

Chapter-1

Introduction

1. Introduction

Energy is a crucial element for the survival of human civilization and the advancement of technologies. The energy demand is increasing exponentially due to urbanization, industrialization, changes in lifestyle, and rapid population growth. It is also predicted that the energy demand will increase by 50% at the end of 2050. Fossil fuels-based energy sources like coal, oil, and natural gas are the world's primary energy sources contributing 127 million metric tons (MMT) [1]. It is well known that fossil fuel-based energy resources are insufficient and unsustainable to meet this energy demand due to their limited availability, high extraction rate compared to restoration, and considerable contribution to anthropogenic global warming. The Inter government panel on climate change has reported that emissions of greenhouse gases from human activities are responsible for approximately 1.1°C of global warming from 1850 - 1900. The report also indicates that global temperature is predicted to rise by 1.5°C or more over the next 20 years [2].

According to the statistical review of world energy [3], primary energy consumption growth slowed to 1.3% last year, less than half the rate of growth in 2018 (2.8%). China was by far the most significant energy driver, accounting for more than three-quarters of the net world increase. India and Indonesia were the following two most significant contributors to growth. At the same time, the United States and Germany had the most significant reductions. The primary energy needs of a developing country like India, which has a population of over 1.30 billion people, are for power and transportation fuels such as petroleum products. The need for energy is constantly expanding in the agriculture, industrial, transportation, and residential sectors. As per the report published by the ministry of petroleum and natural gas economic and statistics division 2019-2020, India is the third largest consumer in the world after china and USA. It is also the fastest rising energy user, utilizing around 806.1 million tons of oil equivalent (MTOE) each year. India's

primary energy consumption is met mostly by coal, crude oil, natural gas, and renewable energy, accounting for 5.8% of global consumption. The overall output of petroleum products in 2018-2019 was 32.47 thousand metric tons, while consumption was 213.21 thousand metric tons. Table 1.1 provide the specifics of crude oil and petro-production from 2013 to 2019, while its consumption of different products is presented in Table 1.2. These data show that crude oil output has not grown at the same rate as consumption, putting India in 3rd place among global crude oil importers in 2020.

Table 1.1: Production of crude oil in India in Thousand Metric Tons (TMT)

State/Region	2013	2014	2015	2016	2017	2018	2019
State wise crude oil production (TMT)							
Andhra Pradesh	301	258	295	273	322	299	252
Arunachal Pradesh	116	84	57	58	52	43	52
Assam	4869	4492	4239	4153	4341	4353	4113
Gujarat	5230	4751	4444	4590	4597	4622	4675
Rajasthan	8549	9059	8674	8288	7876	7832	7024
Tamil Nadu	225	237	255	269	341	375	415
Offshore	18519	18662	19271	18412	18369	17163	16110
Total	37810	37541	37235	36042	35898	34687	32641
Entity wise crude oil production (TMT)							
Onshore	19291	18879	17964	17630	17529	17524	16531
of which							
ONGC nomination	6860	6243	5804	5913	6016	6053	6064
OIL nomination	3644	3359	3284	3206	3376	3344	3131
Pvt/JVs-PSC regime	8788	9277	8876	8512	8137	8127	7336
Offshore	18519	18662	19271	18412	18369	17163	16110
of which							
ONGC nomination	15639	16009	16615	16199	16422	15256	14457
Pvt/JVs-PSC regime	2880	2653	2656	2212	1947	1907	1653

Chapter-1 Introduction

Total crude oil production	37810	37541	37235	36042	35898	34687	32641
of which							
ONGC nomination	22498	22252	22420	22112	22438	21309	20521
OIL nomination	3644	3359	3284	3206	3376	3344	3131
Pvt/JVs-PSC regime	11668	11930	11531	10724	10084	10035	8989

Source: Oil and Natural Gas Corporation Ltd., Oil India Limited and GGH

Table 1.2: Consumption of petroleum products in India in Thousand Metric Tons (TMT)

Products	2012-13	2013-14	2014-15	2015-16	2016-17	2017-18	2018-19
LPG	15601	16294	18000	19623	21608	23342	24907
Naptha	12289	11305	11082	13271	13241	12889	14131
MS	15744	17128	19075	21847	23765	26174	28284
ATF	5271	5505	5723	6262	6998	7633	8300
SKO	7502	7165	7087	6826	5397	3845	3460
HSD	69080	68364	69416	74647	76027	81073	83528
LSD	399	386	365	407	449	524	598
L & G	3196	3305	3310	3571	3470	3884	3668
FO & LSHS	7656	6236	5961	6632	7150	6721	6564
Bitumen	4676	5007	5073	5938	5935	6086	6708
PC	10135	11756	14558	19297	23964	25657	21346
Others	5509	5956	5870	6352	6593	8339	11723
All products total	157057	158407	165520	184674	194597	206166	213216

Notes: Consumption includes sales by all companies & direct private imports. LPG – Liquefied Petroleum Gas, MS – Motor Spirit, ATF – Aviation turbine fuel, SKO – Kerosene, HSD – High-Speed Diesel, LSD – Light Speed Diesel, L & G – Lubricants & Greases, FO & LSHS – Fuel Oil & Low Sulfur Heavy Stock, PC – Petroleum coke, **Source:** Petroleum Planning & Analysis cell, New Delhi.

The price of petroleum products such as diesel, kerosene oil, gasoline, and jet fuel has risen quickly in recent years, with a net growth of more than 2.12 times from 2010 to 2020. As a result, there is an urgent need for renewable and sustainable alternatives for liquid

transportation fuels in order to reduce the strain on the nation's economy and achieve sustainable development. Another concern that has compelled attention to be directed in this manner is GHG emissions. Every year, the world emits around 50 billion tons of GHG emissions. The energy sector accounts for around three-quarters of worldwide CO₂ emissions. Almost 40% of it is related to burning fossil fuels for power generation to meet the needs of the residential, commercial, and industrial sectors. The transportation sector, which includes road transportation, aircraft, shipping, rail, and pipelines for fuels and commodities, accounted for an additional 16% of total CO₂ emissions globally. The usage of coal has boosted global CO₂ emissions, particularly in Asian countries. China, India, the United States, and the United Kingdom have collectively raised global CO₂ emissions by 85 %. The usage of coal in the energy mix is primarily motivated by its low cost. Aside from that, energy efficiency and the shortcomings of present laws have also contributed to the rise in CO₂ emissions in Asia. Generally, the combustion of 1 liter of gasoline emits 2.3 kg CO₂, whereas the combustion of 1 liter of diesel emits 2.68 kg CO₂ [4]. Petroleum products must be replaced by renewable energy supplies to minimize CO₂ emissions in the environment. Furthermore, by-products of fossil-fuel combustion constitute the world's most serious danger to children's health and future, as well as important contributors to global inequity and environmental injustice [5]. The ongoing depletion of fossil fuel sources is one of the primary drivers of price increases in petroleum products such as gasoline, diesel, and kerosene. To reduce GHG concentrations in the atmosphere, either fuel quality must be improved, or fossil fuels must be substituted with renewable energy sources. One feasible answer appears to be the combination of biofuel and fossil fuel.

Over the last two to three decades, considerable global research and development efforts have been dedicated toward creating diverse renewable energy supplies to meet energy demand while reducing environmental issues. Renewable energy resources such as

biomass, solar, wind, and hydro have been highlighted as possible resources for a country like India. Biomass is a natural carbon fuel that releases CO₂ during burning, which the plants utilize as a food source. In return, plants release O₂ through photosynthesis [6]. Moreover, among different categories of renewable energy sources, biomass has captured the imagination of policymakers and researchers worldwide. The fact that they are renewable and sustainable sources of energy, in addition to their inexhaustible nature and broad accessibility in different forms, has made the cynosure of all extant energy policies and policymakers [7]. India has surplus forest and agricultural land that accounts for 500 million metric tons per year of accessibility of biomass; globally, around 10-14 % of energy supply has been garnered through biomass [8]. India's power generating potential from agricultural and agro-industrial leftovers is estimated to be around 18,000 MW. The potential for surplus power production by bagasse cogeneration in sugar mills is projected to be approximately 8,000 MW with gradual higher steam temperature and pressure and efficient project setup in new sugar mills and modernization of existing ones. As a result, the overall projected potential for biomass power is around 26,000 MW. [9]. The best possible way for waste remediation is to use biomass for power generation, fuel, and value-added products that provide vital employment to local people in the process [7]. The majority of India's population lives in rural areas. According to the 2011 census, 68.84 % of India's population lives in rural areas. Because India has 0.638 million villages, biomass will be an important alternative as a renewable source of energy when planning for village electrification. MNRE, Government of India, has adopted initiatives such as central financial aid and fiscal incentives to promote the use of bio-energy from agriculture leftovers, plantations, and diverse urban and industrial waste. MNRE is employing a mechanism for delivering subsidies based on co-generation and biomass gasification.

India is primarily an agricultural economy and has made spectacular progress in becoming more or less grain surplus. Because of the availability of high-yielding hybrid seeds, improved agricultural techniques, agrochemicals and fertilizers, and improved irrigation systems, India's output of key grains has grown significantly, and the nation has become a food surplus. This has also resulted in massive amounts of other forms of agro-wastes, mainly hay and stalks. As per the recent report published by the Indian Renewable Energy Development Agency Limited (IREDA) certain common agricultural wastes in India are (million tons/per annum): straws of various pulses and cereals – 225.50, bagasse – 31.00, rice husk – 10.00, ground nut shell – 11.10, stalks – 2.00, various oil stalks – 4.50, and others – 65.90 [10]. MNRE is encouraging the use of biomass-based power plants to generate energy from locally accessible biomass. These power plants are built in rural regions where surplus biomass such as small wood chips, rice husk, arhar stalks, cotton stalks, seed hulls, fruit peels, and other agro-residues are available to supply the unmet need for electrical energy for lighting, water pumping, and microenterprises such as telecom towers. Various biomass power production facilities have been established in various Indian states to meet the country's energy needs. Table 1.3 displays the biomass potential of several states. Because of the increased use of farm machinery, a lack of understanding, and ineffective waste management rules, this vast amount of biomass is not being profitably utilized for energy generation and value-added manufacturing products. Given the environmental concerns and rising costs of crude petroleum and petrochemicals, it is vital to provide scientific evidence to promote the use of such wastes as an energy source.

Table 1.3. State-wise and source-wise installed capacity of grid interactive biomass power

Installed Capacity of Grid Connected Biomass/ Bagasse Power Plants up to 31.03.2019 [11]			
Andhra Pradesh	378.20	Telangana	158.10
Bihar	113.00	Punjab	194.00
Chhattisgarh	228.00	Rajasthan	119.30
Gujarat	65.30	Tamil Nadu	969.00
Haryana	121.40	Uttarakhand	73.00
Karnataka	1783.60	Uttar Pradesh	1957.50
Madhya Pradesh	93.00	West Bengal	300.00
Maharashtra	2499.70	Odisha	50.40
Total			9103.50

1.1 Biomass

Biomass is described as bio residue produced by water-based vegetation, forest or organic waste, agricultural production waste, agro or food industry waste. In India, many biomass resources are available in various forms. Biomass is a renewable resource that is continually created by photosynthesis using solar energy, CO₂ in the atmosphere, and H₂O in the soil [12–14]. Biomass is a heterogeneous combination of organic components with a tiny proportion of inorganic matter. Typical dry biomass comprises 30–40% oxygen, 30–60% carbon, and 5–6% hydrogen by weight.

Meanwhile, nitrogen, sulfur, and chlorine, together with other inorganic elements, make up around 1% of the biomass [15]. Carbon (C) contributes mostly to the total heating value of biomass since it derives from atmospheric CO₂ during photosynthesis [16]. Hydrogen (H) is a key component of biomass because it is incorporated into the chemical structures of carbon and phenolic polymers. It is converted to water (H₂O) after burning [16]. Nitrogen (N) is a fertilizer that returns to the soil and improves plant growth and output. Sulfur (S)

is a nutrient that is present in amino acids, proteins, and enzymes and is essential for plant development. Photosynthesis releases oxygen (O), which is a critical component of biomass composition [16]. They can be easily categorized as grasses, woody plants, fruits, vegetables, manures, seed hulls, and aquatic plants based on their availability in nature. Algae and *Jatropha* are now also employed in the production of biodiesel. The primary sources of biomass energy are agricultural crop residue, energy plantation residue, and municipal and industrial waste [17]. Fig. 1.1 depicts the numerous biomass classifications available in India.

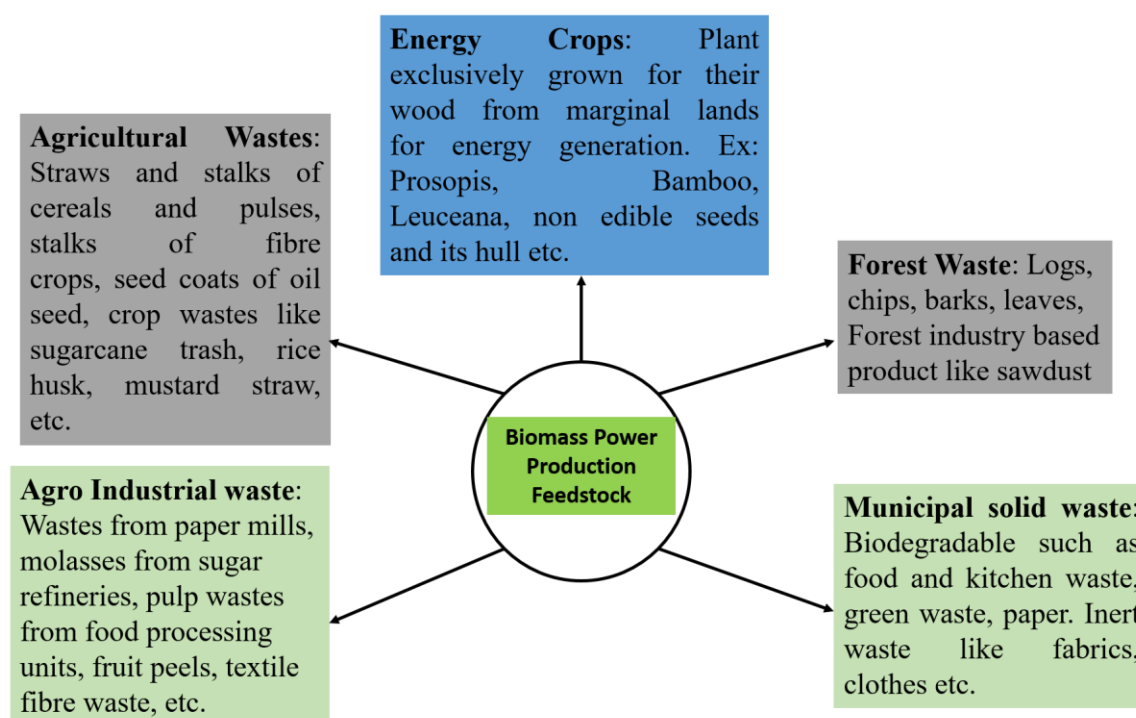


Fig. 1.1: Classification of available biomass resources in India

1.2 Chemical composition of biomass

Lignocellulosic biomass is composed of cellulose (40 – 50 wt. %), hemicellulose (15 – 30 wt. %), lignin (16 – 3 wt. %), and extractive compounds (1 – 10 wt. %) [18]. The chemical structure of biomass can be seen in Fig. 1.2.

1.2.1 Cellulose

Cellulose, the most prevalent component of biomass, is thought to provide a nearly infinite supply of chemicals and energy [19]. Cellulose is found in plant cell walls and accounts for around one-third of all plant material [20]. Cellulose is made up of linear polymers in which glucose units are linked together by β -1,4 glycosidic ester linkages [21]. Native cellulose has a molecular weight of 100000 on average [14,22]. The structure of cellulose chains allows for intramolecular and intermolecular hydrogen bonding [23]. Furthermore, the hydrogen and van der Waals bonds in the cellulose structure give cellulose great strength and resilience to biological assaults. Because of its crystal structure, cellulose is not water-soluble and is resistant to hydrolysis [24]. Cellulose is a critical resource in the creation of paper and cardboard. Furthermore, cellulose derivatives are employed in asphalt, laminates, optical films, medicines, meals, and textiles [25].

1.2.2 Hemicellulose

Hemicellulose, commonly known as polyose, is the second most major component of lignocellulosic biomass [26]. Hemicellulose is a heteropolysaccharide composed of β -1,4-linked sugar units [27]. Hemicellulose is made up of uronic acid, hexoses, and pentoses and has a heterogeneous structure [28]. Hemicellulose has a lower degree of polymerization than cellulose, is highly soluble in alkali media, and is rapidly hydrolyzed [28]. Although hemicellulose is amorphous and hydrophilic, it functions as an interfibrous connective substance that supports cellulose microfibrils [29]. Furthermore, hemicellulose has been shown to establish covalent connections with the functional groups in lignin and interact with cellulose via hydrogen bonds [20].

1.2.3 Lignin

Aside from cellulose, lignin is the most prevalent aromatic polymer in plants [20]. Lignin is a complicated polymer with a three-dimensional amorphous structure made up of

phenylpropane units [30]. Lignin accounts for 16 – 33% of the weight of wood [31]. Lignin has a significantly high molecular weight, which makes measurement challenging [30]. Lignins are polymers formed by the dehydrogenation of p-coumaryl, sinapyl, and coniferyl [32]. Coniferyl alcohol and a trace of coumaryl alcohol make up softwood lignin. Hardwood lignin is made up of coniferyl and sinapyl alcohols, as well as a trace of coumaryl alcohol. Because of its complex structure and varied bonds, lignin is more resistant to microbial degradation than polysaccharides [33]. However, when depolymerized properly, lignin becomes a rich source of valuable chemicals, fuels, and additives [34].

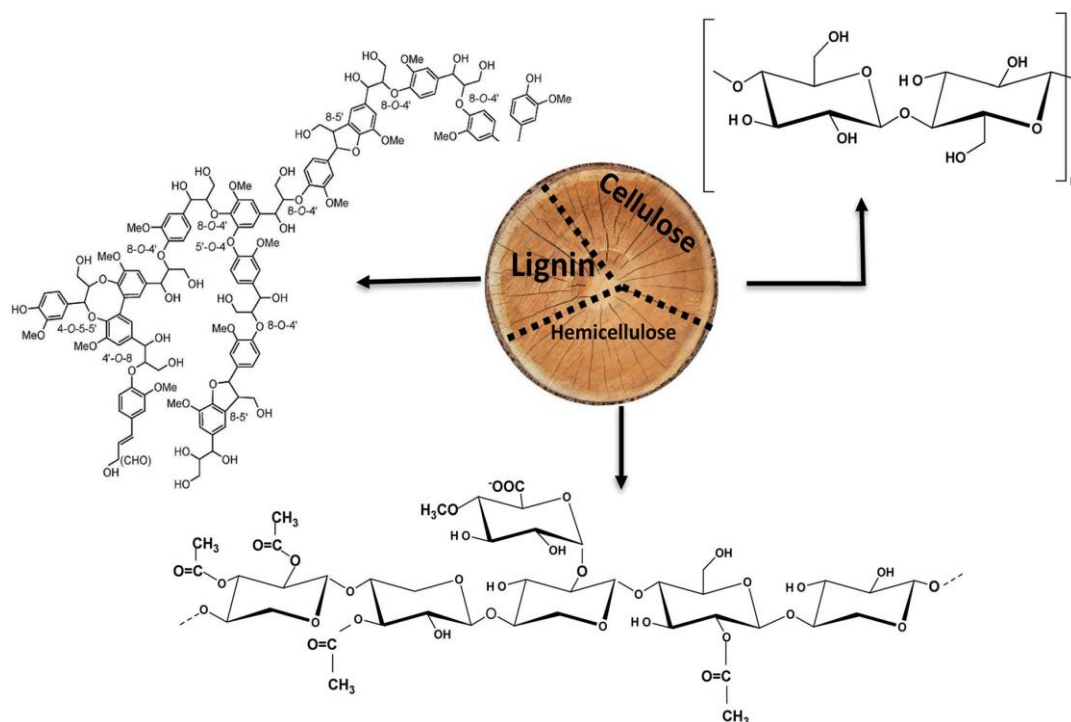


Fig. 1.2: Chemical structure of biomass [35]

1.2.4 Extractives

The word "extractive substances" refers to a broad range of chemicals that may be extracted using polar and/or nonpolar solvents [20]. These extracts are often composed of chemicals with low molecular weights. Extractive compounds include lipids, free fatty acids, waxes, resins, tannins, gums, terpenoids, avonoids, stilbenes, tropolones, and volatile

hydrocarbons typically account for a tiny percentage of the weight of wood [36]. Extractives operate as intermediates in digestion, protecting from insect assault and microbial degradation [26]. They also contribute to the features of the biomass, such as its color, smell, and flavor.

1.3 Technologies for converting biomass to energy

The potential of biomass in India demonstrates that numerous feedstocks are accessible for conversion to bio-fuels as well as power generating applications. Many techniques exist for biomass conversions, which depend on the kind and quantity of biomass feedstock, environment, economic conditions, etc. The conversion of biomass to energy is accomplished via two primary process technologies: thermochemical and bio-chemical. The third approach for obtaining energy from biomass is mechanical extraction.

1.3.1 Biochemical conversion technologies

Biochemical conversion of biomass entails using bacteria, microbes, and enzymes to convert biomass into a gas (biogas) or liquid (bioethanol) fuel [37]. This process is significantly slower than thermochemical and does not need much energy. Fermentation (formation of ethanol or other low molecular weight alcohols) or digestion are the two processes involved in biochemical conversion (biogas production) [14]. Bacteria take oxygen from the biomass and produce methane, carbon dioxide, and solid products during anaerobic digestion. Microorganisms acquire oxygen from the air and emit carbon dioxide, heat, and solid products during aerobic digestion. Prior to fermentation, pretreatment is often employed to minimize the recalcitrance biomass, followed by hydro-lyase enzymes releasing sugars from polysaccharides. The sugar is then transformed into ethanol or other compounds with the assistance of yeasts or other microbial agents [37].

1.3.2 Thermochemical conversion technologies

The following fundamental processes are utilized in the thermochemical conversion of biomass: combustion, gasification, torrefaction, pyrolysis, and hydrothermal methods.

1.3.2.1 Combustion

Combustion is the process of burning biomass in the air to transform the chemical energy stored in biomass into heat energy, mechanical power, and electricity via various processes and equipment such as furnaces, stoves, steam turbines, boilers, etc. The combustion process occurs as a consequence of a chemical interaction between biomass and oxygen, and the major by-products of the process are carbon dioxide and water. Although any sort of biomass can be burned, combustion is only practical for biomass with a moisture level of less than 50% unless the biomass is pre-dried. Biomass with high moisture content is more suitable for biological conversion processes [38].

1.3.2.2 Gasification

Gasification is the partial oxidation of biomass at high temperatures, often in the range of temperature (800 – 900°C), to produce a combustible gas mixture. Gasification generates gases like H₂, CO, H₂O, CO₂, and CH₄, which are used to generate energy, heat, chemicals, and liquid fuels [39,40]. The biomass integrated gasification/ combination cycle (BIG/CC) is a promising idea in which gas turbines convert gaseous fuel to electricity with a high overall conversion efficiency. Because the volume of gas to be cleaned is decreased in BIG/CC systems, the gas is cleaned before being combusted in the turbine, enabling more compact and less expensive gas cleaning equipment.

1.3.2.3. Torrefaction

Torrefaction is a thermochemical process in which biomass is heated in the temperature range of 200 – 300°C under an inert environment, residence time less than one hour at a relatively slow heating rate (less than 15°C/min) [41]. The product gained after torrefaction

has improved physicochemical properties such as low moisture content, high calorific value, hydrophobic nature, and low H/C and O/C ratio. It has high grindability, lower moisture sorption characteristics, and low transportation and storage costs [42]. Bio-oil obtained from pyrolysis of torrefied biomass has less moisture content and a lower O/C ratio [43]. It has lower organic acids and high hydrocarbons, sugar, and phenol. Furthermore, torrefaction increased the proportion of CH₄ and H₂ in syngas while decreasing CO₂ production, implying that torrefaction significantly improved syngas quality during pyrolysis of torrefied biomass [44].

1.3.2.4 Pyrolysis

Pyrolysis is one of the thermochemical processes by which biomass is converted into higher-value products such as bio-oil, gases, char, and other heavy organic compounds at a moderate temperature range of 300 – 700°C in an inert atmosphere. The bio-oil obtained after pyrolysis constitute essential chemicals such as hydrocarbons, phenols, alkanes, and oxygenated compounds such as ketones, esters, and ethers [45]. The bio-oil may be utilized in engines and turbines and is also being investigated as a feedstock for refineries. However, there are several issues that must be addressed, such as corrosivity and low thermal stability. Certain applications may need upgrading bio-oils by decreasing the oxygen content and eliminating alkalis by hydrogenation and catalytic cracking of the oil [46]. Pyrolysis is classified into three types: conventional/slow pyrolysis, fast pyrolysis, and ultra-quick/flash pyrolysis. Slow pyrolysis is commonly used to change solid materials while reducing the amount of oil generated. Fast pyrolysis is the thermal degradation of carbonaceous materials at moderate to high heating rates in the absence of oxygen. It is the most widely used approach in both research and practice. Bio-oil is the main product. The product yields are as follows: liquid condensates – 30 – 60 %; gases (CO, H₂, CH₄, CO₂, and light hydrocarbons) – 15 – 35%; and char – 10 – 15%. Ultra-fast pyrolysis, also known

as flash pyrolysis, is a kind of pyrolysis with an exceptionally quick thermal breakdown and a high heating rate. Gases and bio-oil are the principal products. Heating rates can range from 100 to 10,000 °C/s, and residence periods are brief. The product yields are as follows: liquid condensate (10 – 20%), gases (60 – 80%), and char (10 – 15%).

1.3.2.5 Hydrothermal methods

Hydrothermal treatment techniques are chemical and physical conversion processes that are carried out in liquid or supercritical water at high temperatures (200 – 600 °C) and pressures (5 – 40 MPa) [46]. Hydrothermal approaches have been developed to reduce the cost and time necessary for biomass drying [47]. Carbonization, gasification, and liquefaction are the three types of hydrothermal methods. Hydrothermal carbonization is a wet pyrolysis process in which biomass requires no pre-drying, heated under relatively low temperature (180 – 320°C) in autogenous pressure. The solid product obtained is called hydrochar. It has improved performance than raw biomass like high energy density, high dewaterability, and high combustion rate. It is easily separated from the liquid product due to its hydrophobicity and friable properties. The hydrogen and oxygen content gets lowered due to decarboxylation and dehydration reactions [48]. It is used in carbon sequestration, bioenergy production, soil improvement, and wastewater treatment. The reaction mechanism related to the HTC process is still unknown; however, the primary reactions during HTC are dehydration, hydrolysis, decarboxylation, condensation polymerization, and aromatization [49]. Hydrothermal gasification is a thermochemical technique for transforming biomass into gaseous products such as carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and methane (CH₄) [50]. Gasification is often carried out at temperatures ranging from 400 – 700 °C in order to get high yields of methane or hydrogen [46,51]. Hydrothermal liquefaction is a thermochemical process that produces a liquid product known as bio-oil at moderate temperatures and high pressures [52]. This process

aims to break down biomass with a high moisture content into tiny molecules and lower the oxygen concentration of the biomass in order to obtain liquid fuels or valuable compounds [53,54]. In this process, biomass and O₂ are rapidly oxidized or mineralized to generate CO₂ or H₂O, while toxic combustion products, such as NO_x, are transformed into innocuous chemicals. Liquefaction is typically conducted for 10 to 60 minutes at temperatures ranging from 280 to 380 °C and pressures ranging from 7 to 30 MPa [55].

From the above discussion, it is clear that India possesses a vast supply of agro-residues that are now being underutilized. Furthermore, owing to ignorance, negligence, lack of sufficient technology, absence of a clear-cut policy for agro-waste management, and poor execution of current legislation, a large amount of agro-residue is directly burned in the fields by farmers. Fig. 1.3 depicts the direct burning of various agricultural wastes in the field. Burning this agricultural residue in the field emits CO, CO₂, SO_x, NO_x, and particulate matter as fly-ash, which reduces soil fertility by diminishing microbial ecology. As a result, scientific data must be generated in order to improve existing technology or develop new technology for exploiting this vast amount of accessible biomass as a renewable energy source. This condition is met by the results reported in this thesis.



Fig. 1.3: Burning of various agricultural wastes in the field