Chapter 1

Introduction

1.0 Introduction

The global energy system has undergone a remarkable transformation since the industrial revolution, characterized by significant modernization and mechanization. This shift has greatly influenced human developmentand the global economy, as the accessibility and supply of energy resources play a crucial role in shaping both. Over the years, new energy sources have been developed, beginning with fossil fuels, followed by the development of hydropower, nuclear power and more recently, various renewable energy technologies. Alongside the diversification of energy sources, energy production and consumption scale has increased significantly. The energy demand rises worldwide with the population growth and economic development [1]. Approximately 80% of global energy demand is met by fossil fuels, such as oil, coal, and natural gas. However, according to the International Energy Agency's World Energy Outlook 2023, global reliance on fossil fuels is expected to decline significantly. The ongoing transition toward clean energy technologies is projected to reduce the share of fossil fuels in meeting global energy demand by 73% by 2030 [2]. Additionally, the depletion of fossil fuel resources and the production, transport, and processing of oil and gas resulted in 5.1 billion tonnes of CO_2 equivalent emissions in 2022, accounting for just under 15% of the global energy sector greenhouse gas emissions [3]. To meet climate goals and achieve net-zero emissions by mid-century, it is essential to develop and implement energy-efficient, environmentally friendly technologies across various economic sectors.

Renewable energy sources, including solar, wind, hydropower, and biofuels, are the available options for transitioning to low-carbon, sustainable energy systems. Expanding the use of renewable energy can help to address significant policy challenges such as energy security, climate change, and affordability. However, deploying these energy sources need policy support due to supply chain disruptions, increased costs, and financial incentives. Bioenergy derived from biomass, carbon-rich organic material found in plants represents the largest renewable energy source. It accounts for 55% of global renewable energy and over 6% of the total energy supply. Plants absorb the carbon contained in the atmosphere through photosynthesis, and when biomass is used for energy production, this carbon is released back into the atmosphere during combustion. This cycle positions modern bioenergy as a promising near-zero-emission fuel. In the Net Zero Emissions by 2050 Scenario, bioenergy utilization is expected to increase significantly and replacing fossil fuels [3].

Bioenergy is recognized as an essential and versatile component of the clean energy transition, playing a crucial role in efforts to decarbonize various sectors. Its applications range from solid biofuel and biogases used for power and heat generation in households and industrial settings to liquid biofuels in the automobile, aviation, and shipping industries. However, in line with the Net Zero Emissions (NZE) scenarios, the growth of bioenergy generation needs to be carefully managed to prevent adverse impacts on biodiversity, freshwater systems, food availability, and quality of life. As such, policy support needs to be directed exclusively toward bioenergy that effectively reduces lifecycle greenhouse gas emissions while avoiding unacceptable environmental, social, and economic impacts. Sustainability frameworks are crucial for phasing out the traditional use of biomass and scaling up various sustainable feedstock supplies. In the NZE Scenario, sustainability restrictions limit bioenergy generation to 100 Exajoules (EJ), representing approximately 20% of the total energy supply by 2050 [4]. While traditional biomass utilization is being phased out, the consumption of modern bioenergy is projected to double by 2050, due to its potential as a drop-in alternative fuel in existing industrial setups. The supply of advanced feedstock has significantly increased, driven by increasing investment and the commercialization of advanced conversion technologies. This highlights the necessity of further exploring sustainable bioenergy generation and utilization approaches, particularly in relation to low-value and environmentally friendly energy sources.

1.1 Biomass as sustainable energy sources for biofuel production

1.1.1 Biofuels

Biofuels play a crucial role in addressing the world's pressing energy and environmental challenges in the ongoing transition to a sustainable and clean energy system [5]. The Global Biofuel Alliance (GBA) launch at the G20 summit in 2023 represents a significant milestone for both India and the international community in promoting global biofuel adoption and addressing climate change [6]. Biofuels are sourced from various biomass materials and offer a renewable and potentially carbon-neutral alternative to traditional fossil fuels. This renewable aspect can significantly reduce global greenhouse gas emissions and enhance energy reliability and security. The demand for biofuels is projected to increase by 38 billion litres between 2023 and 2028, representing an approximate 30% increase compared to the previous five-year period. By 2028, total biofuel demand is expected to reach 200 billion litres, reflecting a 23% increase. This growth is primarily driven by renewable diesel and ethanol, which account for two-thirds of the increase, while biodiesel and biojet fuel make up the remaining share [3]. This expansion is mainly driven by favourable government policies to reduce greenhouse gas emissions, decrease oil imports, and promote domestic agriculture. As illustrated in Fig. 1.1, of the total increase in biofuel demand from 2023 to 2030, biodiesel and renewable diesel will contribute 42% (260 kb/d), ethanol 35% (210 kb/d), and biojet fuel 23% (140 kb/d).

Biofuels can be categorized into four distinct generations, each based on the type of feedstock, the methods of conversion used, and the operational parameters involved [7,8]. Fig. 1.2 presents the various biofuel sources and end products.

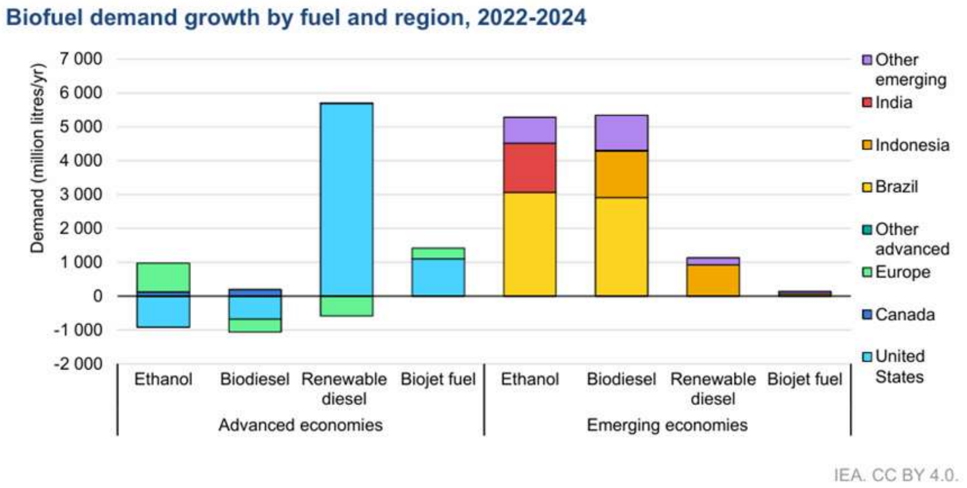

Fig. 1.1 Biofuel demand and growth by fuel and region, 2022 to 2024 [9]

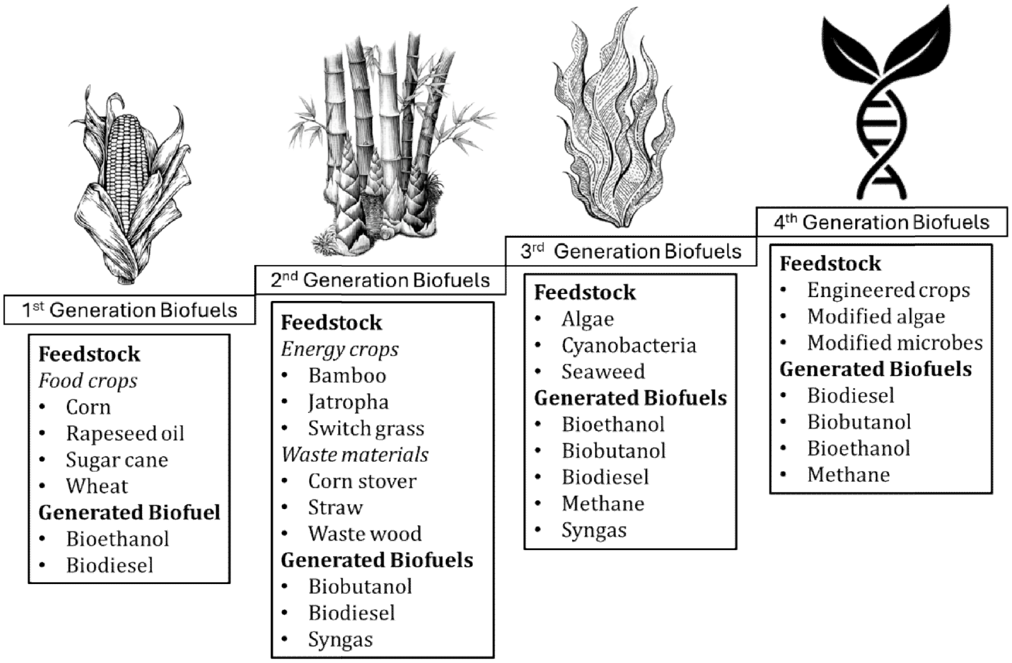

Fig. 1.2 Biofuel sources and end products shaping production pathways

- *First-generation biofuels (1G)*: These are derived from food crops. Biodiesel is produced by extracting oils from crops such as rapeseed, soybeans, and palm oil. At the same time, bioethanol is produced through the fermentation of sugar and starch-rich crops like sugarcane and corn [10]. Although 1G biofuels can be blended with gasoline and used in existing engines with minimal modifications, they have significant drawbacks. One primary concern is the potential for a negative net energy balance. The production process can release more carbon dioxide than the crops capture during their growth, undermining their environmental benefits. Additionally, using food crops for biofuel production raises the ‘*food versus fuel*’ dilemma. The diversion of arable land and resources toward fuel crop cultivation can lead to higher food prices, ultimately affecting the availability of food and livestock feed [11, 12].

- *Second-generation biofuels (2G)*: These are derived from non-edible lignocellulosic energy crops, which include agricultural residues (such as corn cobs and wheat straw), forest residues (like wood chips and sawdust), and dedicated energy crops cultivated explicitly for biofuel production, such as switch grass and miscanthus [13]. As a result, 2G biofuels are widely viewed as a sustainable alternative to the increasing carbon footprint and ethical concerns associated with first-generation biofuels. However, 2G biofuels face significant challenges due to technical difficulties in the pre-treatment and conversion processes. These challenges lead to higher production costs and lower overall yields, which make 2G biofuels less economically competitive. Ongoing research and technological advancements aim to enhance the efficiency of these processes and reduce their associated costs [14].
- *Third-generation biofuels (3G)*: These are produced from microalgal and cyanobacterial biomass, which can naturally generate alcohols and lipids converted into biodiesel, bioethanol, or other high-energy fuel products. This type of biomass has several advantages over traditional plants. Algae and cyanobacteria require minimal land for cultivation, absorb carbon dioxide, and have high lipid content, making them efficient for biofuel production. Additionally, this can be utilized in wastewater treatment processes, providing an environmental benefit. However, there are drawbacks to use these microorganisms, including energy-intensive production processes, high production costs, and susceptibility to contamination by other microorganisms, and challenges in scaling up production for commercialization [15].

- *Fourth-generation biofuels (4G)*: These are genetically engineered crops, such as modified algae and plants, specifically designed to enhance biofuel production. These biofuels offer several advantages, including the potential to absorb more carbon dioxide than they emit, eliminate the conflict between food and fuel, and produce higher yields, which positively contribute to the environment. However, 4G biofuels are still in the early stages of development and face several challenges, such as economic viability, technical complexities, public acceptance, and the need for infrastructure development [16,17].

1.1.2 Impact of biofuel utilization

Recent strategies for expanding biofuel production have been thoroughly examined in the context of sustainable development and clean energy transition scenarios. While biofuels can reduce dependence on fossil fuels and lower greenhouse gas emissions, large-scale production presents significant challenges regarding environmental, economic, and social sustainability. Fig. 1.3 presents the various scenarios of impact of biofuel utilization.

Raw material competition: Biofuel production, which depends on edible and non-edible biomass feedstock, is vital in sustainable renewable energy. However, establishing large-scale bio-refineries to meet the increasing fuel demand has led to increased competition with other industries, such as food, livestock, and paper, using similar raw materials. This competition can lead to increased costs for biomass feedstock, causing inflation in the prices of essential goods. The growing demand for biomass also drives intensive agricultural practices, gradually depleting soil fertility and productivity. The use of heavy machinery in large-scale biomass cultivation exacerbates this issue by compacting the soil, reducing its porosity and aeration. Furthermore, the shift toward monoculture cultivation decreases plant diversity and results in significant habitat loss for many species. Therefore, raising awareness and understanding of biofuel technologies is crucial for effectively addressing and mitigating the economic challenges associated with the food versus fuel debate [18].

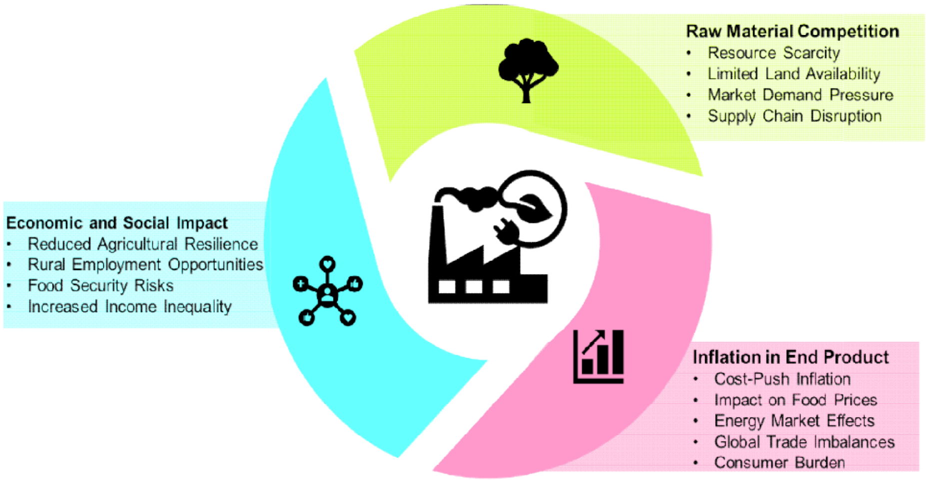

Fig. 1.3 Impact of biofuel utilization

Inflation in end product price: The rising costs of biofuel derived from edible crops are leading to increased production expenses, which in turn increase the cost of the final product. It is essential to consider alternative inputs, such as using oil-derived food waste and ensuring the availability of non-food feedstock for biofuel production to mitigate these costs and address the food versus fuel debate. Some biofuel sources that do not directly compete with the food chain or compete with food production make them viable options. However, their production typically requires advanced machinery and significant investments. Third and fourth-generation biofuels present promising alternatives, but developing these options is often time-consuming and requires specialized expertise [19].

Economic and social impact: All biofuel production facilities depend on common raw materials, which create a ripple effect across various sectors. This competition drives up the cost of biomass, leading to increased prices for biofuel end-products, food, and other essential goods. This inflation disproportionately impacts middle-class and lower-income populations, who spend a significant portion of their income on necessities. Furthermore, the increased demand for raw materials can strain agricultural systems, potentially leading to the over exploitation of agricultural land, migration, disruptions to social structures, deforestation, and other environmental consequences [20].

Biofuel production offers significant environmental advantages and plays a vital role in sustainable development. However, it needs to be managed carefully to prevent unintended food shortages or negative impacts on vulnerable populations. Striking a balance between biofuel production and other essential needs is crucial to maximizing its benefits while avoiding adverse consequences.

1.1.3 Thermal conversion processes of lignocellulosic biomass

The thermal decomposition of organic materials in biomass is crucial for biofuel production. This thermochemical conversion process generates valuable solid, liquid, and gaseous products. Additionally, it provides opportunities for generating renewable electricity, including biomass co-firing in existing coal power plants and supporting decentralized electrification projects in developing countries [21]. Thermal decomposition can be classified into three main processes: combustion, gasification, and pyrolysis. Each of these processes operates under specific conditions that affect both their efficiency and product types. A summary of these operational conditions and their respective yield products is presented in Table 1.1. Optimizing parameters such as temperature, pressure, heating rate and catalyst usage is essential for enhancing the selectivity of desired products while minimizing unwanted byproducts [22].

Table 1.1 Characteristics of thermochemical conversion methods

Thermochemical conversion methods	Combustion	Pyrolysis	Gasification
Temperature	>1073 K	673-1073 K	973-1573 K
Atmosphere	Oxidation	Absence of oxidation	Partial oxidation
Reaction medium	Air	None	Air, CO_2, pure oxygen and/or Steam
Yield product	CO_2 and H_2O	CO, CO_2, H_2O and light hydrocarbons	CO, CO_2, H_2, CH_4, hydrocarbons
Advantages	• Relatively simple and can achieve high conversion of feedstock into energy. • Flexible feedstock quality. • Co-firing of lignocellulosic biomass is compatible with existing infrastructure.	• Adapts to flexible fuels and yields versatile products. • Co-pyrolysis of feedstock assists in CO_2 removal and upgrades the bio-oil. • Generated biochar can be used for carbon sequestration	• Produces synthesis gas with high potential for conversion into value-added products. • Typically, prevents the formation of NOx, SOx, and halogenated compounds. • Flexibility in scale, from small, decentralized units to large industrial plants.
Disadvantages	• Possible generation of GHG, short-lived climate pollutants, contributing to environment pollution. • High pollution control cost. • High risk of fouling and corrosion, leading to increased operational cost.	• Composition of the product is complex. • Lower calorific value of bio-oil limiting its suitability as high-energy fuel. • Energy intensive can offset net energy gain from the biofuels.	• High formation of tar and ash formation. • High capital investments and maintenance cost. • Complex technology which requires precise control on operational parameters.

Combustion

During combustion, biomass is thermally degraded in the presence of air, which converts its stored chemical energy into heat and gases. The thermal energy, produced at temperatures exceeding 1073 K, is used in various industrial applications such as furnaces, steam turbines, and boilers [20]. Biomass combustion is a versatile energy source that can generate heat, power, and steam, making it suitable for small-scale operations and large industrial facilities. One of the main advantages of biomass combustion is its high fuel flexibility, which allows for using different types of biomass. However, for efficient combustion, the moisture content of the biomass needs to be optimum. Additionally, co-generation, the simultaneous production of heat and power, enhances the overall efficiency of biomass combustion plants. This method optimizes energy output by simultaneously generating heat and electricity. The net energy conversion efficiency of a biomass combustion power plant typically ranges from 20 % to 40 %, even when co-fired with coal. However, this efficiency can increase to around 50 % when using biomass integrated gasification combined with gas–steam cycles [23]. Further efficiency improvements can be achieved by co-firing biomass with coal in power plants, which results in higher energy conversion rates. Notably, this practice has led to a 93% reduction in carbon dioxide emissions when biomass is co-fired with coal [24]. This significant decrease is due to the alkaline ash produced from biomass, which captures sulphur dioxide and carbon dioxide generated during combustion. However, a significant limitation of biomass combustion is the substantial emission of greenhouse gases, particulate matter, nitrogen oxides (NOx), sulphur oxides (SOx), and heavy metals. These emissions contribute to environmental pollution, climate change, and health risks. Additionally, biomass conversion through this method poses a high risk of agglomeration, fouling, and corrosion in reactors and industrial components, increasing operational and maintenance costs. Researchers are actively working to address these challenges through pre-treatment techniques and carbon capture technologies, although these solutions often involve high operational expenses [25]. Furthermore, significant maintenance costs are associated with mitigating these limitations.

Pyrolysis

Biomass pyrolysis occurs in the absence of oxygen or air at elevated temperatures ranging from 673 to 1073 K. This method produces three main products: solid char, liquid tar, and gaseous compounds. Pyrolysis is a chemical reaction that precedes combustion and gasification [26]. The proportions of these products vary based on the type of feedstock used and the operating conditions, including temperature, heating rate, and residence time. During the pyrolysis process, moisture is evaporated at temperatures below 473 K, resulting in simultaneous drying and a reduction in the molecular weight of the biomass. At 573 K, amorphous cellulose in the biomass begins to break down into carbonyl and carboxyl radicals, as well as carbon monoxide and carbon dioxide. As the temperature increases from 573 to 773 K, crystalline cellulose decomposes, producing char, tar, and gases. Hemicellulose also breaks down during this range, yielding soluble polymers, volatile gases, char, and tar. At temperatures above 773 K, lignin and other organic materials with strong chemical bonds decompose, forming methanol, acetic acid, water, and acetone [27]. Temperature is a key parameter strongly correlated with changes in the structure and physicochemical properties of biochar during the pyrolysis process [28].

Gasification

Biomass gasification is a complex thermochemical conversion process in an exothermic partial oxidation atmosphere. This process operates under optimized conditions to achieve a high yield of synthesis gas (syngas or producer gas), which primarily consists of significant fractions of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). Gasification typically occurs at temperatures above 973 K, in environments controlled by air, carbon dioxide, oxygen, and/or steam [29]. During the gasification process, approximately 63-75 wt% of the biomass is converted into syngas, while the remaining 25-37 wt% is transformed into carbonaceous solid residues, including char and soot particles, as well as condensable products like tars (1-10 wt%) [30, 31]. The produced syngas can be cleaned and used directly as engine fuel or processed into value-added biofuels [21]. Additionally, it can be converted into liquid biofuels via the Fischer-Tropsch process or used to generate heat or energy for power plants [32]. The key stages in biomass gasification include drying, pyrolysis, oxidation, and reduction, each involving various parallel and sequential reactions. In the drying stage, moisture from the biomass begins to evaporate at temperatures up to 423 K, releasing some organic compounds. The temperature influences the rate of moisture evaporation in this zone. As the temperature increases, the chemical bonds in carbonaceous materials such as lignin and cellulose begin to break down in an oxygen-deficient environment, releasing volatile materials that consist of complex molecules containing hydrogen, carbon, and oxygen. In the pyrolysis stage, compounds break down into smaller species at temperatures ranging from 523 to 973 K, producing gases including carbon dioxide and tar [33]. The output from this process includes tar (a liquid, sticky substance) and fixed carbon, known as biochar. In addition to the gaseous products undergoing oxidation during the oxidation stage, part of the biomass reacts with oxygen. This reaction generates heat and produces carbon monoxide (CO) and carbon dioxide (CO_2). Large and complex molecules, such as tar, break down into lighter gases through exothermic chemical reactions. The gasification medium interacts with the products produced during pyrolysis, generating the heat necessary for endothermic reactions. In the final reduction stage, the remaining char reacts with the hot gases, producing synthesis gas (syngas) that is rich in carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). The temperature during this reduction stage ranges from 973 to 1273 K. This process involves gas-solid (heterogeneous) and gas-phase (homogeneous) reactions. The following equation summarizes the chemical reactions during biomass gasification [33].

Oxidation zone

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -406 kJ\ mol^{-1} \qquad [1.1]$$

$$2C + O_2 \rightarrow 2CO \qquad \Delta H = -123\ kJ\ mol^{-1} \qquad [1.2]$$

Reduction zone

Water-gas reaction

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 131.4\ kJ\ mol^{-1} \qquad [1.3]$$

Boudouard reaction

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H = 172.6\ kJ\ mol^{-1} \qquad [1.4]$$

Water-gas shift reaction

$$CO_2 + H_2 \leftrightarrow CO + 2H_2O \qquad \Delta H = 42\ kJ\ mol^{-1} \qquad [1.5]$$

Methane formation reaction

$$C + 2H_2 \leftrightarrow CH_4 \qquad \Delta H = -75\ kJ\ mol^{-1} \qquad [1.6]$$

The hot gas stream exiting the gasifier contains the primary components of gas products and various impurities. These include tar, condensable aromatic and polyaromatic hydrocarbons, and heavier hydrocarbons. Additionally, the stream features vapour-phase products such as nitrogen compounds (NH_3 and HCN), halogen compounds (HCl and Cl), alkalis, and heavy metals. The presence of these compounds can result in equipment blockages, reduced system efficiency, and higher maintenance costs. Acid gases can cause corrosion in both the gasifier and downstream processing equipment. Tar compounds tend to condense outside the gasifier at temperatures between 523 and 573 K. During biomass gasification, a significant amount of char, a solid residue, is produced [34]. This process is associated with high maintenance costs and substantial expenses related to tar removal. Biomass gasification is complex and requires good control of various operational parameters to generate syngas that meet specific standards. To achieve the desired quality and yield of gas, optimising factors such as heating rate, temperature, pressure, gasification medium, oxidizer-fuel ratio and feedstock composition is essential. The intricate nature of the process, along with the need for a specialized gasifier system and continuous monitoring, further contributes to the overall complexity and cost of operation.

1.2 Petroleum coke

According to the World Energy Outlook Report, the International Energy Agency (IEA) forecasts that global refining capacity will increase from 102.7 million barrels per day (b/d) to 106 million b/d by the end of this decade [2]. Refining a single barrel of crude oil is estimated to produce approximately 20 kg of petroleum coke (petcoke) as a byproduct [35]. The rising processing of heavy crude oils in refineries has renewed interest in the delayed coking process, resulting in a significant increase in petcoke production. Petcoke is a carbon-rich by-product that resulted from processing heavy residues with high sulphur, metal content. It is primarily produced to maximize distillate yields. The disposal and utilization of petroleum coke (petcoke) present significant challenges due to its high sulphur content (5-7 wt%) and vanadium content (approximately 500 ppm). Delayed coking is essential for converting heavy residues into lighter products, making it crucial to find economically viable and environmentally safe methods to utilize petcoke. The rising crude oil prices highlight the need to extract maximum value from every refinery stream [36, 37]. Petcoke has a high heating value, ranging from 30.3 to 34.9 MJ kg^{-1}, greater than coal (24.5 - 30.3 MJ kg^{-1}). Its low ash content, high carbon content, and affordability make it an attractive fuel option. However, petcoke also has significant drawbacks, including low reactivity and high levels of sulphur and vanadium. The utilization of petcoke, like other fossil fuels, generates higher amount of greenhouse gas (GHG) emissions, which limits its widespread use for thermal power generation. Consequently, the utilization of petcoke needs to be pursued in an economically viable and environmentally safe manner.

1.3 Literature review

This study aims to investigate and analyse the properties of Bambusa *tulda* (B. *tulda*) and petroleum coke (petcoke) and their potential for blending in gasification processes. The performance and sustainability of gasification depend on various operational parameters. Therefore, this research systematically examines these parameters to optimize the blending ratio of B. *tulda* with petcoke. The literature review focuses on the following topics:

a) Kinetic study of biomass and petcoke pyrolysis under N_2 and CO_2 atmospheres: This section report on thermal degradation, the effects of heating rates, and the determination of kinetic triplets, including activation energy, pre-exponential factors, and kinetic models.

b) Single particle combustion: This section covers the flame behavior, the influence of blending ratios on mass degradation and combustion times, and the effect of the surface area-to-volume ratio on combustion behavior.

c) Gasification of carbonaceous materials: This section discusses the impact of operational parameters on the gasification of carbonaceous materials. It focuses on the effects of catalyst loading, temperature, and pressure during CO_2 gasification and the influence of blending different raw materials.

1.3.1 Thermal behaviour and kinetic study

Engineers and researchers need to identify the key factors that influence the effectiveness and yield of biomass conversion processes by gaining insights into the kinetics of these processes. This understanding is essential for designing efficient gasification and pyrolysis reactors [38, 39]. The most straightforward and widely used method for studying the kinetics of pyrolysis is thermo-gravimetric analysis (TGA). TGA is an effective technique for examining the solid-phase degradation of biomass, as it is relatively easy to perform and provides significant information on the thermal behaviour of the fuel sample [40, 41]. Investigating the kinetic behaviour of lignocellulosic biomass enhances the understanding of its thermal degradation and the kinetic reactions involved during pyrolysis [42]. Furthermore, it provides to develop more efficient thermochemical process-based reactors. Thermo-gravimetric analysis (TGA) can be conducted using two methods: (a) isothermal and (b) non-isothermal processes. Non-isothermal processes typically allow for better control of temperature and heating rate, leading to more accurate estimations of kinetic parameters than isothermal methods. Therefore, this study utilizes a non-isothermal process due to its accuracy and efficiency in identifying kinetic parameters. Kinetic parameters derived from a non-isothermal process can be estimated using various methods, which are primarily classified into model-fitting and model-free (Iso-conversional) techniques. The Iso-conversional method is a widely used approach for determining the kinetic parameters of reactions and offers several advantages over other methods. One of the main benefits of the Iso-conversional method is that it eliminates the difficulties of making initial assumptions about the form and rate order of the kinetic equation. This makes it suitable for analysing reactions where the reaction mechanism is not defined, or for which the reaction mechanism is complex. Another advantage of the Iso-conversional approach is its ability to reduce systematic errors when determining Arrhenius parameters. This is because the Iso-conversional method uses a constant conversion level, which can help to reduce the errors that can arise from using different conversion levels in the analysis [42, 43]. Iso-conversional methods can incorporate differential or integral approaches to evaluate data obtained from TGA analysis. TGA is generally conducted using a non-isothermal Iso-conversional method with a consistent heating rate [44, 45].

Ounas *et al.* (2011) studied the thermal degradation and kinetics of olive residue and sugarcane bagasse using non-isothermal thermogravimetric analysis (TGA) under a nitrogen atmosphere [39]. The findings indicate that pyrolysis occurs in three stages: moisture evaporation, primary devolatilization, and a slight continuous devolatilization phase. The initial mass loss of 4-5% is attributed to moisture removal at temperatures below 430 K. Significant weight loss, caused by the degradation of lignocellulosic components, occurred between 473 K and 673 K. The decomposition sequence is identified as starting with lignin, followed by hemicellulose (433-633 K) and cellulose (513-663 K). The final weight loss was measured at 76.6 % for olive residue and 83.3 % for sugarcane bagasse. The derivative mass loss (DTG) curves represented the rate of mass degradation at various heating rates ranging from 2 to 50 K min^{-1}. As the heating rate increased, the maximum pyrolysis rate and the temperature at which this peak occurred also increased. This behaviour can be attributed to the complex structure of biomass, which consists of components that decompose at specific temperature ranges during pyrolysis, resulting in distinct peaks in the curves. Mishra *et al.* (2018) found that during the pyrolysis process, the second stage of thermal decomposition of lignocellulosic components, such as hemicellulose, cellulose, and lignin involves two simultaneous exothermic processes after the initial drying stage [46]. These processes result in the release of a higher quantity of volatile matter. White *et al.* (2011) observed that cellulose degradation occurs in two phases [47]. In the first phase, the bonds break into monomers at a lower temperature, producing gases like CO, CO_2, and carbonaceous compounds. In the second phase, at a higher temperature, integration of bonds leads to the formation of liquid products. Lignin decomposition occurs in the third stage, which progresses significantly slower over a wide temperature range. This slower rate is likely due to its association with phenolic hydroxyl groups. The heating rate is a critical parameter during the devolatilization of fuel particles. Analysing the thermal decomposition process provides insight into the mechanisms governing thermochemical conversion under different heating rates. Increasing the heating rate shifts the reaction zone to higher temperatures, leading to a greater yield of volatile matterfor biomass. Conversely, a lower heating rate allows volatile compounds to remain in the reactor for longer period. This extended residence time enables thermal gradients to penetrate the inner core of the particles, promoting secondary reactions such as cracking, re-polymerization, and re-condensation, which result in increased char formation [46, 48].

Lu *et al.* (2022) studied the pyrolysis kinetics and thermal behavior of cornstalk, noting that thermal hysteresis occurs across the biomass cross-section due to its poor thermal conductivity [49]. The pyrolysis process and the associated degradation reaction kinetics are complex, which can create resistance at low heating rates. However, this resistance can be overcome at high heating rates, leading to enhanced mass and heat transfer and, ultimately, higher conversion rates. The Devolatilization Index is used to evaluate the effect of heating rate on volatile release during pyrolysis. A higher heating rate corresponds to a higher Devolatilization Index. Additionally, the Devolatilization Index measures the efficiency of a thermal conversion process, with higher Devolatilization Index values indicating a faster release of volatile matter [50]. These findings are consistent with Chen *et al.* (2017) and El-Sayed *et al.* (2023) [44, 51]. Lee *et al.* (2021) studied the kinetic behavior of torrefied Kenaf in a Thermogravimetric Analysis (TGA) under various heating rates and atmospheres [52]. The initial degradation phase is primarily due to the thermal decomposition of hemicellulose and cellulose, while the subsequent phase is associated with lignin degradation. At temperature below 900 K, the mass loss behaviour of the samples in the CO_2 atmosphere is similar to that in the N_2 atmosphere. However, above 900 K no further mass loss occurs in the N_2 atmosphere, whereas additional mass loss is observed in the CO_2 atmosphere, suggesting the presence of secondary reaction in the remaining char. Furthermore, the heating rate significantly influenced the behavior of the TG (thermogravimetric) and DTG (differential thermogravimetric) curves and the maximum decomposition rate. At higher heating rates, the peak shifted to higher temperatures due to shorter reaction times and thermal delays. This thermal delay, coupled with heat resistance, creates thermal hysteresis, which leads to an increased maximum mass loss rate during decomposition and a decreased conversion rate. As the heating rate increased, the temperature difference between the sample's surface and interior increased, hindering the internal decomposition process due to insufficient energy transfer. From the DTG curve, the Devolatilization Index (D_i) is determined to investigate the behaviour of volatile matter release corresponding to different heating rates. For both atmospheres, the thermal parameters, such as peak temperature, maximum weight loss, and D_i increased as the heating rate increased due to thermal hysteresis. In addition, the devolatilization performance under CO_2 atmosphere lowered at higher heating rates compared to N_2 atmosphere. The analysis showed that the CO_2 atmosphere resulted in lower maximum mass loss rate, a delayed initiation temperature and reduced D_i across different heating rates, indication that the presence of $\mathrm{CO_2}$ reduced the reactivity.

The relationship between heating rates and kinetic parameters such as activation energy, pre-exponential factors, and reaction models is derived from the Arrhenius equation. The combination of these three kinetic parameters is called the kinetic triplet [53, 54]. Muigai *et al.* (2021) conducted a comprehensive kinetic analysis using isoconversional methods, including Flynn–Wall–Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Friedman, with biomass materials such as *Eichhornia crassipes* (water hyacinth, WH), *Thevetia peruviana* (yellow oleander, TP), and *Saccharum officinarum* (sugarcane bagasse, SCB) [55]. The variation in activation energy with respect to conversion (α) indicates that multiple simultaneous reactions occur during pyrolysis. These changes can be attributed to the thermal degradation of different structural components of biomass, including hemicellulose,

cellulose, and lignin. The total activation energy recorded for WH, TP, and SCB is 187.74 – 329.71 kJ mol^{-1}, 182.28 – 389.24 kJ mol^{-1}, and 191.33 – 293.49 kJ mol^{-1}, respectively. The reaction model for the biomass samples is analysed using the Criado master plot. During pyrolysis, each biomass underwent two consecutive reactions. Both wood chips (WH) and tea powder (TP) followed a three-dimensional heat diffusion (D3) mechanism in the conversion range of $\alpha \leq 0.6$, transitioning to a third-order reaction (F3) at $\alpha \geq 0.6$. In contrast, sugarcane bagasse (SCB) showed a stronger correlation with a two-dimensional diffusion (D2) mechanism within the ≤ 0.6 range, and then transitioned to both second-order (F2) and third-order reactions (F3) at $\alpha \geq 0.6$. The correlation with the D3 mechanism is associated with the thermal degradation of cellulose and hemicellulose at low temperatures, where degradation initiates at random points within the sample and propagates through hot gas diffusion. The transition to the ordered reaction models F2 and F3 likely signifies further degradation of cellulose. Kissinger's equation was employed to determine the pre-exponential factor (A), which ranged from 2.88×10^{18} to 4.40×10^{33} s^{-1} for WH, 3.4×10^{18} to 1.47×10^{27} s^{-1} for SCB, and 2.88×10^{18} to 4.40×10^{33} s^{-1} for TP. The wide variation and high values of the pre-exponential factor reflect the reactions' complexity and indicate the biomass's significant reactivity during pyrolysis [55].

Rammohan *et al.* (2022) utilized different isoconversional methods to study the kinetics of *Delonix regia* (DR) biomass through TGA experiments and also investigate kinetic triplets [56]. The study determined the apparent activation energy of the biomass sample using various methods: Differential Friedman, Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), Starink (STK), and Distributed Activation Energy (DAE). The activation energy is found to be in the range of 202.34–205.89 kJ mol^{-1}. The experimental data for conversions from 0.1 to 0.7 exhibited high correlation coefficients ($R^2 > 0.98$), indicating a good fit. In contrast, the conversion at 0.8 displayed deviations, likely due to the formation of secondary reactions that generate significant amounts of solid residues (char and ash) during pyrolysis.

The wide variation in activation energy and pre-exponential factors with conversion is attributed to the thermal degradation of the primary components of the biomass sample. Moreover, increasing the heating rate significantly affects the activation energy and pre-exponential factors, as a higher rate enhances molecular collision rates, thereby accelerating the pyrolysis of DR biomass. Criado's master plot is applied to confirm that the pyrolysis of the biomass sample follows a multi-step reaction mechanism. The experimental data exhibited a second-order reaction (F2) trend for conversions from 0.1 to 0.2, followed by a first-order reaction (F1) and two-dimensional diffusion (D2) for conversions from 0.3 to 0.4. As the conversion progressed to 0.6 to 0.7, the mechanism shifted towards volume contraction (R3) and second-order reaction (F2), ultimately reaching a higher-order reaction (>F5) up to 0.8 conversions. Thus, the master plot analysis reveals that the pyrolysis of the biomass sample involves a multi-step reaction mechanism [56].

Patidar *et al.* (2022) observed fluctuations in the reaction parameters during the kinetic study of the mustard stalk (MS) pyrolysis using the FWO and KAS methods [48]. These fluctuations can be attributed to the complex multi-step reactions (including competitive, parallel, and continuous reactions) that occur during pyrolysis. The increase in reaction parameters from 0.1 to 0.6 is likely due to the increased endothermicity associated with the process. However, a decline trend is observed when the conversion ranges from 0.7 to 0.9, which can be due to the exothermic reactions occurring during this stage of the biomass sample pyrolysis. Specifically, the activation energy for the FWO method increases from 49.892 kJ mol^{-1} to 169.27 kJ mol^{-1}. In contrast, the KAS method increases from 41.444 kJ mol^{-1} to 168.26 kJ mol^{-1} as the conversion factor changes from 0.1 to 0.6, after which it begins to decline. The higher values of the pre-exponential factor (A), ranging from 2.4×10^5 to 1.19×10^{17} s^{-1} for the FWO method and from 3.30×10^4 to 9.53×10^{16} s^{-1} for the KAS method, indicate a shift toward more complex reactions. This reflects the complexity of thermal degradation reactions, as the values of the pre-exponential factor vary significantly compared to the critical value of around 10^9 s^{-1}. The solid-state kinetic model's differential plot and the combined master plot for conversions ranging from 0.1 to 0.9 revealed that the differential master plot did not align well with any existing model, indicating the presence of multiple parallel reactions during pyrolysis. However, the combined master plot effectively captured the reaction mechanism. The z-master plot suggests that the thermal decomposition of the biomass sample involves multiple reactions, with conversions from 0.1 to 0.9 closely matching a multi-diffusion model [48].

The use of carbon dioxide as a pyrolysis medium has gained attention for several reasons, particularly its ability to enhance reactivity and conversion rates and its potential for recycling and utilization. Integrating CO_2 recycling within the pyrolysis process is considered environmentally friendly and energy-efficient, as it does not require external energy sources and produces no additional CO_2 emissions due to complete recirculation within the system. Additionally, the presence of CO_2 results in varying degrees of carbonization, which can alter the physicochemical properties of biochar. Many researchers have utilized Thermogravimetric Analysis (TGA) to study the interaction between biomass samples and CO_2 during the thermal degradation that occurs in the pyrolysis process [40]. Lee *et al.* (2017a) studied the effect of introducing CO_2 as a pyrolysis medium on the thermal degradation of peat, comparing it to the use of N_2 through thermogravimetric analysis (TGA) [57]. At a temperature of 903 K, no significant differences are observed in the physical characteristics, such as the onset and end temperatures of thermal degradation of peat. Consequently, both the TGA and derivative thermogravimetry (DTG) curves in N_2 and CO_2 atmospheres are nearly identical. However, as indicated by the DTG curve, at temperatures above 903 K, the thermal degradation rates in CO_2 are higher than in N_2 atmosphere. This trend shifted slightly at temperatures above 1001 K, reflecting the initiation of the Boudouard reaction, which reached its maximum reaction rate at 1117 K. This observation aligns with the Boudouard reaction, which is thermodynamically favourable at temperatures above 993

K. It is important to note that the mass loss above 1001 K under CO_2 conditions cannot be solely attributed to the Boudouard reaction, as continuous mass degradation occurred above 1001 K under N_2 conditions. Further investigation suggested that the influence of CO_2 on thermal degradation during peat pyrolysis follows a hierarchical process. This process begins with homogeneous reactions (i.e., reactions between CO_2 and volatile organic compounds released during peat pyrolysis). It progresses to heterogeneous reactions (i.e., reactions between CO_2 and the surface of the peat) [57]. In another study conducted by Lee *et al.* (2017b) confirmed that there is a notable difference in thermal degradation when nitrogen (N_2) and carbon dioxide (CO_2) are used as pyrolysis mediums [58]. Using CO_2 during the pyrolysis of agricultural waste significantly affects all the pyrolytic products by creating favourable conditions for the thermal cracking of volatile organic compounds, which enhances syngas production. These experimental findings suggest CO_2 could serve as initial feedstock for waste management, energy recovery, and biochar production. Furthermore, this CO_2-based approach may have broader applications in energy production and air pollution control [58].

Singh *et al.* (2022) conducted co-pyrolysis experiments using a thermogravimetric analyser to explore the co-pyrolysis potential and kinetic characteristics of banana leaf biomass (BLB) and petroleum coke (PC) [59]. Blending PC with BLB increased the heating value to 23.45 MJ kg^{-1} compared to using BLB alone. BLB is characterized by a high ash content of 7.26 %, which presents challenges such as lower heat generation, reduced energy conversion efficiency, and higher waste generation. However, when blended with PC, the ash content was reduced to 3.23 % due to a synergistic interaction, highlighting the viability of the biomass and petcoke blend. Further evidence of the synergistic interaction between BLB and PC can be seen in their activation energies. BLB exhibited activation energy of 195.87 kJ mol^{-1}, while PC had higher activation energy of 258.97 kJ mol^{-1}. Upon co-processing, the activation energy decreased to 158.04 kJ mol^{-1}, which reflects a 32-37% reduction and indicate a favourable synergistic interaction between the fuel samples. Thermodynamic analysis also confirms the production of stable and energy-efficient products, supporting the effective utilization of PC when co-pyrolyzed with BLB. Additionally, unlike PC, BLB contains a negligible amount of sulphur, as indicated by ultimate analysis. This difference suggests significantly lower emissions of sulphur-based gases when using the PC and BLB blend compared to PC alone. Controlled co-pyrolysis provides a pathway to unlock the true potential of petcoke as an energy source, with emissions lower than those from traditional burning methods [59]. Wang *et al.* (2018) found that the high content of alkali and alkaline earth metals content in biochar ash plays a significant role in accelerating the gasification process [60]. As biochar is consumed during gasification, its ash gradually precipitates and comes into contact with petcoke, which enhances the reaction. This acceleration is attributed to the catalysis involving carbon and water in the petcoke. Furthermore, in addition to the synergistic effect of the elevated potassium content, the increased specific surface area and carbonaceous structure of biochar also enhance its gasification reactivity.

1.3.2 Single particle combustion

Riaza *et al.* (2014) investigated the combustion characteristics of biomass, focusing specifically on the volatile combustion phase [61]. Upon ignition, the release and combustion of volatile components in the biomass lead to a flame that gradually increases in size and brightness, eventually enveloping the entire particle. This volatile ignition occurs at temperatures significantly lower than the wall of the furnace. Following the volatile phase, the char combustion phase begins, which exhibits reduced luminosity. In a subsequent study by Riaza *et al.* (2020) combustion experiments are conducted using various types of biomass to compare burnout times and changes in particle size and shape [62]. The results indicated that all biomass samples exhibited a similar pattern of homogeneous ignition with two distinct sequential stages: the volatile flame and char combustion. However, the duration of the volatile flame stage is influenced by the biomass composition, volatile matter content, and pyrolysis kinetics. Notably, olive residue and black pellets demonstrated a shorter period of volatile ignition but had longer char combustion and overall burnout duration. This is attributed to their lower volatile matter content and higher fixed carbon composition than pine, eucalyptus, and willow. The temperature reached during the char combustion stage is significantly higher than during the volatile combustion stage. This elevated temperature partially melts the particles, causing them to become more rounded due to surface tension. Riaza *et al.* (2017) investigated the ignition and combustion behavior of bituminous coal and biomass by measuring the duration of various combustion stages [63]. The findings revealed two distinct stages of combustion: volatile combustion and char combustion. During the volatile combustion stage of biomass, a large, smooth flame envelops the entire surface, resulting in a prolonged volatile combustion time, which accounts for 40 to 50 % of the total burnout time. In contrast, coal exhibits more homogeneous ignition and has significantly shorter volatile combustion duration, taking only 10 to 20 % of the total burnout time due to its lower volatile matter content. The density and porosity of the raw materials play a crucial role in releasing volatile matter from the particles. Biomass, which has a low density and high porosity, releases volatile substances smoothly, leading to a progressively increasing flame. On the other hand, high-density and highly porous coal emits volatiles in a jet-like manner. Furthermore, biomass can achieve a burnout time comparable to coal due to its high volatile matter content and reactivity, even with larger particle sizes [63].

A study conducted by Panahi *et al.* (2019) aimed to evaluate the burning rates of biomass char and their structural characteristics by analysing the combustion behavior of small biomass fuel particles exposed to elevated temperatures (greater than 1000 K) at high heating rates [64]. These conditions closely resemble those found in pulverized fuel utility boilers used for power generation. The study involved selecting individual particles of known size, shape, aspect ratio, and mass from five different types of raw and torrefied biomass. These particles are introduced into a transparent, electrically heated drop-tube furnace, which underwent rapid heating, ignition, and combustion in the air. The temperature-time profiles of the individual particles are recorded using pyrometry to determine their combustion rates. It is observed that the combustion behavior of raw and torrefied biomass occurs in two distinct phases: volatile matter combustion and char oxidation. Capturing the volatile flame temperature of raw biomass has been challenging due to its low luminosity, which results from devolatilization products such as CO_2, CO, H_2, and light hydrocarbons. However, larger biomass particles allowed for the pyrometric detection of volatile flame temperatures, with torrefied biomass flames being hotter due to differences in pyrolysis composition. Torrefied biomass chars exhibited longer burnout times than raw biomass chars, which can be due to their higher fixed carbon content and structural properties, such as porosity and aspect ratios. The combustion duration for raw biomass is generally shorter, with chars burning at peak temperatures. Morphological analysis revealed that torrefied biomass chars are had thinner walls, while bulk density and ash content measurements highlighted significant differences between raw and torrefied biomass. These findings emphasize the influence of particle size, shape, and structure on combustion dynamics, providing critical insights for optimizing biomass combustion in industrial applications [64].

Das *et al.* (2020) conducted a study investigating the combustion characteristics and duration of various biomass and coal fuel blends through single-particle combustion experiments [65]. The research identified two distinct phases of combustion: the flaming (volatile) zone and the char combustion zone. These phases occur during the mass degradation of fuel mixtures. The study found that, as the coal content in the fuel mixture increased, mass degradation during the flaming zone decreased noticeably. This reduction can be attributed to lower volatile matter content of coal. Furthermore, the duration of combustion varied depending on the amount of coal blended into the fuel mixture, which is also influenced by the density of coal. The study utilized fuel samples with three different particle diameters to examine the effect of surface area-to-volume ratio on combustion behavior. The results indicated that decreased particle diameter increased the burning rate per unit mass. This improvement is due to the higher surface area-to-volume ratio, which enhanced the effective surface area available for combustion, ultimately resulting in a higher combustion rate [65].

Gurel *et al.* (2022) investigated the single-particle combustion of agricultural biomass and lignite coal, focusing on the influence of particle mass and thermal pre-treatment methods such as torrefaction and pyrolysis [66]. After ignition, all fuel samples displayed two-phase combustion, and the total burnout time varied depending on the fuel type and the pre-treatment process. The total time included both volatile and char combustion phases. For olive residue (OR) and almond shell (AS), volatile combustion accounted for approximately 18% of the total burnout time, while for Tunçbilek lignite (TL), it accounts only 10%. The higher hydrocarbon content in TL resulted in longer volatile combustion times when comparing particles with the same volatile matter content to those of raw and torrefied biomass fuels. Char combustion times are found to be longer for fuels that underwent slow pyrolysis, as this method produces thermally stable, carbon-rich chars, leading to extended burnout times. Fast pyrolysis increased OR and AS burnout times by approximately 13 and 10 seconds, respectively, while it had a minimal effect on TL. The resemblance in burnout times between fast pyrolyzed OR, AS chars and raw TL indicates the potential for co-firing these fuels in existing power plants. Although particle shape and aspect ratio had little impact on combustion times, the variability in biomass fuels complicates the precise determination of burnout times. This highlights the significant role that pre-treatment methods play in optimizing the combustion characteristics of different fuels [66].

Mahapatra *et al.* (2018) investigated how the properties of biomass, such as size and density, affect both flaming (volatile release) and glowing (char combustion) times during combustion [67]. Flaming time indicates the pyrolysis rate, which increases with a higher effective exposed surface area per unit volume of biomass. The study compared flaming times across various biomass samples with different physical characteristics and found that a higher surface area-to-volume ratio, associated with smaller particle diameters, led to an increased pyrolysis rate, enhanced volatile release, and faster production of pyrolysis products. Consequently, this resulted in a reduced residence time during combustion. However, this reduction significantly impacted the cracking of higher molecular weight compounds, contributing to an increased tar fraction [67].

Mack *et al.* (2023) studied the combustion behavior of individual wood particles under oxyfuel conditions relevant to grate incineration [68]. The study examined the effects of particle sizes (4 mm, 6 mm, and 8 mm) and different $O_2/CO_2/H_2O$ atmospheres. The combustion experiments are conducted at 1193 K, with varying O_2 concentrations (10–50 vol %) in O_2/CO_2, $O_2/CO_2/H_2O$, and O_2/H_2O atmospheres. This study provides valuable insights into how variations in oxygen levels and the addition of steam affect particle size, flame temperature, burnout times, and char combustion behavior. In dry oxyfuel atmospheres, both flame and char temperatures increase with higher oxygen concentrations, although this effect is less pronounced for larger particles. Char combustion durations decrease with increased oxygen concentration, and this effect is more pronounced in larger particles due to enhanced gasification. Burnout times for volatile matter remain constant for 4 mm particles but extend for larger particles; in particular, steam contributes to longer flame durations for 6 mm and 8 mm particles in low-oxygen conditions. In larger particles, intra-particle temperature gradients are more pronounced due to low thermal conductivity, negatively impacting heat transfer efficiency. In both dry and wet air combustion, larger particles take longer to convert completely compared to oxyfuel atmospheres. Transitioning to oxyfuel operation could improve throughput in grate incineration systems by reducing conversion times without increasing thermal stress [68].

Momeni *et al.* (2013) investigated the influence of particle shape and surrounding conditions on the conversion processes and combustion properties (oxidizer temperature and oxygen concentration) of single biomass particles [69]. The findings indicate that spherical particles take the longest time for conversion of similar volume or mass due to their lower surface area-to-volume ratio. In contrast, non-spherical particles allow for quicker and more complete conversion, provided sufficient residence time exists. In practical applications, the fuel particles used for co-firing in power plants typically have similar diameters but vary in length. In this context, spherical particles exhibit the highest surface area-to-volume ratio, which promotes faster and more complete burnout. On the other hand, cylindrical particles with varying lengths tend to share similar conversion characteristics due to their comparable surface area-to-volume ratios. Furthermore, increasing the oxygen concentration enhances the homogeneous combustion of volatile matter and improves char oxidation, intensifying local heat release around the particle. As a result, higher gas temperatures and oxygen concentrations are expected to benefit all stages of biomass combustion. However, the effect of oxygen concentration on char oxidation is more significant at lower temperatures. This phenomenon, known as '*thermal deactivation'*, occurs because char reactivity decreases with rising pyrolysis temperatures. At higher temperatures, the carbon structure within the char becomes more organized and graphite-like, leading to a reduction in active sites. Varunkumar *et al.* (2011) studied the combustion characteristics of wood spheres and pellet cylinders with varying densities [70]. The results indicated that the higher-density pellet cylinder exhibited a longer burn time than the lower-density wood sphere.

Research has increasingly focused on the combustion behavior of various carbonaceous materials, including biomass and coal. In a study conducted by Tripathi *et al.* (2022), the single-particle combustion of refuse-derived fuel (RDF) is examined [71]. The findings revealed that particle size significantly influences RDF combustion. Specifically, as the particle diameter increases, the heat flux to the particle decreases, resulting in a slower burning rate per unit mass. Furthermore, larger particle diameters can reduce devolatilization and increase flaming time. The ratio of glowing time to flaming time for RDF is similar to that of biomass but is four times lower than that of coal. Although the glowing time of RDF is comparable to biomass, the reasons behind this similarity differ. The extended glowing time observed in biomass is due to its higher fixed carbon content, while in RDF, it is primarily attributed to the higher ash content. The ash forms a film around the porous char, which creates resistance to char combustion and ultimately prolongs the glowing phase [71]. Kumar and Nandi (2022) investigated the combustion characteristics of coal, petcoke, biomass, and their trinary blend to identify the synergistic effects of blending on overall combustion performance [72]. The study revealed that increasing the percentage of biomass in the fuel mixture resulted in a more significant synergistic effect. Higher biomass content is also advantageous because it allows for a gradual release of energy during combustion, which helps reduce thermal damage to boiler tubes and refractory bricks. Liu *et al.* (2019) examined the characteristics of a single petcoke particle [73]. The study found that petcoke has a compact structure with no noticeable pores or cracks. However, during the gasification process, visible pores develop, and their size increases as the petcoke transforms. The gasification rate also increases with larger pore sizes, enhancing the contact area with the gasification medium. These studies aim to understand the thermal degradation and combustion characteristics of coal, petroleum coke, char, and other carbon-rich materials. The findings provide valuable insights into burning rates, ignition times, and overall combustion efficiency, which are crucial for optimizing the use of these materials in industrial applications.

1.3.3 Effect of operational parameters on co-gasification

In recent years, extensive research has focused on the co-gasification of biomass and petcoke. This research is motivated by addressing climate change and promoting sustainable energy sources. Scientists have explored how blending biomass with petcoke can effectively overcome many challenges, otherwise using these materials individually. The complementary physicochemical properties and reactivity of biomass and petcoke, along with alkali and alkaline earth metals, enhance their combined, clean, and efficient utilization. Additionally, operational parameters play a crucial role in influencing the gasification process. It is important to fine-tune factors such as temperature, pressure, gasification medium, and catalysts to optimize this conversion process. The specific impacts of these parameters will be discussed in the following sections.

Feedstock properties

The low gasification reactivity of petcoke limits its utilization. However, blending petcoke with biomass can enhance its reactivity significantly. This improvement in reactivity arises from the interaction with free radicals, as well as with volatile matter that is rich in hydrogen and oxygen. Additionally, the presence of alkali and alkaline earth metals (AAEMs) such as sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca) in biomass can further catalyse this process [74, 75]. Other factors, like the higher specific surface area and carbonaceous structure of biochar, also contribute to the increased gasification reactivity of petcoke due to a synergistic effect [60].

Temperature

Temperature plays a crucial role in regulating the syngas composition and gasification processes performance. Higher temperatures enhance endothermic reactions, increasing syngas production [76]. The chemical reactions involved are interdependent and competitive, with their rates influenced by temperature based on the as Gibbs's free energy. Consequently, the distribution of products such as char, gas, and tar is significantly affected by gasification temperatures. The Boudouard reaction becomes more prominent as the temperature increases, while the water-gas shift (WGS) reaction tends to decrease. This shift increases carbon monoxide (CO) production while the formation of carbon dioxide (CO_2) and hydrogen (H_2) declines [77]. High temperatures can negatively impact methanation reactions, reducing methane (CH_4) generation. As gasification temperatures increase, the combined content of hydrogen and methane decreases while the carbon monoxide (CO) content in the syngas increases [78]. Additionally, elevated temperatures promote the thermal cracking of tar through heat absorption reactions, which helps to reduce tar formation. Tar is a complex mixture of organic compounds produced during the devolatilization stage, ranging from low-molecular-weight hydrocarbons to high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) with high boiling points. Higher gasification temperatures decrease tar yields by initiating secondary reactions that thermally break down tar compounds into lighter gases such as hydrogen, carbon monoxide, and methane [79]. Understanding these temperature-dependent processes is essential for optimizing gasification conditions to enhance syngas quality and minimize undesirable by-products. This knowledge enables gasification to become a more efficient and environmentally friendly technology for energy generation.

Pressure

The reactor pressure and the partial pressure of the gasification medium play a crucial role in determining gasification performance and the quality of syngas produced. Operating at high pressure increases the density of the reacting gases, enhances reaction rates and improves the overall efficiency of the gasification process [32]. Also, higher pressure during gasification improves heat transfer within the bed section, increasing conversion rates and supporting various gaseous reactions, including tar reforming [80]. In industrial applications, high pressure is typically employed to produce syngas with a higher calorific value. Despite the significant advantages of using pressure in gasification, there are also considerable drawbacks. The complexity of pressurized gasification systems can lead to operational challenges, difficulties in fabrication and control, and potential instability. These issues may cause system failures and high operational and maintenance costs [81].

Gasification medium

The volume percentage and higher heating value of syngas depend on the gasification medium used in the gasification process. Common gasification mediums include air, oxygen, carbon dioxide, steam, and various mixtures. Air is the most commonly used gasification medium due to its availability and low cost. However, the nitrogen content in air reduces the heating value of the resulting syngas. In contrast, using oxygen leads to higher reaction temperatures, faster reaction rates, and higher heating values than air. Steam gasification typically produces syngas with heating values ranging from 10 to 18 MJ/Nm^3, resulting in higher hydrogen yields than air gasification. Research has indicated that combining steam with air or oxygen yields a higher concentration of combustible gas components and enhanced calorific values [76]. Using carbon dioxide as a gasification medium generates syngas with properties similar to those produced by a steam/air mixture. A significant advantage of using CO_2 in gasification is that it supports CO_2 recycling, reduces emissions, and contributes to climate change mitigation efforts [82].

Catalyst

A catalyst is introduced during the gasification process to accelerate the rate of gasification reactions without undergoing any chemical change. It optimizes the process by allowing it to proceed along a low-energy pathway [83]. This optimization can occur with or without the removal of inherent elements present in the carbonaceous material. The catalyst enhances the gasification process reactivity and effectively contributes to catalytic tar cracking by lowering the activation energy. Common catalysts used in gasification include alkali metal or metal oxide catalysts, carbon-based catalysts, and transition metal-based catalysts, such as those containing nickel, platinum, zirconium, rhodium, ruthenium, and iron. Molten alkali carbonate (MAC) salts, including potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and lithium carbonate (Li_2CO_3), are frequently used in catalytic gasification with air, carbon dioxide, or steam agents. In addition, materials such as ZSM-5 zeolite, olivine, and cement can be employed depending on the production method [84, 85]. Numerous studies have explored the role of molten alkali carbonate (MAC) salts, such as K_2CO_3, Na_2CO_3, and Li_2CO_3, as catalysts in the thermochemical conversion of carbonaceous materials [86-88]. A preliminary literature review has focused on the catalytic effects of MAC salts when carbon dioxide is used as the gasifying medium. The stability of metal alkali carbonate (MAC) salts at high temperatures and their high heat capacity make them promising candidates for gasification processes. Potassium carbonate (K_2CO_3) is particularly favored among these salts due to its effective catalytic properties. The gasification process using MAC salts involves the melting of the alkali carbonate catalyst and its subsequent absorption onto the carbon surface [89-91]. Mckee *et al.* (1982) have contributed significantly on understanding of the gasification mechanism of K_2CO_3 when carbon dioxide (CO_2) is used as the gasifying medium [92]. At high gasification temperatures, K_2CO_3 melts and forms a thin molten film within the pores of the char. This film facilitates oxygen transfer between the char and CO_2, directly linking the catalyst and the carbon. Potassium undergoes a redox cycle, an oxygen transfer process that alternately reduces and oxidizes, as detailed in equations 1.7- 1.9 for CO_2 gasification [93]. The catalyst extracts oxygen from the gasifying agent (in this case, CO_2) and delivers it to the carbon surface, producing carbon monoxide (CO). Fig. 1.4 illustrates the schematic representation of the CO_2 gasification pathway using K_2CO_3.

$$K_2CO_3 + C \leftrightarrow 2K + CO + CO_2 \qquad [1.7]$$

$$2K + CO_2 \rightarrow K_2O + CO \qquad [1.8]$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \qquad [1.9]$$

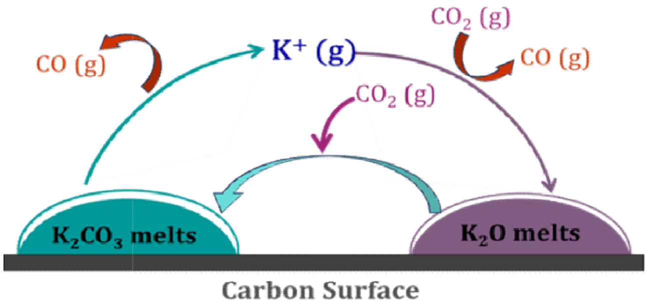

Fig. 1.4 Illustration of CO_2 gasification pathway influenced by K_2CO_3 catalyst

Safar *et al.* (2019) investigated the catalytic effects of potassium during the thermochemical conversion of biomass [94]. The study found that potassium is a highly effective and durable catalyst for char gasification. The study showed that biomass treated with K_2CO_3 had increased pyrolysis reactivity and reduced the ignition and burnout temperatures compared to untreated biomass. Nzihou *et al.* (2013) observed that adding K_2CO_3 and Na_2CO_3 to biomass before pyrolysis can break down its regular cellular structure, thereby enhancing the reaction rate of the resulting char during gasification [95]. Zhou *et al.* (2018) studied the impact of K_2CO_3-loaded sawdust in thermogravimetric and pyrolysis experiments [96]. The kinetic analysis revealed that catalyst-loaded sawdust significantly reduced activation energy at lower temperatures and altered the pyrolysis pathway. Additionally, using a potassium catalyst during gasification effectively reduces and suppresses tar formation, comprising various organic compounds. Elliot *et al.* (1986) examined the effect of K_2CO_3 on tar [97]. The study found that the concentrations of heavier polycyclic aromatic hydrocarbons (PAHs) and phenolic tar components decreased by a factor of 5 to 10. This reduction may occur due to the inhibition of tar formation or the catalysis of its decomposition. Similarly, Bach-Oller *et al.* (2019) investigated the influence of K_2CO_3 on tar reduction and found that potassium inhibited the conversion of lighter aromatics into heavier PAH clusters [98]. This process ultimately reduces the formation of undesirable products such as C_2 hydrocarbons, heavy tar, and soot. Optimizing operational parameters can significantly enhance the efficiency of co-gasifying biomass and petcoke. Researchers have explored these parameters to identify the optimum conditions for maximizing gasification reactivity and syngas quality while minimizing operational costs and environmental impacts.

Co-gasification effectively converts biomass and petroleum coke (petcoke) into high-quality alternative energy sources. Petcoke is known for its aromatic nature and exhibits a heavy aromatic-to-aliphatic ratio, making it a less reactive carbonaceous material. Aromatic carbons are less reactive than aliphatic carbons [77]. The low gasification reactivity of petcoke significantly limits its industrial applications. In contrast, the aliphatic carbon species in biomass possess relatively weaker bonds than the stronger, heat-resistant aromatic compounds in petcoke. This complementary characteristic of biomass and petcoke enhances their reactivity during co-gasification [37]. Furthermore, biomass contains a high amount of volatile matter, allowing it to devolatilize rapidly when co-gasified with petcoke. The process occurs through the thermal cracking of the weakest covalent bonds present in the organic matter of biomass, which rapidly generates a multitude of free radicals. These free radicals can react with the organic matter of the biomass and the petroleum coke (petcoke), facilitating decomposition and gasification reactions within the petcoke. Additionally, the hydrocarbon-rich lightweight molecules produced from the devolatilization of biomass and the cracking of volatiles may interact with the volatiles from petcoke. This reaction helps to prevent recombination and the formation of less reactive, secondary char [99]. Furthermore, biomass ash contains alkaline and alkaline earth metals (AAEMs), which act as natural catalysts. These AAEMs, including calcium, potassium, magnesium, and sodium, participate in cross-linking reactions with oxygen-containing functional groups, disrupting the microcrystalline structure of char. This process allows potassium to alter the carbon structure of petroleum coke (petcoke), facilitating its conversion [100]. Moreover, sodium and potassium react with carbon monoxide and carbon dioxide during gasification to form carbonates, which can help reduce emissions in the resulting product gas. The rapid diffusion of these elements through the carbon matrix creates micropores and mesopores, thereby increasing reaction rates. The presence of sodium can also enhance hydrogen generation by accelerating the water-gas shift reaction and aiding in the cracking of tar. High temperatures (1173 K and above) significantly boost the catalytic effect of potassium [37]. These interactions between biomass and petcoke, driven by volatile materials and alkali and alkaline earth metals (AAEMs), promote the gasification process and are referred to as the synergistic effect. The potential benefits of converting petcoke with biomass contribute in the following ways:

- *Sustainable energy source:* Sustainability can be achieved by partially replacing refinery byproducts with renewable raw materials.
- *Conversion efficiency:* The high reactivity of biomass compensates for the low reactivity of petroleum coke, leading to improved thermal conversion efficiency.
- *Synergistic effect:* The alkali and alkaline earth metals (AAEMs) in biomass and petroleum coke create a synergistic effect that optimizes the thermal cracking of

higher hydrocarbons. This synergy minimizes fouling, agglomeration, and equipment corrosion, ultimately enhancing overall performance.

- *Emission and waste reduction:* Combining biomass with petroleum coke reduces sulphur emissions commonly linked to petcoke while decreasing waste from the forestry, agriculture, and oil sectors, thereby fostering a circular economy.

1.4 Research motivation

Biomass and petroleum coke have different physical and chemical properties, which lead to varying behaviours during thermochemical conversion. Biomass is widely recognized as a renewable resource essential for the transition to clean energy. However, its commercial application faces challenges, including supply chain issues and inherently low energy density. Furthermore, the low reactivity and high CO_2 emission of petcoke can compliment the conversion process. Blending biomass with petroleum coke for thermochemical conversion to address these challenges presents a promising approach to generating alternative fuels. The characteristics of both the feedstock and the blended fuel samples play a crucial role in downstream processing. Therefore, a comprehensive understanding and optimization of the thermochemical conversion process are essential for designing and operating future industrial production systems. This work investigated the thermochemical conversion of biomass and petroleum coke based on a literature survey and identifies areas for further research. The primary objectives of this study are:

a) Experimental and kinetic analysis of Bambusa *tulda* and petcoke pyrolysis in carbon dioxide and nitrogen atmosphere.

b) Experimental study on combustion characteristics of Bambusa *tulda* and petcoke at varying blending ratios.

c) Effect of operational parameters and petroleum coke blending on the recycling of CO_2 during fixed-bed gasification of bamboo char.

Biomass and petroleum coke samples are collected from Assam, Northeast India. The feedstock samples underwent physicochemical characterization, including proximate and ultimate analyses and calorific value determination before starting the experimental work. Single particle combustion experiments examined how various process parameters, such as particle size, density, and blending ratios affect flame behavior, mass degradation, and ignition mass flux. The understanding of these factors is crucial, as each stage of mass degradation during the combustion of carbonaceous fuels occurs over a specific time scale influenced by the parameters mentioned. It is important to note that combustion times can vary depending on the fuel type, the size of the fuel samples, and the characteristics of the combustion system. A comprehensive understanding of combustion time is essential for various applications, including optimizing the combustion process, improving efficiency, and reducing emissions. It is crucial to determine three key factors: activation energy (Ea), the pre-exponential factor (A), and the kinetic model $f(\alpha)$ to understand the kinetics of pyrolysis, This study primarily employs thermo-gravimetric analysis (TGA), a technique that provides insights into solid-phase degradation, chemical reaction rates, and the mechanisms involved in pyrolysis. By comprehending these mechanisms, it becomes possible to control reactions in industrial settings, improve process design, and optimize product yield. Most literature focuses on using nitrogen (N_2) as a gas agent to investigate the kinetic mechanisms, reactivity, and structural properties of biomass and petroleum coke (petcoke). However, there is limited research on N_2 and CO_2 effects on the pyrolysis of biomass and petcoke from Northeast India, mainly using thermogravimetric analysis (TGA) and fixed-bed pyrolysis systems. The role of CO_2 in biomass degradation is complex and influenced by various factors, including the type of feedstock, reactor design, and process parameters. While some studies suggest that CO_2 can facilitate biomass degradation, others report minimal effects on the process. Therefore, the understanding that CO_2 enhances product quality lacks precision without a thorough comparative analysis. Gasification is a thermochemical conversion process that transforms carbonaceous materials such as biomass, coal, and petroleum coke (petcoke) into a mixture of combustible and non-combustible gases. The main product of this process is synthesis gas, along with other valuable fuels and chemicals. Various operational parameters, including the gasification medium, catalyst, pressure, temperature, heating rate, and residence time, needs to be optimized to achieve efficient gasification. Utilizing CO_2 as a gasification medium offers several advantages, as it serves both as a carbon source and an oxidant in multiple chemical reactions, enhancing the conversion of carbon-based materials. Furthermore, using CO_2 can help reduce greenhouse gas emissions and increase carbon monoxide production through the Boudouard reaction. The study also investigates the influence of molten alkali carbonate (MAC) and its catalytic effects when used with CO_2 as the gasification medium. The stability and high heat capacity of MAC salts at elevated temperatures make them a promising catalyst for the gasification process.

1.5 Thesis layout

The thesis is structured into six chapters. **Chapter 1** introduces biofuels, discussing the various sources for their production and the processes involved in their generation. The literature review is divided into three sections, each addressing a specific aspect pertinent to the current study. The first section examines the kinetic analysis of biomass, specifically investigating how the type of feedstock and the presence of N_2 and CO_2 atmospheres influence the kinetic triplet. The second section reviews studies on the combustion of individual particles derived from different raw materials. Finally, the third section focuses the impact of different operational parameters on the gasification process, particularly how blending various carbonaceous raw materials affects the outcome.

Chapter 2 provides a detailed overview of the materials and experimental setup used for combustion, pyrolysis, and gasification experiments. It also outlines the methodologies implemented to study the kinetic triplets, providing a comprehensive overview of the experimental procedures and analytical techniques used in this research.

Chapter 3 presents the findings from pyrolysis experiments conducted using a thermogravimetric analyser and a fixed-bed pyrolysis system. This chapter explores mass degradation behavior, examines the effects of different heating rates, and determines kinetic triplets through isoconversional methods, such as Friedman, FWO, and KAS. The biochar produced in fixed-bed pyrolysis is characterized using various characterization techniques to study the effects of different pyrolysis atmospheres on its properties. Furthermore, this chapter explores the impact of blending petcoke with biomass on the kinetic triplets, as determined through thermogravimetric analysis under the same experimental conditions used for biomass alone.

Chapter 4 presents the results of the single-particle combustion experiments, analysing how different blending ratios and particle sizes influence various factors. These factors include combustion time, flame behavior, mass degradation profile, ignition mass flux, surface area-to-volume ratio, and ash characteristics.

Chapter 5 presents the results regarding the impact of operational parameters such as pressure, temperature, and gasification mediums on gasification. It also examines how catalyst loading affects syngas yield and conversion during the gasification process. Additionally, the chapter investigates how these parameters influence the gasification of various blending ratios of raw materials.

Chapter 6 highlights the main contributions of this study and proposes possible areas for future research in the field.

1.6 Summary

This chapter provides a detailed overview of biofuels and their production methods, including combustion, pyrolysis, and gasification. It explores various operational parameters, such as pressure, temperature, gasification medium, and catalysts affect on the gasification process. The literature review indicates that these parameters affect the yield of synthesis gas (syngas) and enhance overall gasification efficiency. Co-gasification is an effective method for converting biomass and high-carbon raw materials into high-quality alternative energy sources. The section discussing single-particle combustion emphasises the importance of physicochemical properties, such as particle size, density, and surface-to-volume ratio as critical factors that influence combustion performance. Combustion consists of two primary phases: the volatile combustion phase and the char combustion phase. The properties of the fuel sample influence the duration of each phase. A review of kinetic studies in the literature emphasizes the significance of thermal degradation during the devolatilization stage of biomass. This stage involves the release of low molecular-weight compounds, such as hemicelluloses, cellulose, and lignin. Blending carbon-rich raw materials, such as coal and petcoke, under various pyrolysis conditions creates a synergistic effect that affects both reactivity and the characteristics of kinetic triplets. Additionally, this blending modifies the properties of the resulting char. It has been shown that mixing biomass with different high-carbon raw materials in thermochemical conversion processes can improve the quality of the final product and contribute to a more sustainable energy source.