Pyrolysis of Biomass and the use of Pyrolysis Oil as an Alternate Fuel: A Review

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Abstract: *Pyrolysis is a thermochemical conversion process where biomass is converted into liquid (bio-oil), solid (bio char), and gaseous products (pyro-gas) under oxygen-depleted condition due to the application of heat. The composition and yield of pyrolysis products depend upon the operating parameters of the pyrolysis process and types of biomass. In pyrolysis process, it is essential to explore the effect of operating parameters on product yield and instinct about their optimization. The present study reviews the influence of operating parameters on product yield from existing literature on the pyrolysis biomass as well as product characterization and upgrading. The major operating parameters include pyrolysis temperature, heating rate, sweeping gas flow rate, and particle size of biomass. The study concludes that most biomass residues are suitable for pyrolysis and all the operating parameters play an important role in the yield of products and their characterization.*

1. INTRODUCTION

Energy plays a crucial role in economic and industrial development of a country. Nowadays, global demand for energy is increasing rapidly due to the industrialization and growth of world population. Currently, the annual world energy demand is approximately 0.55 quadrillion MJ, and it is expected to rise over 50% by 2030. At present, around 90% of world energy demand is fulfilled by fossil fuels (coal, petroleum, and natural gas). The continuous use of fossil fuels is a serious threat to their limited world reserve as well as responsible for energy insecurity and environmental concern over global warming due to the release of greenhouse gases during their combustion. Hence, it is realized that energy should be renewable, cost-effective, convenient, safe, and sustainable. To overcome the demand for energy as well as the environmental threats, other available alternative energy sources must be utilized efficiently. Nowadays, several nations all over the world have started to replace the fossil fuel-based energy sources with renewable, sustainable, alternative, and carbon-neutral energy sources. Renewable energy sources such as biomass and waste, solar, wind, hydropower, and geothermal play a vital role in world energy balance. Among these, biomass and waste hold a share of around 12%. However, in the near future, it may appear as the most promising alternative to fossil fuels. Biomass is nontoxic, carbon neutral, biodegradable, and abundantly available with a yearly production of 10^{11} to 10^{12} tons on the land area all around the world. Moreover, biomass contains very less quantity of sulfur, nitrogen, and ash, so it releases low amounts of SO_x, NO_x, and soot in comparison to the fossil fuels. Biomass is the only energy resource which produces fuels in the form of liquid, solid, and gases.

2. LITERATURE REVIEW

Meier and Faix (1999) who briefed the updates for the pyrolysis of lignocellulosic biomass.

Bridgwater and Peacocke (2000) summarized the features of fast pyrolysis and provided the history of major processes developed since 1970.

Bridgwater (2003) described the design consideration to optimize the operation of pyrolysis reactors.

Babu (2008) described the chronological improvements in the theoretical study on kinetic modeling, heat and momentum transfer for plasma, and conventional pyrolysis.

Isahak et al. (2012) described the characteristics of biomass, the design of reactors, product formation, and its upgradation for pyrolysis of biomass. Sharma et al. (2015) provided a critical review on the mathematical modeling studies of biomass pyrolysis, process parameters, and catalytic studies.

Murugan and Gu (2015) reviewed the research and development activities in India toward the growth of pyrolysis technology since three decades. These reviews covered mainly the state of the art for the developments of pyrolysis reactors, optimization procedures, and developments and industrialization of biomass pyrolysis in different countries. However, a review on pyrolysis of biomass describing in place of describing it should be describe the impact of operating parameters on the products is missing from the literature, since properties of pyrolysis

products (bio-char, bio-oil, and fuel gas) depend upon the operating parameters.

Different types of biomass such as corncob, wheat straw, rice straw, coconut shell, hornbeam shell, etc. have also been exploited to produce bio-oil, bio-char, and pyro-gas through pyrolysis using different reactors and operating conditions.

3. METHODOLOGY

Biomass is any organic matter—wood, crops, seaweed, animal wastes—that can be used as an energy source. Biomass is probably our oldest source of energy after the sun. For thousands of years, people have burned wood to heat their homes and cook their food. Biomass gets its energy from the sun. All organic matter contains stored energy from the sun. During a process called photosynthesis, sunlight gives plants the energy they need to convert water and carbon dioxide into oxygen and sugars. These sugars, called carbohydrates, supply plants and the animals that eat plants with energy. Foods rich in carbohydrates are a good source of energy for the human body. Biomass is a renewable energy source because its supplies are not limited. We can always grow trees and crops, and waste will always exist.

3.2 Types of Biomass

3.2.1 Wood and Agricultural Product

Most biomass used today is home grown energy. Wood— logs, chips, bark, and sawdust—accounts for about 44 percent of biomass energy. But any organic matter can produce biomass energy. Other biomass sources can include agricultural waste products like fruit pits and corncobs. Wood and wood waste are used to generate electricity. Much of the electricity is used by the industries making the waste; it is not distributed by utilities, it is a process called cogeneration. Paper mills and saw mills use much of their waste products to generate steam and electricity for their use. However, since they use so much energy, they need to buy additional electricity from utilities.

3.2.2 Solid Waste

Burning trash turns waste into a usable form of energy. One ton (2,000 pounds) of garbage contains about as much heat energy as 500 pounds of coal. Garbage is not all biomass; perhaps half of its energy content comes from biomass, which are made from petroleum and natural gas. Power plants that burn garbage for energy are called waste-to-energy plants. These plants generate electricity much as coal-_red plants do, except that combustible garbage—not coal—is the fuel used to fire their boilers.

3.2.3 Landfill Gas and Biogas

Bacteria and fungi are not picky eaters. They eat dead plants and animals, causing them to rot or decay. A fungus on a rotting log is converting cellulose to sugars to feed itself. Although this process is slowed in a landfill, a substance called methane gas is still produced as the waste decays. New regulations require landfills to collect methane gas for safety and environmental reasons. Methane gas is colorless and odorless, but it is not harmless. The gas can cause _res or explosions if it seeps into nearby homes and is ignited. Landfills can collect the methane gas, purify it, and use it as fuel. Methane can also be produced using energy from agricultural and human wastes. Biogas digesters are airtight containers or pits lined with steel or bricks. Waste put into the containers is fermented without oxygen to produce a methane-rich gas. This gas can be used to produce electricity, or for cooking and lighting.

3.2.4 Ethanol

Ethanol is an alcohol fuel (ethyl alcohol) made by fermenting the sugars and starches found in plants and then distilling them. Any organic material containing cellulose, starch, or sugar can be made into ethanol. The majority of the ethanol produced in the United States comes from corn. New technologies are producing ethanol from cellulose in woody fibers from trees, grasses, and crop residues.

`Today nearly all of the gasoline sold in the U.S. contains around 10 percent ethanol and is known as E10. In 2011, the U.S. Environmental Protection Agency (EPA) approved the introduction of E15 (15 percent ethanol, 85 percent gasoline) for use in passenger vehicles from model year 2001 and newer. Fuel containing 85 percent ethanol and 15 percent gasoline (E85) qualifies as an alternative fuel. There are more than 10 million _exible fuel vehicles (FFV) on the road that can run efficiently on E85 or E10. However, just under 10 percent of these vehicles use E85 regularly.

3.3 Biomass as a Source of Renewable Energy and Its Conversion Routes

Biomass is regarded as one of the oldest and abundantly available sources of energy. In the present time, it is the third largest source of energy. Biomass as direct energy source shares up to 40–50% of energy usage in domestic and industrial energy system in many developing countries, which have large forest and agriculture land.

Biomass can be renewed into the various forms of energy and other value-added products through two main conversion processes such as thermochemical and biological conversion. The physical conversion process is the other conversion process to convert biomass into energy. The

choice of the conversion process is mainly dependent upon the quantity and type of biomass as well as the form of energy
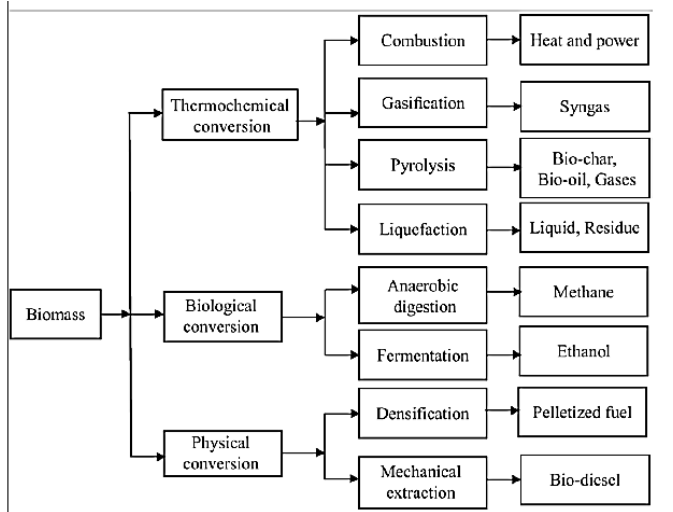

Fig. 1.1: Main processes for biomass to energy conversion

Thermochemical conversion processes are most commonly employed for converting biomass into higher heating value fuels. In the biological conversion process, biomass is converted into methane, biomethanol, bioethanol, or biobutanol with the help of enzymes or microorganisms. In comparison with biological and physical conversion processes, thermochemical conversion of biomass to energy is the most favorable. Thermochemical conversion of biomass is categorized into four processes such as:

1. Combustion
2. Gasification
3. Pyrolysis
4. Hydrothermal liquefaction

The advantages and disadvantages of combustion, gasification, pyrolysis, and hydrothermal liquefaction are summarized in Table 1.1. It shows that among different thermochemical processes, pyrolysisis one of the most promising and a feasible process as it produces fuel in the form of liquid, solid, and gaseous products with various utilization options.

Table1.1: Advantages and disadvantages of combustion, gasification, pyrolysis, and hydrothermal liquefaction

	ADVANTAGES	DISADVANTAGES
	Produced process heat can be used directly for	Emissions problems

	power generation	
	Industrially mature and commercial technology	Heat cannot be stored and it must be used immediately
		Larger gas cleaning equipment is required because of large volume of gaseous products
Gasification	Lower emissions	High capital cost
	Lower process operating temperature than combustion so better control of process	Complex operation as oxygen separation units is required
	Less gas cleaning equipment is required because of comparatively smaller volume of gaseous products	Costs associated with steam and oxygen
	Char produced from the low temperature gasification which can be consumed as activated carbon or soil amendment	High ash content feedstock can result in agglomeration
Pyrolysis	No emissions	Relatively less industrial experience of technology
	Lower operating temperature than gasification and combustion	High heating value (HHV) of bio-oil is lower than heavy oil
	Variety of	Separate up

	products in the form of solid (bio-char), liquid (bio-oil), gas (pyro-gas)	gradation step for bio-oil is required
	Bio-oil can be stored and more easily transported than solid biomass and syngas	Bio-oil is immiscible with hydrocarbons
	Bio-oil can be used as a fuel for power, as a biofuels and chemicals production	Long-term storage of bio-oil is difficult because of its corrosive nature
	Energy density of bio-oil is higher than syngas	
	Bio-char can be used as solid fuels, activated carbon, or soil amendment	
	Potential integration in bio refinery	
Hydrothermal liquefaction	Lower oxygen content in bio-oil as compared to the pyrolysis bio-oil	More expensive and complex process than pyrolysis
	Less processing of biomass is required	Requires high pressure and long residence time

3.4 Pyrolysis and Its Reaction Mechanisms

Pyrolysis is a thermochemical conversion process, which converts biomass into bio-oil, bio-char, and pyro-gas in the absence of oxygen. The word pyrolysis is derived from the Greek words "pyro" means fire and "lysis" means breaking or decomposition. In pyrolysis, thermal decomposition of biomass involves the complex interaction of heat and mass transfer which constitute several chemical reactions resulting into the condensable vapors (bio-oil), gaseous products (pyro-gas), and solid charcoal (bio-char). The main chemical reactions which occur during the pyrolysis of biomass are decarboxylation and decomposition of hemicellulose, cellulose, and lignin. Decarboxylation starts at 250 °C, where CO is released and left aliphatic or aromatic char. Hemicellulose decomposed first within the temperature range of 220–315 °C followed by the cellulose between 315 and 400 °C and finally lignin in between 100 and 900 °C. Decomposition of these compounds produces their monomer units, which are further decomposed into volatile products such as CO, CO , condensable vapors (liquids), and tars. During biomass pyrolysis, many chemical reactions which occur in series and parallel include dehydration, de-polymerization, decarboxylation, isomerization, aromatization, and charring. In general, biomass pyrolysis occurs in three steps: (i) evaporation of free moisture, (ii) primary decomposition (char formation, de-polymerization, and fragmentation), and (iii) secondary reactions (vapor cracking and re-polymerization)

3.4.1 Evaporation of Free Moisture

Removal of free moisture (water vapor) from biomass occurs in the form of dehydration. It starts at 100 °C leaving behind the amorphous carbon in the char.

3.4.2 Primary Decomposition

At the start of pyrolysis, different chemical bonds present in biomass are broken, which results in the release of volatiles and rearrangement reactions. These are the primary reactions which consist of char formation, de-polymerization, and fragmentation.

3.4.2. (a) Char Formation

This includes the conversion of biomass into solid residue, which results due to the formation and rearrangement of benzene rings into stable polycyclic structures. The release of non-condensable gases occurs during these rearrangement reactions.

3.4.2. (b) De-polymerization

De-polymerization involved in the breakage of polymers unites into the individual monomers, which results in the decrease of the degree of polymerization in the chains and produces volatiles. These volatiles are frequently recovered into liquid fraction. De-polymerization reactions occur between the temperature range of 250 and 500 °C.

3.4.2. (c) Fragmentation

It refers to the destruction of bonds within the monomer units of polymers which convert into non-condensable gas and linear compounds. Such type of breakage of ring/bonds generally occurs above 600 °C temperature.

3.4.3. Secondary Reactions

Volatile compounds generated during de-polymerization or fragmentation step are not stable under the reactor temperature, and they may be further involved in secondary reactions. These reactions occur in the vapor phase and/or between the vapor and solid phase. These are particular to cracking and recombination (re-polymerization) reactions. In cracking reactions, volatiles undergo breaking of chemical bonds to form the lighter molecular weight components. In recombination reactions, the volatiles recombine to form higher molecular weight components such as polycyclic hydrocarbons. Furthermore, additional solids such as secondary char are promoted to form when the recombination of volatiles occurs inside the pores of the solid residue. Figure 1.2 shows the reaction pathways for pyrolysis of biomass.
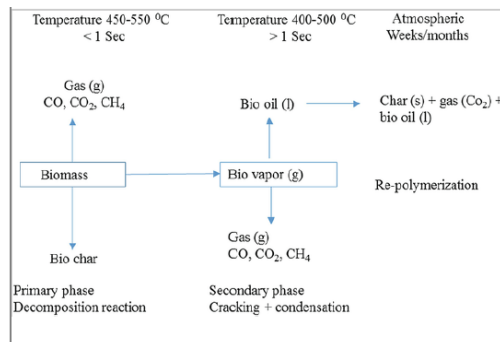

Fig 1.2: Reaction pathways for pyrolysis of biomass

3.5. Effect of Operating Parameters on Product Yield of Pyrolysis Process

Many factors affect the pyrolysis rate with product distribution and their quality. These factors can be summarized as the types of biomass, operating parameters (temperature, heating rate, biomass particle size, sweeping gas flow rate), and physicochemical properties of biomass. Here, we have discussed the effects of operating parameters on pyrolysis product distribution. The optimization of reaction conditions can enhance the yield of any of the three pyrolysis products. The effects of operating parameters on the product yield are summarized below

3.5.1 Temperature

Temperature is the most important and significant parameter in the pyrolysis. It is known from the available literature that pyrolysis temperature plays a key role in the product yield. Temperature provides the required heat for decomposition of biomass. It is known that when the temperature of a molecule exceeds its boiling point, it forms vapor. Therefore, with an increase in the reactor temperature, possibilities for the conversion of different molecules of biomass into vapor phase increase. In pyrolysis process, the temperature difference between the reactor inside and the fresh feedstock provides the driving force for heat transfer for the decomposition and fragmentation of biomass. With an increase in reactor temperature, this temperature difference increases and consequently the rate of decomposition of biomass increases. It is observed from the literature that bio-oil yield increases with an increase in pyrolysis temperature, attains a maximum value at around 500–550 °C, and decreases thereafter. The yield of bio-char is found maximum at the lower temperature of around 350 °C; furthermore, it decreases with an increase in temperature. Gaseous product yield increases continuously with an increase in temperature and maximum yield found at a higher temperature.

The characteristic properties of the bio-oil, bio-char, and gaseous product yield with an increase in operating temperature are because of the following reason. During pyrolysis, different types of reactions (primary and secondary) and de-volatilization of biomass take place, and the produced vapor further undergoes different secondary reactions. When condensed, the condensable compounds produce bio-oil. Non-condensed molecules produce gaseous products. Secondary reactions help to increase gaseous product yield by producing non condensable molecules. At lower temperature, the primary reactions predominate, and with the increase inreaction temperature, vapor formation increases. Consequently, the condensation of the vapors increases, which results in higher bio-oil yield. However, with an increase in temperature, the incidence of secondary reactions also increases. Thus, after a certain temperature range, the bio-oil production decreases when secondary reactions predominate. A temperature exists at which the condensation of produced vapor to the liquid product becomes optimum, resulting in maximum bio-oil yield.

With an increase in temperature, more volatiles are formed as discussed above. Consequently, residual biomass (bio-char) reduced. The yield of bio-char always decreases as temperature and heating rate increases, which is due to the significant loss of volatile matter or secondary decomposition of char at a higher temperature. Secondary decomposition of the char at a higher temperature produces

non-condensable gases, which contribute to the increase in gaseous product yield. The yield of gaseous products increases with an increase in temperature since at higher temperature secondary cracking reactions of pyrolysis vapors and secondary decompositions of char occur, which results in an overall increase in gaseous products' yield.

The composition of bio-oil varies remarkably with temperature. It is well known that bio-oils are a mixture of several chemical compounds. These chemical compounds are mainly alkanes, alkenes, carboxylic acids, aromatic, aliphatic and aromatic nitriles, and polycyclic aromatic hydrocarbons (PAHs).

3.5.2 Heating Rate

The heating rate is an important parameter in pyrolysis process. Rapid heating and cooling of primary vapors are required to minimize the possibilities of secondary reactions which reduce the liquid yield and have a negative impact on its quality, whereas slow heating favors the higher char yield. Biomass pyrolysis with high heating rate decreases he limitations of heat and mass transfer as well as controls the secondary reactions. High heating rate produces more volatiles by fast endothermic decomposition of biomass, which reduces the time required for secondary reactions (tars cracking or re-polymerization). This results in the faster removal of high molecular char and volatiles from the decomposing biomass and left fewer amounts of char.

3.5.3 Biomass Particle Size

It is obvious that biomass is a poor conductor of heat; thus in some pyrolyzer, sand is used as a media for quick heat transfer. In batch pyrolyzer, where no sand is used for heat transfer media, heat is transferred from the surface of the pyrolyzer wall to the biomass through its surface. Thus, the higher surface area of biomass particles increases the heat transfer. Smaller particles possess more surface area than the bigger particles, and hence heat transfer is higher when the smaller particle-sized biomass is used in pyrolyzer.

Due to this reason, more vapors are formed during pyrolysis, which result in less char and more gaseous products when particle size is smaller. With an increase in particle size, the heat transfer reduces, as a result, the rate of vaporization decreases, which gives more char formation and less gas formation. Furthermore, larger particle-sized biomass results in high-temperature gradients inside the particles; thus all the mass of the particle does not attain similar temperature when compared to smaller particle-sized biomass. Large particle-sized biomass also requires a high activation energy. Due to these reasons, more char formation takes place and the vaporized products become

relatively more condensable as compared to that of lower particle size feedstock. This is the probable reason for which bio-oil yield does not vary significantly due to the variation in particle size.

3.5.4 Sweeping Gas (N_2) Flow Rate

The reactive environment of pyrolysis process can affect the nature and composition of the pyrolysis products. The interaction between the pyrolysis vapors with surrounding solid responsible for secondary exothermic reactions which lead to the formation of char. Pyrolysis conditions that support quick mass transfer are useful to minimize these reactions such as vacuum pyrolysis, fast purging of pyrolysis vapors, and rapid quenching of hot vapors. Inert gases such as N_2, Ar, and water vapor are used for the rapid purging of hot pyrolysis vapors. In most of the studies, N_2 gas is generally used due to its low cost.

In pyrolysis, the biomass first forms volatile vapors, which are carried out from the reactor by an inert gas like N_2 and condensed to produce bio-oil. The uncondensed vapors along with the carrier gas result in gaseous products. At lower N_2 flow rate, the residence time of the volatiles in the hot reactor zone is higher, as a result, higher N_2 flow rate, the residence time of the vapor in the reactor hot zone decreases; consequently, more vapor formation takes place, which result in lower char yield and higher gas yield.

At a higher residence time, vapors in the reactor hot zone are converted to either smaller molecules by cracking or partial oxidation and generate more gaseous product as well as bigger molecules through re-polymerization, re-condensation, etc. The relative contribution of these secondary reactions depends on the vapor residence time. The decrease in residence time reduces the contribution of re-polymerization reactions. Further, if the residence time is too less, the re-polymerization reactions may not be considerable, which results in the lower production of bio-oil. Thus, with an increase in N_2 flow rate, initially the yield of bio-oil increases because of the formation of more vapors and their condensation as well as polymerization. However, after certain N_2 flow rate, the yield of bio-oil decreases as the contribution of re-polymerization reactions reduces .

3.6 Types of Reactors

The type of reactors has an important impact in the mixing of the biomass and catalysts, residence time, heat transfer and efficiency of the reaction towards achieving the final desired product. Most plastic pyrolysis in the lab scale were performed in batch, semi-batch or continuous-flow reactors such as fluidized bed, fixed-bed reactor and conical spouted bed reactor (CSBR). The advantages and downsides

of each reactor would be discussed in the following subsections.

1. Batch and semi-batch reactor

Batch and semi-batch reactor Batch reactor is basically a closed system with no inflow or outflow of reactants or products while the reaction is being carried out. High conversion in batch reactor can be achieved by leaving the reactant in the reactor for an extended time which is one of its advantages. However, the disadvantages of batch reactor are the variability of product from batch to batch, high labor costs per batch and the difficulty of large scale production.

In contrast, a semi-batch reactor allows reactant addition and product removal at the same time. The flexibility of adding reactants over time is an added advantage of the semi-batch reactor in terms of reaction selectivity. The disadvantage of semi-batch reactor is similar with the batch reactor in terms of labor cost, thus it is more suitable for small scale production.

Some researchers preferred to use batch reactors or semi-batch reactors in plastic pyrolysis laboratory scale experiment due to the simplest design and ability to control the operating parameters easily. Pyrolysis in batch reactor or semi-batch reactor normally performed at temperature range of 300–800°C for both thermal and catalytic pyrolysis. Some researchers added catalysts to the biomass to improve hydrocarbon yield and for product upgrading. In catalytic pyrolysis, the catalyst was mixed together with the plastic sample inside the batch reactor. The drawback of this process would be a high tendency of coke formation on the surface of the catalyst which reduced the catalyst efficiency over time and caused high residue in the process. Besides that, it was also a challenge to separate the residue from the catalyst at the end of the experiment.
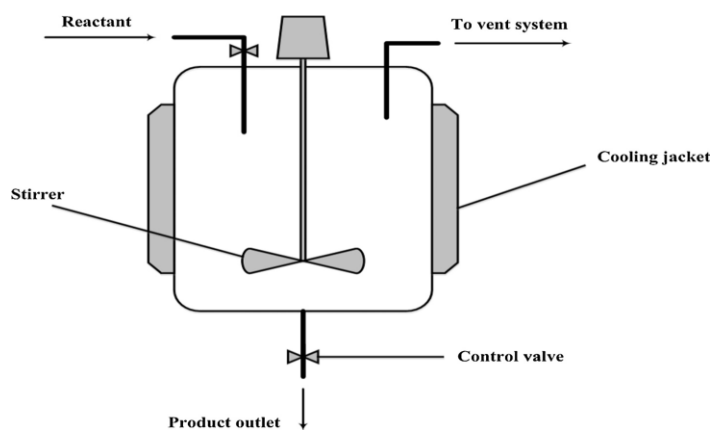

Fig. 1.3: Batch and semi-batch reactor

2. Fixed and fluidized bed reactor

In fixed-bed reactor, the catalyst is usually in palletized form and packed in a static bed as shown in Fig. 1.4. It is easy to design but there are some constraints such as the irregular particle size and shape of biomass as feedstock that would cause problem during feeding process. Besides, the available surface area of the catalyst to be accessed by the reaction is also limited. However, there were several researches chose to use fixed-bed reactor for the plastic pyrolysis. In certain conditions, the fixed-bed reactors are merely used as the secondary pyrolysis reactor because the product from primary pyrolysis can be easily fed into the fixed-bed reactor which generally consists of liquid and gaseous phase.

On the other hand, fluidized bed reactor solves some of the problems occur in fixed-bed reactor. In contrast to fixed-bed reactor, the catalyst in fluidized bed reactor sits on a distributer plate as illustrated in Fig. 1.5 where the fluidizing gas passes through it and the particles are carried in a fluid state. Therefore, there is better access to the catalyst since the catalyst is well-mixed with the fluid and thus provides larger surface area for the reaction to occur. This reduces the variability of the process conditions with good heat transfer. Besides, it is also more flexible than the batch reactor since frequent feedstock charging can be avoided and the process does not need to resume often. Hence, as for conventional design scale, fluidized bed reactor would be the best reactor to be used in the pilot plant due to the lower operating cost

Therefore, fluidized bed reactor is concluded to be the best reactor to perform catalytic plastic pyrolysis since the catalyst can be reused many times without the need of discharging, considering catalyst is a very expensive substance in the industry. Besides, it is more flexible than the batch reactor since frequent feedstock charging can be avoided for continuous process and the process does not need to resume often. Hence, fluidized bed reactor would be the most suitable reactor for large scale operation in terms of economic point of view.
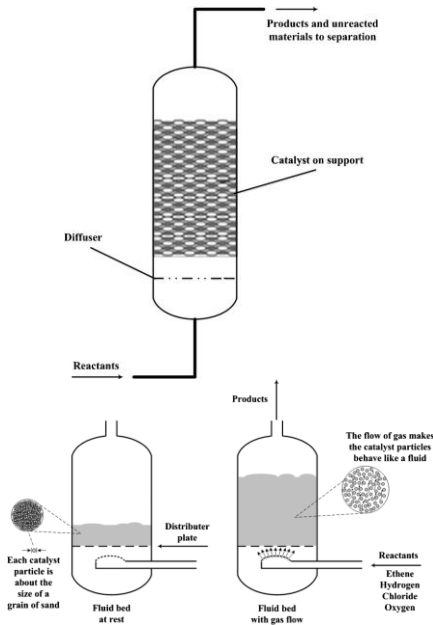
Fig. 1.4: Fixed bed reactor

Fig. 1.5 Fluidized bed reactor

3. Conical spouted bed reactor (CBSR)

Conical spouted bed reactor (CSBR) provides good mixing with the ability to handle large particle size distribution, larger particles and difference in particle densities. There were some researchers used CSBR for their catalytic cracking of plastic experiments. CSBR had lower attrition and low bed segregation than the bubbling fluidized bed. It also had high heat transfer between phases and minor defluidization problem when handling sticky solids. However, a variety of technical challenges during operation of this reactor have been encountered such as catalyst feeding, catalyst entrainment and product (solid and liquid) collection that make it less favorable Additionally, its complicated design that requires many pumps to be used in the system makes it unfavorable due to the high operating cost involved.
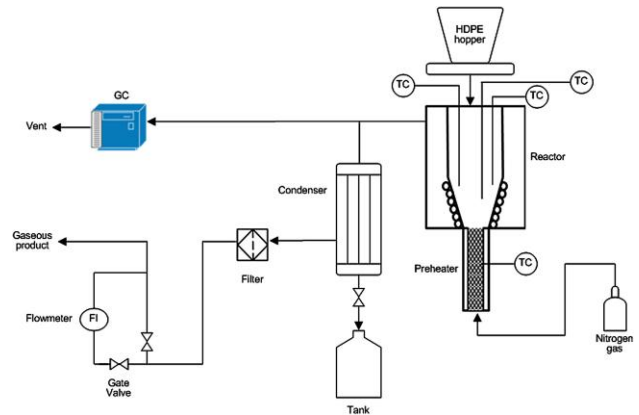

Fig.1.6: Conical spouted bed reactor

3.8. Pyrolysis Product Characteristics

The important products of biomass pyrolysis are bio-char, pyro-gas, and bio-oil. Characteristics and utilization potential of these products are described below:

3.8.1 Bio-char

Bio-char is the solid residue left after pyrolysis of carbonaceous biomass. The properties of bio-char mainly depend on the process and the biomass used. It is usually characterized for bulk density, proximate and ultimate composition, heating values, and surface properties. Thermal decomposition removes the moisture and volatile matter contents from biomass, and the remaining solid char has different properties than the parent biomass. Significant differences are mostly observed in the surface area, porosity, pore structures, and physio-chemical properties such as proximate and ultimate composition It has high carbon content with calorific value in the range of 17–36 MJ/kg, as a result of which it can be utilized as a potential source of energy and may internally provide heat for pyrolysis process. In addition, it can also be used as a precursor for activated carbon production and in the purification of wastewater through adsorption. In recent years, bio-char has gained enormous attention as it can be utilized as a fertilizer and also improves the quality of soil by increasing the retention time and availability of water and nutrients in the soil . In many cases, it also increases the crop growth.

3.8.2 Gaseous Products/Pyro-gas

It mainly consists of CO, CH_4, CO_2, and H_2 with the heating value of 6.4–9.8 MJ/kg and internally utilized as process heat for pyrolysis. It can also be used as synthesis gas with extensive reforming.

3.8.3 Bio-oil

Bio-oil is a dark brown color, free-flowing organic liquid, which contains oxygenated compounds and is immiscible with other petrochemical liquid fuels. It is highly viscous, acidic, relatively unstable, corrosive, and chemically complex in nature It has a distinctive smoky odor. The heating value of bio-oil is lower than the conventional petroleum fuels due to the high water and oxygen content. Bio-oil contains various chemical compounds such as water, water-insoluble lignin fragments, alcohols, aldehydes, carboxylic acids, ketones, carbohydrates, furfurals, and phenols. Table 1.3 represents the typical chemical compositions of bio-oil.

Major components	Quantity (wt.%)
Water	20–30
Lignin fragments	15–30
Aldehydes	10–20
Carboxylic acids	5–10
Carbohydrates	2–5
Alcohols	2–5
Ketones	1–5
Phenols	1–4
Furfurals	2–5

Table 1.3: Typical chemical compositions of bio-oil

Bio-oil finds its utility in numerous places such as in power and chemical sectors. These include usage as a fuel in furnaces and boilers to powering diesel engines. Although the utilization of bio-oil as the transportation fuel is feasible in the form of methanol and Fischer-Tropsch fuels, more research is required in this field. Furthermore, another benefit of bio-oil is that it can be used in the extraction of a number of chemical products. A general overview of the applications of bio-oil is shown in Fig. 1.7
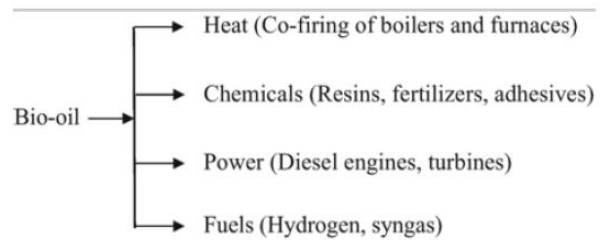

Fig. 1.7: Applications of bio-oil

3.9 Upgradation of Bio-Oil

Considering the above discussion on the properties of bio-oil, it is clear that the fuel quality of bio-oil is lower than the petroleum fuels. Recently, there are several studies that have been done on the upgradation of bio-oil. Table 1.4 [52] shows the current technology used for the upgradation of bio-oil. The characteristics as well as advantages and disadvantages of each technique are also described below.

3.9.1 Hydrotreating

Hydrotreating (HDT) is a nondestructive/simple hydrogenation process used to improve the quality of bio-oils by alteration of their boiling range. In this process, bio-oil reacts with hydrogen at moderate temperature up to 500 °C and low pressure in the presence of the catalyst to remove the oxygen present in bio-oil. The commonly used catalysts for this process are sulfide CoMo or NiMo supported on alumina or aluminosilicates. The main problems that arise due to the use of these catalysts are the instability of alumina and aluminosilicates in the high water content environment of the bio-oil and sulfur stripping from the catalysts. Other suitable catalysts such as Ru/C, Pd/C Pt/SiO2/Al2O3 , vanadium nitride and Ru[58] have also been used for hydrotreating. is process operates at mild conditions, but the yield of bio-oil is relatively low. Moreover, this process generates a large amount of coke, char, and tar, which are responsible for deactivation of catalysts and reactor clogging.

3.9.2 Hydrocracking

Hydrocracking is a thermal process (>350 °C) in which hydrogenation accompanies cracking which occurs at relatively high pressure (100–2000 psi). Hydrocracking of bio-oil produces a wide range of products due to the combination of catalytic cracking reactions with hydrogenation and the multiplicity of reactions. This process is performed by dual-function catalysts in which silica-alumina or zeolite (HZSM-5, HY) catalysts provide the cracking function. In addition, platinum and tungsten oxide catalyze the reactions, and nickel provides the

hydrogenation function. Alumina is mostly used as a support for catalyst. This process is more effective for production of a large amount of light product. However, it requires more severe conditions of temperature and pressure to deal with acids, which is not economical and energy efficient.

3.9.3Steam Reforming

This process converts the petroleum fractions to more volatile products with higher octane number and represents the combined effect of various reactions such as cracking, isomerization, and dehydrogenation. In this process, hydrocarbons are converted into syngas (CO + H_2), by reaction with steam at high temperature. Commercial nickel catalysts show good activity in the processing of bio-oil. Hydrogen production from steam reforming of bio-oils has been extensively studied by the National Renewable Energy Laboratory (NREL) in fixed-bed and fluidized-bed reactor along with the reaction mechanisms. Hydrogen is a clean energy resource and crucial in the chemical industry. The increasing focus on reforming the water fraction of bio-oil looks promising.

3.9.4 Supercritical Fluids

Supercritical fluids have the ability to dissolve materials which are not usually soluble in either gaseous or liquid phase of the solvent and hence to promote the liquefaction/gasification reactions. Supercritical fluids have the ability to improve the yield and quality of bio-oil and have demonstrated a great potential for producing bio-oil with much higher caloric value and lower viscosity. Water is the cheapest and most commonly used supercritical fluid in hydrothermal processing, but utilizing water as the solvent for liquefaction of biomass has the following drawbacks: (1) lower yield of the water-insoluble oil product and (2) yields bio-oil that is very viscous and has high oxygen content. To improve the quality and yield of bio-oil, utilization of organic solvents such as ethanol, butanol, acetone, and methanol has been adopted. All these solvents have the ability to significantly affect the quality and yield of bio-oil, although the process of upgrading bio-oil using supercritical fluids is environment friendly and required relatively lower temperature. However, this process is not economically feasible on a broad scale due to the high cost of the organic solvents.

3.9.5 Esterification

Esterification of bio-oils with low molecular weight alcohols is an effective approach to improve their qualities. In the last few years, a lot of work has been done to upgrade the bio-oils by esterification. Zhang (2006) demonstrated the solid acid/base catalyst to esterify the bio-oil under atmosphere pressure and found that the acidity, density,

heating value, and storage stability of the bio-oil improved remarkably.

3.9.6 Emulsification

Emulsification is a simplest technique, where the bio-oil is emulsified with diesel using a surfactant. However, it is considered as a short-term approach, because this process is not economical, and corrosion issues are associated with this technique.

3.10 Objective of the Project

1) Identification of the desired biomass

2) Characterization of identified biomass

3) Pyrolysis of the identified biomass

4) Characterization of byproducts of pyrolysis

5) Use of byproducts of pyrolysis such as char, oil and gas

6) To raise awareness in developing countries like INDIA on biomass and its possible reuse for conversion into fuel, this could be generated and marketed at cheaper rates compared to that of the available diesel or oil in the market

3.11 Statement of the Project

Pyrolysis of Biomass and the Use of Pyrolysis Oil as an Alternate Fuel.

3.12 Scope of the Project

1) The obtained fuel could be utilized in diesel generators, vehicles such as tractors and also passenger vehicles such as cars

2) The fuel has to be refined at the industrial establishments, based on the results of which small scale industry can be established

3) As there is a high demand of crude oil and due to its sky reaching prices, we could take up this project to setup large or small scale industries and produce the fuel locally at much cheaper rates directly benefiting the National economy and also a step towards SWACHH BHARAT by recycling the Biomass

4) The application of this project could help in reducing the dependency on the gulf countries and promote a step towards innovation

4. CONCLUSIONS

Pyrolysis process follows indirect thermal decomposition mechanism by which biomass under oxygen-depleted condition can be converted into three major products such as bio-oil, bio-char, and pyro-gas. The yield of these pyrolysis products depends upon the operating parameters such as temperature, heating rate, biomass particle size, and sweeping gas flow rate. Temperature is the most important operating parameter in the pyrolysis process, and intermediate temperature between 500 and 550 °C maximizes the bio-oil yield in the products. Low- and high-temperature ranges favor the formation of char and gases, respectively. Overall, moderate pyrolysis temperature, high heating rate, and short vapor residence time maximize the yield of bio-oil in the product. Sweeping gas flow rates do not much influence the yield of bio-oil. However, it reduces the volatile residence times, which helps to minimize the secondary cracking and re-polymerization of vapors. Moreover, a rapid quenching of hot pyrolysis vapors is crucial for high bio-oil yield. The optimum pyrolysis product yield which varied for different biomass depends upon the reactor types and operating parameters. Studies have also been carried out for properties and application of pyrolysis products as well as the up gradation of bio-oil.

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