



A REVIEW ON PYROLYSIS OF BIOMASS WITH A FOCUS ON OPERATING PARAMETERS, PRODUCT CHARACTERIZATION AND ITS APPLICATION

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Abstract: Biomass pyrolysis is an emerging technology that can be used for the production of the carbon neutral fuels and to replace the existing fossil fuels. Global concern for the clean energy fuel is growing day by day. Products obtained from the pyrolysis of biomass are bio oil, biochar and biogas. Biomass pyrolysis products have variety of usage with no such harmful waste product. Extensive research has been carried out on the biomass pyrolysis and various factors affecting it. This review paper aims to study the pyrolysis process, biomass and their composition. Furthermore, the factors affecting the pyrolysis process such as temperature, particle size, heating rate and sweeping gas are also studied. The composition of pyrolysis products and their application in different field are also studied. It is evident from literature that the biomass has a potential to meet the future energy requirements by using pyrolysis process.

1. INTRODUCTION

In the social and economic development of the nation, energy plays an essential role as energy is prime required element for every sector. On a broad scale fossil fuel, nuclear energy and renewable energy resource are some contemporary and extensively used energy resources (varma et al 2016, & saeidy et al 2004). Global energy demands have been fulfilled by the fossil fuels mainly but depleting fossil fuels, global warming and increase in greenhouse gases compelling the need for the search of an alternative fuel which is also a carbon-neutral energy resource (kabir et al 2016). Usage of renewable energy has been around 14 percent of the total energy demand around the globe (thakur et al 2017). It has been increasing gradually over the globe to check and curb the carbon dioxide emission as well as to meet the current energy demand (varma et al 2019). Biomass has emerged as the best renewable source of energy because of its abundance in nature, ease of availability, eco-friendliness and carbon neutrality (danje et al 2011). Biomass is considered as carbon-neutral energy resource because it consumes CO₂ during photosynthesis and releases it while burning (Uddin et al 2018). Generally, biochemical and thermochemical processes are employed for producing energy from biomass. Biochemical conversion process employs biological catalysts and organisms for producing desired energy-rich products such as ethanol from biomass. The Biochemical process includes aerobic digestion, anaerobic digestion and fermentation (munir et al 2009, saeidy et al 2004). Thermochemical processes are using heat and chemical catalyst for the energy production. Gasification, liquefaction, pyrolysis and combustion are some thermochemical conversion processes used for the production of biofuels from the biomass. Although, biochemical conversion process is more economical and environmental friendly than thermochemical process but yield and production rate is quite low. While, thermochemical conversion process is more efficient than biochemical processes so they are more preferential and popular (saeidy et al 2004, varma et al 2016, Damartzis et al 2011). The pyrolysis process is the most promising of the above since it produces no waste. As it provides the best solution by utilizing agricultural and forest residue for energy production (Bamboriya et al 2019, Abnisa et al 2014). In the pyrolysis process, biomass feedstock and waste plastics are converted into bio-oil can serve as a forerunner for fuels and chemicals in industries (Kabir et al 2016). Pyrolysis has potential to production of bio-oil of 75 mass % yield at the moderate temperature of around 500°C (Cepeliog˘ullar et al 2013). Pyrolysis is the thermochemical breakdown of molecules in the absence of oxygen in an inert atmosphere at average temperature around 400 to 600°C (Yousef et al 2020, varma et al 2016). Products obtained from pyrolysis are biochar, biogas and bio-oil in which the main product is bio oil. Biochar can be used in soil amendment as well as to produce activated carbon and biogas which can be used industrially and domestically both (Munir et al 2009). Pyrolytic oil contains a good proportion of alkanes, hydrocarbons, phenols and its derivative aromatics, amines, alcohols and oxygenated compounds (Tripathi et al 2016).

Bio-oil has emerged as a potential alternative for fossil fuel but there is still a need for up-gradation of bio-oil because of its low calorific value, high oxygen content, corrosion problem, instability, lower high heat value (HHV), lower volatility and

delayed ignition time in engine (Han et al 2013). The up-gradation of bio-oil can be done either by high-pressure hydrogenation process and catalytic cracking or by co-pyrolysis of biomass with synthetic polymers like waste plastics, waste polyethylene etc (Cepeliogullar et al 2013, Patil et al 2017). Co-pyrolysis can be considered as an imperative emerging technology for utilizing the energetic and organic value of the waste (Dubdub et al 2020). Disposal of the waste plastic is a quite challenging problem that the world is facing which also triggering climate change and global warming. Landfilling and incineration are used for plastic waste management but neither of them is economical and eco-friendly. Instead, they could pollute the land and air (Bamboriya et al 2019, Saha et al 2006). Recycling is a preferential and potential alternative over landfilling and incineration. Recycling treatment of the waste plastics is classified into three types i.e. mechanical, chemical and thermal treatment. Mechanical treatment is the pre-treatment for the size reduction of the plastics. Chemical treatment includes extraction of polymer components from the waste plastics but due to low recycling rate, use of a lots of chemicals, higher energy consumption, higher CO₂ emission and the product obtained cannot find its application in a wide range thus this treatment is also not considered very much efficient and eco-friendly. Thermal treatment is combustion, gasification, pyrolysis etc where combustion produces heat and power but it causes some environmental problems, while gasification produces char but with low value however, pyrolysis produces value-added energy products such as gaseous fuel, liquid fuel and char (from which activated carbon can be derived). Pyrolysis comes under tertiary recycling; it converts polymeric and cellulosic derived material into feedstock quite easily. Another advantage of pyrolysis is that it reduces the volume of the waste and process is carried out at low temperature when a catalyst is used (Chattopadhyay et al 2008, Mishra et al 2020, Bridgewater et al 1999). The prime objective of this study is to analyse basics of pyrolysis process, biomass, key process operating parameters, products of pyrolysis and bio oil application.

2. PYROLYSIS PROCESS PRINCIPLES

Pyrolysis is derived from the greek words pyro means fire and lysis means decomposition (Mckendry et al 2002). During the thermochemical process of biomass pyrolysis, an inert atmosphere is created. It is a complex process that involves the thermal cracking of biomass feedstock (Dange et al 2011). In absence of air, biomass converted into volatile products and char within the temperature range of 500-800°C (Uddain et al 2018, Babu et al 2008). There are three stages of pyrolysis process, firstly raw material is fed into reactor, second one is the changes the organic mass underwent and then separate the product generated. Pyrolysis of biomass is a set of different parallel and competing reactions. Biomass pyrolysis is categorised as heterogeneous chemical reaction where reaction dynamics and chemical kinetics can be influenced by three major elements i.e. rupture and redistribution of chemical bonds, changing reaction geometry and interfacial diffusion of reactants and products. It involves the splitting of C-C bonds and the bonding of C-O bonds in which a portion of biomass is converted to carbon while the rest is oxidised and hydrolysed (Uddain et al 2018, Zaror et al 1982, Mohan et al 2005). An oxygen free medium favour heating of the biomass to temperature over its thermal stability limit and also prevents combustion (Saeidy et al 2004).

In the earlier literatures, term pyrolysis is considered synonymous to carbonization where solid char is the main product but now a days bio oil has become the principal product replacing char (Guedes et al 2017). Pyrolysis process involves heat and mass transfer mechanisms where initially heat is transferred from heat source to the particle surface and then to its inside which results as an increment in the inside temperature of the particle which removes the moisture of the biomass (Babu et al 2008, Yeman et al 2003). Pyrolysis process mechanisms can further be divided as primary and secondary process. Due to increase in inside temperature of the particle of the biomass, there is a commencement of primary pyrolysis reactions which involves fragmentation, char formation and depolymerisation (Han et al 2013). By the effect of heat, biomass is fragmented and devolatilized into its main constituents. Benzene rings are formed in char formation process, these rings unite together to form a residue called char, an aromatic structure. The polymers are cleaved into single monomeric units till the volatile molecules are produced. This process is known as depolymerization process. Lastly, small chain organic compounds and gases are produced by the covalent bond linkage of the polymers within the monomeric units in the fragmentation process (Mohan et al 2005, Babu et al 2008, Guedes et al 2017). Those reactions which influence the cellulosic biomass directly are termed as primary pyrolysis reactions. In the primary reactions, breakdown of cellulose, hemicellulose and lignin takes place which forms primary products and intermediates. Primary pyrolysis involves removal of H₂O, carboxyl group and H₂. Various hydroxyl, carboxyl and carbonyl groups are formed in primary pyrolysis (Saeidy et al 2004, Babu et al 2008). Primary pyrolysis at high temperature releases volatiles. Then heat transfer takes place between hot volatiles and cooler unpyrolyzed fuel oil. These interactions results in the initiation of secondary pyrolysis which is autocatalytic in nature. Secondary reactions affect the intermediates. Primary reactions and secondary reactions occurs simultaneously and competitively (Gudese et al 2017, Yemen et al 2003, Kan et al 2018). When fragmentation and depolymerisation occur in nature, volatile compounds are not stable at reactor temperatures. A secondary pyrolysis is then carried out, which involves cracking and recombination. In cracking breakdown of the volatile compounds into lower molecules takes place while in recombination process, volatiles are combines to form higher molecular weight compounds. These higher molecular weight compounds can either be volatile or non-volatile in nature. While in some cases, due to condensation of volatile compounds in cooler area of fuel, char can be produced which is called as secondary char (Munir et al 2009, Mohan et al 2005, Yeman et al 2003). Depending upon the operating conditions used, pyrolysis can be classified into three types: slow, fast and flash pyrolysis (Jahirul et al 2012).

1) **Slow pyrolysis:** Slow pyrolysis, termed as carbonisation, has been traditionally used for the production of charcoal (Grange et al 1996, Raveendran et al 1996). Conventional slow pyrolysis process has been in use since thousands of years and it has slow heating rate (Guedes et al 2017, Yeman et al 2003). In this kind of pyrolysis, thermal decomposition of the organic components of the biomass is slow and irreversible (Grange P et al 1996). Thermal breakdown of biomass takes place at lower heating rate, longer residence time and at relatively lower process temperature (300°C-700°C). The particle size in the range of 5 to 50 mm is used in slow pyrolysis, because of which repolymerization reactions gets enough time to maximize the solid yield (Jahirul et al 2012, Raveendran et al 1996). However, slow pyrolysis is not much suitable for the production of good quality bio oil as due to long residence time cracking of primary products occurs which is likely to affect the bio oil quality and yield. It also demands extra energy inputs because of its low heat transfer and higher residence time (Tursi et al 2019).

2) **Fast Pyrolysis:** In fast pyrolysis biomass is heated rapidly at high temperature with high heating rates (410-200°C/s), short residence time, (0.5-10s) and oxygen deficiency (Thakur et al 2017, Raveendran et al 1996). When pyrolysis is performed at high temperature, bio oil is formed but oil yields may be affected by pyrolysis temperature alterations, types of biomass, mechanism of heat transfer, size of the feed particle and residence time (Jahirul et al 2012, Babu et al 2008). Biomass is breakdown into

aerosols, vapours and charcoal. These vapours and aerosols are rapidly cooled and condensed produce a pyrolysis liquid. Fast pyrolysis requires finely grinded biomass feed particles to achieve high heat transfer rate (Thakur et al 2017, Guedes et al 2017). High heating rates, high heat transfer, rapid cooling of vapours, very short vapour residence time and the precision of temperature control are some features of the fast pyrolysis (Tursi et al 2019). Lower energy costs, lower capital investment cost and improved efficiency and environmental friendliness are some key feature of fast pyrolysis technology (Jahirul et al 2012). Fast pyrolysis has acquired immense popularity for the generation of fuels (liquid state) and the range of speciality chemicals. Liquid fuels are stored and transported quite easily and economically (Tursi et al 2019).

3) **Flash Pyrolysis:** in flash pyrolysis biomass is heated at higher heating rates (103-104°C/s) with higher reaction temperature between 450-1000°C and shorter residence time (0.5 s) (Raveendran et al 1996, Tursi et al 2019). Flash pyrolysis is a promising process and is entirely different from the conventional pyrolysis process (Yaman et al 2003, Sudha et al 1999). Flash pyrolysis has a rapid thermal processing technique which has a very short vapour residence time a high level of thermal activity with a fast quenching, it conserve starting important depolymerisation products (Sudha et al 1999). In the flash pyrolysis particle size is kept small i.e. in range of 2-3mm and dried feedstock with 10% moisture content to expose particle for the rapid heating, heat transfer and quenching of hot pyrolysis vapours (Jahirul et al 2012). The majority of the products produced from flash pyrolysis process are gaseous (Yeman et al 2003). Flash pyrolysis oil is generally used in direct combustion in boilers or gas turbines (Verma et al 2012). Corrosiveness, poor thermal stability and increase in viscosity of oil are some technical limitations which arises during flash pyrolysis (Tursi et al 2019).

3. BIOMASS

Among the renewable energy resources, it is the single resource which can be converted into all the three states of fuels (saeidy et al 2004). Biomass is present in abundance and can be used without the damaging environment in any major way. It does not have any risk of major accidents as the nuclear and oil energy do (White et al 2011). Biomass is the organic material derived from the plants in which energy from the sunlight is stored in the form of chemical bonds by the photosynthesis process. When the chemical bonds are broken, the substance releases their stored energy (Akhtar et al 2012). Biomass is also defined as waste derived from organic and inorganic compounds, such as organic manure, sludge, waste paper etc (Uddain et al 2004). Hence, all the biodegradable organic material derived from plants, animals, micro-organisms, non-fossil organic waste from industry or municipal corporation and agricultural products or residues fall under the category of biomass (Mohan et al 2006). Biomass contains a complex mixture of lignin, cellulose, hemicellulose and extractives along with a small number of inorganic compounds which decompose or pyrolyze at different rates, different mechanisms and pathways (Tripathi et al 2016, Thakur et al 2017). Being able to transform extensively available biomass into energy is quite attractive prospect for the countries like India. The most common raw materials are forest and agricultural residues for the pyrolytic process (Kan et al 2016, Verma et al 2012). There can be two ways to classify biomass; firstly on the types of the biomass exists in nature and secondly on the basis of the use and application of the biomass feedstocks. Generally the former one is the most used classification. So on this basis, biomass is classified as

- a) Wood and woody biomass
- b) Aquatic biomass
- c) Herbaceous biomass
- 1) Agricultural crop residue
- 2) Energy crop residue
- d) Animal and human waste biomass
- e) Biomass mixture

Woody biomass is consisting of trees, barks, root residues and leaves of the woody shrubs. It can be obtained from forests. The structure of the woody tissue is fibrous in nature. Since wood has low thermal conductivity, the temperature gradient within the solid increases sharply along with the thickness of biomass material (Kan et al 2018, Zhou et al 2006, Zhao et al 2011). Aquatic biomass is high moisture content material which includes microalgae, macroalgae and emerging plants. Since they are high in moisture content, they are more suitable for wet processing techniques such as fermentation. Aquatic biomass has high hydrogen content as well hence it is suitable for the production of hydrogen. In aquatic biomass, sulphur content is less and good nitrogen content (Saeidy et al 2004, Akhtar et al 2012, Zhau et al 2006). The most common raw materials for the pyrolysis system are forestry and agriculture residues. They are heterogeneous in nature and show significant variations in chemical and physical structure within the single piece of the biomass material (Kan et al 2016). Most of the agricultural crop residue such as olive oil residue, corncob, hazelnut bagasse, tea waste, cotton etc can be transformed into valuable products (Zhao et al 2011).

3.1 COMPOSITION OF BIOMASS:

Biomass is the matrix of organic resources and small amount of minerals, also containing carbon, hydrogen, oxygen, nitrogen, chlorine and sulphur (Mohan et al 2006). Cellulose, hemicellulose and lignin are the major organic components of the biomass (Grange et al 1996). During pyrolysis, when sugar units break thermally, hemicellulose and cellulose forms volatile products mainly and char is mainly formed by lignin (Sharypov et al 2002). Cellulose is the polymer of glucose, containing the units of (1,4)-D-glucopyranose in a linear chain with an average molecular weight of around 100000. (1,4)-D-glucopyranose units are connected as 1-4 in β -configuration. Cellulose is found to be insoluble in water. Cellulose provides the skeletal structure to the most of the biomass. Approximately 50% of the cell wall material is formed by cellulose (Mckendry et al 2002). Hemicellulose is a matrix of heterogeneously branched complex polysaccharides consisting of sugars such as glucose, xylose, mannose, arabinose, galacturonic acids, methyl glucuronic with an average molecular weight less than 30,000. Hemicellulose is tightly and non-covalently binds with microfibril surface of each cellulose. It is soluble in dilute alkali solutions. Generally, the monomeric units in hemicellulose are 50-200 with a few simple sugar residues. Xylan is the most abundant one found 10 to 30% of the dry weight basis in softwoods and hardwoods (Yeman et al 2003, Mckendry et al 2002). Lignin is a highly branched, amorphous and high molecular weight substance having three carbon chains on the ring of six carbon atoms called phenyl propane. There can be three structures possible depending upon the number of methoxyl groups attached. Lignin degrades over a wider range of the temperature while cellulose and hemicellulose over a narrow temperature range. Lignin is insoluble in sulphuric acid so for separating lignin from the complex strong sulphuric acid treatment is taken. Lignin content in soft woods and hardwoods ranges

from 20% to 40% by weight (dry basis) and from 10% to 40% by weight in herbaceous species (Bridgwater et al 1999, Yeman et al 2003, Mckendry et al 2002). It is easy to separate and recover cellulose in its pure form while due to structural changes during processing, separation and recovery of hemicellulose and cellulose is quite difficult (Thakur et al 2018, Akhtar et al 2012, Grange et al 1996). Thakur et al. 2017 concluded that high cellulose and high hemicellulose content in vetiver grass leads to high bio-oil yield. Pyrolytic behaviour of the biomass is affected by the composition of the cellulose, hemicellulose and lignin (Varma & Mondal et al 2015,). Low lignin, high cellulose and hemicellulose content are favourable in enhancing the rate of decomposition. During pyrolysis, decomposition of cellulose and hemicellulose starts at lower temperature range of 315 -400 °C and 220 -315 °C, respectively (Varma et al 2018). Lignin break down at higher range of temperature which is around 500-900°C (Danje et al 2011). Composition of the hemicellulose, cellulose and lignin changes from one biomass to another. Relative proportion of hemicellulose to lignin in sugarcane bagasse is 3.48 while cellulose to lignin is 4.25 (Varma & Mondal et al. 2016). Hui et al 2011 reported that in *P. Australis* composition of cellulose is high and lignin content is low. Some reported cellulose, hemicelluloses and lignin content in different biomass is shown in Table 1.

Table 1. Cellulose, hemicelluloses and lignin content in different biomass

S no	Biomass	Cellulose	Hemicellulose	Lignin	Reference
1	Vetiver grass	39.14%	48.57%	11.02%	Thakur et al. 2017
2	Pine needle	34.5%	29.1%	31.7%	Varma & Mondal et al. 2016
3	Phragmites australis	43.05%	30.68%	20.34%	Hui et al. 2011
4	Sugarcane bagasse	42.9%	38.2%	13.8%	Mohomane et al.2017
5	Softwood	39.2%	23.6%	37.2%	Mohomane et al. 2017
6	Wood saw dust	47.62%	39%	11.23%	Varma & Mondal et al.2016
7.	Hazelnut	42.6%	28.7%	44.4%	Demirbas et al.1998

Initial moisture content of the biomass can significantly affect the behaviour of the biomass during pyrolysis and the physicochemical properties of the bio oil. Biomass moisture content varies with biomass type and storage method. Based on the moisture content in biomass, its energy change route is decided. High moisture content biomass is suitable for the 'wet/ aqueous' conversion process i.e. biochemical conversions like fermentation. This is because, energy obtained from the end product would be smaller in comparison to the energy used in drying the product. While dry biomass is more suitable for the thermochemical conversions like gasification, pyrolysis or combustion. Woody herbaceous plants with low moisture content are the most suitable option for the biomass for thermochemical processes (varma et al 2016, Akhtar et al 2012). Usually, moisture content of the green biomass is about 50-60%. By using solar drying, moisture content can be reduced to 3-12%. Moisture content of the biomass for the pyrolysis process should be less than 10%. Additional heat is needed if the humid content of the biomaterial is high. This would affect the pyrolysis process quite adversely (Uddain et al 2018, Babu et al 2008).

4. PYROLYSIS PROCESS OPERATING PARAMETERS

4.1 Temperature

Effect of temperature on the product yield in the pyrolysis process is quite vital and decisive. Temperature provides the heat needed for the fragmentation and decomposition of biomass. Difference of temperature between the feedstock and inside temperature of reactor acts as an driving force for the same (Mckendry et al 2002). When the temperature is low i.e. less than 300°C, breakdown takes places within the biomass at the heteroatom sites which forms the heavy tars. However, at the temperature above 500°C, heavy decomposition of the biomass takes place which results in the formation of the various types of the compounds. With increase in temperature, conversion efficiency of the biomass also increases. The reason behind it can be the extra energy available to rupture bonds (Babu et al 2008). For the optimum yield of the liquid, the required range of the temperature is around 400 to 550°C. However, there may be small variation in temperature range with different biomass. Increasing temperature has an optimistic effect on the liquid yield but at temperature above 600°C, bio-oil and biochar produced gets converted into gases. This happens because the secondary cracking of the volatiles takes place (Guedes et al 2017, Kan et al 2018). When the temperature exceeds 700°C, the carbon content in the bio oil increases in the form of polycyclic aromatic hydrocarbons (Jahirul et al 2012, Raveendran et al 1996). bridgwater et al.1999 obtained the maximum product yield (50%) at temperature of 500 to 520 °C for most forms of the woody biomass. Sharypov et al. 2001 obtained maximum yield of the light liquids at the temperature 400°C for the biomass/ plastic mixture conversion. In the final product distribution, types of polymers and origin of biomass plays an important role. Zhou et al 2006 observed that Chinese pine wood saw dust begins to react at temperature around 250°C while plastics start to decompose at higher temperature around 400°C. Bilbao et al 1987 performed the pyrolysis experiment in an isothermal experiment at low preheating rate under the temperature range 230-300 °C. They observed very small amount of cellulose decompose at very low temperature while nearby all solids degrade at temperature higher than 300°C

4.2 Heating Rate

In addition to the temperature of the biomass, the heating rate at which it decomposes into product is another important factor (Babu et al 2008, Pradhan et al 2013). Slow heating rate is favourable for the higher char yield while high heating rate favours more volatiles (McKendry et al 2002). Heating rate in conventional pyrolysis is quite lesser than the heating rate in fast pyrolysis. Higher rate of the heating causes the faster degradation of biomass which triggers yield of volatiles. By endothermically fragmenting biomass so quickly, secondary reactions have less time to react (Babu et al 2008). Secondary reactions have a negative impact on yield and quality thus, in order to control secondary reactions, primary vapours need to be heated and cooled rapidly (McKendry et al 2002). Mass and heat transfer limitations are reduced in fast heating rates which favours the bio-oil production (Raveendran et al 1996). Utmost generation of bio oil is seemed to achieve at higher heating rates (Pradhan et al 2013).

Varma et al 2019 reported that with increased in heating rate to 50°C/min from 10°C/min the yield of oil also raised to 44.16% at 500°C temperature of pyrolysis process for wood sawdust(Tsai et al 2007).Chen et al 2014 studied the effect heating rate on oil yield. They found the little increase in yield with increase in heating rate (Verma and Mundal et al 2017). Pradhan D. et al 2013 observed the maximum yield of mahua seeds (59.95%) in a semi batch reactor which was operated at the temperature of 525°C with heating rate of 10°C/min(Qi et al 2006). Mishra et al 2020 suggested lower heating rates for better heat transfer at intra particle level. Because of better heat transfer and mass transfer, lower heating rates ensure efficient pyrolysis (Tripathi et al 2016).

4.3 Particle size

In biomass pyrolysis, nature of biomass and type of the pyrolysis process decide the appropriate size of the particle. In the case of rapid pyrolysis, in order to achieve uniform heating, smaller size particles are preferred (Isahak et al 2012). Heat transfer is higher in smaller particle size biomass feed comparative to larger particle size as smaller one possess more surface area comparative to larger one(McKendry et al 2002). It is observed that greater temperature gradient exists for the larger size particles which can decrease the bio oil yield. Larger size particle also require higher activation energy (Isahak et al 2012). Varma et al 2019 observed that for wood sawdust, utmost generation of the bio oil is observed at the moderate particle size of the feed particle. Generally, particle size does not have any considerable effect on the bio oil yield. The difference of 3% was found in the bio oil yield between smaller size particle feed (dp lesser than 0.25) and bigger particle feed (dp bigger than 1.7)(Tsai et al 2007). Tsai et al 2005 observed the optimum generation of the bio oil (>40%) at particle size < 0.50mm of rice husk in fixed bed pyrolysis system (Bridgewater et al 1998). Varma et al 2016 observed that at the constant temperature of 500°C with heating rate of 50°C/min the yield of the bio oil for smaller particle size (< 0.25mm) is obtained as 37.75% and 41.23% for the particles of the larger size (range 1- 1.7mm)(Czernik et al 2004). While at the size of particles ranging between 0.5 to 0.6mm the utmost yield of the oil is achieved i.e. 45.03%.

4.4 Sweeping gas:

Sweeping gases are used to provide inert atmosphere. Inert gases like N₂, Ar, water vapours are used as sweeping gases to provide inert atmosphere. Use of N₂ is most common in the practise as sweeping gases due to its cost efficiency (Akhtar et al 2012, Tsai et al 2007). Interaction between the surrounding environment and escaping pyrolysis vapours encourages the secondary exothermic reactions which causes char formation. In order to curb such secondary reactions, rapid mass transfer conditions are adopted such as rapid quenching of the hot vapours using inert gases. Escaping pyrolysis hot vapours are removed from the reaction zone by using inert gases which results as reduction of the secondary reactions such as repolymerization (Babu et al 2008, Bridgewater et al 1998). Varma et al 2019 studied the effect of nitrogen flow rate on oil yield of wood sawdust using pyrolysis process. Yield of gaseous product is Increases with rise of nitrogen flowrate while yield of biochar decreases with increase in nitrogen flowrate. The yield of product gases increases to 32.16% from 22.59% and yield of char is decrease from 37.15% to 28.92 wt % as nitrogen flowrate increases to 200 cm³/min from 50 cm³/min, respectively. However, amount of bio oil produced increases first with N₂ flowrate then achieve maximum value afterwards decreases with an increment in N₂ flowrate. The Maximum value (44.25 wt%) of bio oil observed at N₂ flowrate of 100cm³/min (Tsai et al 2007).Varma &mondal et al. 2017, studied the pyrolysis of sugarcane bagasse in a semi batch reactor. They found that residence time of volatiles vapours is influenced by nitrogen flowrate. They observed that when N₂ flowrate increases from 50 to 100 cm³/min, amount of the bio oil increased to 5% i.e. from 39.5% to 44.95%,but when N₂ flowrate further increased to 200cm³/min yield of bio oil decreased by 41.89%. This happens due to the improper condensation of volatiles at higher temperature (Czernik et al 2004).

5. PRODUCT CHARACTERISTICS:

The major biomass pyrolysis products obtained are oil, char and biogas. The characteristics of the product are discussed below:

Biogas: In the process of the pyrolysis incondensable gases are obtained which constitutes CO₂, CH₄, CO, H₂ and light hydrocarbons. These gases are called as biogas (Guedes et al 1996). The production of biogas in slow pyrolysis is about 10% to 35%, while in flash pyrolysis with higher temperature, higher yield is possible. To maximize the yield of biogas, higher temperature with long residence time and lower heating rates are required Higher moisture content affects the biogas production undesirably. Gaseous products are produced less when biomass is moist. Biogas is a sustainable fuel that can be used in combustion process in industries. Biogas can also serve as energy or heat source for the pyrolysis process itself. The heating value of the biogas is about 6.4 to 9.8 MJ/Kg with extensive reforming it can be used as synthesis gas(McKendry et al 2002, Jahirul et al 2012, Tursi et al 2019, Varma et al 2018).

Bio char: In the pyrolysis process the solid product is char. When hemicellulose and lignin are decomposed thermally, then there is a considerable mass loss of volatiles and what leaves after is an vague rigid grid of carbon called as char. It constitutes 91% to 63% of carbon and 10% to 30% of oxygen. In biochar, carbon is present in two structures firstly as amorphous aromatic structure and secondly as crystalline graphene structure. Pyrolysis conditions such as biomass type, feedstock particle size, heating rate, flowrate of inert gas, shape and type of reactors significantly affects the biochar's physical conditions. Presence of high content of carbon makes it suitable to be used in generation of heat. The calorific value of biochar ranges from 17 to 36 MJ/kg. Biochar can be used for internal energy source for heat generation in pyrolysis process as well. bio char can be utilized as a forerunner in activated carbon production and adsorption based waste water purification. It can be used in the production of hydrogen rich gas, manufacturing of carbon nanotubes and in improving soil fertility through alteration of soil pH. There are numerous benefits of using char for soil enrichment. These includes reduction of leaching of nitrogen in groundwater, reduction in nitrous oxide emissions, increased capacity of cation exchange for better fertility of soil, increased retention of water and surge in the number of soil beneficial microbes (McKendry et al 2002, Mohan et al 2006, Jahirul et al 2012, Tursi et al 2019, varma et al 2018).

Bio oil:In biomass pyrolysis the liquid product formed by the condensation of vapours is called bio oil,bio crude or biomass pyrolysis oil, which is an amalgamation of multiple components of different size molecules derived from depolymerization and decomposition of cellulose, lignin and hemicellulose. There are several benefits of using bio oil such as a positive CO₂ balance in biomass fuels, can be used in small power generation units too.Being a liquid fuel it is easy to store and transport.Compared to biomass gasification fuel it has high energy content and can be used in ongoing and existing power plants. There is a difference between the composition of the petroleum derived fuels and bio oils (Tursi et al 2019, Qi et al 2006). Bio oil, a miscible blend, consists about 75 to 80 wt% polar organics and 20 to 25 wt % water(Bridgewater et al 1999). Bio oil is an organic liquid free flowing in nature, dark brown in colour and has a smoky odour. It shows immiscibility with other petrochemical liquid fuels

(Varma et al 2018). Characteristic properties of bio oil include high viscosity, corrosive, complex chemical structure, acidic and relatively unstable in nature. It is a blend of aldehydes, alcohols, carboxylic acids, ketones, carbohydrates, phenols, water and lignin fragments (Bridgewater et al 1999). Its high water to oxygen content leads to lower heating values (Thakur et al 2017, Mckendry et al 2002). As a fuel its water content is a key concern, as higher amounts of water will negatively impact the fuel's ability to burn. The existence of the polar groups in the bio oil is indicated by its higher oxygen content which results as higher boiling points, higher viscosity and relatively poor chemical stability (Isahak et al 2012, Varma et al 2018).

Some of the characteristics of bio oil make it less appropriate to used as a fuel such as suspended char, alkali metals, sensitivity with higher temperature, high viscosity, lower pH, layering or partial separation of phases, not compatible with polymers etc. Suspended char leads to problems like equipment blockage high CO emissions, erosion, combustion problems etc.. While, lower pH results in corrosion problems of pipe work and vessels. Alkali metals cause deposition or coating of solids in boilers, engines and turbines. Bio oil's sensitivity towards higher temperature can cause blockage and decomposition because of liquid fragmentation on hot surface. However by adopting some modification techniques these problems can be rectified (Varma et al 2018 & Bridgewater et al 1998 & Czernik et al 2004).

6. APPLICATION OF BIO OIL

Biomass fuels are carbon neutral in nature. Bio oil is liquid in state so it can be stored and transported quite easily and readily. Biomass fuels have relatively low sulphur content in comparison to fossil fuels. Bio oil has better potential for efficient high production of energy compared to other biomass fuels like black liquor or hog fuel (Qi et al 2006). Due to its acceptable emission levels and economic feasibility, bio oil can be appropriate fuel option for boilers. Bio oil can be co fired with fossil fuels. To commercialize bio oil, availability of better quality of bio oil at an attractive price is a must (Bridgewater et al 1998). In slow and moderate speed diesel engines, bio oil can be used as a fuel. Modified bio oil may be efficiently used in gas turbines which is currently using gaseous and liquid petroleum fuels. Gas turbines have a wide range of appliances including in aircraft, production process in industries and in power generations (Tursi et al 2019). Slow and medium speed engines can also operate on low grade fuels, they are fuel flexible. Bio oil combined with diesel fuel, with the help of surfactants can also be used in transportation. Bio oil can become promising fuel in future with some advancement and upgradation. Wood pyrolysis liquids also acts as major source of chemicals such as methanol, acetic acid, turpentine and tar (Czernik et al 2004)

7. CONCLUSION

The future of energy is in biomass. Fuels obtained from biomass are carbon neutral in nature. To harness energy from biomass, biomass pyrolysis process is found to be most promising one. It produces three state products with no waste product left behind. Type of biomass, moisture content, composition of biomass, temperature, heating rate, sweeping gas all has their significant effect on the pyrolysis process and its products. For the maximum bio oil production, optimum temperature of about 400 to 500°C is needed. For the efficient pyrolysis, lower heating rate is required. Various studies confirmed that intermediate particle size is required for the maximum oil production. Sweeping gas is used to remove the hot vapours in order to suppress the secondary reaction. Products obtained from the pyrolysis are bio oil, biochar and biogas. Bio oil is considered as main product which can be conveniently used as a fuel. Presently with a few modifications and upgradation, bio oil can be used as fuel in furnace, boiler and diesel engines. However transportation fuel can also be one of the applications of bio fuel. Further research, improvement and upgradation in technology are needed. In future, with advanced technology bio oil can be used to make as transport fuel but it still need some time. Bio oil can also be used in extraction of chemicals from it. Biochar is another product of the biomass pyrolysis with various usages. It can be used as source of energy internally, water purification and soil amendment are possible uses for this product. Similarly biogas produced can also be used as a fuel in combustion processes. Thus, biomass pyrolysis can said to be a very potential thermochemical process to meet the future requirements. However, more studies and research are still needed to understand the potential of bio oil and its application in real field. The authors hope that this review paper will inspire investigations in these fields.

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