Review Article

A Review on Pyrolysis for Sustainable Biomass Conversion

ABSTRACT

The use of bio-energy is rapidly increasing which is become a crucial significant way to replace fossil fuel. The depletion of fossil fuel responsible for initiating the utilization of the sustainable energy which has been available in surrounding of human beings. The employment of such sustainable energy can be possible from waste procreated by living creature and that is feasible because of thermal decomposition processes, comprise the gasification, combustion, pyrolysis process for the production of biochar. The present study portrayed the very promising thermal decomposition process that is the pyrolysis process. The two main pyrolysis process explained where basic feedstock that is biomass invested. This feedstock may have diverse versions as natural live or dead plants, wastage of animals, organic waste etc. All these feedstocks are responsible for the emission of some amount of carbon which relates to the different modes of operation used in the pyrolysis biomass conversion process. The bio product varies due to the effect of various operating condition such as temperature, heating rate, feedstock, reactors configuration, reaction time. Demand for bio products rising in daily life Due to this circumstance Sustainability of products become prominent while exploited in the proper application such as soil amendment, soil fertility, climate change mitigation and waste management. This review demonstrates the pyrolysis process to convert simple biomass to sustainable biochar, bio-oil and syngas with the variation of the amount of product depending on different pyrolysis processes.

***Keywords**: Sustainable energy, Thermal Decomposition Process, Pyrolysis process, Feedstock, Modes of operation.*

1. INTRODUCTION

Energy is a significant demand for present industrial societies for incredible development. Agriculture, transportation, renewable sectors require extensive energy in the form of fossil fuels. The energy demand becomes effective as the growth of population that becomes more challenging. [1,2]states population increased as 7.3 billion people to 9 billion in 2050 and 11.2 billion by the year 2100 and approximately demand for determinate sources will increase by 2.8 times of present demand. Fossil fuels are most required over the worldwide industrial societies which are a finite practical convenient source of energy [3]. Depletion of Coal, oil and gas are the evidence for growing global warming with air pollutants such as NO_x, SO_2 and Hg and many chemical fertilizers [4]. Alternative energy source becomes a necessity for those; biomass is an acceptable source as another option in the renewable field [5].

Biomass is a sustainable source formed by living species just as animals and plants that are organic materials originating from living matters. Biomass comprises not only biological organisms but also has organic extractives, cellulose, ligninand animal waste from poultry farms, pig farms, cattle farm, sludge and waste wood[6]. Biomass traditionally includes green waste which is abundant resources due to the presence of high carbon content, low moisture, low or even no sulfur content, economic cost and preserve the environment clean as Fig.1[7]. This figure explains all the resources of biomass to produce a diverse product in bio-energy. It is an environmentally friendly and effective alternative substitute for fossil fuels. Biomass produces three types of fuels, could be liquid fuel, gaseous fuels, solid fuels[8]. Biomass comprising 63% of RES used in industrial area includes oil-based biomass and solid biomass at a greater level. According to [9], In 2016, the overall oil equivalent In 2016, India's overall energy consumption was 724 million tons of oil equivalent (Mtoe) consumption in India was 724 million tons is looking forward to gaining 1921 Mtoe on the word by 2040 with an approximated growth rate of 4.2% per annum. Based on this survey china and USA on the top of all country and India was the fourth-largest energy consumer in the world. The biomass is also produced the gaseous fuels by the burning procedure. The biomass emitted CO2 gas by using thermal degradation processes. According to [10] CO_2 emission from biomass increases 6% from 33Gt during 2015 to 35Gt during 2050 receiving current and planned policies. The main reward is that biomass fuel is carbon neutral or even carbon negative.

Biochar is the product of biomass which is generated by using the thermochemical decomposition of biomass such as slow pyrolysis and fast pyrolysis [11]. The pyrolysis is the vital thermal decomposition method for generation of any organic liquids, gases and solid. Pyrolysis concern rapid heating at a maximum temperature of raw biomass in the absence of oxygen. The biochar is very inexpensive and environment friendly. Biochar benefits in terms such as soil remediation, waste management, carbon sequestrations, energy production, and greenhouse gas reduction with several developments in biomass application[12]. [13]explained that Biochar is beneficial in agriculture considering the level of 50% carbon stay in the soil as stable biochar balanced.

Biomass contributes 14% primary energy production all over the world although it is inadequately wasting through the unsustainable application. Due to this circumstance Sustainability of products become prominent while exploited in the proper application such as soil amendment, soil fertility, climate change mitigation and waste management [14]. Biochar is a carbon-neutral energy source, because of the fact, biochar generated along with CO2 which was available in the surrounding environment is then released by the process into the atmosphere, along with a zero-net balance of CO2 emissions. While using biochar in soil application carbon sustainability is a significant parameter to consider [15].This review paper describes all the pyrolysis system for the production of sustainable biochar/ bio-oil/ syngas. The different pyrolysis processes is used to in correspondence with temperature for create diverse bioproduct for various application in regarding soil, environment, agriculture, renewable energy.

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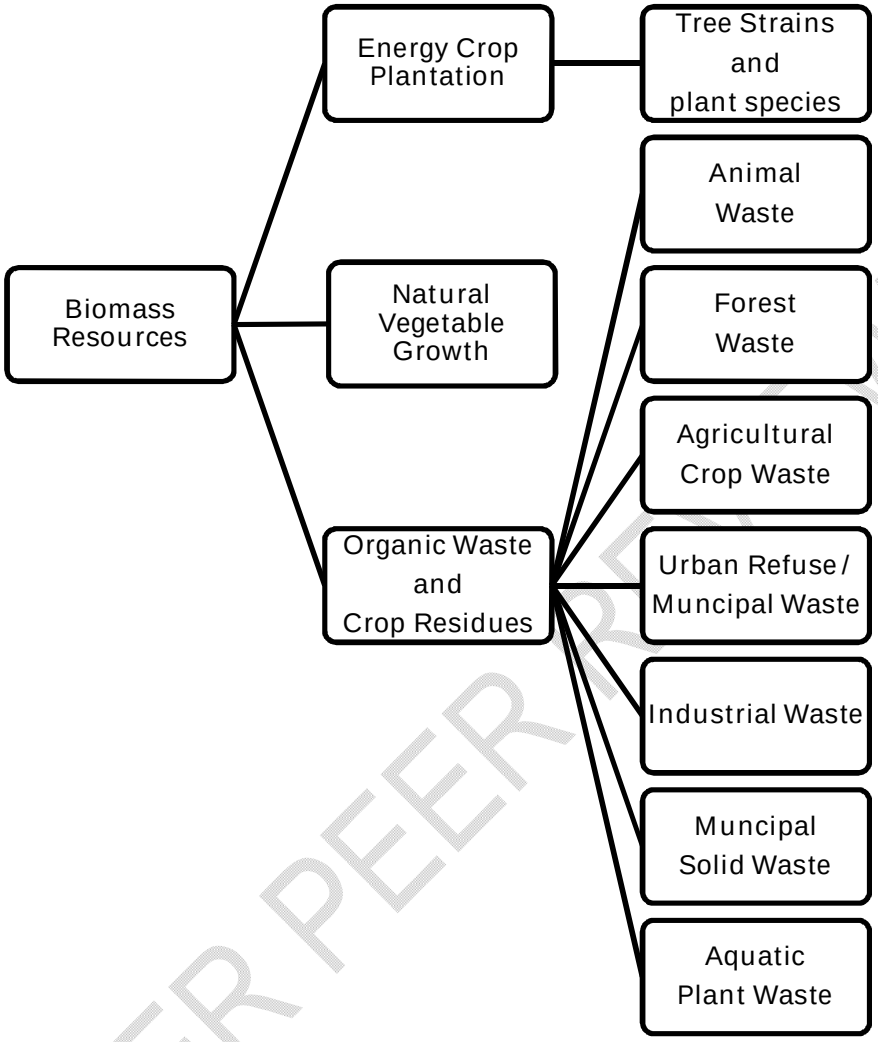

Fig.1. Biomass Resources [7]

2. BIOMASS – RESOURCE FOR SUSTAINABLE DEVELOPEMENT

The biomass is interesting industrialized demand which rise day by day as the energy source for world. Now days this demand the fossil fuel remain 80% of the primary energy in world, from which 58% consumed by the transport sector[16]. Depletion of the fossil fuel increased the inspiration toward the alternative, renewable, sustainable, efficient and cost-effective energy sources.to meet the energy demand reliably then it done in natural sustainable manner using various forms of energy[17]. Availability of this source at all time is responsible on Renewable energy sources which expounds naturally as solar energy, wind energy, hydro energy, geothermal energy, biomass energy has been successfully developed[18,19].

In the Global world some part of waste management done by using this waste as high potential biomass for generation of bioenergy. Due to this reason biomass become

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fourth largest source of primary energy. the increasing utilization of the biomass as bio-energy used to possible the sustainable development in rural area[20,21].

The development which satisfiesrequirement of energy at present without comprising proficiency of future generation to meet their needs is sustainable development.[22].

3. BIOCHAR PRODUCTION TECHNOLOGY

The chemical compounds found in biomass experiences many kinds of procedures as cross-linking, thermal decomposition and depolymerisation such process of converting the sustainable biomass into a carbon-rich solid waste introduced as biochar[23]. The mentioned process is also responsible for the production of condensable and non-condensable organic products. The condensed organic product consists of bio-oil and non-condensed product consist of gaseous products contain hydrogen, carbon oxide, carbon monoxide and Hydrocarbon compound[24]. Biochar have different properties according to the thermochemical operating parameters and properties of verities of feedstocks[25]. As [25], Some ordinary feedstocks comprise switchgrass, mixed pine chips, raw wheat straw, wheat straw pellets, corn hulls, pecan shells, groundnuts shell, bark, rice, sugarcane, paper sludge, cow manure, poultry manure, poultry litter, sewage sludge, and aquaculture waste. The thermochemical process as Fig.2 consists of combustion, gasification, pyrolysis where the pyrolysis produced biochar at least oxygen with slightest moist. There are diverse pyrolysis types according to the different feedstock used [26], includes slow pyrolysis, fast pyrolysis as [27], microwave-assisted pyrolysis, flashed pyrolysis as[28], intermediate pyrolysis and vacuumed hydro pyrolysis.[29]emphasise that the pyrolysis process yield bio-oil and bio-gas furthermore solid biochar. The author also explained that the pyrolysis procedure is a very efficient procedure to produce all states of the product instead of gasification and combustion.[30]gives the approximated ratio of production of process gasification which contains 85% gaseous products,10% solid char and only 5% liquid. However, the process pyrolysis holds solid bio-char (25–35%), liquid bio-oil (30–55%) and gaseous products syngas(10–40%).

Pyrolysis is illustrated as the thermal decomposition of biomass sources under torpid oxygen. Consequently, these techniques developed as an efficacious way to generate the biochar, bio-oil and syngas instead of fossil fuels[31]. The distinct products are exploited by many applications such as bio-oil utilized in vehicles, trains, boats and aircraft as an alternative option for diesel and petrol[32–34]. Supplementary products of pyrolysis such as solid char or carbonaceous materials and gaseous carbon oxide (CO2) are too utilized as the source in many applications. Primarily the pyrolysis techniques can be categorized based on the subsequent units which required in downstream processing. Figure 3 shows classification of pyrolysis techniques. The pyrolysis technique fundamentally composes by three main types that are slow pyrolysis[35], intermediate pyrolysis and fast pyrolysis[36]. As Table (1) slow pyrolysis and intermediated pyrolysis specify its individual remarkable specification that it provokes a large amount of bio-char wile in fast pyrolysis results in higher liquid bio-oil yield. Thus, slow and intermediate pyrolysis is the best option for the production of biochar. For the higher biochar production, there are conditions for existing pyrolysis process which illustrated as Fig.3. From Fig.3 we can state that the heating rate and temperature must be in control or as specified otherwise it affects products.

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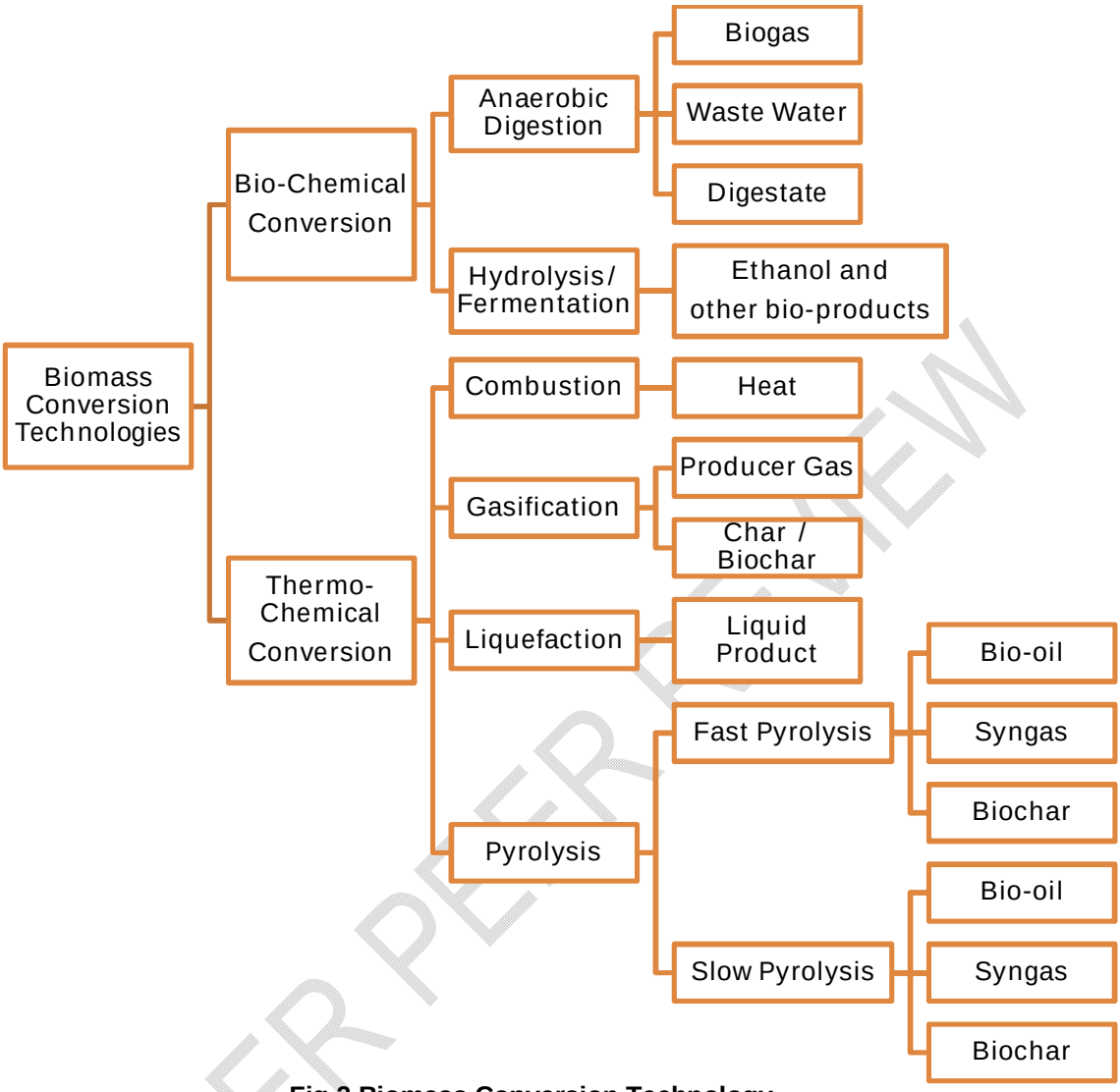

Fig.2 Biomass Conversion Technology

Table1 Comparison of Pyrolysis Technologies with their Specification

Mode	Condition	Liquid (Bio-oil)	Solid (Biochar)	Gas (Syngas)
Fast pyrolysis	moderate temperature (~ 500°c) short vapour residence time (<2s)	75% (25% water)	12%	13%
Intermediate Pyrolysis	Low-moderate temperature Moderate hot vapour residence time	50% (50% water)	25%	25%
Slow Pyrolysis	Low-moderate temperature (300-500°c) Long residence time (4-30 min)	30% (70% water)	35%	35%

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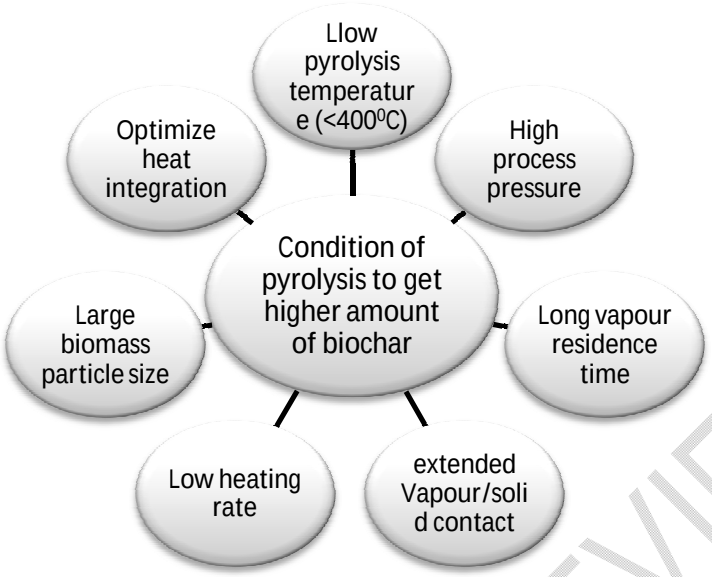

Fig. 3 Different Conditions for the Pyrolysis Process

4. OPERATIONAL CONDITIONS FOR PYROLYSIS

Pyrolysis process called as carbon-negative processes because this process involves the carbon form environment which then enters into the soil as fertilizer and then emitted in the environment in very less amount but if the waste does not utilize as biochar, then it emitted a higher amount of carbon in an environment this whole cycle can be explained by Fig.4.

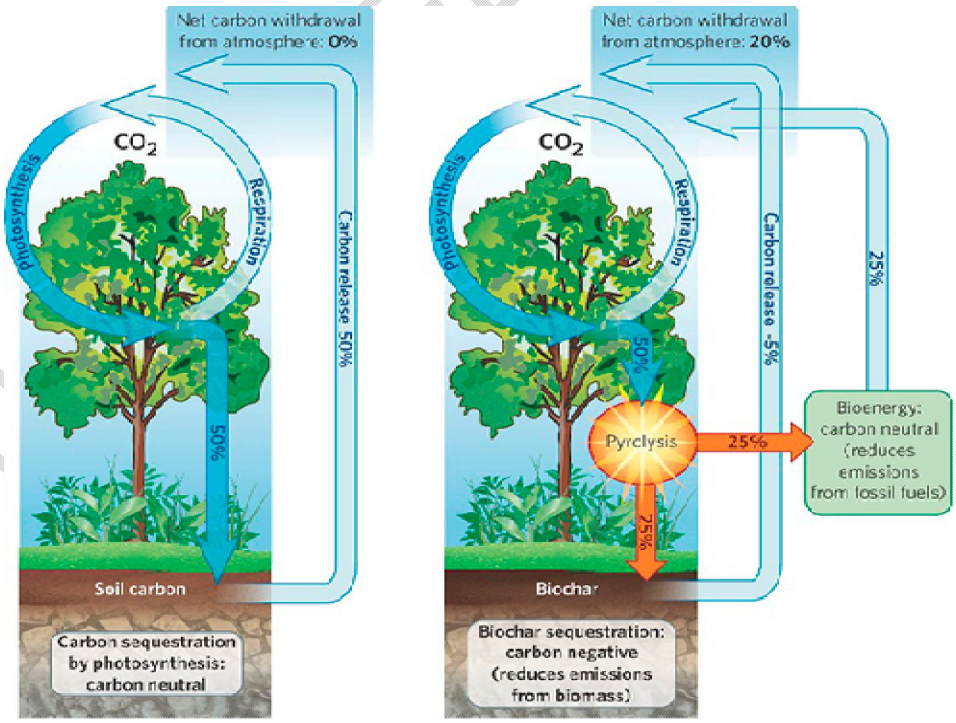

Fig.4. Environmental cycle with regards to carbon content

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The amount of carbon emission depended on modes of operation that is a process to be used for the production of biochar which is as Fig.5.

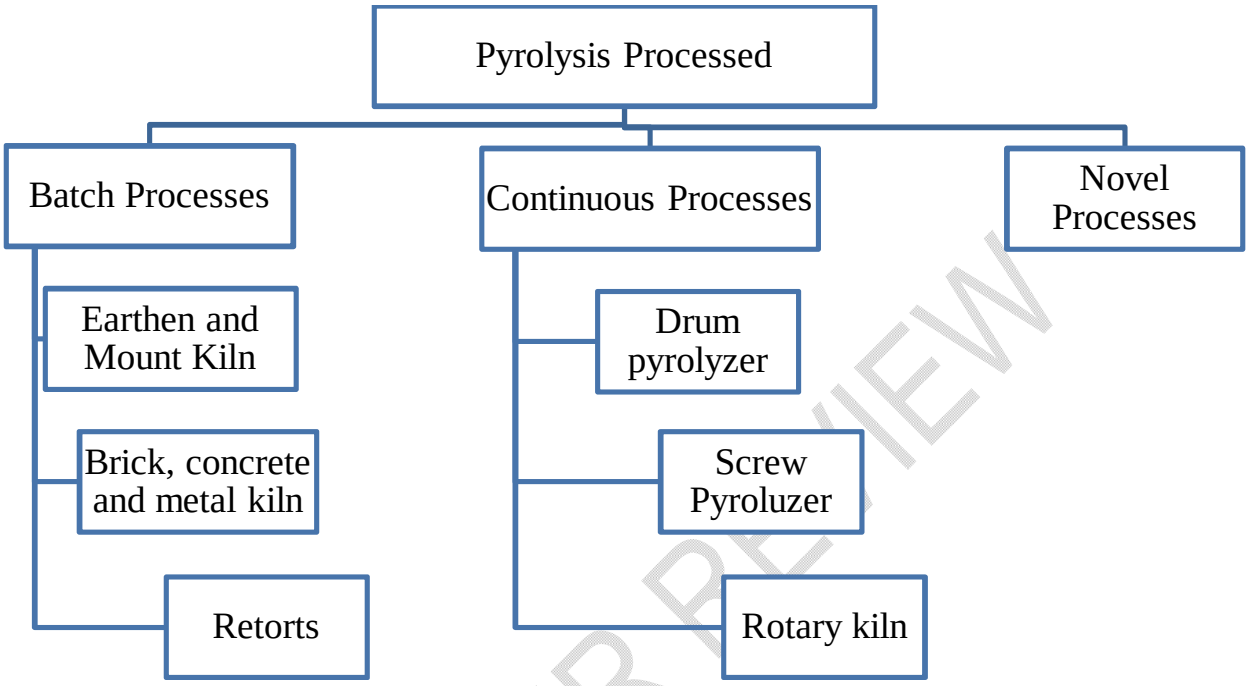

Fig.5. Pyrolysis process

Biochar Production technologies are responsible for many other productions with different modes of the procedure[37]. These processes are classified as Fig.5. which include batch process, continuous process, novel process. The process is working with different reactor types like earth pits and mounds, brick, concrete, screw type and metal kilns retort etc. Working with these reactors Biochar found in a variety of applications, such as animal farming, soil conditioning, soil substrates and industrial uses, depending on their feedstocks, heating rate, temperature and many other characteristics.

Firstly, the batch process is the process for the production of a higher amount of charcoal acquired in batch earth, brick or metal kilns. There are kilns which are antiquated but Modern batch devices can obtain mean emissions. If the process functioning correctly, it imparts the benefits of lower cost, ease of operation, relatively low emission.

Another process is a continuous biochar production process which is also called continuous flow process because it works consistently with mechanical or heat treatments. This process is responsible for producing continuous operation with the maximum amount of bio-char, efficient energy, economic reasons[38]. The continuous process is prominent for industrial application to fulfil the requirement of continuous heating for a large amount of available material. The continuous process having exceptional advantages over the batch process due to the simplicity of operation, regularity in the manufacture of the product in superior quality, low cost, less processing time.

The novel process is a convenient way to convert biomass to biochar in significantly lower processing time that is it proceeds quickly due to this is defined as flash carbonization. Flash carbonization process includes the flash firing of biomass bed with elevated pressure. This ignited flashed fire is then shifted upward direction to opposed the flow of air in a downward direction by using elevated pressure[39,40].

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5. SLOW PLYROLYSIS

Slow pyrolysis can be proceed by using some kind of operation include such as earthen and mound kiln, Brick, concrete and metal kiln, retorts.[41] Investigated the selective catalytic reduction at low temperature regarding modified cotton biochar and commercial activated carbon[42,43]. In this paper author utilized the fixed bed reactor which heated the cotton raw material at temperature 600°C with a heating rate of 5°C /min. similarly for biochar, this raw material heated at temperature 800°C with a heating rate of 5 ^{o}C /min for 2h. While another mode of operation reported[44] that traditional kiln technology has temperature of <400 ^{o}C. This kiln technology gives carbon yield in proportion of 24.9 and 37.4%.the designed kiln in this paper accelerated the significant lower emission of a product of imperfect combustion. Carbon from this slow pyrolysis system is utilized to sustain the process with efficient cost, eco-friendly environment. Due to cost-effectiveness, the traditional kiln is the best way to sustain the product in an application in a rural area. The slow pyrolysis also carried by using stove in domestic application,[45]Present the experimental analysis of the growth of rice husk biochar. As part of this study, rice husk is an essential feedstock for a yield of biochar by using a stove. The biochar is then employed for the crop production in the soil which increased the height of the plant in drought condition. It offers tremendous growth in the biochar application regarding soil fertility. The another[46] Prescribed was important to live and dead vegetation for controlling the fire during the combustion process. This combustion process relates to the pyrolysis process regarding to live and dead fuels. This study [44]carried a practical model with slow pyrolysis which is shown in Fig. 6 involve metal tube which placed electrically heated programable furnace for heated the sample plant with definite temperature which controls by the thermocouple. This structure also includes gas condensers, filters, reactors. This practical pyrolysis model was separated within two groups based on the pyrolizer apparatus for nitrogen atmosphere. The first group initiate yield of tar and light gas which was originated by heating the dead longleaf pine litter with a temperature of (400–800 °C) and heating rate of (5–30 °C min−1) another one group pyrolyzed the 14 live or dead plant species with the pyrolizer apparatus. A gas chromatograph equipped with a mass spectrometer (GC–MS) and a gas chromatograph equipped with a thermal conductivity detector (GC-TCD) were utilized to examine tar and light gas individually while light gas includes CO and CO_2 followed by CH_4 and H_2[47].

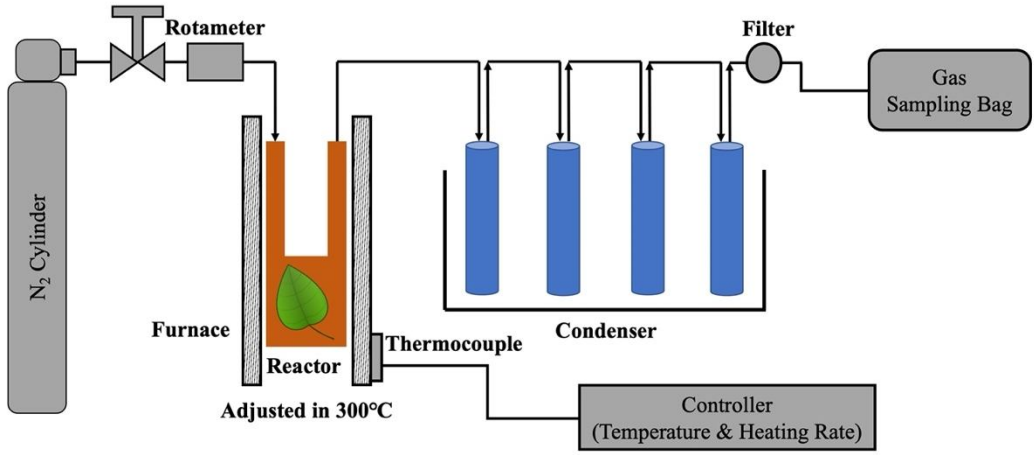

Fig.6. Model of slow pyrolysis with pyrolyzer apparatus.[44]

[48]found the heating value for generation and effect on properties of char.as the heating rate of the production increases the production of char get decreased however it strengthens

the carbon content which presents in biochar. [48] This paper compares the biochar product with different feedstock as sugarcane bagasse, casuarina leaves, coconut coir pith, groundnut shell, rice husk, sawdust, and wheat husk. This all feedstock heated on temperature from 300°C to 550°C for the respective time in the lap of 10 min to 60 min which produced char with carbon content above 75%. [49]used coconut wood as feedstock to heated by using batch reactors on the temperature of 375°c, 475°c and 575°c for the respective time of 5 min^{-1}, 10 min^{-1} and 20 min^{-1}. The 6694.49 cal/g of biochar was produced at the temperature of 575°c for 5 min^{-1} which concludes that Heating rate and final temperature affects the production of char.[50] explained many metallurgical processes for the emission of higher CO2 carbon using fossil carbonaceous material. This paper having the semi-continuous carbonization process which was structured to produced charcoal by using high temperature for heating the of Fruit cuttings feedstock material in a certain amount for the production of sustainable energy. The carbonization processes which remark in this research was operated on very high temperature more than 900 °C for producing high-quality charcoal. The gas-tight double screw reactor having a length of 2.3 m used in this experiment was heated on a very higher temperature by using two types of heating procedure external and electrical heating process. These two processes were separated within three heating zone by temperature which was adjusted separately. The schematic structure of this experimental unit is as shown in Fig. 7. The result contains a higher amount of charcoals with high carbon contents (>85%) and low volatiles amount (b10%).[51] Specified that when the heating rate pyrolysis increases the production of char decrease and the release of volatile matter increases. By concern char quality, boosting the temperature intensity the ash content and carbon content. The temperature has great importance while producing biochar with a premium grade of carbon.

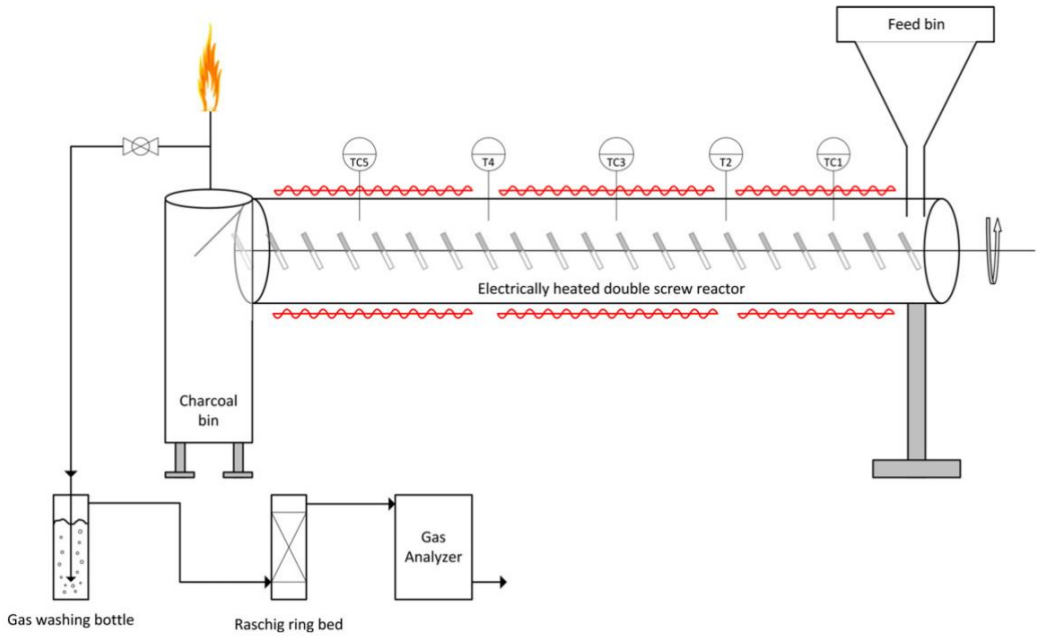

Fig. 7.Schematic view of slow pyrolysis modelwith screw reactor [47].

6. FAST PLYROLYSIS

Fast pyrolysis is the temperature-dependent process wherein any type of feedstock heated on higher temperature swiftly in a very low oxygen level[51]. The advanced fast pyrolysis is preparing for high yield biofuel with the aid of a high heating rate with a

temperature around 500^{0}C. [52] Fast pyrolysis required 30 to 1500 ms processing time by employing the 500^{0}C reactor temperature.[53] Established fast pyrolysis biochar system in the UK for carbon abatement and electricity production. This system used for ten types of feedstocks in small medium and large-scale process chain which offer grater carbon abatement. This research shows greater carbon abatement which provides 10–25 % of carbon content. The another operation used in fast pyrolysis as [54] which is specified process by using black wattle residues which performed at temperature 380 – 580^{0}C inside the screw feeder which having feeding rate of 120 to 240 rpm. Experimental products can be calculated by employing yield and selectivity calculation formulae which as bellow

$$yield(wt\%) = \frac{weight\ of\ biooil\ fraction}{weight\ of\ feedstock} \times 100$$

$$selectivity(wt\%) = \frac{amount\ of\ desire\ product}{weight\ of\ feedstock} \times 100$$

The above analytical procedure for measuring the yield of each product, which was defined using GC-MS in identifying the various compounds using. There is a special instrument Algilent 7890/GCMS5978 for bio-oil analysis. [55]ascertained that bioenergy is usual renewable energy which is rarely used by world for proper globalization. The biomass has appreciable potential to issue energy for evolution of advancement and civilization. The energy is provoked by employing various thermochemical conversion alternatives which includes the various gasification and pyrolysis process. This research work on pyrolysis process which includes a computational fluid dynamic model which developed by using a computer simulation tool to analyse and upgrade with Advanced System for Process Engineering (ASPEN) PLUS which is as Fig.8[52]. This pyrolysis process is responsible for production of bio-oil, biochar and syngas according to temperature and type of feedstock. This research gives different energy sources by using four different feedstock including bio-oil up to 58%, syngas 24.90%, biochar 17.08%. Another fast pyrolysis process [56] utilized the high grown waste crop that is wheat straw within fluidized bed reactor of fast pyrolysis system. This wheat straw was employed for bioenergy production mainly in liquid form by using faster reactor. This system has a significant segment that is biomass feeder, fluidized bed reactor (FBR) with for heating the feedstock also the shell and tube type condenser used for the recovering the bio-oil. The result of this model has a great amount of bio-oil that is 42 wt% while char contains was 27.1 wt% with a temperature of 500°C. This model was assayed by GC-MS and FTIR to identify chemical compounds such as phenol, alkanes, alcohols, aromatic, alkenes, hydrocarbon, furnol, and esters compounds available in bioenergy product.[57]selected four crops according to their yield potential but only two crops are used for the pyrolysis process. the bench-scale fluidised bed rig and product mass balances fast pyrolysis testing process is used for Arundodonax (giant reed) and Cynaracardunculus (cardoon) crop. Both this crops gives variation in product content on various temperatures. For cardoon and giant reed feedstock, the pyrolysis gives the better result in biofuel and char. for giant reed at the temperature of 4250C with the minimum particle size the yield organic liquids is 45.8% and char is 19.3% while at a temperature of 5560C with the higher amount of particle size the yield organic liquids is 38.9% and char is 13.1%.

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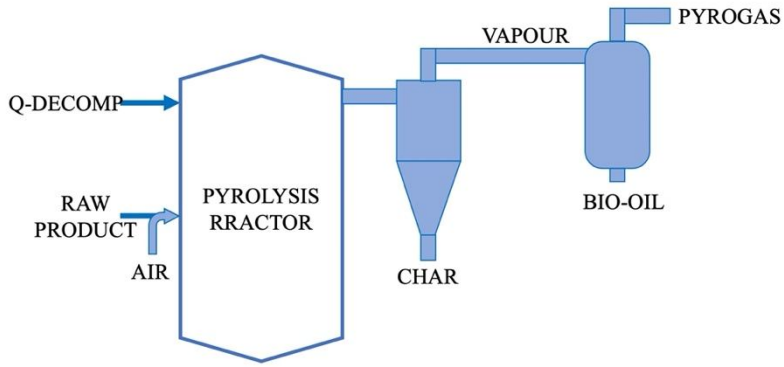

Fig.8. Computerized ASPEN PLUS model for biomass pyrolysis[52]

The result become more nettle after washing Arundodonax which was 58.7% organic liquid at 4600C reactor temperature. For another crop of cardoon at the temperature of 499^{0}C, the organic liquids content 30.6% and char content 18.0% which was failed due to bed agglomeration another testing on temperature 4440C which content organic liquids 45.1% and char content 15.6% the fast processing structure was mention in Fig. [57].

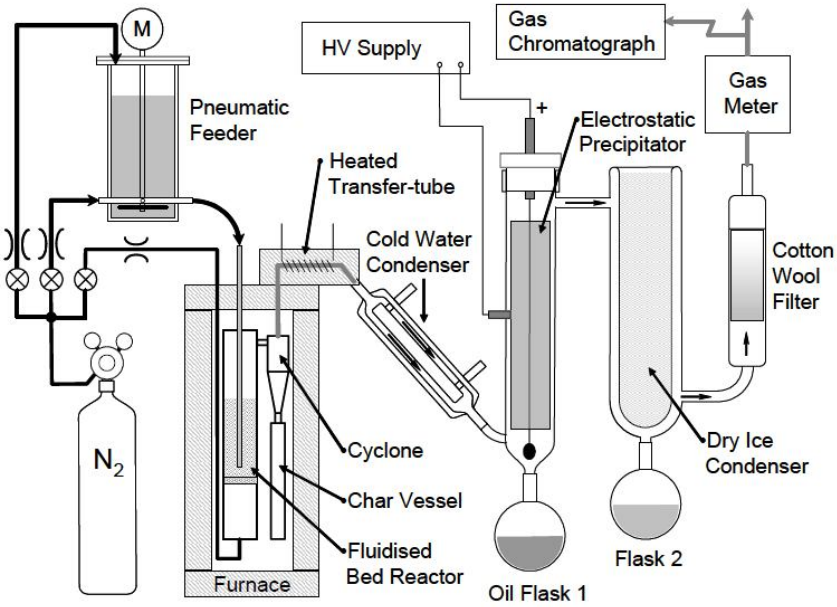

Fig.9. 100 g/hr Bench scale pyrolysis rig [57]

7. PLYROLYSIS PRODUCTS

Conventional pyrolysis technology has two main types which are slow and fast pyrolysis belongs to thermal decomposition. The throughputs of this pyrolysis process having different ration for both pyrolysis processes. Slow pyrolysis traditionally it takes more time to yield the final product that is charcoal (biochar). While the process which obtains the yield product within less residence time that is fast pyrolysis contain highly the liquid product (bio-oil). Fast pyrolysis having a high heating rate that is the temperature required for the procedure of pyrolysis should be higher which heated the feedstock for a rapid result.

So from the discussion of the slow pyrolysis and fast pyrolysis we can define the products average response. Pyrolysis obtain the product with an absence of oxygen and less moist which include an array of solid(biochar), liquid (bio-oil) and gaseous products(syngas)[58,59]. From this, all product liquids yields are most valuable energy factor because of its high energy density and flexibility while transport, storage, and use. But in the scarce thermal decomposing process have a result of a great amount of charcoal as the final yield from biomass such as fruit cutting wood. The pyrolysis can yield any type of product which depends on the type of feedstock which was invested.

7.1 BIOCHAR

Char is the major part of pyrolysis which having average amount product in every processes. The yield char can be depending on the availability of feedstock or type of feedstock. The temperature requires to heated the feedstock should be very low less than > 4000C.the feedstock contain wood, agriculture raw material, crop residues. The pyrolysis process used to generate higher charcoal is slow pyrolysis because of its slow residence time. The time required to burn or heated the feedstock must be far long to create the higher quality charcoal products. The char fraction having involution of inorganic material ashes to vary the product quantity, unsorted organic solids and carbonaceous residues to produce organic char by thermal decomposition process. The charcoal generated by the pyrolysis process must be handling carefully otherwise the ash content in char having higher ratio.

In the pyrolysis process slow pyrolysis must be suit to generated higher quality charcoal along with lower heating rate. The residence time must be greater to generated charcoal without low ash content.

Yet fast pyrolysis produces smaller particle sized char with higher volatility following higher temperature and higher heating rate. The ash content for char yield in fast pyrolysis rangesbetween 6–8 times greater than in the original feed with higher alkali content. The char content is 12 %only in fast pyrolysis where in slow pyrolysis it becomes 35%[60–63].

7.2 BIO-OIL

Bio-oil is the essential product come into liquid state that may contain mixture of water and organic chemicals. Water contain must be in range of 15-35 % wt while organic component contents are acids, alcohols, ketones, esters, sugars, guaiacols, furans, phenols, alkenes, aromatics, syringols, nitrogen compounds and miscellaneous oxygenates. The liquid product must be generated with low oxygen but if there is high presence of oxygen that is 35–40% then lower the energy density. The amount of product totally depends on feedstock; pyrolysis process and heating temperature which also effect on viscosities of bio oil rangesbetween of 10–100 cp at 401°c.the content of methanol in bio-oil reduce the viscosity and density. Heating feedstock with proper temperature is responsible for yield bio-oil product with heating value of 17mj kg^{-1}.

The slow pyrolysis techniques yield the bio-oil with the low temperature of 300-400 0c.this bio-oil content 30% of oil and 70% of water content that is very low oil can generated. The reason behind this result may be affect because of slow heating rate, low temperature and slow process with high residence time.

While fast pyrolysis performance used to achieve the higher oil content with the higher temperature that is ~5000c.the oil content affect by higher heating rate and speed of process that is short vapour residence time of < 25 .the fast pyrolysis content 75% of oil and only 25% of water mixture[31,64–69].

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7.3 GASES

Gases product generated by using pyrolysis process which contains many kinds of gases carbon dioxide, carbon monoxide, hydrogen, methane, ethylene, ethane, minor amounts of higher gaseous organics and water vapor

The gases may produce by using pyrolysis process with high temperature and long residence time that is slow pyrolysis. Slow pyrolysis responsible to produce gases state by using higher temperature above the 5000C with high vapour residence time. This process performs under the very low or zero content of oxygen.by using the slow pyrolysis the gas yield product having 35% to 85% average amount. However, the gas product by using fast pyrolysis having lower amount that is upto 13 % of gases may generated, because the fast pyrolysis required very low residence time. By using fast pyrolysis 53% wt CO_2, 39% CO, 6.7% hydrocarbons with presence of methane and 0.8% H_2[61,70–72].

8. CONCLUSION

The energy is global demanding requirement for living being which increasing rapidly. The bio-energy has been fulfilling the energy requirement by using waste of industries, agriculture, animals. This feedstock / Biomass utilized as renewable source for production of bio-energy in terms of liquid, solid and gases form. Biomass comprises not only biological organisms but also having the organic extractives, cellulose, lignin, animal waste from poultry farms, pig farms, cattle farm, sludge and waste wood. Biomass contributes 14% primary energy production all over the world. The sustainable biomass would be responsible for various applications such as soil amendment, soil fertility, climate change mitigation and waste management.

Biochar is the major product initiated by thermochemical decomposition of biomass. This thermal decomposing process includes pyrolysis system. The pyrolysis performs the vital thermal decomposition method for generation of any organic liquids, gases and solid. This paper helps to conclude the proper pyrolysis system as required specification. The various modes of operation within batch process, continuous process, novel process. this operation may includedifferent reactor types like earth pits and mounds, brick, concrete, screw type and metal kilns retort kiln used in pyrolysis system organized for yield of product in liquid, solid and gases form. This study specified that for generation of liquid state product mostly fast pyrolysis employed while for yield of char slow pyrolysis essential procedure due to its long term of working. Biochar benefits in terms such as soil remediation, waste management, carbon sequestrations, energy production, and greenhouse gas reduction with several developments in biomass application, however the liquid oil is efficient to handle store and transport.

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