

# Chapter 11

## Effective Utilization of High-Grade Energy Through Thermochemical Conversion of Different Wastes



A. Santhoshkumar, R. Muthu Dinesh Kumar, D. Babu, Vinoth Thangarasu and R. Anand

**Abstract** Waste disposal is a major problem in most of the countries. Thus, waste to energy conversion will fulfill the future energy demand as well as resolve the pollution issues. This work mainly involved in the extensive study on pyrolysis and gasification of biomass and hazardous e-waste into useful energy and its impact on the environment. Microwave-assisted pyrolysis (MAP) technique has attracted the research society because of its energy efficient process and more viable route for converting the waste into potential products. Similarly, this chapter provides the assessment of biomass and e-waste volarization route to produce syngas using different gasification strategies. In addition, this study focused on the pyrolysis and gasification parameters like temperature, equivalence ratio, and particle size, which influence the product yield and emission formation. In general, pyrolysis and gasification of biomass and e-waste produce the volatile products, and it leaves the solid residue like char and ash. As an implementation, this study explained the conversion of waste residue from pyrolysis and gasification into useful products like activated carbon, silicon carbide, and zeolite, which can be used as the catalyst in microwave process and some other applications. At the end, the study covers the utilization of pyrolysis fuel and syngas in compression ignition engines with advanced technologies like CRDI and dual fuel strategies. CRDI and dual fuel mode combustion are the appropriate methods to reduce the engine emissions and enhance the engine efficiency.

**Keywords** Biomass · E-waste · Microwave-assisted pyrolysis Gasification · Syngas · Engine

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**Nomenclature**

ABS	Acrylonitrile–butadiene–styrene
ASTM	American Society for Testing and Materials (ASTM)
BFRs	Brominated flame retardants
CAG	Comptroller and Auditor General of India
CFC	Chlorofluorocarbon
COHb	Carboxyhemoglobin
CPV	Concentrator photovoltaics
CRDI	Common rail direct injection
CRTs	Cathode ray tube
CSP	Concentrated solar power
DME	Direct methyl ether
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-ray analysis
ER	Equivalence ratio
FPSPS	Free-pressureless spark sintering technique
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
HCBs	Hexa-chlorobenzenes
HDPE	High-density polyethylene
HIPS	High impact polystyrene
HPLC	High-performance liquid chromatography
MAOS	Microwave-assisted organic synthesis
MAP	Microwave-assisted pyrolysis
MB	Methylene blue
MSW	Municipal solid waste
MWS	Maxwell–Wagner–Sillars
NMFs	Nonmetallic fractions
NMR	Nuclear magnetic resonance spectroscopy
OECD	Organisation for economic cooperation and development
PAH	Polycyclic aromatic hydrocarbons
PBDD/Fs	Polybrominated dibenzo-p-dioxins and dibenzofurans
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and dibenzofurans
POPs	Persistent organic pollutants
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SiC	Silicon carbide
TBBPA	Tetrabromobisphenol
TGA	Thermogravimetric analysis
WCO	Waste cooking oil

WEEE	Waste electrical and electronic equipment
WPCBs or WCB	Waste printed circuit boards
XRF	X-ray fluorescence

## 11.1 Introduction

Biomass is one of the major renewable energy sources which fulfill about 14% of the energy requirement. In case of rural areas, up to 90% of energy demand is fulfilled by biomass. In the year of 2050, most of the peoples in the world are predicted to live in the developing countries, and biomass is expected to remain a major source of energy contribution to the large populations (Balat and Ayar 2005). To recover energy from the biomass and recently plastic waste, gasification technology is focused as a sustainable waste management technique; hence, it will be able to reduce the toxicity of waste, the burden on landfills, and also the environmental hazards (Seltenrich 2016). Plastic waste management is increasing day by day, so it must be urgently addressed. Low degradability of plastic waste causes enormous problem in marine environments (Andrady 2015). Likewise, in Europe over the last decade recycled plastic contribute energy sector have increased from 55% and also dumping of waste plastics reduced by nearly 40% (Hestin et al. 2017). Plastic polymers are extensively used in the current world such as in automobiles, packing, agriculture, electronics, building materials, and so forth. This massive consumption was promoted to the production of an increased amount of e-waste, especially in more developed countries. Industrialization and population growth increasing the energy demand, petroleum products consumption, and disposal of e-waste were described in energy demand and scenario. E-waste is defined as discarded waste electronic and electrical equipment during the manufacturing and repairing process. The e-waste is mostly collected from household and business equipment with circuitry or electrical components. The e-waste contains plastics, different metals like copper, tin, lead, cadmium, beryllium, mercury, and flame retardant additives like bromine, chlorine, fluorine, and iodine that affect the landfill and ecological system. Thermochemical conversion processes are the best alternative to meet the energy requirements by converting wastes into most valuable products (Joshi et al. 2016).

The e-waste contains lots of different constituents and elements, creating an intricate heterogeneous waste containing plastics, metals, and ceramics. Conventional procedures of recycling e-waste (i.e., separating, shredding, and sorting) generates a residual material that still contains valuable metals, they often turn out to be landfills (Lee et al. 2007; Cui and Forssberg 2003). Recycling of e-waste also causes environmental problems pertaining to the presence of various halogenated and nonhalogenated flame retardants (Schlummer et al. 2005). The flame retardant is used for preventing the flame propagation on the plastic materials. The halogenated flame retardant infers to a chemical mixture which contains

halogen atoms (bromine, fluorine, chlorine, and iodine), and they are not electrolytic in nature. Nonhalogenated flame retardants like phosphorus, phosphate, and nitrogen are widely used in plastics. These halogenated and nonhalogenated components pollute the environment during the direct combustion of plastics. Moreover, polymers have been identified in e-waste such as high impact polystyrene, acrylonitrile butadiene styrene, polystyrene, polyvinyl chloride, polycarbonate, and polypropylene (Alston et al. 2011). The pyrolysis process can probably be utilized to convert plastics into diesel-like fuel or other more valuable products (Anuar Sharuddin et al. 2016) and surely be considered as an important process of restoring and reuse of the polymeric content of the e-waste (Muhammad et al. 2015; Martinho et al. 2012; Al-Salem et al. 2009). In the realm of pyrolysis, microwave-assisted pyrolysis is an efficient process which gives some advantages over conventional pyrolysis process—e.g., it offers a volumetric heating that improves heating efficiencies (Appleton et al. 2005). Two different types of microwave absorbers (i.e., “C” based, “Fe” based) were used to study the microwave-assisted pyrolysis of e-waste and different experimental setups used to increase the quality and quantity of liquid fraction and to reduce the solid residue (Rosi et al. 2018).

In traditional pyrolysis technique, the heating mechanism is less efficient and slower as it is based on conduction and convection. Energy efficient volumetric heating can be attained in microwave pyrolysis due to the diffuse character of the electromagnetic field; it heats all the substances uniformly (Domínguez et al. 2007). In the realm of pyrolysis, the microwave-assisted pyrolysis (MAP) is an efficient process which gives some advantages over conventional pyrolysis process offers volumetric heating that improves heating efficiencies (Jones et al. 2002). According to Paradela et al. (2009), e-waste plastics were mixed with pine biomass with the purpose of maximizing liquid yields by studying the experimental conditions. The primary intention behind the co-pyrolysis is to improve pyrolysis oil liquid fraction and its properties (i.e., a mixture of varieties of plastics and pine residue).

Microwave heating had intensive functions in food, ceramic, and chemical processes industries in recent days. Microwave heating is resulting from the conversion of magnetic attraction energy to thermal power, and additionally, the effectiveness of the conversion depends upon the nonconductor nature of substances. In many cases, the energy consumption in microwave-assisted heating could be a smaller quantity than that of other heating processes and so the handling time is shorter (Rattanadecho et al. 2007). Compared to conventional heating, microwave-assisted heating is having many advantages like faster heating rate and faster rate of reaction. Municipal solid waste is used in pyrolysis process, and different susceptors have used for increasing the efficiency of microwave pyrolysis process. For municipal solid waste activated carbon, solid beads, fly ash, aluminum are the suitable susceptors (Suriapparao and Vinu 2015). Several types of research were described by Wang et al. (2014) the use of pyrolysis oil in internal combustion engines for a better replacement of the diesel fuel. For efficient utilization of energy, it is essential to consider the quality and quantity of energy.

Conversion of waste plastics into value-added products using gasification in the bubbling fluidized reactor produces syngas which mainly consists of  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ , and  $N_2$ . The generated syngas can be converted to fuels like methanol and dimethyl ether (Sansaniwal et al. 2017). An astounding favorable position of gasification contrasted with pyrolysis is the more noteworthy adaptability to together valorise plastics of various syntheses or blends or plastics blended with different feedstocks. Therefore, composition and application depend on several factors such as gasifying agent, catalyst, bed material, and reactor configuration. Syngas produced from gasification of plastics have an average heating value in the range of 6–8  $MJ/m^3$  (Sancho et al. 2008; Arena and Di Gregorio 2014; Arena et al. 2010; Xiao et al. 2007).

An exhaustive literature search is already done, and further study is needed throughout the full project tenure to get updated with current research in the proposed area. Conventional procedures of recycling e-waste will generate a residual material that still contains valuable residues; they often turn out to landfill. Polymers have been identified in e-waste residues such as high impact polystyrene, acrylonitrile butadiene styrene, polystyrene, polyvinyl chloride, polycarbonate, and polypropylene. Current investigation work shows that the thermal conversion process called pyrolysis is an effective way to recover energy from the e-waste. However, the pyrolysis oil can be replaced as diesel fuel was addressed and its application for use in a diesel engine. The performance and combustion characteristics of the CI engine with pyrolysis oil as fuel was comparable to the standard diesel fuel. Several types of research described the use of pyrolysis oil in internal combustion engines for a better replacement of the diesel fuel. Among various possible technological developments, a common rail direct injection (CRDI) system has to lead the technological revival. CRDI systems have been observed to significantly reduce specific fuel consumption and soot emissions as compared to conventional diesel operation, however, with a tendency of increased  $NO_x$  formation (Roy et al. 2014).

## **11.2 Environmental Impact of Waste Disposal and Energy Conversion**

### ***11.2.1 Global Energy Status and Scenario***

World energy demand has been increased due to the rise in population and technological advancement. Approximately, 80% of the energy demand could be fulfilled by the fossil fuels. More utilization of fossil fuel coupled with a steady rise in energy demand and an increase in carbon dioxide ( $CO_2$ ) and carbon monoxide ( $CO$ ) emissions are becoming the real threat for the ecosystem. The  $CO_2$  and  $CO$  emissions are the main contributor to the environmental pollution and global warming (Anand 2017). Depletion of fossil fuels and environmental threat have

spurred research interest in alternative renewable energy sources. The alternative renewable sources are solar energy, wind energy, tidal energy, geothermal energy, and hydropower energy (Zhang et al. 2003). According to the energy survey, the world energy demand could be fulfilled by 77.9% of fossil fuel and remaining renewable energy sources. The energy production in terms of percentage is oil—35%, coal—29%, natural gas—24%, nuclear energy—5%, and hydropower—6% remaining solar and other sources (Lin et al. 2011). The world population will increase from 74 billion to 92 billion in 2040 according to the energy outlook 2018 survey. Global energy demand will increase by about 25% from 2016 to 2040 for non-OECD countries. Due to the rise in population, the electricity demand will be rise by 60% from 2016 to 2040 (Administration, U.S.E.I 2018).

Solar energy is a promising and freely available renewable energy source to manage the energy crisis. It is superior to the other sources in terms of availability, accessibility, cost-effectiveness, capacity, and efficiency (Kannan and Vakeesan 2016). According to the international energy scenario, 40,000–60,000 MW decentralized rooftop solar PV could be installed in India by 2022 (Shrimali and Rohra 2012). Solar, nuclear energy, and conservation of energy will be meeting the Indian energy demand over the next 20 years (Parikh and Parikh 2011). Estimated CAG of Indian energy demand could be pegged around 3.1% from 2009 to 2035 (International Energy Agency 2012). Indian government is imposing the policy and takes the initiative for the implementation of solar power technology like CSP and CPV. It is solving the energy problem like deficit, energy inequity, and energy security as observed by Sharma et al. (2012). As per the NISEM scenario, the total estimated solar power generation in India is 749 GWP, and its target is 100 GWP solar power in India by 2022 (National Institute of Solar Energy 2014). The estimated annual solar power generation could be 459,900 Million units, and the theoretical annual power generation is 918,573 Million units. By 2030, 12,875 MW wind power may be achieved in India (Singh 2018).

As per the Ministry of Statistic and Programme Implementation, the total estimated wind power generation in India is about 102,772 MW but present wind energy power generation is 23,439 MW. The wind power production is depending on site, wind profile, and master height (Ministry of Statistics and Programme Implementation 2015). Estimated small hydropower generation in India is 19,749 MW, and present installed capacity of the small hydropower in India is 3800 MW by 2014 (Ministry of Statistics and Programme Implementation 2015). Estimated biomass and cogeneration power generation in India is about 17,538 MW and present capacity of biomass electricity generation is 4013 MW in India. The total expected power generation from renewable energy sources in India is about 725,660 Million units and theoretical power generation from renewable sources in India approximately about 13, 13,604 Million units (Ministry of Statistics and Programme Implementation 2015).

### ***11.2.2 Environmental Impact of Waste Disposal***

Increase in electronic waste is concern over across the world. Each year globally about 300 million tons of e-waste is produced, and about 10% only recycled. In the world, India is the 5th major producer of e-waste. Roughly each year India is dumping 18.5 lakh metric tons of e-waste, which includes 12% of telecom equipment and 70% of computer devices of the total e-waste, and 18% of mobile e-waste (Mundada et al. 2004). In recent days, electrical and electronic wastes are drastically increased due to population and industrialization. The e-waste is recycled through incineration or pyrolysis process, and non-recycled e-waste is landfilled. E-waste contains lots of heavy metals, brominated flame retardant, and other toxic and hazardous substance. Landfilled causes environmental pollution (Wang and Xu 2014a). The presence of halogenated and nonhalogenated flame retardants in electrical and electronic waste causes environmental pollution and burning gases harmful to human health as noticed by Weber et al. (Weber and Kuch 2003). WEEE is recycled through melting, regeneration, and crushing. The MNFs, WPCBs have hazardous ingredient, which causes environmental pollution, and e-waste contains acrylonitrile butadiene styrene, polystyrene, and polyvinyl chloride (Guo et al. 2009).

Disposal of municipal solid waste (MSW) is one of the major issues not only in India but also in the whole world. The higher rate of population growth, global urbanization, degree of industrialization, and public habits increased the productivity of municipal solid waste (Pandey et al. 2016). According to the life cycle analysis, collection of MSW, storage of MSW, transportation of MSW, Processing of MSW is too difficult. MSW is the potential source for the power generation; it consists of food, paper, wood waste, clothes, rubber, plastics, and daily discharge materials. 90% of MSW is not disposed of properly or mannerly, it is simply dumped in open spaces, which causes environmental hazards, and it is created problem to the public health (Klein 2002). In USA, 90–95% of MSW is converted into useful energy. According to the survey, 3.98 million tons of MSW is recyclable, 3.32 million tons of MSW is landfilled, and 0.60 million tons of MSW is incinerable. According to the World Bank survey, the solid waste increases from 1.3 billion tons to 2.5 billion tons by 2025. In India, 0.1 million tons of MSW/day per capita is produced (Akolkar 2005).

Last few decades, the plastics usage has been drastically increased due to its better characteristics. In total, WEEE waste consists of about 30% of plastic due to its numerous behavior like lightweight and noncorrosive in nature. More landfilling of plastic waste reduced the area and polluted the environment and affected the human health. Especially, BFRs affected the nervous and reproductive systems of mammal (Stegeman et al. 1993). Syamsiro et al. (2014a) synthesized the pyrolysis oil from MSW using Y-zeolite and normal zeolite as catalyst. MSW collected from last disposal place in Indonesia. The results revealed that HDPE waste produced maximum liquid fraction. Presence of catalyst in the reaction reduces the liquid fraction, whereas gases fraction slightly increased as compared to non-catalytic process. MSW-based pyrolysis oil has better calorific value compared to low-grade oil and biomass feedstock.

### ***11.2.3 Importance of Waste to Energy Conversion***

In the modern world, due to population and technological advancement, more quantity of waste is produced. The different wastes such as cooking waste, municipal solid waste, plastic waste, automobile waste, electronic or e-waste, and agricultural waste were discarded in the landfill directly. Many researchers have been working on waste to energy conversion technique to meet the world energy demand by utilizing the energy from wastage (Pandey et al. 2016). The most important waste to energy conversion techniques are physical method, thermal conversion method, biological method, and chemical method. In the physical method, the solid waste is converted into pellet, wood chips, and wood briquettes, respectively. Thermal conversion method is classified into three types such as direct combustion, pyrolysis, thermal gasification, and plasma arc gasification. The biological method consists of fermentation and anaerobic digestion. In the chemical method, waste material is converted into useful energy through transesterification and esterification process (Mohn et al. 2008).

The solid waste undergoes combustion or incineration process produces heat energy which can be utilized for the conversion of water to steam. It is used in power generation through the gas turbine (Suksankraisorn et al. 2004). Pyrolysis process is also known as dry distillation or thermal cracking. In the pyrolysis process, the solid wastes are heated with the absence of oxygen. The output of the pyrolysis process is methane, hydrogen, hydrocarbon, charcoal, vinyl chloride and cock, liquid fuel, and solid residue (Liamsanguan and Gheewala 2008). Thermal gasification is the process of converting waste into energy by heating the solid waste at above 700 °C with the presence of limited oxygen. The gasification process outputs are carbon monoxide, hydrogen, and carbon dioxide gases, and they are used in power generation (Management of Solid Waste in Indian Cities 2005). The biological methods are fermentation and anaerobic digestion. Fermentation is the metabolic process which converts sugar into useful product such as acid, gases, and alcohol in the presence of yeast and bacteria. The output gases from the fermentation are used in power generation. Anaerobic digestion is the process of converting biodegradable waste into useful energy. It produced methane and carbon dioxide gases (Boundy 2011).

#### **11.2.3.1 Chemical Method in Waste to Energy Conversion**

Waste cooking oil (WCO) is generated from various places such as restaurant and domestic; it is about approximately 10 million tons produced from USA every year, 4.5 million tons from China, 0.7–10 million tons produced from Middle East European countries, India—0.6 million, Malaysia—0.5 million, Japan—0.57 million, Ireland—0.15 million, and Canada—0.12 million per year, respectively (Gui et al. 2008; Kulkarni and Dalai 2006). A large amount of waste cooking oil is dumped by fast food shops and restaurants across the world resulting in



environmental hazards. As the oil is dumped into the water sources, oil layers get formed on the water surface; thus, it prevents the exchange of oxygen across the water surface. The ineffective way of disposing the WCO results in obstruction of drainage pipes which causes soil and water pollution (Babu and Anand 2017). Thus, it is essential to properly recover and reuse the waste cooking oil. When the waste cooking oil is reused, it gets oxidized and produces toxic contents, which leads to health problem in human being (Babu and Anand 2017).

Transesterification is the process of converting waste cooking oil (triglycerides) into biodiesel (methyl ester). Waste cooking oil-based biodiesel could be one of the promising alternative fuels for diesel engines. Maximum biodiesel yield of 97.4% was obtained from sunflower based waste cooking oil using sodium methoxide as a catalyst under molar ratio of 1:6, temperature of 55 °C, 150 min of time, catalyst concentration of 1.5 wt% and 975 rpm of stirrer speed as noticed by Babu and Anand (Babu and Anand 2017). Biodiesel was synthesized from waste cooking oil using KBr impregnated CaO catalyst. The optimum yield of 83.3% was obtained at 1.8 h of reaction time, molar ratio of 1:12, temperature of 50 °C, and catalyst amount of 3 wt% (Mahesh et al. 2015). The optimum biodiesel yield of 97% was obtained from palm oil-based waste cooking oil using KOH catalyst under temperature of 45 °C, reaction time of 3.5 h, stirrer speed of 200 rpm, and molar ratio of 0.4:1 (Kannan and Anand 2012).

### 11.2.3.2 Pyrolysis Technique in Waste to Energy Conversion

Pyrolysis is the process of converting waste to energy through heating the solid waste with the absence of oxygen. The products are liquid oil, gaseous fuel, and solid char. The product yield is varied based on the operating parameters as noticed by Demirbas (2004a). Microwave pyrolysis is the effective method compared to the conventional heating method in the pyrolysis process. In traditional pyrolysis technique, the heating mechanism is less efficient and slower as it is based on conduction and convection whereas, in microwave pyrolysis due to the diffusion characteristics of the electromagnetic field, heat dissipated throughout the area (Rosi et al. 2018). Thus, microwave pyrolysis provides equal distribution of heat and efficient heat transfer. It only heats the dipole material. So, the hotness was created in the mark substantial and the efficiency of the process is higher than conventional heating (Lam et al. 2010). Microwave pyrolysis technique is one of the best methods in waste to energy conversion technique when compared to conventional pyrolysis process. It converts the e-waste into diesel-like fuel for diesel engines as renewable energy source (Andersson et al. 2012).

Demirbas (2008) extracted the diesel-like fuel from waste engine oil by pyrolysis process. Pyrolysis process converts industrial or solid waste into quality and more desirable product. The maximum yield of 41.8% was obtained at 620 K used alumina-based catalyst. The octane number of the waste engine oil is greater than the gasoline fuel. Flash point is lower than the gasoline fuel. Sharma et al. (2014) examined the liquid hydrogen mixture produced from waste plastic grocery bags

through the pyrolysis process. The product consists of paraffinic hydrogen (96.8%), olefinic hydrogen (2.6%), and aromatic hydrogen (0.6%), respectively. The pyrolysis oil boiling point range is 290–340 °C, the heating value is 46.18 MJ/kg, and it is more than conventional diesel fuel. The experimental studies concluded that pyrolysis blended diesel is suitable for conventional diesel engines. Kalargaris et al. (2017) studied that waste plastic can be a renewable energy as it has higher heating value. It can be converted to useful oil by pyrolysis process and utilized in an internal combustion engine to create mechanical power and heat. The oil is produced by fast pyrolysis method, and the properties of this oil are similar to the diesel oil. Pyrolysis oil derived from plastic was used as an additive to diesel and operated on advanced injection timing in diesel engine resulted in the brake thermal efficiency and emissions all are improved.

## **11.3 Thermochemical Conversion of Wastes and Its Pollution Formation**

### ***11.3.1 Impact of E-waste and Biomass Incineration***

The consumption of plastic has been increasing quickly in the last few years due to its lightweight, their capability to be easily formed, and noncorrosive behavior. These excellent properties are replacing the importance of the metals and wood. The global yearly consumption of plastics in the 1950s has been amplified about 20 times to nearly 100 million tons from 5 million tons (Syamsiro et al. 2014b). The e-waste contains lots of different constituents and elements, creating an intricate heterogeneous waste containing plastics, metals, and ceramics. Conventional recycling of e-waste (i.e., separating, shredding, and sorting) generates a residual material that still contains valuable metals, which often turns into a landfill Cui and Forssberg (2003). Different types of plastics were found in the examined electronic equipment rendering to Wang and Xu (2014b) as reported that the dominant polymers contained were high impact polystyrene (HIPS), polypropylene (PP), polycarbonate blends (PC/ABS), polystyrene (PS), and acrylonitrile–butadiene–styrene (ABS). With regard to large refrigeration and air conditioning appliances, cathode ray tube televisions and monitors had the minimum numbers of various polymers, with up to about 11 different types, while printers, typewriter equipment, and central processing units have 14 different polymers according to Vilaplana and Karlsson (2008). In the small electronic equipment case, Dimitrakakis et al. (2009) found the number reached 20 different types. Moreover, metals, color additives, and halogenated flame retardants were also found in electrical and electronic equipment.

Besides with this unusual kind of materials, the various additives (i.e., inorganic and organic) are as well added to polymeric plastics, which are often harmful substances, can change the properties of the material such as melting point, color,

density, and flammability, for legal, cost and/or design purposes. These artificial additives may be dyes (e.g., Cd, ZnO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>), halogenated flame retardants (often chlorinated/brominated organic compounds added with Sb<sub>2</sub>O<sub>3</sub> or polychlorinated biphenyls), and several plasticizers or stabilizers (e.g., compounds of Cd, Ba, Pb, Zn, and Sn, or polychlorinated biphenyls) (Erickson and Kaley 2011). Incineration and gasification will result in emissions of hydrocarbons, brominated dioxins, heavy metals, and polyaromatic hydrocarbons. Widmer et al. (2005) said that recycling of e-waste also causes environmental problems about the presence of various nonhalogenated and halogenated flame retardants. Yang et al. (2013) investigated that dehalogenation has become an essential topic in the recycling of e-waste plastics using pyrolysis. E-Waste plastics have been a significant ecological problem because these polymers usually comprise of toxic brominated/chlorinated flame retardants which might cause severe ecological contamination, specifically the formation of hazardous substances like polybrominated dibenzodioxins/furans. According to Rahaman et al. (2001), burning of e-waste plastics will result in emissions of hydrocarbons, brominated dioxins, and heavy metals.

Furthermore, heavy metals such as lead, copper, and mercury present in the e-waste lead to pollute the environment and ecological system and cause the serious health hazards to humans. Most of electrical and electronics devices contain hazardous elements such as lead, brominated flame retardants (BFRs), polyvinyl chloride (PVC), cadmium, chromium, mercury, and beryllium. The significant quantity of lead is found in cathode ray tube which is commonly used in computer monitor, and television screens use CRTs. Continuing usage of these materials may affect the human organ systems like nervous and endocrine systems, bones, reproductive, and kidney. Moreover, among these, few of them are highly carcinogenic. Improper disposal of e-waste along with domestic waste (landfilled instead of recycling/incinerated) without any control will pollute the soil, air, and water and create the long-lasting effect on the environment (Needhidasan et al. 2014).

At the point when biomass is burned, their harmful constituents are freed into breathable air discharges and the dangerous fiery remains debase groundwater. The dumping of incomplete incineration ash on landfills is riskier due to the presence of poisonous content. The water is used to filter this unwanted content. Incinerator clinker has been advanced for such applications as fixings in bond, fill for recovering mines, compost, charcoal, mechanical tile, and street base. These are riskier than landfilling, bringing sully nearer to where they can hurt individuals (Saidur et al. 2011) incineration is a waste treatment process that includes the ignition of natural substances contained in biomass materials. High-temperature waste treatment and incineration are called thermal treatment. Incineration of biomass materials converts into ash, flue gas, and heat. The flue gas carries the solid form of ash which is an inorganic component of the biomass. Before they are exhausted to the atmosphere flue gas must be cleaned. In some cases, electric power is generated by using the heat generated in the incineration of biomass (Fytili and Zabaniotou 2008). Incineration with vitality recuperation is one of a few waste to vitality (WtE) advances, for example, gasification, pyrolysis, and anaerobic processing.

Working principle of incineration and gasification remains the same. The main product from the gasification is the combustible gases (Fytli and Zabaniotou 2008). So, the best alternative is to convert the waste into the most valuable products with the help of thermal conversion processes such as pyrolysis and gasification.

### ***11.3.2 Pyrolysis of E-waste and Biomass***

Advanced technologies of thermochemical processes cover a widespread of modern innovations and produce either petrochemical feedstock or fuels. Recent days, thermolysis or pyrolysis (thermal cracking) is gaining renewed attention, like the fact that the added value of petroleum fuels and its valuable potential products from e-waste plastics and biomass.

#### **11.3.2.1 Conventional Pyrolysis Techniques**

Investigation on pyrolysis process has been developed by means of numerous kinds of conventional heating mechanism. The conventional heating mechanism is tubular or fixed bed reactors melting containers, blast ovens, and electric and gas heaters. In this mechanism, thermal energy is supplied externally and heats all the substances inside the reactors. In this circumstance, heating is not entirely directed to the substantial and these outcomes in lowering the efficiency of the process (Lam and Chase 2012). So, these processes are used for the pilot production. Current pyrolysis technique has numerous advantages over incineration and steam reforming technique and shows high potential in the field of waste energy recovery. However, there are so many challenges associated with pyrolysis techniques. Engine oil with less thermal conductivity range from 0.15 to 0.30 W/mK requires more processing time for pyrolysis to occur. In electric pyrolysis, the external source is applied which heats up all the substance including the chambers; this results in overall energy losses and formation of toxic compounds (PAH) (Domeño and Nerín 2003) and char (Ramasamy and T-Raissi 2007), which results in coking and fouling of the system. Besides, in conventional way, pyrolysis process distributes the heat in an uneven way, which led to poor control over heating process, and final pyrolysis process depends on the actual process condition applied on the waste materials (Lázaro et al. 2000).

#### **11.3.2.2 Microwave Pyrolysis**

Pyrolysis occurring in the absence of oxygen is thermal decomposition procedure to extract liquid oil, gaseous fuel, and solid char (Demirbas 2004b). The yields of these three products vary according to the variation of operation parameter (Bridgwater et al. 1999). There are various methods available for heating the

wastes. Among them, conventional heating and microwave heating are conducted. Real-world wastes can be treated very efficiently in microwave pyrolysis as compared to the conventional pyrolysis. In traditional pyrolysis technique, the heating mechanism is less efficient and slower as it is based on conduction and convection whereas, in microwave pyrolysis due to the diffuse character of the electromagnetic field, it heats all the substances equally. Thus, microwave pyrolysis provides equal distribution of heat and efficient heat transfer and heating methods can be controlled easily. It only heats the dipole material. So, the hotness was created in the mark substantial and the efficiency of the process is higher than conventional heating (Lam and Chase 2012).

Minkova et al. (2001) observed that microwave assisted pyrolysis offers an alternative view in the heating of the molecule where the electromagnetic field infiltrates and strongly collaborates with the dipoles arrangement. Because of the high preference of water atoms with microwaves, humidity content inside a particular biomass molecule is focused explicitly by accidental microwaves. Microwaves evaporate humidity in the deepness of the molecule, before volatilizing natural substance. The mist produced is quickly discharged into the surrounding zone, clearing volatiles, as well as making special diverts in the carbonaceous strong that expansion its absorbency. Thus, supports the arrival of volatiles at small temperatures, and consequently, its response with the mist delivered which primes to partial oxidation and creation of perpetual gases ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ).

Microwave pyrolysis has the advantages in the recycling treatment of different wastes, and some of the characteristics of the process include an increase in the chemical reactivity, high-temperature capabilities, in situ treatment of wastes, fast heating, waste volume reduction, etc. Handling of domestic and hazardous industrial waste and nuclear waste can be done by microwave heating. Microwave technology can be applied for control of CFC, methane, and greenhouse gases via microwave catalysis reactions. Wastes which cannot be burned such as concrete, ash, etc., that mostly contain dialectic material can be melted by microwave irradiation (Fernandez et al. 2011). The heat is making its way from the outer most layer to the innermost layer in conventional heating. The microwave heating is not the same as conventional heating. It is basically conversion of energy, not a heat transfer. Microwave can penetrate materials and deposit energy. In microwave heating, electromagnetic energy is transferred to thermal energy. So, the heat generation is done for the whole volume of the material. Microwave heating recognizes the heterogeneous reactions, and conventional heating helps in homogeneous reactions (Zhang and Hayward 2006).

It is observed by Menéndez et al. (2002), Domínguez et al. (2007) that microwave pyrolysis is used to obtain greater gas yield and lesser carbonaceous residue. That demonstrates the efficiency of microwaves in heterogeneous processes. At the higher temperatures, the heating method has the least differences. So, in the case of microwave heating, at lower temperature also, the efficiency is higher (Dominguez et al. 2008). Microwave heating has higher heating rates because no time is wasted in heating the surrounding area. The rate of heating influences devolatilization

(high heating rate improves devolatilization), the residence time of volatile (higher the rate, shorter the time). High heating rate gives high liquid yield and deposition of refractory material is reduced on the inner surface (Allan et al. 1980). If a material has a significant moisture content, microwave pyrolysis shows a unique pattern in the heating process of particle. Water molecules have good harmony with microwaves. The steam generated, by the vaporization of moisture in the core of the particle, is swiftly exited into the adjacent area. It not only sweeps vaporescent but also makes favorable channels in the solid which increases the permeability that favors the liberation of vaporescent at low temperatures (Minkova et al. 2001).

### 11.3.2.3 Challenges of Energy Recovery from the Pyrolysis

Biological, thermal, and other treatments are the promising technologies widely used to convert and recover energy from waste materials. Carbonization, pyrolysis, and gasification are called as thermal treatment process except for incineration process (Mohan et al. 2006). Majority of biomass energy is produced from green wastes (64%) and solid waste (24%), and remaining are agricultural waste and landfill gases (Demirbas 2000). Important chemical properties for waste treatment include elemental analysis, pyrolysis product, higher heating value, heat of pyrolysis, and heating values of char and volatiles. Some of the properties vary with species concentration, growth, and combustion environment. High moisture content in the biomass affects the pyrolysis process and the end product of pyrolysis. The calorific value of the bio-oil is greatly influenced by the moisture content of the biomass feedstock. In general, moisture content below 15% is processed in the pyrolysis process (Jahirul et al. 2012). Hence, drying process is carried out before pyrolysis. In contrast, high temperature in the drying process results in thermal oxidative reactions. Thermal stability of biomass was affected due to oxidative reaction which results in lower heating value and lower flame temperature (Dobele et al. 2007). Green waste decomposition can be characterized by particle size, specific gravity, ash content, element content (C, H, O, and N), structural content (cellulose, hemicellulose, and lignin), and extractive content. Char is formed due to the presence of inorganic compounds (Environmental Protection Agency 2007). Heat content in green waste is greatly influenced by the presence of organic compounds. Extractive content increases the higher heating values of the wood fuels.

Microwave pyrolysis produces more H<sub>2</sub> and CO compared to conventional pyrolysis process which is called as syngas (Huang et al. 2008). Polycyclic aromatic hydrocarbon produced also less in the microwave pyrolysis. The yield of pyrolysis oil and syngas is 8.52 and 73.26 wt%, respectively, which are higher than that of the conventional pyrolysis process. Simpler constituents are produced in the bio-oil from microwave. The syngas and methane gas produced in microwave pyrolysis are 65.2 and 22.41 and 30% higher heating values than pyrolytic gas from conventional method (Shi et al. 2014). There is a relationship between microwave power and calorific value on the solid residue. Caloric values of solid residues ranged from 18.51 to 19.66 MJ/kg are recorded when microwave power was 200–350 rpm,

which is higher than that of rice straw (15.26 MJ/kg). Calorific value of the residue decreased from 17.44-16.78MJ/kg during microwave pyrolysis process with the power of 400-500 W due to the removal of volatile content. Microwave power is high some of the fixed carbon can be pyrolysis and microwave upgraded pyrolysis has demonstrated its potential as an elective strategy for biomass transformation (Huang et al. 2008).

#### 11.3.2.4 Effect of Pyrolysis and Its Pollution Formation

Numerous amounts of studies were carried out to study the thermal decomposition of e-waste plastics printed circuit board and analyze the product obtained, but few of them reported the toxicity of the gaseous product evolved during the process. There could be a chance of brominated substances and furnace or other by-products containing TBBPA emission during the combustion and pyrolysis process. More attention required for pyrolysis of hazardous emission (EPA 2008). Limited research works have been carried out on PBDD/Fs (brominated dioxins and furans) emission during the combustion and pyrolysis of hazardous wastes (Ortuño et al. 2014; Duan et al. 2011). Further research work is necessary to find the influence of metals and brominated components in the emission of halogenated pollution in the e-waste plastics pyrolysis and combustion.

At elevated temperature, the gaseous product can be varied greatly, which contains methane, ethylene, benzene, toluene, acetylene, carbon oxides, and other hydrocarbons. However, ploy cyclic aromatic hydrocarbons (PAHs) were also formed at elevated temperature in the pyrolysis, and it was represented by non-desired pollution. The higher PAH pollutants formed for the different hazardous wastes above 850 °C of the pyrolytic temperature (Conesa et al. 2009). A relatively higher naphthalene yield or emission factor can be noticed at the same temperature. Nevertheless, no research work has investigated the formation of pollutant emissions resulting from the thermal treatment of substances combining biomass and metal-free wastes. Only limited work has analyzed the pollution formation of biomass and other kinds of municipal solid waste during the pyrolysis process (Soler et al. 2018). Maasikmets et al. (2016) reported that the combustion of municipal solid waste results in high emission of PCDD/Fs and hexachlorobenzenes (HCBs). Edo et al. (2017) assessed torrefaction of municipal solid waste combined with wood pellets and waste wood emits the PCDD/Fs. Lundin et al. (2013) studied the organic pollutants (POPs) emissions formation and reduction of persistent during the biomass combustion with waste products from paper industry and pulps. The total yield of chlorinated benzene for WCB sample is varied from 0.01 to 17 mg/kg, however for NMF-WCB sample, the mono-, di- and trichlorobenzene is varied from 0.42 to 34 mg/kg.



### ***11.3.3 Thermochemical Reactors for Gasification of E-waste and Biomass***

Presently fossil fuels in power industries, as well as automobile industries, are used widely but at a cost of damaging the environment by adding more and more deposited carbon into the atmosphere. Biomass gasification has the potential to convert renewable biomass solid waste into combustible gases which can be used to power those industries. Many countries including India are trying to combine the use of surplus biomass in power industries and started integrated gasification combined cycle method.

The technologies associated with plastic gasification are essentially those already established for the gasification of other feedstock, such as the coal and biomass. However, the plastic characteristics include: high volatility, sticky behaviour, low thermal conductivity and tar formation are the major challenges in the conventional gasification techniques (Lopez et al. 2018). Gasifier design for handling plastics should have the following features: (i) high heat transfer rate for plastic depolymerization, (ii) operating conditions that are controlled in a better way, and (iii) appropriate retention time for cracking of tar (Lopez et al. 2018). The main biomass gasification technologies are updraft, downdraft, cross-draft, fixed bed, and fluidized reactors (Sansaniwal et al. 2017). Gasification of plastic is very difficult in updraft and downdraft gasifiers. fluidized beds have special features and therefore widely used in gasification of plastic (Wilk and Hofbauer 2013). Gasifier reactors are used to generate heat from the thermochemical reactions to produce the mixture of combustible gases for power generation. Gasifiers are mainly classified based on bed and flow. On the basis of bed, they are classified as fixed and fluidized bed. Whereas on the basis of flow, they are classified as updraft, downdraft, and cross-draft flow gasifier. For example, the fixed bed reactors are used with downdraft gasifier.

#### **Fixed bed gasifier**

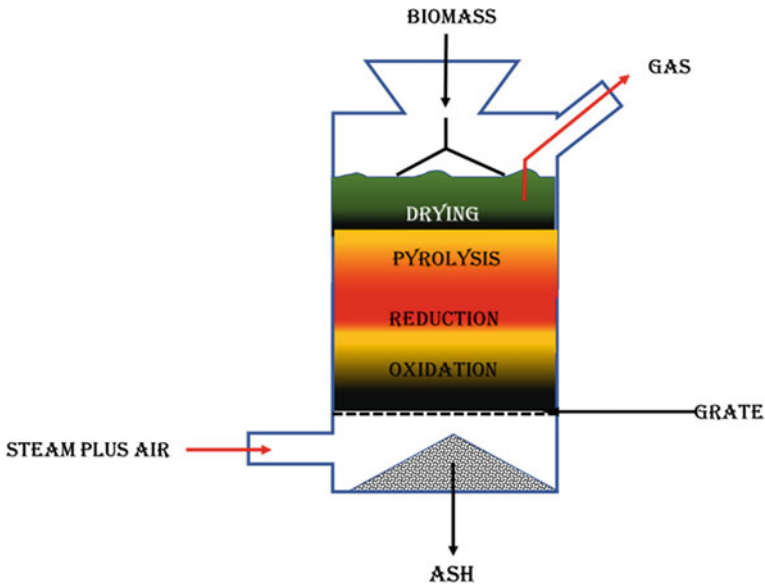
The usage of fixed bed gasifier in plastic gasification processes is associated mainly in their design, operation and limited investment cost, poor heat transfer, limited gas to solid contact, continuous operation. These are challenges which are to be rectified for implementing the process (Friengfung et al. 2014). Very few studies have been carried out in the fixed bed gasifier with the co-processing of plastic waste with biomass (Straka and Bičáková 2014). Burra and Gupta (2018) examined gasification of biomass with plastics wastes. Polycarbonate, polyethylene terephthalate, polypropylene, and pine wood are gasified in their study and found that co-gasification led to enhance H<sub>2</sub> production up to three times the individual gasification with no loss of carbon conversion. Ahmed et al. (2011) investigated coprocessing of mixture of wood chips and polyethylene feedstocks in a fixed bed reactor at 900 °C. Moreover, they studied the synergistic on hydrogen yield and gasification efficiency of biomass and plastic wastes. The optimum plastic content in the feed was evaluated as 60 and 80% only.



Parparita et al. (2015) investigated polypropylene and biomass waste composites in a dual-fixed bed reactor in the ratio of 0.5 each with steam as a gasifying medium in the temperature range of 700–850 °C with iron cerium iv oxide (Fe–CeO<sub>2</sub>) as a catalyst. 2.55 m<sup>3</sup>/kg of gas yield is reported with gas composition (% vol.). Gas composition is hydrogen—40, carbon monoxide—5, carbon dioxide—16, methane—6, and with the heating value of 35.5 MJ/m<sup>3</sup>. Ponzio et al. (2006) investigated updraft fixed bed gasifiers (60 kg/h) using biomass (0.45) and waste polyolefin (0.55) with air as a gasifying medium operated in the temperature range of 800–930 °C with ER of 0.19–0.24. The gas yield of 2.6–3.4 m<sup>3</sup>/kg was reported with gas composition (% vol.) of H<sub>2</sub>: 10–15, CO: 15–14, CO<sub>2</sub>: 8, CH<sub>4</sub>: 6–5, tar content reported to be high in the range 11.2–22 g/m<sup>3</sup>. He et al. (2009) examined the waste polyethylene in a fixed bed reactor (0.3 kg/h) using nickel aluminum oxide as a catalyst (Ni/γ-Al<sub>2</sub>O<sub>3</sub>) with a standard pressure of 1.33 operated in the temperature range of 700–900 °C. The gas yield is varied from 1.22 to 2.04 m<sup>3</sup>/kg and is reported with gas composition (% vol.) H<sub>2</sub>: 17–37, CO: 20–27, CO<sub>2</sub>: 35–21, CH<sub>4</sub>: 21–10 and higher tar content of 13–106 g/m<sup>3</sup>. The lower heating value reported in the range is 11.3–12.45 MJ/m<sup>3</sup>. Moreover, compared to fixed bed, research activities in plastic gasification are usually carried out in the fluidized bed gasifier reactor (Hackett et al. 2012).

### 11.3.3.1 Updraft Gasifier

In updraft gasifiers, steam, oxygen, and air may be used as a gasifying agent; it is introduced at the bottom of the reactor for the interrelation with the biomass feedstock which is fed in the top of the reactor. The reaction bed is supported with metallic grate that is provided in the bottom of the reactor as shown in Fig. 11.1. The producer gas is drawn at the upper side with high calorific value (Pereira et al. 2012). The particle size used in these gasifier ranges from 2 to 50 mm. The operating pressure is in the range of 0.15–2.45 MPa and retention time is 15–30 min (Malik and Mohapatra 2013; Mondal et al. 2011). To avoid overheating inside the reactor and also to get quality end product, evaporation of steam is carried out into the combustion zone. This type of gasifiers has the highest thermal efficiency due to the passage of hot gases through the reactor, which leaves the gasifier unit at low temperature (Anis and Zainal 2011). Due to an elevated temperature which is achieved in the bottom of the reactor, low ash content is produced nearly equal to ash discharge point (Mandl et al. 2011). The high tar content is produced from the gasifier and is not suitable for engine applications (Brachi et al. 2014). Gunarathne et al. (2014) experimented with a pilot scale updraft gasifier using biomass pellet as feedstock and produced high syngas with a heating value of 7.3–10.6 MJ/N m<sup>3</sup>. A countercurrent gasifier has four distinctly defined zones starting from bottom partial oxidation zone at the bottom then reduction zone followed by pyrolysis then at the top is drying zones, studied by Huang et al. (2017). The combustible gases produced in the reduction zone leave the gasifier as a mixture of gases with the volatiles produced in the pyrolysis zone and steam in the



**Fig. 11.1** Schematic view of updraft gasifier

drying zone. The producer gas produced in updraft gasifier is rich in hydrocarbons and has a higher heating value which makes it more suitable for heating applications, for example, in industrial furnaces but for generating electricity the producer gas needs to be thoroughly cleaned. The advantage of updraft gasifier is ease of construction and high thermal efficiency. The sensible heat is recovered by direct heat exchange with help of entering biomass feed, which is then dried and pre-heated, and undergoes pyrolysis before entering gasification. The excess amount of tar presence in raw gas is the disadvantage of updraft gas producer. Therefore, substantial cleanup is necessary for the fuel gas if further processing is to be carried out (Samiran et al. 2016)

### 11.3.3.2 Downdraft Gasifier

In downdraft gasifiers, biomass feedstock material is passed from the top whereas air is passed downward and producer gas leaves from the bottom of the gasifier. Because air is passed in the same direction as that of biomass feedstock, it is also called cocurrent gasifier. There are four zones, namely, drying, pyrolysis, oxidation, and reduction as shown in Fig. 11.2. Oxidation zone is below the pyrolysis zone and reduction zone is below the oxidation zone, as studied by Khosasaeng et al. (2017). A clean mixture of combustible gases in the exit stream is obtained. Its main advantage is that the producer gas is produced with low tar content formed during devolatilization of the material which is thermally cracked (Buragohain et al. 2010).

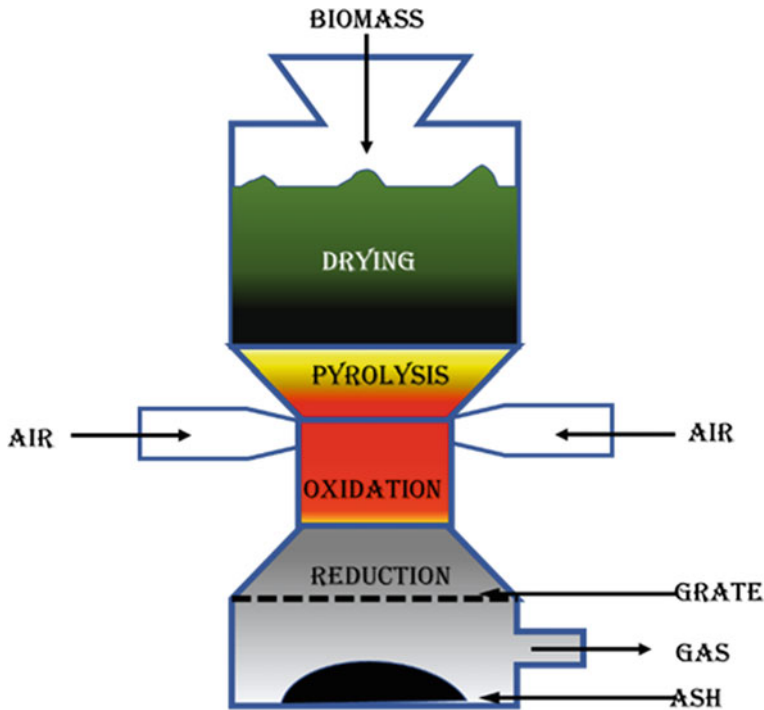


Fig. 11.2 Schematic view of downdraft gasifier

Lower tar content is suitable for gas engines and turbines (Hebden and Stroud 1982). The position of the oxidation zone is thus a critical parameter in the design of downdraft gasifier. The feedstock requirement for gasifier reactor is associated with the size of the throat. The particle size of the feedstock ranges in 1–30 cm (Couto et al. 2013). The downdraft gasifier is not appropriate for large-scale plants because of the throat size limitation for the scale-up process (Martínez et al. 2012). The feedstock material used for downdraft gasifier should have low moisture content up to 30% and low ash content of less than 1% weight (Boateng and Mtui 2012). The downdraft gasifiers are suitable for the conversion of biomass to high volatile fuel for the generation of power (Prasad et al. 2014). The elevated temperature at the exit of the gasifier in the downdraft gasifier enables low tar content of about less than  $0.5 \text{ g/m}^3$  (Olgun et al. 2011). This lower tar content makes it advantageous for electricity production by using internal combustion engine (Martínez et al. 2012). Oxidation zone with high temperature results in melting of some ash constituents (Di Blasi and Branca 2013). Syngas is produced in the downdraft gasification in the range of  $4\text{--}5 \text{ MJ/N m}^3$  with residence time of around 900–1800 s with carbon conversion efficiency of around 93–96% (Huang et al. 2017; Siedlecki et al. 2011).

### 11.3.3.3 Cross-Draft Gasifier

Cross-draft gasifier has some advantage over updraft and downdraft gasifier, but they are not of superlative type. It is one of the simplest types of gasifier where biomass fuel enters from the top of the reactor followed by drying, pyrolysis, oxidation, and reduction zones. Air may be used as gasifying medium enters through sides rather than from top or bottom as shown in Fig. 11.3. Less ash content is produced in the gasifier and has a separate ash pin, reduction zone hence reduces the biomass fuel used for operation (Srivastav 2013). The advantage of the cross-draft gasifier is a fast response to load, flexible gas production. They are unable to handle high tar content and small particle size biomass material. The carbon dioxide reduction is also poor in the cross-draft gasifiers (Anil 1986).

#### Fluidized bed

In fluidized bed gasifiers, the biomass feedstock is brought into an inert bed of sand, char, etc., or other fluidized bed. The biomass feedstock is fed into this fluidized bed depending upon the density and size of the biomass feedstock. Biomass feedstock is fed in two ways: one way is above the bed and other is directly into the bed depending upon how it is affected by the bed velocities, as suggested by Warnecke (2000). The process is normally carried out at a maintained temperature of bed media between 550 and 1000 °C. When the biomass feedstock is kept under such temperature conditions, the reactions in the drying zone and pyrolysis zone start and proceed rapidly, producing the gaseous components of the biomass feedstock at relatively low temperatures. The char which is remained after

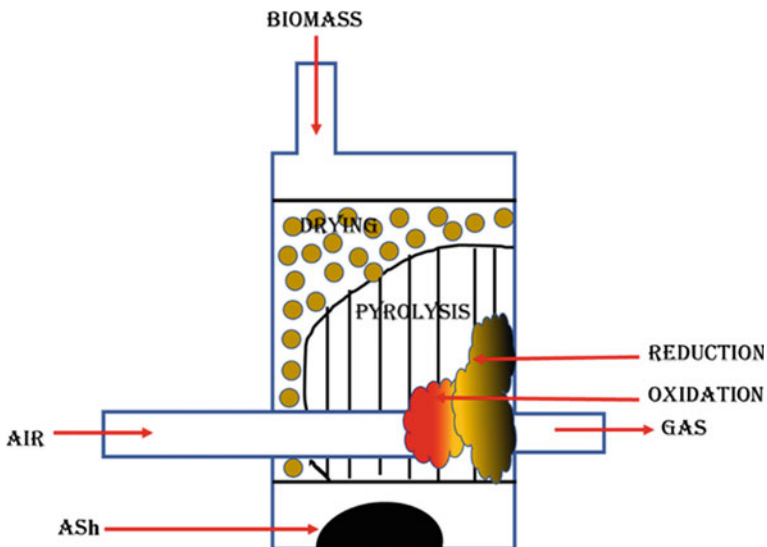


Fig. 11.3 Schematic view of cross-draft gasifier

pyrolysis zone is oxidized within the bed to produce the heat energy for other zones to continue the process like drying and devolatilization reactions.

Suda et al. (2010) suggested that the mechanism of fluidized bed gasifier is actually a hotbed made of sand particles which are continuously agitated by air that helps in producing more heat. The nozzles are located at the bottom of the bed for air distribution. fluidized bed gasifiers are having advantage on fixed bed gasifier because they produce more heat in short time with a uniform high-temperature bed of 800–1000 °C due to the abrasion phenomenon between sand particles and biomass. Generally, two kinds of fluidized beds have been utilized as a part of gasification specifically, bubbling fluidized beds and circulating fluidized bed (Molino et al. 2016). Plastic gasification generally preferred for bubbling fluidized bed. Even though, circulating fluidized beds have special features such as high yield and low tar content (McKendry 2002). Plastic gasification generally preferred for bubbling fluidized bed. The primary points of interest of bubbling fluidized reactor deal with high heat and mass transfer rate, better gas–solid contact, excellent control of temperature, and flexibility. This reactor is always operated with air as a gasifying agent when co-gasification carried out with biomass or coal (Martínez-Lera et al. 2013). Arena et al. (2010) investigated bubbling fluidized bed with a capacity of 100 kg/h using polyethylene as feedstock in sand bed material. The equivalence ratio of 0.2–0.31 and operating temperature of 845–897 is maintained which produced a gas yield of 3–4.3 m<sup>3</sup>/kg with gas composition (% vol.) of H<sub>2</sub>: 9.1–9.5, CO: 2.8–2.2, CO<sub>2</sub>: 9.1–10.4, and CH<sub>4</sub>: 10.4–7.1. Tar content of 81–160 g/m<sup>3</sup> is recorded with lower heating value of 6.3–7.9 MJ/m<sup>3</sup>.

#### 11.3.3.4 Challenges of Energy Recovery from Gasification

Although there is various technology available in the world to recover energy from waste matter, gasification has been developed as a capable method to establish ecological waste management scheme that will able reduce pollution in the environment and maximize the energy recovery from waste materials. The co-gasification of coal, plastics, and biomass has been recently focused in an effort to generate high calorific syngas from gasification technology. Kannan et al. (2013) investigated co-gasification blends of polyethylene and polyethylene terephthalate. Better cold gas efficiency and heating value have been produced from steam as a medium compared to polyethylene gasification with steam and air as a medium. By varying the blend ratio of feedstock material, it is likely to envisage quality of the syngas thus according to the application feedstock material is selected. Blending polyethylene and polyethylene terephthalate showed the optimistic effect on heating value and producer gas yield. The H<sub>2</sub>/CO molar ratio is a key parameter for using producer gas in several applications through proper selection of biomass feedstock and an oxidizing agent.

The integration of small-scale downdraft gasification system with internal combustion engines produces electricity and heat from the biomass waste. The biomass feedstock material used for the gasification is pellets of redwood having a lower heating value of 17 MJ/kg. The experimental result showed a maximum yield

of syngas of  $33.6 \text{ N m}^3/\text{h}$  has been reported in the gasifier. The maximum exergy and energy analysis of the integrated system have been found to be 15 and 32% from the thermodynamic analysis. Moreover, gasification system creates a bottom ash in a considerable amount that may be harmful to the atmosphere and safety issues if appropriate perseverance is not made. Along these lines, this work additionally centered around the reutilization of ash keeping in mind the end goal to diminish the earth and wellbeing concerns related with its transfer, making the general procedure all the more ecologically inviting. From elemental analysis, gasification with redwood pellets showed a considerable silica amount, influencing it to end up a profoundly potential hotspot for combining compound containing silica gel. The aluminum silicate compound of zeolite is formed from the hydrothermal reaction of bottom ash which can be effectively used as an adsorbent material.

Synthesis of zeolite using hydrothermal method is used in zeolite synthesis, and this method is used in the collection of ash from the redwood pellets gasification. 5 g of ash mixed in the ratio of 2:1 with 10 g of anhydrous NaOH and grounded into a fine powder with the help of mortar and pestle. The dry mixture is taken in an alumina crucible and placed in a tubular furnace at a temperature lying between 400 and 650 °C for 1 h and 30 min. The resultant mixture is once again grounded to a fine powder before mixing with a little amount of  $\text{NaAlO}_2$  and 90 ml of deionized water and stirring is done at an rpm of 500 (Hong et al. 2017). The resultant slurry mixture is then transferred to an autoclave which is made up of Teflon-lined stainless steel and kept in an oven at a temperature lying between 100 and 160 °C for a specified reaction time. After that, the reactor is allowed to cool sufficiently for a certain time in order to handle the slurry safely, and finally, it is to be filtered with vacuum unit and washing is done until pH of 7 or 8 is reached. The drying of the final product is carried out in an oven at a temperature of 100 °C overnight (Maneerung et al. 2018).

In order to evaluate the adsorption capabilities of prepared zeolites, a cationic dye which consists of an aqueous solution of methylene blue (MB) is used to perform the adsorption experiments. The batch type of adsorption experiments performed with original bottom ash and zeolite by using 25 mg of sample and 100 ml of a solution which consists of 60 mg of methylene blue. The continuous stirring of adsorption mixture was done at 300 rpm over a specific time period. From that point onward, a gathering of the supernatant was carried out at certain time interim and the color grouping remained was then analyzed by using UV-visible spectrophotometer (wavelength close to 664 nm). The direct relationship between methylene blue fixation and absorbance unit was built up utilizing standard arrangements arranged by the various weakening of the first methylene blue arrangement. The rate expulsion of color and the particular adsorption capacity,  $q_t$  (mg/g) were then ascertained utilizing the accompanying condition (Molina and Poole 2004).

### 11.3.3.5 Influence of Gasification and Its Pollution Formation

Gasification facilities share the natural issues as like those related with mass consume incinerators, including water contamination, air contamination, transfer of slag, and other side effects (Lata et al. 2006). Gasification process includes tremendous measures of water for cooling purposes and furthermore incorporates well-being, security, and scent issues. The last major natural effect of biomass vitality might be that of loss of biodiversity. Tar is the major problem associated with the biomass gasification process (Balat et al. 2009). During gasification, tars, antacid mixes, incandescent light, and overwhelming metals are discharged and can cause ecological and operational inconveniences (Arena et al. 2009). Asadullah (2014) reported that biomass gasification technology generates diverse kind of ecological effect and perils, for example, harmful, fire, blast, and natural dangers.

#### Air pollution

Biomass ash, dust, fly ash/char, and gaseous emission are released into surroundings as air pollutants during biomass gasification that leads to unpleasantly influence both condition and human well-being. The producer gas leaving the reactor will enter into an air pollution control (APC) system for post process gas cleaning. The wet scrubber system has successively achieved low emission standards during biomass gasification system (Bridgwater 1995).

#### Dust

Dust will be generated during feedstock preparation, handling, storage, and fly ash removal (Gunarathne et al. 2014). The treatment of strong materials is an infamous wellspring of airborne particles, particularly when the solids are dry and friable. A few kinds of gasifiers may deliver hot particles as a result of glitch or hardware issues. These may touch off combustible materials and cause a fire (Technical report Central Pollution Control Board 2008). Lata et al. (2006) announced that residue can cause lung harm, aggravation of skin and eyes and may frame hazardous blend with air. The gasifier should not create in excess of 2–6 g/m<sup>3</sup> of residue (Deutsche Gesellschaft für Sonnenenergie et al. 2005). Di Blasi et al. (1999) reported that the use of non-woody biomass in gasification results in high measure of sulfur, chlorine, and cinder, in contrast to gasification of woody biomass. Sulfur and chlorine have the few negative effects on condition (Sutton et al. 2001). Nitrogen and sulfur are available in a significant number of the results and the comparing oxides are created amid burning of the fuel gas; these oxides (NO<sub>x</sub> and SO<sub>x</sub>) can have a negative ecological effect.

#### Carbon monoxide poisoning

Carbon monoxide is a major constituent of producer gas and is the most widely recognized reason for gas harming. It is predominantly poisonous due to the

absence of color or smell. Carboxyhemoglobin (COHb) framed as 80–90% of consumed CO ties with hemoglobin, which is a particular biomarker of presentation in blood. Hemoglobin partiality for CO is 200–250 times that for oxygen. Epidemiological and clinical information show that CO from smoking and work related exposures ecological may provide for cardiovascular mortality and myocardial localized necrosis (Mishra et al. 2015).

Health and environmental effects associated with selected aromatic hydrocarbons (tar)

Output put gas from biomass gasification process is cleaned by water scrubbing. The developed organic compounds enter the cooling stream with flue gas dust particles. The disposal and treatment of this waste through gasification are tedious process due to the presence of toxic compounds. It will affect human health and the environment. The maize cobs are used as feedstock in downdraft biomass gasification process and the condensates were collected and cooled by producer gas and it was kept in cooler at about 2 °C for 24 h before analyzing with gas chromatographer. The chemical compositions of producer gas are 1,3 + 1,4-dimethyl benzene, naphthalene, toluene, benzene, ethylbenzene, and 1,2-dimethyl benzene. Among these, naphthalene and xylene concentration were found higher than permissible exposure limit (PEL), which are hazards to both human health and surroundings, but the concentration of benzene, toluene, and ethylbenzene was below the permissible limits (Menya et al. 2014).

## 11.4 Factors Affecting Thermochemical Conversion Process

### 11.4.1 Factors Affecting Microwave Pyrolysis

The pyrolysis yield was varied depends on temperature, heating rate, residence time, and the addition of microwave absorber on the pyrolysis process. The following sections explain the individual factors and its effect on the pyrolysis process.

#### 11.4.1.1 Influence of Temperature on Pyrolysis Yield

Miandad et al. (2016) stated that pyrolysis of polystyrene waste at 400 °C for 75 min of reaction time yields 8, 16, and 76% of gas, char, and liquid oil by mass, respectively. Increasing the pyrolysis temperature to 450 °C increases the gas and liquid yield to 13 and 80.8% by mass, respectively, but decreases the char yield to 6.2% by mass. The optimum temperature and response time was found to be 450 °C and 75 min. higher temperature exhibits the formation of gaseous product due to secondary cracking and higher kinetic energy.



In the polyethylene pyrolysis, there was no wax produced above 600 °C related to the lower temperatures shown by Williams and Williams (1997). Lighter components were produced by breaking down the massive wax. The amount of gas increases with increase in the temperature. A wide variety of smaller organic molecules were generated due to high temperature which increases the gas formation as the molecules break down and secondary reaction (Miandad et al. 2016). The amount of oil and wax decreases with an increase in pyrolysis temperature. The increase in temperature above 800 °C promotes the secondary chemical reactions in the pyrolysis process which influence the formation of smaller chain hydrocarbons and hydrogen. The hydrogen and smaller chain hydrocarbons contain higher energy content (Calorific value) compared to longer chain hydrocarbons. Singh and Ruj (2016) also observed the same results where high temperatures result in the high formation of gas with an increased amount of smaller chain hydrocarbon compounds in the products. Adrados et al. (2012) found that the cracking reduces because of the residence time deficiency on increasing the temperature in the compounds and reactor as well as aromatic compounds in the form of wax having large molecular chains were obtained in oil product.

#### 11.4.1.2 Effects of Heating Rate on Pyrolysis Yield

The microwave heating and conventional heating are distinguished based on differential heating rates of the material being heated. Microwave heating shows a higher heating rate because microwave energy is transferred directly to the material by means of molecular interaction with the electromagnetic field, which does not waste time for heating the environment. Therefore, significant time and energy savings are achieved in microwave pyrolysis. High heating rates improve the devolatilization of material which decreases the conversion time. The residence time of volatiles is regulated by heating rate also. The shorter residence time, the faster the volatiles, and the higher heating rate reaches to the regions of external cold in bringing down the activity of vapor phase products belongs to secondary reactions which gives high liquid yields and decreased deposition on the char's internal surface of the refractory condensable material (Dobelet et al. 2007).

Slow pyrolysis process can be described with parametric conditions such as 400 °C of temperature and heating rate of (0.1–1 °C/s) with residence time of more than 30 min. The composition of slow pyrolysis product is found as 35% biochar (solid), 30% bio-oil (liquid), and 35% syngas (Marcilla et al. 2013). Demirbas and Arin (2002) stated that flash pyrolysis has the fast heating rates with the temperatures of (400–600 °C). Vapor retention times are typically under 2 s. Compared to slow pyrolysis, extensively less tar and gas are delivered. The circumstances under which the fast pyrolysis happens to result in the generation of low water and char content bio-oil, with the expanded energy esteem. Rapid cooling of the pyrolysis vapors provides the pyrolysis oil. Compare to conventional electrical pyrolysis, microwave

pyrolysis has higher heating rate, efficiency and provides uniform volumetric heating of the substances. The microwave-assisted pyrolysis increases the gas production and decreases the char formation due to hot spot formations (Appleton et al. 2005).

### **11.4.1.3 Effects of Microwave Absorber on Pyrolysis**

The pyrolysis process products can be altered or tailored by incorporating receptors in the material. Dielectric properties of product determine the heating mechanism of the process, so it must be considered, because all these factors play a role in interaction with volatiles (Dominguez et al. 2008). A spent catalyst can change over waste oil into diesel oil. Lesmana and Wu (2015) reported the pyrolysis of waste oils within sight of a spent impetus, and also the recovery properties of the spent impetus, for example, the sort of recovery (in situ and ex situ) and time and temperature for spent impetus recovery. The yield of pyrolysis oil was higher than 60% when waste oil was pyrolyzed at 370 °C.

The addition of proper susceptors in microwave method can increase the yield value of the liquid oil. Previous experiments conducted on pyrolysis of waste engine oil as observed by Tripathi et al. (2015) examined that yield of saturated hydrocarbons is 40, 55, and 50%, respectively, at the temperatures of 300, 400, and 500 °C, and also reveal that aromatic benzene derivatives are high content at the higher and lower temperatures and chain length decreases as temperatures increase. This shows the temperature at which the work should be carried on. It clearly shows that the temperature must be around 400 for maximum output of saturated hydrocarbons. Domínguez et al. (2006) study the effects of char and graphite on pyrolysis oil yield. It observed that the maximum yield was obtained in char as a receptor in microwave pyrolysis method as compared to graphite receptor. Moreover, it was noticed that graphite cracking the aliphatic chains and converted into lighter species. The rate of reaction depends upon the size and shape of the mesh (Hussain et al. 2010). On the other hand, Wan et al. (2009) studied the effect of different catalysts on microwave pyrolysis, corn stover, and aspen wood used as a feedstock in microwave pyrolysis. It was found that the catalysts to speed up the heating participate in the so-called in situ upgrading of pyrolytic vapors.

## **11.4.2 Factors Affecting Gasification**

### **11.4.2.1 Effects of Equivalence Ratio on Syngas**

The comparability proportion is the actual proportion of air to biomass, as for the stoichiometric requirements of biomass gasification (Mevisse et al. 2009). Narváez et al. (1996) reported that CO and H<sub>2</sub> divisions in syngas upgraded when equivalence ratio (ER) esteems were diminished. However, the yield of vaporous items will diminish as well when the ER is lessened underneath the limit, which is the

commencement of pyrolysis. Higher ER brings about the lower yield of CO and H<sub>2</sub>, with an expansion in CO<sub>2</sub>, which in turn diminishes the warmth substance of the Syngas. By differentiating, higher ER enhances the breaking of tar because of higher O<sub>2</sub> accessibility for unpredictable species to respond with. Be that as it may, an inconsequential impact of ER was found on nitrogenous items, amid gasification. Zhou et al. (2000) revealed a small increment in smelling salts (NH<sub>3</sub>) yield at a temperature of 800 °C, utilization of sawdust as the feedstock material when the ER was increased from 0.25 to 0.37. Gasification is ruled by the pyrolysis process having comparability proportion lower than 0.2 and ruled by ignition with identicalness proportion higher than 0.4.

#### 11.4.2.2 Effects of Biomass Size and Moisture Content

In fixed bed gasifiers, there is a constraint in measure related to the biomass (Kaupp and Goss 1981). For case, positive properties of maker gas are accomplished at the feedstock size of 1–2 cm amid peach pruning gasification (Yin et al. 2012). Hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) substance expanded with the reduction in the size of peach pruning. There is a perception that little size biomass fundamentally builds the vitality proficiency of gasification process (Alauddin et al. 2010). The small size biomass yields more producer gas as compared with bigger size biomass for specific gasification time. Warmth exchange region increments with molecule estimate lessening, in this way upgrades unstable, discharged amid pyrolysis process (Hernández et al. 2010). There may be a chance of high weight drop issue in the gasification of little size biomass and in addition high residue content in producer gas. The issue of inadmissible develop gasification bed in the reduction zone additionally emerge with little size and low-thickness biomass (Biagini et al. 2015). Homogeneity of biomass measure likewise influences the execution of gasifier. The proficiency of gasifier increments as expanding the level of homogeneity of biomass estimate (Belonio 2005).

In most fuels, there is little selection in wet content since it is decided by the fuels type, its origin, and treatment. It is fascinating to use fuel with low wet content as a result of heat loss thanks to its evaporation before the chemical change is appreciable and also the heat budget of the chemical change which impedes the reaction. For example, for fuel at the temperature of 250 °C and the exit temperature of raw gas from gasifier at 3000 °C, 2875 kJ/kg of heat is required for heating and evaporating the wetness. Besides, impairing of the heat budget of the gasifier, high wetness content conjointly develops a load on filtering and cooling the instruments with the increment in the pressure drop across these units owing to compressing liquid. Biomass with over 30% dampness content decreases calorific estimation of producer gas because of the inefficient process of pyrolysis during biomass gasification (Lata et al. 2006). Nature of producer gas in term of quality of heating value can be influenced by the dampness content of biomass. Biomass with high dampness content yields producer gas with low calorific value or heating values (Warnecke 2000). Warmth required for finishing pyrolysis process is

deficient in light of the fact that more warmth is consumed by feedstock for driving off dampness amid drying process. The maker gas from rice husk with dampness content of 15% has higher CO and H<sub>2</sub> rate than the maker gas from rice husk with the dampness of 30% (Mevisen et al. 2009).

#### 11.4.2.3 Effects of Gasification Temperature

The temperature of gasification temperature can be influenced by proportionality proportion. The gasification temperature can be influenced by proportionality proportion. Increase in temperature increases the proportion of proportionality due to the upgrade of the combustion procedure in the oxidation zone (Guo et al. 2014). The elevated temperature in gasifier is advanced tar splitting and improved endothermic single gasification rate, which helps in yielding producer gas with enhanced warming quality (Liu et al. 2012). The levels of ignitable gas are CO and H<sub>2</sub> increments with expanding gasification temperature (Wang et al. 2015). By and large, not surprisingly, the oxidation zone has the most elevated temperature among different zones, while the temperatures everything being equal amid gasification. The wavering happens because of the automatic nature of downdraft gasifiers (Balu and Chung 2012). For normally suctioned gasifier, air flow rate to the oxidation zone varies amid gasification which is relied upon bed porosity and suction fan limit. The variety of air flow rate modifies warm discharged amid oxidation process, therefore, gasification temperature swayed.

Temperature plays an important role in operating parameters, which puts an effect on the composition of gases and conversion of carbon throughout the gasification and oxidation reactions. Heating value, gas yield, the efficiency of cold gas, and finally yield of char and tar in the process of gasification are influenced by the temperature. This effect relies on the thermodynamic behavior associated with the reactions and the balance between exothermic and endothermic reactions (Lata et al. 2006; Belonio 2005; Basu 2010; Wood and Branch 1986). There is a restriction to how high the temperature for the gasification process can go up to (tolerable level) due to its impact upon (1) the unstable issue content in fuels; (2) materials of development utilized as a part of the gasifier; (3) the creation of undesired-capable gases, for example, NO<sub>x</sub>; and (4) its impact on the fiery debris combination (Warnecke 2000; Paethanom et al. 2012; Kim et al. 2014). High gasifier working temperature has been accounted for reasonable high biomass carbon change which eventually lessens the tar substance and delivers more flammable gases (Paethanom et al. 2012). Hydrogen focus has been seen to be expanded at first and after that steadily diminished with the expansion in the temperature.

#### 11.4.2.4 Effects of Biomass Consumption Rate

The rate of biomass utilization is influenced via air stream rate and estimation of biomass. The utilization rate of biomass is corresponding to air current rate and

conversely corresponding to the biomass measure (Tinaut et al. 2008). As the flow rate of air increments, accessibility of oxygen expands which enhances the rate of oxidation. This implies biomass utilization rate heightens with expanding air flow rate. The littler size of biomass upgrades the process of oxidation because of bigger add up to response zone per unit volume of biomass.

## 11.5 Synthesis of Microwave Absorber from Waste Residues

### 11.5.1 *Microwave Heating of the Carbon-Based Material*

Based on the existing studies, the microwave heating of carbon-supported materials may be categorized into two classes named as solution heating and stable solid heating. The section of microwave absorber determines the type of heating required. Solution heating is characterized by means of microwave-assisted organic synthesis (MAOS), and the opposite is stable solid heating, where the key objectives are stable carbons and metals. Solution and stable heating fluctuate to a great extent due to the additional reactions that take place during the heating process. Microwave heating is especially associated with the dipole rotation of polar solvent molecules. Conversely, freely rotatable dipoles are not available in carbon-rich solids. Therefore, the movement of electrons generates heat either through Joule heating within the grain or arc generation at segment boundary barriers (Kim et al. 2014).

Microwave heating involves with dipolar polarization and ionic conduction of the microwave absorbing material. Water and major solvents like dimethylformamide and ethanol tetrahydrofuran have dipole substance in nature (Kim et al. 2014). The dipoles are rotating when the microwave is applied, and the rotation will delay to the modification of electrical field which is the reason for heat dissipation due to friction. Further, the solution is additionally heated by ions exist in the ionic conduction phenomenon. In the case of solids supported by carbon does not contain free rotary dipoles, so that microwave heating cannot be explained beyond the limit due to the interaction between microwaves and electrons is critical. The Maxwell–Wagner–Sillars polarization [MWS] called surface polarization is the main cause of solid heating supported by carbon. Moreover, semiconductivity function is obtained in the carbon-supported solids due to delocalized pi electrons inside the graphitic vicinity (Wallace 1947; Ganguli and Krishnan 1941). Thus, carbon-supported solids heated by Joule heating play important role in the microwave phenomena. In these cases, in contrast to solution heating, microwave heating could be very effective and selective due to the fact the target material entirely absorbs the microwave power.

Conducting materials, for example, metals with redirect microwaves and results that unable to execute the conversion of microwave vitality to heat (Clark et al. 2000). There may be a variation in the response of bulk metals and metal

nanoparticles to microwaves. In the microwave process, the skin depth can be a quantity of the depth of microwave penetration during which the incident radiation decreases to 36.8% of its incentive from the surface (Metaxas and Meredith 1983). If the skin depth value of a material is less than its thickness that begins the microwave heating on its surface. Particle size observation studies depicted that skin depth value of bulk materials is within the order of microns (Mishra et al. 2006). However, micro- and nanometal powders well interact with microwaves pores since the pores and skin depth of the metals will increase with a decrease in its particle size (Gupta and Eugene 2011). The heating of bulk metals with the aid of microwaves is not an easy task, and it is likely to heat nanosize metal powders.

In the heat transfer concerns, the microwave is an attractive susceptor. The literature study illustrated that SiC susceptor provides the heat to the core metal through the conduction and radiation (Janney et al. 1992). It denotes that effective utilization of microwave absorber which results in lower heating potency. The effectiveness may be further enhanced by a selection of suitable microwave vessels. Especially the vessel materials itself has a tendency to convert the microwave into heat means, the vessel plays a vital role in hybrid microwave heating. Heating materials comprise of polar molecules are used for microwave heating which promotes higher heat transfer characteristics with cost economic. In addition to this, the materials with a high dielectric loss factor may be applicable to various processes in view of microwave heating. Among the existing absorber, carbons are excellent microwave absorbers which would be created or changed by microwave heating. Furthermore, carbon materials have a potential capability to convert microwave strength into heat, and so it would also act as a microwave receptor to indirectly heat the material which is transparent to microwaves. In continuation with this, carbon materials could be used as microwave receptors in different process applications such as pyrolysis of organic wastes, soil remediation, catalytic heterogeneous reactions, and biomass. The dielectric loss tangent of different carbons is greater than the loss factor of distilled water (distilled water  $\tan \delta = 0.118$  GHz and 298 K) and it is lesser than coal (Menéndez et al. 2010).

Among the different carbon-based materials, graphite is a strongly suggested microwave absorbing substance that can withstand higher temperatures and also gives off higher heating rates. Graphite with carbon substances are evident to produce a microplasma but at the same time as they are heated in presence of microwaves (Menéndez et al. 2010). The microplasma has generated while adding carbon-based material like graphite. During this process, the small dimension (10–1000  $\mu\text{m}$ ) plasma was generated because several electrons might jump out of the material because of their higher kinetic energy. The ionization of the atmosphere due to the arcing that visualizes the spark output for a short time and a small spatial region. However, during this process, few more electrons may come out from the core materials. This is due to driving force existed in the electrons caused by higher kinetic energy. If it is continuous, ionizing the electrons which are the so-called micro-plasma, they exist for a short period of time. This could be visualized by sparks or arc formation existed during the process (Menéndez et al. 2010, 2011), although graphite or other carbon items were used for supporting the microwave

pyrolysis (Menéndez et al. 2004; Domínguez et al. 2005). Considering the microplasma, it has a behavior of arc formation during the pyrolysis which could adversely affect the equipment. In order to avoid this circumstance, it is advisable to use the graphite with other substances to enhance the heating effectiveness without arc formation. However, graphite mixed with different materials, which requires an in-depth examination throughout the microwave heating. A high-grade graphite powder combined with either microwave absorbing material or non-microwave absorbing material can be used for creating the crucibles. This would increase the heating value of microwave heating. Several studies reported about microwave engrossing materials named as char or graphite to SiC that increase the conversion efficiency of microwave to heat (Revesz et al. 2002). The alumina or zirconia can be combined with silicon carbide for executing microwave heating at different temperature (Vandervoort et al. 2007; Fall and Shulman 2003). However, there is no report existing for investigating the microwave heating of mixtures including graphite.

### ***11.5.2 Synthesis of Carbon-Based Material from Ash and Char***

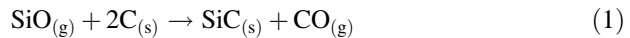
Carbides are widely known for its stability in thermochemical process with high wear resistance and hardness among the all other modern ceramics (Martínez et al. 2006; Sun and Gong 2001). The silicon carbide (SiC), non-oxide ceramics can be formed as whiskers or fibers by different thermal processes (Martínez et al. 2006; Silva and figueiredo 2001). The two primary methods followed in this process to make silica carbide are (i) mixing silica and carbon at 1300–1500 °C inert atmosphere (Martínez et al. 2006; Freitas et al. 2004) and (ii) mixing of carbon and silica at 1300–1550 °C in the chlorhydric atmosphere (Martínez et al. 2006). Another way widely known is thermal decomposition (pyrolysis) in a controlled atmosphere of rice husk (RH), comprises above 90% of silica. The fine SiC whisker or elements forms in length between 10 and 80 μm and diameter between 0.5 and 1 μm can be obtained from this process (Kirk-Othmer 1996; Gorthy and Mukunda Pudukottah 2004). Vapor–liquid–solid (VLS) process was also used to produce the SiC whiskers in the presence of transition metals such as Fe, Co, and Ni as catalysts. In this process, the vapor is transported to the liquid catalyst as precursors which is positioned at the tip of the whiskers, the integration of the component into the precipitation of the solid crystal and liquid at the solid–liquid interface. The existence of liquid catalyst discriminates this process from other whiskers growth process. The SiC whiskers are commonly in cubic structure which is mounting in  $\langle 1 \times 1 \times 1 \rangle$  direction (Li et al. 2016).

The SiC is prepared by temporarily bonding a stoichiometric mixture of micronized (<20 μm) metallic silicon and carbon. The temporary binders such as polyvinyl alcohol, methyl cellulose, sodium silicate, polyethylene glycol, and the



SiO<sub>2</sub> sol can be used for bonding silicon and carbon. The SiC precursor is formed into green bodies by using common technologies such as pelletizing, extrusion, and granulation. For the production of open cell foams or 3D structures using existing methods such as pelletisation, extrusion and granulation (Schwartzwalder and Somers 1963; Studart et al. 2006). In this process, the slurry is synthesized by using the similar raw material, but a significant quantity of temporary binders and rheological additives has used to attain the essential viscosity and thixotropy for the slurry. The outcome structure is then dried out at atmospheric temperature and subsequently undergoes thermal treatment at atmospheric pressure under inert condition in a furnace up to 1360 °C. Continuous heat treatment of 1 hour is essential for the preparation of self-adhesive porous SiC. The temperature should be maintained below the melting point of 1400 °C for SiC during heat treatment process. The high carbon yield resin converted into amorphous carbon in the pyrolyzed condition, which combines and bind the silicon and carbon particles together (Duong-Viet et al. 2016).

SiO is formed above 1000 °C when the metallic silicon may react with remaining traces of oxygen. The SiO gas further reacts with the carbon structure forms into SiC and CO according to Eq. 3, further the CO is reacted with metallic silicon forms into SiO and SiC according to Eq. 4.



The oxidative treatment carried out for SiC for 2 h in air at 800 °C to remove the unreacted carbon residue in their matrix (Duong-Viet et al. 2016). The activation carbon obtained from rice husk can be activated with chemical or physical methods. The chemical impregnation of rice husk ash with KOH or NaOH at 650–850 °C results in activation with extremely high surface area (Brunauer–Emmett–Teller (BET) 1413–3014 m<sup>2</sup>/g) (Guo et al. 2002). The increase pore size in rice husk and removed the silica by using of KOH or NaOH. Similarly, activation carbon is also synthesized from tire-derived char (TC) by using the following method. In this process, a preliminary assay is performed to determine which environment, alkaline or acidic, is better to reduce the Zn content of the tire-derived char. Then the tire-derived char samples were subjected to demineralization by following methods (López et al. 2013).

- 1 M ((NH<sub>4</sub>)H(CO<sub>3</sub>) (NH<sub>4</sub>)CO<sub>2</sub>NH<sub>2</sub>)) ammonium carbonate solution with a concentration of 25 or 50 g/L, and a TC concentration of 12.5 or 25 g/L.
- Char concentration of 20 or 25 g/L and 1 M or 2 M solution of H<sub>2</sub>SO<sub>4</sub>.
- 1 or 2 M HCl, with a char concentration of 20 g/L.
- A mixture of concentrated commercial HNO<sub>3</sub> (69% HNO<sub>3</sub>) plus 1 M H<sub>2</sub>SO<sub>4</sub>, and a TC concentration of 20 g/L.
- A mixture of commercial concentrated HNO<sub>3</sub> and water, and a TC concentration of 20 g/L.



20–25 g of TC is mixed in a demineralizing solution for 2 h by using stirrer at room temperature. The pretreatment of 20 g TC for 24 h in 16 ml of  $\text{HNO}_3$  is involved in  $\text{HNO}_3/\text{H}_2\text{SO}_4$  treatment. finally, the mixture of one litre of 1 M  $\text{H}_2\text{SO}_4$  is added and the mixture is shaken for 2 h. The pretreatment of 20 g of TC with 16 ml of  $\text{HNO}_3$  (Panreac, 65% pure; density 1.41 g/mL) for 24 h is involved in demineralization process by  $\text{HNO}_3/\text{H}_2\text{O}$ . The mixture is shaken for 2 h by adding 1 l of distilled water. Zn content is reduced significantly in the TC sample, which is corresponded to the one prepared by  $\text{HNO}_3/\text{H}_2\text{O}$  demineralization treatment (DTC-NW). It was stimulated by KOH chemical treatment (López et al. 2013).

Agricultural waste or residues contains organic compounds from organic sources such as rice straw, sugar cane, coconut shell, bagasse, and others (Sudiana et al. 2017). Rice husk is one of the alternative material which can be potentially used in microwave absorber fabrication. The production of AC-SiC nanowire from agricultural waste is through a novel free-pressureless spark sintering technique (FPSPS) which is manifested below. In this process, one gram of Si powder is mixed with 20 ml of ethanol and exposed for a time of 3 min to 20 kHz ultrasonic frequency. The obtained liquid solution is mixed with already available biomass and is stirred or distributed by using mechanical means. Then vacuum drying is used to dry the sample and silicon-treated stalk samples will be added to graphite. Then FPSPS processing is carried out by heating as well as cooling at a specific rate of 20, 50 and 100 °C. In the vacuum dryer, it is held at 1300, 1500 and 1600 °C and the applied pressure will be around 5 MPa (Bradbury and Olevsky 2010).

### 11.5.3 Dielectric Properties of Carbon-Based Materials

The Magnetic and Electric field components are perpendicular to each other in all electromagnetic waves and microwaves. Materials can be classified according to the component of the electric field interaction with the microwave field in three ways: i) Microwave-transparent insulators that pass through the medium without losses, (ii) conductors-reflect micro-waves cannot penetrate and (iii) absorptions. Microwave heating is also referred to as dielectric heating because dielectrics are the materials which absorb microwave radiation (Thostenson and Chou 1999). These include dipole orientation, atomic polarization, electronic polarization, ionic conduction, and interfacial or Maxwell–Wagner polarization mechanisms. The transfer of electromagnetic energy to thermal energy occurs only in dipole and Maxwell–Wagner polarizations at microwave frequencies (Mijović and Wijaya 1990). The Maxwell–Wagner polarization exhibits on the boundary of two dissimilar dielectric materials or freely movable charged particles such as  $\pi$ -electrons in the solid carbon material (Zlotorzynski 1995).

The accumulation of the charge, at the material interface, is produced and the energy is dissipated in the form of heat. This is due to the so-called Maxwell–Wagner effect, i.e., when the charged particles cannot couple to the changes of phase in electric field. The communication of microwaves with metal powder or

metals might be further contributed to the energy absorption effect (Marken et al. 2006). In the irradiated sample, the polarization occurs when the effective current is out of range with reference to the applied field by a difference (termed  $\delta$ ). This difference describes the loss factor or dissipation factor, or the dielectric loss tangent represented by  $\tan \delta$ . The study of dielectric parameters is most essential in order to select optimal condition in designing microwave absorber which influences the absorption through heat dissipation. Magnetic parameters such as permeability and magnetic loss influences absorption. Hence, the material is described only the mixed dielectric material of carbon and resin, and the function of magnetic loss and permeability in microwave absorption will not be discussed (Meredith 1998).

#### Permittivity

The relation between the dielectric material capacitance and the microwave propagation is described by the permittivity of a substance. The mathematical representation of both real and imaginary part in a material and the quantity of electrostatic energy stored in a unit volume for a given applied field are determined by the real permittivity “ $\epsilon$ ”, also known as dielectric constant. The permittivity of imaginary part is represented by  $\epsilon''$  in mathematical equation. The energy loss is described by the lag in the polarization upon wave propagation as it passes through a dielectric material. The ratio of natural permittivity of the material,  $\epsilon$ , to permittivity of free space  $\epsilon_0$  is the relative permittivity of a material,  $\epsilon_r$  (Yusof 2004).

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (3)$$

The most common formula for complex permittivity of a substance is written as

$$\epsilon_r = \epsilon_r' - j\epsilon_r'' \quad (4)$$

#### Loss Tangent, $\tan \delta$ .

The dissipation of power or energy from the incident waves are represented by loss or  $\tan \delta$ . The loss factor is a most important parameter in microwave absorption, which converts incoming microwave energy into heat. The conductivity and permittivity of the material influences the overall losses based on dissipation as noticed by Neelakanta and Park (Neelakanta 1995). In general, an efficient absorber material would have a considerable amount of loss factor. The ratio of the loss aspect to stored component of absorptive material is termed as dissipative factor or the loss tangent, and it is commonly expressed as (Vinoy and Jha 1995)

$$\tan \delta = \frac{\sigma + \omega\epsilon''}{\omega\epsilon'} \quad (5)$$

Especially with pure dielectric where losses are very low, the influence of conductivity inside losses is considered zero. A dielectric with small loss is considered to have  $\sigma \ll \omega\epsilon''$  with  $\sigma \approx$  zero. Therefore, for pure dielectric:

$$\tan \delta = \frac{\omega\epsilon''}{\omega\epsilon'} \quad (6)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (7)$$

It has reverse properties with  $\sigma = \infty$  and  $\sigma \gg \omega\epsilon''$  in the case of conductor. The loss tangent for conductor is then:

$$\tan \delta = \frac{\sigma}{\omega\epsilon'} \quad (8)$$

The reflection loss (RL) in dB unit could evaluate the microwave absorbing potential; if the RL values of an absorber are lower than 10 dB (90% absorption), the absorber works properly in the microwave field. Due to the low complex permittivity, the microwave absorbing properties are poor which cannot disperse electromagnetic energy efficiently (Ding et al. 2012).

#### 11.5.4 Factors Influencing Dielectric Properties

Dielectric properties of the materials may be affected by some of the parameters such as temperature, frequency, moisture content, and density as in the circumstance of wet materials like biomass (Nelson and Trabelsi 2012).

##### Frequency

Dielectric constant and loss factor of material are momentarily varying with frequency, but low-loss and transparent materials are exceptions (Nelson and Trabelsi 2012). The relationship between the frequency and dielectric properties depends on the loss mechanism(s), involved. Debye equation is the predominantly used one which relates the polar materials permittivity and frequency (Metaxas and Meredith 1983).

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau} \quad (9)$$

where  $\epsilon_s$  and  $\epsilon_{\infty}$  are the dielectric constants at d.c (static) and high frequency, respectively, and  $\tau$  represents the relaxation time in seconds.

Relaxation time can be defined as when the applied field is removed, the time needed for the dipole to return to a random alignment (Nelson and Trabelsi 2012). Intermolecular forces are substantially associated with relaxation time, and these are

affected by temperature (Gabriel et al. 1998). At higher frequency, the dielectric constant starts to drop due to that the molecules are not able to rotate with significant amount before the field is reversed. At very low and very high frequencies the loss factor tends to zero. Dielectric properties of heterogeneous materials are complex in nature due to the involvement of more than one loss mechanism at the same time. The conductive and dipolar losses are the dominant factor at lower and higher frequencies, respectively (Adam 2017).

#### Temperature and moisture content

Studying the influence of temperature on dielectric properties is essential because the temperature is changing under electromagnetic heating. Molecules mobility and their intermolecular forces are adversely affected by temperature. Energy storage and dissipation of molecules are affected by temperature (Nelson and Trabelsi 2012; Gabriel et al. 1998). Applied frequency and loss mechanism involved are the factors which affect the influence of temperature on the dielectric property (Nelson and Trabelsi 2012). Polarization losses are exhibited by polar materials; relaxation time increases with decreasing in temperature. Intermolecular forces between molecules get weaken and rotation ability of molecules increases with increase in temperature (Adam 2017). Dielectric properties of biomass generally depend on the water content. Hence, at low-temperature dielectric properties of biomass can be understood by studying the temperature effects on polar materials dielectric properties. Moreover, free water is not only responsible for biomass water content. Compared free water, the bound water has less polarization ability which in turn lower dielectric constant and loss factor due to restricted movement (Metaxas and Meredith 1983; Bergo et al. 2012).

The physical structure and chemical composition of biomass are significant changes which start with drying to char formation during the pyrolysis process. In this, the physical structure and chemical composition of raw biomass are entirely different from final one. These changes adversely influence the dielectric properties of biomass. Effect of pyrolysis temperature on loss tangent of wood mass at 2.45 GHz microwave oven was investigated by Robinson et al. (2015). They reported that increasing the temperature up to 120 °C, a significant drop in loss tangent was observed which is due to evaporation of moisture content. When the temperature is raised above 200 °C a second reduction was observed followed by meager loss materials get evaporated between 250 and 480 °C. After that rapid increment of loss tangent was observed at above 500 °C due to good microwave absorptivity of char which was formed by carbonization of biomass (Adam 2017).

#### Density

The packing density of granular and pulverized solids are greatly affected their dielectric properties and also increases the permittivity. This is because of less void fraction and permittivity than solid fraction in the mixture at higher packing density, which results in increases in the overall permittivity of the mixture. Different forms of biomass such as sawdust, chips, shavings, logs, and pellets. The density of

biomass is varying with their size and shape. Also, dimensions of the feedstock for processing are decided based on factors such as the form at which the material feedstock is available, processing requirements, and the economic considerations (Nelson and Trabelsi 2012; Adam 2017; Nelson 2005).

### ***11.5.5 Microwave Enhancement of Carbon Catalyst Reaction***

Carbon-supported substances are activated carbon, carbon fiber, and others that contain a specific segment of graphitic which can be expanded by raising the temperature of heat treatment process (Kim et al. 2014; Marsh and Rodríguez-Reinoso 2006). In this manner, microwave heating of different carbon-supported materials is also described. Activated carbon, char, and biomass are for the most part frequently connected with absorbents during the microwave heating. Reclamation of NO<sub>x</sub>-saturated activated carbon and char was extensively stated in the 1990s (Cha and Kong 1995; Kong and Cha 1996). Restored activated carbon and char in the microwave heating efficiently provide sufficient energy for several cycles. Guo and Du (2012) stated within a minute regeneration of NO<sub>x</sub>-saturated char was done while the input power was over 300 W. Additionally, Menéndez et al. (1999a, b) suggested refurbishment of a simple property of activated carbon by using getting rid of oxygenated functionalities. The carbon and oxygen substance of oxidized activated carbon were enhanced from 84.50 to 97.82% and 14.98 to 1.56%, respectively, after exposure to 1.5 min of microwave irradiation. Temperature over 900 °C was attained approximately in a minute when the activated carbon was irradiated by 1000 W due to high carbon content. In conventional heating, 900 °C was attained at 3 h. Organic chemicals, dye, and SO<sub>2</sub> were removed in microwave radiation with the use of activated carbon (Hua-Shan and Chih-Ju 1999; Liu et al. 2004). The use of activated carbon increases the regeneration efficiency after repeated cycle (Ania et al. 2004), porous structure preservability (Ania et al. 2007) and improve the representative strengths included with the short time required (Zhang et al. 2007). Recently, activated carbon conversion from biomass was reported with the aid of microwave heating (Yagmur et al. 2008; Li et al. 2008). Carrott et al. (2001) mentioned the elemental composition of activated carbon fibers differed due to rapid heating over 800 °C/min, and improvement in the carbon content was noticed. Li et al. (2009) used carbon fiber as a microwave absorber for the remediation of crude oil contaminated soil.

Microwave pyrolysis was conducted continuously over a long duration; the carbonaceous char was trapped within the reactor. Increasing amount of char in the reactor will influence the pyrolysis yield and products. The volatile material present in the char during microwave pyrolysis of waste engine oil could act as a catalyst and microwave absorbent and improve the heating rate. Also, promote the heterogeneous reaction in the pyrolysis gases evolved from the pyrolysis process,

leading to different composition in the oil yield observed in the process. This work also suggested inorganic metal containing char can potentially use as a catalyst for thermal cracking (Domínguez et al. 2006; Lam et al. 2015). The presence of Fe, Ni in the char improves the catalytic effect of heterogeneous reaction like methane decomposition reaction will be reported by different studies (Muradov et al. 2005; Avdeeva et al. 2002). In addition, the valuable gases  $H_2$  and syngas were produced in microwave pyrolysis of sewage sludge and coffee hulls in presence of char catalyst (Domínguez et al. 2007, 2008; Menéndez et al. 2007).

The high carbon and relatively low volatile content were reported in pyrolysis of waste oil at 550 °C. XRF analysis discovered that metal oxides including mainly of CaO,  $Fe_2O_3$ ,  $Al_2O_3$ , ZnO,  $SiO_2$ , MgO, and NiO are present in the metallic char. The energy-dispersive X-ray spectroscopy for the metallic char revealed the existence of metalloid (Si), metals (Mg, Cu, Al, Fe, Ca, Pb, Ni, Zn), nonmetals (C, P, O, S), and halogen (Cl). Metal elements like Al, Cu, Fe, Mg, and Ni were already reported in many studies for their catalytic effect in the pyrolysis process (Muradov et al. 2005; Avdeeva et al. 2002). The metallic char added to the pyrolysis reactor led to the hot spot formation in the pyrolysis of waste engine oil promote the heterogeneous reaction in between the waste engine oil and metallic char to produce higher yield of CO and  $H_2$  and lesser yields of  $CH_4$  and  $CO_2$  and. Also, the formation of lower chain hydrocarbons in both pyrolysis fuel (i.e.,  $C_5$ – $C_{10}$  hydrocarbons) and non-condensable gases was reported. Moreover, the metals get converted into metal oxides and absorb the sulfur existing in the oil.

The microwave absorber (silicon carbide, magnetite, and manganese dioxide) and microwave non-absorbing powders (alumina, titanium, and zirconia) along with graphite powder are investigated and compared with pure materials. The graphite–silicon carbide was found to have better microwave heating characters than other combinations. The weight ratio of 1:1 (graphite powder to microwave absorber) has chosen for their work. Similarly, graphite–magnetite combination showed superior heating rate pure iron oxides. The average rise in temperature of 60 °C/min attained while using a pure iron oxide ( $Fe_3O_4$ ). Cheng et al. (2002) reported  $Fe_3O_4$  heated in both E and H fields. Most of the iron oxides such as FeO and  $Fe_2O_3$  are heated in E field. On further addition of graphite with  $Fe_3O_4$ , the heating rate of the substance becomes stronger and formation of microplasmic impacts the graphite.  $Fe_3O_4$  converted into FeO during microwave heating of graphite– $Fe_3O_4$  composite and graphite and Fe could be consumed. The FeO is the poor microwave absorber and affects the heating rate subsequently, due to the fact that it cannot be used as crucible material. On the other hand, the mixture provided uniform heating and did not go through any massive change in the weight and chemical composition during the process. Also, the same results were obtained when SiC–graphite mixture reused repeatedly, hence its dielectric properties of this mixture unchanged. Weight ratio ranging among 40–50% exhibits the higher heating rate of the mixture. SEM and XRD analysis confirmed that graphite and SiC chemical response does not change during the process. Hence, SiC with graphite aggregate is more suitable for making microwave crucible and susceptors (Chandrasekaran et al. 2013).

### ***11.5.6 Regeneration of Carbon Material***

Activated carbon (AC) is a naturally synthesized material obtained by calcination of biomass and extensively used as a catalyst support and adsorbent due to its huge surface area per unit mass and great adsorbing ability (Thomas and George 2015). Generally, AC materials are directly burned to produce steam or thrown as wastes which will initiate the secondary pollute formation. Instead of utilizing AC in incineration or throwing as waste it can be regenerated, by doing so the adsorbing ability of AC can be reactivated and substantially secondary pollution formation also minimized. The regeneration of AC can be achieved through oxidization, thermal, microwave, and biological regeneration methods. Among these methods, the biological and oxidization way of regeneration are more time-consuming and economically not suitable (Sabio et al. 2004). However, microwave irradiation is an efficient regeneration method, but it is not widely used due to its limited application. Thermal regeneration is the well-known and popularized method used in AC regeneration (Dehdashti et al. 2011). In this, the process is carried out in a muffle furnace. The optimum regeneration temperature and time were found by conducting a series of experiments which involve:

- Drying at around 105 °C,
- Pyrolysis under N<sub>2</sub> atmosphere, and
- Gasification of residual organics by an oxidizing gas, such as steam or carbon dioxide (Guo and Du 2012; San Miguel et al. 2001).

The AC is obtained by carbonization of biomass materials under an N<sub>2</sub> atmosphere at 800 °C. The carbonization process evaporates the moisture content and decomposes and eliminates the low volatile matters which are adsorbed on the carbon surface (San Miguel et al. 2001). The final AC contains carbonized char in the carbon pores which is strongly linked with AC structure. Generally, steam or CO<sub>2</sub> or mixed of both is used as a mildly oxidizing agent in the process of controlled gasification of carbon at 800 °C (San Miguel et al. 2001). Water vapor can be used to eliminate the carbonated carbon, at elevated temperature. The remaining carbonated carbon will be oxidized by reacting with water vapor. Finally, the obtained AC has its original adsorption capacity and carbon pore structure. Compared to steam generation, all the phenolic compounds cannot be eliminated by pyrolyzing at 700–900 °C which will result in AC with the lower surface area per unit mass. It can be concluded that steam generation is the effective and cost-effective method to produce AC with the large surface area and high porosity (Cheng et al. 2007).

## **11.6 Characterization of Alternate Fuels Derived from Thermochemical Conversion**

### ***11.6.1 Physical Properties***

#### **11.6.1.1 Density**

The density is defined as the mass per unit volume. In order to measure the weight of the sample, the electronic weighing machine is employed having an accuracy of  $\pm 0.1$  g. First, the sample whose density has to be measured is taken in 50 mL of volume. Then the sample quantity weight is measured in the electronic weighing machine, and then again, the process is repeated for 40, 30 mL volume of sample fuel. This is done to ensure that the value is very accurate.

#### **11.6.1.2 Viscosity**

Brookfield viscometer DV3T model was used to calculate the kinematic viscosity of different liquid fuels. Viscosity is defined as the resistance offered by one layer to another while in motion. This property was measured as per the ASTM D445 standard. 16 mL of liquid fuel was poured into a spindle and cylindrical cup type arrangement and was subjected to continuous shear stress. The temperature of 40 °C should be maintained according to ASTM standard which is taken care by the water bath arrangement. The value of the viscosity was directly given on the screen display.

#### **11.6.1.3 flash and fire Point**

To find the flash and fire point of different liquid fuels, the open cup Cleveland apparatus is used. ASTM D93 standards have used for conducting the experiment. A practical detonation source will cause the vapor of the trial to burn at a flash point. The flash point is determined by warming an example of the fuel in a container and passing the flame over the surface of the sample. If the temperature is at or above the flash point, the vapor will ignite and an easily detachable flash can be observed. The flash produced need not sustain for a long time. Whereas, fire point is the minimum temperature at which vapor of the fuel steadily burns at least for five seconds once ignited.

#### **11.6.1.4 Cloud and Pour Point**

The apparatus as per ASTM D97 and ASTM D2500 standards were used for the tests. Pour point is a minimum temperature below which a liquid loses its flow characteristics. Cloud point is the lowest temperature at which the first crystal formation starts. A freezer which can cool below 0 °C is used, where the



temperature is decreased in steps of 3 °C, till a cloud or haze or wax crystal is formed at the bottom of the test tube containing fuel. The temperature at which the cloud forms is called cloud point. After cloud point, the temperature is reduced in steps of 1 °C till the temperature at which the fuel stops moving when the test tube is tilted. This temperature is the pour point.

#### 11.6.1.5 Acid Value

Acid value is defined as 1 mg of potassium hydroxide (KOH) which is required to neutralize 1 g of chemical substance; it measured the carboxylic acid group in the chemical component. In acid value testing, two solutions have to prepare like burette solution and beaker solution. In beaker solution, taking 1:3 ratio of diethyl ether and ethanol and adding lesser than 1 g of testing fuel along with two drops of phenolphthalein color indicator. In burette solution, 0.1 N of KOH solutions dissolved in deionized water. The burette solution is titrated with beaker solution. The standard methods are available to determine the acid value such as ASTM D974, ASTM D664, and European Standard EN 14104. The acid value is the parameter in which found the free fatty acid of raw oil as well as biodiesel. This parameter directly affects the biodiesel property like viscosity, density, calorific value, and cetane number, and also affects the engine emission, performance, and combustion characteristics. Fatty acid causes dehydration or peroxide in biodiesel, because normally biodiesel contains more unsaturated contents. So, it easily reacts with oxygen and makes sledge, fatty acid and corrodes the engine components.

### 11.6.2 Ultimate Analysis and Proximate Analysis

Elemental composition of fuel is determined by ultimate analysis. The ultimate analysis is one of the vital components when considering biomass powers properties. It evaluates the level of N, S and to think about the natural effect of biomass. Also, it helps to estimate the percentage of C, H, O and heating value of the biomass fuels (Sheet 2008). Table 11.1 shows the ultimate analysis of different types of biomass. The ultimate analysis shows the contents of the organic constituents along with ash and moisture. It provides a convenient and uniform system for comparing and evaluating the fuels. The ultimate analysis gives the chemical composition of the biomass fuels (Kirubakaran et al. 2009). The accompanying ASTM norms are accessible for assurance of ultimate analysis of biomass fuels (Basu and Basu 2010).

Carbon, hydrogen	E-777 for refuse-derived fuels (RDF)
Nitrogen	E-778 for RDF
Sulfur	E-775 for RDF
Moisture	E-871 for wood fuels
Ash	D-1102 for wood fuels

**Table 11.1** Ultimate analysis of different types of biomass types (wt% dry basis) (Demirbas 2004b; Haykiri-Açma 2003)

S. No.	Biomass	C	H	O	N	S
1	Lignite	65.20	4.50	17.50	1.3	4.1
2	Spruce wood	51.40	6.10	41.20	0.3	0.0
3	Hazelnut shell	50.80	5.60	41.10	1.0	0.0
4	Corn cob	49.00	5.40	44.20	0.4	0.0
5	Corn stover	49.40	5.60	42.50	0.6	0.1
6	Tobacco stack	49.30	5.60	42.80	0.7	0.0
7	Tobacco leaf	41.20	4.90	33.90	0.9	0.0
8	Almond shell	47.90	6.00	41.70	1.1	0.06
9	Saw dust	53.60	6.6	35.50	1.5	0.1
10	Rice husk	46.90	5.20	37.80	0.1	0.04

### Proximate analysis

The fundamental characteristics of any fuel are determined by proximate and ultimate analyses. The proximate analysis shows the quantity of combustible constituents and noncombustible constituents. It also provides the basis for estimating its commercial value. The proximate analysis examination is critical to contemplate the burning marvel of biomass (Kirubakaran et al. 2009). For example, Ash remains substance in biomass fills can cause start and ignition issues. It also gives as the gross composition of biomass and also easy to measure. For wood fuels, we can use standard E\_870-06. Separate ASTM standards are applicable for the determination of the individual component of biomass.

Volatile matter E\_\*&@ for wood fuels  
 Ash D-1102 for wood fuels  
 Moisture E-871 for wood fuels  
 fixed carbon Determined by difference

Fixed carbon content is different from ultimate analysis carbon. In proximate analysis it is referred to us char yield does not include carbon in the volatile matter. Proximate analyses of various samples are mentioned in Table 11.2 (Jenkins et al. 1998).

**Table 11.2** Proximate analysis of different types of biomass types (wt% dry basis) (Jenkins et al. 1998)

S. No	Biomass	Fixed carbon	Volatile matter	Ash
1	Alfalfa stems	15.81	78.92	05.27
2	Wheat straw	17.71	75.27	07.02
3	Rice hulls	16.22	63.52	20.26
4	Rice straw	15.86	65.47	18.67
5	Switch grass	14.34	76.69	08.97
6	Sugar cane bagasse	11.95	85.61	02.44
7	Willow wood	16.07	82.22	01.71
8	Hybrid poplar	12.49	84.81	02.70
9	Almond shells	20.71	76.00	03.29
10	Almond hulls	20.07	73.80	06.13

### 11.6.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique which is used in the thermal analysis to study and observe the various chemical and physical changes through the changes in the weight of the materials with temperature and time. This analysis has been used widely during the pyrolysis process to study the biomass decomposition and its constituents (Collard and Blin 2014). Thermogravimetric analysis can also be used to carry out proximate analysis of several types of biomass matters which include determining the volatile matter, ash content, fixed carbon, and the presence of moisture (García et al. 2013). As per the earlier study, the enthalpy for pyrolysis process can be said as the minimum energy which is required to carry out pyrolysis. It can be stated as the sum of the energy which is required for heating the biomass matter up to the reaction temperature in pyrolysis which is necessary to drive the reaction in pyrolysis process. Differential scanning calorimetry (DSC) is used for determining the enthalpy for pyrolysis. The measurements were carried out in an SDT apparatus which is a combination of DSC-TGA device that measures the change in weight and heat flow as the functions of temperature. Before performing the analysis, drying of the samples was carried out in an electric oven at a temperature of 105 °C for 1 h.

The purpose of drying was the prediction of accurate enthalpy values for the pyrolysis process independent of the moisture content. On a dry basis, enthalpy for the pyrolysis process is generally reported because of the variation of moisture content when it goes for processing. Generally, the moisture content of the feedstock would be around 6–12% on dry basis. The moisture content can be found without drying of the feedstock. The moisture content and enthalpy value deviated more as compared to the experimental value. The deviation of the enthalpy value is due to moisture content available in the feedstock. The enthalpy associated with heating and evaporating the moisture present in the biomass matter can be summed with the enthalpy for pyrolysis. This can be achieved by the calculation latent heat

for evaporation of water and sensible enthalpy for heating the water present in the biomass up to the temperature of 100 °C, after that multiplying the sum by the fraction of water in the biomass matter (Chen et al. 2014; He et al. 2006). The major outputs from the TGA-DSC measurements were the change in weight and heat flow as a function of temperature. The calculation of enthalpy for pyrolysis can be done by integrating the heat flow curve over the temperature range of pyrolysis as mentioned below:

$$Q_{py} = \int_{T_0}^{T_{py}} \frac{H(T)}{dT/dt} dT \quad (10)$$

where

$Q_{py}$  is the specific enthalpy for pyrolysis (J/g),  
 $T_{py}$  and  $T_0$  are the final and starting temperatures, respectively (°C),  
 $H(T)$  is the specific flow of heat to the sample at temperature  $T$  (W/g), and  
 $dT/dt$  is the constant heating rate.

The heat flow values were also used for the calculation of the specific heat capacity, ( $T$ ), of the biomass matter as a function of temperature as given below:

$$(T) = \frac{-H(T)}{dT/dt} \quad (11)$$

Kinetics is a useful tool for characterization and performance estimation. Thermal analysis such as differential scanning calorimetry and thermogravimetric analysis is used as an effective tool for the kinetic parameters determination. During pyrolysis reactions, the conversion was described by kinetic models. These kinetic models are complex and computationally rigorous, but they are more detailed and accurate. Various kinetic models can be found on pyrolysis of different feeds in the open literature (Sharma and Rajeswara Rao 1999).

Ozawa (1965) mentioned that the variable heating rate methods are also called iso-conversional methods. Moreover, the advantages of these models are that they apply to complex, multi-staged reactions and provide activation energy and pre-exponential factor, excellent reliability, and easy to manually perform. However, isoconversional methods assume reaction order as one and they take lengthy calibrations. Inversely single heating rate methods have simple calibration, the simple rapid experiment is sufficient to study the kinetics, and they provided all the three parameters (i.e., pre-exponential factor, and order of reaction, and activation energy). Moreover, the drawback of the single heating rate models is they have poor reliability, applicable only to nth order reactions. From this, the advantages of both the models are suitable for the computer the pyrolysis kinetic parameters. Rosi et al. (2018) investigated that the styrene polymers such as high impact polystyrene and acrylonitrile butadiene styrene; both of which are significant e-waste components plastics. So, these two plastic types have been employed to investigate the behavior of kinetics.

### 11.6.4 Chemical Constituent's Analysis

Gas chromatography and mass spectrometry (GC-MS) is a systematic method that conglomerates the structures of gas chromatography and mass spectrometry to recognize different matters inside a test trial. From the GC-MS results, the amount of alkane, alkene, ketone, and cycloalkane can be found. More the alkane means more efficiently the fuel will be ignited as the C–H bond is a single bond. However, more the alkenes mean the fuel will not readily ignite as C–H bond is a double bond. The presence of avoidable elements like alkene, cycloalkane, and ketone which directly affects the properties of the fuels could be quite low. The data obtained from GC-MS can be used to find out the total percentage of carbon number range. The total percentages of different levels of carbon number range will indirectly signify whether the improvement or deterioration in the values of properties such as viscosity and calorific values (Pittman et al. 2012). Additionally, it can identify trace elements in materials that were earlier assumed to have fragmented beyond identification. Like liquid chromatography–mass spectrometry, it permits inquiry and recognition even of small quantities of an element. In recent developments, the multidimensional hyphenated chromatographic methods have improved considerably the value of data collected from every sample. Furthermore, complex samples contain constituents with different characteristics; an individual method cannot offer the full analysis. Therefore, a mixture of analytical methods such as gas, high-pressure liquid, gel permeation chromatography, Fourier-transform infrared spectra, and nuclear magnetic spectroscopy is acquired to evaluate the bio-fuel composition (Ware et al. 2017). Appropriate classification of bio-fuel constituents appraising the analytical approach which applied for their identification tends to their classification in approximately four divisions: (1) the medium polar monomer identifiable by GC, around 40 wt%, (2) polar monomers also identifiable from HPLC (or GC after derivation) in the region of 10–15 wt%, (3) 20–30 wt% of water determined from the Karl-Fischer technique, and (4) oligomeric components, around 20 wt% also observed from HRMS or GPC. Although traditional GC and HPLC have offered certain information on the bio-fuel constituents and still are applied for qualitative and quantitative analysis, the actual elucidation of bio-fuel production has observed using the application of LC or LC GC × GC, combined with mass spectroscopy (Michailof et al. 2016). Atomic absorption spectroscopy (AAS) is a Spectro analytical technique used for the quantifiable determination of the chemical elements present in the sample using the absorption of light (optical radiation). Atomic absorption spectroscopy (AAS) is conducted for diesel, e-waste, and pyrolysis oil to know the percentage amount of other metals such as lead, iron, chlorine, and bromine. AAS analysis for e-waste, waste oil and pyrolysis oil are important to know the kind of harmful halogenated metals present in the feed as well as in the produced pyrolysis oil and further methods of elimination of these metal contents in the pyrolysis oil can be employed. Inductively coupled plasma is a method which is used for detecting the metal and nonmetal content at concentrations as low as one part in 1015. This can be done by

ionizing the sample by inductively coupled plasma. Compared to atomic absorption spectrometry, this test gives more accurate and sensitive value (Oasmaa et al. 1997).

### ***11.6.5 Heating Value***

The amount of heat produced on complete combustion of 1 g of fuel is called heating value or calorific value. The product of combustion is cooled to normal condition and water vapor leaves without being condensed is called lower calorific value or net calorific value. Higher heating value (HHV) is the quantity of heat released when unit quantity of fuel is completely burned at atmospheric temperature under stoichiometric conditions; the water vapor produced during combustion is being condensed when reaches to the initial temperature. HHV includes latent heat of evaporation of condensed water vapor. Higher heating value is used in boilers and lower heating value is used in internal combustion engine. Liquid and solid fuel calorific values are measured by bomb calorimeter, and gases fuel calorific value is measured by Junkers gas calorimeter. Chemical composition, moisture content, and molecular structure are the parameters affect the calorific value of the fuels. The waste cooking oil and pyrolysis oil calorific value are measured by using IKA 2000 model bomb calorimeter. A bomb calorimeter is a constant-volume type calorimeter used in computing the heat of burning of a particular response or simply to measure the calorific value of a fuel. Bomb calorimeters are built in such a way that it can withstand the large pressure that produced within the calorimeter due to reaction or burning of fuel. Electrical energy is used to burn the fuel, and as the fuel is burning, it will warm up the nearby air, which enlarges and outflows through a tube that primes the air out of the calorimeter. When the air is evading through the copper tube, it will also warm up the water. The change in temperature of the water permits for computing the calorie content of the fuel.

## **11.7 Performance, Combustion, and Emission Analysis of Syngas and Pyrolysis Fuel in Dual Fuel CI Engine**

### ***11.7.1 Effective Utilization of Pyrolysis Fuel in CI Engine***

Kalargaris et al. (2017) studied that pyrolysis fuel derived from waste plastic can be used as the best alternative fuel because of its higher heating value. It can be converted to useful oil by pyrolysis process and utilized in an internal combustion engine to create mechanical power and heat. The oil is produced by fast pyrolysis method, and the properties of this oil are similar to the diesel oil. Pyrolysis oil derived from plastic was used as an additive to diesel and operated on advanced injection timing in diesel engine resulted in the brake thermal efficiency and emissions all are improved. The motor ignition attributes, performance, and exhaust emissions were broke down and related to diesel fuel action. The outcomes

demonstrated that the locomotive could keep running on plastic pyrolysis oil at rated load introducing similar performance to diesel. Mani et al. (2009) studied pyrolysis oil derived from plastic was used as an additive to diesel and operated on advanced injection timing in diesel engine resulted in the brake thermal efficiency and emissions all are improved. The motor ignition attributes, performance, and exhaust emissions were broke down and related to diesel fuel action. Shukla et al. (2016) described the use of plastic pyrolysis oil in internal combustion engines for a better replacement of the diesel fuel.

Researchers started opting for dual fuel strategy to challenge emission problems occurring in conventional diesel engines. The combustion phase and combustion duration will be controlled by reactivity gradient with port injection of a low reactive fuel like CNG combining direct injection of an extremely reactive fuel in cylinder (Wu et al. 2011). Auto-ignition of fuel can be restricted by higher octane number (ON) of the fuel which always indicates a high resistance toward self-ignition. This extends the upper load limit of the dual fuel engine effectively with less EGR operation. It can be concluded that the natural gas with good reserves and high-octane number is the best choice of the port injection fuel (Machrafi et al. 2008). To meet the current environmental legislations, it is highly required to reduce  $\text{NO}_x$  emissions in the exhaust gas. It is required to obtain energy conservation with low emission and high efficiency. Present developments in the CI engine combustion allow it to use alternative gaseous fuels such as CNG (natural gas), LPG (liquefied petroleum gas), DME (dimethyl ether), and hydrogen which help to resolve the emission problems (Ryu 2013).

The diesel ignited natural gas engine has the maximum explosion pressure lower than that of the original diesel engine. Due to the higher flame propagation speed of gaseous fuel, combustion duration will have decreased in CI engine combustion at rated load. Soot and  $\text{NO}_x$  emissions are lower when compared with the original diesel engine. Whereas at Low loads, the diesel ignited natural gas engine has higher unburned HC and CO emissions (Papagiannakis and Hountalas 2008). Among different possible technologies in the CI engine combustion, common rail direct injection (CRDI) systems can be lead to the technological revival. Compared to conventional diesel engine operation, CRDI system has been reported to reduce the specific fuel consumption and smoke emission significantly. However,  $\text{NO}_x$  formation is increased. Dual fuel strategies at rated load will decrease the  $\text{NO}_x$  formation but it is not suitable for lower load due to higher HC emissions.

### ***11.7.2 Energetic Utilization of Syngas in Dual Fuel Engine***

Syngas is produced through the gasification process by partial burning or oxidation of coal and biomass feedstock. It consists of hydrogen and carbon monoxide gases. The composition of gases mainly depends on feedstock particle size, flow rate, moisture content, and reactor, operating condition, catalyst, and residence time as noticed by Shilling and Lee (2003). The drawback of syngas is inferior calorific

value and density. The heating value can be increased by supplying pure oxygen during gasification process; then, the heating value increases by 9–13 MJ/N m<sup>3</sup>. The syngas is free from oxides of sulfur, little amount of oxide of nitrogen. It is diatomic molecule, and it is produced from residual oil, natural gas, petrol coke, coal, and biomass. Syngas offer sustainable development in automobile and energy sector as observed by Pradhan et al. (2015).

Mahgoub et al. (2015) investigated the influence of syngas on diesel engine performance and emissions characteristics. The engine was operated at dual fuel mode with different engine speed like 1200, 2000 and 3000 rpm. The experimental results revealed that power output was decreased for syngas fuel due to its lower heating value and density compared to conventional diesel. The syngas will be a promising renewable source of energy for future due to its feedstock availability. It can be used as a substitute fuel in diesel engine under dual fuel mode as noticed by Sahoo et al. (2011). Sahoo et al. (2012) studied the influence of syngas on diesel engine performance, emissions, and combustion characteristics operated at dual fuel mode. The engine test was carried out at different engine load and different syngas composition. The results showed that 100% hydrogen syngas produced a good performance, but nitric oxide emission was increased. 50 and 75% hydrogen syngas showed good engine performance is about 16.1 and 18.3%, respectively. At 25 and 50% CO presence, syngas provides more CO and UBHC emission due to CO fraction in syngas composition.

Power output and engine performance and emissions depend on hydrogen and carbon monoxide percentage in syngas. The higher proportion of hydrogen syngas is emitted more nitric oxide emission compared to carbon monoxide syngas. The faster combustion due to increased hydrogen fraction resulted in more in-cylinder pressure and temperature in cylinder; high adiabatic flame temperature of hydrogen also influenced the formation of nitric oxide emission as observed by Shudo (2008). Azimov et al. (2011) studied the effect of different compositions of syngas and equivalence ratio on diesel engine under dual fuel mode. Hydrogen and carbon monoxide proportion in syngas affect the engine performance and emissions characteristics. The higher percentage of hydrogen in syngas improved the combustion efficiency and reduced the CO and UBHC emissions, whereas nitric oxide was increased due to complete combustion led to higher in-cylinder temperature and pressure. The presence of CO in syngas improved the engine performance up to a certain limit. Higher percentage on CO in syngas reduced the engine performance; similarly, emission of CO and UBHC emissions was increased. The above literature studies clearly stated that 50–75% hydrogen syngas can provide better efficiency under dual fuel mode. Hence, syngas will be a predominant renewable energy source and better substitute fuel for conventional diesel engines.



## 11.8 Conclusions

The methods and techniques to extract energy from e-wastes and biomass and their optimization can surely support the energy sector and satisfy a part of energy demand. Microwave heating provides more benefits compared to the conventional pyrolysis of e-waste and biomass. The volumetric heat generation and hot spot formation influence the product yield and pyrolysis oil characterization. The higher gaseous product and solid char are obtained in the microwave pyrolysis compared to conventional pyrolysis. The gaseous products evolved in the microwave pyrolysis contain higher  $H_2$  and CO yields. The liquid and gaseous products obtained from the microwave pyrolysis having higher calorific value compared to conventional pyrolysis. The addition of carbon-based material like activated carbon, fly ash, graphite, and SiC in microwave pyrolysis has improved the process efficiency. The higher alkane is formed while using SiC as the microwave absorber. The graphene acts as a good microwave absorber, and it promotes the higher heating rate compared to other microwave absorbers. The higher PAH emission is formed above the pyrolytic temperature  $850\text{ }^\circ\text{C}$  in microwave pyrolysis. Moreover, the metal content present in the waste promotes the methane reforming reaction in the microwave pyrolysis. Further, metals converted into metal oxides leads to sulfur removal. Chlorinated benzenes and PCDD/Fs were detected during the pyrolysis of organic pollutants combined with wood pellets.

Gasification is one of the major approaches to fabricate syngas consists of higher proportion of  $H_2$  to CO from waste biomass. The content of tar observed in this literature mainly depends on the design of reactor, operating conditions, and characteristics of feedstock. The gasification flexibility method is improved significantly when plastic-like materials are combined with coal or biomass. At lower operating temperature than traditional process, the biomass and e-waste from gasification can fabricate a  $H_2$  gas product free from tars. Hence, the production rate of  $H_2$  will be higher at 30 wt% recorded. From different gasification technologies, the syngas is applied to develop power and also produces bottom ash which consists of a significant quantity of silica. From the hydrothermal reaction, this silica can be developed into zeolite and applied as absorbent material. The utilization of different gaseous fuels such as LPG, CNG, and hydrogen with pyrolysis oil in CI engine decreases the emission to great extent. The common rail direct injection (CRDI) system has certain benefits while comparing with the traditional mechanical injection system. The high-pressure injection system improves the homogeneity and turbulence in the air–fuel mixture to determine the lower emission rate and higher thermal efficiency. The use of syngas in diesel engine (dual fuel medium) will reduce the brake thermal efficiency as compared with conventional fuel (diesel) operation. The incrementing of CO constituents in the gas will reduce the  $NO_x$  emission and improves performance due to lower heating. The enhancement of hydrogen in syngas tends to enhance the performance of the engine.

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