wastes are compost, recyclable and non-recyclable wastes from household activities including food wastes, paper, used cooking oil, sewage sludge, biosolid from waste water treatment plants, industries, waste from sewage cleaning [10]. Seaweed and algal waste are considered as another form of waste biomass profoundly available in the water bodies with higher nitrate concentration.

According to United Nations Environment Programme, 5 billion metric tons of biomass is generated every year from agriculture. Canada generates more than a hundred-billion Canadian dollar of GDP from the agricultural products along with more than 27 million metric tonnes of waste biomass [7].

2.2 Biomass as an energy source

Bioenergy represents renewable energy obtained from the biomass and includes solid, liquid, gas fuels obtained either by direct combustion or with use of conversion techniques.

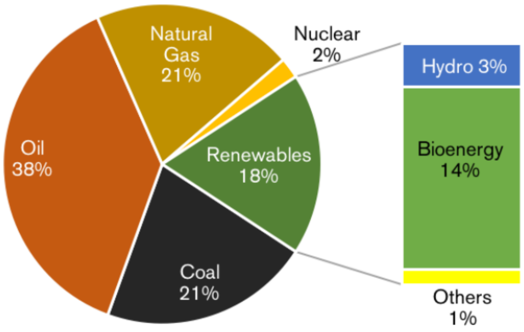


Figure 2.1: Global energy consumption scenario in 2013(*Source: WEC 2016*)

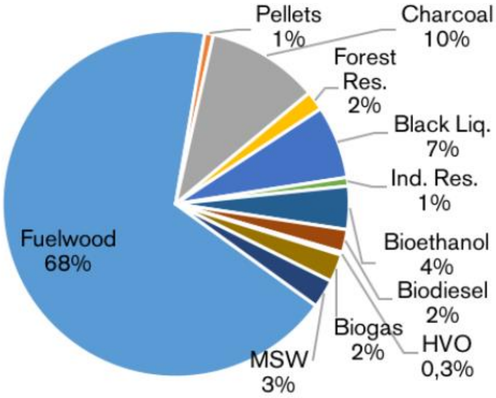


Figure 2.2: Primary energy supply of biomass resources globally in 2013 (*Source: World Energy Council 2016)*

In the global energy consumption scenario shown in figure 2.1, 80 percent of energy is suppled by fossil fuel annually, including 38 percent of oil and 21 percent of coal. 18 percent of bioenergy comes mainly from burning biomass like firewood and pellets in developing and underdeveloped nations [1]. Around 2.6 billion people were dependent on traditional biomass for energy needs. 52 million tonnes of charcoal used for different purposes is from wood. The data on energy supply based on biomass shows that around 90 percent of the total energy supplied by biomass is by woody biomass [1]. The major use of biomass is as fuelwood, charcoal which is the major source for heating and cooking. This is the thermal equivalent of about 1.2 billion tons of oil that constitutes about 25 percent of current global production.

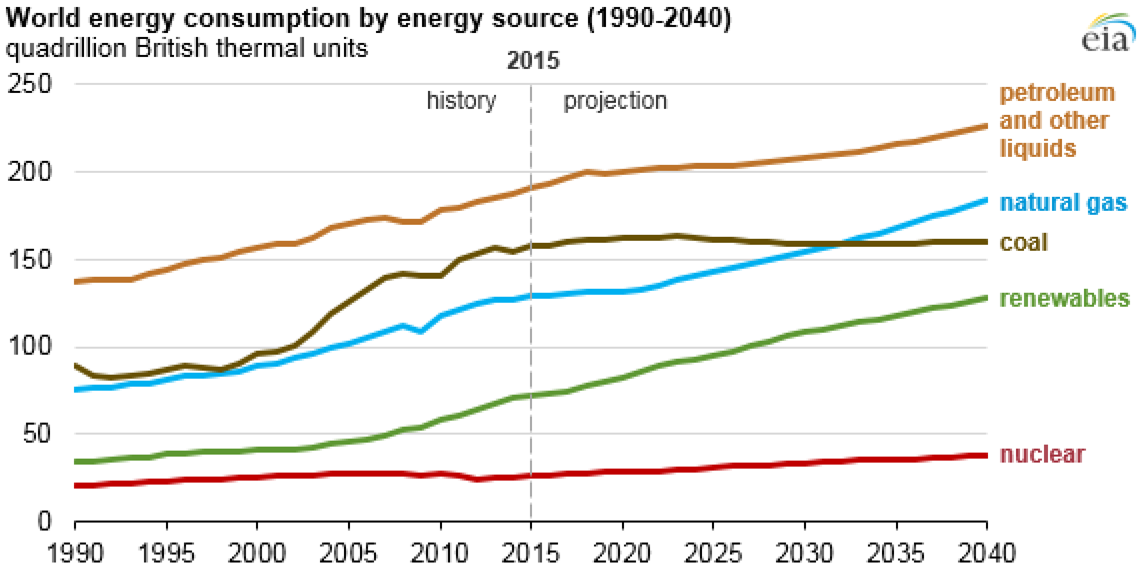


Figure 2.3: World energy consumption by energy source (1990-2040) (*Source: U.S Energy Information Association*)

According to UN, the world population will increase to 9 billion by 2050. With increase in population there will be significant challenges in the food as well as energy sector. U.S Energy Information Administration predicts that world energy use will increase by 28 %

between 2015 and 2040, among which most of the increase will be prominent in non-OECD countries, with renewables being the fastest growing energy source [11]. The consumption of renewables is projected to quadruple over the next 20 years [12]. Renewable energy and hence biomass are estimated to be the fastest growing energy source with an average increase of 2.2 percent per year between 2015 and 2040 [11] as shown in figure 2.3.

Global energy needs rise more slowly than in the past but still expand by 30% between today and 2040 and renewable energy will be the source of energy.

2.3 Biomass in composites application

Apart from energy generation, biomass can be used for obtaining chemicals and composites materials when properly treated. The use of biomass accounts to about 10% in chemical industry while that in polymer composites world is negligible.

Carbon is an important element in the material production industry. While there are other non-renewable sources that could supply the raw feedstocks, biomass is the only renewable source to provide carbon-based material [13]. Utilizing waste biomass and their products (through biological, chemical or thermochemical conversion processes) as a constituent element in composite material to offer better mechanical and thermal properties is key to a greener future. Specific properties of biomass-derived materials are combined with that of parent materials to offer superior qualities such as low density, high mechanical properties, excellent specific strength and recyclability as compared to the conventional materials [14]. Even though, biomass hold higher potential to be used in material, limited work has been done so far. The ongoing extensive researches in the field of bio composites are trying to justify the same taking financial factor in consideration.

2.3.1 Some research examples in composites

Among many innovative researches, biodegradable film producing biodegradable pot (BioPot) for seedlings plantation [15], heat insulator from coconut fibers and natural rubber [16] are some. In the latter, 5 to 60 weight percent of latex was experimented. 30 percent latex content in coconut fiber was found to be suitable for heat application as it absorbed 95 percent of the heat. Use of rice husk ash and coconut fibers in concrete has also been studied showing change in mechanical properties and stiffness of the material [17]. Wood cement composites particleboard production using supercritical carbon dioxide was also studied [18]. The cement bonded particleboard was manufactured by conventional cold pressing method and the internal bond strength increased from 0.3 MPa to 1.3 MPa.

Different compatible fillers have been experimented in many researches with some promising findings, however. In a study, fly ash was used with calcium carbonate as filler in epoxy and hardener with discontinuous glassfibre and found that they reduce the compressive strength and increase the impact strength of the material [19]. The wool composites exhibited better heat and fire-retardant properties, flax composites showed higher tensile and flexural strength and a mixture of both provided enhanced quality in both flame retardant and mechanical performance [20]. Another study showed the addition of ammonium polyphosphate as a filler material increases the heat absorptivity significantly reducing the heat release rate [21]. The bending property and flexural stress are greatly influenced by Al_2O_3 in carbon fibre and epoxy composites [22].

These examples of increased interest towards the newer and greener materials including natural fibers are the realization of their numerous advantages in performance as well as their friendly contribution towards the environment.

2.3.2 Hindrances and probable solutions in composites research

Despite the booming biocomposites market offering the unique, biodegradable, environmentally friendly products, there are still areas, which needs improvement for it to compete with the existing fossil fuel-based products. Reproducibility and machinability are pivotal detriments which are currently resisting the commercialization effort. Lack of enough information regarding the performance and properties of each constituent and the resultant biocomposites material is also to blame for adversity to limit the development of the material [23]. Other vital factors that have impacted the biocomposites world are poor moisture resistance, low impact strength [8, 23-28], inconsistency in natural fibers properties [29]. The influence in mechanical properties due to weak bonding between non-polar polymeric matrices and polar natural fibers, the incapability to withstand higher temperature leading to poor thermal stability [29, 30, 31] are other drawbacks of the green composite materials.

The suitable and appropriate materials selections for engineering applications will not only be cost effective and saves manufacturing time; it also increases product life and enhances the productivity and performance [32, 33, 34]. Researches are trying to find the appropriate combination and composition of the constituent matrices and reinforcement along with the fillers and additives to propose the better material properties. For example, in a study by Gupta & Singh [35], it was found that flexural and dynamic mechanical properties were found to increase due to incorporation of Polylactic Acid (PLA) coated sisal fibres while in another PLA-hemp composites experiment, the impact properties increased with low adhesion and reduced flexural strength [36]. Hence, not all matrices and reinforcements are compatible with each other. Similarly, fillers and additives can sometimes create adverse effects on adhesion and various mechanical properties.

Various techniques including chemical treatments, hybridization technique and techniques to incorporate filler materials have been tried in numerous studies to overcome these drawbacks in composite materials [35]. As far as additives are concerned, low cost filler materials may offer an added dimension in improving the mechanical and chemical properties of the material reducing the material cost simultaneously [19, 37]. As discussed above, limited number of materials is found to be compatible as fillers in material systems containing fibers [38] although numerous materials can be used as fillers in polymers [39]. This bonding incompatibility between fillers and matrices may result in weak adhesion and poor strength. It may also result in uncontrollable and unpredictable performance [19]. Based on these results, Das & Bhattacharyya [40] proposed nanoindentation to study the detailed interfacial mechanical properties to effectively optimize the engineering design of the composites.

2.4 Thermochemical conversion process

Thermochemical conversion process is a process of changing physical and chemical properties of biomass applying heat. In general, biomass-to-energy conversion technologies deal with feedstocks varying greatly in bulk density, size, moisture content, and intermittent supply. Therefore, modern industrial technologies are often hybrid fossil-fuel/biomass technologies which use the fossil fuel for drying, preheating and maintaining fuel supply when the biomass supply is interrupted. Thermochemical processes such as pyrolysis, torrefaction, hydrothermal carbonization, gasification convert raw biomass into more convenient form of energy carriers. These carriers possess either high energy density reducing transportation costs or have more predictable and convenient combustion characteristics allowing them to be used in internal combustion engines and gas turbines. Different thermal conversion processes are discussed below:

2.4.1 Torrefaction

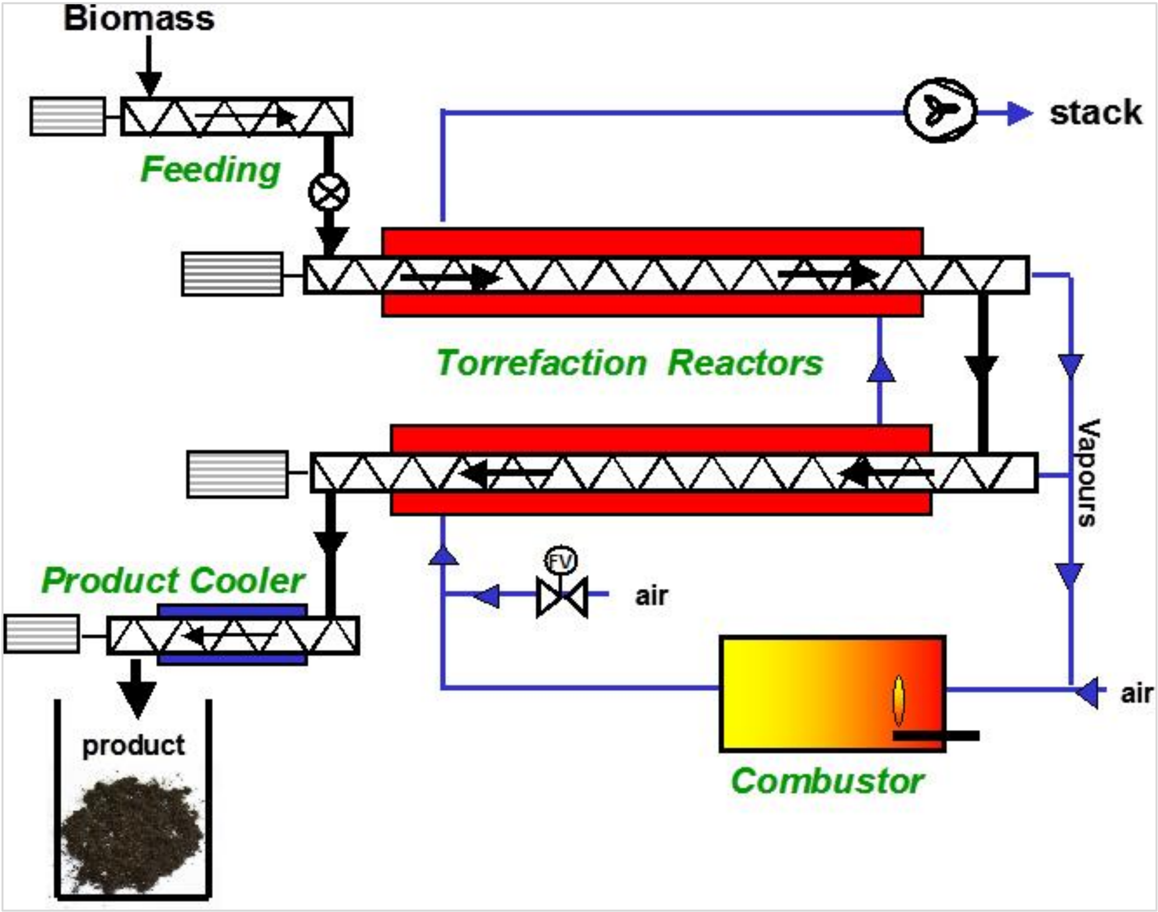


Figure 2.4: Schematic diagram of torrefaction process [44]

It involves heating of biomass below 300 °C in absence of oxygen at lower heating rate and with a residence time of 30 minutes to 2 hours [41]. Its main benefit is that it increases the energy density of biomass by reducing the moisture content. The torrefied biomass is lighter in weight, easier to handle and more brittle which makes grinding easier and less energy is required for processing. The product is hydrophobic, so the transportation and storage are easier. Torrefaction process results in a mass loss (dry basis) of 20-30% and an energy of 10-15% is consumed during the process [42]. The volume of torrefied biomass is only reduced by 10-20% as compared to raw biomass and torrefied product results in high ash content which results corrosive deposits on boiler tubes.

2.4.2 Gasification

It is a process of heating biomass at temperatures higher than 750 °C with controlled supply of air to produce carbon monoxide, carbon dioxide and hydrogen. The resulting gas is called syngas or producer gas which can be burnt directly as a fuel. The syngas can be used for production of electricity in gas turbine, gas engine, as a reduction gas in steel industry, production of natural gas by methanation.

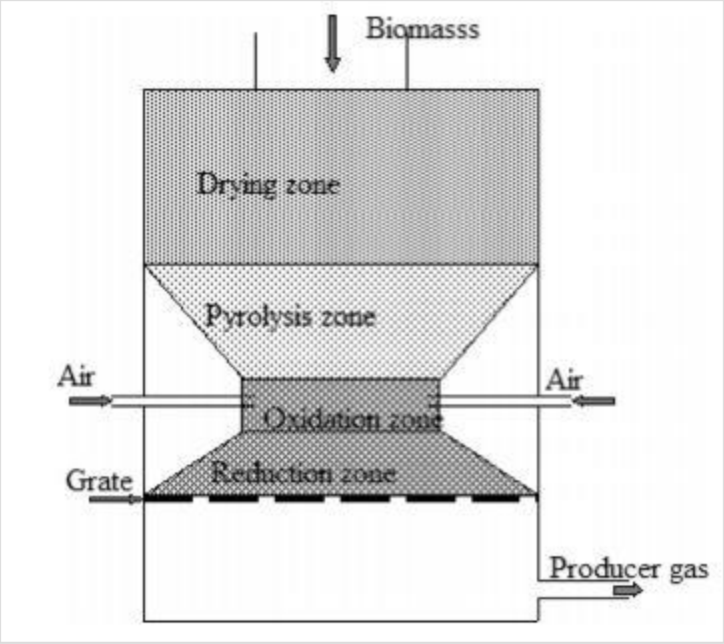


Figure 2.5: Schematic diagram of a downdraft gasifier [45]

The cost associated with gasification is high and its disadvantage is that it increases the greenhouse gases. The tar formation due to higher molecular weight volatile causes fouling effect and produces environment pollutants [43]. The corrosion associated during the combustion process is its another demerit.

2.4.3 Hydrothermal carbonization

It is a process of heating biomass at a temperature above 180 °C at a pressure higher than 2.5 MPa and with residence time of 15 to 120 minutes. The main advantage of this process is that it is suitable for handling high moisture content feedstock [46,47, 48]. The pressure in the process ensures that water is always in the subcritical region. The end products from this process are biochar, syngas and nutrients. As no drying of biomass is required, lesser energy is consumed. The carbon efficiency is higher compared to other conversion processes which means the biochar captures maximum carbon.

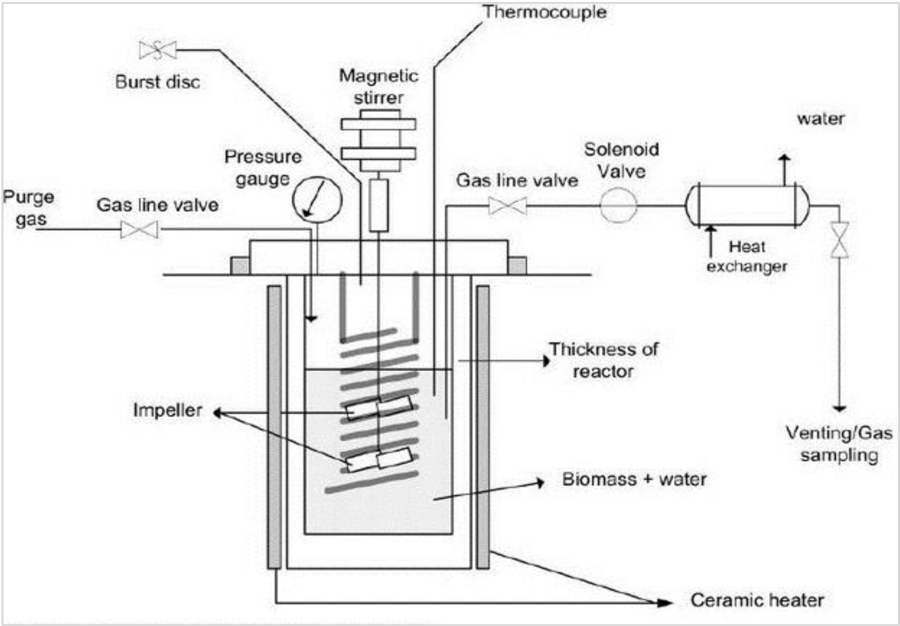


Figure 2.6: Schematic diagram of autoclave reactor for hydrolysis of palm shell [49]

2.4.4 Pyrolysis

It is process of thermal decomposition of biomass at temperatures higher than 400 °C in inert environment in absence or limited supply of oxygen with residence time above 30 minutes. The end products are biochar, biooil and syngas. As the process is carried out in high temperature, the biomass compounds are degraded. Pyrolysis is a versatile technique as compared to other processes for handling waste biomass from agricultural and forestry industries to produce biofuel and biomaterial products. The process is relatively simpler and quicker.

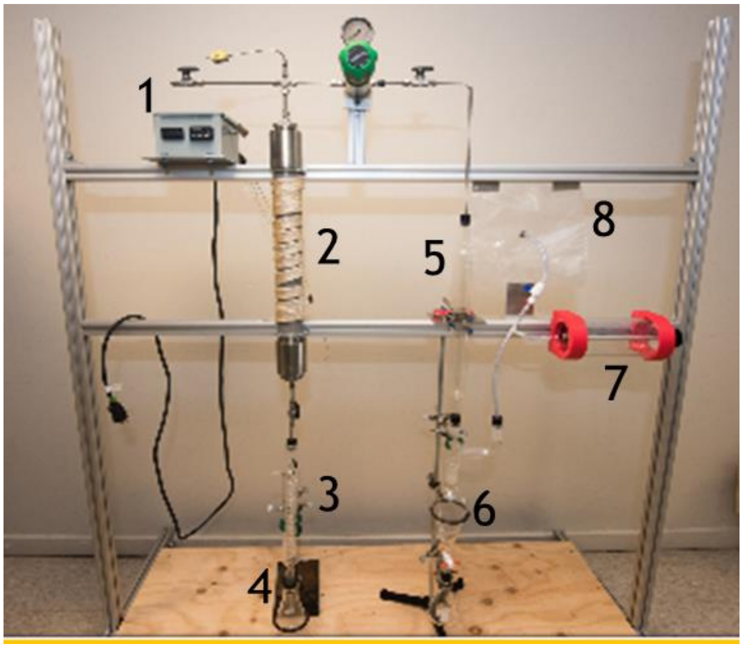


Figure 2.7: System setup for pyrolysis process. 1) Temperature, heating rate and Residence time controller, 2) Reactor, 3) & 5) Condensers, 4) & 6) Biooil collectors 7) & 8) Syngas collectors)

The products obtained from pyrolysis are solid fuel (biochar), liquid fuel (biooil) and gaseous fuel (syngas) [41]. As the pyrolysis temperature is reached, the decomposition of biomass takes place. The solid product remains in the reactor chamber 2) whereas the condensable vapor condenses to biooil and non-condensable vapor leaves the chamber as gas. Condensed biooil is collected in collector 4) and 6), and the uncondensed gas is collected in gas bag 8) through gas syringe 7). The system temperature, heating rate and holding time is determined by the settings on controller 1). The quality and quantity of pyrolysis products depend on the properties of biomass, temperature, pressure heating rate, residence time, presence of catalyst and the design of the reactor.

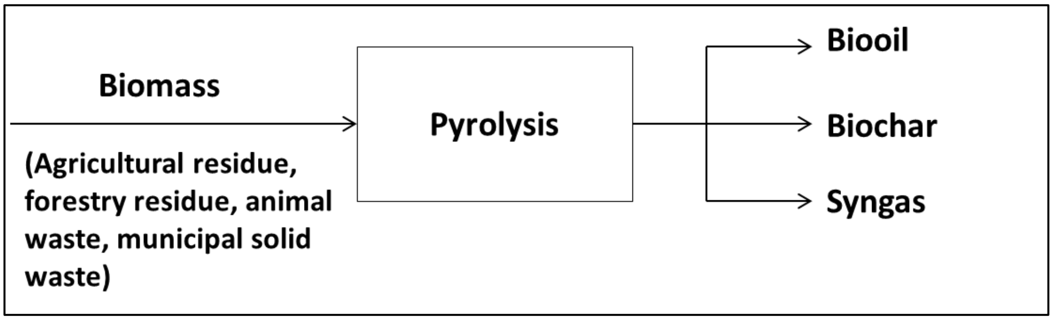


Figure 2.8: Pyrolysis process and pyrolytic products flowchart

2.4.4.1 Pyrolytic products

I. Biochar: It is a carbon rich solid product obtained from pyrolysis process, has heating value in the range of 25-32 MJ/kg on dry basis [41]. The physical and chemical properties of biochar are dependent on the type of feedstock, heating temperature and residence time. It can be used as a biofuel for space heating, for cooking, as a carbon sequester for soil amendment, to control pollution by applying in wastewater treatment plant and as a fuel stock to run co-firing boilers by mixing it with coal. When spread on the soil, it holds the nutrients and prevents the fertilizers from leaching thus reducing the use of excess fertilizer in the soil. Biochar is being studied for its application in the scientific researches to innovate novel materials with improved mechanical and fire retarding properties.

II. Biooil: It is a clear brownish pale liquid product of pyrolysis process that contains mixture of hydrocarbons and water content. It is obtained by condensing the volatile gases produced during the pyrolysis process. Biooil can become a reliable jet fuel source, a fuel source to run boiler, furnaces, hot air generators and modified engines that can handle acidic nature of the fuel. It can be used to extract numerous hydrocarbons and chemicals by separation. The main disadvantage of the biooil is the complex refinery process. The water molecules attached to the hydrocarbons are difficult to be removed. The acidic nature of this liquid fuel causes corrosive effects in the inner linings of the piston cylinders and damages the engine parts.

III. Syngas: The uncondensed gas remained after the condensation of volatile gas during the pyrolysis process is syngas. The major components present in this fuel gas are Carbon dioxide, Carbon monoxide and hydrogen. Other combustible hydrocarbons are also present in low concentrations. Syngas can be used for heating and to run small scale power generators. It can be collected and can be used in place of natural gas. During the pyrolysis process, syngas can be circulated back to the input so that the energy required during the process can be reduced [41, 50].

Lee et al. [51] have demonstrated the possibility of use of agricultural waste (e.g., red pepper [*Capsicum annuum L.*] stalk) for waste management, energy recovery, and biochar fabrication through pyrolysis process. Pyrolysis process is even more practical conversion process to lower down the viscosity of oil [52]. By mechanically fluidized reactor pyrolysis, Hossain [53] has recovered valuable products including pesticides, antioxidants and activated carbon from crop waste demonstrating an example of a biorefinery, a sustainable process for converting biomass into value added bio-based products. Shie et al. [54] have researched the carbon-containing sunflower-oil cake, a biomass waste, to convert into syngas and liquid oil as bioenergy sources and raw material to further produce chemical feedstocks.

2.4.4.2 Pyrolysis classification

A. Based on the source of heat, pyrolysis process can be classified as follows:

I. Allothermal pyrolysis process

It is a process in which the feedstock biomass is thermally segregated into various products by the application of external source. The external source can be coal, electricity, solar, exhaust gas etc.

II. Autothermal pyrolysis process

It is a process that uses biomass as the fuel source to run the pyrolysis process. This process is effective in remote area where no electricity is available, or the unit price of external sourced energy is high.

B. According to the rate of heat and final temperature, pyrolysis processes are of following types:

I. Slow pyrolysis

It is a pyrolysis in which biomass is heated slowly in the absence of oxygen at temperature of about 400 ° C with heating rate of 10 °C/s for long residence time of about 5-30 minutes [55]. The production of char is the primary goal. It is of two types: carbonization and conventional pyrolysis. In carbonization, biochar is the main product whereas in conventional pyrolysis involves all three products (biochar, biooil and syngas).

Table 2.1: Classification of pyrolysis method [56]

Method	*Temperature (°C)*	*Residence Time*	*Heating rate (°C/s)*	*Major products*
Conventional/slow pyrolysis	Med-high 400-500	Long 5-30 min	Low 10	Gases Char Biooil (tar)
Fast pyrolysis	Med-high 400-650	Short 0.5-2 s	High 100	Biooil Gases Char
Ultra-fast/flash pyrolysis	High 700-1000	Very short < 0.5 s	Very high >500	Gases Biooil

II. Fast pyrolysis

It is a rapid thermal decomposition of biomass at temperature of 400-650 °C, short residence time 0.5-2 second with heating rate of 100 °C/s in which biooil is the main product. If biooil is the product of interest, then the peak temperature should be below 650 °C and it can be up to 1000 °C if gas is the required product. The end products constitute 30-60% liquid, 15-35% gases and 10-15% char [55]. Higher heating rate, temperature range, short residence time of vapor in reactor and rapid quenching of products are the factors that increase the liquid yield [41].

III. Ultra-fast, or flash pyrolysis

It is an extremely rapid thermal decomposition pyrolysis at higher temperature of 700-1000 °C, short residence time <0.5 seconds with a high heating rate of 100-1000 °C/s [41]. The main products are gases and biooil. The yield constitutes 10-20% liquid, 60-80% gas and 10-15% char [55].

C. Based on the production frequency, pyrolysis processes can be:

I. Continuous pyrolysis

The feedstock is fed continuously after a cycle is run. In the continuous reactor, the feed materials are input from one part and the products are led out from other part of the reactor.

II. Batch pyrolysis

The feedstock is fed manually and is suitable mostly for laboratory experiment. In the batch reactor, the materials are fed into the reactor in batches for pyrolysis either at the start of the process or after all the fed materials are processed.

D. Based on the type of reactors used, pyrolysis processes are of following types:

I. Fixed bed pyrolysis

In fixed bed pyrolysis, the feedstock is fed in the fixed bed reactor which is heated externally. The process is simple and is effective for uniform biomass feedstock. It is mostly used as a batch pyrolysis in research and small-scale heat and power application. Heat is supplied from external source or by allowing limited combustion in oven.

II. Non-fixed (Rotating bed/moving belt) pyrolysis

In non-fixed pyrolysis, the feedstock rotates about the axis of the circular reactor or moves over a horizontal hot surface. The feedstock and bio oil production are continuous, so this is mostly used in petroleum and chemical processing industries. The by-product fly ash is carried out along with vapor and gases.

E. Based on the chemical addition to influence the process, pyrolysis is of following types:

I. Catalytic pyrolysis

This pyrolysis use catalysts with the biomass. Catalyst in pyrolysis causes change in decomposition behaviour of biomass changing quantity and quality of the end products. It enhances the quality of char and reduces the tar production. Use of catalysts can reduce the moisture content in biooil and can reduce the corrosion in the reactor. Some of the examples Calcium Oxide, Nickle Oxide, etc.

II. Non-catalytic pyrolysis

The feed material is only the biomass and the decomposition of biomass mostly depend on the temperature and residence time. When biomass is only heated, there are possibilities that end products cause corrosion in the reactor and the products obtained may not be controllable. It is due to

2.4.4.3 Pyrolysis reactors

The reactor is the main component of any pyrolysis process. It is the place where actual cooking of the biomass takes place. The reactors control temperature, heating rate of the biomass which determines the nature of products. Different types of pyrolysis reactors are:

I. Fixed bed reactor

It is a reactor in pyrolysis process with immobile bed of feedstock. In comparison to fluidized bed reactor it has longer residence time, lower gas velocity and lower ash carryover. The heater controls the reactor temperature and thermocouple is used to monitor its temperature during the process. Nitrogen or inert gas is used as the carrier gas and decomposed products are carried out by the carrier gas.

II. Fluidized bed reactor

It consists of a bed of sand particle which is supported by a porous plate and the primary combustion air is supplied from the lower section of the reactor. The feedstock is fed into the fluidized bed at temperature of 600-900 °C and the gas is passed through cyclone for removal of particles. It is then sent in the condensation unit where the vapors condense to form oil. In this reactor, the residence time of vapors and solids are controlled by the fluidizing gas flow rate. The advantages of fluid-beds are uniform temperature inside the reactor and a uniform heat transfer in all particles. 75% biooil can be obtained with this reactor. Two types of fluidized bed reactors are in use: i. bubbling fluidized bed and ii. circulating fluidized bed reactor. In bubbling fluidized bed, the biomass is fed into a bed of hot sand which is fluidized by inert gas. The fluid bed allows high transfer to biomass solid and 70-75% liquid is obtained from dry wood feedstock. Circulating fluidized bed works in the same principle of bubbling fluidized bed but the solid is recycled in a continuous cycle having loop seal and cyclone [41, 50]. The main advantage of the circulating fluidized bed process is that combustion heat can be reused in the inert bed solids.

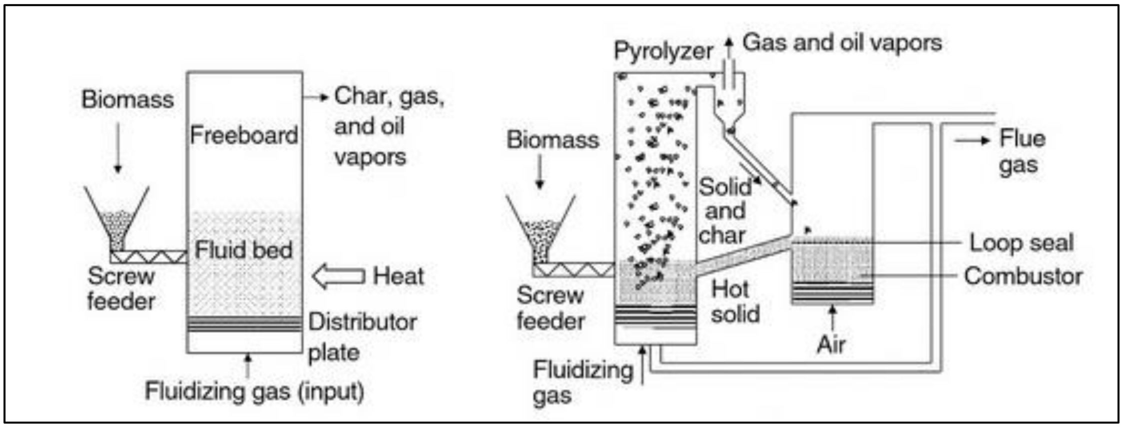


Figure 2.9: Bubbling fluidized bed & circulating fluidized bed reactors [57]

III. Screw kiln

Screw kiln is the recent and has been widely accepted type. An extruder is used to screw the feedstock from a feeder in an oxygen free environment. The extruder is heated by external heat sources. Solid residues and pyrolysis products are separated and collected from the other end of the extruder. The small diameter of the extruder and good mixing of the materials make the radial temperature gradient negligible. The process is relatively stable and does not use bed material as in the fluidized bed reactor. The feeding rate can be controlled by adjusting the rotation speed of the extruder, which also determines the residence time.

2.5 Pyrolysis system used in this research

Based on the operating principle, pyrolysis process can adhere various kinds of reactors.

For the bioenergy study, a fixed bed pyrolysis has been implemented. Muffle furnace was used as source of heat.

For biocomposites study, two-stage rotating drum pyrolysis reactors was implemented. The first stage was to remove moisture and the second drum performed the actual pyrolysis process. Heat was supplied by wrap heaters wrapping around the reactors. Details of the setup has been presented in methodology of each study in next chapter.

2.6 Biomass feedstocks for pyrolysis

The various potential sources of biomass have been tabulated below:

Table 2.2: Biomass feedstocks for bioenergy and biomaterials [58-60]

Origin	*Feedstock*	*Type*
Forestry	Woody biomass residues: Stem wood and primary forest residues, landscape residues: whole trees, timber, thinning, branches, harvest losses (unmerchantable wood), stumps and coarse roots etc.	Residues
Forestry	Woody biomass: forests and other wooded land, including tree plantations and short rotation forests for stem wood production	Dedicated Feedstocks
Agriculture	Lignocellulosic crops: short rotation coppice (willow, poplar, eucalyptus etc.), red canary grass, miscanthus, giant reed, switch grass etc.	Dedicated Feedstocks
Agriculture	Sugar crops: sugar cane, sugar beet, sweet sorghum etc.	Dedicated Feedstocks
Agriculture	Starch crops: corn, wheat, industrial sweet potatoes, barley, rye, millet, rusby or virginia mallow, cassava etc.	Dedicated Feedstocks
Agriculture	Oil crops: coconut, palm, palm kernel, soybean, sunflower, linseed, rapeseed, castor etc.	Dedicated Feedstocks
Agriculture	Grasses: green plant materials, grass silage, immature cereals, plant shoots etc.	Dedicated Feedstocks
Agriculture	Agricultural surplus	Residues

Agriculture	Animal manure (wet and dry)	Residues
Agriculture	Herbaceous residues, partly now being left on the land or burned: wheat straw, bran, barley straw	Residues
Agriculture	Grass from permanent (semi-natural) grasslands	Residues
Agriculture	Fruit and grain waste biomass: olive stonnes, cherry pits, grape waste, nut shells, olive oil mill residues etc.	Residues
Process wastes Forestry	Wood processing industry lignocellulosic by-products and residues: sawdust, cutter savings, grinding powder, bark, woodchips, wood dust etc.	Residues
Process wastes Forestry	Pulp and paper industry by-products and residues: bark, black liquor and other sludges etc.	Residues
Process wastes Forestry	Agro-industrial side-streams: beet pulp, bagasse, corn cobs, corn stover, olive mill cakes, cassava waste water, palm oil mill effluent, groundnut waste, soybean waste, orange peel waste, potato peel waste	Residues
Organic waste	Organic waste from industry and trade (excluding agro-industrial and pulp and paper industry) including woody fractions such as bulk transport packaging, recovered demolition wood etc.	Residues
Organic waste	Sewage sludge (from industry and households)	Residues
Organic waste	Oil-based residues: animal fat from food industries, used cooking oil from restaurants, households and others etc.	Residues
Organic waste	Municipal solid biodegradable waste (from private households and gardens) including woody fractions such as food left overs, waste paper, discarded furniture etc.	Residues
Aquaculture	Municipal solid biodegradable waste (from private households and gardens) including woody fractions such as food left overs, waste paper, discarded furniture etc.	Dedicated Feedstocks

A. Agro-processing wastes

Agriculture not only contributes to the economy greatly, it also generates excessive amount of wastes. It basically includes organic wastes such as weed, straws, leftover stalks etc. that have low water content (below 10%). Animal wastes in agro-processing industry can be animal dungs, dead bodies, bones, and flesh. The agricultural products processing industries produce wastes like molasses, potato peals, oilcakes, husk, stalk and nutshells, etc. Crambe and meadowfoam oilcakes processed as feedstock to run the pyrolysis process represent the agro-processing wastes.

B. Forestry wastes

Forestry residues are generated during clearing for logging roads, extracting stem-wood for pulp and timber and include small trees, branches, woods left in after forest cleaning, pulp and paper processing residue.

There are also the following types of forestry residues that have application in the production of bio-based products and bioenergy:

- Residues from harvest operations left in the forest after stem wood removal (branches, roots etc.);
- Complementary fellings (emerging from the difference between the maximum sustainable harvest level and the actual harvest quantities for round wood production);
- Wood wastes from a range of sources (e.g. construction or demolition wastes, waste from manufacturing of wood-based products) [61].

The sawmill industry generates large quantity of sawdust as the process waste which is pelleted for their ease of transportation. A sac of spruce pellets representing the forestry wastes was purchased from local market and utilized as another feedstock to generate biochar for biocomposites material application.

2.7 Application of pyrolytic products

Biochar, biooil and syngas, generated from the pyrolysis process have numerous useful applications.

The carbon sequestration [62-66] for improving C:N ratio of soil [67, 68, 69] to waste water treatment by filtration [62, 70, 71] to briquets for energy application, all of these uses of biochar have been investigated and proven by many researchers. Water retention, nutrient efficiency, cation exchange capacity (CEC), microbial activity, and associated GHG and nitrogen emissions properties of biochar were discussed in the past studies [62, 73-75].

2.7.1 Biochar as an energy source

Waqas et al. [75] carried out pyrolysis of agricultural waste like date leaves, grass clipping, coconut leaf, ornamental plant residue at 250, 350 and 450 °C and heating values of biochar were 24, 23.64 and 23.08 MJ/kg respectively. Boumanchar et al. [76] studied the heating values of six kinds of biomass and two types of biochar and the results show that the heating value for biomass ranged from 12.16 and 20.53 MJ/kg and that of biochar was 27.39 for biochar 1 and 32.60 MJ/kg for biochar 2. Tsia et al. [77] studied pyrolysis of exhausted coffee residue from coffee industry for its potential as biofuel and higher heating value of 31.9 MJ/kg was obtained. Ahn et al. [78] studied the use of wood biomass char in direct carbon fuel system where the performance of char in terms of power density was 60-70% to that of coal. This study suggests that biochar could be alternative fuel source that can complement the fossil fuel in many energy applications. As a fuel, it can be used in coal fired boilers and co-firing with coal.

2.7.2 Biochar for soil amendment

Biochar as a soil amendment help retain water and mineral in the soil preventing leaching of nutrients, reduce fertilizer consumption, sequester carbon and reduce the emission of greenhouse gases. Colantoni et al. [79] performed pyrolysis on pelletized grape vine and sunflower husk at 400 and 500 °C and concluded that pyrolysis has a significant effect on the concentration of phosphorous and potassium in the biochar. The phosphorous concentration in biochar obtained from pyrolysis of sunflower husk at 500 °C increased by 230% and that obtained from grape vine at 500 °C increased by 194% and similar trend was observed for potassium concentration. This increase in the concentration makes the biochar suitable for use as fertilizer to improve the crop yield. The use of biochar in soil can reduce the dependency on inorganic fertilizers. Laird et al. [80] studied the impact of biochar on nutrient leaching and concluded that use of biochar can reduce the leaching of N, P, Mg and S.

2.7.3 Biochar as a carbon sink

Plants act as carbon storage, but the direct combustion of agricultural/ forestry residue releases the carbon dioxide back into the atmosphere contributing to the global warming. Soil act as the only source where biochar can be stored for a long time [81]. Biochar on the other hand stores carbon and act as a carbon sink in the soil. Converting the biomass into char converts the carbon to more stable form. Woolf et al. [82] stated that production of biochar and its application in soil reduces carbon dioxide emission by 12%. Lehman et al. [83] stated that biochar sequesters about 50% of initial carbon in the biomass. Carbon retention after direct burning is only about 3% and that from biological decomposition is around 10-15% making biochar a best source for carbon sink.

2.7.4 Biochar as a potential filtering agent

The use of biochar as activated carbon for metal removal is being studied in the present days. Berger [84] studied the biochar obtained at 450 °C from chopped Salix for filtration of greywater treatment and suggested that biochar can be used as alternative to activated carbon for organic and phosphor removal. Berger further puts forth that the porosity and high surface area of biochar results in its higher contaminant absorptivity.

2.7.5 Biochar in material applications

Polymers are materials consisting long chain of macromolecules which are used in paints and adhesives industry, home appliances, automobile and packaging industries. 85% of polymer used today are thermoplastics and their uses are widely spread because of their low cost, flexibility and their formability [85]. Mostly it is used in electrical appliances and to make automotive parts. The polymers used these days are materials blended with other polymers or with various filler materials. Fillers are added in material to improve its characteristics like processability, durability, mechanical properties like compressive strength, tensile strength, abrasive resistance along with the reduction in material cost. Composites are two or more materials with different properties combined to produce a newer material which has more superior properties than the individual properties [86]. Wood is a natural composite consisting of long cellulose fibre held together by amorphous lignin and cement, concrete, glass, reinforced plastic are examples of artificial composite. Composites contain fibers as reinforcement and the matrix (binder) that holds the fibers together [87].

Use of filler may reduce the cost of composite and obtain the desired mechanical properties like fire retardant and smoke performance, water resistance, surface smoothness, improves the surface and provides dimension control to the material. In recent days, the use of inorganic fillers like calcium carbonate, kaolin, alumina trihydrate, calcium sulphate is increasing in composites [86]. While these inorganic fillers are widely used, renewable and environmentally friendly biochar can be a sustainable alternative source of filler material in the future.

Biochar is cheaper filler material that can dramatically influence the of biocomposites material characteristics. Khalil et al. [8] claims that due to high carbon content in Jatropha, their carbon black and activated carbon can be used as filler in composite fabrication. Its undebatable that the biochar makes its application in substantial number of fields. The hydrophobic nature of biochar is an advantage for use as filler and its surface area allows the matrix to be stable. In the field of biocomposites, even though the biochar is already conceived as a constituent (filler, additive) element, it is yet to convince the material industry. Higher proportion of thermally stable biochar to a woody biomass with fire retardants to neat Polypropylene significantly improved the flammability and certain mechanical properties, such as flexural strength and tensile/flexural moduli [88]. In similar study of biocomposites with biochar, reduced weight with low moisture and improved surface adhesion of biocomposites demonstrated notable mechanical characteristics such as advance impact properties and top-class tensile and flexural strength with higher biochar percentage [89].

2.7.6 Biochar in concrete application

Concrete is a mixture of cement, sand, brick or stone, ballast and water which when placed in forms allows being cure and becoming hard. The cement and water form a paste which binds the material when its hardened. The binding material is cement, the stone is the coarse aggregate and matrix is the mortar used in concrete. Concrete have high compressive strength and good thermal and water resistance. The materials for concrete are easily available and are cheap. Materials like silica, limestone, glass has been added in concrete to improve its mechanical properties. 4100 million metric tons of cement is produced worldwide [90] and the raw materials include Calcium oxide, silicon dioxide, and iron oxide. These raw materials are mixed in a rotatory kiln at temperature around 1400 °C and gypsum is added to the cement. This process emits the carbon dioxide to the atmosphere. According to the Intergovernmental Panel on Climate Change, IPCC, for every tonne of cement produced there is a one and a quarter tonnes equivalent of CO_2 released [91].

Biochar obtained at 300 °C was added to mortar (2% by weight of cement) by Gupta et al. [92]. The results showed improvement in early compressive strength, ductility suggesting the use of biochar as carbon sequestering admixture in concrete. Akhtar et al. [93] used biochar obtained from poultry litter, rice husk and pulp and paper mill sludge in the concrete and the results showed an increase in flexural strength by 20%.

2.7.7 Biochar in nanotube application

Khan et al. [94] compared the mechanical and electrical properties of composite with biochar and multiwall carbon nanotubes as fillers dispersed in epoxy resin. Pristine biochar and heat-treated biochar were used. Pristine biochar was obtained from pyrolysis of maple wood and heat-treated biochar was obtained after heating biochar at 950 °C in presence of nitrogen for 4 hours. Biochar pellets were grinded and dispersed in epoxy resin. An overhead mixer at 2000 rpm was used for dispersion of fillers in the matrix for 2 minutes. The trapped gas bubbles were removed by sonication and degassing was carried in low vacuum chambers for 20 minutes. Composite was molded in dog bone shape and was cured at 60 °C for 4 hours.

Table 2.3: Composition used for composites preparation (Khan et al. 2017) [94]

S.N.	*Sample ID*	*Resin(g)*	*Hardener (g)*	*Filler (g)*
1	Blank epoxy	66.67	33.33	0
2	2%	65.33	32.67	2
3	4%	64	32	4
4	20%	53.33	26.67	20

2%, 4% and 20% (wt.) of biochar was used for composite preparation and its mechanical properties was compared with blank epoxy. For tensile strength, samples were measured with a load cell of 10 kN and a strain rate of 5 mm/min according to the standard ASTM D-638 protocol. Ultimate tensile stress and elongation at break was found to be improved with use of 2% biochar. The Young's modulus increased by 41% as compared to the blank epoxy for sample with 20% biochar. The addition of filler changed the brittle property of epoxy resin into ductile property.

2.7.8 Biochar as a filler in polymer composites

Pandey et al. [89] studied the characteristics of hybrid composite made of sisal fiber with epoxy as matrix and softwood biochar as filler. The weight percent of sisal fiber used was 2 gram and epoxy used was 93, 88 and 83 grams. 5%, 10% & 15% biochar (weight fraction) was used as filler. Longitudinal and orthogonal fiber orientation of the sisal fiber was used, and hand lay up process was used for composite manufacturing. A mold of dimension 150 x 130 x 5 mm^3 was used for composite preparation. Epoxy resin mixture and hardener were mixed in the ratio of 10:1 (weight) and constant weight (%) of 2 grams of sisal fiber was used. Epoxy was stirred using a magnetic stirrer and biochar was then added. The sisal fibers were placed with mold and epoxy resin mixture with biochar was poured to it. Sample was cured for 12 to 15 hours.

Table 2.4: Composition used for composites preparation (Pandey et al. 2016) [89]

S.N.	*Sisal(gm)*	*Biochar % weight fraction*	*Epoxy(gm)*
1	2	5%	93
2	2	10%	88
3	2	15%	83

The longitudinal fiber showed improved mechanical properties as compared to the orthogonal fiber composite. Tensile strength of longitudinal fiber with 5% biochar showed highest tensile strength of 14.4 MPa, flexural strength with 10% biochar was higher with 21.2 MPa, flexural modulus was maximum with 5% biochar and impact properties was found maximum for 15% biochar.

2.8 Chemical and thermal behaviour of biochar-added composites

Das et al. [95] studied the waste derived biochar added composites for chemical and thermal characterization. Biochar with moisture content 1.88% weight, pine wood, Polypropylene (PP) and Maleic anhydride grafted polypropylene (MAPP) were used for the preparation of composite. Polypropylene, wood, biochar, and MAPP were mixed in a high intensity mixer. It was then melted and blended in a twin-screw extruder and composite planks were hot pressed moulded at 195 °C. 6 to 30% biochar was used to produce wood PP biochar composite and found that addition of biochar increased the thermal conductivity of composite and reduced the surface roughness of the composites. Their results from transmission electron microscopy showed no significant variation in diffraction pattern among the different composites specimens.

Das et al. [96] in another study characterized the mechanical, thermal, chemical and morphological properties of the biochar added biocomposites. In this case, pine saw dust, sewage sludge, and poultry litter were pyrolysed to produce biochar. Pine wood biochar was produced by pyrolysis at 900 and 350 °C for 1 hour and at 470 °C and 420 °C for 10 minutes. For biocomposite manufacturing, the process discussed above was repeated with 42% polypropylene, 30% landfill pine wood, 24% biochar and 4% MAPP. The poultry litter biochar biocomposites had high values of tensile/flexural strength, tensile/flexural modulus, and impact strength as compared to other composites. The tensile strength of pine wood biochar (900 °C) added composite increased from 24 to 26 MPa as compared to the wood polymer composite, flexural strength decreased from 47 MPa to 42 MPa and flexural modulus increased from 2.2 to 3.8 MPa. The addition of biochar enhanced the tensile and flexural strength.

2.9 Morphology and flame retarding character of biochar-added composites

In another study, Das et al. [97] added biomass waste (rice husk, coffee husk, coarse wool and landfill wood) with biochar and polypropylene to identify most suitable biomass to use in composites. The biochar was prepared from pyrolysis of landfill pine wood at 900 °C for 1 hour. In this study too, 42% polypropylene, 30% biomass, 24% biochar and 4% MAPP was used. Thermogravimetric analysis, tensile modulus and strength tests were carried out according to ASTM D638 protocol, three-point bending test for flexural strength test was done based on ASTM D790 protocol. TGA for individual biomass and that with biomass and biochar showed that composite had higher onset temperature than the individual biomass which is because of thermally stable biochar. The addition of biochar made the composite more thermally stable. They also studied the fire properties of individual biomass and that of composite. The fire characteristics was studied with peak heat release rate (PHRR) and time to ignition (TTI) provided the time a material takes to catch fire under radiative heat. The biomass ignited rapidly while the biochar did not ignite under the radiative heat. The time to reach PHRR for biomass was 25-57 seconds with PHRR in the range of 188–430 kW/m^2 and time for biochar was 305 seconds with PHRR 33 kW/m^2. The biochar was found to be inert and did not ignite under radiative heat. Similarly, all the biochar-based composites showed shorter time to PHRR and TTI as compared to PP. The flexural strength, tensile moduli, flexural moduli of the composite was higher than that of PP. The addition of biochar in rice husk and wood increased the tensile strength, flexural strength, tensile/flexural moduli. The tensile and flexural strength for rice husk with biochar was 32.7 MPa, 62.6 MPa and for wood with biochar was 35.8 and 67.2 MPa. The addition of biochar improved the mechanical properties of the composite. The Scanning Electron Microscopy showed that in wool biochar composite, the biochar hindered the interaction of wool and PP which caused the wool biochar to have less tensile strength compared to other composite. SEM also shows the mechanical interlocking of biochar with PP for all the composite which enhanced the tensile/flexural moduli compared to the PP. Overall, the wood-based composites was found to have enhanced mechanical properties and good resistance to fire characteristics.

Table 2.5: Summary of previous works on biocomposites

Biomass Type	*Composite Material*	*Characterization technique*	*Major Finding*	*References*
Maple wood biochar	Epoxy + resin + hardener + biochar	ASTM D-638 protocol for tensile stress.	Improved tensile stress and elongation at break	Khan et al. (2017) [94]

	As shown in table		for 2 wt.% load of biochar	
Softwood biochar	Epoxy + biochar + epoxy As shown in table	Tensile/flexural strength, tensile/flexural modulus	Improved mechanical properties for longitudinal fiber as compared to orthogonal fibers	Pandey et al. (2016) [89]
Waste derived biochar	Polypropylene + wood + biochar + MAPP	Brunauer Emmett Teller (BET),	Increased the thermal conductivity of composite and reduced the surface roughness of the composite	Das et al. (2015) [95]
Pine saw dust, sewage sludge, and poultry litter biochar	42% polypropylene + 30% landfill pine wood + 24% biochar + 4% MAPP	ASTM D638-tensile modulus and strength, ASTM D790-flexular modulus and strength	Enhanced tensile and flexural strength of composite	Das et al. (2016) [96]
Landfill pinewood biochar	42% polypropylene + 30% biomass + 24% biochar + 4% MAPP	TGA, ASTM D638, ASTM D790-flexular modulus & strength, ASTM E1354 for fire properties	Thermally stable composite, shorter time to PHRR and TTI as compared to PP, flexural strength, tensile moduli, flexural moduli of the composite	Das et al. (2018) [97]

2.11 Application of biooil

Biooil is another product obtained during the pyrolysis of biomass and finds its applications as combustion fuels used in boiler, engines, gas turbine, jet fuel and as a source of hydrocarbons and other chemicals. Islam et al. [98] studied the biooil produced from pyrolysis of different biomass like pine seed, date seed, plum seed, nutshell, hay of catkin, rice husk, jute stick, saw-dust, wheat straw and linseed residue. The energy content of biooil ranged between 20 to 33 MJ/kg and the density of the biooil was in the range of 900 to 1224 kg/m^3. The viscosity was closer to that of diesel hence suggesting that pyrolysis oil could be used as alternative fuel after necessary upgradation and refinery processes. Pyrolysis of date seed was studied by Joardder et al. [99] and the 1042.4 kg/m^3 density and 28.636 MJ/kg heating value of oil were revealed, and these values correlates to that found by Islam et al. The advantage of the biooil as a source of energy is that it is easy to store and transport as its flash point is comparatively higher than that of the fossil fuels. The attached water molecules with hydrocarbons are difficult to be separated and removed, the acidic nature resulting corrosion in linings of pistons and cylinders and engine parts are some serious drawbacks of the biooil to be used as a fuel source. While there are some problems associated with the use of biooil directly in diesel engine and gas turbine like poor cetane number [100], various chemical methods are being carried out to upgrade the quality of biooil for its use.

2.12 Application of syngas

Syngas, a mixture of carbon monoxide, carbon dioxide and hydrogen, is another product obtained from pyrolysis process. Hot syngas can be used directly to generate industrial steam, heat production in industries, boilers operation and electricity generation via steam turbine. Syngas can be circulated to heat the thermal plants. Hlavsová et al. [101] studied the syngas production of nine compost feedstocks obtained from no-hybrid and hybrid perennial grasses and heating value of 16.23 to 17.43 MJ/kg was obtained. The demerits of using syngas as a direct source to run engine are: it contains tar. The removal of tar requires water and the addition of moisture content corrodes the internal parts of the power plants.

2.13 Summary

With the increasing dependency on fossil fuel and the limited source of oils, alternative forms of energy must be used in order to have a sustainable future. The problems like emission of greenhouse gases from the use of fossil fuel, direct combustion of product, use of fossil-based materials has shifted the focus from widely used fossils to advantageous renewable source of energy. Pyrolysis is one of the conversion technologies which produces biochar, biooil and syngas, all of which has its application in the energy sector. With proper design and development of the biomass conversion technologies, the energy crisis problem as well as the climate change enhanced by emission of greenhouse gases can be solved. Not only in the energy sector, but biochar can be used to replace inorganic materials, and cement in certain fraction. This replacement helps in reduction of the harmful gases along with improving the physical and mechanical properties of the materials.

Chapter 3

Materials and Method

3.1 Materials and method for energy application study

3.1.1 Feedstock

Crambe (Crambe Abyssinica) and Meadowfoam (Limnanthes Alba) oilcake samples used in this study was provided by Nature Crops International. The oilcakes were crushed into powder of mean size 425 microns and were used for all the experiments. The product characterization and analysis are necessary to evaluate the energy value that can be extracted from these waste by-products. The raw crambe and meadowfoam sample was characterized by proximate and ultimate analysis and the data is presented in Table 3.1.

Table 3.1: Proximate and ultimate analysis of raw crambe and meadowfoam oilcakes

	FC	*M*	*Ash*	*VM*	*C*	*H*	*O*	*N*	*S*	*HHV*
Crambe	7.45	6.09	5.5	80.96	49.76	7.51	37.25	4.92	0.56	22.77
Meadowfoam	9.51	6.89	8.22	75.38	44.21	5.00	46.29	4.08	0.42	18.65

[FC = fixed carbon %; M = moisture %; VM = volatile matter %; C = carbon %; H = Hydrogen %; O = Oxygen %; S = Sulphur %; HHV = Higher Heating value MJ/kg]

3.1.2 Experimental method for pyrolysis

The pyrolysis experiments were carried out in absence of oxygen at the temperatures of 450 °C and 550 °C. The steel tube of 9 mm internal diameter and 160 mm long was used as the reactor for the pyrolysis experiment. The reactor was kept inside a closed furnace (Paragon Sentry Xpress 4.0, USA). The furnace temperature was controlled by the temperature controller attachment on the furnace and the internal temperature inside the tube was measured by centrally placed 1/8” diameter and 24" long K type thermocouple (Omega CHROMEGA®- ALOMEGA®304 SS Sheath, Part# KQSS-18G-24, USA). The temperature was recorded in a computer by K type ±0.5% of reading or ±1.0 °C accurate Universal Thermocouple Connector (Omega UTC-USB, Model# UTC-USB, USA). Samples size of 7 grams weight in maximum was collected. The raw samples were first heated at 110 °C for an hour to remove the moisture. After the removal of moisture, the heating rate was kept at 600 °C /hour (10 °C per minute) while the final temperature was set to 450 °C and 550 °C for 2 samples from each biomass (crambe and meadowfoam oilcakes). The residence time was set to 30 minutes at each desired temperature. The resulting gas was condensed first in a tube and the remaining uncondensed gas was collected in a 1000 ml syringe (Model# S-1000, USA).

3.1.3 Analytical methods

All the solid products were subjected to the proximate, ultimate and bomb calorimeter analysis. Similarly, gases collected at different temperatures from both the feedstocks were subjected to the gas chromatography analysis. Ultimate analysis of liquid biooil was conducted, and its heating value was calculated using Organic Elemental Analysis Equipment (Thermo-Fisher Flash 2000 CHNS-O Analyser, USA).

3.1.3.1 Gas product analysis

The gas samples collected in the syringe were analyzed by a multi-gas chromatograph with thermal conductivity detector (SRI 8610C Multi-gas #1 Configuration, USA). The collected sample was deposited by the Helium gas stream as a carrier gas first into the Silica gel column, with the column oven holding at 40 °C, where the ethane, propane, butanes, pentanes, and carbon dioxide were retained. The remainder of the sample containing H_2, O_2, N_2, CH_4, and CO continued onto the Molecular Sieve column. During a chromatographic run with the sampling valve in the inject position, the H_2, O_2, N_2, and methane present were the first to elute through the columns and into the detector due to the Silica gel's long retention of C, CO_2 and other higher hydrocarbons at 40 °C. The sampling valve actuated back into the loading position immediately following the elution of the CO peak, which reversed the sequence of the columns prior to the detector, and sent the components preparing to elute from the Silica gel packed column (ethane, propane, etc.) to the detector without passing them through the Molecular Sieve packed column. At the same time, the Silica gel packed column temperature was ramped to promote the rapid elution of the remaining components. The Multiple Gas Analyzer with a TCD detector provides analyses in the 250 ppm to 100% range for fixed and natural gases.

Each gas sample was tested 3 times. The CO_2 gas obtained from crambe at 450 °C deviated by 0.78% while rest were below 0.5%. The maximum variance of 0.05% was observed again in CO_2. At 550 °C, highest deviated value was 0.17% in methane and the corresponding variance representing the largest value was 0.029%.

Similarly, the tests performed in gases obtained from meadowfoam pyrolysis at 450 °C had CO_2 with the overall high standard deviation having value of 0.41%, the maximum variance of 0.17% was observed for the same compound. Gas obtained at 550 °C was analysed and the standard deviation and variance were par below 0.4% and 0.16% respectively.

3.1.3.2 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere. This analysis was performed on a TGA instrument (TA Instruments TGA Q500, USA) under two different conditions: a) under dry air and b) under nitrogen up to 1000 °C using a heating rate of 10 °C per min. The TA Instrument TGA Q500 had a weighing precision of +/- 0.01% and sensitivity of 0.1 µg.

About 20 mg of each sample of crambe and meadowfoam oil cakes were placed in a standard platinum crucible. For dry air tests, oxygen flow rate was set at 50 ml per min while the nitrogen flow rate was kept at 50 ml per min for TGA test in a nitrogen environment.

3.1.3.3 Proximate, ultimate and heating value analyses

Raw and biochar were analyzed by a Flash 2000 CHNS-O Analyser and by bomb calorimeter (Parr 6100 Calorimeter, USA). The chromatography column of CHNS Analyser connected to highly sensitive thermal conductivity detector ensures wide detection range from 100 ppm to 100%. Calorimeter is calibrated with the relative Standard Deviation of 0.0982% with 10 times the standard sample run.

The proximate analyses of oilcake and biochar samples were performed using standard procedures i.e., ASTM D3174-12 for ash analysis [102] and ASTM D3175-11 for the volatile matter [103].

The elemental analysis experiments were repeated six times for each substance. The hydrogen in the crambe char obtained at 450 °C had maximum standard deviation (S.D.)

of 1.07% and maximum variance of 1.155 while deviation for others were below 1%. Similarly, the maximum S.D. of 1.88 and variance of 3.54 was observed in carbon in biochar collected at 550 °C. In case of meadowfoam oilcake pyrolysis, the elements in char samples at 450 °C and 550 °C had S.D. and variance well below 1%.

For energy value calculation in bomb calorimeter, the actual sample tests were repeated thrice and 0.65MJ/kg of maximum standard deviation value was observed while analysing crambe char at 550 °C.

3.1.3.4 Analysis of biooil

Flash 2000 CHNS-O Analyser was used to perform the liquid sample analysis. The analysis gave the organic elements C, H, N, S, and O (from difference) percentage. The net heating value (NHV) and higher heating value (GHV) of liquid samples in kilocalorie per kilogram were also found from the same equipment.

3.1.3.5 Wastewater analysis (Solid concentration and turbidity)

This preliminary work was conducted to understand the novel approach of using biochar in wastewater treatment. At first, 50 ml of wastewater sample was taken in a beaker. Biochar from above pyrolysis experiment at 450 °C for crambe was added on top of the wastewater in the beaker. Initially, the biochar floated on the water but slowly a phenomenon of flocculation was observed between the biochar and solid in wastewater. The samples were kept at the room temperature for 24 hours. Two distinct zones were detected, on the top was clear water and below solid with biochar. The clear water sample was removed using a pipette. To calculate the solid concentration, 20 ml of water sample was transferred to the beaker. The water sample was filtered using 0.45-micron filter paper. The filter paper was placed in a crucible and weighted. The filter paper was kept inside the oven at 103 °C to remove the moisture. The difference between the weight of the filter paper and the dried sample gave the total suspended solids. The filtered water was dried at 103 °C and the weight difference before and after drying beaker gave total dissolved solids. The sum of dissolved and suspended solids gave the total solids in the water sample. The turbidity of the water sample was measured using Turbidity Meter (Hach 2100Q Handheld Turbidity Meter, USA). The instrument was calibrated for better accuracy.

3.2 Materials and method for biocomposite study

3.2.1 Feedstock

Spruce wood pellets were purchased from local retail shop and used as feedstock. A 17 oz non-woven E-glass fabric, two layers ±45° fiber orientation, held together by a light stitching glass fiber tape (727-10), C105-B Epoxy Resin and a fast hardener compatible for fiber glass (C205-B) was purchased from the Marine Source, a local supplier.

3.2.2 Experimental method for biocomposite preparation

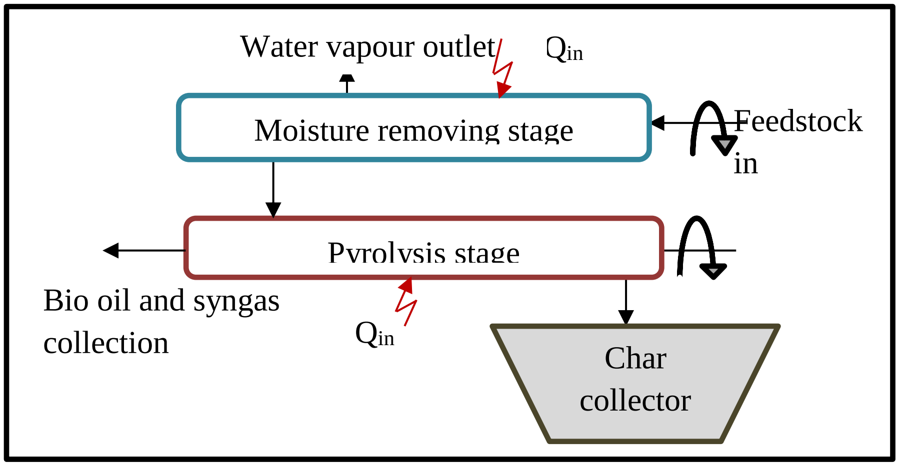


Figure 3.1: Schematic diagram of double-stage pyrolysis working principle

Feedstock was fed into the upper drum heated at 150 °C through screw feed system. The optimized motor speed and slanting of the drum made sure that the biomass remained inside the reactor for 30 minutes before it was expelled to the pyrolyzer drum through a connector channel connected to the other end. The water vapour was ejected to the atmosphere from the upper left top port. The pyrolyzer drum was heated and maintained to 400 °C. A continuous adjusted shaft rotation and fixed slanting of the rotating bed kept the dried biomass in pyrolysing stage for 30 minutes. The syngas was expelled through the left end and the biochar was collected through the outlet on the other end as shown in the schematic diagram above.

3.2.3 Blend preparation

All the blends were prepared by mixing in a calculated volume proportion in a beaker. A ratio of 5:1 was maintained in between epoxy resin and hardener. Filler additives at various proportions were added to the resin and the mixture was stirred at 2000 rpm for 2 minutes. The prepared solution in addition to the hardener was poured onto the glassfibre mat.

3.2.4 Composites preparation

Three distinguished sets of composite materials are prepared with various proportion of filler additives (biochar). In each sample, 58% wt. epoxy was maintained. The poured mixture over the rectangular biaxial 727-10 glassfibre mat was processed by hand layup vacuum infusion technique to evenly distribute the solution over and into the mat and to remove the surplus resin.

Table 3.2: Different samples with altered biochar composition (% by weight of epoxy)

Sample No.	*Percentage of Biochar*	*Percentage of Epoxy*
Sample 1	0	58
Sample 2	5	58
Sample 3	10	58

The composites were cured subjected to the vacuum pressure for 12 hours and then left them to cure for 36 hours. The obtained composites samples were cut into the required sample sizes for testing and analysis purpose.

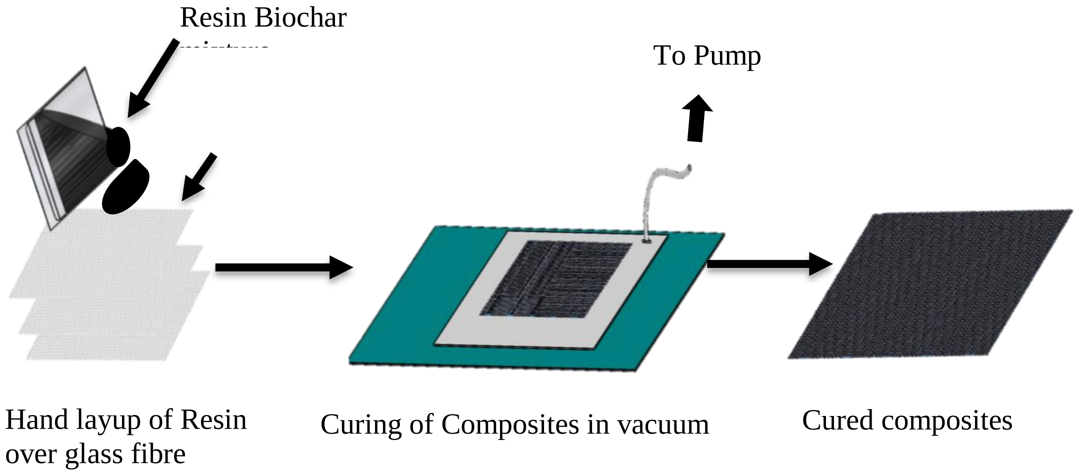


Figure 3.2: Schematic diagram of the composite preparation technique.

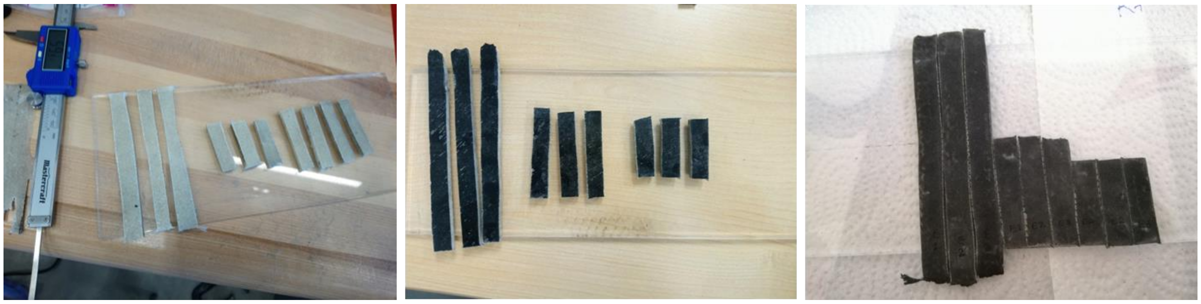


Figure 3.3: Specimen of GFRP without biochar (left), with 10% biochar (middle) & 5% biochar (right).

3.2.5 Characterization

3.2.5.1 Scanning electron microscopy

The morphology of the composites was examined using scanning electron microscope (SEM) (JEOL 6400, USA) utilizing secondary electron (SE) and backscattered electron (BSE) modes.

3.2.5.2 Thermogravimetric analysis

The thermal stability of the composites (in powdered form) was analyzed by thermogravimetric (TG) studies. The analyses were carried in TA instruments Q500 thermal analyzer. The measurements were performed on 6 to 10 mg of the samples from room temperature to 900 °C in nitrogen atmosphere. The heating rate was 5 °C/min.

3.2.5.3 Dynamic mechanical analysis (DMA)

The viscoelastic properties of all composites samples were measured using TA instruments TAQ-800, dynamic mechanical analyzer.

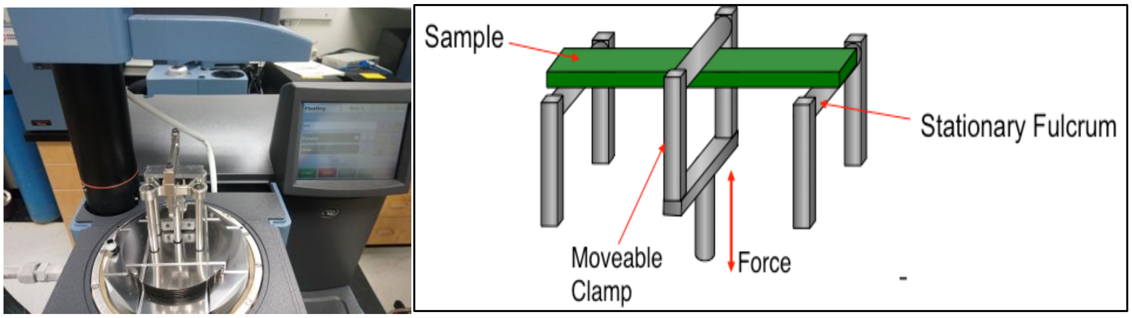


Figure 3.4: TA Q800 in action for three-point bending test (left) and schematic diagram for the three-point bending test setup (right)

Rectangular specimens of Size (15.0000 mm by 11.2233 mm by 3.5767 mm for Resin & Glassfibre composites), (15.0000 mm by 12.2167 mm by 3.8100 mm for composites with

5 % biochar) and (15.0000 mm 12.9233 mm 3.3200 mm for composites with 10% biochar) were used for the analysis. The analyses were done in three-point bending clamp at a frequency of 1 Hz. The samples were heated from 30 °C to 175 °C at a heating rate of 3 °C/min.

3.2.5.4 Flame test

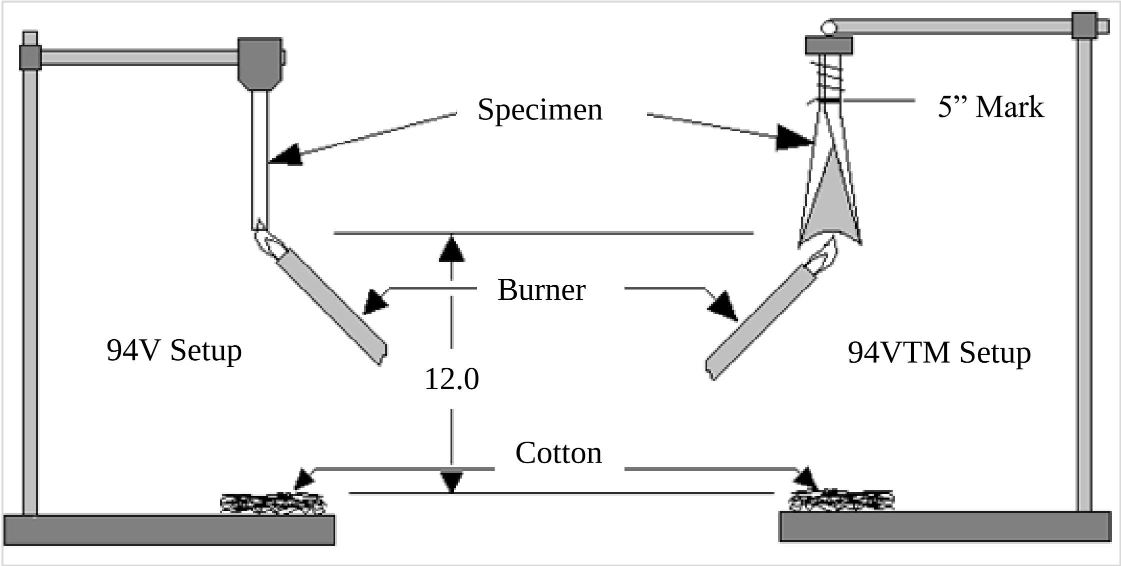


Figure 3.5: Schematic of vertical burning test for 94V and 94VTM classifications

UL94 vertical Flame Test was performed with reduced exposure time. A set of 5 specimens were subjected to a 20mm flame in accordance with the prescribed test procedures. After the flame is removed from the specimen, after-flame and afterglow times were measured. If flaming particles or drops fall from the specimen to a piece of surgical cotton which was placed below, it was noted whether the cotton ignited.

Table 3.3: Criteria conditions for vertical burning tests

Criteria Conditions	*94V-0*	*94V-1*	*94V-2*
Total flaming combustion for each specimen	≤ 10 sec	≤ 30 sec	≤ 30 sec
Total flaming combustion for all 5 specimens of any set	≤ 50 sec	≤ 250 sec	≤ 250 sec
Flaming and glowing combustion for each specimen after second burner flame application	≤ 30 sec	≤ 60 sec	≤ 60 sec
Cotton ignited by flaming drips from any specimen	NO	NO	YES
Glowing or flaming combustion of any specimen to holding clamp	NO	NO	NO

Chapter 4

Results and Discussion

The result and discussion chapter are divided into two sections: first will discuss the results obtained from the pyrolysis study of meadowfoam and crambe along with preliminary investigation for using biochar on treating wastewater. The following section will discuss the results for the biocomposite using biochar as a filler material.

4.1 Products yield

The percentage of products from the pyrolysis of crambe and meadowfoam oilcake at 450 °C and 550 °C is shown in Table 4.1. Solid yield from pyrolysis of crambe at 450 °C was 28.62%, which was slightly lower than the pyrolysis of meadowfoam oilcake (35.21%).

Table 4.1: Products yield from pyrolysis at 450 °C and 550 °C

	Crambe		*Meadowfoam*	
Products	*450 °C*	*550 °C*	*450 °C*	*550 °C*
Solid (%)	28.62	26.65	35.21	31.09
Liquid (%)	59.66	61.27	49.8	56.95
Gas (%)	11.72	12.08	14.99	11.96

During the process, higher liquid yield was observed in crambe as compared to meadowfoam. The solid yield decreased with an increase in pyrolysis temperature for both feedstocks, while liquid yield increased during the same change in temperature. In a similar slow pyrolysis process of wood, straw, green wastes and algae, raw biochar yield was seen to decrease with the intensity of the pyrolysis process (i.e. residence time and highest treatment temperature). The volatile matter content of the produced biochar decreased with pyrolysis temperature, whereas ash and fixed carbon contents increased [104-106].

4.2 Analysis of solid products

Proximate, ultimate and heating value analysis of the solid product is presented in Table 4.2 below.

Table 4.2: Analytical results of the solid product from oilcakes pyrolysis

	Crambe Char		*Meadowfoam Char*	
Pyrolysis Temperature (°C)	*450*	*550*	*450*	*550*
Proximate Analysis (wt.%)				
Moisture Content	1.74	0.97	1.66	1.44
Volatile Matter	18.45	17.51	24.59	18.50
Ash	18.68	21.35	22.22	24.13
Fixed Carbon	61.13	60.17	51.52	55.94
Ultimate Analysis (wt.%)				
C	60.74	66.1	61.52	62.87
H	2.01	2.84	2.82	1.98
N	5.97	6.57	5.35	4.76
S	0.04	0.6	0.17	0.12
O	31.24	23.89	30.14	30.27
Bomb Calorimeter				
Gross HHV (MJ/Kg)	24.45	23.10	23.20	23.17

Results from the proximate analysis showed fixed carbon in crambe oilcake increased from 7.45% to 61.13% in biochar, and from 9.51% in meadowfoam oilcake to 51.52% in resulting biochar. A heating value for the solid product was in the order of 24 MJ/kg for both crambe and meadowfoam, which was close to the heating value of low-quality coal. Thus, crambe and meadowfoam biochar can be used to produce energy for replacing fossil fuel. However, higher ash content could be a problem that might lead to fouling and corrosion of heat exchanger tubes.

The ultimate analysis of biochar samples from different temperature pyrolysis of crambe oilcake showed that the carbon content in biochar increased when the process temperature was raised. Traces of sulfur were observed in biochars obtained at both the temperatures. Nitrogen was observed to be present in about same quantity (5.97 and 6.57 percent at 450 °C and 550 °C respectively). 2.01% and 2.84% hydrogen were detected in biochar obtained at 450 °C and 550 °C, respectively.

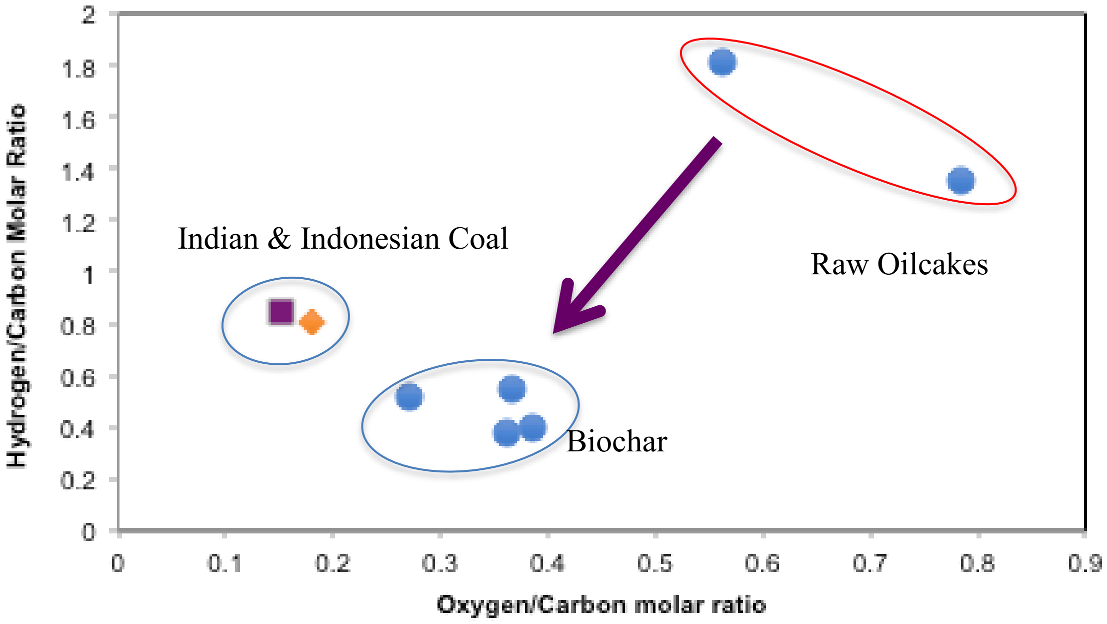


Figure 4.1: Van Krevelen diagram (H:C vs. O:C ratio) of the solid samples

The Van Krevelen diagram shown in figure 4.1 confirms the improvement in energy value and applicability of biochar as a replacement of certain coals. This is because of the reduction of H/C and O/C ratio in in them as compared to the raw samples.

4.3 Analysis of liquid products

The ultimate analysis of biooils from the pyrolysis of the crambe and meadowfoam oilcakes at 450 °C and 550 °C is presented in Table 4.3. The liquids collected, after drying the sample by heating at 120 °C for an hour, during the pyrolysis process were used as samples for further analyses.

Table 4.3: Ultimate analysis of biooils from pyrolysis of oilcakes in percentage

	Crambe		*Meadowfoam*	
Temperature (°C)	*450*	*550*	*450*	*550*
Nitrogen	5.37	5.58	5.75	5.58
Carbon	64.58	67.34	70.86	73.02
Hydrogen	10.7	10.17	9.98	9.96
Sulphur	0.27	0.33	0.42	0.54
Oxygen	19.08	16.58	12.99	10.9
HHV (MJ/kg)	37.59	37.77	38.71	39.45

The elemental analysis of biooil obtained by pyrolyzing crambe oil cake at 450 °C showed 64.58% of carbon and the percentage went up to 67.34% at 550 °C. Hydrogen composition was found to be about 10% at both the temperatures. Traces of sulfur (0.27% and 0.33%) were observed in samples at consecutive temperatures. Similarly, biooil from meadowfoam oilcake pyrolysis contained 70.86% of carbon at 450 °C, which slightly increased (73.02%) at 550 °C. Hydrogen was again averaged to about 10% for both the liquid samples at all temperatures. The changes in pyrolysis temperature did not alter the sulfur content whose value was marginal (0.42% and 0.54%). Both feedstocks yielded liquid containing about 5.5% nitrogen. Oxygen was calculated from the difference.

Liquid sample from crambe pyrolysis at 450 °C contained higher oxygen concentration (19.08%). The value was 16.58% in from Crambe at 550 °C. Similarly, 10 to 15 % of oxygen was observed in biooil samples from the meadowfoam oilcake pyrolysis at both the temperatures. The results from ultimate analysis of biooil from crambe and meadowfoam showed similarity in elemental compositions of biooil obtained from pyrolysis of rapeseed oilcake [107, 108]. The gross heating value GHV of the biooil samples were obtained from CHNS Analyser.

The HHV of crambe biooil was found to be 37.59 MJ/kg and 37.77 MJ/kg at 450 °C and 550 °C respectively. Similarly, the heating value of biooil at 450 °C and 550 °C was 38.71 MJ/kg and 39.45 MJ/kg for meadowfoam. In a similar study, rapeseed pyrolysis at 450 °C showed 33 MJ/kg [106], and 36.4 MJ/kg when pyrolyzed at 500 °C [109].

4.4 Analysis of gas

The composition of gas collected during pyrolysis of crambe and meadowfoam are shown in Table 4.4 below. The results showed that the gas consists of mainly carbon dioxide (CO_2) along with carbon monoxide (CO) and methane (CH_4) and a small fraction of ethane and ethene with other gases unidentified by gas chromatography. With an increase in temperature, an increase in CO concentration was observed with decrease in CO_2 concentration. The origin of CO_2 was mainly because of decomposition of cellulose–hemicellulose. The CO was mainly formed from secondary cracking of volatiles and by a reduction of CO_2 ($C + CO_2 = 2CO$) [75, 108, 110]. Low gas yield and a high percentage of

CO_2 resulted in low energy value in gas; however chemical energy with CO, methane and higher hydrocarbon can be used to provide the energy needed for the pyrolysis process.

Table 4.4: Composition of gas collected from pyrolysis of oilcakes in percentage

	Crambe		*Meadowfoam*	
Compounds	*450 °C*	*550 °C*	*450 °C*	*550 °C*
CH_4	7.67	7.15	9.39	11.25
CO	10.17	15.54	7.99	18.85
C_2H_6	3.32	3.44	2.26	2.96
CO_2	62.93	51.04	74.41	64.25
C_2H_4	3.26	3.62	1.92	1.99
Other gases	12.64	19.20	4.02	0.68

4.5 Thermal decomposition of oilcakes

The TGA results of crambe and meadowfoam in presence of air and nitrogen are shown in Figure 4.2. The TGA analysis for crambe oilcake samples in presence of air showed three major weight loss steps, generally observed in biomass oxidation during TGA experimentation (Fig. 4.1), which agreed with other authors Cao et al. [111], Ucar and Ozkan [107] and Duman et al. [112]. The first change in slope was observed around 175 °C, which was marked by the start of the release of volatiles and its subsequent oxidation. The weight loss below 175 °C was caused by moisture loss. The second change occurred around 520 °C, which represented the oxidation of biochar. The sharp slope during biochar oxidation phase suggested its higher reactivity, which makes it a better fuel for energy generation. A similar trend was observed from TGA analysis of meadowfoam oilcakes in presence of air.

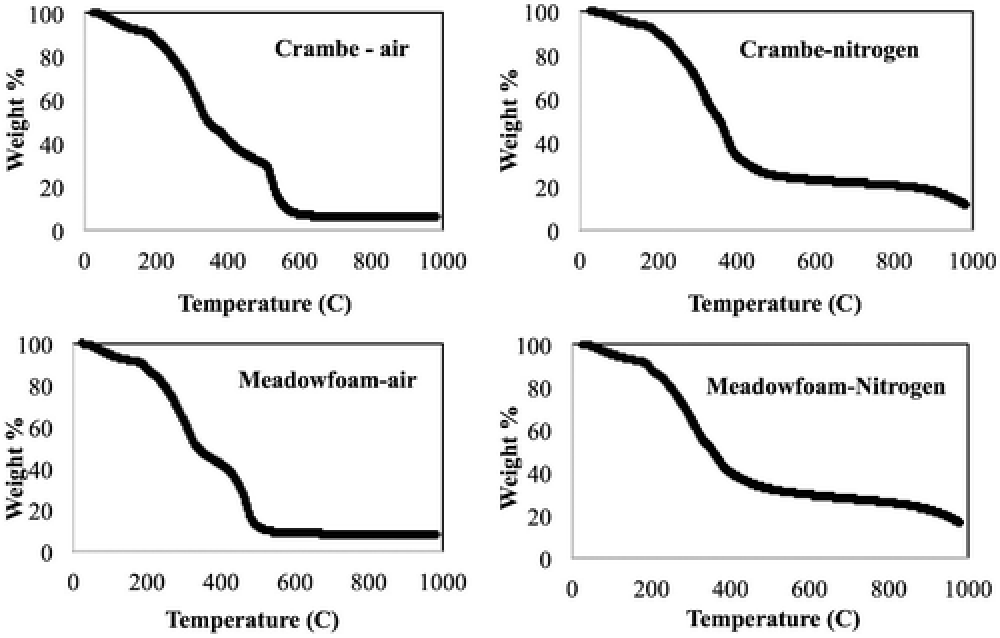


Figure 4.2: TGA of crambe and meadowfoam under air and nitrogen

TGA analysis in nitrogen environment was carried out to determine the pyrolysis temperature for enhancing the biochar yield. The TGA analysis of crambe and meadowfoam oilcake in nitrogen environment showed the three-step process as follows moisture loss, the release of volatiles, and slight weight loss due to volatile release at a higher temperature. As seen from TGA analysis, around 400-550 °C, most of the volatiles were released, leaving solid biochar and ash. This was the main reason for selecting 450 °C and 550 °C for pyrolysis process. The yield of biochar, volatiles, and gas obtained from pyrolysis experiments represented in Table 4.1 resembled very well with solid yield shown by TGA analysis. In a similar TGA analysis of the crambe [111], 7.16% moisture, 73.36 % of the volatile matter in dry mass and 17.69% fixed carbon in dry mass was reported. The results were very similar to the findings of the current study.

4.6 Wastewater treatment: Biochar is a potential remedy

The distribution of total suspended and dissolved solids in the raw wastewater and the water sample after char treatment is shown in Figure 4.3. As compared to raw wastewater, the total solid concentration was lower in the water sample after biochar treatment. Total suspended solid was reduced by 94% as compared to the raw wastewater. The flocculation between the biochar and the suspended solid in the wastewater resulted in the settling of the suspended solids, leaving very low suspended solids in water. However, higher dissolved solids were observed in water treated with biochar. The probable reason could be the dissolution of alkali minerals present in biochar. The char from crambe was high in ash content and it is possible that some of the alkali content dissolved in water to increase total dissolved solids. Further investigation needs to be performed.

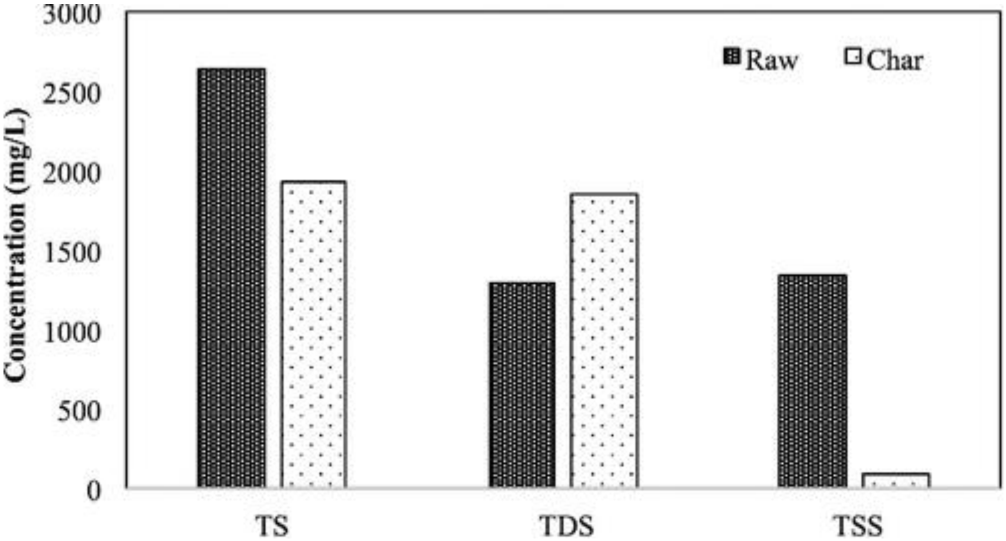


Figure 4.3: Solid concentration in water sample before and after biochar treatment

The measured turbidity was 1798 NTU for raw wastewater sample, which reduced to 50 NTU after treatment with biochar. Furthermore, the foul odour was eliminated after biochar treatment of the wastewater. These are some preliminary observation with high significance to an agro-processing industry in PEI, especially those, which uses a large amount of fresh water. Results obtained would allow the industry to recycle treated water for processing, reducing the consumption of freshwater, and ensuring sustainability of their process.

The following section discusses the results obtained from the study of using biochar as a filler material in a composite. SEM analysis is followed by TGA, DMA and fire-retardant analysis to study the thermal and mechanical properties of resulting biocomposite material.

4.7 Scanning electron microscopy (SEM) analysis

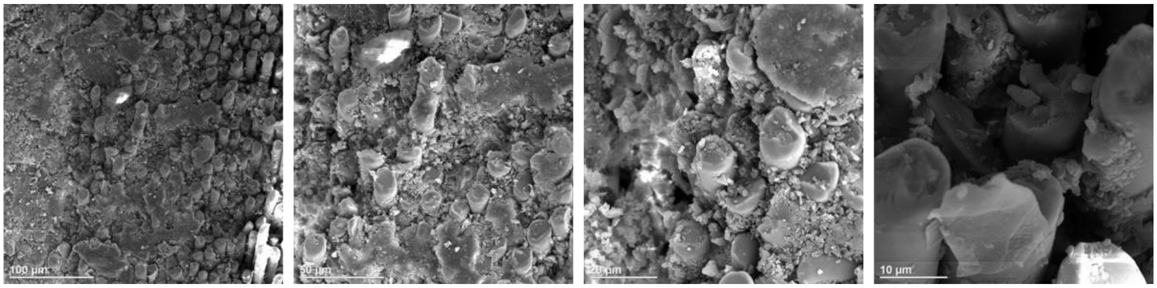


Figure 4.4 (a) SEM images of AC10 (100 μm, 50 μm, 20 μm and 10 μm respectively).

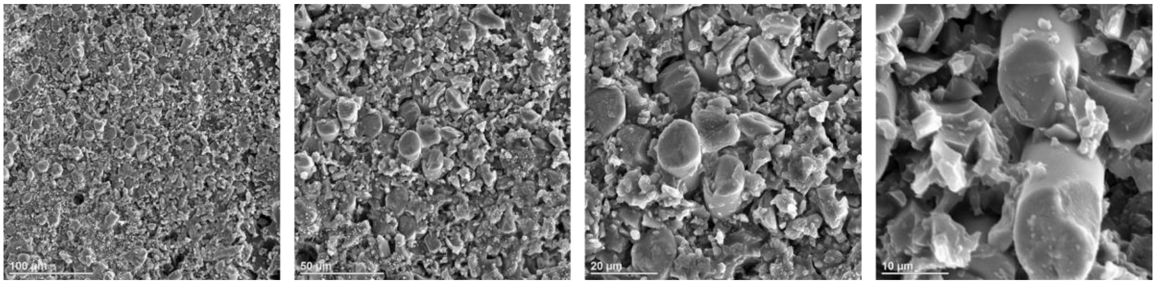


Figure 4.4 (b) SEM images of AC5 (100 μm, 50 μm, 20 μm and 10 μm respectively).

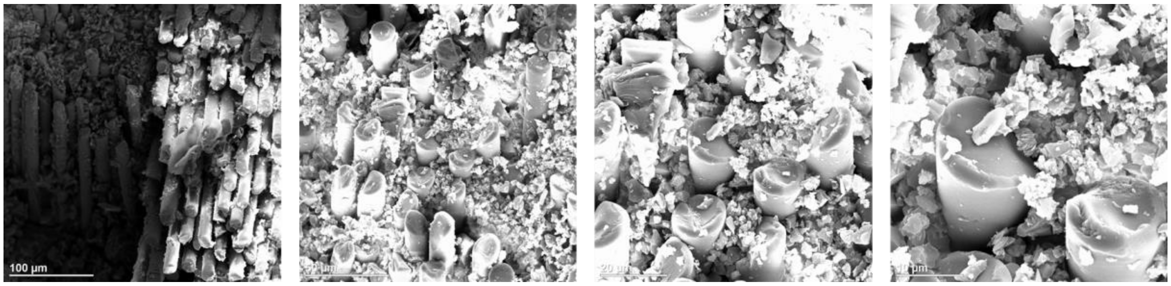


Figure 4.4 (c) SEM images of BC5 (100 µm, 50 µm, 20 µm and 10 µm respectively).

(**Note:** AC10 represents Glassfibre Reinforced Polymer (GFRP) with 10% Activated carbon, AC5 is GFRP with 5% Activated carbon, BC10 is GFRP with 10% biochar, BC5 is GFRP with 5% biochar.)

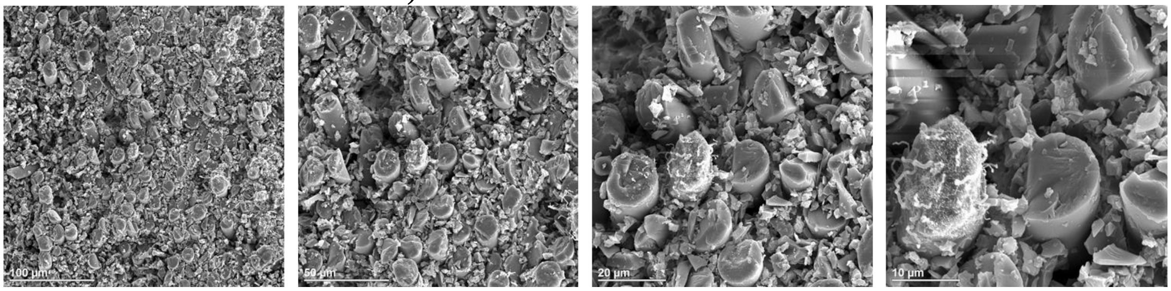


Figure 4.4 (d) SEM images of BC10 (100 µm, 50 µm, 20 µm and 10 µm respectively).

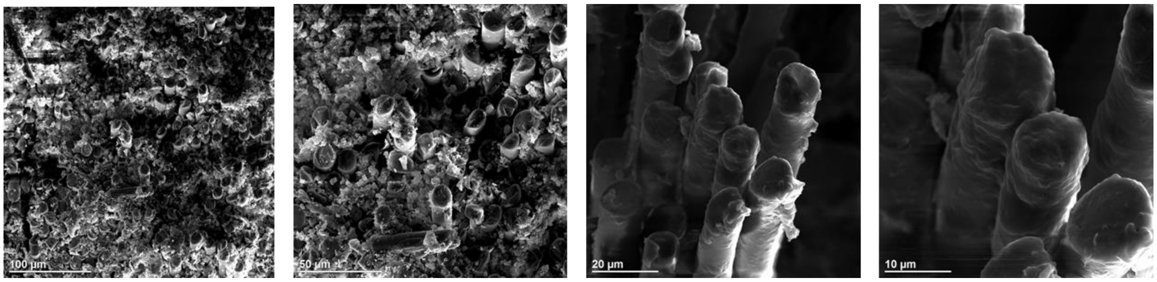


Figure 4.4 (e) SEM images of GFRP (100 µm, 50 µm, 20 µm and 10 µm respectively).

Figures in 4.4 (a, b, c, d) show that the scanning electron microscopy (SEM) images of the fabricated composite structures, including activated charcoal- reinforced (10 vol.% and 5 vol.%; AC10 and AC5), and in-house pyrolysed biochar-reinforced (10 vol.% and 5 vol.%; BC10 and BC5), respectively. It is noted that the micrographs were taken across the depth of the structures. In all four samples the presence of glass fiber, reinforcing particles, and polymer matrix is evident; however, looking at the high-resolution images, it is clear that BC10 provides a higher ductility in the structure. This is important as the evidence of ductility is a sign of high mechanical interlocking of micron-scale char in the polymer molecular chain, conforming the observation made by Bowlby et. al. [113]. Comparing 4.4 (e) with the above, the long fibers are in random orientation, which when devoid of mean free path between the neighboring fibers can lead to premature fiber breakage and ultimate failure.

4.8 Thermogravimetric analysis of the composites

As shown in figure 4.5 and 4.6 below, the initial weight loss at around 100 °C is because of the evaporation of the moisture present in the sample. The second weight loss occurred in the temperature range of 265-275 °C. In case of resin and glass fiber composites, this mass loss is because of the oxidation of resin while in case of biochar additives, additional oxidation of biochar results in higher weight loss per degree centigrade rise in temperature as shown in figure 4.6. The oxidation of resin continues until 515 °C where another peak is observed in derivative weight loss curve. During the same course, the higher peak for BC10 sample can be explained due to the additional oxidation of the biochar in the composites. More importantly, the major degradation of composites with filler additives is shifted slightly towards the higher temperature. This explains a better thermal stability of doped composites. More than 40% residue in all samples is due to the presence of thermally stable glassfibre.

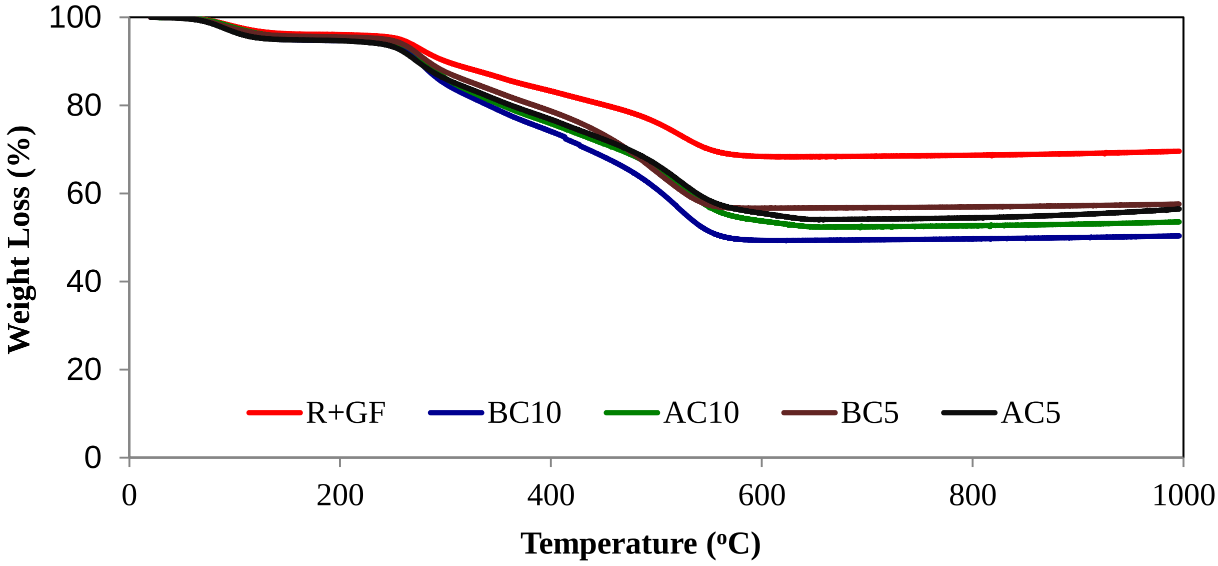


Figure 4.5: TGA thermal decomposition of the composites with temperature.

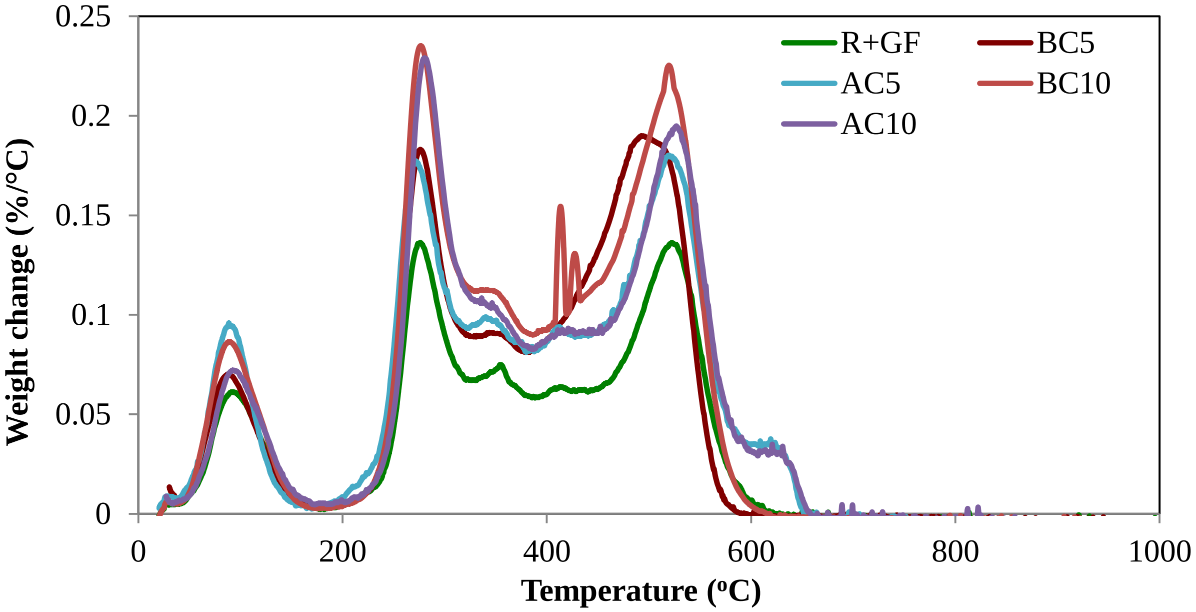


Figure 4.6: TGA (DTG) results of various composites

4.9 Dynamic mechanical behaviour of the composites samples

Fiber loading, their orientation, nature of fiber-resin bonding interface, nature of filler materials (compatibility) determines the dynamic mechanical properties of the fibre-reinforced composites. DMA analysis of the biochar-based composite material is carried out to study the transitions occurring and mechanical properties, especially the viscoelastic behaviour of the composites over a spectrum of temperature. The viscoelastic behaviour represented by the variation of storage modulus, loss modulus and loss factor (tan delta) as functions of temperature helps to understand the interfacial bonding between the reinforcement fibers (glass fibers), polymer matrix, and filler material (biochar).

4.9.1 Dynamic storage modulus (E')

Figure 4.7 shows the variation of the storage modulus of the composites material with temperature, which indicates the stiffness of the composite material. The storage moduli curves were seen to follow similar pattern, decreasing down to minimum after certain temperature. The composites sample with 10% biochar (BC10) and with 10% activated charcoal (AC10) showed an increase in storage modulus while for the composites samples with the 5% biochar (BC5) and the 5% activated charcoal (AC5), the modulus were lower compared to that of the composites with no added filler material. A 36% and a 28.5% increase in storage modulus were obtained in AC10 and BC10 respectively. Increase in storage modulus with higher char concentration is attributed to the higher dispersion of resin. This may also be due to the improvement in the stiffness of the matrix due to the reinforcement effect caused by the fillers that transferred stress at the interface as suggested by Hameed N et al. 2007 and Joseph PV et al. 2003 [113, 115].

The lower storage modulus in BC5 as compared to that of R+GF composites suggests formation of agglomerates and void around filler materials. The viscosity of the resin and char mixture as well as the method implemented to make composites can be the reason for such effect.

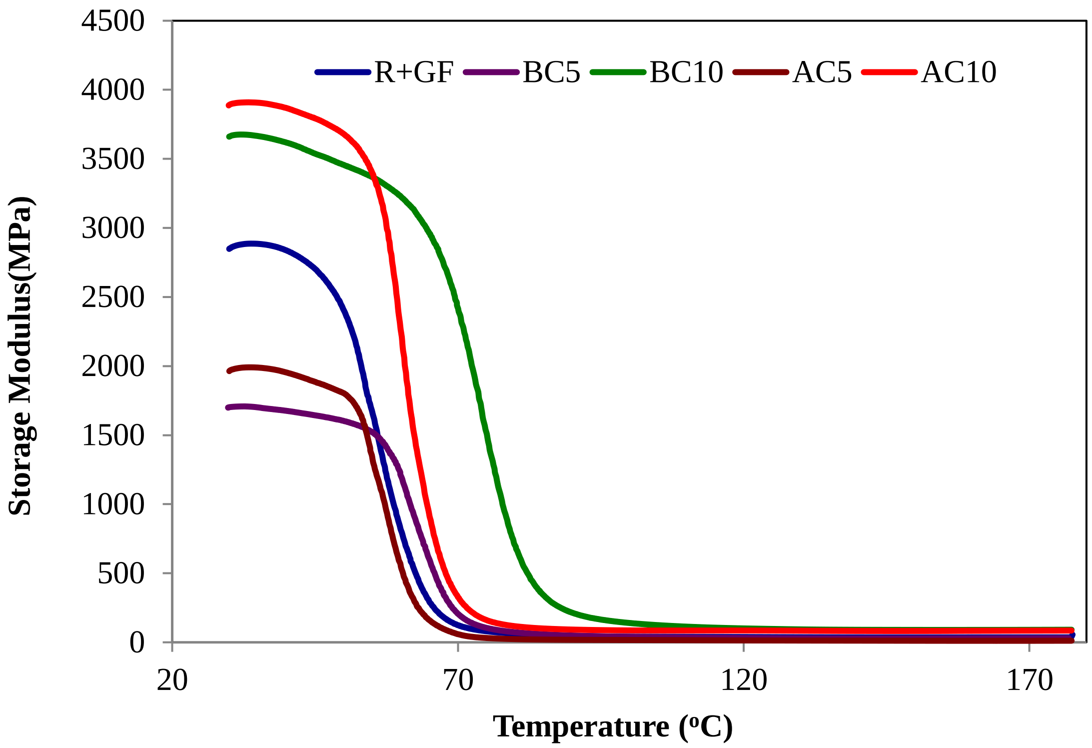


Figure 4.7: Change in storage modulus of composites as a function of temperature.

In general trend, it is observed that the storage modulus gradually decreases with increase in temperature until the temperature reaches the glass transition point where a sharp drop is observed. This drop represents the transition from the glassy state to the rubbery state. This transition is caused due to the increase in the molecular activity of the polymer chains at and above transition temperature [114]. Storage modulus in general depends on the content of the filler material, dispersion and the interfacial bonding and this explains for the storage modulus to be higher in composites samples with fillers. Higher surface area of biochar provides better dispersion of polymer matrix, resulting in stronger interfacial bonding and higher storage modulus. Higher percentage of biochar improves the dispersion resulting in higher storage modulus for 10% biochar as compared to the composite with 5% biochar. Also, for 10% char addition; the glass transition temperature is shifted towards higher temperature. This shifting is due to the displacement of resin having lower glass transition temperature with thermally stable biochar in the composites.

4.9.2 Loss modulus (E”)

Loss modulus is defined as the measure of energy dissipated as heat per cycle under deformation. The pattern of loss modulus in various composite as a function of temperature is illustrated in figure 4.8 below. The trend of all curves convinces that the loss moduli increase from room temperature to their maximum when the temperature reaches the glass transition temperature. Here, the higher molecular activity and significant deformation contributes to the rise in the loss moduli of the composites.

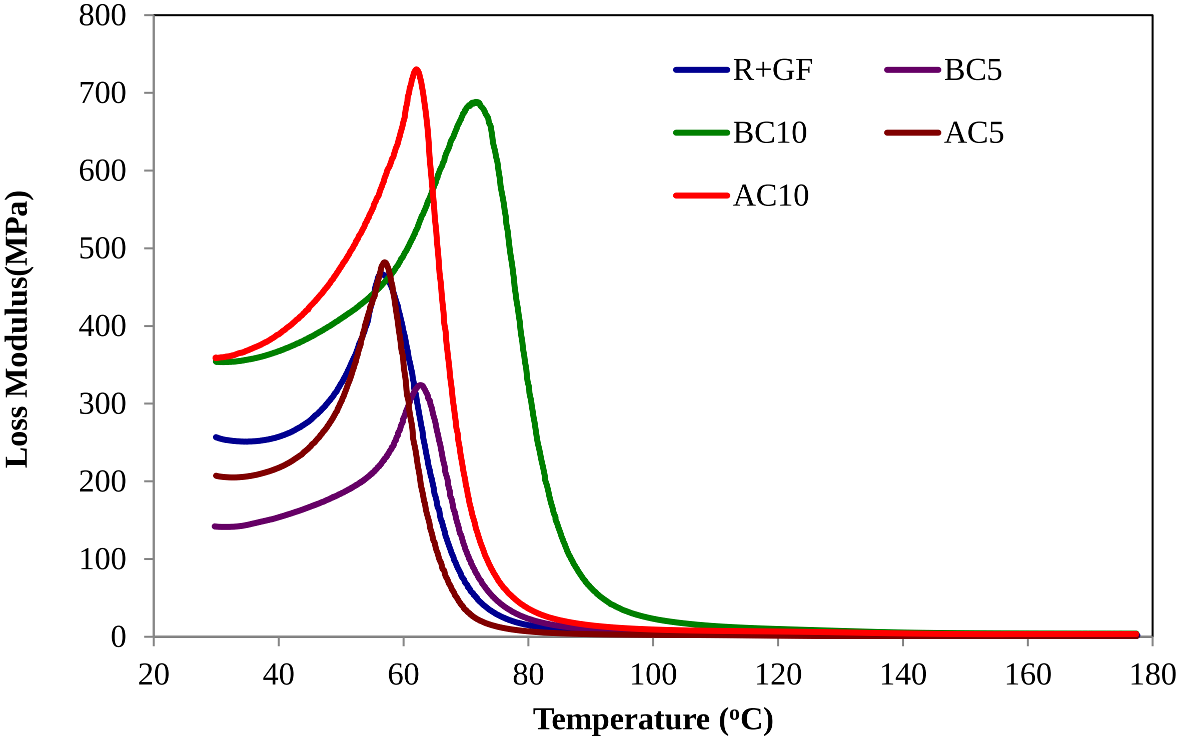


Figure 4.8: Change in loss modulus of the composites as a function of temperature.

Furthermore, the loss modulus in that transition region is comparatively higher for BC10 composite, which could be due to increase in the internal friction promoting energy dissipation [114]. It can also be attributed due to presence of voids and the stress transfer to the additives in the resin-fiber transition during the course. High modulus resulting filler compositions (AC10 and BC10) constrain on the segmental mobility of polymeric molecules at the relaxation temperature leading to higher loss modulus values. The higher peaks in case of BC10 and AC10 is due to the massive filler doping of the composites. A poorly compatible additive in high concentrations results to reduction in mechanical properties in polymer matrices [116, 117].

4.9.3 Loss Factor (Tan δ)

The loss factor is a damping property that shows a balance between the elastic and viscous phases in polymeric materials. Loss factor (also called Tan δ) is the ratio of E” to E’.

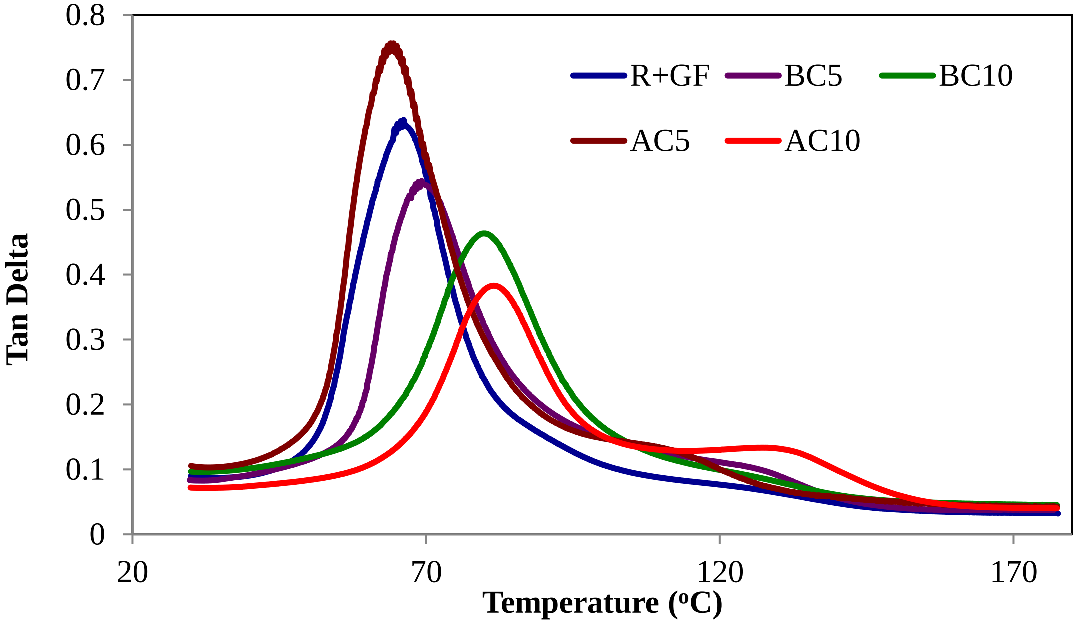


Figure 4.9: Loss factor of various composites as a function of temperature.

The curves shown in figure 4.9 demonstrate the energy dissipated, calculated in terms of the recoverable energy, and it shows mechanical damping or internal loss (friction) in any viscoelastic system [118].

Because below glass transition temperature, the deformation is elastic in nature and the polymer molecules are free to move, this resulted in lower damping over that region. The gradual rise in loss factor with the increase in temperature up to the glass transition temperature is due to damping upsurge caused by the relaxation process. The higher energy dissipation takes place in the relaxation process resulting in higher damping values. Damping is affected by the distribution of fiber, fiber/matrix interaction and formation of void. Among the Tan delta curves, the lowest peak indicates good interfacial adhesion between the matrix and reinforcement, which is seen to obtain in case of BC10 composites. Tan delta values are higher for BC5 as compared to BC10 composites, which indicates a possibility of poorer interface between the char and the polymeric matrix, higher inclusion of void and improper distribution of fiber in the former case.

4.10 Flame-retardant property of the composites

Table 4.5 and Table 4.6 shows the results of fire-retardant test conducted on the composite samples following the modified UL94 vertical flame test. The difference between the two tables is the initial flame exposure time. The results in table 8 shows the after-flame time obtained when exposed to 20mm flame for 10 second while Table 9 shows the results for 5 second flame exposure. According to the UL94 test, the material fails all three vertical tests (94V-0, 94V-1, 94V-2) if total flaming and glowing combustion time for each sample after second flame application is more than 60 seconds.

Table 4.5: UL94 with 10 seconds flame exposure

Sample	*R + GF*	*BC 5%*	*BC 10%*	*AC 5%*	*AC 10%*
After-flame time (Sec)	190	180	210	195	200

As can be seen from table 4.5, when the exposure time was set for 10 seconds, the after-flame time for each sample was higher than 60 sec and hence, each of the composites is categorized as flammable. However, comparing the after-flame and glow times, it was higher for the composites with biochar 10%, which was even higher in the composites with 10% activated carbon. Since activated charcoal is more reactive, it will result in faster oxidation as compared to biochar. Therefore, another set of tests were carried out with 5 seconds flame exposure only on biochar-based composites samples mimicking the UL94 tests. The results are presented in Table 4.6.

Table 4.6: Modified UL94 test with 5 seconds flame exposure

Sample	*R + GF*	*BC 5%*	*BC 10%*
After flame time for specimen (Sec)	10	10.6	8.1
After flame plus afterglow time for each individual specimen after the second flame application (sec)	70.1	154	271.3

In case of modified test, with 5 sec exposure of flame the fire extinguished after 10, 10.6 and 8.1 sec in composites without filler, with 5% and 10% biochar respectively. The sample was again exposed to 10sec after the first flame died. The flame took 70, 154 and 271.3 sec for composites without filler, with 5% and 10% biochar samples respectively to die. The modified test clearly shows that if the concentration of biochar is increased in the composite, it will help to retard the fire. It is recommended that future work should be carried out with higher biochar concentration.

Chapter 5

Conclusions

1) The pyrolysis study of the crambe and meadowfoam oil cakes was carried out at 450 °C and 550 °C. Biochars obtained from these feedstocks were found to have a higher carbon content between 60% – 66% with heating value in the range of 24 MJ/kg. Biochar can be used as energy source to replace fossil fuel in heating applications.
2) Biochar application for wastewater treatment showed 94% reduction in total suspended solid and 97% reduction in turbidity with removal of foul smell. However, the dissolved solids were found to be higher in the treated water.
3) The liquid biooil was found to have a heating value in the range of 37 MJ/kg. This biooil can be used as fuel for energy application, or further refined to produce transportation fuels.
4) Gas produced during pyrolysis can be used to provide heat for auto-thermal operation of pyrolysis system.
5) By utilizing the waste from one agro-processing industry to solve wastewater issues in another with by-product going into soil application, a circular bio-economy has been established with new product and process developments and potential for creation of new industry.
6) Higher storage moduli in composites with higher additives concentration was experienced which was due to the reinforcement effect caused by the fillers by transferring stress at the interface. The formation of agglomerates and void around filler materials was the reason for lower storage modulus in BC5 as compared to

that in virgin composites. The higher loss modulus in the glass transition region for BC10 composite was the result due to increase in the internal friction.

7) The elastic deformation zone below glass transition temperature (Tg), where the polymer molecules are free to move, has lower damping. The damping increment due to relaxation process with the temperature rise is responsible for the peaking of loss factor up to Tg. The distribution of fiber, fiber/matrix interaction and formation of void have effect on relaxation process that dissipates higher energy. Greater value of Tan delta suggests a possibility of poorer interface between the char and the polymeric matrix, higher inclusion of void and improper distribution of fiber.
8) The modified flame test suggested that the increased biochar concentration in the composites can help to retard the fire. It is recommended that future work should be carried out with higher biochar concentration.

Chapter 6

Future Works

The results from the research suggest the application of biochar in the field of energy and composites material applications. The study has shows that biochar from agro-processing waste could be used as valuable energy source for replacing fossil fuel. The present study does limited analysis on bio0il properties produced as a by-product during pyrolysis process. The future work can investigate developing ways for improving the quality of biooil to be used as a transportation fuel. This may include identifying and introducing catalysts to upgrade biooil and for biorefinery purpose.

The work on biocomposites showed increase in stiffness, lower damping and fire-retardant properties in composites with higher biochar concentration. However, the work has been done with only up to 10 percent biochar concentration. It is recommended that future work be performed with higher concentration of biochar. Also, future study could look into other applications of biochar in composites such as acoustic properties for its, absorptivity, transmissivity and reflectivity of sound waves. Study on properties of biochar to absorb harmful gases when used in composites as an enclosure can be performed in the future.

References:

1) World energy resources bioenergy. World energy council. 2016. Available at: https://www.worldenergy.org/wp-content/uploads/2017/03/WEResources_Bioenergy_2016.pdf (Accessed on 11 May 2018).

2) Dyer J, Mullen R, Chapman K. Oil in biomass: a step-change for bioenergy production?. American oil chemists' society. 2012. Available at: https://www.aocs.org/stay-informed/read-inform/featured-articles/oil-in-biomass-a-step-change-for-bioenergy-production-april-2012 (Accessed on 27 January 2018).

3) Park Y, Jeon J, Kim S, Kim J. Biooil from rice straw by pyrolysis using fluidized bed and char removal system. fuel. 2004;49(2):801.

4) Ward J, Rasul MG, Bhuiya MMK. Energy recovery from biomass by fast pyrolysis. procedia engineering. 2014; 90:669-674. doi.org/10.1016/j.proeng.2014.11.791.

5) Ramachandran S, Singh SK, Larroche C, Soccol CR, Panday A. Oil cakes and their biotechnological applications—a review. bioresour technol. 2007; 98:2000–2009. doi.org/10.1016/j.biortech.2006.08.002.

6) Karyn L. Glucosinolates. Nutraceuticals: efficacy, safety and toxicity. 2016; 40:551-554. doi.org/10.1016/B978-0-12-802147-7.00040-1.

7) Prince Edward Island's agriculture industry. Agriculture and agri-food Canada. 2012. Available at: http://publications.gc.ca/ (Accessed on 27 January 2018).

8) Khalil HPSA, Aprilia NAS, Bhat AH, Jawaid M, Paridah MT, Rudi D. Jatropha biomass as renewable materials for biocomposites and its applications. Renewable and sustainable energy reviews. 2013; 22:667–685.

9) Biomass at a glance. National energy education development. Available at: http://www.need.org/ (Accessed on 25 February 2018).

10) Available at: http://www.esru.strath.ac.uk/EandE/Web_sites/03-04/biomass/background%20info4.html (Accessed on 25 February 2018).

11) International energy outlook. US Energy Information Administration; 2017.

12) BP energy outlook. British petroleum; 2017.

13) Isikgor FH, Becer CR. Lignocellulosic biomass: A sustainable platform for production of bio-based chemicals and polymers. Polym. chem. 2015; 6:4497-4559

14) Faruk O, Bledzki AK, Fink H-P, Sain M. Biocomposites reinforced with natural fibers: 2000–2010. Prog Polym Sci. 2012; 37:1552–1596.

15) Norashikin MZ, Ibrahim MZ. The potential of natural waste (corn husk) for production of environmental friendly biodegradable film for seedling. World academy of science, engineering & technology. 2009; 34:176.

16) Yuhazri YM, Sihombing H, Razak JA, Mujahid AZA, Balamuragan AG, Nor NM, Shohaimi A. Optimisation of coconut fibers toward heat insulator applications. Global engineers & technologists review. 2011; 1:35-40.

17) Domke PV. Improvement in the strength of concrete by using industrial and agricultural waste. IOSR journal of engineering. 2012; 2(4):755-759.

18) Hermawan D, Hata T, Kawai S, Nagadomi W, Kuroki Y. Manufacturing oil palm fronds cement-bonded board cured by gaseous or supercritical carbon dioxide. J Wood Sci. 2002; 48:20-24.

19) Gupta N, Brar BS, Woldesenbet E. Effect of filler addition on the compressive and impact properties of glass fibre reinforced epoxy. Bull. Mater. Sci. 2001; 24:219–223.

20) Kim NK and Bhattacharyya D. Development of fire resistant wool polymer composites: Mechanical performance and fire simulation with design perspectives. Materials and Design. 2016; 106:391-403.

21) Rajaei M, Kim, NK, Bhattacharyya D. Effects of heat-induced damage on impact performance of epoxy laminates with glass and flax fibres. Composite structures. 2017; 185:515-52.

22) Saha A, Roy PC, Modak N. Three point bending test of fibre reinforced particulate Composites. International journal of scientific & engineering research. 2016; 7:17-19.

23) Gupta MK, Srivastava RK. Mechanical properties of hybrid fibres reinforced polymer composite: A review. Polym plast technol eng. 2016; 55:626-642.

24) Gupta MK, Srivastava RK, Bisaria H. Potential of jute fibre reinforced polymer composites: A review. I J fib text res. 2015; 5:30-38.

25) Gupta MK, Srivastava RK. A review on characterization of hybrid fibre reinforced polymer composite. American J polym sci eng. 2016; 4:1-7.

26) Ahmed KS, Vijayarangan S. Tensile, flexural and interlaminar shear properties of woven jute and jute-glass fabric reinforced polyester composite. J mater process technol. 2008; 207:330-335.

27) Kalia S, Kaith BS, Kaur I. Pretreatments of natural fibers and their application as reinforcing material in polymer composites—A review. Polymer engineering and science. 2009; 49:1253-1272.

28) Al-Oqla FM, Salit MS, Ishak MR, Aziz NA. A novel evaluation tool for enhancing the selection of natural fibers for polymeric composites based on fiber moisture content criterion. BioResources. 2015; 10(1):299-312.

29) Al-Oqla FM, Sapuan SM, Ishak MR, Nuraini AA. A decision-making model for optimal reinforcement condition of natural fiber composites. Fibers polym. 2015; 16(1):153–163.

30) Al-Oqla FM, Sapuan SM. Polymer selection approach for commonly and uncommonly used natural fibers under uncertainty environments. JOM. 2015; 67(10):2450–2463.

31) Mohanty A, Misra M, Drzal L. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. J Polym Environ. 2002; 10(1–2):19–26.

32) Al-Oqla FM, Omari MA. Sustainable biocomposites: challenges, potential and barriers for development. green biocomposites, green energy and technology. 2017; 13-29.

33) Jahan A, Ismail MY, Sapuan S, Mustapha F. Material screening and choosing methods–a review. Mater des. 2010; 31(2):696–705.

34) Al-Oqla FM, Omar AA. A decision-making model for selecting the GSM mobile phone antenna in the design phase to increase over all performance. Prog electromagnet res C. 2012; 25:249–269.

35) Gupta MK, Singh R. Flexural and dynamic mechanical analysis (DMA) of polylactic acid (PLA) coated sisal fibre reinforced polyester composite. Materials today: proceeding. 2018; 5:6109-6114.

36) Durante M, Langella A, Formisano A, Boccarusso L, Carrino L. Dynamic-mechanical behaviour of bio-composites. Procedia engineering. 2016; 167:231-236.

37) Xanthos, M. Functional fillers for plastics. 2010. Wiley Verlag, Weinheim, Germany.

38) Gupta N, Karthikeyan CS, Sankaran S, Kishore. Correlation of processing methodology to the physical and mechanical properties of syntactic foams with and without fibers. Materials characterization. 1999; 43:271-277.

39) Katz HS, Milewski JV. Handbook of fillers for plastics. 1987. Reinhold:Von Nostrand.

40) Das O, Bhattacharyya D. Interface/interphase in polymer nanocomposites. Scrivener publishing LLC. 2017; 337–378.

41) Basu P. Biomass gasification, pyrolysis and torrefaction: Practical design and theory. 3rd Edition; Academic press. 2018.

42) Blackwood technology. Available at: http://www.blackwood-technology.com/technology/what-is-torrefaction/ (Accessed on February 2018).

43) Milne AT, Abatzaglou N, Robert E. Biomass gasifier tars: their nature, formation, and conversion.1998. 10.2172/3726.

44) Available at: http://www.btgworld.com/en/rtd/technologies/torrefaction (Accessed on 25 January 2018).

45) Prasad L, Subbarao P, Subrahmanyam J. Pyrolysis and gasification characteristics of Pongamia residue (de-oiled cake) using thermogravimetry and downdraft gasifier. Applied Thermal Engineering 63. 2014; 379-386).

46) Reza MT. Hydrothermal carbonization of lignocellulosic biomass. 2011. Master

thesis report, The graduate school of University of Nevada, Reno.

47) Basso D. Hydrothermal carbonization of waste biomass. 2016. Doctoral school in environmental engineering, University Trento, Italy.

48) Kambo HS, Dutta A. Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. Applied Energy. 2014; 135: 182–191.

49) Kean et al. Hydrogen from Palm shell. BioResources. 2013. 8 (2). 1831-1840. DOI: 10.15376/biores.8.2.1831-1840.

50) Pandey A. Handbook of plant-based biofuels. CRC: New York. 2015.

51) Lee J, Xiao Y, Cho SH, Kim JK, Lee SS, Tsang D, Ok YS, Kwon E. Pyrolysis process of agricultural waste using CO_2 for waste management, energy recovery, and biochar fabrication. Applied energy. 2017; 185(1):214-222. doi.10.1016/j.apenergy.2016.10.092.

52) Sharma YC, Singh B. Development of biodiesel: Current scenario, renewable and sustainable energy reviews. 2009; 13:1646-1651.

53) Hossain MM. Recovery of valuable chemicals from agricultural waste through pyrolysis. Electronic thesis and dissertation repository. Ontario (CA): The University of Western Ontario; 2016.

54) Shie JL, Chang CY, Tu WK, Yang YC, Liao JK, Tzeng CC, Li HY, Yu YJ, Kuo CH, Chang LC. Major products obtained from plasma torch pyrolysis of sunflower-oil cake. Energy & fuels. 2008; 22(1):75-82.

55) Biomass pyrolysis. Penn State University. Available at: https://www.eeducation.psu.edu/egee439/node/537 (Accessed on 27 January 2018).

56) Available at: https://www.e-education.psu.edu/egee439/node/537 (Accessed on 28 January 2018).

57) Biomass gasification and pyrolysis: practical design and theory- Prabir Basu.

58) IEA bioenergy- Task 42 biorefinery, 2012, Available at: http://task42.ieabioenergy.com/ (Accessed on 27 January 2018).

59) BACAS, 2011 Available at: https://www.bacas.org.uk/reports/ (Accessed on 5 February 2018).

60) Biomassfutures, 2012. Available at: http://www.biomassfutures.eu/ (Accessed on 5 February 2018).

61) Deliverable 5.2: Benchmark and gap analysis of criteria and indicators (C&I) for legislation, regulations and voluntary schemes at international level and in selected EU Member States. S2BIOM, D 8.1, 2015. Available at: http://s2biom.alterra.wur.nl/doc/S2Biom_D5_2_Benchmark_and_gap_analysis_Main_report_30_Mar.pdf (Accessed on 11 January 2018).

62) Ayub S, Ali SI, Khan NA. Adsorption studies on the low cost adsorbent for the removal of Cr(VI) from electroplating wastewater. Environmental pollution control journal. 2002; 5(6):10 – 20.

63) Ajmal M, Rao RAK, Siddiqui BA. Studies on removal and recovery of Cr (VI) from electroplating wastes. Water research. 1996; 30(6):1478-1482.

64) Tan WT, Ooi ST, Lee CK. Removal of chromium (VI) from solution by coconut husk and palm pressed fibre. Environmental technology. 1993; 14:277-282.

65) Khan NA, Shaaban MG, Hassan MHA. Removal of heavy metal using an inexpensive adsorbent. Paper presented at: Proc. UM research seminar; 2003; University of Malaya, Kuala Lumpur, Malaysia.

66) Ayub S, Ali SI, Khan NA. Efficiency evaluation of neem (Azadirachtaindica) bark in treatment of industrial wastewater. Environmental pollution control Journal. 2001; 4(4):34 – 38.

67) Weber W Jr., Pirbazari M, Melson, G. Biological growth on activated carbon: an investigation by scanning electron microscopy. Environ. sci. technol. 1978; 12 (7):817-819.

68) Huggins TM, Haeger A, Biffinger JC, Ren ZJ. Granular biochar compared with activated carbon for wastewater treatment and resource recovery. Water research. 2016; 94:225-232.

69) Li WW, Yu H, Rittmann B. Chemistry: reuse water pollutants. Nature. 2015; 528:29-31.

70) Ren ZJ, Umble AK. Water treatment: recover wastewater resources locally. Nature. 2016; 529:25.

71) Deng Y, Zhang T, Wang Q. Biochar adsorption treatment for typical pollutants removal in livestock wastewater: a A review. Engineering applications of biochar. 2017; doi.10.5772/intechopen.68253.

72) Quinn D. Biochar: industrial applications. Whole fuels energy corp. 2015. Available at: http://whole-energy.com/wp-content/uploads/2015/04/Biochar-White-Paper-Mar-6.pdf (Accessed on 25 April 2018)

73) Ajila CM, Brar SK, Verma M, Prasada Rao U. Sustainable solutions for agro processing waste management: An overview. Environmental protection strategies for sustainable development. strategies for sustainability. Dordrecht (NL): Springer; 2012. doi.org/10.1007/978-94-007-1591-2_3.

75) Waqas M, Aburiazaiza AS, Miandad R, Rehan M, Barakat MA, Nizami AS, Development of biochar as fuel and catalyst in energy recovery technologies. Journal of cleaner production. 2018; 188:477-488.

76) Boumanchar I, Chhiti Y, Alaoui FEM, Ouinani AE, Sahibed-Dine A, Jama FBC, Bensitel M. Effect of materials mixture on the higher heating value: Case of biomass, biochar and municipal solid waste. Waste management. 2017; 61:78-86.

77) Tsai W, Liu S, Hsieh C. Preparation and fuel properties of biochars from the pyrolysis of exhausted coffee residue. Journal of analytical and applied pyrolysis. 2012; 93:63-67.

78) Ahn SY, Eom SY, Rhie YH, Sung YM, Moon CE, Choi GM, Kim DJ. Utilization of wood biomass char in a direct carbon fuel cell (DCFC) system. Applied energy.2013; 105:207-216.

79) Colantoni A, Evic N, Lord R, Retschitzegger S, Proto AR, Gallucci F, Monarca D. Characterization of biochars produced from pyrolysis of pelletized agricultural residues. Renewable and sustainable energy reviews. 2016; 64:187-194.

80) Laird D, Fleming P, Wang B, Horton R, Karlen D. Biochar impact on nutrient leaching from a midwestern agricultural soil. Geoderma. 2010; 158:436-442.

81) Nanda S, Dalai AK, Berruti F, Kozinski JA. Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials. Waste biomass valor. 2016; 7:201-235.

82) Woolf D, Amonette J, Street-Perrot A, Lehmann J, Joseph S. Sustainable biochar to mitigate global change. Nature communications. 2010; 1:1-9.

83) Lehmann J, Gaunt J, Rondon M. Bio-char sequestration in terrestrial ecosystems. Mitig. adapt. strat. glob. change. 2006; 11: 395–419.

84) Berger C. Biochar and activated carbon filters for greywater treatment – comparison of organic matter and nutrients removal. 2012. Master thesis report, Swedish University of agricultural sciences.

85) Xanthos, M. Polymers and polymer composites. In functional fillers for plastics, 2nd ed.; Xanthos, M., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010; pp. 1–18.

86) Composite Lab. Available at: http://compositeslab.com/composite-materials/additives-fillers/ (Accessed on 19 December 2017).

87) Composite Materials, The Royal Society of Chemistry. Available at: www.RSC.org (Accessed on 15 April 2018).

88) Das O, Kim MN, Kalamkarov AL, Sarmah AK, Bhattacharyya D, Biochar to the rescue: balancing the fire performance and mechanical properties of polypropylene composites. Polymer degradation and stability. 2017; 144:485-496.

89) Pandey A, Telang A, Rana RS. Mechanical characterization of bio-char made hybrid composite. Int. journal of engineering research and application. 2016; 6:26-31.

90) Cement production globally and in the U.S. from 2010 to 2017 (in million metric tons). Available at: https://www.statista.com/statistics/219343/cement-production-worldwide/ (Accessed on 25 April 2018).

91) Available at: http://rammedearthconsulting.com/rammed-earth-cement-co2.htm (Accessed on 21 January 2018).

92) Gupta S, Kua HW, Low CY. Use of biochar as carbon sequestering additive in cement mortar. Cement and concrete composites. 2018; 87:110-129.

93) Akhtar A, Sarmah AK. Novel biochar-concrete composites: Manufacturing, characterization and evaluation of the mechanical properties. Science of the total environment. 2018; 616-617:408-416.

94) Khan A, Patrizia S, Simone Q, Massimo R, Mauro G, Alberto TF, Carlo R, Charles QJ. Low-cost carbon fillers to improve mechanical properties and conductivity of epoxy composites. Polymers. 2017; 9(12):642. doi.org/10.3390/polym9120642.

95) Das O, Sarmah AK, Bhattacharyya D. A novel approach in organic waste utilization through biochar addition in wood/polypropylene composites. Waste management. 2015; 38:132-140.

96) Das O, Sarmah A, Bhattacharyya D. Biocomposites from waste derived biochars: Mechanical, thermal, chemical, and morphological properties. Waste management. 2016; 49:560-570.

97) Das O, Kim NK, Hedenqvist MS, Lin RJT, Sarmah AK, Bhattacharyya D. An attempt to find a suitable biomass for biochar-based polypropylene biocomposites. Environmental management. 2018; 62:403–413.

98) Islam MN, Joardder MUH, Hoque SMN, Uddin MS. A comparative study on pyrolysis for liquid oil from different biomass solid wastes. Procedia engineering. 2013; 56:643-649.

99) Joardder MUH, Halder PK, Rahim A, Paul N. Solar assisted fast pyrolysis: a novel approach of renewable energy production. Journal of engineering. 2014. doi.org/10.1155/2014/252848.

100) Venderbosch R, Prins W. Fast pyrolysis technology development. Biofuel bioprod. biorefin. 2010; 4:178-208.

101) Hlavsová A, Corsaro A, Raclavská H, Juchelková D, Škrobánková H, Frydrych J. Syngas production from pyrolysis of nine composts obtained from nonhybrid and hybrid perennial grasses. The scientific world journal. 2014; 2014.

102) American society for testing and materials (ASTM). Standard test method for ash in the analysis sample of coal and coke from coal. West Conshohocken (PA): ASTM International; 2012. ASTM D3174-12.

103) American society for testing and materials (ASTM). Standard test method for volatile matter in the analysis sample of coal and coke. West Conshohocken (PA): ASTM International; 2012. ASTM D3175-11.

104) Stolarski M, Krzyżaniak M, Śnieg M, Christou M, Alexopoulou E. Production costs and residues evaluation of Crambe abyssinica as an energy feedstock. Environmental biotechnology. 2014; 9(2):59-64.

105) Gercel HF. The production and evaluation of biooils from the pyrolysis of sunflower-oil cake. Biomass and bioenergy. 2002; 23:307-314.

106) Raja SA, Kennedy ZR, Pillai BC, Lee CLR. Flash pyrolysis of jatropha oil cake in electrically heated fluidized bed reactor. Energy (Oxford). 2010; 35(7):2819-2823.

107) Ucar S, Ozkan A. Characterization of products from the pyrolysis of rapeseed oil cake. Bioresource technology. 2008; 99:8771-8776.

108) Cao L, Yuan XZ, Jiang LB, Li CZ, Xiao ZH, Huang ZL, Chen XH, Zeng GM, Li H. Thermogravimetric characteristics and kinetics analysis of oil cake and torrefied biomass blends. Fuel. 2016; 175:129-136.

109) Jiang H, Song L, Cheng Z, Chen J, Zhang L, Zhang M, Hu M, Li J, Li J. Influence of pyrolysis condition and transition metal salt on the product yield and characterization via Huadian oil shale pyrolysis. Journal of analytical and applied pyrolysis. 2014; 112:230-236.

110) Yaman S. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy conversion and management. 2004; 35:651-671.

111) Ozcimen D, Karaosmanoğlu F. Production and characterization of biooil and biochar from rapeseed cake. Renewable energy. 2004; 29:779-787.

112) Duman G, Pala M, Ucar S, Ucar S, Yanik J. Two-step pyrolysis of safflower oil cake. Journal of analytical and applied pyrolysis. 2013; 103:352-361.

113) Hameed N, Sreekumar PA, Francis B, et al. Morphology, dynamic mechanical and thermal studies on poly(styrene-co-acrylonitrile) modified epoxy resin/glass fibre composites. Composites: part A.2007; 38:2422–2432.

114) Bowlby LK, Saha GC, Afzal MT. Flexural strength behavior in pultruded GFRP composites reinforced with high specific-surface-area biochar particles synthesized via microwave pyrolysis. Composites: part A: Applied science and manufacturing. 2018; 110:190-196

115) Joseph PV, Joseph K, Thomas S, Pillai CKS, Prasad VS, Groeninckx G, Sarkissova M. The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Composites part A: applied science and manufacturing. 2003; 34:253-266, doi.org/10.1016/S1359-835x(02)00185-9.

116) Dai JF, Li B. Synthesis, thermal degradation, and flame retardance of novel triazine ring-containing macromolecules for intumescent flame-retardant polypropylene, J appl polym sci. 2010; 116 (4):2157-2165.

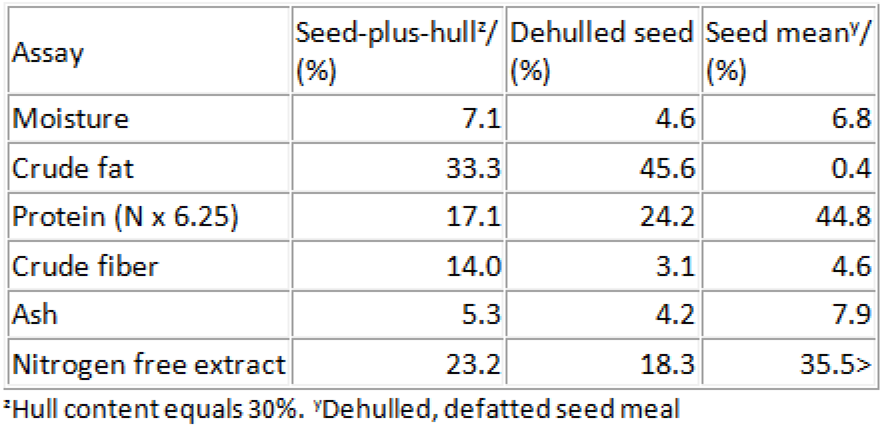
117) Isitman NA, Kaynak C. Nanoclay and carbon nanotubes as potential synergists of an organophosphorus flame-retardant in poly (methyl methacrylate), Polym degrad stab. 2010; 95 (9):1523-1532.

118) Ehrenstein GW, Riedel G and Trawiel P. Dynamic mechanical analysis (DMA). Thermal analysis of plastics. 2004; Pages 236-299.

Appendices

Appendix A: Some Physical and chemical properties of feedstocks

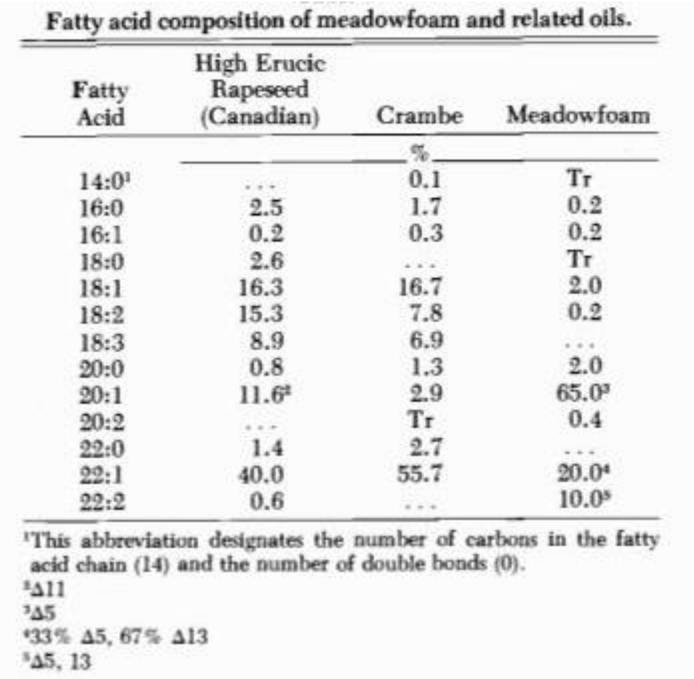
Analyses of Crambe seed and seed meal (Source: David DuByne, Crambe, Oil Seed Crops. Available on http://www.oilseedcrops.org/crambe/)



Assay	Seed-plus-hull[z]/ (%)	Dehulled seed (%)	Seed mean[y]/ (%)
Moisture	7.1	4.6	6.8
Crude fat	33.3	45.6	0.4
Protein (N x 6.25)	17.1	24.2	44.8
Crude fiber	14.0	3.1	4.6
Ash	5.3	4.2	7.9
Nitrogen free extract	23.2	18.3	35.5>

[z] Hull content equals 30%. [y] Dehulled, defatted seed meal

Fatty Acid Composition of Meadowfoam and Crambe compared with Rapeseed (Source: Meadowfoam (Limnanthes alba): Its Research and Development as a Potential New Oilseed Crop for the Willamette Valley of Oregon, Station Bulletin 648, November 1981)



Fatty acid composition of meadowfoam and related oils.

Fatty Acid	High Erucic Rapeseed (Canadian)	Crambe	Meadowfoam
		%	
14:0[1]	. . .	0.1	Tr
16:0	2.5	1.7	0.2
16:1	0.2	0.3	0.2
18:0	2.6	. . .	Tr
18:1	16.3	16.7	2.0
18:2	15.3	7.8	0.2
18:3	8.9	6.9	. . .
20:0	0.8	1.3	2.0
20:1	11.6[2]	2.9	65.0[3]
20:2	. . .	Tr	0.4
22:0	1.4	2.7	. . .
22:1	40.0	55.7	20.0[4]
22:2	0.6	. . .	10.0[5]

[1] This abbreviation designates the number of carbons in the fatty acid chain (14) and the number of double bonds (0).

[2] $\Delta 11$

[3] $\Delta 5$

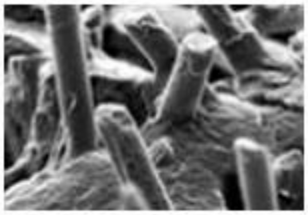
[4] 33% $\Delta 5$, 67% $\Delta 13$

[5] $\Delta 5$, 13

Appendix B: Technical Data of Glassfibre

Glassfibre (727 Biaxial Tape) technical data:

17 oz non-woven E-glass fabric. Two layers ±45° fiber orientation, held together by a light stitching. Ideal for repairs, tabbing and reinforcing.



Glass composition (weight %)

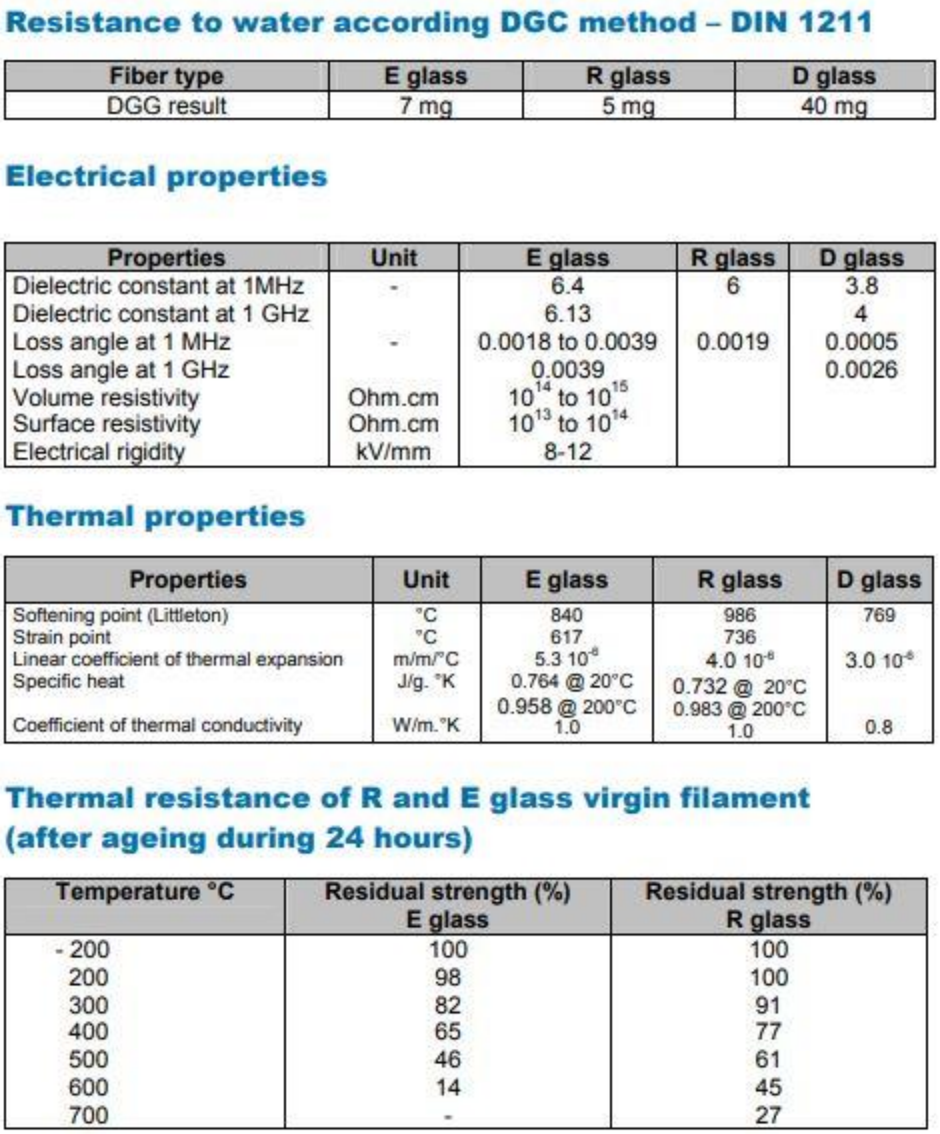
Composition	E (glass)	R (glass)	D (glass)
Silica SiO_2	53 to 57	58 to 60	72 - 75
Aluminia AL_2O_3	12 to 15	23.5 to 25.5	-
Calcium Oxide CaO + Magnesium Oxide MgO	22 to 26	14 to 17	-
Boron Oxide B_2O_3	5 to 8	-	up to 23
F_2	0 to 0.6	-	-
$Na_2O + K_2O$	< 1	-	< 4
Fe_2O_3	≈ 0.5	-	-
Miscellaneous	-	<2	< 1

Physical properties

Properties	Unit	E glass	R glass	D glass
Density	g/cm_3	2.60	2.53	2.14
Hardness *(Vickers 50 g - 15 s)*	-	5.6	6.2	-
Sound velocity	m/s	5680	5940	-

Mechanical properties

Properties	Unit	E glass	R glass	D glass
Virgin filament tensile test	MPa	3400	4400	2500
	ksi	493	638	363
Impregnated strand tensile test	MPa	2400	3400	1700
(calculated on fiber cross section)	ksi	348	493	246
Tensile modulus	GPa	73	86	55
	msi	10.5	12.5	8
Tenacity *(sized yarns)*	cN/Tex	Min. 50		
Elongation at break for sized yarns according to binder system	%	2.2 - 2.5		
Elastic recovery	%	100	100	100



Resistance to water according DGC method – DIN 1211

Fiber type	E glass	R glass	D glass
DGG result	7 mg	5 mg	40 mg

Electrical properties

Properties	Unit	E glass	R glass	D glass
Dielectric constant at 1MHz	-	6.4	6	3.8
Dielectric constant at 1 GHz		6.13		4
Loss angle at 1 MHz	-	0.0018 to 0.0039	0.0019	0.0005
Loss angle at 1 GHz		0.0039		0.0026
Volume resistivity	Ohm.cm	10^{14} to 10^{15}		
Surface resistivity	Ohm.cm	10^{13} to 10^{14}		
Electrical rigidity	kV/mm	8-12		

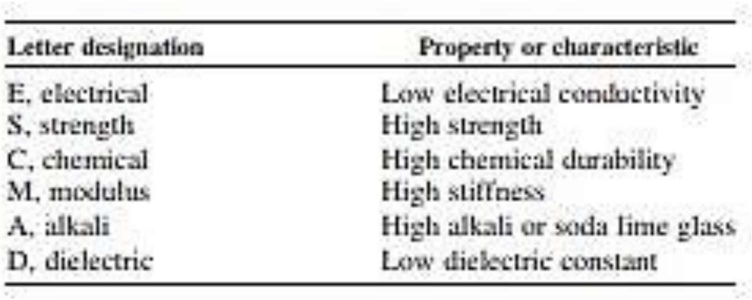
Thermal properties

Properties	Unit	E glass	R glass	D glass
Softening point (Littleton)	°C	840	986	769
Strain point	°C	617	736	
Linear coefficient of thermal expansion	m/m/°C	5.3 10^{-6}	4.0 10^{-6}	3.0 10^{-6}
Specific heat	J/g. °K	0.764 @ 20°C 0.958 @ 200°C	0.732 @ 20°C 0.983 @ 200°C	
Coefficient of thermal conductivity	W/m.°K	1.0	1.0	0.8

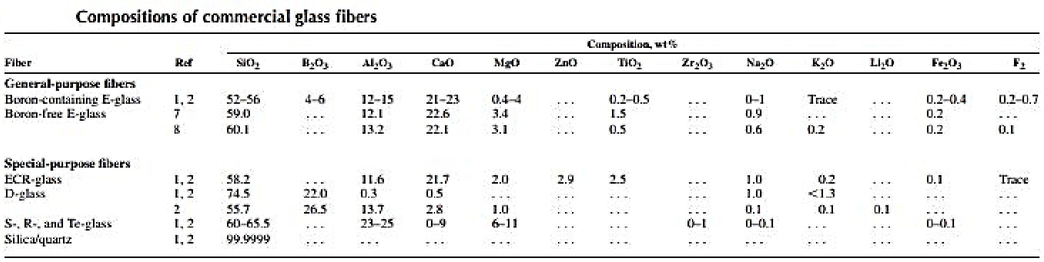
Thermal resistance of R and E glass virgin filament (after ageing during 24 hours)

Temperature °C	Residual strength (%) E glass	Residual strength (%) R glass
- 200	100	100
200	98	100
300	82	91
400	65	77
500	46	61
600	14	45
700	-	27

(Source: http://glassproperties.com)

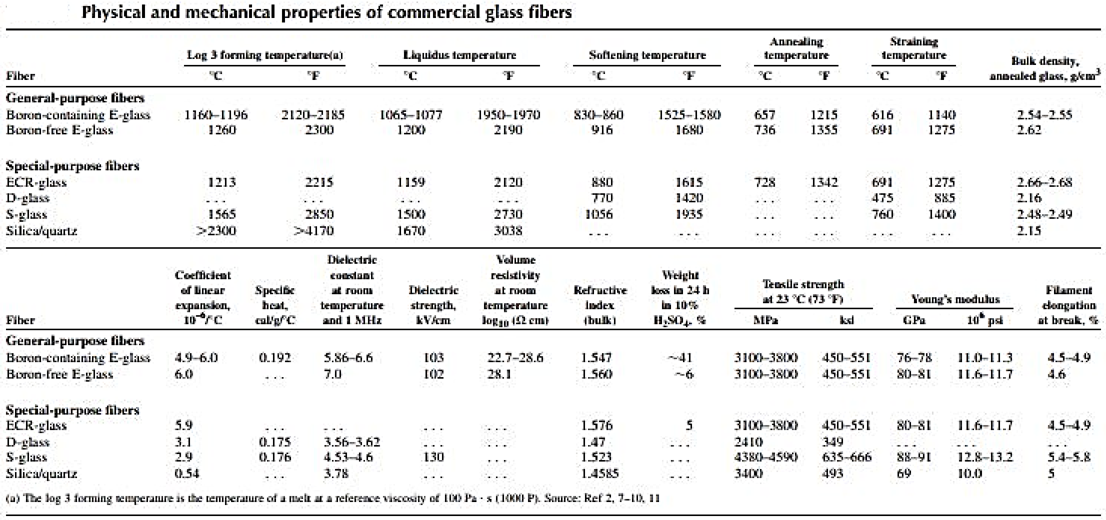


Letter designation	Property or characteristic
E, electrical	Low electrical conductivity
S, strength	High strength
C, chemical	High chemical durability
M, modulus	High stiffness
A, alkali	High alkali or soda lime glass
D, dielectric	Low dielectric constant



Compositions of commercial glass fibers

		Composition, wt%												
Fiber	**Ref**	**SiO_2**	**B_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**ZnO**	**TiO_2**	**Zr_2O_3**	**Na_2O**	**K_2O**	**Li_2O**	**Fe_2O_3**	**F_2**
General-purpose fibers														
Boron-containing E-glass	1, 2	52–56	4–6	12–15	21–23	0.4–4	...	0.2–0.5	...	0–1	Trace	...	0.2–0.4	0.2–0.7
Boron-free E-glass	7	59.0	...	12.1	22.6	3.4	...	1.5	...	0.9	...	...	0.2	...
	8	60.1	...	13.2	22.1	3.1	...	0.5	...	0.6	0.2	...	0.2	0.1
Special-purpose fibers														
ECR-glass	1, 2	58.2	...	11.6	21.7	2.0	2.9	2.5	...	1.0	0.2	...	0.1	Trace
D-glass	1, 2	74.5	22.0	0.3	0.5	...	...	...	...	1.0	<1.3	...	...	...
	2	55.7	26.5	13.7	2.8	1.0	...	...	...	0.1	0.1	0.1	...	...
S-, R-, and Te-glass	1, 2	60–65.5	...	23–25	0–9	6–11	...	...	0–1	0–0.1	...	...	0–0.1	...
Silica/quartz	1, 2	99.9999	...	...	...	...	...	...	...	...	...	...	...	...



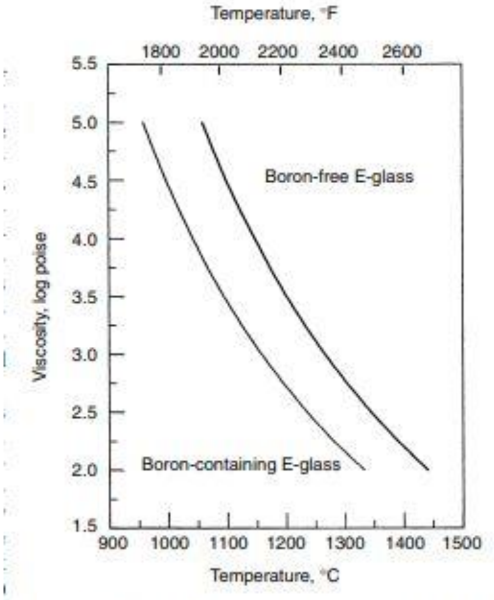
Physical and mechanical properties of commercial glass fibers

	Log 3 forming temperature(a)		Liquidus temperature		Softening temperature		Annealing temperature		Straining temperature		
Fiber	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**Bulk density, annealed glass, g/cm^3**
General-purpose fibers											
Boron-containing E-glass	1160–1196	2120–2185	1065–1077	1950–1970	830–860	1525–1580	657	1215	616	1140	2.54–2.55
Boron-free E-glass	1260	2300	1200	2190	916	1680	736	1355	691	1275	2.62
Special-purpose fibers											
ECR-glass	1213	2215	1159	2120	880	1615	728	1342	691	1275	2.66–2.68
D-glass	...	...	...	...	770	1420	...	...	475	885	2.16
S-glass	1565	2850	1500	2730	1056	1935	...	...	760	1400	2.48–2.49
Silica/quartz	>2300	>4170	1670	3038	...	...	...	...	...	...	2.15

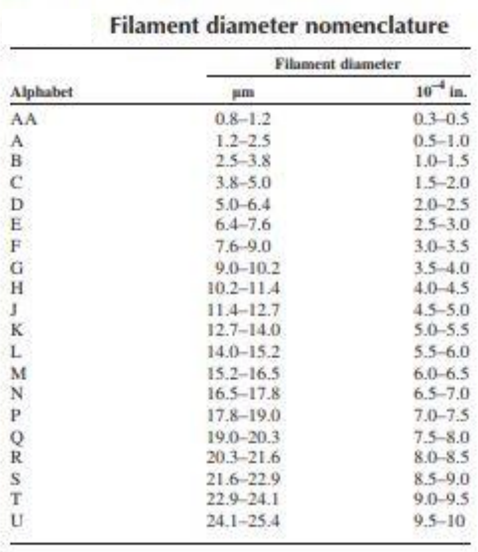
								Tensile strength at 23 °C (73 °F)		Young's modulus		
Fiber	**Coefficient of linear expansion, 10^{-6}/°C**	**Specific heat, cal/g/°C**	**Dielectric constant at room temperature and 1 MHz**	**Dielectric strength, kV/cm**	**Volume resistivity at room temperature $\log_{10}$ (Ω cm)**	**Refractive index (bulk)**	**Weight loss in 24 h in 10% H_2SO_4, %**	**MPa**	**ksi**	**GPa**	**10^6 psi**	**Filament elongation at break, %**
General-purpose fibers												
Boron-containing E-glass	4.9–6.0	0.192	5.86–6.6	103	22.7–28.6	1.547	~41	3100–3800	450–551	76–78	11.0–11.3	4.5–4.9
Boron-free E-glass	6.0	...	7.0	102	28.1	1.560	~6	3100–3800	450–551	80–81	11.6–11.7	4.6
Special-purpose fibers												
ECR-glass	5.9	...	...	...	...	1.576	5	3100–3800	450–551	80–81	11.6–11.7	4.5–4.9
D-glass	3.1	0.175	3.56–3.62	...	...	1.47	...	2410	349	...	...	...
S-glass	2.9	0.176	4.53–4.6	130	...	1.523	...	4380–4590	635–666	88–91	12.8–13.2	5.4–5.8
Silica/quartz	0.54	...	3.78	...	...	1.4585	...	3400	493	69	10.0	5

(a) The log 3 forming temperature is the temperature of a melt at a reference viscosity of 100 Pa · s (1000 P). Source: Ref 2, 7–10, 11

(Source: ASMI Standards)



Viscosity of boron-free and boron-containing E-glass



Filament diameter nomenclature

	Filament diameter	
Alphabet	**μm**	**10^{-4} in.**
AA	0.8–1.2	0.3–0.5
A	1.2–2.5	0.5–1.0
B	2.5–3.8	1.0–1.5
C	3.8–5.0	1.5–2.0
D	5.0–6.4	2.0–2.5
E	6.4–7.6	2.5–3.0
F	7.6–9.0	3.0–3.5
G	9.0–10.2	3.5–4.0
H	10.2–11.4	4.0–4.5
J	11.4–12.7	4.5–5.0
K	12.7–14.0	5.0–5.5
L	14.0–15.2	5.5–6.0
M	15.2–16.5	6.0–6.5
N	16.5–17.8	6.5–7.0
P	17.8–19.0	7.0–7.5
Q	19.0–20.3	7.5–8.0
R	20.3–21.6	8.0–8.5
S	21.6–22.9	8.5–9.0
T	22.9–24.1	9.0–9.5
U	24.1–25.4	9.5–10

(Source: ASMI Standards)

Appendix C: Technical Data of Polymer

About 105 Epoxy Resin® / 205 Fast Hardener® (General Description)

105/205 Epoxy is used for general coating and bonding applications at lower temperatures and to produce a rapid cure that develops its physical properties quickly at room temperature. 105/205 forms a high-strength, moisture-resistant solid with excel lent bonding and barrier coating properties. It will wet out and bond to wood fiber, fiberglass, reinforcing fabrics, foam and other composite materials, and a variety of metals. 105/205 Epoxy can be thickened with WEST SYSTEM fillers to bridge gaps and fill voids and can be sanded and shaped when cured. With roller applications, it has excellent thin film characteristics, allowing it to flow out and self-level without "fish-eyeing." Multiple coats of 105/205 Epoxy create a superior moisture barrier and a tough, stable base for paints and varnishes. It is formulated without volatile solvents resulting in a very low VOC content. It has a relatively high flash point, no strong solvent odor and does not shrink after curing. It is not intended for clear coating natural finished wood.

Handling Characteristics

Mix ratio by volume (300 Mini Pump ratio)	5 parts resin : 1 part hardener
by weight	5.19 : 1
Acceptable ratio range by weight	4.83 : 1 to 6.20 :1
Mix viscosity (at 72°F) ASTM D-2393	975 cps
Pot life (100g at 72°F)	9 to 12 minutes
Working time, thin film*	60 to 70 minutes
Cure to a solid, thin film*	6 to 8 hours
Cure to working strength	1 to 4 days
Minimum recommended temperature	40°F (4 °C)

*Epoxy cures faster at higher temperatures and in thicker applications.

Physical Properties of Cured Epoxy

Specific gravity	1.18
Hardness (Shore D) ASTM D-2240	83
Compression yield ASTM D-695	11,400 psi
Tensile strength ASTM D638	7,900 psi
Tensile elongation ASTM D-638	3.4%
Tensile modulus ASTM D-638	4.08E+05
Flexural strength ASTM D-790	14,100 psi
Flexural modulus ASTM D-790	4.61E+05
Heat deflection temperature ASTM D-648	118°F
Onset of Tg by DSC	129°F
Ultimate Tg	142°F

(Source: https://www.westsystem.com)

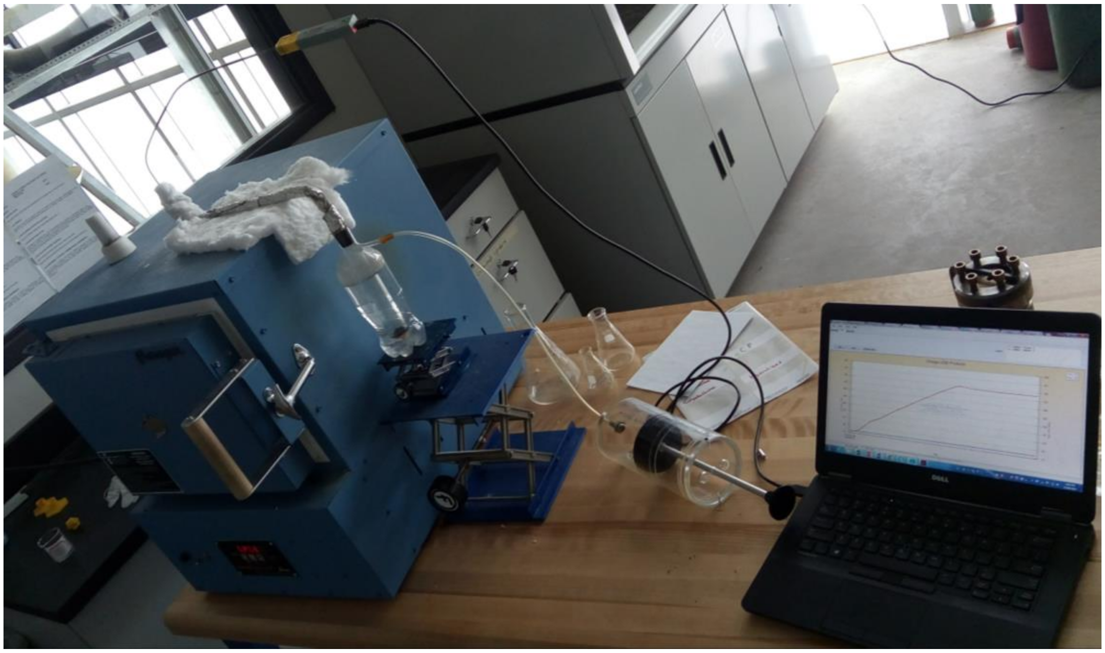
Appendix D: Photographs of feedstocks

Bags of meadowfoam and crambe oilcakes made available by Nature Crops International.

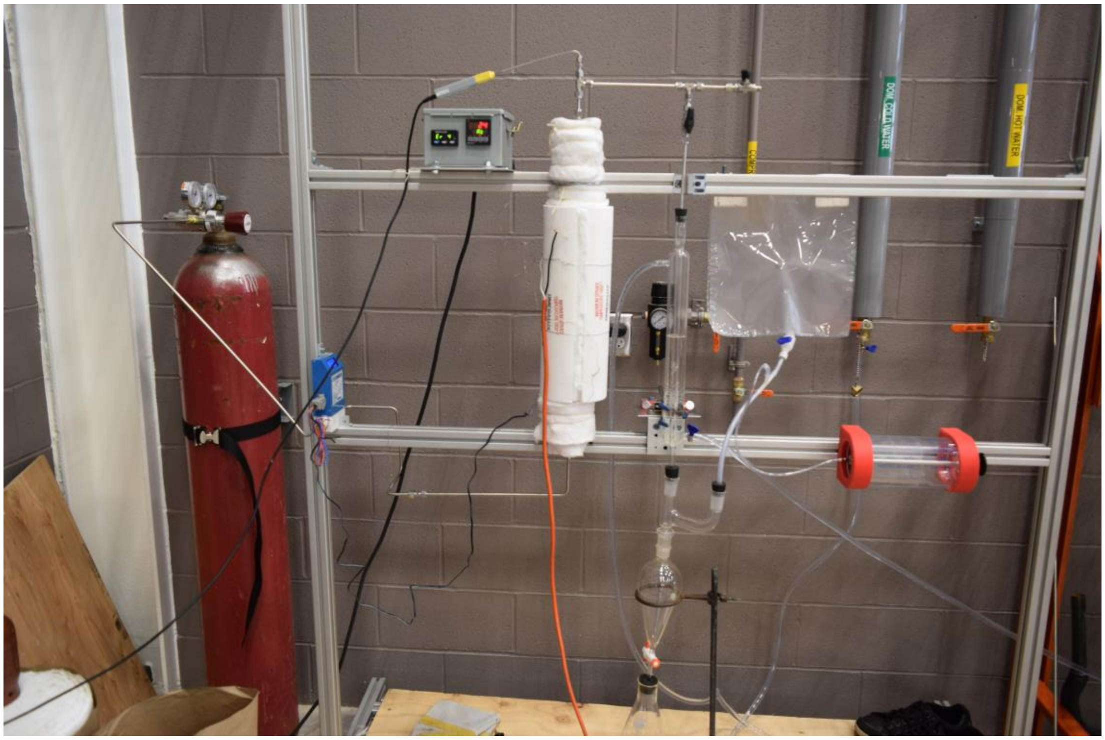
Grinded feedstock samples.

Spruce pellets pyrolysis feedstock for char production for composites application.

Appendix E: Photographs of different lab setups used



Muffle furnace pyrolysis for energy study.

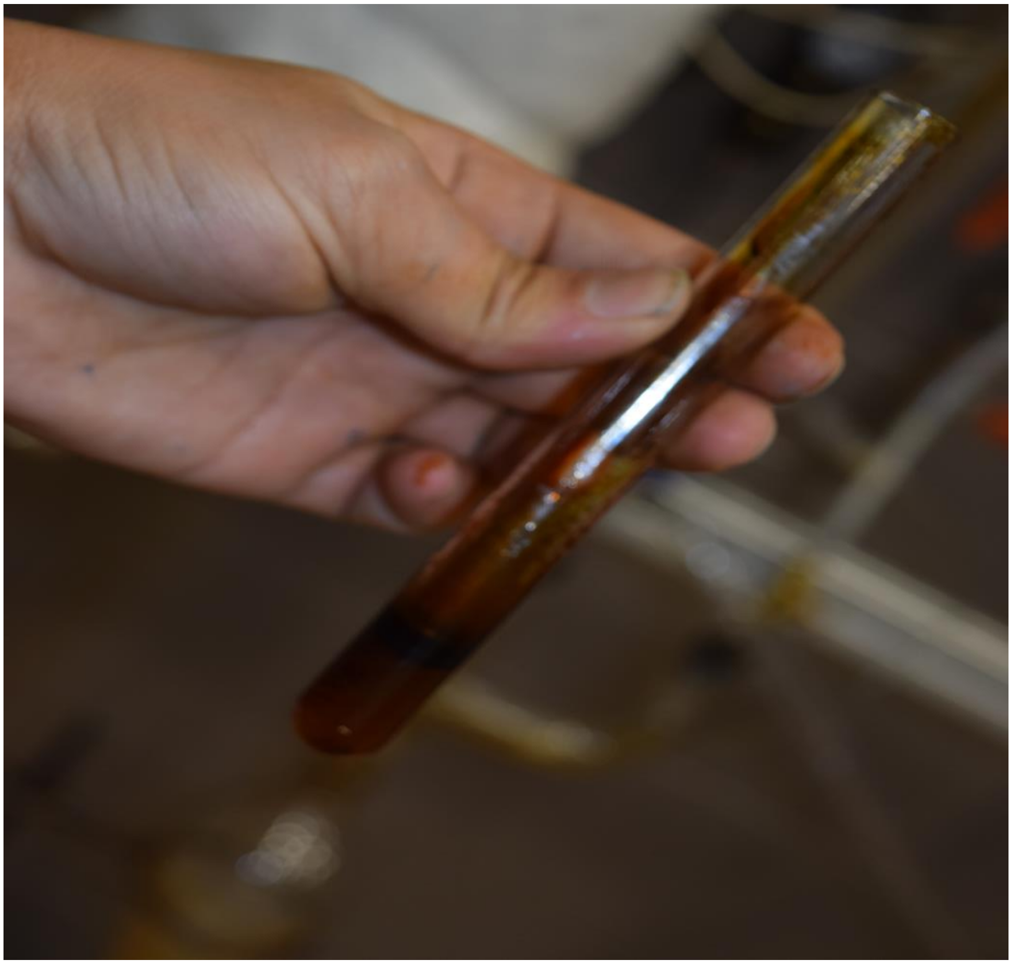


Pyrolysis set up being run to collect syngas for analysis.

Two-stage rotating drum pyrolysis in operation.

Appendix F: Photographs of pyrolytic products

Grinding and screening of produced biochar for biocomposites application.



Collected biooil sample for analysis.

Igniting Syngas showing good combustibility.

Collection of produced pyrolytic products for analysis.

Appendix G: Photographs of Composites making process and accessories.

Accessories for composites production.

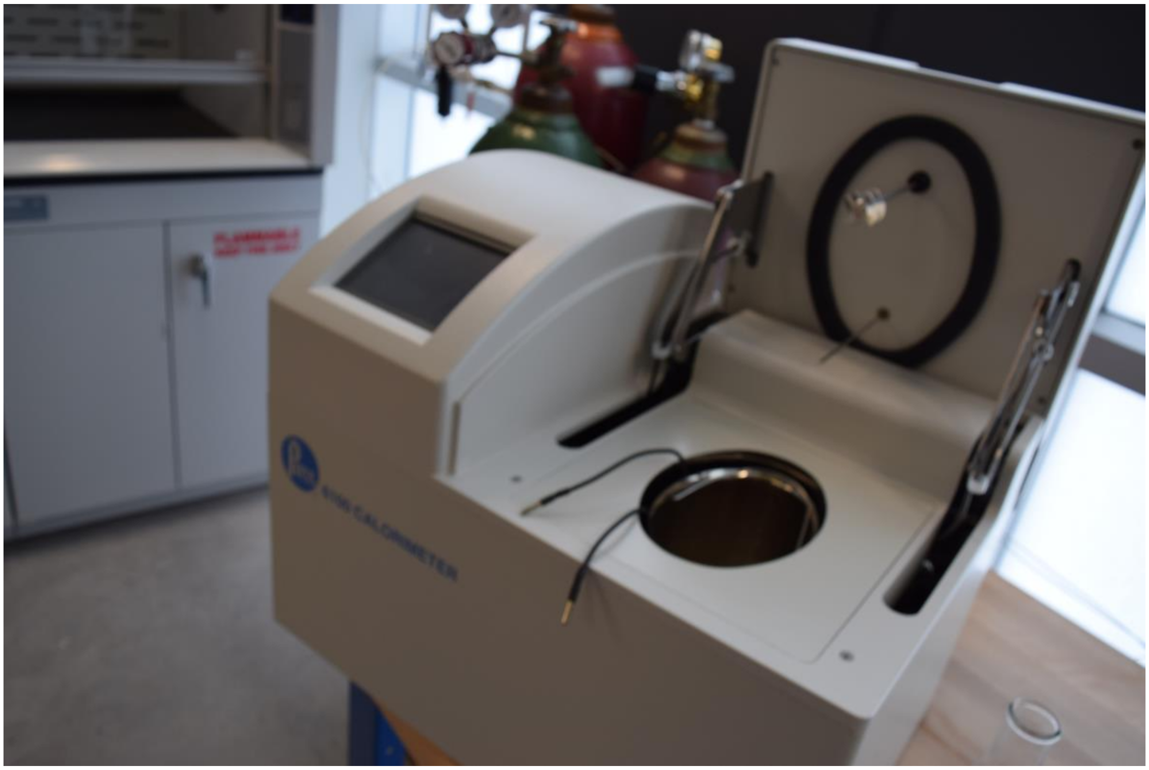
Vacuum infusion technique being applied to produce composites material.

Composites samples being cured (Left), A cured Sample (Centre) & Sample held in vices to be cut in sizes for analysis (Right).

Appendix H: Photographs of tests being performed

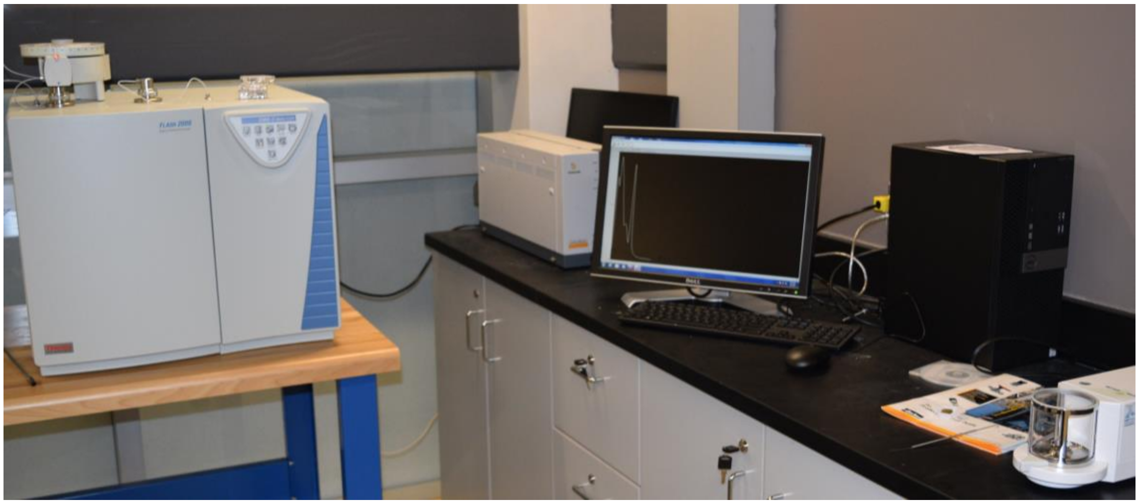
Sample preparation for the proximate analysis.

Muffle Furnace running Proximate Analysis.



Parr Bomb Calorimeter set up for calorific value determination of different samples.

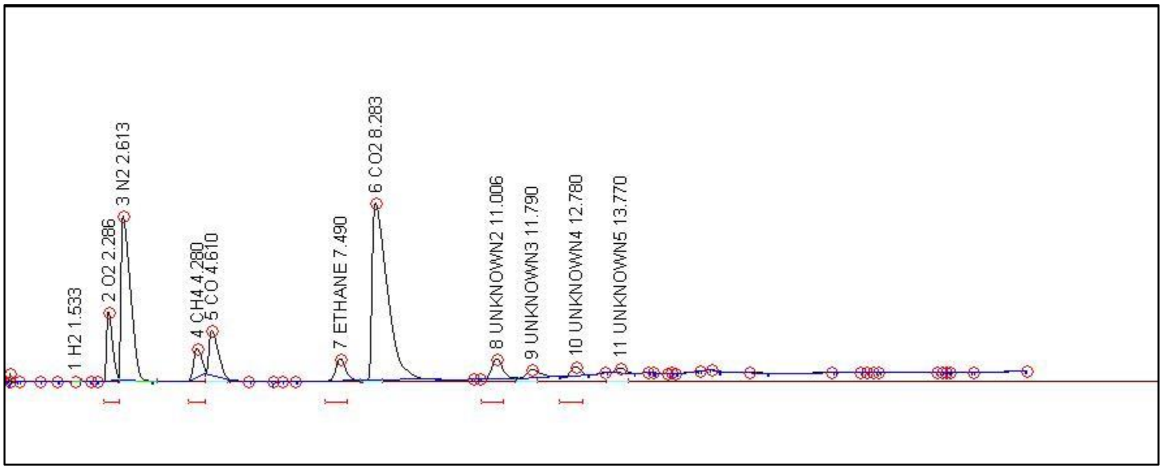
Bomb for Bomb Calorimetry Analysis being prepared.



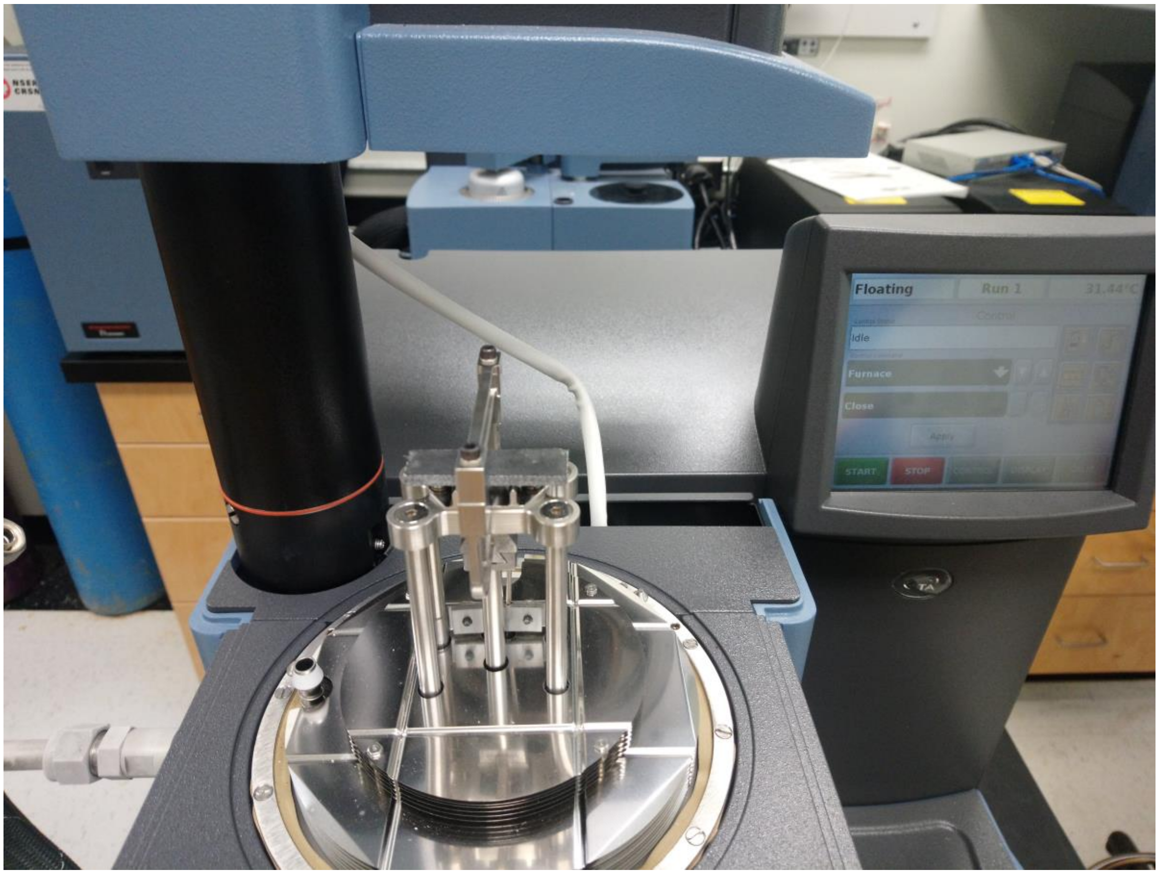
Elemental Analysis for CHNSO determination in the samples being performed.

TGA Analysis being done.

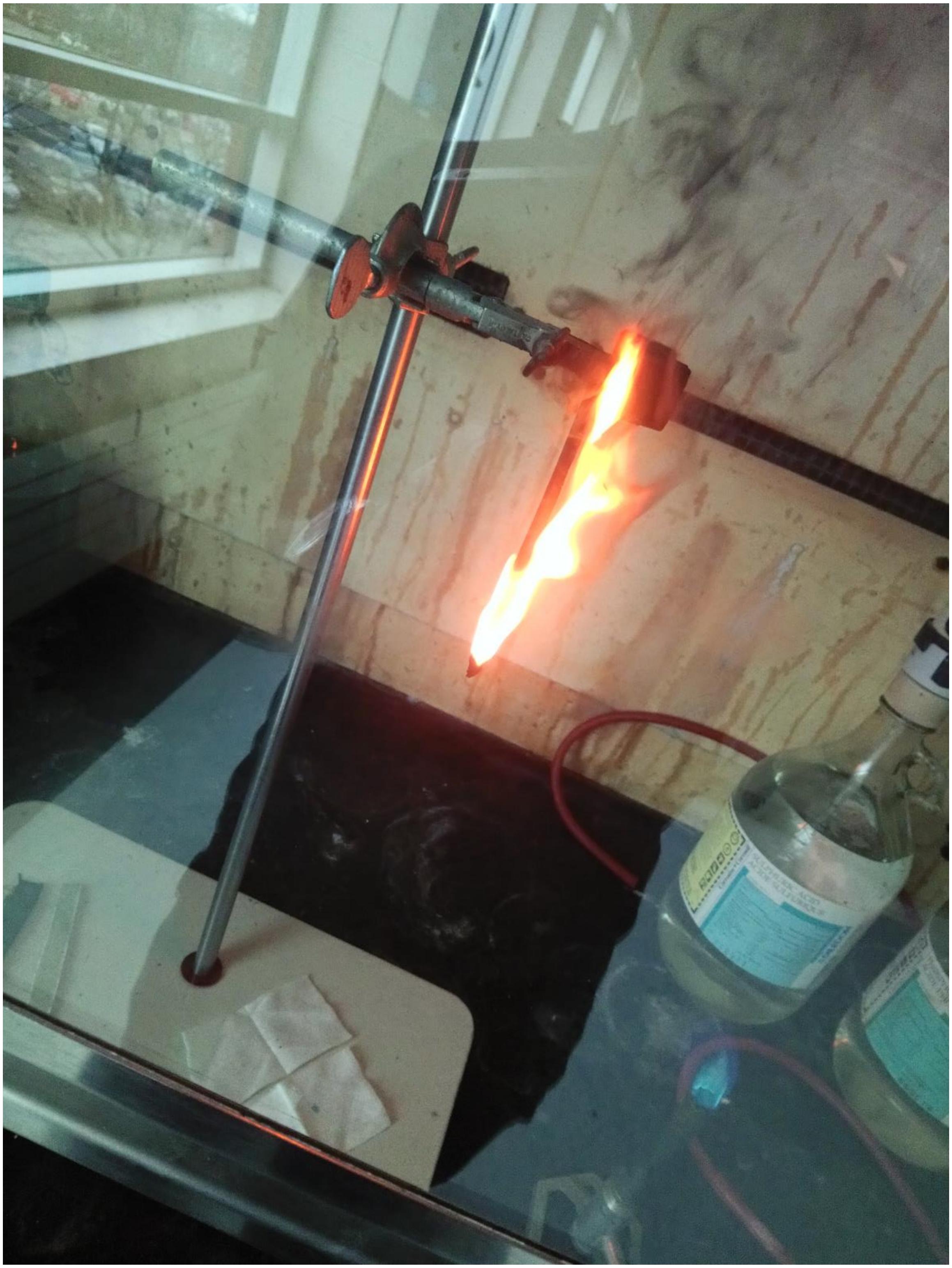
Gas analysis being performed in Gas Chromatograph.



Gas Composition detected during the Gas Chromatography Analysis.



A sample ready to be DMA tested.



Vertical flame test being performed.

CURRICULUM VITAE

Name: Raj Kumar Dahal

Education: Bachelor’s Degree in Mechanical Engineering, Pulchowk Campus, Institute of Engineering, Tribhuvan University, Kathmandu, Nepal, (2006-2011)

Publications & Presentations:

1. **Journal Papers**
   - I. Dahal RK, Acharya B, Farooque A. *Biochar: a sustainable solution for solid waste management in agro-processing industries.* Biofuels. 2018. doi: 10.1080/17597269.2018.1468978.
   - II. Bhatt D, Shrestha A, Dahal RK, Acharya B, Basu P, MacEwen R. *Hydrothermal Carbonization of Biosolid from Waste Water Treatment Plant*. Energies. 2018 (Under Review).
   - III. Dahal RK, Acharya B, Saha G, Bissessur R. *Application of Biochar in Glassfibre Reinforced Polymer Composites: Thermal and Dynamic Mechanical Studies* (Under Review).
   - IV. Dahal RK, Cameron J, Pandian A, Acharya B, Srividya PK. *Catalytic effect of nano nickel oxide and calcium oxide on properties of pyrolytic products.* (Under Review)
2. **Presented Conferences**
   - I. Dahal RK. 3 Minute Thesis presentation. 67th Canadian Chemical Engineering Conference. 2017. Edmonton.
   - II. Dahal RK, Acharya B. *Biochar: A Sustainable Solution for Waste Management in Prince Edward Island*. Canadian Chemical Engineering Conference. 2017. Edmonton.
3. **Seminars and Poster Presentations**
   - I. Dahal RK, Acharya B. *Pyrolysis of waste biomass for energy and biocomposites applications*. Graduate Research Seminar. 2018. University of Prince Edward Island.
   - II. Dahal RK, Acharya B. *Study of Biochar for Energy and Composite Applications*. Engineering Design Expo. 2018

III. Dahal RK, Acharya B. *Biochar: A Sustainable Solution for Waste Management in Prince Edward Island*. Graduate Research Seminar. 2017. University of Prince Edward Island.

IV. Dahal RK, Acharya B. *Pyrolysis of Biomass for Biocomposite Application*. Science Graduate Research Day. 2017. University of Prince Edward Island.