Chapter 1

Introduction

1.1 Introductory Overview

The history of human civilization has been intricately intertwined with the progressive development of new energy sources and various conversion technologies. In antiquity, ancient civilizations heavily relied on the sun as the primary energy source for their sustenance and survival. Solar energy played a crucial role in shaping weather patterns, powering wind currents, and driving water cycles, all of which were harnessed by humans for various purposes. As human civilization advanced through different centuries, new energy sources gradually emerged to complement solar energy. For instance, the discovery and utilization of fire provided early humans with heat and light, marking one of the first intentional harnessing of a non-solar energy source. The invention of simple machines like water wheels in ancient times marked the integration of hydropower into society, effectively tapping into the kinetic energy of flowing water. During the medieval and Renaissance periods, societies started utilizing biomass, like wood and agricultural waste, to store potential energy for heating and cooking. The transformative Industrial Revolution of the 18th and 19th centuries witnessed the widespread use of coal, harnessing the energy stored in it to power steam engines and machinery [1]. At that time, coal-fired factories and steam-powered ships spurred unprecedented economic growth. In the 20th century, the emergence of oil and natural gas as principal energy sources further revolutionized energy production, releasing the concentrated energy stored in fossilized organic matter.

1.2 Fossil Fuels Depletion and Environmental Sustainability

Today, global energy demand is growing tremendously. Global energy consumption experienced notable growth in 2022, showing a 2.1% increase, surpassing its average growth rate of 1.4% per year during the period 2010–2019 [2]. This surge in demand was largely influenced by three major economies: China, the United States, and India, which together account for nearly 44% of the overall rise in energy demand, as stated in the U.S. Energy Information Administration’s 2022 International Energy Outlook report [3]. However, India is confident that it will encounter notable challenges in the upcoming years. The World Energy Outlook Report 2022 [4] by the International Energy Agency (IEA) projects a tremendous increase in India’s energy demand of more than 3% per year from 2021 to 2030. The country’s burgeoning population, rapid urbanization, and industrialization are primarily responsible for this escalation. Over the past few decades, the global consumption of fossil fuels has seen a significant increase, leading to grave environmental implications. According to the International Energy Agency (IEA) report [5] from 2021, fossil fuels, including coal, oil, and natural gas, still accounted for approximately 80% of the world's total energy consumption. The burning of these fossil fuels releases large quantities of greenhouse gases, such as carbon dioxide (CO_2), into the atmosphere, contributing to global warming and climate change. The United Nations Framework Convention on Climate Change (UNFCCC) estimates that CO_2 emissions from fossil fuel combustion reached a record high of 57.4 gigatons in 2022 [6]. This rise in emissions has been linked to extreme weather events, rising sea levels, disruptions in ecosystems, and an increase in the frequency and intensity of wildfires. Moreover, the combustion of coal for electricity generation results in the release of various harmful air pollutants, such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter, which contribute to air pollution and have adverse effects on human health. Thus, the world faces a twin crisis resulting from both fossil fuel depletion and environmental degradation due to greenhouse gas (GHG) emissions. On one hand, the increasing demand for fossil fuels has led to concerns about their depletion, as these finite resources are being consumed at an alarming rate. With continued reliance on fossil fuels for energy production, there is a pressing need to explore and adopt alternative, renewable energy sources to ensure a sustainable future for generations to come. The continued reliance on fossil fuels presents a critical challenge for global efforts to mitigate climate change and underscores the urgent need to transition to cleaner and more sustainable energy sources.

1.3 Embracing Renewable Energy: A Necessity for the Future

Addressing the above-mentioned twin crisis necessitates a comprehensive approach that involves transitioning away from fossil fuels towards cleaner, renewable energy options and implementing effective strategies to mitigate GHG emissions. Sustainable energy policies, technological innovations, and international cooperation are essential to tackle these intertwined challenges and build a resilient and environmentally responsible future. As a result, there has been a growing shift towards alternative energy sources that are renewable, sustainable, efficient, and cost-effective with fewer emissions. Renewable energy sources, such as solar, wind, hydroelectric, geothermal, and biomass, harness natural processes and energies that are continuously replenished, making them sustainable and environmentally friendly.

Solar energy harnesses the power of the sun through photovoltaic cells and solar thermal systems, providing clean electricity and heat. Wind energy converts the kinetic energy of wind into electricity through wind turbines. Hydropower uses the energy from flowing or falling water to generate electricity. Geothermal energy taps into the Earth’s natural heat to produce electricity and for heating purposes. Biomass energy uses organic materials to generate heat and electricity.

The use of these renewable energy sources facilitates economic and social development in a variety of ways. They offer a reliable and abundant source of energy, reducing dependence on finite fossil fuels and promoting energy security. By diversifying the energy mix, countries can achieve a more stable and resilient energy supply, mitigating the impact of price fluctuations in global fossil fuel markets. Renewable energy investments create new employment opportunities and stimulate economic growth. Furthermore, the renewable energy industry frequently attracts investment and generates revenue by exporting renewable technologies and services. Another important aspect is that the transition to renewable energy sources can have positive social impacts, particularly in remote or underserved regions. Decentralized renewable energy systems empower individuals and communities to generate their own power, fostering energy independence and empowerment. In conclusion, the move towards renewable energy sources offers a promising pathway to address the challenges of fossil fuel depletion and mitigate GHG emissions. Embracing these sustainable alternatives not only helps safeguard the environment but also unlocks economic and social opportunities for a more prosperous and inclusive future.

1.3.1 Biomass as a Source of Renewable Energy

Biomass is a promising and versatile source of renewable energy derived from organic materials, such as agricultural residues, bio wastes generated agro-based industries, animal droppings, forest waste, energy crops, and organic municipal waste. The energy potential of biomass lies in the chemical energy stored during the process of photosynthesis. To utilize this energy, various technologies like combustion, gasification, and anaerobic digestion can be employed, which enable the extraction of heat, electricity, and biofuels from biomass, making it a versatile and renewable energy source. The combustion of biomass releases carbon dioxide, but since the plants absorbed an equivalent amount of CO_2 during their growth, the net emissions are considered carbon neutral, making biomass an environmentally friendly option. Moreover, the use of organic waste materials for energy generation contributes to waste management and reduces landfill disposal. As a distributed energy resource, biomass promotes energy security and rural development, enabling local communities to produce their renewable energy and contribute to decentralized energy systems. However, sustainable biomass utilization requires careful management to prevent negative impacts on biodiversity, land use, and food production. Continued research and technological advancements are crucial for optimizing biomass energy conversion processes and ensuring its integration into a sustainable energy future.

According to the International Energy Agency (IEA), India is the world's third-largest energy-consuming country, with 80% of demand still being met by coal, oil, and solid biomass [5]. The bioenergy capacity in India was nearly 10.7 gigawatts in 2022, an increase of 78 megawatts from the previous year [8]. The country's biomass availability estimations are above 500 million metric tons annually [9]. The use of modern bioenergy has increased on average by about 3% per year between 2010 and 2022 and is on an upward trend [10].

Biomass energy, though touted as a sustainable option, faces some significant challenges. For example, the use of traditional biomass for cooking is still widespread in India, and it can have serious negative impacts on human health and the environment. With the application of modern technologies, biomass can be efficiently converted into a wide range of products, reducing our reliance on conventional fossil fuels and promoting a circular economy. Through processes like biomass gasification, pyrolysis, and fermentation, it is possible to produce biofuels, biogas, and bio-based chemicals, which can serve as renewable alternatives to traditional fossil fuels. Additionally, biomass can be transformed into valuable materials, such as bioplastics, bio-based fibers, and biochemicals, contributing to the reduction of greenhouse gas emissions and the conservation of finite resources. Harnessing the immense potential of biomass through innovative techniques allows us to cultivate a bioeconomy that is both sustainable and diverse. This paves the way for a future that is not only greener but also more resilient, ensuring a lasting positive impact for future generations.

1.3.2 Biomass Integration for a Resilient Biobased Society

Biomass plays a pivotal role in the transition towards a biobased society, holding immense importance in sustainable development and the mitigation of environmental challenges. As a renewable and abundant resource, biomass encompasses a wide array of organic materials. According to a report by the International Renewable Energy Agency (IRENA), biomass supplied approximately 10% of the world's total energy consumption in 2020 [11]. Before the advent of the petrochemical era, renewable feedstocks played a significant role in meeting the global energy and chemical demand. During the 1920-1930s, the chemurgy movement in the United States emerged, promoting the utilization of biomass as a source of chemicals [12]. The movement was driven by the belief that carbohydrates could serve as versatile alternatives to hydrocarbons for various chemical applications. It aimed to economically utilize agricultural surpluses and reduce dependency on non-renewable resources. However, between 1920 and 1950, there was a swift transition to a fossil-fuel-based economy, heavily reliant on non-renewable resources. Nevertheless, the oil crisis of the 1970s triggered a renewed interest in renewable energy sources due to concerns over diminishing fossil fuel reserves, global warming, and environmental pollution. Among the various renewable resources, lignocellulosic biomass emerged as a promising candidate, offering an abundant and cost-effective feedstock for the production of bio-based chemicals, fuels, and energy. It was recognized that biomass could replace or complement fossil resources in the synthesis of carbon-containing raw materials, making it an essential component of a renewable-based economy. However, the increasing consumption of biomass for energy led to concerns about rising feedstock prices, creating a conflict with the need for low-cost raw materials in biorefineries. Nonetheless, the unique composition of lignocellulosic biomass makes it particularly well-suited for extracting value-added chemicals and materials, enhancing the economic viability of a society dependent on renewable resources for its energy and material needs. While biomass alone may not fully address the world's power requirements, its utilization for chemical synthesis represents a crucial step towards a more sustainable and renewable future.

1.4 Solving India's Energy Dilemma: A Focus on Renewable Energy Strategies

India, as one of the world's fastest-growing economies, faces a pressing energy concern with increasing demand and limited fossil fuel reserves. The country heavily relies on imported coal, oil, and natural gas to meet its energy needs, making it vulnerable to price fluctuations and geopolitical uncertainties. Additionally, the reliance on fossil fuels contributes significantly to greenhouse gas emissions and air pollution, posing severe environmental and public health challenges. The US Energy Information Administration (EIA) [3] projecting that by the mid-2040s, India will consume more energy than the United

States. Such a surge in energy demand and an increasing reliance on energy imports could potentially lead India into a state of energy insecurity, warranting careful consideration of energy policies and investments in alternative energy sources to ensure a sustainable and secure future. Moreover, at COP26, held in Glasgow (UK), India made a significant commitment to combat climate change by announcing its net-zero emissions target [14]. According to this commitment, India aims to achieve net-zero greenhouse gas emissions by the year 2070. This ambitious pledge underscores the country's determination to transition towards a more sustainable and low-carbon future, aligning with global efforts to limit global warming and mitigate the adverse impacts of climate change. The announcement reflects India's growing recognition of the urgent need to address environmental challenges and contribute to the collective fight against climate change on an international level.

In response to energy and environmental concerns, India has been actively pursuing renewable energy interventions as a viable and sustainable solution. India has made substantial strides in promoting renewable energy sources to reduce its dependence on fossil fuels and curb carbon emissions. India has implemented a biofuel policy that aims to reduce the country's dependence on fossil fuels and promote the use of renewable energy sources. This policy encourages the use of waste biomass for energy production, which can help the country diversify its energy sources, mitigate greenhouse gas emissions, and secure a more sustainable future [87, 88]. Additionally, the government is making efforts to decarbonize energy-intensive industries by promoting the use of biogas, which can help in management of waste, reduce greenhouse gas emissions, and increase renewable energy production [91]. The Indian National Policy on Biofuels, released in 2018, sets blending targets for ethanol (20% blending by 2030) and biodiesel (5% by 2030) [89]. The policy includes an accelerated national E-20 mandate from 2030 to 2025, which aims to increase the capacity of ethanol production in India from 7 billion liters (BL) in 2021 to 15 BL in 2025 [89]. The Indian Government has also launched the Global Biofuels Alliance to accelerate the deployment of sustainable biofuels [88].

India also has emerged as one of the world's leading solar energy producers, with ambitious solar energy targets. The government's policies and initiatives have also played a crucial role in fostering the growth of renewable energy technologies across the country. Solar parks and incentives for solar rooftop installations have contributed to the significant expansion of solar power in the country. India's wind energy sector has also witnessed substantial growth over the years. India has significant hydroelectric potential, and several projects have also been commissioned to harness this clean energy source. The Government continues to explore new opportunities for sustainable hydropower development while taking into consideration environmental and social aspects.

Overall, the Government has implemented several policies to address its energy trilemma of ensuring energy security, energy affordability, and environmental sustainability, including financial support for clean energy and subsidies for renewables. These initiatives of Govt have led to a substantial increase in renewable energy capacity, contributing to energy security and reducing carbon emissions.

However, challenges remain in realizing the full potential of renewable energy in India. The intermittency of renewable sources, such as solar and wind, requires grid integration and energy storage solutions to ensure a stable and reliable power supply. Additionally, financing and infrastructure barriers, along with land acquisition issues, pose challenges to the smooth implementation of renewable energy projects. Also, the collaborative efforts between the government, private sector, and international partners will be essential to overcome challenges and drive the nation towards a cleaner and greener energy future.

1.5 Biowaste: Generation and Its Management

Biowaste, as a general term, encompasses all biodegradable materials with a biological origin that are discarded. These wastes originate from diverse sources and can be classified into different types such as forestry and agricultural residues, animal waste and droppings, sewage sludge, biorefinery byproducts, food waste as well as kitchen and garden waste, etc.

1.5.1 Weed Biowaste

Biowaste management remains a pressing concern, warranting focused attention. Among the diverse array of biomass sources, invasive weedy plants emerge as a highly coveted feedstock for pyrolytic valorization into fuels and chemicals. This preference stems from their remarkable ability to thrive under various conditions year-round, requiring minimal additional inputs. Further, the escalating threat posed by these plant invasions is becoming more pronounced, fuelled by the global movement of various plant species for gardening, agricultural, or forestry purposes [85] and thus management of such plants becomes all the more important.

The introduction of these plant species to new areas contributes to their establishment and rapid proliferation within natural or semi-natural ecosystems, posing a significant menace to habitats across numerous regions worldwide [85]. These unwelcome intruders not only jeopardize the survival of native species but also vie with agricultural crops for essential resources such as water, nutrients, and space, resulting in considerable economic losses in the agriculture sector. The deleterious impacts extend to the disruption of agricultural food production in agroecosystems and the alteration of natural ecosystems, causing harm to native species through competition or predation [85, 86]. Moreover, weeds contribute to soil degradation, compromise product quality, and pose threats to both humans and livestock [17]. In India, the impact of weeds on crop yield is estimated to be around 31.5%, surpassing losses caused by pests and diseases [15, 16].

Notably, weeds have been categorized based on their association with crops, ecological affinities, life span, and origin. A few examples of these noxious invaders are *Lantana camara, Alternanthera philoxeroides, Parthenium hysterophorus, Cassia uniflora, Chromolaena odorata, Eichhornia crassipes, Tithonia diversifolia, and Prosopis juliflora* etc. [19]. Prolific growth of these weeds is attributed to their quick adaptability to harsh conditions, prolific seed production through various reproductive methods, and the absence of natural predators [87].

Given the substantial detrimental impact of invasive weeds, it is imperative to address their control and management with utmost effectiveness. As the magnitude of this challenge continues to escalate, the urgency to manage these biowastes becomes even more pronounced. Currently, a range of practices is employed for weed management, encompassing cultural, biological, chemical, and mechanical/physical approaches. These methods include stale seedbeds, crop rotation, buried drip irrigation, mulching, tillage, manual removal, seed targeting, and heat/thermal treatment. However, these practices are not without their challenges. High costs, labour-intensive requirements, adverse effects on soil quality, weed resistance to chemicals, and environmental toxicity are significant concerns associated with conventional weed management. A case in point is the management of the pervasive *Parthenium hysterophorus,* covering an expansive 35 million hectares, which would incur an astronomical cost of 182 billion rupees if done manually, as reported elsewhere [20]. Similarly, eradicating Lantana, which spans 13 million hectares, would necessitate 117 billion rupees at a rate of 9000 Rs/ha [21, 22]. These conventional approaches impose substantial financial and environmental burdens.

Hence, an urgent need arises to develop innovative and cost-effective strategies for managing these biowastes without exacerbating environmental concerns and placing undue strain on farmers. The focus should be on pioneering solutions that address the challenges posed by invasive weeds while minimizing their impact on ecosystems. The efforts to harness the potential of invasive weedy plants must be complemented by robust strategies to curtail their spread and mitigate the broader ecological and economic ramifications. By aligning innovative solutions with a comprehensive understanding of the interconnected issues at play, substantial progress can be made toward effective biowaste management while preserving the delicate balance of ecosystems worldwide [85, 86]. These technologies should strive to enhance the economics of production, whether in the realm of biofuels or agriculture. It is crucial to foster advancements that not only address the immediate challenges posed by invasive weeds but also contribute to sustainable and economically viable practices, ensuring a harmonious coexistence between agricultural productivity and ecological well-being.

1.5.2 Waste Valorization: Strategies for Turning Waste into Valuable Resources

The current era faces significant challenges in managing the increasing amounts of waste generated. Existing waste management methods, such as landfilling, recycling, composting, and incineration, present limitations and environmental concerns. Landfilling, for instance, requires vast landmasses and raises fears of greenhouse gas emissions [23, 24]. Moreover, the presence of toxic compounds in certain waste materials, like curcin, lectin, phorbol esters, saponins, and protease inhibitors in Jatropha deoiled cakes [25, 26], hysterin, sesquiterpene lactones, ambrosin, etc., in Parthenium [27], and lantanilic acid and triterpenes in Lantana [28, 29], hinders their use as feed for composting. In light of these challenges, a holistic strategy is needed to address waste management issues and capitalize on the potential benefits of waste utilization.

A promising solution is to utilize these wastes as feedstocks for the production of energy and materials. This approach aligns with the twin objectives of achieving sustainable waste management and generating renewable energy and materials. India’s Biofuel Policy 2018 [30] also emphasizes the production of second-generation biofuels, utilizing byproducts from various processes to reduce conflicts between food and energy production.

1.5.3 Various Pathways of Biomass Conversion

India boasts an abundant availability of feedstock, providing a reliable, cost-effective, and carbon-neutral energy resource for the production of biofuels such as biodiesel, bio-oil, bioethanol, and chemicals. The diversity of conversion technologies further enhances its potential for sustainable energy generation. Each of these technologies has specific requirements, advantages, and disadvantages. Various factors influence the choice of conversion processes, which include: (1) the type and quantity of biomass feedstock; (2) end-use requirements; (3) environmental standards; and (4) techno-economic feasibility [31]. The conversion of biomass to energy is commenced using two main process technologies: biochemical/biological and thermochemical. Moreover, physicochemical technology is also used for producing biodiesel from plant and vegetable oils by trans-esterification and other processes.

1.5.3.1 Biochemical conversion

There are mainly two processes, fermentation and anaerobic digestion, which are used in this conversion process.

1.5.3.1.1 Fermentation

Fermentation is used in various countries for the wide-scale production of ethanol from sugar cane, bagasse, sugar beet, maize, wheat, sweet sorghum, and others. The biomass is first ground and then enzymes are used to convert the starch into sugars, followed by the conversion of the sugars into ethanol using yeast. In this process, the obtained solid residues or sugar cane bagasse are used as animal feed, in the gasification/pyrolysis process as feedstock, or as a fuel for boilers [32]. As the lignocellulosic biomass consists of some longer-chain polysaccharide molecules, the conversion of lignocellulosic biomass, like wood, grass, or other biomass, is more complex and, hence, acid or enzymatic hydrolysis is necessary prior to the fermentation of sugars into ethanol.

1.5.3.1.2 Anaerobic digestion

In this process, organic material is directly converted to biogas, a mixture of mainly methane and carbon dioxide with small quantities of other gases, such as hydrogen sulfide. In an anaerobic environment, bacteria convert the biomass to a gas with an energy content of about 20%—40% of the lower heating value of the feedstock [33]. Anaerobic digestion is a commercially proven technology and is widely used for treating high moisture content (80%—90%) organic waste. Biogas can be directly used in gas engines and gas turbines as well as a fuel for natural gas vehicles. Biogas quality can be upgraded by removing CO_2 with a conversion efficiency of 21% [34].

1.5.3.2 Thermochemical conversion

Thermochemical conversion technologies can be considered more advantageous than biochemical conversion technologies in terms of reaction time, flexibility, and the potential to utilize all types of biomass. Thermochemical biorefineries are composed of one or more thermochemical conversion methods merged to produce valuable hydrocarbons or energy. Such methods are especially important in reducing reliance on fossil resources by efficiently using the available biomass. As a result, high energy-efficient, value-added products can be obtained. The primary aim of thermochemical biorefineries is the production of transportation biofuels as their main product. Various processes are used for the thermochemical conversion of biomass such as combustion, gasification, torrefaction, and pyrolysis; which are shown in **Fig.1.1**

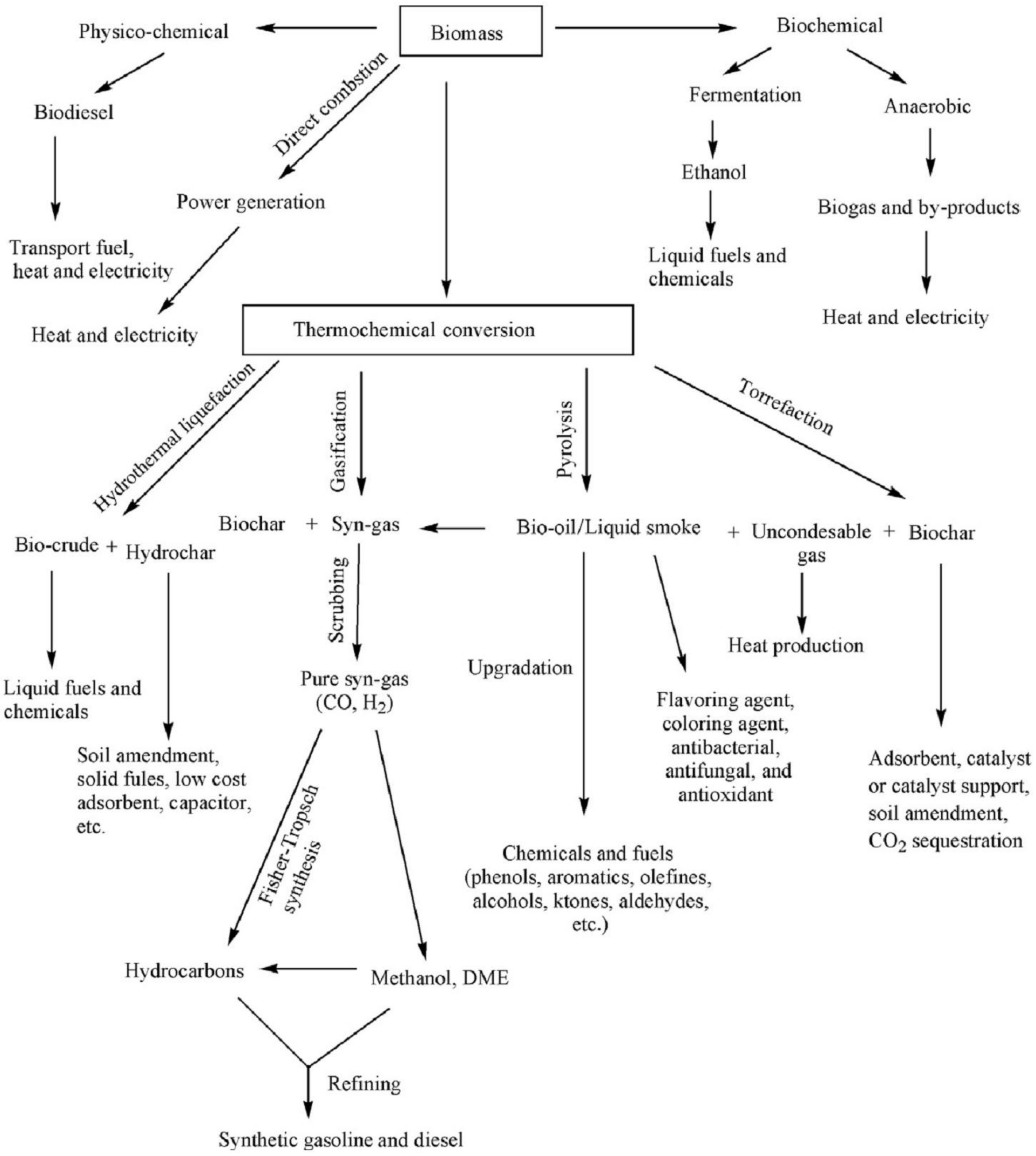

Fig. 1.1: Various conversion routes and utilization of lignocellulosic biomass

1.5.3.2.1 Combustion

The combustion process involves the burning of biomass in the presence of air. Biomass can store chemical energy which, through the combustion process, is converted into heat energy, shaft power, and electricity by employing different methods as well as devices like furnaces, stoves, steam turbines, boilers, and others. Although any type of biomass can be burnt, biomass with a low moisture content is preferred for combustion. Biomass with a higher amount of moisture is suitable for biological conversion processes or hydrothermal liquefaction [35]. Combustion plants from small-scale (e.g., for domestic heating) to large-scale industrial plants in the range of 100–3000 MW are available. Biomass combustion power plants have a bioenergy conversion efficiency of 20%– 40%. The Stirling cycle uses combustion to provide shaft power directly, but the development of the cycle is presently limited to small power outputs. The co-combustion of biomass with coal can also be carried out in existing coal-based power plants, which may be an attractive alternative due to its high conversion efficiency.

1.5.3.2.2 Gasification

Gasification is the conversion of biomass into synthesis gas (a mixture of CO and H_2) by the partial oxidation of biomass (in the presence of limited air or O_2) at a high-temperature range (800 °C–900 °C). This lower heating value gas can be burnt directly or applied in gas engines/gas turbines as fuel. Also, the produced gas can be utilized as a chemical platform for the production of some chemicals, such as methanol, dimethyl ether, and olefins [36]. Biomass-derived syngas are also utilized in the renowned Fisher-Tropsch synthesis-based biomass-to-liquid (BTL) technology for the production of liquid fuels, such as gasoline, diesel, and jet fuel. However, there are some flaws of BTL technology: it may produce poor quality biomass-derived syngas with a low calorific value, low H_2 to CO ratio, low selectivity to desirable olefins, catalyst poisoning, and the formation of tar and methane which can harm the process equipment with long- term operation leading to complicated cleaning steps. These drawbacks of BTL technology draw attention toward the production of syngas from economical natural gas or coal as a feed instead of biomass [37]. Moreover, the major techno-economic barrier for the large-scale implementation of BTL is that it requires large gasification systems, involving high investment and running costs as well as uncertainty in terms of the availability and quality of feedstock [38].

1.5.3.2.3 Pyrolysis

Pyrolysis is a common thermal conversion technique where biomass is thermally decomposed into biofuel products at a moderate temperature range from 350–800 °C in the absence of air/oxygen [39]. In pyrolysis, the major components of biomass, viz., cellulose, hemicellulose, and lignin, consisting of the long chains of carbon, hydrogen, and oxygen compounds break down into smaller molecules in the form of gases, condensable vapors (tars and oils) and char under different conditions [40]. The heavier gases produced in the pyrolysis when cooled at room temperature are condensed into liquid, termed bio-oil; and the gases such as hydrogen and methane, etc., are lighter in weight and remain as gases at room temperature, known as syn-gas (synthesis gas). In the pyrolysis process, product selectivity can be controlled and tuned to suit end-use interests by regulating the various process parameters [41]. The relative proportions of the by-products obtained from the pyrolysis are dependent on different pyrolytic conditions, viz., temperature, residence time, heating rate, feedstocks, pressure and reactor design, etc. [42]. For example, performing pyrolysis of biomass below 450 °C with a slow heating rate leads to the production of biochar in higher amounts. Again, the higher yield of bio-oil can be obtained from pyrolysis by performing at an intermediate temperature between 450 °C to 800 °C along with a high heating rate. Gaseous product formation in large amounts can be possible if the pyrolysis is performed above 800 °C with a high heating rate [40]. The following **Fig.1.2** shows the flow diagram of a pyrolysis unit for different product production.

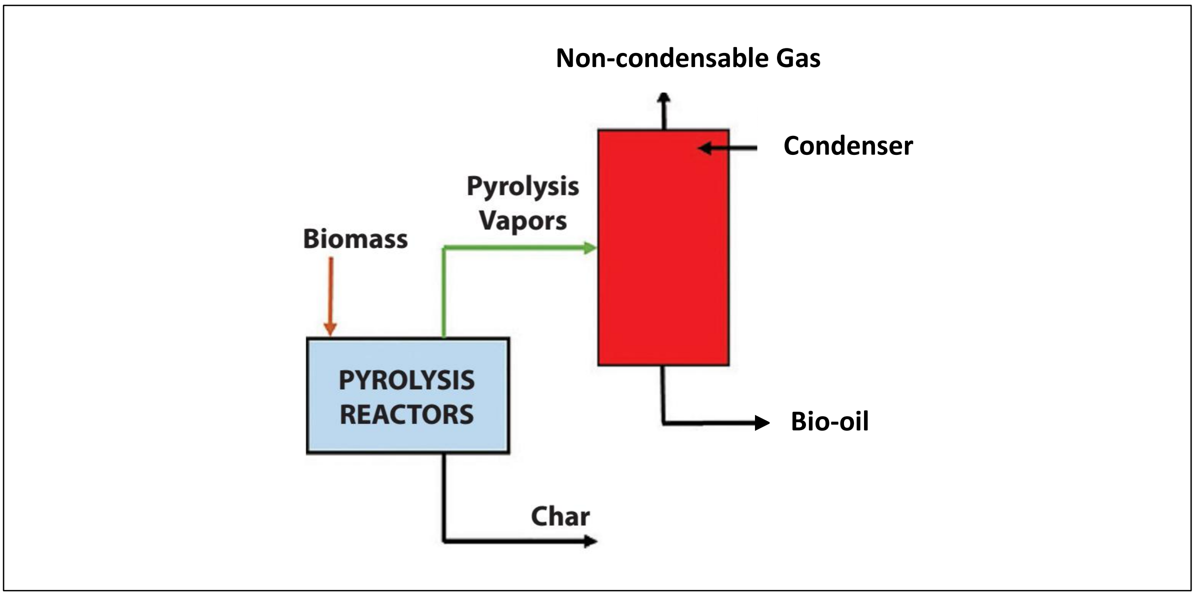

Fig.1.2: Flow diagram of pyrolysis unit for different product formation

1.6 Historical Overview and Evaluation of the Pyrolysis Process

The pyrolysis process dates back centuries and has garnered significant attention due to its potential to convert organic materials into valuable products and energy sources. The history of pyrolysis is rich and varied, with evidence of its usage across different cultures and periods. The roots of pyrolysis can be traced back to ancient civilizations, where it was employed for various purposes. Early civilizations like the Egyptians and Chinese used pyrolysis in the production of charcoal for heating and cooking. Additionally, indigenous cultures in the Amazon rainforest practiced “terra-preta” formation by pyrolyzing agricultural residues, creating fertile soils. During the Industrial Revolution, pyrolysis gained traction in the production of town gas from coal, used for lighting and heating in cities. The development of more efficient retorts and advancements in chemistry further expanded pyrolysis applications. In recent times, pyrolysis has experienced a resurgence due to growing concerns about environmental sustainability and the need to reduce waste. Pyrolysis holds promise in addressing environmental challenges and transitioning toward a more sustainable future as it has the potential to convert organic waste into valuable products and renewable energy. However, further research, technological advancements, and favorable policies are essential to unlock its full potential.

1.6.1 Classification of the Pyrolysis Process

Based on the heating rate, pyrolysis can be classified into three different types:

(i) Fast pyrolysis, (ii) Flash pyrolysis, and (iii) Slow pyrolysis.

1.6.1.1 Fast pyrolysis

Fast pyrolysis of biomass is performed by heating at a moderate to high temperature along with a higher heating rate in the absence of oxygen. Fast pyrolysis is characterized by a short vapor residence time. Fast pyrolysis leads to the formation of 60–75% of liquid fuels along with 15–25% of solid fuels. Based on the type of biomass utilized in the pyrolysis, it can also provide gaseous products from 10–20% [42]. Fast pyrolysis is considered promising in the production of liquid biofuels from biomass due to some advantages, including economic feasibility; easy transportation and storage facility; and the application of second-generation biofuel feedstocks are possible in this method [44].

1.6.1.2 Flash pyrolysis

Flash pyrolysis is another type that is carried out at higher temperatures ranging between 450 – 1000 °C along with a higher heating rate in an inert atmosphere. This process can result in solid, liquid as well as gaseous products. The yield of liquid fuels in flash pyrolysis can be obtained up to 75%. The vapour residence time in this particular pyrolysis process is very short [45]. Flash pyrolysis has the drawback of poor thermal stability. Another disadvantage of flash pyrolysis is the viscous nature of the obtained oil, which may be due to the catalytic effect of the char [46].

1.6.1.3 Slow pyrolysis

Slow pyrolysis is performed at a low-temperature range at a low heating rate which provides good quality charcoal/biochar. In this pyrolysis method, the vapour residence time is quite longer than the other pyrolysis which is around 5–30 min [47]. The longer residence time of this process leads to the lower yields of liquid biofuels. Furthermore, the quality of bio-oil produced in this process is very low. The process suffers from low heat transfer values with longer retention time leading to enhanced expenditure by higher input of energy [48, 49].

1.6.2 Pyrolysis Products

The three primary products obtained from pyrolysis of biomass are solid, liquid, and gaseous products [50]. Pyrolysis products are the complex combination of the products produced from the individual pyrolysis of cellulose, hemicellulose, lignin, and extractive fractions present in biomass; each component has its 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 [51]. Products from the pyrolysis process also strongly depend on the water content in the biomass, which produces large quantities of condensate water in the liquid phase [52]. This contributes to the extraction of water-soluble compounds from the gaseous and tar phases, and thus a greater decrease in gaseous and solid products [53].

1.6.2.1 Liquid product

Pyrolysis typically yields a liquid product referred to as pyrolysis oil, bio-oil, or bio-crude. It is generally a dark brown, free-flowing organic liquid consisting of various compounds primarily derived from the depolymerization and fragmentation reactions of three key biomass constituents: cellulose, hemicelluloses, and lignin. Biooil represents a complex mixture of organic compounds, mainly including alcohols, acids, aldehydes, esters, ketones, phenols, and lignin-derived oligomers [7].

A comprehensive understanding of bio-oil is a prerequisite for research aiming to elucidate the mechanism of bio-oil production, its properties, and upgrading techniques [54]. Numerous publications have asserted that distinct chemical compositions of bio-oil are responsible for varying physical properties [71-74]. The primary bio-oil components are distributed as follows: water (20–25%), water-insoluble pyrolytic lignin (25–30%), organic acids (5–12%), non-polar hydrocarbons (5–10%), anhydrosugars (5–10%), and other oxygenated compounds (10–25%). The water content in biooils contributes to their low energy density, reducing flame temperature, and causing ignition and injection difficulties when preheated [13]. Biooils are highly acidic with a pH value of 2.0–3.0, attributed to the presence of hydroxyl-acetaldehyde (up to 10 wt.%), followed by acetic and formic acids (at ~ 5 wt.% and ~ 3 wt.%, respectively) [51]. The precise composition of bio-oil depends on factors such as feedstock type and quality, heat transfer rates, reaction time and temperature, and the efficiency of condensation equipment [51].

Efforts have been made to investigate the feasibility of using bio-oil as a transportation fuel due to its hydrocarbon content [75-78]. Combustion tests using bio-oil and ethanol mixtures at a 20:80 ratio demonstrated no performance decrease [79]. Investigations into bio-oil and diesel mixtures revealed no significant change in fuel properties, albeit with cost disadvantages and the use of energy-intensive surfactants and emulsifiers [80, 81]. Biooil has also been successfully used for heat production, offering longer flames and lower toxic gas emissions upon combustion, making it a viable substitute for conventional fossil fuels with minimal system modifications [82]. Various business houses and researchers worldwide have explored the use of bio-oil in diesel engines with large cylinder bores [83, 84]. Biooil’s lower emission of toxic gases has prompted researchers to consider its use in gas turbines. This potential application has been explored in separate studies conducted in various regions, including Canada, Italy, Germany, and other locations. [82, 84]. However, high acidity, viscosity, moisture content, low thermal stability, and the presence of oxygenated compounds in biooil, may pose problems such as engine and turbine corrosivity. To mitigate these issues, oil upgrading methods involving alkali removal as well as oxygen reduction through processes like hydrogenation, dehydration, fractionation, steam reforming, and catalytic cracking are necessary [56].

Despite substantial progress in upgrading bio-oils, technical challenges such as catalyst deactivation, catalyst lifespan, and low chemical recovery still exist [43, 55].

Bio-oil also holds promise as a platform chemical. Many biomass-derived pyrolysis oils are known to contain polycyclic aromatic hydrocarbons (PAH). Phenolic compounds found in bio-oils have extensive applications in resin and flavoring agent production within the food industry. Syringol and guaiacol are also present in significant concentrations in biomass-derived pyrolysis oils and are utilized in the production of biodegradable polyesters and polyethers [59]. The aqueous phase of bio-oil has been patented and commercialized as a food flavoring and browning agent [61, 80].

1.6.2.2 Gaseous product

The thermal decomposition of biomass results in the generation of both condensable and non-condensable gases. The previous section delved into the discussion of condensable gases, often referred to as liquid products. The non-condensable gas typically contains CO, H_2; minor quantities of other components, including carbon dioxide (CO_2), water, hydrocarbons like CH_4, C_2H_4, and C_2H_6, as well as tar and ash [69]. The specific composition of these components varies depending on the type of biomass used and the conditions of pyrolysis [70]. These constituents originate from a series of endothermic reactions occurring at elevated pyrolysis temperatures. For instance, hydrogen (H_2) forms during the breakdown of hydrocarbons at higher temperatures, while carbon monoxide (CO) and carbon dioxide (CO_2) serve as indicators of oxygen presence in the biomass, primarily resulting from the decomposition of partially oxygenated organic compounds. Therefore, the content of cellulose in the biomass, being a highly oxygenated polymer, significantly influences the production of carbon oxides. Furthermore, the presence of light hydrocarbons may be attributed to the reformation and cracking of heavier hydrocarbons and tar within the vapor phase [53].

1.6.2.3 Solid product

The thermal degradation of lignin and hemicellulose results in a significant loss of mass in the form of volatile compounds, leaving behind a rigid amorphous carbon matrix referred to as char or biochar. The yield of char varies across different temperature ranges. The physical characteristics of char are highly influenced by pyrolysis conditions, including the type of reactors, biomass, drying treatment, particle size of feedstock, chemical activation, heating rate, residence time, pressure, and flow rate of inert gas, etc. [53].

Biochar primarily consists of carbon, along with hydrogen and various inorganic species, organized into two structures: stacked crystalline graphene sheets and randomly ordered amorphous aromatic structures. Within the aromatic rings, elements such as O, N, P, and S are commonly incorporated as heteroatoms, exerting a significant influence on the physical and chemical properties of char [62].

Biochar finds a broad range of applications that yield environmental and agronomic benefits. It possesses several advantageous qualities, including energy production, waste management, carbon sequestration potential, wastewater treatment, and support for catalyst development. The application of char into the soil contributes to soil nutrient maintenance and the mitigation of greenhouse gas emissions, such as CH_4 and CO_2, generated by traditional waste disposal, processing, and recycling operations [63]. The addition of biochar also addresses soil acidity issues and provides potential benefits to soil microorganisms, along with readily available nutrients like nitrogen, phosphorus, and potassium, although this effect diminishes over time. Thus, along with the other applications the production of solid char through pyrolysis helps achieve the dual goals of waste reduction and energy recovery. Additionally, it reduces the weight and volume of the initial biomass feedstock, thereby minimizing the space required for disposal. Char may also be used as a coal substitute for energy production in blast furnace [90].

Biochar has also garnered considerable attention for its potential role as a biosorbent in environmental remediation. Its application as an adsorbent in wastewater treatment and recycling represents an effective method for the separation and reduction of various pollutants—both organic and inorganic—in contaminated water. This approach also offers significant advantages in terms of cost, availability, profitability, ease of operation, and efficiency [65]. Furthermore, the utilization of biochar for adsorbing pollutants such as toxic heavy metals [66] and dye effluents [57] has become a prominent area of research interest. This interest stems from the favourable characteristics of biochar, including its porosity, high specific surface area, and cation exchange capacity [67].

1.7 Methodology for Modelling and Optimization of Pyrolysis Process

It is essential to comprehend the impact of process parameters on the yields and characteristics of pyrolysis products. This is accomplished through the process of modelling and optimization. The pyrolysis process is simulated, taking into account variables such as temperature, residence time, heating rate, and other relevant factors. By manipulating these model parameters, researchers can make reliable predictions regarding product yields and quality. Subsequently, optimization techniques are employed to ascertain the most efficient combinations of parameters. This may entail optimizing desirable products, eliminating undesirable components, or achieving a balance between different aspects. By employing this integrated methodology, researchers can gain insights into the influence of particular variables on the pyrolysis process and determine the optimal configurations for attaining desired results.

Process parameter optimization in any process or methods aims to reduce the number of experiments, minimize time requirements, and cut costs. Traditional or classical optimization methods involve varying one parameter at a time while keeping others constant. Due to the length, large number of experiments, and failure to develop an understanding of the interaction effect; the classical or traditional approach has some disadvantages. In addition to that, the classical way is a time-consuming as well as expensive approach to attain optimum conditions. On the contrary, statistical optimization or mathematical modeling entails the simultaneous optimization of all parameters through a mathematical algorithmic process [92-94]. This methodology is considered an important tool for gathering knowledge on the significance of the factors affecting pyrolyser performance. Generally, response surface methodology (RSM) and artificial neural network (ANN) are two statistical tools, which are employed for experimental design, statistical modelling and optimization of all the process parameters together [95, 96]. They enable us to predict and establish a relationship between one or more responses with independent factors [97, 98].

1.8 Importance of Kinetics and Thermodynamics in Biomass Pyrolysis

The growing interest in the thermal utilization of bio-waste, driven by the need to recover materials and energy while reducing greenhouse gas emissions, has spurred research in the field of biomass decomposition kinetics for thermochemical energy production. A few theoretical calculations based on thermogravimetry provides valuable insights into the thermal degradation mechanisms of biomass and its various molecular fractions that store chemical energy [99]. Biomass pyrolysis, which involves a complex interaction of competitive and concurrent reactions, requires a thorough understanding of solid-state pyrolysis kinetics. This knowledge is essential for elucidating the structure and composition of the biomass constituents and for assessing the feasibility, design, and scaling of industrial applications. In this context, researchers have developed hypothetical models that treat the overall performance of pyrolysis as the combined behaviour of individual components [100].

A pyrolysis kinetic study seeks to uncover how thermal decomposition occurs, whether it involves one or more processes and the range of conversions that take place. Kinetic models provide characteristic constants that define these processes [68]. Various kinetic parameters, including process conditions, heat and mass transfer limitations, sample heterogeneity, and systematic errors, influence biomass pyrolysis. Researchers have employed different isoconversional methods, such as Friedman, Flynn–Wall–Ozawa, and Kissinger–Akahira–Sunose, to calculate the activation energy for pyrolysis of various types of biomass.

From the kinetic data, it is possible to determine the thermodynamic parameters which are important to define the availability of the process and understand the variation of enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) with conversion [58]. These parameters in addition to kinetic parameters (such as activation energy, and pre-exponential factor) are useful in determining the nature of the pyrolysis process in terms of energy requirements and energy balance [60, 64]. For example, the information of ΔH provides an estimation of the energy consumed by pyrolysis to convert the biomass into bioenergy products. A deeper understanding of the reaction kinetics and thermodynamic aspects is indispensable to the design and optimization of a large-scale pyrolysis system [64].

1.9 State of the Art

Thermochemical conversion of biomass, particularly pyrolysis, has emerged as a promising strategy for sustainable energy production and waste valorization. While extensive research has been conducted on conventional lignocellulosic biomass, such as agricultural residues and forestry waste, the potential of invasive weed species like *Tithonia diversifolia* remains relatively unexplored. Existing studies on biomass pyrolysis have employed various techniques, including kinetic modeling and catalytic pyrolysis. However, the application of these techniques to invasive weed species, especially *Tithonia diversifolia*, is limited. Additionally, a comprehensive understanding of the interplay between pyrolysis conditions, product distribution, and reaction mechanisms is still evolving. Furthermore, the optimization and modelling of pyrolysis processes using methods such as Response Surface Methodology (RSM) and Artificial Neural Networks (ANN) has gained significant attention. Nevertheless, comparative studies evaluating the efficacy of these techniques in predicting pyrolysis product yields are scarce.

1.10 Benefits of the Research

This research aims to address critical knowledge gaps in the thermochemical conversion of *Tithonia diversifolia*, an invasive weed species. By studying its pyrolysis kinetics, mechanisms, and the impact of catalysts like metal-impregnated ZSM-5, this research contributes to the development of efficient and sustainable bioenergy production technologies. The findings will enhance our understanding of the pyrolysis process, optimize operating conditions, and improve the quality of bio-oil. Additionally, this research promotes the utilization of invasive weed biomass, mitigating its negative ecological impact and contributing to a more sustainable and circular bioeconomy.

1.11 Research objectives

The objectives of this thesis are as follows:

(a) To evaluate physicochemical properties of *T. diversifolia* biomass for its suitability in a pyrolyric conversion process.

(b) To investigate the effect of operating conditions on the pyrolysis of *T. diversifolia*.

(c) To compare the artificial neural network (ANN) and response surface methodology (RSM) for evaluation of the predictive capability of bio-oil yield.

(d) To investigate the kinetics, reaction mechanism, and thermodynamics of *T. diversifolia* pyrolysis.

(e) To determine the effect of catalysts on the pyrolytic conversion of biomass by elucidating the kinetics, thermodynamics, and mechanisms of the catalytic pyrolysis process.

1.12 Organization of the Thesis

This thesis is structured into five chapters, each serving a distinct purpose.

Chapter 1 serves as an introduction and background of the research.

Chapter 2 presents a comprehensive review of existing literature. This review covers a range of topics, including the pyrolysis of lignocellulosic biomass with a special emphasis on the current state-of-the-art review of pyrolysis of invasive weed species. It discusses various factors that influence the performance of thermochemical conversion of biomass, different methodologies used to optimize pyrolysis oil yield, the various types of catalysts and their properties affecting pyrolysis reactions, and the kinetics and thermodynamics of biomass pyrolysis. Upon reviewing the literature, research gaps have been identified, and research objectives have been formulated.

Chapter 3 is dedicated to outlining the research methodologies employed in this study.

Chapter 4 is further divided into four subchapters. These are:

- **Chapter 4A**, focuses on biomass characterization, encompassing physico-chemical and biochemical analysis. It also delves into the effect of operating conditions on biomass pyrolysis.
- **Chapter 4B** conducts a comparative assessment of artificial neural networks (ANN) and response surface methodology (RSM) of bio-oil yield obtained in biomass pyrolysis.
- **Chapter 4C** investigates the reaction kinetics, mechanisms, and thermodynamics of biomass pyrolysis.
- **Chapter 4D** explores the influence of catalysts on biomass pyrolysis, presenting the experimental results as well as their effect on kinetics, mechanisms, and thermodynamics.

In **Chapter 5**, the thesis concludes by summarizing the results along with the prospects of the research.

The appendices provide several tables for reference. These include tables that explore the impact of various parameters on product yield and GC-MS tables of bio-oils.

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