1.1. Introduction

Energy has always played a key role in the development and evolution of human society. Modern civilization is especially dependent on energy and some of the most distinct characteristics of the society, such as an increase in population, energy consumption, environmental impact and climate change, communal complexity, affluence and the gap between poor and rich peoples, are directly or indirectly influenced by availability, accessibility and the affordability of energy sources [1]. Since the dawn of the industrial era, the increasing ability to harness and use different forms of energy has transformed the living conditions of billions of people, enabling them to enjoy a higher level of comfort with liberty to perform productive tasks for a better livelihood. For the last 200 years, the steady growth in energy consumption has been closely attached to increasing levels of prosperity and economic opportunity of the world. Arrival of fossil fuels, viz. oil, natural gas and coal as new and cheap sources of energy played a key role in the establishment of an industrialized economy [2]. Currently, more than 80% of the primary energy consumed in the world is obtained from fossil fuels of which 57.7% alone is consumed in the transportation sector. With an increase in economic activity, industrialization, and population, it is to be expected that these will eventually increase the pressure on fossil fuels. Further, the global economic status is directly affected by increase in crude oil prices due to increasing demands of energy. Use of fossil fuels is also responsible for the emission of a significant amount of pollutants in the atmosphere, including greenhouse gases (GHG). Increasing anthropogenic GHG is believed to trigger many harmful effects to the environment including a rise in sea level, frequent climate change, retreat of glaciers, loss of biodiversity, etc. [3]. Thus, increasing fossil fuel consumption despite its non-renewable nature along with increasing GHG emissions due to its wide-spread use have led to a shift in attention towards an alternative energy source, which is renewable, sustainable, efficient, and cost-effective in nature with lesser GHG emissions [4]. Basically, there are adequate amounts of renewable energy sources to provide all of the world's energy supplies and are more evenly distributed as compared to fossil fuel resources. Also, the energy that can be

extracted from renewable resources is three orders of magnitude higher than the current global energy need. However, the main challenge is to develop the method to effectively and economically capture, store and use the energy when required [5]. Diverse renewable energy sources currently provide about 9% of the US, 26% of India's and 19% of the world's energy need (IEA, 2012). Different technologies, viz. hydroelectric systems, biomass energy systems, wind power, solar thermal systems, photovoltaic systems, passive energy systems, geothermal systems are currently adopted to provide the renewable energy from various renewable resources [6]. It is estimated that by the year 2040, approximately, half of the global energy supply will come from renewable resources [7]. The renewables are the primary, domestic and clean or inexhaustible sources of energy, out of which the biomass and biomass derived materials, have been pointed out to be one of the most promising alternatives. Biomass, in many ways, can be considered as a form of stored solar energy that results from the subsequent accumulation of available atmospheric CO₂, water and sunlight through the process called photosynthesis. Worldwide biomass production is estimated at 146 billion metric tons per year which stands at 4th position amongst the sources of energy [8]. Further, the biomass can be recommended as the perfect equivalent to petroleum for the production of fuels and fine chemicals with a net zero emission of CO_2 [9]. Thus, biomass becomes an invaluable source of energy to provide the initial feedstock in the development of a large bio-energy industry, offering an environmentally acceptable way of disposing unwanted and often polluting biowastes. Biomass provides a potential source of biofuels by using biochemical, chemical and thermo-chemical procedures which can replace the petroleum fuels easily. Moreover, various value added chemicals, such as reducing sugars, furfural, ethanol and other products, can also be derived from biomass during the process of biofuel production [10].

1.2. Importance of Biomass

Biomass can be used directly (e.g. burning wood for heating and cooking) or indirectly by converting it into a liquid or gaseous fuel (e.g. alcohol from sugar crops or biogas from animal waste). The net energy available from

biomass when it is combusted ranges from about 8 MJ/kg for green wood to 20 MJ/kg for dry plant matter to 55 MJ/kg for methane as compared with about 27 MJ/kg for coal. Annually, photosynthesis stores 5–8 times more energy in biomass than man currently consumes from all sources [10]. Biomass represents only 3% of primary energy consumption in industrialized countries. However, much of the rural population in developing countries, which represents about 50% of the world's population, is reliant on biomass, mainly in the form of wood for fuel. Biomass accounts for 35% of primary energy consumption in developing countries, raising the world's total of 14% of primary energy consumption [8]. The earth's natural biomass replacement represents an energy supply of around a year, of which currently only 2% is used as a fuel. According to the United Nations Conference on Environment and Development (UNCED), biomass could potentially supply about half the present world primary energy consumption by the year 2050.

During the photosynthesis process, plants use only a small portion of sun's energy to fix 200 billion tons of carbon into terrestrial and aquatic biomass with an energy content of 3000 billion GJ/y. Up till now, only 1/10th of world's biomass energy is consumed, while the rest is left unexploited [11]. These large amounts of energy not only can supplement a country's energy resources but also can efficiently provide a wide range of chemical feedstock for chemical industry. Furthermore, it is eco-friendly and avoids biological imbalance. The potential energy that is stored in a plant biomass can be utilized by burning it directly or by means of various processes to obtain biofuels. Therefore, biomass can be considered as one of the desirable options for most of the countries around the world. A significant amount of biomass is generated in the East Asian countries, namely, Bangladesh, China, India, Indonesia, Philippines, Thailand, and Vietnam, where the principal resources of biomass wastes are residues from agriculture and forest industries, animal manure from medium and large-scale livestock farms and municipal solid waste (MSW). Potential of lignocellulosic biomass for bio-energy production in India have been evaluated for the past decades with inclusion of updated technologies. Biomass accessibility in India is

estimated to be around 915 million metric ton which includes agricultural, forestry, and wasteland residues, the power potential of which is estimated at 33,292 MW [12]. About 32% of the total primary energy use in the country is still derived from biomass and more than 70% of the country's population depends on it for their energy needs. The Indian Ministry of New and Renewable Energy (MNRE) has initiated a number of programs for promotion of efficient technologies for conversion of biomass to biofuels for use in various sectors. Biomass power generation in India is an industry that attracts investments of over Rs. 1 billion USD (nearly 600 cores INR) every year, generating more than 5000 million units of electricity and yearly employment of more than 10 million men in rural areas. As per MNRE, the current availability of biomass in India is estimated at about 500 Mt per year. Studies sponsored by the Ministry has estimated surplus biomass availability at about 120–150 million tons per annum covering agricultural and forestry residues corresponding to a potential of about 18,000 MW [13].

1.3. Biomass resources

The term "Biomass" covers a range of organic materials recently produced from plants and animals that feed on the plants. Biomass resources include wood and wood wastes, agricultural crops and residues, forest and wood processing residues, municipal solid waste (MSW), animal wastes including human sewage, municipal solid waste (MSW) (excluding plastics and non-organic components), wastes from food processing, energy crops, short rotation forests, aquatic plants and algae. The average majority of biomass energy is produced from wood and wood wastes (64%) followed by MSW (24%), agricultural waste (5%) and landfill gases (5%). Biomass resources that can be divided into the following broad categories are depicted in Fig. 1.1.

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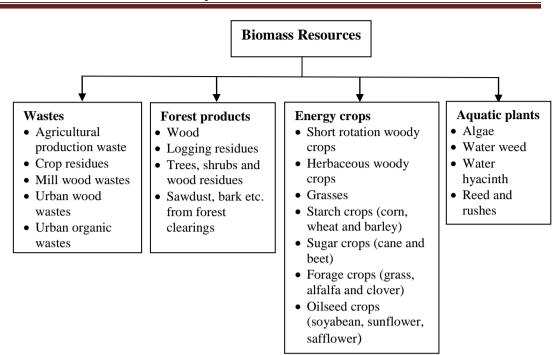


Fig. 1.1: Various resources of biomass

Although total renewable now accounts for nearly 18% of global primary energy supply, out of this over 55% is supplied by traditional biomass (fuel-wood and charcoal for domestic use, rice husks and other plant residues and animal wastes) and about 30% by large hydropower. Solar, wind, modern biomass, geothermal, small hydro (below 10 MW) and ocean energy all together account for only 12% of total renewable. Traditional and modern biomass together contributes about 12% of today's world energy supply, while in many developing countries; its contribution is in the range of [8].

1.3.1. Forest residues

According to FAO, in the year 2014, the total global wood fuel production was 1,864 million m³. It is estimated that approximately 53% of this volume is utilized as fuel wood, mainly in developing countries. The remaining 47% is used as industrial raw material [14]. The residues obtained from the forest processing industries can be divided into two wide categories: (i) logging residues, produced from logging activities and (ii) industrial by-products (i.e. wood processing

wastes) generated by wood processing firms during the manufacture of sawn wood, plywood, particleboard, etc.

Logging residues include stumps, off-cuts, saw dust, etc. Not all of the logging residues can be used for bioenergy production due to technical constraints, ecosystem functions, and other uses such as animal fodder and fertilizer. There are also environmental concerns considering an extensive long term use of logging residues. For instance, leaving appropriate levels of logging residues protects soil quality and eliminates the need for the use of fertilizers.

Wood processing wastes such as discarded logs, bark, sawdust, off-cuts, etc., on the other hand, are generated through sawmill and plywood mill processing activities. According to the OECD/IEA [15], the use of wood processing wastes as feedstock for second-generation biofuels would be attractive since they are normally concentrated at the various mills, and their collection would not be complicated or costly.

1.3.2. Urban wastes and other wastes

Urban wastes are generated by people living in towns and cities during their daily activities. Urban wastes can be categorized into four major types, namely, municipal solid waste (MSW), sewage sludge, food waste, and fat, oil and grease (FOG). In India, production of urban waste has direct impacts on public health of the country. With crowded cities and significant poverty, millions of people in Indian cities are directly exposed to the harmful effects of all urban wastes that are dumped into land and water bodies without proper treatment. With increasing urbanization in the country, there is heightened environmental awareness on both the generation and disposal of urban wastes. The availability of the various types of urban wastes is discussed below:

Municipal solid waste (MSW) is generated by households, commercial and industrial sectors as a result of the concentration of population, and activities in urban areas. Large quantities of both solid and liquid food wastes are generated by the food industry, hotels, restaurants and the confectionary industry in the country. They include foods that do not meet specified quality control standards, peelings and scraps from crops, fruits and vegetables. Most of the solid food wastes normally enter the waste dumps.

Sewage is nothing but the byproduct of wastewater treatment plants. Increasing urbanization and industrialization causes an enormous increase of wastewater all around the world. This pollution is subsequently accumulated as sewage sludge. The most common methods of extracting energies from sewage sludge are anaerobic digestion, co-digestion, and incineration methods.

Livestock manure refers to animal garbage. The quantity of manure produced generally depends on the amount of fodder eaten, the quality of fodder, and the live weight of the animal. These can be processed in an environmentally acceptable way through anaerobic digestion to generate biogas,

Fat, oil and grease (FOG) or urban grease waste are generated as byproducts from food preparation activities. These wastes can be classified into two categories, namely, yellow grease and grease trap waste [8]. Nowadays, pyrolysis is considered as an innovative alternative for treating such waste and to obtain different chemicals and fuels. The energy produced in pyrolysis of urban wastes can be considered as cleaner than the conventional incineration plants since lower amounts of NOx and SO₂ are produced due to inert atmosphere of the pyrolysis process and also the opportunity to wash syngas before its combustion.

1.3.3. Energy crops (woody energy crops and perennial herbaceous crops)

Energy crops having potential as feedstock for biofuel production can be grown on land which is not suitable for agricultural crops for reducing the competition among the agricultural and energy crops for arable land. These include sugarcane, sweet sorghum, maize and cassava for bio-ethanol, oil palm, coconut, sunflower, soybean and *Jatropha* for biodiesel. Apart from these, various species of grass like bermuda grass, elephant grass, esparto grass, giant cane, switchgrass etc. with high energy values have been reported as a feedstock for pyrolysis. Planting of energy crops, for instance, could increase vegetation coverage, and substantially improve the local environment such as reduction of

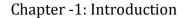
soil erosion. But, extensive use of tillage, fertilizers and irrigation could lead to the deterioration of the physical and chemical properties of soil, such as reduced soil fertility, accumulation of toxic substances, and reduced organic matter. Residues left on the farms improve the soil by returning the nutrients, and also inhibit weed growth. The development of cellulosic ethanol and pyrolysis oil, however, may cause some of the farmers to remove huge amounts of agricultural crop residues for sale in order to increase their income which will have detrimental effect on soil health [15].

1.3.4. Aquatic biomass

The interest in the exploitation of aquatic biomass (microalgae, macroalgae or seaweed, aquatic plants such as Ipomoea) for energy production has grown considerably due to their larger productivity per hectare with respect to the terrestrial biomass. Earlier aquatic biomass has been cultivated and used at industrial level as a source of chemicals, food for humans or animal feed. Recently, aquatic biomass has been receiving increasing attention as a source of biofuels due to the need to shift from first-generation biofuels (biodiesel and bioethanol produced from edible biomass) to non-food sources that may grow without the use of arable land. Aquatic biomass can grow in freshwater or in waste streams in order to contribute to a better utilization of the waste stream. Much research has been carried out on aquatic biomass to evaluate its potential as alternative biofuel feedstock that involved the researchers to develop new technologies for production and processing of biooil, biodiesel, bio-alcohol, biohydrogen as major fuel. Among the aquatic biomass, microalgae are attracting much attention as they are photosynthetic renewable resources, with high lipid content and faster growth rate than terrestrial biomass [16]. Major nutrients (nitrogen and phosphorus) required for cultivation of microalgae can easily be obtained from wastewater. Algae cultivation does not require any herbicides or pesticides application. Therefore, cultivation of microalgae plays a dual role of wastewater remediation and increase the production of biofuel crops. Moreover, microalgae do not compete with the food products as they can be cultivated on non-arable land. Production of microalgae is also helpful to reduce the waste CO₂ from the environment (1 kg of dry algal biomass utilizes about 1.83 kg of CO_2) [17]. Thus, the microalgae biomass can be considered as an attractive alternative to traditional forms of biomass for biofuel production.

1.4. Biofuels

Biofuels are being investigated as a suitable alternative of fossil fuels because of their renewable and biodegradable nature [18]. They are commonly divided into primary and secondary biofuels (as shown in Fig. 1.2). Fuel-wood comes under the category of primary biofuel with various applications. It can be used in an unprocessed form mostly for heating, cooking or electricity production. The term secondary biofuel is usually referred to solid (charcoal), liquid (biooil, bioethanol, and biodiesel) or gaseous (biogas, syngas and bio-hydrogen) fuels predominantly produced from renewable biomass [19]. Liquid biofuels may offer a promising alternative to petroleum based fuels and their respective names biooil, bioethanol and biodiesel are given according to the adopted technique of production. They are able to be used in vehicles and various industrial processes. The secondary biofuels can be classified into three generations: first, second and third generation biofuels on the basis of different parameters, such as the type of processing technology, type of feedstock or their level of development [18].



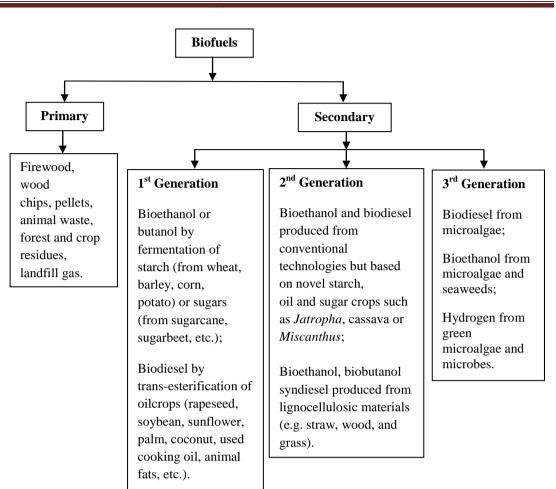


Fig. 1.2: Classification of biofuels

1.4.1. First-generation biofuels

First-generation biofuels are those which are made from feedstock that are used as human food. They are generally made from the edible part of the biomass such as sugars, grains or seeds. Typical first-generation biofuels are sugarcane ethanol, starch-based or corn ethanol, biodiesel, and pure plant oil (PPO). Among the first generation biofuels, bioethanol is one of the dominant liquid, representing approximately 85% of the global biofuel production, while biodiesel accounts for the rest 15% [17]. But there are some economic and environmental limitations associated with the production systems. The rapid expansion of global biofuel production from the food crops has raised the cost of certain crops and food stuffs. In addition, the rigorous use of land with high dose of fertilizer and pesticide applications, water can create significant environmental problems. These harmful

environmental and social consequences encourage the mankind to search nonedible resources of biomass for production of biofuels [20].

1.4.2. Second-generation biofuels

Second-generation biofuels are generally produced from lignocellulosic biomass, which are either non-edible residues of food crop production or nonedible whole plant biomass. Major sources includes agricultural residues, forest harvesting residues or wood processing waste such as leaves, straw or wood chips as well as the non-edible components of corn or sugarcane and short rotation energy forestry. The main advantage of producing second-generation biofuel from non-edible feedstock is that it does not compete with food production and hence limits the direct food versus fuel conflicts associated with first generation biofuels. The exploitation of total above-ground biomass for production of secondgeneration biofuels provides a better land use efficiency in comparison to first generation biofuels. Moreover, lower cost of feed material and use of non-edible biomass favors to promote the second-generation biofuels [4, 20].

1.4.3. Third-generation biofuels

Biofuels derived from microalgae are known as third generation biofuels which are considered to be a feasible alternative energy source for fossil fuel with no major drawbacks coupled with the first and the second generation biofuels. The algae are cultured to act as a low-cost, high-energy and entirely renewable feedstock. Oil productivity of microalgae cultures can able to beat the yield of the oilseed crops, e.g. microalgae in an open pond production can yield biodiesel of 12,000 l/ha compared with 1190 l/ha for rapeseed [17]. Unlike the conventional crop plants (which are usually harvested once or twice a year), microalgae have a very short harvesting cycle (\approx 1–10 days depending on the process), thereby allowing multiple or continuous harvests with considerably increased yields [21]. Furthermore, microalgae have the ability to grow on wasteland and water that are not suitable for food production, consequently minimizing the stress on already exhausted water sources. Thus, it can be estimated that microalgae will have the potential to produce more energy per acre than conventional crops [22].

1.5. Conversion technologies

The conversion of biomass into energy can be accomplished by a number of different technologies, each with its specific requirements, advantages and disadvantages. The type of biomass required is largely determined by the energy conversion process and the form in which the energy is required. Various biomass conversion technologies are shown below in Fig. 1.3.

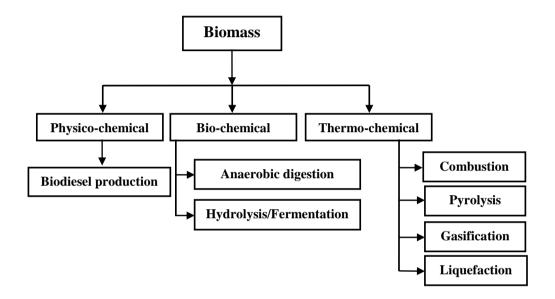


Fig. 1.3: Various biomass conversion technologies

Biomass can be converted into useful forms of energy by using a number of different processes. Factors that influence the choice of conversion process are: the type and quantity of biomass feedstock; the desired form of the energy i.e. end-use requirements; environmental standards; economic conditions; and project specific factors. In most of the situations, it is the form in which the energy is required that determines the process route, followed by the available types and quantities of biomass. Biomass can be converted into three main products [23]:

- energy-power/heat generation
- transportation fuels
- ➤ as a chemical feedstock.

Conversion of biomass to energy is undertaken using three main processes (as shown in Fig. 1.3), such as physico-chemical, bio-chemical and thermochemical. There exists a large scope for exploitation of biomasses for their conversion into bio-fuels e.g. bio-diesel, biooil and bioethanol by using physicochemical, thermo-chemical as well as bio-chemical conversion routes [24]. The physicochemical conversions are trans-esterification and other processes to convert plant and vegetable oils to biodiesel, the bio-chemical conversion includes fermentation and anaerobic digestion; and thermal conversion processes consists of combustion, fast and slow pyrolysis, gasification and liquefaction.

Thermochemical conversion technologies can be considered as more advantageous over biochemical conversion technologies based on the potential to utilize almost all types of biomass and recover both energy and chemical value of the feedstock. In this regard, pyrolysis can be considered as a viable option, in which the product selectivity can be controlled and tuned to suite end-use interests by regulating the various process parameters [25]. Pyrolysis lies at the heart of all thermo-chemical fuel conversion processes and is assumed to become an avenue to petroleum type products from biomass resources. Pyrolytic oil may be used directly as a liquid fuel, added to petroleum refinery feedstock, or catalytically upgraded to transport grade fuels [26]. Moreover, the kinetics of the reaction, reactor design, product distribution, composition and their properties can be established [27]. Thus, pyrolysis can be considered as an important conversion technology for bio-refineries and applied as a primary unit to convert biomass into biooil that has been used as feedstock for further processes as in chemical recovery. The solid char and non-condensable gases that are coproduced along with the liquid fraction during pyrolysis also show versatile applications in the fields of science and technology. The biorefinery perception covers the complete utilization of biomass with zero waste and leads to a whole range of valuable products including food, feed, fuels, chemicals, intermediate products (platforms) and sophisticated products (e.g. polymers) similar to fossil oil refineries. Pyrolysis has the ability to treat the side streams that originate from other processes.

Considering all aspects, it is expected that pyrolysis can be placed at the center of a biorefinery process for supply of fuel, chemicals and other ingredients.

Pyrolysis has wide flexibility regarding feedstocks for its operation and as such this method can ensure adequate urban solid waste management which has posed as one of the key challenges of the century for sustainable development [28]. Pyrolysis may also offer a host of opportunities particularly in semi-urban and rural areas, where solid waste management is characterized by low waste collection coverage, lack of treatment and inadequate disposal. Pyrolysis offers a viable option for treatment of biowaste and converting them into solid, liquid and gaseous fuel, which reduces the waste substances from disposal sites and could also become a probable source of income. Thus, there remains an immense scope for establishing either a central processing unit or a peripheral unit of pyrolysis based bio-refineries in such areas with abundantly available bio-resources as feedstock. Furthermore, the pyrolysis based bio-refineries are comparatively easier to build and operate.

The liquid product obtained during pyrolysis can be used to generate heat and power by blending with conventional fuels. The solid char produced as a byproduct from waste biomass is a carbon enriched material anticipated to be used as a soil amendment to sequester carbon and boost the soil quality. Addition of char (biochar) to soil can improve soil quality by raising soil pH, increasing moisture holding capacity, attracting more beneficial fungi and microbes, improving cation exchange capacity (CEC), and retaining nutrients in soil [29-30]. Biochar may persist in soil for long periods of time since it is very resistant to microbial decomposition and mineralization. Therefore, the use of sustainable biochar as a soil amendment is an innovative and highly promising practice for sustainable agriculture [31]. Biochar has the capacity for remediation of contaminated water and provides additional benefits to the environment. Biochar which requires less investment as compared to activated carbon, absorb hydrocarbons, other organics, and some inorganic metal ions is a promising and emerging wastewater treatment technology [32].

1.6. History of pyrolysis

Mankind has used pyrolysis and related processes for thousands of years. The earliest known example is the use of charcoal, produced as an unintentional residue from cooking fires, for cave drawings by Cro-Magnon man some 38,000 years ago [33]. In Bronze Age, intentionally produced charcoal was used for smelting metals. Nowadays, charcoal is still heavily used in metallurgy process. For thousands of years charcoal has been preferred as a cooking fuel. Prior to the development of petrochemicals, pyrolysis, or 'wood distillation', was a source of many valuable organic compounds for industrial and medicinal uses; and some high value liquid products, such as flavorings, are still produced by wood pyrolysis [34]. Since the Victorian times pyrolysis and gasification processes have been used to extract synthetic crude oil and gaseous products from coal. But recently much attention has been focused on identifying suitable biomass and organic wastes as feeds for pyrolysis and related thermal treatment processes for energy recovery or bio-fuel production [35]. Pyrolysis co-product, the solid char has also been used in agriculture for thousands of years. The fertile Terra preta (dark earth) soils of the Amazonian region results from incorporation of char into otherwise poor soils. The resulting soils have long-lasting fertility that has been related to the stability of carbon in the soil [23]. It is this observation coupled with the search for carbon sequestration techniques for climate change mitigation that has led to recent interest in pyrolysis-derived char, or biochar [35].

1.7. Pyrolysis process

Pyrolysis is a process of thermochemical decomposition of organic material at higher temperatures (400–800 °C) in the absence of oxygen. It is a very complex process and consists of both simultaneous and successive reactions when organic material is heated in a non-reactive atmosphere. In this process, thermal decomposition of organic components in biomass starts at 350–550 °C and goes up to 700–800 °C in the absence of air/oxygen [23]. Temperature plays a crucial role in the product distribution of pyrolysis process. Maximum yield of pyrolysis products can be obtained by altering the conditions as following: solid pyrolysis

char (a low temperature, low heating rate process), liquid pyrolysis oil (a low temperature, high heating rate, short gas residence time process), and fuel gas (a high temperature, low heating rate, long gas residence time process) [27]. Table 1.1, indicates the product distribution obtained from different modes of pyrolysis showing the considerable flexibility achievable by changing process conditions [37].

Mode	Conditions	Liquid	Solid (char)	Gas
Fast	~ 600 °C, short hot vapor	75 wt.% (oil)	12 wt.%	13 wt.%
	residence time < 2s			
Conventional	~500 °C, moderate hot vapor	50 wt.% in two	25 wt.%	25 wt.%
	residence time $5 - 30$ m	phases		
Carbonization	~ 400 °C, long hot vapor	30 wt.% (oil)	35 wt.%	35 wt.%
	residence time hours, days			
Gasification	~ 750-900 °C, moderate hot	3 wt.%	1 wt.%	96 wt.%
	vapor residence time 5s			
Flash	<650 °C, hot vapor	75 wt.%	12 wt.%	13 wt.%

Table 1.1: Product weight yields (dry wood basis) obtained by different modes of pyrolysis of wood [35, 37]

1.7.1. Conventional Pyrolysis

residence time < 1s

Conventional or slow pyrolysis has been applied for thousands of years in traditional charcoal making process by using pits, mounds or kilns. In this process, the liquid and gas products are often discarded, which escapes as smoke with resultant environmental issues. Development of conventional pyrolysis during the late 19th and early 20th centuries by using modern reactors has led the process to an industrial level. In conventional pyrolysis, the biomass is heated up to ~500 °C whereas the residence time of vapor varies from 5–30m. Since the vapors do not escape rapidly, the components in vapor phase continue to react with each other which results in the formation of solid char and liquid product along with the non-condensable gases. The process also has wide application in chemical industries so as to extract important liquid products such as acetic acid, methanol and other chemicals, to convert ethylene dichloride into vinyl chloride to make polyvinylchloride (PVC) etc. The advantage of slow pyrolysis over the fast

pyrolysis is that the liquid product does not contain high quantity of reactive tar [38].

1.7.2. Fast Pyrolysis

Fast pyrolysis of biomass is characterized by high heating rates and short vapor residence times (generally <2s). This generally requires a feedstock prepared as small particle sizes (\leq 3mm) and a design that removes the vapors quickly from the presence of the hot solids. Decomposition of biomass produces some vapors, aerosols, and solid residues called char. By condensing the vapors, a dark brown mobile liquid is obtained with heating value higher than that of bioamss [35]. A controlled pyrolysis reaction temperature is used, often in the range of 400–600 °C. Most importantly the biomass used for pyrolysis should have low moisture content (\leq 10% moisture). Fast pyrolysis process can covert the biomass into 60–75 wt.% of biooil, 15–25 wt.% of solid char, and 10–20 wt.% of non-condensable gases with zero waste generation. Moreover, both the biooil and char can be further used as a fuel in various engines and the gas can be recycled back into the process. There are currently a number of different reactor configurations that can achieve this which includes ablative systems, fluidized beds, stirred or moving beds and vacuum pyrolysis systems [35].

1.7.3. Other Technologies

The other technologies except slow and fast pyrolysis that may be used for thermal treatment of biomass and char production covers some other technologies and are discussed below:

1.7.3.1. Carbonization

Carbonization is a process through which organic materials are converted into carbon rich material. In carbonization biomass is thermo-chemically treated in the temperature range between 200–315 °C in the absence of oxygen similar to traditional process used for charcoal production. The biomass spontaneously breaks down and produces charcoal/biochar as the main product. During carbonization the solid product gains much higher energy density than the raw biomass, which lowers the transportation cost of the carbonized biomass. Moreover, carbonized biomass has favorable characteristics such as, hydrophobic nature, similar or closely related properties as coal, easy to crush, grind or pulverize. The by-products contain some condensable gases such as water vapor, formic acid, acetic acid, furfural, methanol, lactic acid, phenol, and other oxygenates. Non-condensable gases such as carbon dioxide, carbon monoxide and small amounts of hydrogen and methane are also obtained [39].

1.7.3.2. Flash pyrolysis

Flash pyrolysis is an improved and modified form of fast pyrolysis. This process can be characterized by rapid de-volatilization in an inert atmosphere, with a very high heating rate of 1000 °C/s or even higher, high reaction temperatures between 450–1000 °C and very short gas residence time which is 0.1–1s [37]. The flash pyrolysis of biomass is a promising process for production of solid, liquid and gaseous fuel from biomass with a liquid (biooil) yield as high as 75%. The rapid heating rate combined with high temperature and low vapor residence time leads to high liquid yield but the char yield gets decreased. The biggest challenge to use flash pyrolysis on the industrial scale is to configure a reactor for flash pyrolysis in which the input biomass particles reside for a very short time under the extremely high heating rate. The problem associated with flash pyrolysis reactors is the stability and quality of biooil as it is strongly affected by the char/ash particle present in the product. Moreover, the char present in the biooil can catalyze the polymerization reaction inside the liquid product causing an increase in the viscosity of oil [40].

1.7.3.3. Gasification

Gasification is an alternative thermo-chemical conversion technology suitable for treatment of biomass or other organic matter including municipal solid wastes or hydrocarbons such as coal. It involves partial combustion of biomass at high temperatures (>700 °C) under controlled amount of oxygen resulting in the production of combustible gases called syngas or producer gas. The gas mainly consists of carbon monoxide (CO), hydrogen (H₂) and traces of methane (CH₄). Since the syngas can be combusted at higher temperatures or even in fuel cells, its production by gasification is more efficient than the direct combustion of the original fuel.

In addition, some trace elements like chlorine, sulphur, nitrogen, sodium, potassium, etc. formed during gasification need to be removed from the gas before being used as fuel in engines because of their corrosive nature [35]. Nitrogen compounds produced during gasification mainly present as ammonia that enhances the formation of NOx emissions during combustion. Similarly, chlorine element not only causes fouling problems but also creates corrosion problems. The occurrence of chlorine in gasification leads to the formation of hydrogen chloride, and condensation of water containing hydrogen chloride on the cooler parts of the equipments cause severe corrosion of the metal surfaces. Furthermore, the alkali components, particularly, sodium and potassium, can cause corrosion of ceramic filters and turbine blades. Therefore, the removal of these trace elements from the gases produced during gasification is an utmost important task [36]. Even if the gasification process is designed to produce gaseous products alone, gasifiers, under some conditions, can produce reasonable yields of char and it has been proposed as an alternative production route to pyrolysis for biochar [35].

1.7.3.4. Hydrothermal liquefaction (HTL)

HTL or direct liquefaction is a promising technology to treat waste streams from various sources or biomass to produce liquid fuels by processing in a hot, pressurized water environment. Typical hydrothermal processing conditions occurs at a temperature range of 523–647 K and an operating pressures from 4 to 22 MPa of pressure. The process is mainly meant to provide a means for treating wet materials without drying and to access ionic reaction conditions by maintaining a liquid water processing medium. The temperature is sufficient to initiate pyrolytic mechanisms in biopolymers while the pressure is sufficient to maintain a liquid water processing phase. Hydrothermal processing is divided into three separate processes, depending on the severity of the operating conditions. At temperature below 520 K, it is known as hydrothermal carbonization. Major product is known as hydro-char which has the similar property with that of coal. At an intermediate temperature range between 520 and 647 K, the process is defined as hydrothermal liquefaction resulting in the production of a liquid fuel known as biocrude. Biocrude is similar to petroleum crude and can be upgraded to the whole distillate range of petroleum derived fuel products. At higher temperatures above 647 K gasification reactions start to dominate and the process is defined as hydrothermal gasification, resulting in the production of a synthetic fuel gas. The overall aim of each conversion process is to generate a product with a higher energy density by removal of oxygen [41].

1.8. Pyrolysis products

The three primary products obtained from pyrolysis of biomass are char, permanent gases, and vapors that condense at ambient temperature to a dark brown viscous liquid called biooil [42]. Pyrolysis products are the complex combination of the products produced from the individual pyrolysis of cellulose, hemicellulose, lignin and extractives fraction present in biomass; each component has its own kinetic characteristics. In addition, secondary reaction products result from cross-reactions of primary pyrolysis products and reactions between pyrolysis products and the original feedstock molecules [38]. Products from pyrolysis process also strongly depend on the water content in the biomass, which produces large quantities of condensate water in the liquid phase [43]. This contributes to the extraction of water-soluble compounds from the gaseous and tar phases, and thus a greater decrease in gaseous and solid product [37].

1.8.1. Biooil

Liquid product obtained through pyrolysis is usually referred to as biooil or bio-crude. Usually, biooils are dark brown, free-flowing organic liquids composed of various molecular sizes of compounds that are primarily derived from the depolymerization and fragmentation reactions of three major building blocks of biomass, namely, cellulose, hemicelluloses, and lignin. The chemistry of pyrolysis oil is qualitatively well known, although detailed quantitative compositions are usually not available. Chemically, biooil is a complex mixture of oxygenated compounds that are classified into these five broad categories: (1) hydroxyaldehydes, (2) hydroxyketones, (3) sugars and dehydrosugars, (4) carboxylic acids, and (5) phenolic compounds [44]. The phenolic compounds are present as monomeric units and oligomers derived from the coniferyl and syringyl building blocks of lignin. Furthermore, the biooils are found to be highly acidic with pH value of 2.0–3.0. This might be due to the presence of hydroxyl-acetaldehyde (up to 10 wt.%), followed by acetic and formic acids (at ~ 5 wt.% and ~ 3 wt.%, respectively) [38].

1.8.2. Char

Thermal degradation of lignin and hemicellulose results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous carbon matrix which is referred as char. For different temperature regions yield of char would be different. Physical characteristics of char are greatly affected by the pyrolysis conditions such as reactor type and shape, biomass type and drying treatment, feedstock particle size, chemical activation, heating rate, residence time, pressure, flow rate of inert gas, etc. [37]. Char mainly consists of carbon along with hydrogen and various inorganic species in two structures: stacked crystalline graphene sheets and randomly ordered amorphous aromatic structures. In the aromatic rings, H, O, N, P and S are commonly incorporated as hetero atoms which have a great influence on char's physical and chemical properties [45].

1.8.3. Gases

Thermal decomposition of biomass produces both condensable and noncondensable gases. The non-condensable gas is known as "syngas" if in a purified form with high carbon monoxide and hydrogen concentrations. If the noncondensable gas is diluted with an inert gas such as nitrogen, it is known as "producer gas" [46]. The gas also contains small amounts of carbon dioxide (CO₂), water, hydrocarbons such as CH₄, C₂H₄, C₂H₆, tar, ash, etc., depending on biomass feedstock and pyrolysis conditions [47]. These components are obtained during several endothermic reactions at high pyrolysis temperatures. H₂ is produced from the cracking of hydrocarbons at higher temperatures. CO and CO₂ are the indicators of the presence of oxygen in the biomass. Those components mainly originate from the cracking of partially oxygenated organic compounds. Therefore, as a highly oxygenated polymer, the amount of cellulose present in the biomass is an important factor determining the amount of carbon oxides produced. The light hydrocarbons such as CH_4 , C_2H_4 , C_2H_6 , etc. may be due to the reforming and cracking of heavier hydrocarbons and tar in the vapor phase [37].

1.9. Mechanism of pyrolysis

In pyrolysis process the long chains of carbon, hydrogen and oxygen compounds in biomass breaks down into smaller molecules in the form of gases, condensable vapors (tars and oils) and solid charcoal. Rate and extent of decomposition of each of the components depends on various process parameters such as, reactor temperature, heating rate, pressure, reactor configuration, feedstock etc. The possible reaction with desirable end product of pyrolysis process can be depicted as [27]

Biomass $\xrightarrow{\text{Inert gas}}$ Solid char (FC, VM, Ash) + Liquid (Org + Aq.) + Gas (CO₂, CO, H₂, CH₄) (Org: Organic phase; Aq: Aqueous phase; FC: Fixed carbon; VM: Volatile Matter)

Lignocellulosic biomass is a complex mixture of three major constituents, viz. hemicellulose, cellulose, and lignin. These constituents are unevenly distributed in the cell wall as a skeleton, linking material and hard solids, respectively. Cellulose macro molecules regularly gather to form tough microfibers that function as the skeletal material of the cell wall, and the inner space is packed with amorphous hemicellulose and lignin linking material. Cellulose connects with hemicellulose or lignin molecules mainly through hydrogen bonds while the connections between hemicellulose and lignin include both hydrogen and covalent bonds. Carbohydrates and lignin link tightly together in lignin-carbohydrate complexes, which results in residual carbohydrate or lignin fragments in extracted lignin or hemicellulose samples. The minor amounts of extractives present in the biomass decompose at different temperature and heating

rate follows different mechanisms and pathways. The thermal degradation order of hemicelluloses, cellulose, and lignin can be summarized as follows [48]:

Hemicelluloses > cellulose > lignin

The reaction mechanisms of biomass pyrolysis are complex in nature but can be defined in three main stages as stated below:

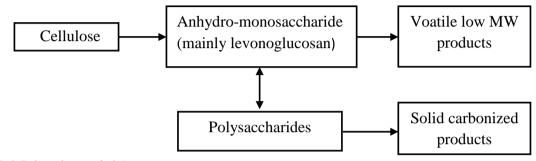
$Biomass \rightarrow Water + Non-reacted residue$	(1)
Non reacted residue \rightarrow (Volatile + Gases) ₁ + (Char) ₁	(2)
$(Char)_1 \rightarrow (Volatile + Gases)_2 + (Char)_2$	(3)

(Subscript 1 & 2 indicates – primary and secondary decomposition respectively)

From the above reactions it can be observed that pyrolysis proceeds in three steps. During the first stage of biomass decomposition, some internal rearrangement such as water elimination, bond breakage, appearance of free radicals, formation of carbonyl, carboxyl and hydro-peroxide groups takes place. The second stage of the solid decomposition corresponds to the main pyrolysis process. It proceeds with a high rate and leads to the formation of the pyrolysis products. During the third stage, the char decomposes to carbon-rich residual solid form at a very slow rate. The formation of secondary charring [Eq. (3)] makes the char less reactive. Furthermore, the experimental runs indicate several endothermic and/or exothermic peaks for biomass pyrolysis. Generally, cellulose pyrolysis is an endothermic process whereas the lignin is an exothermic process. Similarly, wood pyrolysis is an exothermic process and the main cause of heat generation is the secondary decomposition of volatiles, possibly catalyzed by the remaining solid [48].

Among the three major biomass constituents of cellulose, hemicelluloses, and lignin, the decomposition of cellulose has been most widely analyzed and best comprehended [49]. There are many schemes reported in the literature to describe cellulose pyrolysis reactions [50-53]. The Broido-Shafizadeh model [50], Waterloo model [51], and Varhegyi-Antal model [52] are among the most cited mechanisms. Although all three models agree that the formation of anhydrosugars

through depolymerization is competing with char formation reactions, difference could still be found among three mechanisms. Kawomoto et al. [54], proposed a mechanism of char production following the route presented in Fig. 1.4. They found carbonization reactions gradually transformed levoglucosan to methanol and water soluble residue, and eventually into a fraction totally insoluble to water and methanol.



(MW: Molecular weight)

Fig. 1.4: Scheme of cellulose pyrolysis mechanism [54]

1.10. Response surface methodology (RSM) as a tool for optimization

Response surface methodology (RSM) was developed by Box and coworkers in 1951 [55]. This term was originated from the graphical viewpoint generated after fitness of the mathematical model. It is a collection of mathematical and statistical techniques that are useful for modeling and analysis of engineering problems. In this technique, the main objective is to optimize an output variable (response) which is influenced by several input variables (independent variables). The software provides a series of experimental tests, called runs, in which changes are made in the input variables in order to identify the reason behind the changes in the output response. In addition, this method minimizes the number of experimental trails required to evaluate several parameters and their interaction. Errors may be generated due to numerical noise as a result of incomplete coincidence of repeating processes, round-off errors or the different representation of continuous physical occurrences [56]. In RSM, the errors are assumed to be random.

One important objective of RSM is to determine the optimum operating conditions on the control variables that lead to the simultaneous optimization of the predicted values of the responses within a region of interest. Optimization implies the levels of independent variables that results in maximum value of the output variable [57]. Furthermore, the optimum designs are those that are constructed on the basis of a certain condition that refer to the 'closeness' of the predicted response. Optimization reduces the effects of noise. In multi response experiments, the term 'optimum' is sometimes uncertain as there is not any particular method to resolve the data. Conditions that are optimal for one response may be different for other responses or even physically impractical from the experimental point of view. After that the response can be represented graphically, either in the three-dimensional space or as contour plots that help visualize the shape of the response surface.

1.11. Pyrolysis kinetic studies

The trend for material and energy recovery from biomass along with the need to reduce greenhouse gases has led to an increased interest in the thermal exploitation of biomass and/or wastes. The kinetics of biomass decomposition is important in the context of thermochemical conversion processes aimed at production of energy. Thermogravimetry is a study of determining the decomposition profile versus temperature [58]. It gives the mechanisms by which thermal degradation of biomass occurs in the different molecular fractions that stored the chemical energy. The determination of kinetic parameters provides information on the processes taking place as well as the structure and composition of the materials. Study of pyrolysis is based on hypothetical models, where it is considered that the overall performance of pyrolysis is the combination of the behavior of each individual component. Therefore, the determination of the kinetic parameters provides key information of the processes that take place, as well as the structure and composition of its constituents [59]. Furthermore, the analysis of the volatile products of thermal degradation, identifies the gaseous species emitted by the biomass, and thus provides insights to the processes through which such decomposition occurs. A number of reactions occurred simultaneously during the process of pyrolysis which prevents to develop a kinetic model that takes into account all these reactions. A kinetic study aims to reveal how the thermal decomposition takes place (whether one or more processes and what range of conversions occur) through the characteristic kinetic constants provided by the kinetic models [60].

1.12. Application of pyrolysis products 1.12.1. Application of Biooil

Potential application of biooil is in the production of higher value liquid fuels so that the biooil can be used directly in boilers, furnaces, engines and gas turbines. However, the direct use of biooil has been restricted due to presence of some negative properties such as high viscosity, high oxygen substance, highly corrosive, high moisture content, and their thermal instability. These properties may arise due to occurrence of hundreds of compounds that are derived from the depolymerization and fragmentation reactions of cellulose, hemicellulose and lignin components of biomass as reported [61]. In other aspects, characteristic compounds present in the crude biooils include oxygenates (such as acids, esters, alcohols, ketones and aldehydes), sugars, furans, hydrocarbons (such as alkene, aromatics), phenols (such as phenols, anisoles, catechols, guaiacols, syringols, etc.), high molecular weight species (such as cellulose, hemicellulose and lignin) and water [62]. For these reasons, the biooil needs to be upgraded before utilizing it as a fuel in of diesel or gasoline run engines. The main focus of the upgrading is to convert the oxygen rich and high atomic weight lignin into hydrocarbons to match with today's petroleum derived fuels. Furthermore, biooil has another implication to be used as a chemical feedstock and many biomass derived pyrolysis oils are known to contain polycyclic aromatic hydrocarbons (PAH). Phenolic compounds present in biooils have extensive use in the production of resins and flavorings agents in the food industry. Syringol and guaiacol are also found in significant concentrations in biomass derived pyrolysis oils and are used in the production of biodegradable polyesters and polyethers [63]. Usually, various chemical treatments of biooil, such as dehydration, hydrogenation, fractionation, etc. can be used to increase concentration of specific type or class of chemicals as well as to improve stability. Biooil upgrading to hydrocarbons (fuels) is also possible via methods like steam reforming, hydrodeoxygenation and zeolites upgrading in both 'in-situ' (catalyst mixed with biomass feedstock) and 'ex-situ' (vapors passed over a catalyst bed or up gradation of collected oil in a separate reactor) mode [64]. Among the various treatments, fractionation could be a viable process to separate the oxygenated compounds present in the biooil, which causes problem in the case of storage and stability of the oil. Oxygenated compounds can be separated from the biooil by fractionating it into individual chemical classes, viz. aliphatic, aromatic, and polar by using liquid column chromatography technique [63].

1.12.2. Application of solid char

Char has a wide range of application in achieving environmental as well as agronomic benefits. Char possess various beneficial qualities such as energy production, waste management, C sequestration potential, enhancement of soil quality, wastewater treatment, used as a support for catalyst development etc.

Production of solid char through pyrolysis helps in achieving the twin objective of both waste minimization and energy recovery. It also reduced the weight and volume of initial biomass feedstock and thereby reducing the space required for its disposal. Char can also be used as a substitute of coal for energy production. Conversion of waste biomass into char (char is termed as biochar if intended for applications other than energy) and its subsequent addition into the soil helps in maintaining the soil nutrient as well as in mitigation of GHG emissions such as methane and carbon dioxide that are generated from traditional waste disposal, processing and recycling operations [35]. Addition of biochar resolves the soil acidity problem and able to provide a potential contribution for soil microorganisms along with some available nutrients such as N, P, K, though this effect of biochar disappears in the long run.

Biochar derived from waste biomass is also gaining much attention for its function as a biosorbent for environmental remediation. Due to the over growth in population, industrialization, and civilization, the demand for water is increasing

geometrically. Therefore, wastewater needs to be purified and recycled for the purpose as alternative sources of water [65]. Among various treatment technologies, adsorption is a fast and universal method which offers significant advantages like the low cost, availability, profitability, ease of operation, and efficiency [66]. It is widely used as an effective physical method of separation in order to eliminate or lower the concentration of pollutants (organic and inorganic) in the polluted waters by using biochar. Water pollution caused by toxic heavy metals [67] and dye effluents [61] is a worldwide environmental problem because of its adverse effects on human health, as well as on aquatic flora and fauna. Application of biochar for adsorption of these pollutants becomes a major research area due to the biochar's favorable characteristics such as porosity, high specific surface area, cation exchange capacity etc. [68]. The urban storm water runoff treatment can be taken as a realistic example of biochar application for the removal of pollutants which would reduce costs of storm water treatment by avoiding expensive materials (such as activated carbon, complexing agents for improve of removal performance) [69].

1.13. Justification for selection of feedstock

In order to meet the increasing energy demand of the country and to provide energy security, National Policy on Biofuels was announced in December 2009. The major goal of the policy is to facilitate and bring about development and utilization of indigenous non-edible feedstock raised on degraded or waste lands for production of biofuels. In this regard, renewable feedstock shows the ability to supply a significant portion of the global energy and chemical requirement before the beginning of petrochemical era. Among the other sources of energy, biomass is the only renewable resource of carbon from which chemicals, materials, and fuels can be produced using appropriate conversion pathways. In the 1920s through 1930s, the Chemurgy movement in the United States promoted the use of biomass as a source of chemicals with the belief that "anything that can be made from hydrocarbon could be made from a carbohydrate." Therefore, biomass can be considered as a viable option to sustainably accumulate the future energy and material requirements that are

associated with a bio-based economy. Thus, development of new, efficient technologies for producing energy and materials from sustainable resources has encouraged biomass valorization (biorefining) to become an important area of industrial research, and is currently considered as a major step towards the realization of a common sustainable future [70]. Consequently, the availability of feedstock becomes an important factor for successful implementation of any biofuel program. In this regard, the present study aims to emphasize three new feedstocks (*Pongamia glabra* and *Mesua ferrea* seed covers and *Scenedesmus dimorphus*, a microalgae species) in the futuristic energy scenario.

Indian government's approach to biofuel policy is based solely on nonfood feedstocks in order that the possible fuel vs. food security can be avoided. Thus, utmost exclusive emphasis has been given on the utilization of waste and degraded forest and non-forest lands for production of biofuel through cultivation of shrubs and trees bearing non-edible oil seeds. In this respect, India has a vast untapped potential of non-edible oil bearing plant species distributed throughout the country: more than 300 species of trees have been reported to produce oil bearing seeds [71]. Assam, one of the biological hotspots of Northeast India, is enriched with far-reaching forest areas and well-known flora and fauna across the region. Furthermore, the State has also a large array of non-edible oilseed bearing trees and shrub species which are easily accessible for extraction of biodiesel. Some non-edible oil yielding species, particularly found in Assam are viz. koroch (P. glabra), terminalia (Terminalia belerica) and nahar (M. ferrea), etc. The seeds of these species may serve as feedstocks for potential biodiesel industries [72-73]. During processing of seeds, and oil extraction for biodiesel production, a huge amount of bio-wastes like seed covers, deoiled cake, etc., are generated as byproduct which are often discarded as waste material [74]. Utilization of these waste materials for energy production and chemical recovery can be an emerging option with multiple co-benefits, i.e. they are cost effective, renewable and carbon neutral in nature.

The present investigation aims to explore *P. glabra* seed cover (PGSC) and *M. ferrea* seed cover (MFSC) as two potential candidates for bio-energy

generation through thermo-chemical conversion. These indigenous renewable resources are non-polluting and virtually inexhaustible. Gainful utilization of PGSC and MFSC (which are wastes products generated during utilization of *P. glabra* and *M. ferrea* seed oil for biodiesel production) for biofuels and other coproducts through pyrolysis can be one feasible way to enhance the economics of biodiesel production. Furthermore, PGSC and MFSC are lignocellulosic biowastes with not many competitive uses [72].

In addition to various tree species, Assam is also known for having a rich biodiversity of freshwater microalgae. Many microalgae species have been screened and reported for their oil content from the Chandrapur region of Assam [75]. Some of the isolated microalgae strains are Chlorella sp, Selenastrum sp, Scenedesmus dimorphus, Scenedesmus quadricauda, Desmodesmus sp. etc. Microalgae from NE India have been the major objective for most researchers dealing with generation and production of alternative fuels. Algae have become a promising feedstock for biofuel production because of its low price, production of minimum byproducts and waste, non-competition with food industry and biomass productivity, lipid content and fatty acid composition [76]. Production of biodiesel from algal species left solid residues with 10% of mineral content for which the leftover can again be fed back to the growth cycle. Moreover, 60% of waste generated during the biodiesel processing has very limited use which makes the process economically less competitive [77]. Pyrolysis, among the thermochemical conversion has the ability to use the complete organic part of the feedstock generating lesser amount of residues [74]. Among microalgae, Scenedesmus species has the most attractive features for proficient and economic permutation of CO_2 fixation, wastewater treatment and lipid synthesis. Moreover, it seems to be an ideal species due to its ability to grow and tolerate different environmental conditions, and also because it is more resistant to physiological stress consequent to nutrient starvation and light limitation [76]. Thus, there remains a huge scope for initiation of a decentralized pyrolysis based bio-refineries in rural NE India with Scenedesmus dimorphus and other abundantly available bioresources as

feedstock. Pyrolysis based bio-refineries are comparatively easier to build up and operate.

1.14. Objectives of the proposed doctoral research

The present study has been undertaken with the following objectives in mind:

- To study the physico-chemical properties and thermal behavior of selected bio-wastes and microalgae species;
- □ To study the pyrolytic conversion of biomass into products;
- □ To study the characterization of liquid (biooil) and solid char obtained from pyrolysis of biomass;
- □ To study the fractionation of biooil obtained at optimum condition separated by using liquid column chromatography for categorization of its sub-fractions;
- □ To study the application of by-product (biochar) obtained from the pyrolysis of the biomass.

References:

- Bashar, A. K. Energy and It's Various Perspective Including Bangladesh. https://www.academia.edu/9833317/Energy_and_It_s_Various_Perspective_I ncluding_Bangladesh_By_Abu_Khairul_Bashar/ accessed on 25/08/2017.
- Energy Producing Systems: Fossil Fuels. https://dnr.mo.gov/education/energy/documents/fossilfuelpower.pdf/ accessed on 12/09/2017.
- Gullison, R. E., Frumhoff, P. C., Canadell, J. G., Field, C. B., Nepstad, D. C., Hayhoe, K., Avissar, R., Curran, L. M., Friedlingstein, P., Jones, C. D., and Nobre, C. Tropical forests and climate policy. *Science*, 316 (5827): 985-998, 2007.
- 4. Nigam, P. S. and Singh, A. Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science*, 37(1): 52-68, 2011.
- 5. Demirbas, A. Biorefineries: current activities and future developments. *Energy Conversion and Management*, 50 (11): 2782-2801, 2009.
- Pimentel, D., Herz, M., Glickstein, M., Zimmerman, M., Allen, R., Becker, K., Evans, J., Hussain, B., Sarsfeld, R., Grosfeld, A., and Seidel, T. Renewable Energy: Current and Potential Issues Renewable energy technologies could, if developed and implemented, provide nearly 50% of US energy needs; this would require about 17% of US land resources. *Bioscience*, 52(12): 1111-1120, 2002.
- 7. Gupta, R. B., and Demirbas, A. *Gasoline, diesel and ethanol biofuels from grasses and plants.* Cambridge University Press, 2010.
- Demirbaş, A. Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Conversion and Management*, 42(11): 1357-1378, 2001.
- Zhou, C. H., Xia, X., Lin, C. X., Tong, D. S., and Beltramini, J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chemical Society Reviews*, 40(11): 5588-5617, 2011.
- 10. Küçük, M. M. and Demirbaş, A. Biomass conversion processes. *Energy Conversion and Management*, 38(2): 151-165, 1997.

- Reddy, B. S. Biomass energy for India: an overview. *Energy Conversion and Management*, 35(4): 341-361, 1994.
- 12. Ghosh, S. K. Biomass & bio-waste supply chain sustainability for bio-energy and bio-fuel production. *Procedia Environmental Sciences*, 31: 31-39, 2016.
- Ghosh, S. K. Potential of economic utilization of biomass waste in India -Implications towards SDGs. In Seventh Regional 3R Forum in Asia and the Pacific, pages 1-22, Adelaide, SA, Australia, 2016.
- 14. Forest products statistics: Food and Agriculture Organization of the United Nations (FAO-2014). http://www.fao.org/forestry/44134-1f63334f207ac6e086bfe48fe7c7e986.pdf/ accessed on 16/07/2017.
- 15. Domson, O., and Vlosky, R. P. A strategic overview of the forest sector in Ghana Louisiana Forest Products Development Center, Baton Rouge, LA, Vol. 81, 2007.
- Nunoo, F. K. E. and Ameka, G. K. Occurrence of macro-algae in the by-catch of beach seine fisheries at Sakumono, Ghana. *West African Journal of Applied Ecology*, 8(1): 1-7, 2005.
- Duku, M. H., Gu, S., and Hagan, E. B. A comprehensive review of biomass resources and biofuels potential in Ghana. *Renewable and Sustainable Energy Reviews*, 15(1): 404-415 (2011).
- Bhatti, H. N., Hanif, M. A., and Qasim, M. Biodiesel production from waste tallow. *Fuel*, 87(13): 2961-2966, 2008.
- Demirbas, A. Political, economic and environmental impacts of biofuels: A review. *Applied Energy*, 86: S108-S117, 2009.
- 20. Dragone, G., Fernandes, B. D., Vicente, A. A., and Teixeira, J. A. Third generation biofuels from microalgae. *Current Research, Technology and Education Topics in Applied Microbiology and Microbial Biotechnology*, 2: 1355-1366, 2010.
- Schenk, P. M., Thomas-Hall, S. R., Stephens, E., Marx, U. C., Mussgnug, J. H., Posten, C., Kruse, O., and Hankamer, B. Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy Research*, 1(1): 20-43, 2008.

- 22. Ullah, K., Ahmad, M., Sharma, V. K., Lu, P., Harvey, A., Zafar, M., Sultana, S., and Anyanwu, C. N. Algal biomass as a global source of transport fuels: overview and development perspectives. *Progress in Natural Science: Materials International*, 24(4): 329-339, 2014.
- 23. McKendry, P. Energy production from biomass (part 2): conversion technologies. *Bioresource Technology*, 83(1): 47-54, 2002.
- 24. Singh, J., and Gu, S. Biomass conversion to energy in India—a critique. *Renewable and Sustainable Energy Reviews*, 14(5): 1367-1378, 2010.
- 25. Brennan, L. and Owende, P. Biofuels from microalgae—a review of technologies for production, processing, and extractions of biofuels and coproducts. *Renewable and Sustainable Energy Reviews*, 14(2): 557-577, 2010.
- 26. Pütün, A. E., Özcan, A., and Pütün, E. Pyrolysis of hazelnut shells in a fixedbed tubular reactor: yields and structural analysis of bio-oil. *Journal of Analytical and Applied Pyrolysis*, 52(1): 33-49, 1999.
- Balat, M., Balat, M., Kırtay, E., and Balat, H. Main routes for the thermoconversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Conversion and Management*, 50(12): 3147-3157, 2009.
- 28. Lohri, C. R., Diener, S., Zabaleta, I., Mertenat, A., and Zurbrügg, C. Treatment technologies for urban solid biowaste to create value products: a review with focus on low-and middle-income settings. *Reviews in Environmental Science and Bio/Technology*, 16(1): 81-130, 2017.
- 29. Lehmann, J., Gaunt, J., and Rondon, M. Bio-char sequestration in terrestrial ecosystems–a review. *Mitigation and Adaptation Strategies for Global Change*, 11(2): 395-419, 2006.
- 30. Lehmann, J. Bio- energy in the black. *Frontiers in Ecology and the Environment*, 5(7): 381-387, 2007.
- 31. Zheng, W., Sharma, B. K., and Rajagopalan, N. Using biochar as a soil amendment for sustainable agriculture. A report submitted to the Sustainable Agriculture Grant Program of Illinois Department of Agriculture, grant number: SA 09-37, 2010.
- 32. Mohan, D., Sarswat, A., Ok, Y. S., and Pittman, C. U. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and

sustainable adsorbent-a critical review. *Bioresource Technology*, 160: 191-202, 2014.

- 33. Antal, M. J., and Grønli, M. The art, science, and technology of charcoal production. *Industrial and Engineering Chemistry Research*, 42(8): 1619-1640, 2003.
- 34. Bridgwater, A. V. and Peacocke, G. V. C. Fast pyrolysis processes for biomass. *Renewable and Sustainable Energy Reviews*, 4(1): 1-73, 2000.
- 35. Narzari, R., Bordoloi, N., Chutia, R. S., Borkotoki, B., Gogoi, N., Bora, A., and Kataki, R. Biochar: An Overview on its Production, Properties and Potential Benefits. In Biology, Biotechnology and Sustainable Development, pages 13-40, ISBN: 978-93-84443-19-1. Research India Publications, 2015.
- 36. McKendry, P. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*, 83(1): 55-63, 2002.
- 37. Jahirul, M. I., Rasul, M. G., Chowdhury, A. A., and Ashwath, N. Biofuels production through biomass pyrolysis—a technological review. *Energies*, 5(12): 4952-5001, 2012.
- Mohan, D., Pittman, C. U., and Steele, P. H. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy and Fuels*, 20(3): 848-889, 2006.
- 39. Verma, M., Godbout, S., Brar, S. K., Solomatnikova, O., Lemay, S.P., and Larouche, J.P. Biofuels Production from Biomass by Thermochemical Conversion Technologies. *International Journal of Chemical Engineering*, 2012: 1-18, 2012.
- 40. Roy, P. and Dias, G. Prospects for pyrolysis technologies in the bioenergy sector: A review. *Renewable and Sustainable Energy Reviews*, 77: 59–69, 2017.
- 41. Elliott, D. C., Biller, P., Ross, A. B., Schmidt, A. J., and Jones, S. B. Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresource Technology*, 178: 147-156, 2015.
- 42. Fahmi, R., Bridgwater, A. V., Donnison, I., Yates, N., and Jones, J. M. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel*, 87(7): 1230-1240, 2008.

- 43. Demirbaş, A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management*, 41(6): 633-646, 2000.
- 44. Piskorz, J. and Scott, D. S. The composition of oils obtained by the fast pyrolysis of different woods. Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem.;(United States), 32(CONF-870410-) 1987.
- 45. Verheijen, F., Jeffery, S., Bastos, A. C., Van Der Velde, M., Diafas, I., and Parsons, C. *Biochar application to soils: a critical scientific review of effects on soil properties, processes and functions.* European Commission, Joint Research Centre. Institute for Environment and Sustainability, Ispra, Italy, 2009.
- 46. Kasparbauer, R. D. The effects of biomass pretreatments on the products of fast pyrolysis. Iowa State University, 2009.
- 47. Fernández, Y. and Menéndez, J. A. Influence of feed characteristics on the microwave-assisted pyrolysis used to produce syngas from biomass wastes. *Journal of Analytical and Applied Pyrolysis*, 91(2): 316-322, 2011.
- 48. Balat, M. Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis. *Energy Sources, Part A*, 30(7): 620-635, 2008.
- 49. Kan, T., Strezov, V., and Evans, T. J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renewable and Sustainable Energy Reviews*, 57: 1126-1140, 2016.
- 50. Bradbury, A. G., Sakai, Y., and Shafizadeh, F. A kinetic model for pyrolysis of cellulose. *Journal of Applied Polymer Science*, *23*(11): 3271-3280, 1979.
- 51. Piskorz, J., Radlein, D. S. A., Scott, D. S., and Czernik, S. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 16(2): 127-142, 1989.
- 52. Varhegyi, G., Jakab, E., and Antal Jr, M. J. Is the Broido-Shafizadeh model for cellulose pyrolysis true?. *Energy and Fuels*, 8(6): 1345-1352, 1994.
- 53. Diebold, J. P. A unified, global model for the pyrolysis of cellulose. *Biomass* and *Bioenergy*, 7(1-6): 75-85, 1994.
- 54. Kawamoto, H., Murayama, M., and Saka, S. Pyrolysis behavior of levoglucosan as an intermediate in cellulose pyrolysis: polymerization into

polysaccharide as a key reaction to carbonized product formation. *Journal of Wood Science*, *49*(5): 469-473, 2003.

- 55. Chen, Y., Yang, H., Wang, X., Zhang, S., and Chen, H. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: influence of temperature. *Bioresource Technology*, 107:411–418, 2012.
- 56. Response surface methodology: Chapter 3. http://www.brad.ac.uk/staff/vtoropov/burgeon/thesis_luis/chapter3.pdf/ accessed on 09/06/2017.
- Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., and Escaleira, L. A. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, 76(5): 965-977, 2008.
- 58. Rodríguez, R., Gauthier, D., Udaquiola, S., Mazza, G., Martinez, O., Flamant, G., and Tyagi, R. Kinetic models for pyrolysis and combustion of sewage sludge. Proceedings on Moving Forward Wastewater Biosolids Sustainability: Technical, Managerial, and Public Synergy, GMSC, 801-809, 2007.
- Conesa, J. A. and Domene, A. Biomasses pyrolysis and combustion kinetics through n-th order parallel reactions. *Thermochimica Acta*, 523(1): 176-181, 2011.
- 60. Min, F. F., Zhang, M. X., and Chen, Q. R. Non-isothermal kinetics of pyrolysis of three kinds of fresh biomass. *Journal of China University of Mining and Technology*, 17(1): 105-111, 2007.
- 61. Horne, P. A. and Williams, P. T. Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel*, 75(9): 1051-1059, 1996.
- 62. Xu, X., Cao, X., Zhao, L., Wang, H., Yu, H., and Gao, B. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environmental Science and Pollution Research*, 20(1): 358-368, 2013.
- 63. Demirbas, A. Heavy metal adsorption onto agro-based waste materials: a review. *Journal of Hazardous Materials*, 157(2): 220-229, 2008.
- 64. Agrafioti, E., Kalderis, D., and Diamadopoulos, E. Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. *Journal of Environmental Management*, 133: 309-314, 2014.

- 65. Šafaříková, M., Ptáčková, L., Kibrikova, I., and Šafařík, I. Biosorption of water-soluble dyes on magnetically modified Saccharomyces cerevisiae subsp. uvarum cells. *Chemosphere*, 59(6): 831-835, 2005.
- 66. Komkiene, J. and Baltrenaite, E. Biochar as adsorbent for removal of heavy metal ions [Cadmium (II), Copper (II), Lead (II), Zinc (II)] from aqueous phase. *International Journal of Environmental Science and Technology*, 13(2): 471-482, 2016.
- Babel, S. and Kurniawan, T. A. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, 97(1): 219-243, 2003.
- Subramanian, K. A., Singal, S. K., Saxena, M., and Singhal, S. Utilization of liquid biofuels in automotive diesel engines: an Indian perspective. *Biomass* and Bioenergy, 29(1): 65-72, 2005.
- Achten, W. M., Mathijs, E., Verchot, L., Singh, V. P., Aerts, R., and Muys, B. Jatropha biodiesel fueling sustainability? Biofuels, Bioproducts and Biorefining, 1(4): 283-291, 2007.
- 70. Chutia, R. S., Kataki, R., and Bhaskar, T. Thermogravimetric and decomposition kinetic studies of *Mesua ferrea L*. deoiled cake. *Bioresource Technology*, 139: 66-72, 2013.
- 71. Government of India, Ministry of New and Renewable Energy, 2009.
- 72. Sarma, A. K. Biodiesel production from Mesua ferrea L. (Nahar) and Pongamia glabra Vent. (Koroch) seed oil (Doctoral dissertation) (2006).
- 73. Basumatary, S. Non-edible oils of Assam as potential feedstocks for biodiesel production: a review. *Journal of Chemical, Biological and Physical Sciences*, 3(1): 551-558, 2012.
- 74. Umdu, E. S., Tuncer, M., and Seker, E. Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al₂O₃ supported CaO and MgO catalysts. *Bioresource Technology*, 100(11): 2828-2831, 2009.
- 75. Goswami, R. C. D. and Kalita, M. C. Microalgal resources in Chandrapur area, North-East, Assam, India: a perspective for industrial refinement system and a boon for alternative energy generation and mitigation of greenhouse gases. *Archives of Applied Science Research*, 4(2): 795-799, 2012.

- 76. Cicci, A. and Bravi, M. Production of the freshwater microalgae scenedesmus dimorphus and arthrospira platensis by using cattle digestate. Chemical Engineering, 38: 85-90, 2014.
- 77. Babich, I. V., Van der Hulst, M., Lefferts, L., Moulijn, J. A., O'Connor, P., and Seshan, K. Catalytic pyrolysis of microalgae to high-quality liquid biofuels. *Biomass and Bioenergy*, 35(7): 3199-3207, 2011.