Experimental and Theoretical Investigation of the Pyrolysis of Biomass in a Twin Screw Reactor to Produce Green Fuels

A thesis submitted to the
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In

Chemical Engineering

By

Leena Kapoor

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UNIVERSITY OF PETROLEUM AND ENERGY STUDIES
SCHOOL OF ENGINEERING
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DECLARATION

I declare that the thesis entitled “Experimental and Theoretical Investigation of the Pyrolysis of Biomass in a Twin Screw Reactor to Produce Green Fuels” has been prepared by me under the guidance of Prof. Santosh. K. Gupta, Distinguish Professor of Chemical Engineering, UPES. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis on **“Experimental and Theoretical Investigation of the Pyrolysis of Biomass in a Twin Screw Reactor to Produce Green Fuels ”** by **Leena Kapoor** in partial completion of the requirements for the award of the degree of Doctor of Philosophy (Engineering) is an original work carried out by her under our supervision and guidance.

It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

Gupta

Signature of Supervisor

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UPES Dehradun

Dedicated

To

My

Parents

ABSTRACT

The increasing demand for crude oil and dramatic climate changes due to greenhouse gas emissions have attracted the attention of many researchers towards bio energy, i.e., bio fuels. Biomasses are renewable sources of energy which can provide a clean energy that will free our environment from pollution [1]. The use of biomass can be more and more beneficial both technologically and economically as it is easily available and can be converted through thermal or biological processes into numerous forms of energy. Thermochemical conversion was considered the most promising way for high-efficiency conversions of biomasses [2]. Biomass conversion through thermal processes requires heat and catalysts to convert it into useful chemicals, fuels and power. In general, three thermal processes are being used for transforming biomasses into solid, liquid and gaseous products under thermal conditions, i.e., combustion, pyrolysis and gasification [3]. Among these, pyrolysis is the primary process for transforming raw biomass thermochemically; it is also the first step for combustion or gasification processes [4]. The analysis of pyrolysis can be useful for controlling and then optimizing the process [5]. Pyrolysis forms three different products in various quantities: char, tar and gases, the relative proportions of which are fairly dependent on the type of pyrolysis, the characteristics of the biomass and the parameters of the reactions.

The main aim of this work is to estimate the process performance for a few biomasses in terms of product yield and their physio-chemical characterization. This work compares two different types of pyrolysis reactors, i.e., a screw reactor and a fixed bed reactor, for different biomasses. It compares the yields of the products and the quality of bio-oil produced using these pyrolysis methods.

A lab-scale biomass pyrolysis system has been designed and then constructed based on the concepts of auger reactors. The process of fast pyrolysis uses different biomasses to produce bio-oil or pyrolysis oil for different applications as a source of energy and as a chemical feedstock. These are of interest in this study. Here, the pyrolysis of sawdust, bamboo, bagasse, pinewood, mustard and camellia have been investigated through fast pyrolysis in an auger reactor. A temperature of 500 °C has been used to characterize the yields and reactor problems have been pointed out. Desirable design changes have been proposed to overcome these difficulties. Bio char, which is the biofuel, in solid form, is successfully formed in the system. This work reports the product yields of bio-oil and biochar. Bio-oil is one of the crucial products of fast pyrolysis. Pyrolysis experiments can be done with several types of biomass feeds. However, much needs to be studied with twin-screw reactors. Surveying of the literature on biomass fast pyrolysis has been done and the effects of the parameters such as the temperature, the rate of heating, the feed rate and the residence time on the pyrolysis process have been studied.

Further, this investigation reports on the work performed in a twin-screw reactor and a fixed bed reactor. Studies have been made using profiles of temperature near 500 ^{0}C, with the biomass used being mustard, sawdust, camellia, bagasse and bamboo. Solid and liquid biofuel, i.e., biochar and bio-oil, have been analyzed along with proximate and ultimate analyses of biomass feedstocks. Profiling for system limitations has been performed to address problems related to bio-oil production. Suggestions regarding a change in the design of these reactors have been proposed using the solid works software (to optimize the present design). The endeavor is to make changes in the existing design to enhance its efficacy. Nitrogen gas has been used to keep up the velocity profile of particles of biomass in the reactor. The work does not have a conflict between food and fuel as it demonstrates that biomass feeds that are used are chiefly by-products from the sugar industry and wood wastes.

To carry out the analysis on various biomass feedstocks – bamboo, bagasse, sawdust, mustard and camellia, efforts have been made to add further insights on the design and operational parts of the pyrolysis processes. A fixed bed tubular reactor was used to perform experiments by fast pyrolysis at a temperature of 500°C with the residence time of 2 min with continuous flow of nitrogen. The bio-oil and gases that were obtained were analyzed by using GC-MS and GC–TCD. Further, the results that were apparent from these experiments for each of the biomass samples are also compared.

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Chapter 1 Introduction

Biomasses are defined as those materials, exclusive of fossil fuels, which were living organisms that have the potential to be used as a fuel either directly or after converting them. The demand of energy globally is predicted to increase drastically in the near future: the exhaustion of fossil fuel reserves, change in climate across the globe, have converged to create an urgent need to develop a more sustainable energy system which would be based on renewable lignocellulose biomass [1].

Biomass energy has been in use in India since ancient times, basically in the form of the husk, firewood, cow dung cake, and many other natural feedstock [1]. Unfortunately burning of biomass directly produces a high amount of smoke and ash. Consequently, biogas plants were developed as they are pollution-free, i.e., they produce no smoke. The Indian government provided various subsidies to establish biogas plants. Newer technologies like biomass gasification were also developed that converts biomass into syngas.

Due to the increase in the demand in rural areas, power generation plants based on biomass are on a rising trend. The largest Indian population resides in rural areas. Based on a survey in 2018, approximately 66% of the Indian population lives in rural areas[2]. Hence, to plan electrification for around 0.638 million villages in India, biomass can be a vital option. The biomass availability in India is approximately around 500 metric tons per year. Thus, approximately 17,500 MW power can be created by using this biomass[3]. Apart from agricultural waste, biomass can also be taken from other sources like an industrial waste (e.g. bagasse in sugar mills). In India approximately around 550 sugar mills are currently operating, and thus, an expected 73,000 MW energy can be produced by 2030 by using bagasse as biomass [1]. Various other potential sources for biomass include roadside shrubs, road sweeping, agro-based industries, vegetable wastes and plantations, etc [4].

Biofuel has the high potential in energy sector, since the fuel and thus, oxygen required for their operation can be taken from their immediate environment, and this offers great potential as a power source [1]. Energy through biomass is believed to be the most favorable among the renewable energy sources (RES) as it is widely available worldwide. Biomass pyrolysis has an inimitable advantage of producing solid, liquid and gaseous fuels which can be transported, stored and utilized, far away from its place of production. Due to the negligible amounts of nitrogen and sulfur components present in biomass pyrolysis products, its use does not lead to environmental pollution [2].

Thermochemical conversion is considered one of the most promising ways to achieve high-efficiency conversions of biomasses, converting the biomasses into solid, liquid and gaseous products at relatively high temperatures. Accordingly, a few technologies have been developed in the course of time: pyrolysis, combustion, liquefaction, gasification, etc. Pyrolysis is considered to be one of the elementary processes for converting the biomass thermochemically; it is also the primary step in combustion or gasification processes. The *analyses* of the pyrolysis of biomasses can find its uses in controlling and optimizing these processes [5] .

On the basis of the operational conditions, pyrolysis is of mainly three types: slow, fast and flash pyrolysis. Conventional or slow pyrolysis is categorized by slow heating rates, low temperatures and high solids and gas residence times. Fast pyrolysis is categorized by short vapor residence time, high heat transfer and rapid cooling of vapors. Flash pyrolysis is categorized by moderate temperatures and rapid heating rates. Fast pyrolysis, among all the three modes of pyrolysis, provides the highest yield of bio-fuel [6].

The pyrolysis oil that is obtained from biomass is highly complex and oxygenated in nature and is also chemically unstable [7]. The percentage of oxygen present in biomass is around 35-40 by wt. % [6]. The key difference between petroleum fuel and bio-oil is the presence of a large amount of oxygen in bio-oil [8].

1.1 Need for Research

The depletion of fossil resources and an increase in the demand for petroleum fuels have led to an interest in renewable feedstocks. Biomasses are renewable sources of energy, consisting of carbon, hydrogen, and oxygen, having the composition of $C_8H_4O_6$ [9]. Based on the source from which it is obtained, biomass contains some amount of earth metals. Comparatively, biomasses have a high O/C and low H/C ratio than fossil fuels and, therefore, have low energy densities than crude oil [10]. The recovery of energy from biomasses and other wastes is dependent on the thermochemical and biochemical processes; pyrolysis has received considerable importance due to the direct production of liquid fuels [11]. The liquid fuel i.e., bio-oil formed through biomass pyrolysis is higher on the acidic side, has less stability and low energy content [12]. To increase the energy content and bio-oil stability it is essential to develop new technologies.

1.2 Objectives of the Research

The main aim of this work is to produce bio-oil (biofuel) from few renewable sources using reactors that employ fast pyrolysis. The selected approaches are as follows:

- Selection of six different biomasses, namely, bamboo, pinewood, camellia, mustard, sawdust, and bagasse, which are wastes and are readily available in India to produce green fuel (bio-oil). To study, in detail, the physicochemical characteristics, suitability, and availability of these biomasses.
- To investigate the calorific value of bio-oil that is produced from six different biomass samples.
- To study fast pyrolysis in a fixed bed and a twin-screw reactor to produce bio-oil.

1.3 Research Methodology

Numerous work has been done on biomass pyrolysis using various kinds of biomasses [13]. For example residues from agriculture and forests, grasses, barks, seeds, nuts, cellulose, algae, wood, and lignin, have been tested in different reactors under different pyrolysis conditions. Rice husk, wheat straw and bagasse were used in most of these studies [14], however, maximum work has been done using wood as biomass and may be due to easy comparability and consistency of tests [15]. Very few studies exist on biomass pyrolysis of pinewood, bagasse, and their co-products such as bio-oil, bio-char. Further, research is needed to understand the throughput of biomass pyrolysis using these biomasses. Production of bio-oil *via* pyrolysis is yet to be made feasible commercially. Char should be removed from the reactor immediately so as to prevent contamination of bio-oil with solids [16]. A good understanding of biomass pyrolysis is required in order to maximize the production of bio-fuel. Understanding of pyrolysis technology to process agricultural residues, wood wastes and municipal solid waste which are easily available and process-able is needed[17].

The best possible tools for analyzing and developing any complex process are mathematical modeling, simulation, and optimization. Many pyrolysis studies on the modeling of pyrolysis have been reported since 1946. Mostly, they deal with the pyrolysis of woody biomasses [18].

Biomass pyrolysis incorporates several extremely complex reactions with quite a large number of intermediates and end products [19]. Since devising precise reaction mechanisms for biomass pyrolysis is difficult, pyrolysis models are devised in a manner that is more macroscopic and empirical. This research is aimed at studying the effects of various process conditions on the fixed bed and screw reactor using a few sample biomasses.

The aim of this study is to produce a biofuel (bio-oil) that is environmentally safer. The present work deals with the pyrolysis of biomass species that are easily available in India particulary in the Dehradun region. The pyrolysis experiments were conducted in two different reactor configurations i.e., fixed bed reactor and twin screw/moving bed reactor.

1.4 Thesis Outline

This thesis contains the following six sections:

- Chapter 2 summarizes the literature review that has been done to illustrate the general technical know-how of biomass fast pyrolysis and previous research efforts in connection with fixed bed and twin screw (auger) reactors.
- Chapter 3 includes a detailed description of the apparatus, the materials and methodology used for the experimental purpose of the research.
- Chapter 4 features the multi-objective optimization of the reactor.
- Chapter 5 the experimental result along with detailed discussion.
- Chapter 6 includes the conclusions of the research reached and recommendations made for future work.

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Chapter 2 Literature Review

2.1 Introduction

This chapter presents a brief literature review of the different aspects of biomass pyrolysis. Section 2.2 gives an overview of different types of biomass and its energy potential. In Section 2.3, pyrolysis is discussed as the first step in biomass pyrolysis. Section 2.4 is dedicated to related developed work. The bio-oil properties, both chemical and physical, are outlined in Section 2.5. Bio-oil applications are highlighted in Section 2.6. The gaps found from the literature survey are mentioned in Section 2.7, and finally, Section 2.8 deals with the present contribution made by the experiments performed.

2.2 Biomass

Biomasses are renewable sources of energy, consisting of carbon, hydrogen, and oxygen, having a composition of $C_8H_4O_6$ [9] . Based on the source from which it is obtained, biomass also contains certain earth metals. Biomass has a low H/C ratio and a high O/C ratio when compared to crude oil and, therefore, has lower energy density in comparison to crude oil [10].

The energy that is recovered from biomasses and other wastes are based mainly on thermochemical and biochemical processes. Pyrolysis has received much importance because it produces liquid fuel directly[20]. The liquid fuel thus obtained is widely known as bio-oil. It is highly acidic in nature, less stable and has low energy content [21]. The development of new technologies is essential to upgrade it and to decrease its acidity.

The energy obtained from biomass has always been in use in India since pre-historic times, basically in the form of the husk, firewood, cow dung cake and many other natural feedstocks [2]. Using biomass directly in the solid form is not healthy as it produces a lot of smoke and ash. This led to the development of biogas plants as they are pollution-free, i.e., they produce no smoke.

Biomass gives a cleaner alternate energy source that could drastically improve our energy security, economy, and environment, the 3 E’s. The industrial and energy usages of biomass are becoming attractive, technologically and also economically. The use of biomass provides several advantages, such as:

- **Abundance:** Biomass is associated with a secured supply of raw material to the energy system as it is available in most countries abundantly in various forms. Biomass can be considered to be a significant contributor to the energy supply for the nation which, at a later stage, ensures cheaper energy for the industries and greater self-sufficiency.

- **Socio-economic benefits:** include new chances of occupation that will be generated in rural areas of the country.

- **Environmental benefits:** include utilizing biomass for energy as an alternative to decrease the current environmental problems such as an alarming increase in levels of CO_2 in the atmosphere caused by the burning of fossil fuels. Further, bio-fuels contain a minimum amount of sulfur, thus reducing SO_2 emissions.

Biomass is renewable in nature and is basically the only biological petroleum substitute available. In general, biomass refers to trees and plants, forestry and organic residues, agro-industrial, and agricultural and domestic wastes, which include solid and municipal wastes. Biomass conversion processes mainly include reduction of moisture content, which results in increase in its thermal value and preservation potential. Wood and other biomasses can be treated in several ways to provide solid, liquid and gaseous fuels. In general, such methods can be categorized as thermal and biological. The main thermal conversion processes are combustion, pyrolysis and gasification. The biological processes include anaerobic digestion, fermentation and hydrolysis. Conversion of biomass *via* thermochemical processes (combustion, pyrolysis, gasification) is one of the best non-nuclear forms of energy in the future which is renewable with many advantages to ecology. When a compound is decomposed only by the action of heat in an inert atmosphere complete, it is called pyrolysis. Pyrolysis is one of the finest routes for the production of gaseous products, charcoal, tar, and other organics [21]. To design the equipment necessary for pyrolysis, it is important to design models that will describe the kinetics and the mechanisms that will govern the process [22].

Several workers [23] have conducted experimental and modeling studies on biomass pyrolysis. Despite these, no single model has been accepted widely that can predict the reaction rate and can provide prior information about the final conversion of biomass over an extensive range of particle sizes and for a particular species of biomass[24].

A reasonable understanding of biomass pyrolysis has considerable potential to develop a biomass pyrolysis conversion process. Since pyrolysis is the primary step of biomass conversion such as combustion and gasification, a good understanding of this is crucial for the proper and effective use of biomass. For applications of engineering, knowledge of the kinetics of pyrolysis is necessary to predict the pyrolysis behavior of biomass materials precisely, as well as for designing reactors.

2.2.1 Energy potential of biomass residues

The combustion of fossil fuels produces greenhouse gases. CO_2 emissions will, if trends prevail, lead to an excess over 1990 levels by 14% by the end of 2030. It is clear that an energy policy is to be framed to address this unsatisfactory situation. This energy policy will examine the role played by renewable sources. In this context, the European Commission has enhanced its support to programs involving energy efficiency and those using renewable energy sources.

Fig. 2.1 shows renewable energy sources contribution. It is apparent that bioenergy contributes to the highest among all other renewable resources. It is believed that bio-energy is the only renewable source of energy that has the potential to replace fossil fuels because of no net carbon emissions, no sulfur dioxide emissions and thus, serves to lessen greenhouse gas production.

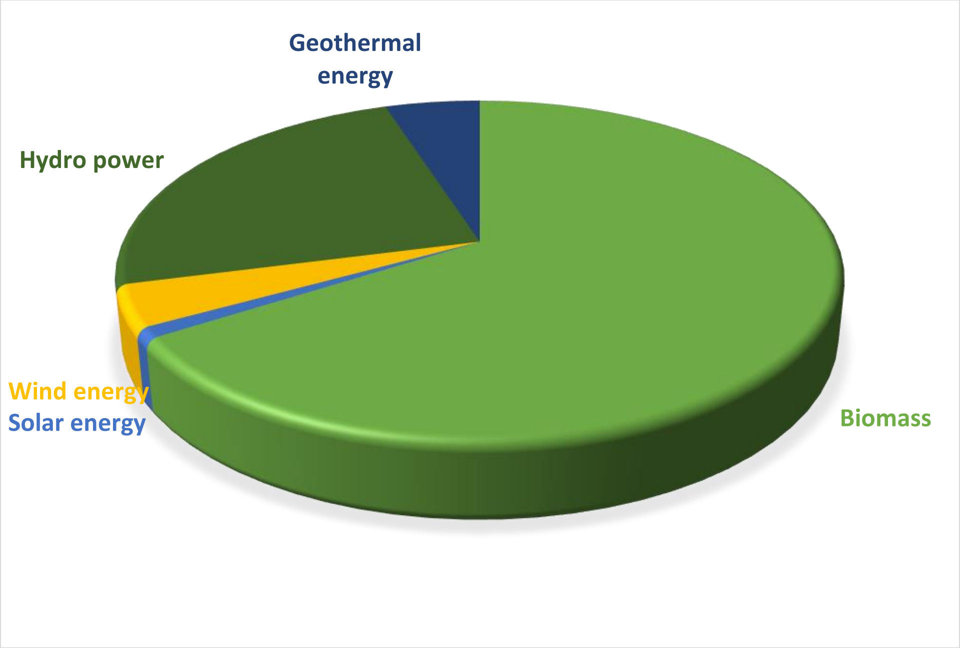

Fig. 2.1 Contribution of the various renewable energy resources [2]

Also, the thing that needs attention is that the current use of sources of renewable materials to produce energy is limited to a certain extent, which is significantly lower than their actual potential. In most countries, the share is largely less than 50% of the available biomass resources[25]. This is primarily because of the high costs for technologies involved in the upgrading of bio-oils. The investment costs can be as high as almost double the cost of fossil-based power plants. Also, a large effort is necessary for the storage and transportation of biofuels because their energy density is low.

2.3 Pyrolysis

2.3.1 Introduction

The decomposition of biomass thermally in the complete absence of oxygen is known as pyrolysis Pyrolysis results in the production of three products mainly solid, liquid and gas. Pyrolysis is of three types, i.e., slow, fast and flash. Slow pyrolysis of biomass results in the production of solid products i.e., char. Flash pyrolysis, also known as short residence time pyrolysis, is usually carried out at moderate temperatures for obtaining gaseous products. Fast pyrolysis is categorized by high heating rates with rapid quenching of the vapor in order to eliminate the production of secondary products.

Pyrolysis technologies have become prevalent only in the last about 20 years in comparison to gasification that is over 200 years old and to combustion technology that is more than 2,000 years old. Pyrolysis must also be seen as complementary to the process of gasification as liquid is generated, which can be stored and transported till its time of use and then can be used continuously as well as intermittently. Gaseous products obtained from gasification cannot be economically stored or transported, so it is most desirable to applications pertaining to baseload.

The process of pyrolysis produces three kinds of products in different amounts: char, tar, and gases, and their relative ratios depend mostly on the biomass characteristics, the reaction parameters and the method of pyrolysis. Liquids obtained from the pyrolysis of biomass are complex mixtures of oxygenated aromatic and aliphatic compounds. Biomass pyrolysis may yield methanol, which comes through methoxyl group of uronic acid and with the breakdown of methyl esters. A systematic pictorial depiction of biomass pyrolysis is shown in Fig. 2.2.

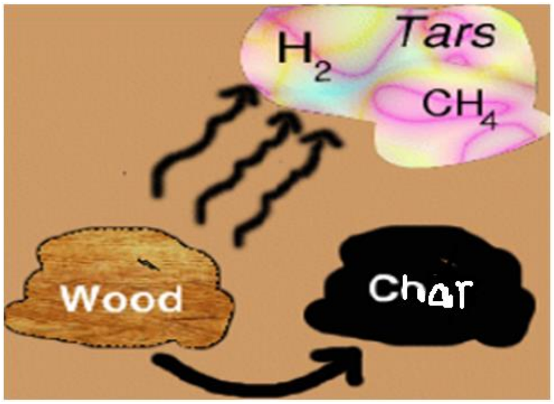

Fig. 2.2 Schematic depiction of the pyrolysis process

Biomass pyrolysis has many applications but the central focus of many studies is on applications related to energy so as to lower the greenhouse gas emission due to the driving force of political commitments made by all countries to decrease air pollution. Apart from its usage as a fuel, the thermochemical process products find use in particular fields. For example, the liquids product obtained from pyrolysis has many applications such as in the production of hydrogen, fine chemicals, adhesives, fertilizers, food flavors, resins, emission control reagents, hydroxyl acetaldehyde, and other commodities. The solid products obtained from pyrolysis finds its use as manure due to the presence of ash, char and unconverted biomass material present in it. As a result of biomass pyrolysis, the calorific value of bio-char thus formed is comparable to those of coke and lignite while the calorific value of liquid product obtained is same as those of methanol and ethanol. The calorific value of gases thus obtained by biomass pyrolysis is comparable to those of coal or producer gas but is much lower than for natural gas. The conditions for pyrolysis define the chemical composition of the products obtained.

2.3.2 Classification of Pyrolysis

Pyrolysis is classified as:

a) **Conventional:** Conventional pyrolysis is the one that results in high amounts of solid products, i.e., char. It is slow and irreversible pyrolysis of biomass. In this type of pyrolysis, the organic material present in biomass is decomposed thermally.

b) **Fast**: Fast pyrolysis is related to liquid product production. The primary goal of fast pyrolysis is to change solid biomass (40-75% on dry basis) to a liquid bio-oil. Of the remaining biomass, 10-20% is converted into char and the remaining 10-30% into an incondensable gas. In this type of pyrolysis process, the biomass is quickly heated to moderate temperatures in the absence of oxygen to yield: char 10-15%; bio-oil, 70-80%, and light gas, 10-15%. Bio-oil thus formed is a mixture of carbonyl and carboxyl functional groups along with phenolic compounds [26].

c) **Flash**: Flash pyrolysis is generally used for the production of gaseous products.

2.3.3 Pyrolysis Reactors

Most of the research work has been focused on testing of different reactor configurations and the development of new reactors. High amounts of bio-oil yield and high efficiency are the primary goals for several workers. Recently published reviews mostly classify the reactors as follow:

- Bubbling fluidized bed reactors
- Ablative pyrolysis
- Entrained flow reactor
- Circulating fluidized bed reactors
- Fixed bed fast pyrolysis reactor
- Screw reactor
- Rotating cone
- Vacuum pyrolysis reactor

Brigdwater [19] has discussed all the reactor configurations in several studies and has discussed the technical aspects, i.e., liquid collection methods, heating rate and char removal methods, with their advantages and disadvantages. Maximino [24] has done a detailed analysis of the fast pyrolysis technology focusing basically on the feedstock characterization that is available in plenty, reactor design, products obtained through pyrolysis and its upgrading.

The commercial processes must necessarily have the stages: proper reception of the feed, its storage, pre-treatment and preparing the feed, conversion of solid biomass into bio-oil through fast pyrolysis process and, finally, upgrading the bio-oil to a desirable marketable end-product such as biofuels. Although each one of these reactors is being studied on a lab-scale, but none of the reactors was found to be superior to the other; however, some reactors have been found more viable for commercial applications than others. Brown and Brown [23] have determined through several studies that five technologies are most suitable and feasible for the commercialization process. These are: a) bubbling fluidized-bed reactors, b) circulating fluidized-bed reactors, c) screw reactors, d) vacuum reactors and e) ablative reactors which can generate adequate amounts of bio-oil. The results obtained from these technologies justify their market attractiveness. Among all these reactors the fluidized-bed technology is considered to be the well-understood while screw reactors are better used for heterogeneous feedstocks. Screw reactor has the ability of easy handling of feed and smooth operations.

2.4 Related work

A considerable amount of work has been done on biomass pyrolysis. Many different biomass feedstocks were chosen for pyrolysis, e.g., bark, wood, nuts, forestry and agricultural residues, seeds and nuts, algae, grass, lignin, and cellulose. All these feedstocks were tested under various pyrolysis conditions and in different pyrolysis reactors. A major portion of research has been done using olive bagasse, wheat straw (agro-biomass), pinewood (woody biomass) biomasses as feed stocks[27]. The intermediate pyrolysis of rapeseed as reported in the literature [28] was studied in fixed bed reactor at a temperature of 550°C with a heating rate 300^0C/min using 0.6 – 0.85 mm particle size under nitrogen flow rate of 100 cm^3/min of . It resulted in about 65% of bio-oil yield. Neem seed pyrolysis was studied in semi batch reactors. It resulted in 38% yield of bio-oil operated at a temperature range of 400-500ºC with a heating rate of 20 ºC/min[14]. The intermediate pyrolysis of groundnut as a feedstock was studied in a fluidized bed reactor with a temperature range of 400-475^0C. It resulted in 63.48 weight % of bio-oil[29]. From all of these studies, the five basic parameters of the resulting oil were identified, i.e., viscosity, pH, density and low heating value (LHV) (24.56 cSt, 4.20, 1.2 kg/m^3, and 31.07 MJ/kg, and, respectively)[11]. It is found from the literature survey that only very few studies have been done on fixed bed and twin screw reactor using fast pyrolysis.

Limited studies are currently being available on the physio-chemical characterization of bagasse, mustard, pinewood, jatropha seeds biomasses and on pyrolysis products such as bio-oil, biochar. Further work is required to be done in order to understand its output comprehensively. Production of bio-oil through pyrolysis is not feasible commercially yet, the fast pyrolysis technology is still an immature technology. In order to compete with traditional fossil fuels, pyrolysis still has to to overcome many technical, social and economic barriers. For removal of solids from bio oil the development of an effective and rapid char separation technique is needed[24]. For pyrolysis processes, various catalysts were developed and used. But most of them were used only on small scales to improve upon the properties of the gas produced for research. This has its own limitations. Research on development of industrial catalyst still needs to be done as no catalysts have been developed so far which can sustain biomass pyrolysis. More research is needed to develop a more efficient technology for the manufacture of chemicals and bio fuels from bio-oil. The requirement is also to develop a catalyst that can remove efficiently the oxygen containing compounds from the bio oil in order to enhance the properties of bio-oil. Much focus has been given to the pyrolysis of biomass because of the opportunity to process agricultural residues, municipal solid waste and wood wastes to cleaner energy[8]. A good understanding of the integral process will allow pyrolysis products not only be maximized but also to be optimized.

Based on the literature survey, the following observations can be:

- Different types of biomass such as red oak, white oak, red maple, beech, sourwood, pinewood, poplar, spruce, timothy grass, switch grass, wheat straw, different straws, municipal sewage waste, aquatic plants, etc., have been utilized for the process of thermochemical conversion.
- Various reactors such as batch reactors, auger reactors, fluidized bed reactors, cone reactors, rotary cone reactors and ablative reactors have been used for the thermochemical process of pyrolysis. All these reactors have different operating conditions, explored to obtain green fuel and bio char for its commercialization.
- Generally, all of these reactors have their own limitations depending on the process conditions, type of feed and type of pyrolysis. So there is no natural choice as to which reactor is to be used. The selection is finally based on the essential requirement of the end products.
- Several attempts have been made to understand the non-isothermal kinetics comprehensively on the basis of thermal decomposition of the material of the biomass by various models and also to determine the kinetic parameters along with different energy analyses, techno-economic analysis of pyro oil, biochar from the pyrolysis process.

2.5 Bio-oil Properties

2.5.1 Chemical Properties

The pyrolysis reactions are generally oxidation reduction reactions in which some amount of biomass is reduced to carbon and the remaining amount is hydrolyzed and oxidized [30]. Pyrolysis generally involves the breakage of carbon-carbon bond and the formation of carbon-oxygen bonds [9]. The bio-oil obtained through pyrolysis is generally composed of a complex mixture of oxygenated hydrocarbons having a certain amount of water. The other compounds present in bio-oil are phenolic compounds, hydroxy aldehydes, carboxylic acids, sugars and hydroxy ketones[31]. The liquid product obtained through biomass pyrolysis are either heterogeneous fluids with an oily phase and an aqueous phase or a single homogeneous phase oil having high water content [32]. It is difficult to characterize bio oil chemically due to high molecular weight species present in them which are mostly complex phenolic compounds. The bio-oils also have polar and many non-volatile components which can only be detected through HPLC or GPC[33]. A thorough analysis of bio-oil involves at least GPC (molecular weight distribution), GC-MS (volatile compounds), FTIR (functional groups), and HPLC (non-volatile compounds).

2.5.2 Physical Properties

These are very well described in the literature. Table 2.1 shows a comparison between bio-oil and petroleum fuel [28].

The water content in bio-oil appears to be natural due to the original moisture present in biomass feed stock and also due to the dehydration reactions that produce up to 15 wt. % and 30 wt. % of moisture. To lower the water content in bio oil the biomass samples used should have less than 10% moisture. The water from bio oil thus produced cannot be removed as such by conventional methods, as the oil that is heated directly generally inclines towards polymerizing. The water present in the oil has opposing effects on its properties: lowering of oil-heating value but on the other hand, improved stability and reduced viscosity. Therefore, it is very crucial to carefully control the moisture content of the biomass and bio-oil[34].

The density of bio-oil is considerably higher in comparison to petroleum oil, which has its own effects on designing and also on the equipment specification (e.g., pumps and atomizers in engines and boilers). The bio oil viscosity generally varies from 35 cP to as high as 1000 cP (at 40 ºC depending on the type of biomasses used, pyrolysis operating conditions and the percentage of light component in oil the viscosity of bio oil varies generally from)[35].

Table 2.1: Properties of petroleum fuel oil and bio-oil [28]

Physical Properties	Heavy fuel oil	Bio-oil
Specific gravity	0.94	1.2

HHV, MJ/Kg	40	16-19
pH	-	2.5
Moisture content, wt.%	0.1	15-30
Viscosity (at 50°C), cP	180	40-100
Elemental composition, wt.%		
C	85	54-58
H	11	5.5-7.0
O	1.0	35-40
N	0.3	0-0.2
Ash	0.1	0-0.2

2.6 Bio-oil applications

Bio-oil can be used directly as a furnace/boiler fuel. It can also be used in turbines and diesel engines for power and heat generation. It has been tested successfully in a diesel test engine, where it acts similarly as diesel in terms of engine emissions and other parameters [27]. Bio-oil can be used as substitute of diesel fuel in engines with little modifications. The combustion of bio oil in turbines has also been reported by many researchers[36].

Bio oil also finds its application in electricity generation by co firing it with coal. Until and unless bio oil is upgraded it cannot be used as a transport fuels [37]. Bio oil after upgrading can be used as a high quality fuel[38]. The methods for bio oil upgrading includes: 1) hydro deoxygenation with the help of hydrotreating catalysts (CoMo or NiMo supported on alumina), 2) blending with other fuels, or 3) zeolite upgrading.

In addition to advantages there are several difficulties in the production of bio fuel *via* fast pyrolysis which in turn complicate the process. The poor energy density of biomass, large scale production of liquid fuel from biomass to meet energy demand is one to the serious problem related to the use of biomass as a transport fuel. One of the attainable solutions goes through the concept that has already been referred to: centralized upgrading in bio refineries. In comparison to petroleum industry, a bio refinery is one which is particularly being used for the production of bio fuels using biomass as feedstock.

2.7 Optimization

Optimization techniques mostly deal in finding the decision (or control) variable using an objective function(s). Optimization techniques have long been applied to problems of industrial importance. Optimization is important to have an efficient design, manufacturing and operation of various engineering activities. In the recent past, several researchers have carried out optimization studies on various pyrolysis reactors using different algorithms. Most of them have used traditional technique. These have a possibility of getting trapped at local optima. The traditional methods for optimization are based on gradients and depend on the initial guess and also on the degree of non-linearity. Therefore, these traditional methods of optimization have limited applications as they do not ensure global optimum solutions. In order to overcome this problem, nontraditional methods for optimization such as Differential Evolution (DE) [38], Evolutionary Computation based on natural phenomenon, Genetic Algorithms (GA) [39] and Simulated Annealing (SA) [40] have been developed. These non-traditional optimization methods have probabilistic conversion rules, i.e., they are stochastic types of algorithms. These non-traditional optimization methods have better global perspectives due to which these types of optimization techniques are gaining much more admiration in comparison to traditional optimization techniques [41]. Also, for a problem having many global optimal solutions many designers are much more interested in finding multiple global solutions instead of single global optima. This may be due to the fact that these global solutions may be suitable for one condition only but may not be valid for some other conditions and also due to the fact that a designer may not be interested in finding absolute global solutions but may be interested in finding solutions having marginally inferior values of the objective function. Thus, as a precautionary measure, it is advantageous to know all the equally good solutions for later applications. While in the case of traditional methods of optimization for finding multiple optimal solutions, the algorithms have to be used multiple times having different initial guesses every time and expecting different optimal solutions every time.

Multiobjective optimization (MO) is one of the best techniques used for solving problems involving more than one objective function. In regard to single objective optimization where an algorithm is used to get an optimal solution, multiple objective optimization generates Pareto sets in which ***all*** the solutions are regarded as *equally good*. In this study, the multi objective optimization problem for a twin screw reactor is solved using the non-dominated sorting genetic algorithm (NSGA-II). NSGA-II is a recent advancement of genetic algorithm which was developed by Kalyanmoy Deb and co-workers [41]. Fig.2.3 shows the flowchart of NSGA-II. The non dominated sorting genetic algorithm is of two types, NSGA and the elitist NSGA-II. These two versions of Genetic Algorithm is widely used for solving several multi objective optimization problems in chemical engineering.

I. **NSGA (or NSGA-I):** Non-Dominated Sorting in Genetic algorithm (NSGA) is a very effective and popular algorithm but lacks due to its computational complexity. It also has the disadvantage of the absence of elitism. The need for selecting an optimal value of a parameter makes its use limited for many researchers. Therefore, a modified version of non dominated sorting in genetic algorithm, i.e., NSGA-II, has been developed and is used in this study. NSGA-II has better sorting algorithm, no sharing parameter needs to be chosen *a priori* and it also incorporates elitism.

II. **NSGA-II** was developed by Kalyanmoy Deb. The main features of NSGA II are:
   - It is a non dominated sorting technique where the sorting is done on the basis of the level of non-domination of all individuals;
   - It implements elitism;
   - In order to have diversity this follows a crowding distance mechanism;

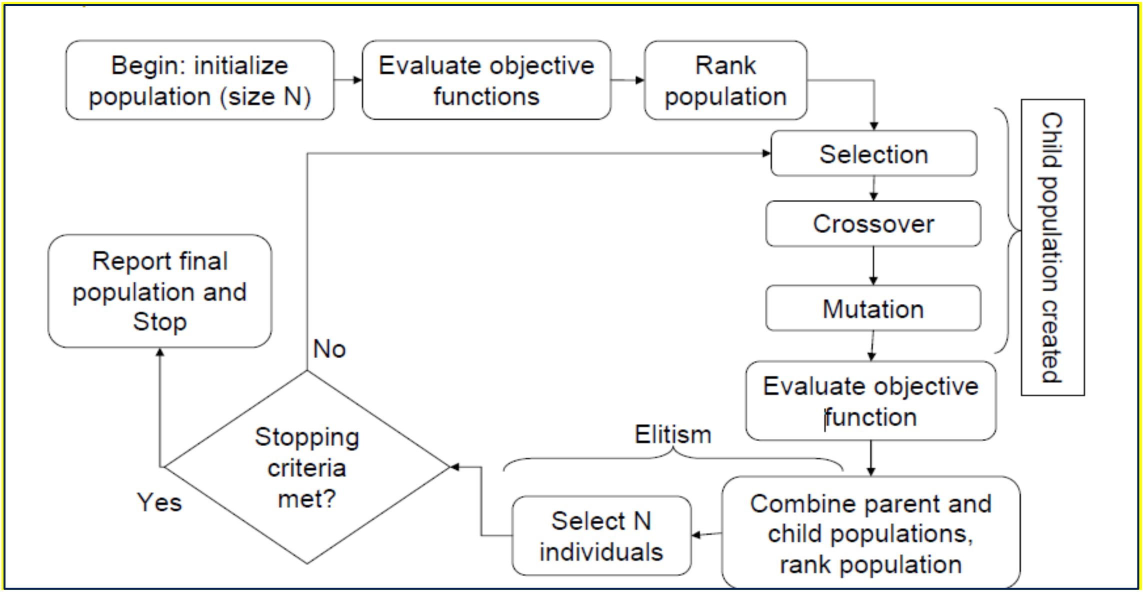

Figure 2.3. Flowchart of NSGA-II

2.8 Gaps as per the literature review

Even after considerable development in the field of biomass pyrolysis over the past few decades, the commercialization of biomass pyrolysis technology still needs a considerable exertion in order to overcome the techno economic barriers. The key challenges for future research in biomass pyrolysis are:

- Selecting biomass properly to achieve high bio-oil yields: Biomass having a low moisture content is mostly chosen so as to reduce the cost for drying and also to improve the quality of oil. In addition, the biomass having high cellulose content results in high production of bio-oil [42].
- Currently little knowledge is available on the physiochemical characteristics of various biomass types like pinewood, mustard, camellia, bagasse, and their co-products like bio-oil, bio char obtained by pyrolysis. Further research is essential to understand its throughput.

- Fast char removal methods must be develop in order to prevent contamination of bio oil with char.

- Various catalysts have been designed, tested and developed for the pyrolysis. These catalysts are used only on a small scale specifically in improving the gas production but no catalyst has been developed yet that can sustain the biomass pyrolysis process on an industrial scale.
- The upgraded bio-oil thus produced using various catalysts needs detailed characterization.
- Efficient technologies to produce bio fuels and chemicals from bio-oil still need to be developed.
- Development of deoxygenated catalysts is also necessary in order to remove the oxygen containing compounds in bio-oil which, in turn would improve the bio-oil properties.

Much of the attention nowadays has been given to biomass pyrolysis technologies as it helps in utilizing the agricultural residues, municipal solid waste and wood waste into clean energy. A deep understanding on biomass pyrolysis techniques will help in maximizing pyrolysis products with its optimization as the next step.

2.9 Present study

A substantial amount of research has been carried out by using different types of reactor worldwide on biomass pyrolysis. A lot of work still needs to be done in a twin-screw or auger reactor. This scanty knowledge has motivated the current activity. This work reports on work performed in a screw reactor and fixed bed reactor, with temperature profiles near about 500℃, with six different biomass samples. Analysis of pyrolysis products, i.e., bio-oil, biochar and pyrolysis gases was done along with the ultimate and proximate analysis of feedstock's. The operational limitations faced during the working of both the types of reactors that is, the fixed bed and the screw reactor, are addressed. Also, design changes in the reactors used for pyrolysis are suggested. It is assumed that these design changes would make the efficacy of the pyrolysis reactors. As the biomass used in the present study are mainly wastes and by-products, this research leads to no conflict between food and fuel. Further, this study has been done in order to perform an analysis on six different biomass feedstocks – bamboo, mustard, camellia, pinewood, bagasse and saw dust experimentally. The analysis of bio-oil and gases produced as a result of pyrolysis by fast pyrolysis was done using GC-MS and GC–TCD. The results for all the biomass samples are also compared.

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Chapter 3 Research Methodology

3.1 Introduction

This chapter explains the experimental facility, the techniques used for measurement with correlations with uncertainties, and the procedure used for experimentation. This chapter also comprises of the detailed characterization and analysis of pyrolysis products obtained.

3.2 Feedstock and materials

The biomass feedstocks that underwent pyrolysis were sawdust, bagasse, bamboo, mustard, camellia and pine wood. These biomass feedstocks came in their natural forms. Bagasse was taken from a sugar industry located in Doiwala village near Dehradun, Uttarakhand, India, while pine wood and saw dust were brought from a carpenter shop located at Saharanpur Chowk, Dehradun, Uttarakhand, India. Camellia was obtained from the interiors of Dehradun city. Other biomass feedstocks, i.e., bamboo and mustard, were brought from Delhi, India. To enhance the formation of the product, the biomass feedstocks were first pre-treated. The biomass feedstocks were dried first to reduce their moisture content and then were sieved in a sieve shaker to a size of 2 mm so as to improve the rate of heat transfer. The experiments were then carried out at 500 ± 10ºC.

3.3 Experimental setup

The present work deals with the study of two different biomass pyrolysis reactors twin screw reactor and fixed bed reactor**.**

3.3.1 Twin screw (Auger) reactor

To perform experiments, a twin screw biomass pyrolysis reactor was used. This reactor was developed to produce bio-oil through fast pyrolysis at a relatively higher temperature under inert conditions. It has the advantage of operating even at lower temperature but suffers from the disadvantage that all the moving parts are in the hot zone of the reactor. The major component of twin screw reactor are:

1. assembly to feed biomass feedstock

2. a sub-system carrying heat for pyrolysis

3. assembly consisting of reactor and twin screws

4. condenser and char tank

Also, following utilities are used:

1. frog pumps for circulating water in the condenser assembly

2. nitrogen cylinders for maintaining inert atmosphere in the reactor

The reactor body is made up of a horizontal pipe (AISI 316 steel) in which two screws are assembled along the length of the pipe. The length of both the screws is kept equal i.e., 565 mm. To rotate the screws, gears are arranged at both the sides of the horizontal pipe. The rotation of the screws moves the biomass along the reactor, i.e., from the inlet towards the hot zone and then towards the outlet of the reactor.

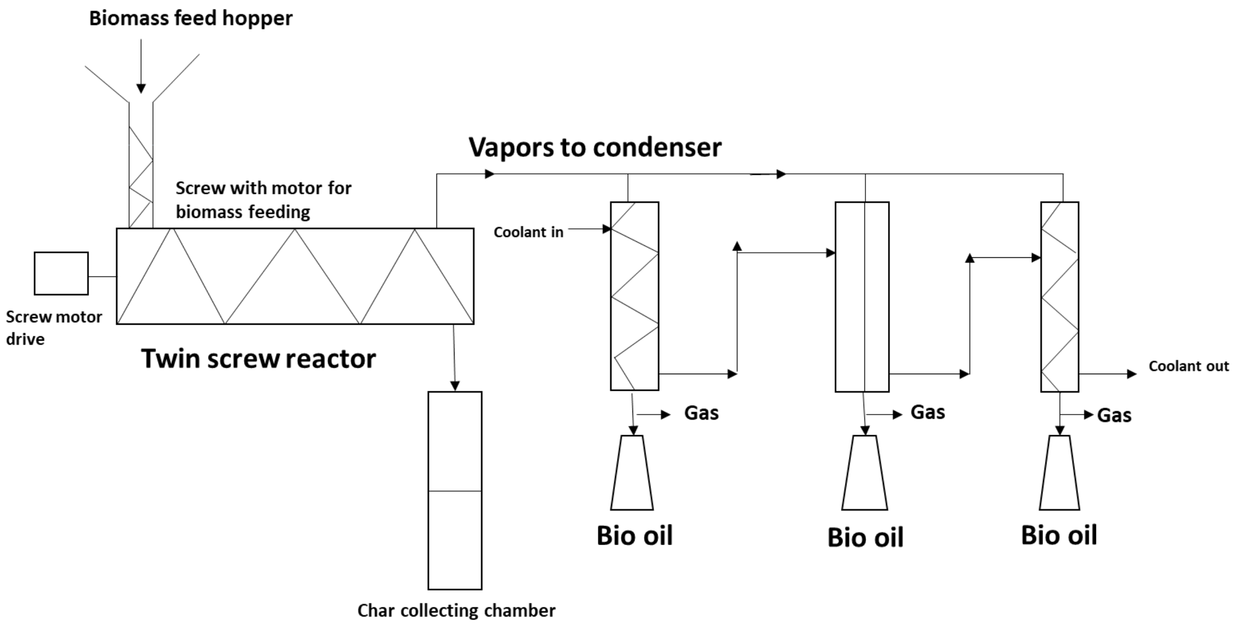


Fig. 3.1. Schematic of the experimental set-up of screw reactor

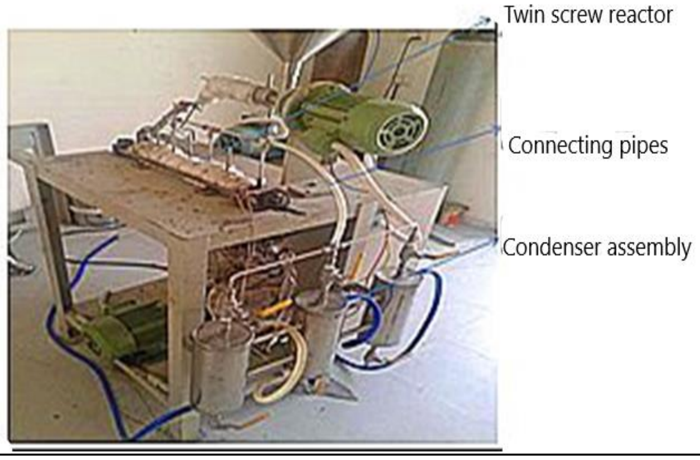


Fig. 3.2. The pyrolysis system in which experiments were carried out

The body of the reactor (horizontal pipe) is wrapped with an electrical resistance wire that defines the reaction zone by providing heat for the reaction. The inside and outside temperatures of the reactor are monitored with the help of thermocouples. A K-type thermocouple is used for temperature measurement. Generally a temperature difference of about 25–30°C was found between the extruder wall and the temperature of the heating coil. The reactor has five orifices; the diameter of each is 0.78 mm. Water pump is used for circulating the water through the condenser. A screw feeder is used for feeding biomass in the reactor. The feed rate for the screw feeder was indicated in RPM on a control panel fixed on the reactor. After the completion of reaction, hot vapors are made to pass through the condenser unit in order to get liquid product i.e., bio-oil while the solid product i.e., bio-char is collected in a cylindrical enclosed flask attached to the reactor. The non-condensable gases move to an exhaust system.

3.3.1.1 System components

The material of construction for the auger reactor is stainless steel for all wetted parts of the reactor and the feeding system. The reactor stand is constructed of mild steel. The insulation used in the main reactor system is ceramic fiber. All the heating parts are first wound with glass tape before winding with high-temperature flexible heaters. A flexible heater of 1,200 mm length was wound on the reactor with ceramic fiber insulation.

- **Biomass feeding system**

The biomass feeding system is shown in Fig. 3.3. The hopper has a rotating screw inside (at the pipe end) to ensure uniform injection of biomass to the reactor. The hopper has a feeding capacity of a maximum of 5 kg/hr. The screw in the hopper also encourages the mixing of the biomass feedstock used into the assembly of the reactor system. The screw is linked to a 0.5 HP motor with a variable frequency drive (VFD) to control its RPM.

Fig 3.3. Biomass feeding hopper

- **Screw system in the reactor**

The twin screws are constructed of SS. One of the screws is shown in Fig. 3.4. The screws are of length 20 in., and diameter, approximately 28 mm. A 1.5 HP motor is used with a reduction gearbox to rotate the reactor screws. The RPM is controlled with a VFD and displayed *via* a display on the control panel. The motor is mounted on the stand at the bottom. Three probes at different locations of the reactor measure the temperatures which are displayed on the control panel. A PID controller has been used to control temperature at the pre-determined desired values. The reactor is wound with electrical heating coil as mentioned above. This heater provides additional heating and avoids heat losses. Nitrogen purging is done at the feed end of the reactor to ensure an inert atmosphere and unidirectional flow of the vapors. The char i.e. solids exit the reactor from the other end and are collected in a cylindrical tank.

Fig. 3.4. One of the screws used in the reactor

- **Condenser system**

The product collecting system present at the downstream of the unit consists of thee parallel SS condenser systems, as shown in Fig. 3.5. The first and third units have coils inside for the vapors to flow and the second one has a straight SS tube inside. Cooling water flows co-currently on the inside of the condensers through inlets and outlets provided.

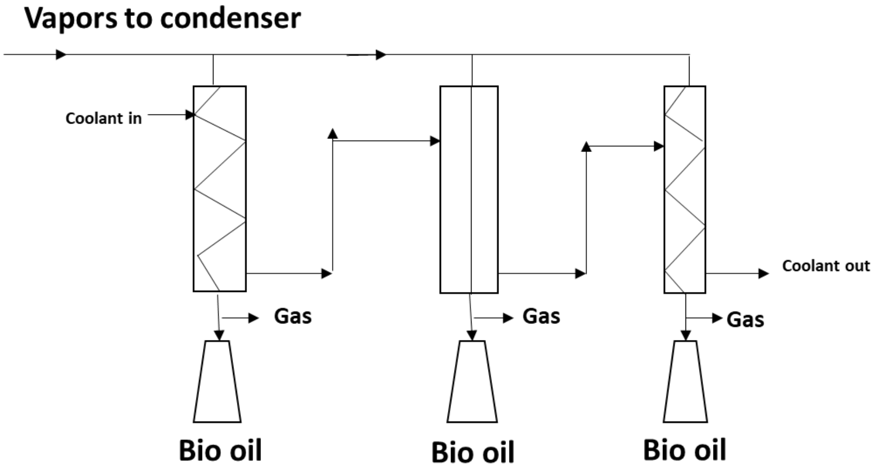


Fig 3.5. Condenser units

- **Heating coils**

The heating coils used in the reactor system are HTS/AMPTEX heavy AMOX insulated duo tape. A maximum temperature of 750℃ is achieved in the heating coils.

- **Nitrogen**

Nitrogen is used as purge gas. The nitrogen also acts as a carrier gas to carry the hot condensable vapors. The nitrogen has a purity level of 99.99 %. A valve used to regulate pressure of nitrogen. The pressure of nitrogen was kept above atmospheric pressure.

3.3.2 Fixed Bed Reactor

This reactor system consists of a vertical tube made of Inconel 800 as shown in Fig. 3.6. Biomass pyrolysis experiments were also being performed in this reactor system at a temperature of 500 ± 10ºC (in duplicate runs). The inner diameter of the tube is 25mm and its length is about 3ft. An electrical resistance coil provides heat for the reaction with a power of 2 KW at single phase, 220 V. The highest temperature that is achieved in the fixed bed reactor is found to be around 1,100ºC. Heating zone for this reactor is 1.5 ft long having PID controller for temperature monitoring. Three thermocouples are positioned with digital temperature indicators. The reactor outlet is connected with two glass condensers, where cold water is circulated for quenching the vapors obtained to finally get the desired bio-oil. The solid obtained within the reactor is cooled and is then weighed. The gas formed is measured by taking a difference.

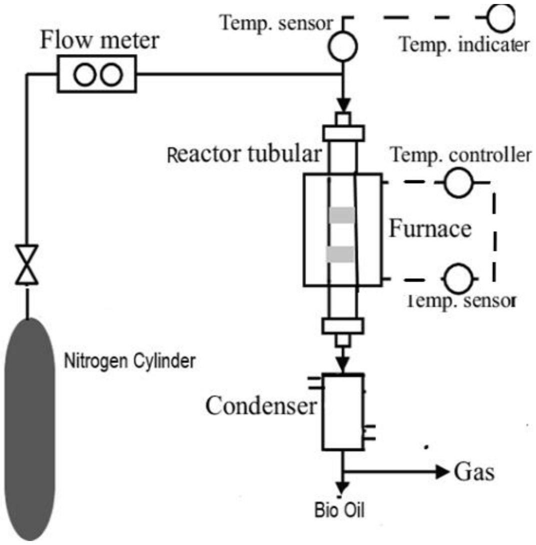


Fig 3.6. The schematic diagram shows the fixed bed reactor

3.4 Feedstock analysis and characterization

To determine the elemental composition in the biomass samples, elemental analyzer (Perkin Elmer, 2400 series II) was used. The elemental analysis of biomass feedstock is shown in Table 3.1.

Table 3.1 Elemental analysis of biomass feedstock

Samples	C	N	H	S	O
	Ultimate analysis (wt. %)				
Bamboo	44.90	0.72	6.038	0.018	48.342
Mustard (Khari)	46.31	4.45	7.055	0.036	42.149
Camellia	38.90	0.71	5.875	0.165	54.35
Pinewood	48.96	0.32	4.761	0.05	34.51
Sawdust	43.17	0.09	5.081	0.04	36.87
Bagasse	44.61	0.86	5.671	0.02	43.52

Table 3.2 Proximate analysis of biomass feedstock

Samples	Volatile matter	Ash	Moisture	Fixed Carbon	Calorific Value (MJ/Kg)	
	Proximate analysis (wt. %)				Experimental	Theoretical
Bamboo	76.72	2.57	10.25	10.84	16.8	16.2
Mustard (Khari)	70.78	14.98	6.86	7.38	20.24	19.06
Camellia	80.20	4.78	0.49	14.53	16.12	13.02
Sawdust	70.31	6.98	9.37	17.75	15.15	16.02
Pinewood	58.23	2.3	12.95	21.84	18.1	17.86

Bagasse	71.7	3.2	6.8	19.2	17.2	16.31

The proximate analysis for biomass samples was done as per standard ASTM methods and the results thus obtained are tabulated in Table 3.2. The amount of moisture present in the biomass samples significantly affects the conversion of biomass *via* pyrolysis, so the moisture has to be removed before carrying out pyrolysis. The ash content in biomass usually helps in catalyzing secondary pyrolysis reactions which, in turn has major influence on product yield while the volatile matter content and fixed carbon present in the biomass samples shows the ease with which biomass feedstocks can be burnt.

The calorific value of all biomass feedstocks are determined through experiments in a bomb calorimeter. The theoretical value of calorific value was found with the help of modified Dulong equation:

$$\text{CV (MJ/kg)} = \frac{33.5 \times \text{wt.\%C}}{100} + \frac{142.3 \times \text{wt.\%H}}{100} - \frac{15.4 \times \text{wt.\%O}}{100} \qquad (1)$$

The TGA analysis for selected biomass samples for present study is done in a TGA instrument (TGA-Q600) with N_2 flowrate maintained at 40 ml/min at a heating rate of 10° C/min. The sample size taken was 10 mg. All the selected samples for the present study were heated to 1,000°C. Fig 3.7 to be referred to results for TGA.

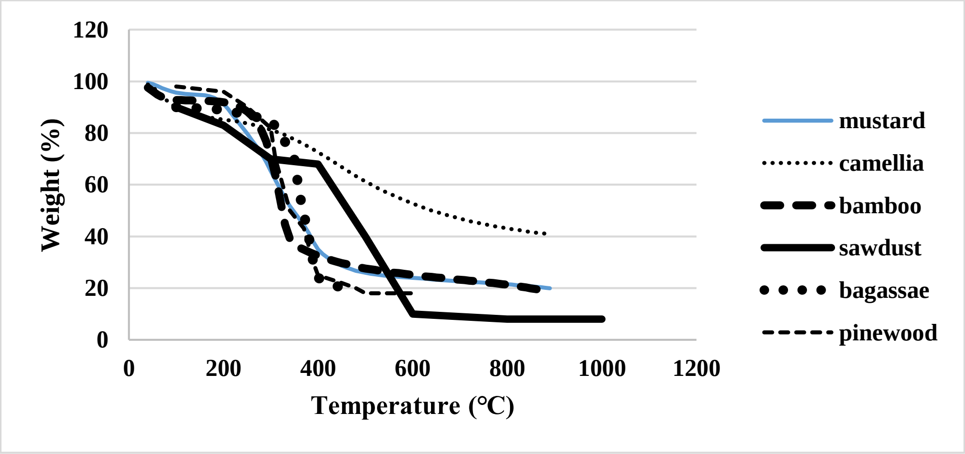


Fig. 3.7. Results for TGA for the six feedstocks

3.5 Operating conditions for the reactor

- **Temperature**

The temperature is been found to be an important parameter that influences the pyrolysis process[43]. The biomass particles are reacted when comes in contact to the hot inner wall of the reactor. It is also very important to note the differences between the inside and outside temperature of the reactor. The reactor outside temperature was found to be higher than the inside temperature as the heating coils are wrapped in the outer periphery of the reactor which increases the reactor outlet temperature. Also due to the heat transfer of biomass particles while they pass through the reaction zone make the temperature of reactor higher than the reaction temperature.

The temperature of the reactor generally controls the overall temperature of the system. Based on the trial experiments run conducted the bio oil yield is found to be maximum a temperature of 500℃±10℃. Optimal rates of reaction are also very crucial for favorable product distribution. All the experiments were performed at atmospheric pressure.

- **Biomass feed rate**

The rate at which biomass is fed is also an important parameter for pyrolysis. The biomass feed rate generally effects the yield and also the composition of the pyrolysis products. For twin screw reactor the biomass feed rate is proportional with the velocity of screws.

It is found in the present study that with high rotation velocities, the biomass particles are only slightly pyrolyzed due to a lower time of contact of biomass particles with the hot wall while by lowering the rotation velocity of screws more successful thermal degradation of feed samples results. As the rotation of the twin screw is reduced, the contact time of the particles with the hot wall increases and thus, more, successful thermal degradation of feed samples results. Thus, to get a consistent degradation of all feedstock in the reactor, the rotation velocity of screws should be kept constant and low, as far as possible.

- **Nitrogen rate**

Trial runs were performed in the screw reactor using different biomass samples so as to obtain reasonable operating conditions for biomass pyrolysis experiments to be performed which, in turn, will help in getting a significant bio-oil conversion. The flow rate for nitrogen gas was maintained 526 mL/min. The nitrogen flowrate was set as such so that it does not carry ash particles and char to the condenser unit. Also, this helps in keeping the residence time of about 2s for the fast pyrolysis reaction. The exact operating conditions at which experiments are run are given in Table 3.3. Each of the six samples was tested three times.

Table 3.3 Operating conditions for both the reactors

Operating conditions	**Fixed bed reactor**	**Twin screw reactor**
Temperature (°C)	500	500
Nitrogen (mL/min)	526	526
Residence time	2 min	2 s
RPM	-	55

- **Reproducibility**

The pyrolysis runs performed in both the reactors, i.e., fixed bed and twin screw reactor, were all done in duplicate so as to attain more trustworthy results. If the product fraction thus obtained are in agreement then that sample yield was recorded. Otherwise, the experimental run was repeated.

The choking of biomass in the feeding column results in the locking of the twin screws due to the trapping of biomass particles between the screw gap/pipe lead to a reduction in the repeatability of some tests and in special cases sabotaged the whole test.

3.6 Experimental procedure

Before starting the experiments the operating conditions like temperature of reactor, biomass feed rate, screw velocity in case of twin screw reactor) , nitrogen flow rate were predefined.

The first step followed to perform the experiments was preparation of biomass samples that is the biomasses used were first crushed, sieved and dried completely. The temperature of the reactor was then set in the control panel attached with the reactor which ultimately raises the reactor temperature to the required set limit. The temperature in the reactor is monitored with the help of thermocouples arranged along the reactor length. Four thermocouples were being used in the case of fixed bed reactor and two thermocouple were used in case of twin screw reactor. The temperature of the reactor was maintained constant throughout all the experimental runs with the help of temperature control panel. The coolant used were then pumped along the condensers. The nitrogen supply was then opened to maintain the inert atmosphere inside the reactor. The rotational motor in case of twin screw reactor was then switched on to rotate the twin screws in the reactor. In case of fixed bed reactor the pre weighed biomass samples was kept inside the reactor for various time intervals while in case of twin screw reactor the biomass sample is fed in to the feeding hopper from where it moves inside the reactor with the help of screw arrangement. As the twin screw rotates the biomass samples moves inside the reactor where pyrolysis reaction takes place. The experimental run was considered to be completed when no biomass sample is observed in the feeding hopper and no gaseous product is visible at the exhaust of the reactor. At this stage the heater and rotational motor (in case of twin screw reactor) are switched off. The nitrogen supply is then stopped. The coolant pumped is then switched off. The bio oil and char thus obtained are then collected and weighed. After the collection of bio oil and char the whole reactor assembly was cleaned up properly with acetone.

3.7 Results and Discussion

3.7.1 Product yield

Bamboo, camellia, mustard, pinewood, sawdust and bagasse were pyrolyzed at the conditions mentioned in Table 3.3. The results are summarized in Table 3.4. A considerable amount of liquid is obtained in both the reactors, i.e., auger and fixed-bed reactor. From table 3.4 it can be observed that the product yield i.e liquid and gas are found to be different based on the reactor type. The liquid yield decreases (from 2 to 10 wt. %) while the gas yield increases (from 2 to 10 wt. %) in the fixed bed reactor when compared to screw reactor. This results due to high heating rate in twin screw reactor.

The quantity of bio-oil and char that are produced by using the pyrolysis reactors is also calculated by weighing the biomass samples before and after each of the experiments. The product yields are then calculated on the basis of the weight of the products formed and the weight of the initial samples taken. The results are also shown in Fig 3.8 and Fig 3.9.

Table 3.4 Experimental results from the pyrolysis of biomass in both the reactors

Sample	Product Yields (wt. %)					
	Fixed bed reactor			Screw reactor		
	Bio char	Bio oil	Gases	Bio char	Bio oil	Gases
Bamboo	32	48	20	33	51	16
Mustard	29	40	31	29	43	28
Camellia	31	39	30	32	45	23
Saw dust	28	41	31	25	47	28
Pinewood	24	46	30	24	52	24
Bagasse	36	30	34	29	39	32

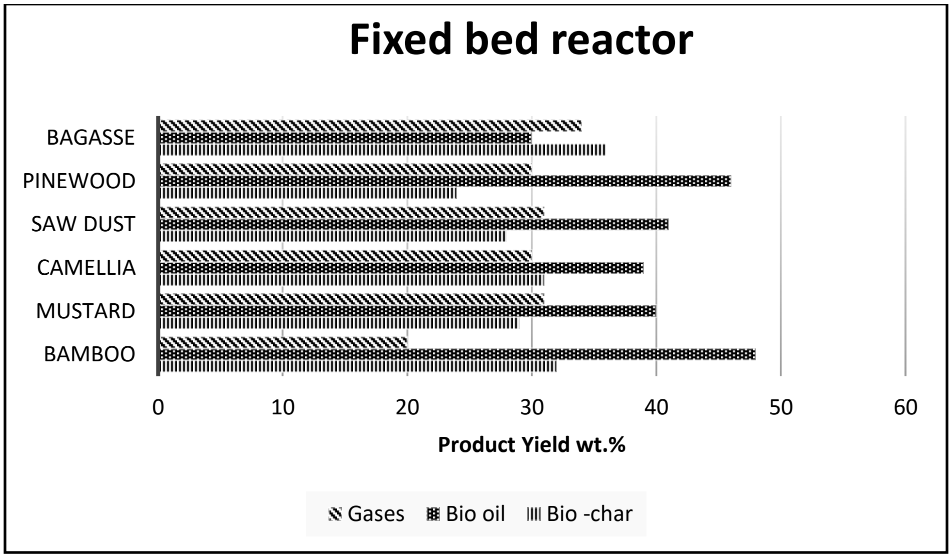


Fig 3.8. Overall product yield obtained from fast pyrolysis using the fixed bed reactor (operating conditions as in Table 3.3)

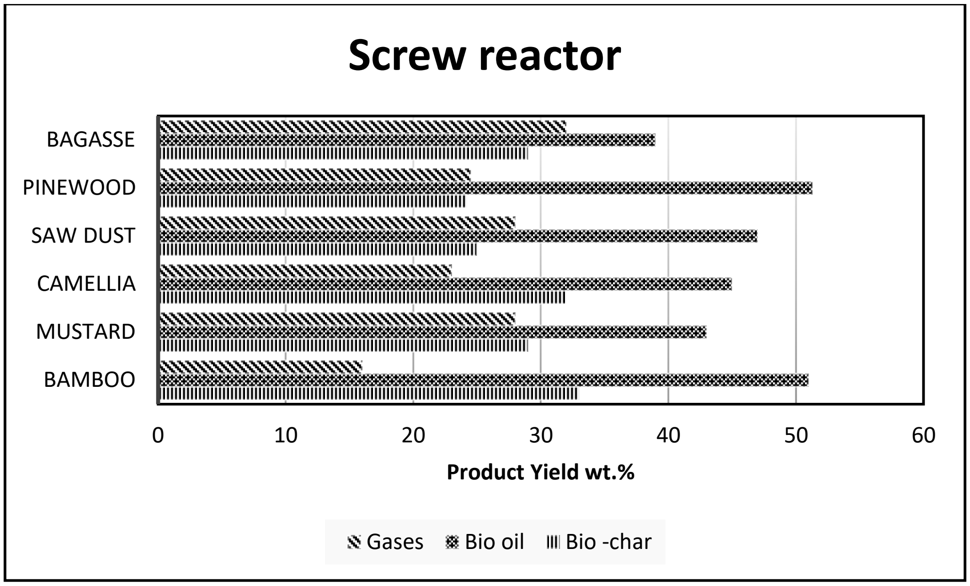


Fig 3.9. Overall product yield obtained from fast pyrolysis using the screw reactor (operating conditions as in Table 3.3)

3.8 Analysis of bio-oil and bio char

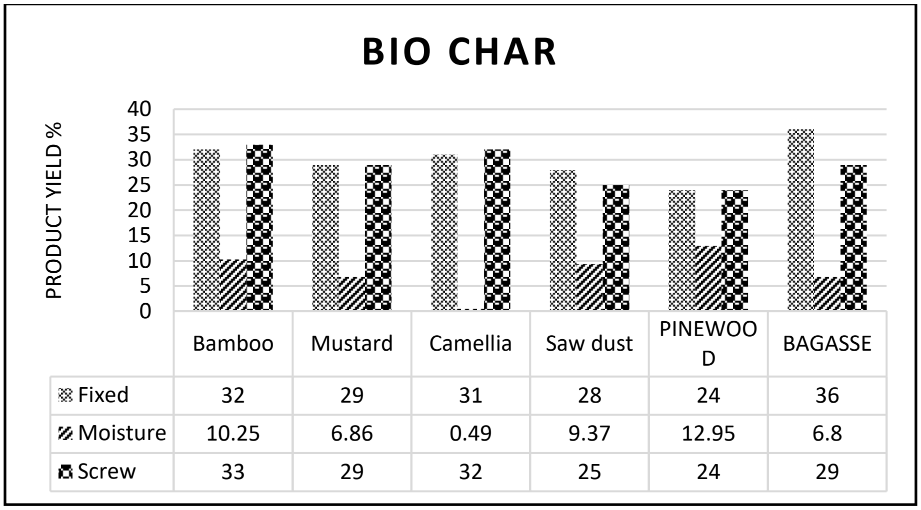
The product streams obtained through fast pyrolysis consists of organic condensate better known as bio oil, solid commonly known as char and gaseous products known as non condensable gases. In term of mass balance the overall product yield has been reported in Section 3.6. It has been observed that various types of feedstocks produce different amounts of char, bio-oil and varying gas compositions.

The samples taken from all the biomasses have shown similar composition which indicates good process stability. The percentage of the lighter components was found to be lower in the case of the twin-screw reactor in comparison to a fixed bed reactor as also being observed by other workers[44].

The screw reactor is associated with a fast heating rate and long residence times of the vapors, which results in the formation of a severe product. Slow heating rate results in gradual degradation of biomasses.

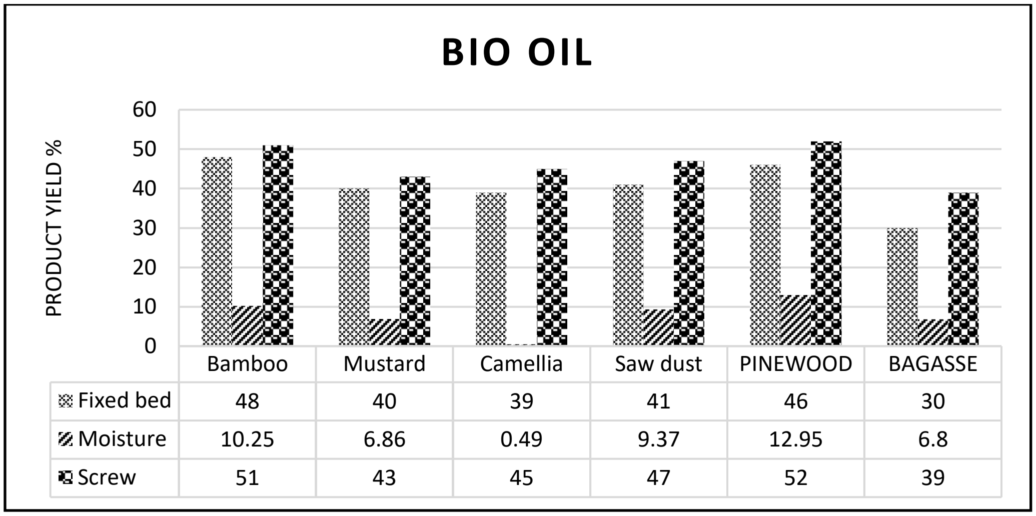
3.9 Moisture content effect on product yield

The moisture content present in biomass significantly effects the heat transfer rate which, in turn, influences the product yield. In this study it was found that high moisture content of biomass leads to high liquid yields. Consequently, biomasses such as pinewood, sawdust and bamboo are more favorable in bio-oil production (related to the lignin content). The ratios of moisture content, ash content, volatile matter and fixed carbon content of various biomasses have an important effect on the product yields. The biomass containing high volatile matter results in high quantities of bio-oil and syngas, whereas fixed carbon increases the bio char production. Fig. 3.10, 3.11 and 3.12 shows the effect of moisture content on bio-char, bio-oil and pyrolysis gases yield.



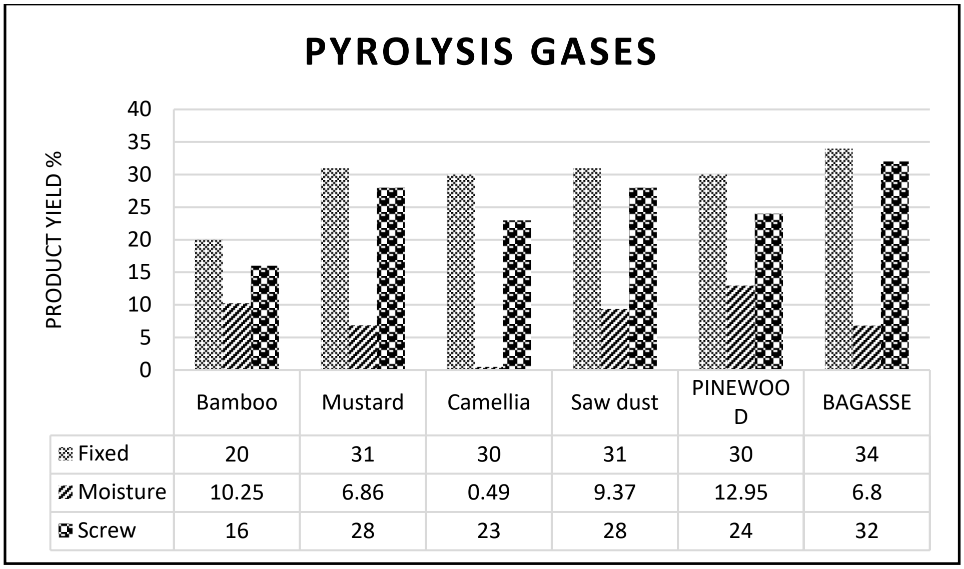
	Bamboo	Mustard	Camellia	Saw dust	PINEWOOD	BAGASSE
▩ Fixed	32	29	31	28	24	36
▨ Moisture	10.25	6.86	0.49	9.37	12.95	6.8
▦ Screw	33	29	32	25	24	29

Fig 3.10. Effect of moisture content on biochar (Operating conditions as in Table 3.3)



	Bamboo	Mustard	Camellia	Saw dust	PINEWOOD	BAGASSE
▩ Fixed bed	48	40	39	41	46	30
▨ Moisture	10.25	6.86	0.49	9.37	12.95	6.8
▦ Screw	51	43	45	47	52	39

Fig 3.11. Effect of moisture content on bio-oil (operating conditions as in Table 3.3)

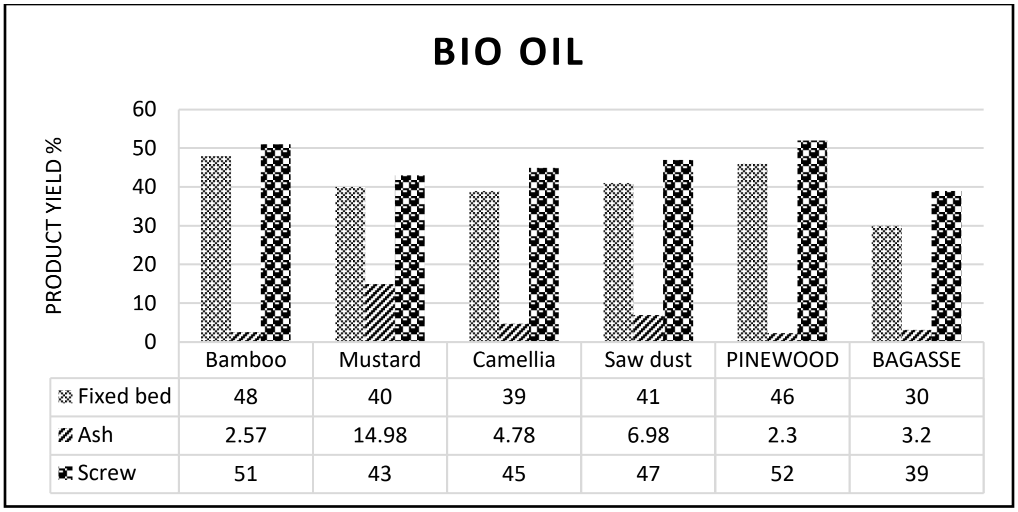


	Bamboo	Mustard	Camellia	Saw dust	PINEWOOD	BAGASSE
▩ Fixed	20	31	30	31	30	34
▨ Moisture	10.25	6.86	0.49	9.37	12.95	6.8
▦ Screw	16	28	23	28	24	32

Fig 3.12. Effect of moisture content on pyrolysis gases (operating conditions as in Table 3.3)

3.10 Effect of ash content of biomass on product yield

The highest bio-oil yield found using screw reactor was with pinewood (52 wt. %) and the lowest with bagasse (39 wt. %). This may be due to the presence of low ash content (2.3 wt. %) and high cellulose content in pinewood which got converted into bio-oil. As a consequence of high ash content, the agro biomasses such as camellia, mustard and bagasse presented lower yields of bio-oil (see Table 3.2). Figures 3.8 and 3.9 represents the overall product yields obtained from fast pyrolysis of different biomasses. On the other hand by using fixed bed reactor configuration the maximum amount of bio oil was produced with bamboo. The yields of biomasses obtained in the present study is comparable to those obtained in other studies [45] involving screw reactors and fixed-bed reactors.

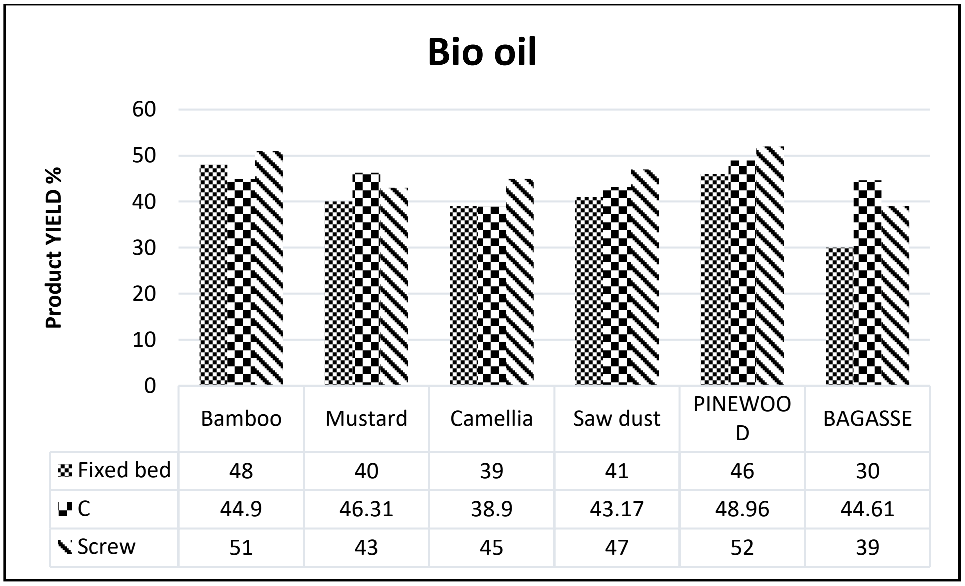


	Bamboo	Mustard	Camellia	Saw dust	PINEWOOD	BAGASSE
Fixed bed	48	40	39	41	46	30
Ash	2.57	14.98	4.78	6.98	2.3	3.2
Screw	51	43	45	47	52	39

Fig 3.13. Effect of ash content on bio-oil yield (operating conditions as in Table 3.3)

3.11 Effect of the carbon content of biomass on product yield

The carbon, oxygen, hydrogen, nitrogen and ash content significantly affect the pyrolysis products. It was found that the biomass feedstocks with low nitrogen and mineral contents results in high bio-oil and syngas production. Fig 3.14 shows the effect of carbon content on bio-oil yield.



	Bamboo	Mustard	Camellia	Saw dust	PINEWOOD	BAGASSE
Fixed bed	48	40	39	41	46	30
C	44.9	46.31	38.9	43.17	48.96	44.61
Screw	51	43	45	47	52	39

Fig 3.14. Effect of the carbon content of biomass on bio-oil yield (operating conditions as in Table 3.3)

3.12 Gas Chromatography

The components present in bio-oil produced from biomass pyrolysis was found through Gas Chromatography-Mass Spectrometry study using the NIST library. Components such as aldehydes, carboxylic acids, ketones, phenols, esters and amides were found to be the main chemical groups present in bio-oils. It was observed that pinewood biomass contains significant amounts of phenolic components which is due to lignin content found in pinewood in comparison to other biomasses used in this study.

Similar results were observed when compared to other studies [27]. GC-MS analysis, thus, reveals that bio-oil from various biomasses consists of mainly ketones, alkane, alkyne, amines, alkene, imine, alcohols and heterocyclic compounds, as listed in Table 3.5.

Through GC-MS analysis, it is observed that bio-oils obtained from various biomass samples have similar components with little amount of variation in the saturate and aromatic percentage. It is found that the aromatics and saturates percentage were less in bio-oil produced from the fixed bed reactor in comparison to bio-oil obtained from the moving bed reactor due to early removal of pyrolysis products from fixed bed reactor.

Through this study it is also observed that hydrocarbons are the most abundant product found in bio-oils. Other authors had found naphthalene, fluorine and other polycyclic aromatic compounds in bio-oil but in the present study, none of these hydrocarbons was detected. This may be due to the different biomass types, short gas residence times and low reaction temperatures.

The calorific value of bio-oils obtained *via* pyrolysis in both the systems is found to be high, i.e., comparable to light fuel oil and, thus, can be used as a synthetic liquid fuel.

The bio char thus produced consists of initial mineral matter formed due to process severity. The ash content in bio char is found to be high and has similar value as that reported by other authors[46]. The ash percentage was found to be 9% to 15% based on the characteristic of the biomass feed.

GC-MS was performed on an Agilent 6890 N unit with a GC column 25 μm thickness, DB – 1701, 60 mm X 0.25 mm.

Table 3.5: GC-MS analysis of different compounds present in bio-oil produced from both the reactors

Compound Name	Molecular Formula
Cyclopropane	C_3H_6
Cyclobutane	C_4H_8
Heptane	C_7H_{16}
1,2,3-Trimethylcyclopentane	C_8H_{16}
Octane	C_8H_{18}
4-Methyloctane	C_9H_{20}
1-Undecene	$C_{11}H_{22}$
Undecane	$C_{11}H_{24}$
Dodecene	$C_{12}H_{24}$
Tetradecane	$C_{14}H_{30}$
Icosane	$C_{20}H_{42}$
Ethane	C_2H_6
1-Tetradecene	$C_{14}H_{28}$
1-Octadecene	$C_{18}H_{36}$
Ethylene	C_2H_4
1-Hexadecyne	$C_{16}H_{30}$
1-hydroxy-2-propanone	$C_3H_6O_2$
2-butanone	C_4H_8O
1,3-cyclopentanedione	$C_5H_6O_2$
2,5-Cyclohexadienone	C6H6O
1,4-Cyclohexanedione	C6H8O2
Carbon-dioxide	CO_2
Methane	CH_4
Water	H_2O
Nitrogen	N_2
Carbon-monoxide	CO

Hydrogen	H_2
Oxygen	O_2
Nitric-oxide	NO
Sulfur	S
Sulfur-dioxide	SO_2
Carbon-graphite	C
Levoglucosan	$C_6H_{10}O_5$
2,2,4-trimethyl-1,3-dioxalane	
Carboxylic anhydrides	
Furans	
Saccharides	

3.13 Calorific value

The calorific values were determined experimentally and theoretically (HHV) for all the biomass feedstocks used in this study. The calorific value thus determined from both sources have an error of ±5 percent. It is found from the present study that pinewood and bamboo bio-oil resulted in high calorific values in comparison to respective biochars and biomasses. The biochars have high calorific value in comparison to biomass samples due to the presence of a lower percentage of H and O than C, which significantly increases the energy value of the fuel as more energy is contained in C-C bonds than in C-O and C-H bonds[47]. Fig. 3.14 shows the calorific values of bio-oils obtained from the pyrolysis of bamboo, mustard, camellia, pinewood, bagasse, and sawdust. Bridgwater (2011)[19] stated that a higher heating value of bio-oil is produced from higher temperatures and shorter times.

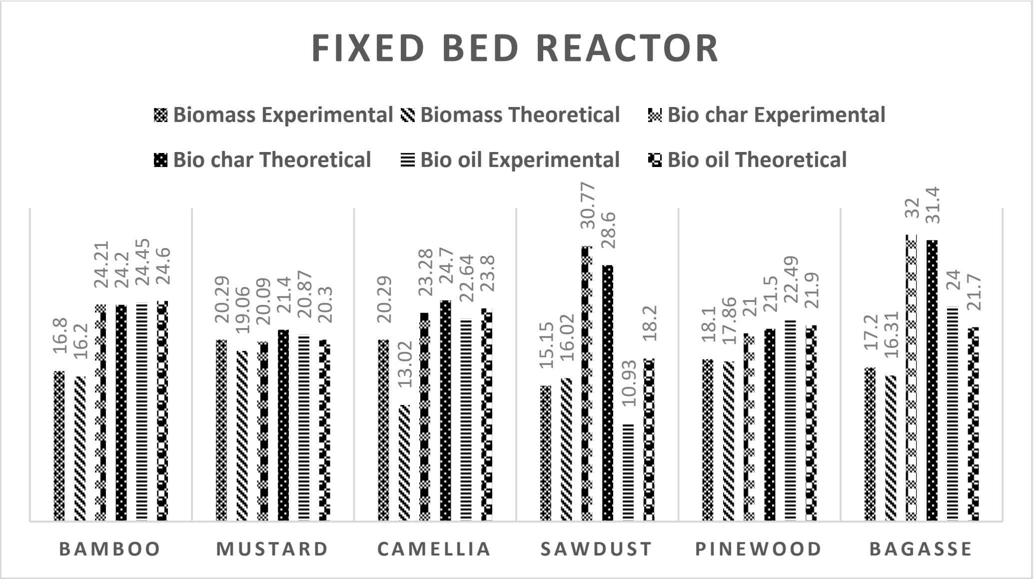


Fig 3.15 Experimental and theoretical calorific values of biomass samples and products in the fixed bed reactor (operating conditions as in Table 3.3)

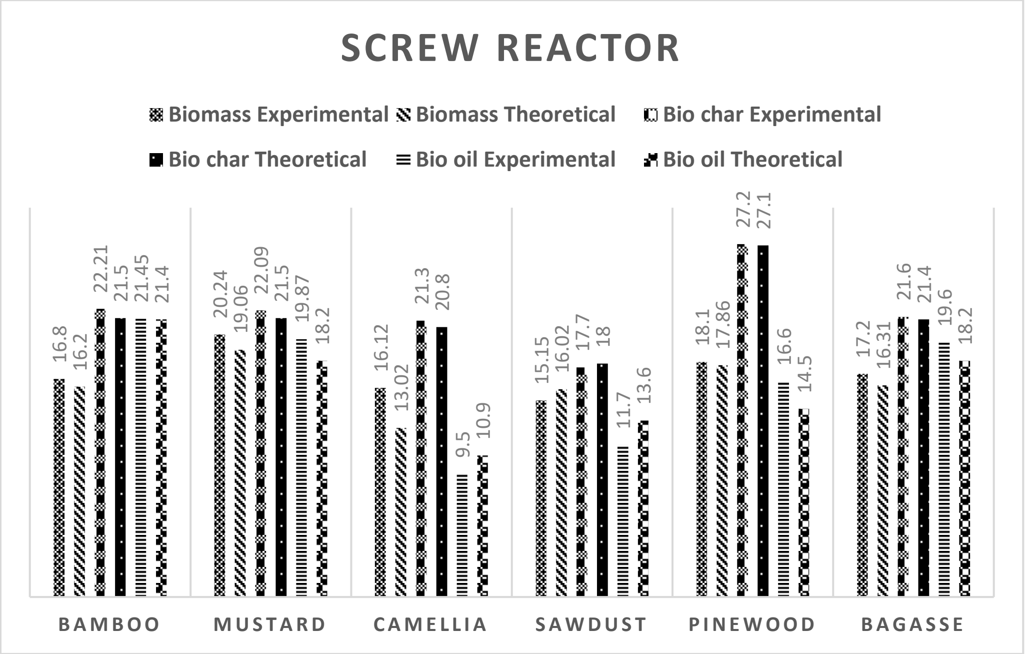


Fig 3.16. Experimental and theoretical calorific value of biomass samples and products in a screw reactor (operating conditions as in Table 3.3)

3.14 Discussion

The biomass pyrolysis experiments were performed in two different reactor types i.e., fixed bed and twin screw reactors operating under similar temperature conditions and in an inert atmosphere. The twin screw reactor or moving bed reactor can process up to 1kg/hr of biomass feedstock. This reactor operates in a continuous mode with good process stability and reproducibility observed during experimentation. The results obtained from both the reactor types were compared. It was found that complete biomass conversion was achieved in both the reactor types. The char yields obtained from both the reactors were found to be similar but different liquid and gas yields were obtained in both the reactors. It is observed that when biomass pyrolysis is performed in the twin screw reactor there is an increase in the liquid yield, i.e., the bio-oil produced is more in comparison to similar experiments performed in a fixed bed reactor, whereas there is a decrease in the gas yield in the screw reactor in comparison to the fixed bed reactor. This may be due to the severe cracking of pyrolysis products in twin screw reactors due to the faster heating rates and longer gas residence times in the reactor. All the experiments performed in both the reactor configurations were completed satisfactorily with no problem faced in the reactors during long working time. On characterization of pyrolysis products it is found that char obtained comprises of mainly carbon while the liquid product, i.e., bio-oil is a mixture of hydrocarbons. The pyrolysis gases comprised of a mixture of carbon monoxide, hydrogen, carbon dioxide and nitrogen. The pyrolysis conditions were kept the same in all the experimental runs except the feed rate of biomass samples in the screw reactor.

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Chapter 4 Multi-objective optimization

4.1 Multi-objective optimization

Multi-objective optimization problems usually deal with more than one competing objectives. The Pareto optimal set is regarded as one of the best ways of presenting the results of these. Pareto sets provide a set of *equally good* solutions, i.e., in this set of solutions, none of the solutions is better than the other solution. With Genetic algorithm (GA) a Pareto set can be generated in a single run with minimal increase in computational time. GA mimics natural genetics[48].

The real optimization problems faced in industries usually deal with more than one objectives. To solve such problems one of the best ways is to generate Pareto optimal sets that provide a spectrum of trade-offs of the competing objectives. Pareto optimal sets provide equally good solutions, i.e., no solution is better than the other one unless some other criterion is used for comparison.

Multi-objective optimization problems can be solved using several methods. In this study, a more recent version of the NSGA-II (Non-dominated Sorting Genetic Algorithm) has been used to obtain the Pareto set.

In this work, a problem involving multi-objective optimization is solved using NSGA-II. The problem involves two objectives: a) to maximize the bio-oil yield, and b) to minimize the biochar yield. Four process variables (called decision variables) are used, as described later.

4.2 Formulation of the optimization problem

Four decision (process) variables (x_i, $i = 1 – 4$) are chosen for the present study. A simple problem involving a multi-objective optimization function of these process variables is solved using a multi-objective genetic algorithm. The problem solved is to obtain the maximum bio-oil yield ($Y_{\text{bio oil}}$) and to minimize the biochar yield (Y_{biochar}). The temperature of the reactor, T_{HC}, rate of flow of nitrogen, Q_{N2}, auger speed, ω_{A} and biomass feed rate, m_{HC}, are used as the decision variables, x_i, i=1-4.

The multi-objective optimization problem to be solved is described below

$$\text{Max } I_1 (x_1, x_2, x_3, x_4) = Y_{\text{bio oil}}$$

$$\text{Min } I_2\ (x_1, x_2, x_3, x_4) = Y_{\text{biochar}}$$

where

$x_1 = T_{HC}$ (°C)

$x_2 = Q_{N2}$ (sL/min)

$x_3 = \omega_A$ (rad/sec)

$x_4 = m_{HC}$ (kg/hr

subject to constraints:

$$500 \leq T_{HC}\ (°\text{C}) \leq 630$$

$$1.5 \leq Q_{N2}\ (\text{sL/min}) \leq 2.5$$

$$25 \leq \omega_A\ (\text{rad/s}) \leq 30$$

$$9.4 \leq m_{HC}\ \ (\text{kg/hr}) \leq 21.9$$

To investigate the values of the bio-oil yield and the biochar yield, the following normalized model equations are used. These are given by [46] for an auger reactor:

$$I_1 = Y_{\text{bio oil}} = 66.9 + 7.36\left(\frac{T_{HC}-525}{50}\right) + 0.63\left(\frac{Q_{N2}-2.5}{0.5}\right) - 0.52\left(\frac{\omega_A-30}{2.5}\right) + 2.28\left(\frac{m_{HC}-15}{3}\right) + 1.24\left[\left(\frac{T_{HC}-525}{50}\right)\left(\frac{\omega_A-30}{2.5}\right)\right] - 0.64\left[\left(\frac{T_{HC}-525}{50}\right).\left(\frac{m_{HC}-15}{3}\right)\right] - 2.36\left(\frac{T_{HC}-525}{50}\right)^2 - 0.73\left(\frac{m_{HC}-15}{3}\right)^2 \qquad \text{(a)}$$

$$I_2 = Y_{biochar} = 20.55 - 7.29\left(\frac{T_{HC}-525}{50}\right) - 0.89\left(\frac{Q_{N2}-2.5}{0.5}\right) - 2.77\left(\frac{m_{HC}-15}{3}\right) - 1.31\left(\frac{T_{HC}-525}{50}\right)\left(\frac{\omega_A-30}{2.5}\right) + 1.03\left(\frac{T_{HC}-525}{50}\right)^2 + 1.17\left(\frac{m_{HC}-15}{3}\right)^2$$

(b) (4.1)

It may be added here that ideally, the data taken on the auger reactor in *this* study should have been used for MOO, but this was not possible since experiments could be carried out for only one set of conditions (values of T_{HC}, Q_{N2}, ω_A and m_{HC}).

4.3 Input data for NSGA-II

We have chosen two objective functions, i.e., maximization of the bio-oil produced and minimization of the biochar. The computer code used for NSGA II minimizes *all* the objective functions, so we need to transform the maximization of bio-oil into a minimization problem. The most popular form to convert a maximization problem into a minimization one is to use: min is $f_1 = 1/(1 + I_1)$[49]. Mathematically the optimization problem can be written as follows:

$$\text{Min } f_1 = 1/\,(1 + I_1) = 1/(1+Y_{\text{bio oil}})$$

$$\text{Min } \mathrm{I}_2 = \mathrm{Y}_{\text{biochar}}$$

Here, I_1 is the original objective function while f_1 is the modified objective function (to be minimized).

The Pareto set was produced for the present multi-objective problem using different initial populations and different combinations of the *computational* parameters of NSGA-II. The best results produced have been discussed and shown here.

Table 1 shows the computational parameters used in the present study. The values presented in the table were kept unchanged for *all* the other optimization runs in this study.

Table 4.1. Reference values of the computational parameters in NSGA-II

Maximum number of generations, N_{gen}	50
Population size, N_{pop}	400
Crossover probability, P_{cross}	0.8
Mutation probability, P_{mute}	0.0001

The Matlab™ program used consists of the model equations and the code for NSGA II.

4.4 Results

It is observed from Fig. 4.1 that when one goes from the point, A, to point, B, the yield of bio-oil increases (desirable), but the yield of biochar also increases (undesirable). Hence, these points comprise of a Pareto set. The Pareto-optimal sets obtained by maximizing the bio-oil yield and minimizing the biochar yield are presented in Figs. 4.1-4.3. These figures show a smooth and well distributed Pareto set being generated by NSGA-II over a wide range of variables. With different combinations of the computational parameters, the

Pareto set shown in Figure 4.3 is observed to be the best. The Pareto sets generated from all of these studies ultimately become an identical front; though with minor variations (mainly in the range of the Pareto set).

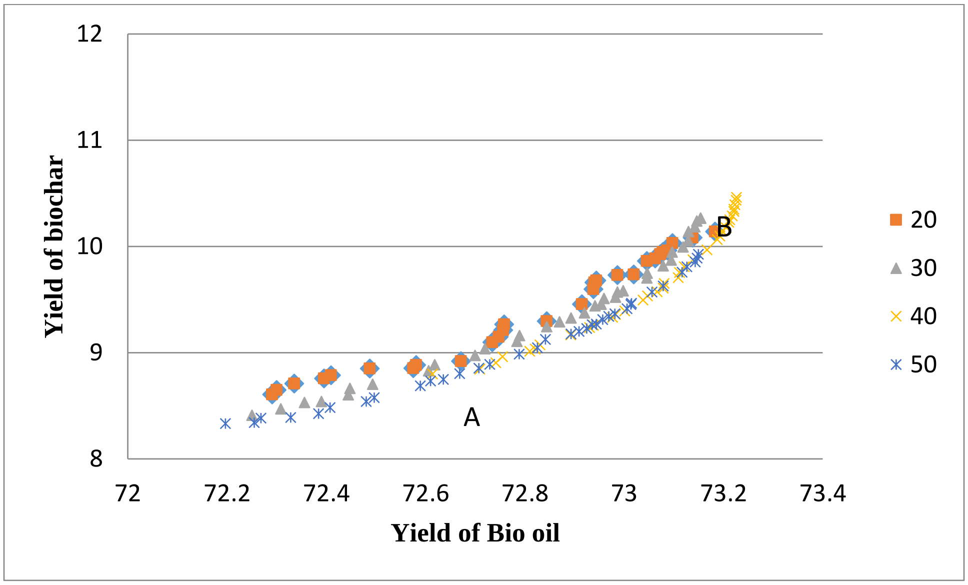

Fig. 4.1 Pareto set at different generations with a population size of 100. Reference values in Table 4.1 used for the other computational parameters

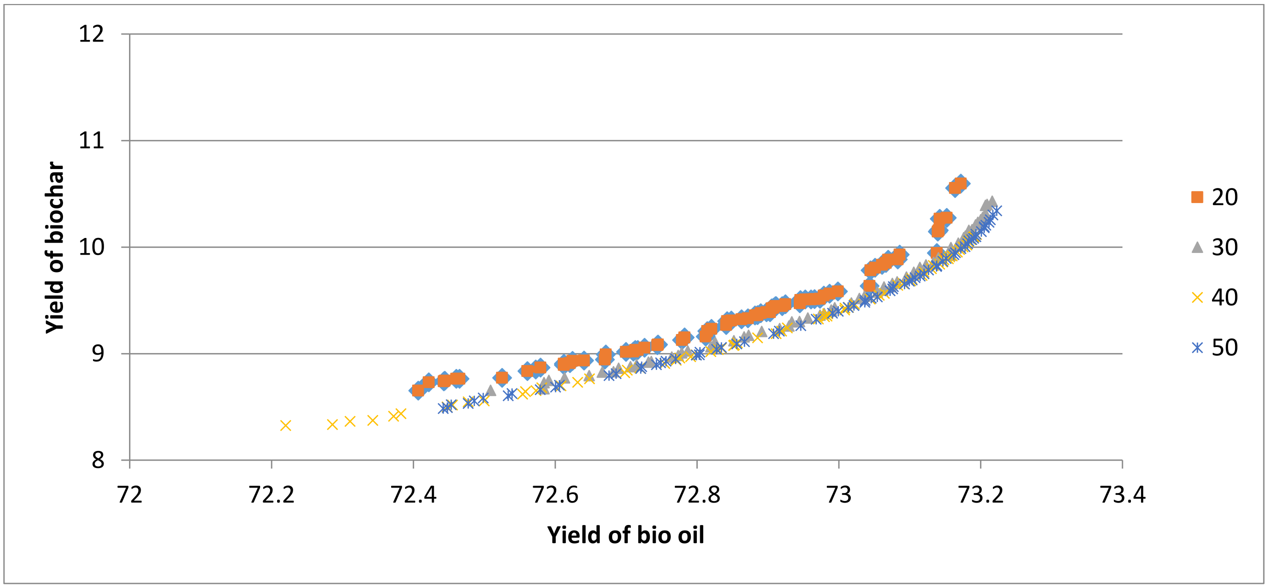

Fig. 4.2 Pareto set at different generation numbers and a population size of 200. Reference values in Table 4.1 used for the other computational parameters

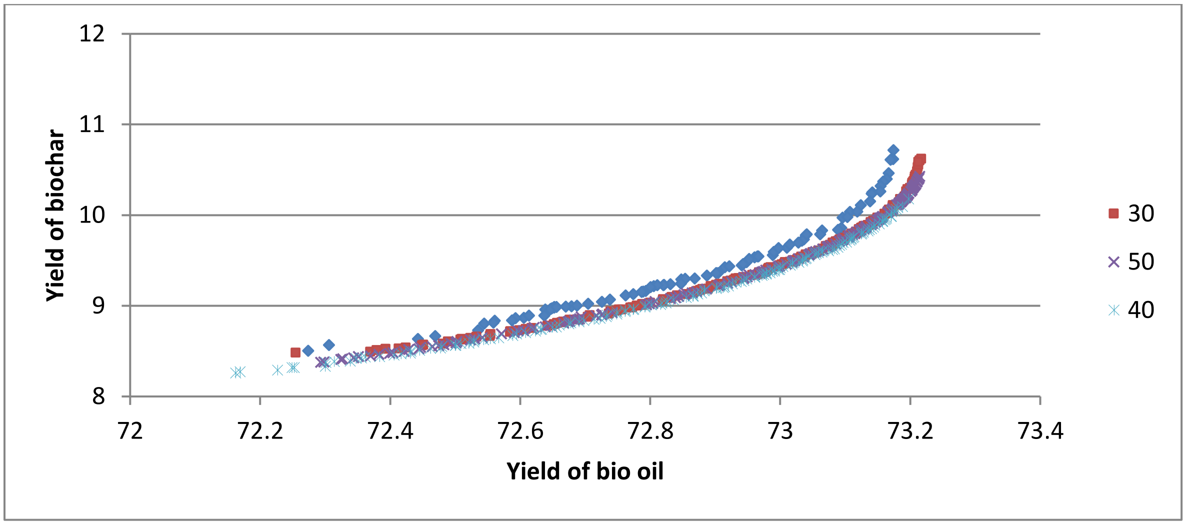

Fig. 4.3 Pareto set with different generation numbers and population size of 400. Reference values in Table 4.1 used for the other computational parameters

It is found that NSGA-II is sensitive to the values of several computational parameters, namely, N_{gen}, P_{cross}, and P_{mute}. It is observed that as N_{gen} is increased from 10 to 50, the population of solutions converge to the final Pareto set, as shown in Figure 4.3.

This *preliminary* study shows the existence of Pareto sets for the pyrolysis problem. A more extensive study can be carried out once more experimental data is taken on the auger reactor, and an appropriate curve-fit equation becomes available.

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Chapter 5 Results and Discussion

5.1 Results and discussion

This work demonstrates that different biomasses can be successfully converted to bio-oil. Two reactors have been studied, the twin-screw (auger) reactor and the fixed bed tubular reactor. The composition and yield of bio-oil are observed to be sensitive to processing conditions. In the present study the agro biomasses, which were otherwise a waste having low energy value due to higher water content, have been pyrolyzed into high energy content bio-oils. The presence of high water content in these agro biomasses restrict their use as potential feedstocks.

It is observed that different types of feedstocks produce different amounts of biochar, bio-oil and gas compositions. Also, the results obtained in different reactor configurations, i.e., screw reactor and the fixed bed reactor, are different. The operating conditions for pyrolysis in both the reactors were 500℃ and an inert atmosphere. The screw reactor can process up to 1kg/hr of feedstock and operates in a continuous mode. On comparing the results obtained in both types of reactor, it was found that complete conversion of biomasses was achieved. The yield of solid material, that is, bio char, was found to be similar in both the reactor configurations. In screw reactor the high heating rate was achieved which results in high bio-oil yield[50]. The pyrolysis conditions were the same in all the experimental runs except the feed rate of biomass samples in the screw reactor.

The pyrolysis of six different biomasses chosen for the present study was done in both the reactors, i.e., the twin screw reactor and the fixed bed reactor. It is observed that a higher bio-oil yield was found for pinewood, bamboo and sawdust due to their high volatile matter content. It is found that pinewood and bamboo biomasses resulted in maximum bio-oil yield (52 wt. %) and lowest biochar yield (24 wt. %). This is due to the presence of high cellulose and hemicellulose content in biomass which results in high bio-oil yields in comparison to biomass with high lignin content [26]. The high volatile matter in these biomasses also favors high bio oil production. A high ash content results in a decreased production of bio-oil while the production of char and gas increases. Thus, a higher bio-oil yield can be obtained in biomasses having higher amounts of volatile matter and a lower amount of ash.

It is found that if biomass feeding rates are increased for a moving bed reactor, the bio-oil production decreases due to the shorter residence time in the condenser and, consequently, insufficient quenching. So an optimum value of the biomass feed rate has to be determined. Also, in the case of the moving bed reactor, the percentage of lighter compounds is found to be higher in comparison with those in the fixed bed reactor.

The presence of nitrogen as an inert gas helps in controlling the secondary reactions and also ensures the absence of oxygen during the pyrolysis reaction[43]. On increasing the flow rate of nitrogen it acts like a carrier gas which decreases the residence time of the vapor in the reactor.

5.2 Recommendations for future work

This study has indicated some limitations, namely, dealing with fast heating rates and good outflow of vapors from the reactors. It is observed that faster heating rates can be achieved by heating the reactors internally through resistance wire rather than heating it externally. The new design for the feeding system, i.e., hopper and feeder arrangement in screw reactors used in the present study, has resulted in pyrolyzing higher amounts of biomass and also helped in continuous operation of the screw reactor.

The pre-heating of nitrogen to higher temperatures and then analyzing its effect on pyrolysis would be interesting to study in the future. A new design for the main horizontal reactor in the case of the screw reactor with more efficient product separation can be a good improvement to achieve better products. Removal of char from the reactor as soon as possible can avoid secondary pyrolysis reactions. A cyclone separator can be connected directly with the main horizontal pipe, i.e., with the reactor in order to separate solids from vapor. The bio-oil calorific value produced *via* the screw reactor can be improved by using a catalyst. Thus, a catalyst bed can be attached in the reactor for further improvement of the quality of the bio-oil.

The amount of experimental data taken on the auger reactor in this study needs to be augmented and then curve-fitted. Further studies that need to be performed to optimize the product yield condition in auger reactors is to study the detailed kinetics with the estimation of the kinetic parameters.

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Research papers from the present study

a) Kapoor, L., D. Bose and A. Mekala. 2017. “Biomass pyrolysis in a twin screw reactor to produce green fuels.” *Biofuels.* doi. No.: doi.org/10.1080/17597269.2017.1345360. 2017 JCR-ISI Impact factor 0.784.

b) Kapoor, L. 2018, Experimental investigation of the pyrolysis of biomass to produce green fuels. *International Journal of Sustainable Energy,* 38 (7), 692-700. doi: /10.1080/14786451.2019.1566235. JCR-ISI Impact Factor 0.43.

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