

A review on mechanism and factors affecting pyrolysis of biomass

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Abstract-In the present worldwide scenario of searching alternative sustainable renewable energy resources to minimize overexploitation of fossil fuel, thus afford has been made in this study to summarize pyrolysis of biomass as a sustainable energy source. Among the thermochemical technologies, pyrolysis greatly reduce reliance on fossil fuel by converting various types of biomass into eco-friendly end products such as bio-oil, pyrolytic gases and bio-char. Based on available literature, its socio-economic benefits, and easy adoptability proved pyrolysis an attractive process in the sequence. This review mainly deals with the mechanisms of biomass pyrolysis (heterogeneous reactions affecting dynamics and kinetics by chemical bonds breakage and redistribution, reaction structure and interfacial diffusion of reactants and products) and some key factors affecting pyrolysis products distribution such as biomass composition, particle size, reaction temperature, heating rate, vapour residence time and reaction atmosphere.

Keywords- Biomass, Pyrolysis, Mechanism, Temperature, Heating rate

1. INTRODUCTION

The worldwide concerned issues such as greenhouse gas emissions, air quality degradation and particulate emission due to consumption of conventional fossil fuels. Therefore, it is realized to find some renewable energy sources which reduce increased massive load on fossil fuel. Now, great efforts have been made by researchers for conservation of fossil fuel through using of various sources of sustainable alternative energy such as hydropower, wind, solar, geothermal and biomass [Wang et al., 2016; Varma & Mondal, 2016b and White et al., 2011]. Biomass is attractively pronounced as eco-friendly, renewable and sustainable energy sources due to is clean, abundant and carbon neutral characteristics [Thakur et al., 2018; Varma & Mondal, 2016c]. An approximate yearly worldwide production estimate of lignocellulose biomass is around 2.2×10^{11} tons [Feng & Lin, 2017 and Torres et al., 2007].

The word Biomass emerges from biological terms *phytomass* (plant) and *zoo mass* (animal). It is an organic (natural carbohydrate polymers and nonedible plant) and biodegradable material produced by photosynthesis process in the presence of sun light and available to us from agricultural crops, forestry materials, animal waste, aquatic plant and algae

[Wang et al., 2016; Dhyani & Bhaskar, 2017; Santos et al., 2015 and Oladeji et al., 2015]. Lignocellulose biomass mainly consists of cellulose (35-50%), hemicellulose (20-35%) and lignin (10-20%) with small inclusion of substances such as moisture, minerals and extractives (e.g., resins, tannins, terpenes, oil and fatty acids) [Feng & Lin, 2017; White et al., 2011 and Alonso et al., 2010]. The conversion of solid biomass to energy can be possible through biochemical processes such as anaerobic/aerobic digestion and fermentation processes to produce CH₄ and C₂H₅OH and thermochemical processes [Kwietniewska & Tys, 2014; Limayem & Ricke, 2012]. The thermochemical processes defined according to oxygen supply and product distribution which include combustion, gasification, liquefaction and pyrolysis [Goyal et al., 2008 and Stevens, 2011]. Among this pyrolysis process has been extensive building as a promising platform for the production of fuels and valuable chemicals from several types of biomass [Garg et al., 2016].

The pyrolysis process thermally depolymerizes the solid biomass to liquid, also known as bio-oil, in absence of O₂ along with biochar and biogases [Kan et al., 2016]. Bio-oil can be used as transportation fuel and heat generation, while biochar can be applied to the agricultural lands as a soil amendment or utilized to produce activated carbon whereas non-condensable

gases used as energy in domestic and industrial application [Varma & Mondal, 2016a]. The main product bio-oil is present in the liquid form, containing a high amount of aromatic compounds, which makes it as a potential source for alternate energy [Anex et al., 2010; Wright et al., 2010 and Brown et al., 2013].

This review is aimed to guide future research on biomass in context of pyrolysis mechanism and parameters influencing pyrolysis that would leads to optimize desired product yield, improve reaction performance, and energy efficiency, and understand product distribution. These parameters are type of biomass, particle size, temperature, pressure, particle heating rate and residence time.

2. MECHANISM OF BIOMASS PYROLYSIS

The thermal conditions, reactor designs and reaction mechanisms of degradation of the biomass constituents are the complexity of biomass pyrolysis making it a mystery to the researcher. During biomass pyrolysis, following reactions occur in series and parallel, including dehydration, depolymerization, decarboxylation, charring, isomerization and aromatization. It consists of three main stages: (i) evaporation of free moisture, (ii) primary mechanism (char formation, depolymerization and fragmentation) followed by (iii) secondary mechanism (oil cracking and condensation). Biomass decomposition occurs to form solid char at 400-500 °C, which is responsible for chemical bonds to be broken. The secondary reactions proceed with further rising of the temperature of volatile compounds that remain in primary reaction matrix [Kan et al., 2016; Collard & Blin, 2014 and Ferdous et al., 2002].

2.1 Evaporation of free moisture

Dehydration process starts at 100 °C of biomass, due to release of free moisture (water vapour) from biomass and formation amorphous carbon for char [White et al., 2011].

2.2 Primary decomposition

The primary decomposition depends on the geometry of bonds that are to be broken and can be explain by char formation, depolymerization and fragmentation [Collard & Blin 2014].

2.2.1 Char formation

Solid residue named char, formed during the biomass conversion in pyrolysis process, presents an aromatic polycyclic structure [McGrath et al., 2003 and Pastorova et al., 1994]. Fast removal of primary char is necessary because it readily decomposed into secondary char, gas and water and also work as a catalyst for support secondary reaction. Consequently, bio oil yield decreases. The main pathway of this reaction is the benzene rings formation and combination of these rings with polycyclic structure [Kan et al., 2016 and Collard & Blin, 2012]. Figure 1 represents char formation from biomass.

2.2.2 Depolymerization

Depolymerization process consists in the breakdown of large lignocellulosic polymer bond into small aromatic monomers and low molecular weight saturated compounds in temperature range between 300 to 450 °C, which results the chains formation in short range and produced volatiles that are condensable to liquid at atmospheric temperature [Collard & Blin, 2014].

2.2.3 Fragmentation

It consists of the linkage of covalent bonds within the monomer units that results noncondensable gases and formation of linear small chain compounds. At optimum temperatures of around 600 °C active cellulose is breakdown into carbonyls acid, alcohols etc. [Kan et al., 2016 and Collard & Blin, 2014]. Figure 2 represents depolymerization and fragmentation in pyrolysis of biomass.

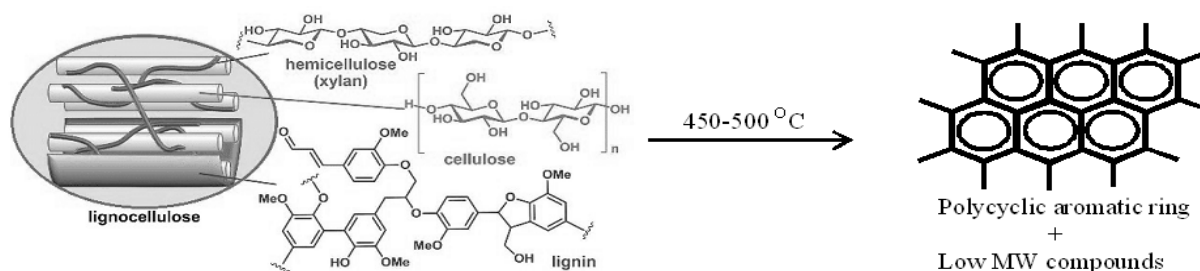


Figure 1 Char formation from biomass [Kuthi et al., 2016; Collard & Blin, 2014 and Jahirul et al., 2012]

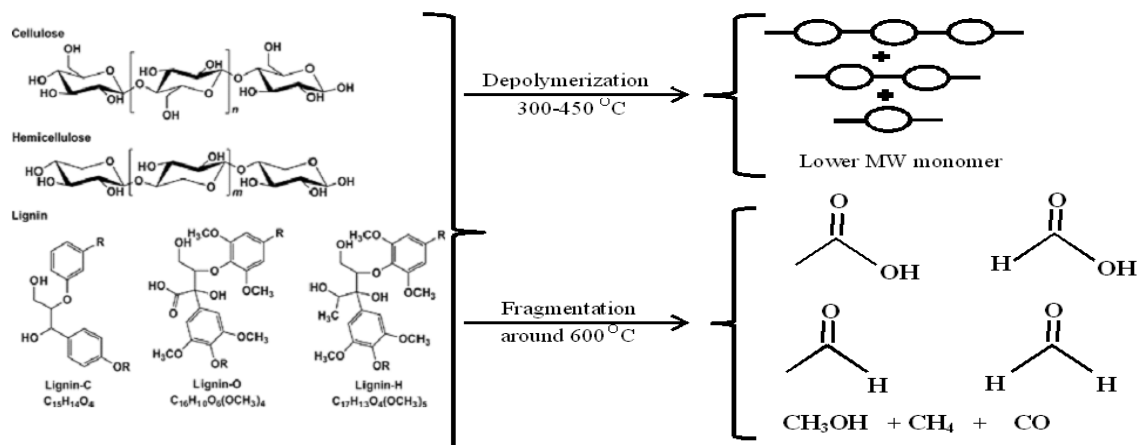


Figure 2 Depolymerization and fragmentation in pyrolysis of biomass [Zhou et al., 2016; Kan et al., 2016 and Collard & Blin, 2014]

2.3 Secondary reactions

Volatile compounds are not stable released during depolymerization and fragmentation process under reactor temperature condition, they can proceed further cracking and repolymerization named secondary reactions. This cracking relates to the destruction of chemical bonds of volatile constituents and formation of new higher molecular weight components and these components can either retain within the polymer or within the volatile compounds. In repolymerization reactions, volatiles recombine and formed higher molecular weight polycyclic hydrocarbons, which sometimes are non-volatile under the reactor temperature condition. Further, recombination process occurs inside the pores of solid residue, this reaction can promote char named secondary char [Nanda et al., 2014; Collard & Blin,

2014 and Jahirul et al., 2012]. Figure 3 reaction mechanisms for pyrolysis of biomass.

3. FACTORS AFFECTING PYROLYSIS

This section mainly deals with the factors such as biomass composition, particle size, temperature, heating rate, vapour residence time and reaction atmosphere that affect performance of pyrolysis reactions.

3.1 Biomass composition

The composition of biomass feedstock should be taken in to consideration when it aimed to produce higher yield of specific product as the physico-chemical characteristics of each component is different in various biomasses. It is preferable to use cellulose and

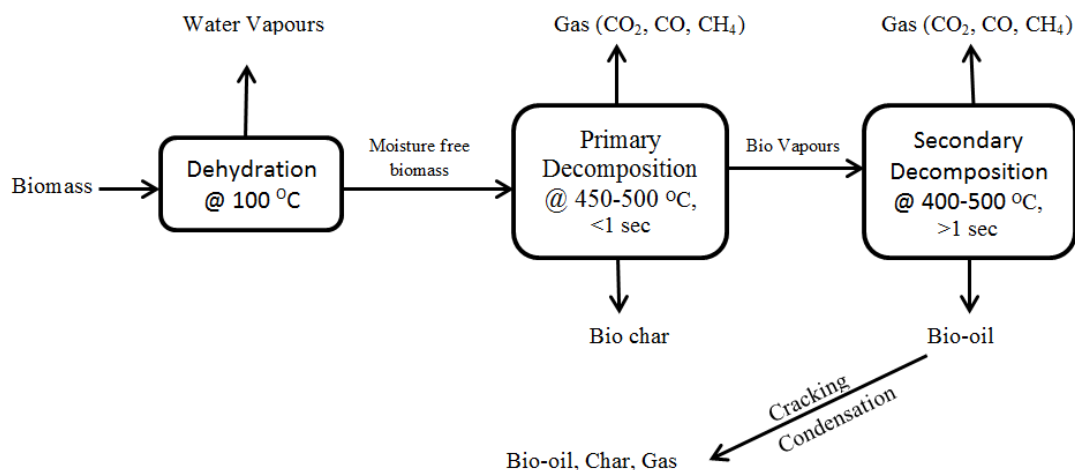


Figure 3 Reaction mechanism for pyrolysis of biomass [Wang et al., 2016; Jahirul et al., 2012 and Venderbosch & Prins, 2010]

hemicellulose containing biomass for high bio-oil yield and lignin for the bio-char [Feng & Lin, 2017; Akhtar & Amin, 2012 and Yang et al., 2006a]. It is also evident that pyrolysis of lignin is difficult as compared to cellulose component and it would also contribute in producing dense and viscous bio-oil [Fehmi et al., 2008 and Wang et al., 2008]. High volatile matter favour high production of bio-oil and syn gas, while, fixed carbon favour bio-char. In addition moisture content affects stability, viscosity, corrosiveness and pH of liquid product [Jahirul et al., 2012 and Bridgwater et al., 1999].

3.2 Particle size

Particle size of biomass also plays a vital role in pyrolysis. It is reported that change in particle size of babool seed feedstock from 0 to 1 mm influence the products yield. The char yield increases from 18 % to 25.8 % whereas, gas and liquid product yield decreases from 37 % to 29 % and 42.7 % to 41.8 %, respectively. It is also reported that maximum bio-oil yield (~ 32 %) is found at particle diameter 0.4 mm. Their findings suggest that small particles (below 0.4 mm) are suitable for obtaining a high bio-oil yield [Garg et al., 2016]. In case of palm kernel and cassava pulp residue, the maximum liquid yield of 53.5 % and 42.4 %, respectively observed at 2.03 mm particle size. Using of particle size < 2.03 mm increases volatile yield but lowers liquid yield, while

particle size > 2.03 mm increases solid char yield. This is due to the fact that in smaller particle range temperature inside particle is less this gives higher yield of gas and higher weight volatiles further decomposed to gas products that significantly decreases liquid yield [Oladeji et al., 2015]. For larger size particle char formation is favoured due to large temperature gradient inside particle imparting poor heat transfer [Sensöz et al., 2006 and Sinha et al., 2000]. These observations are generally concluded that uniform heating rate in small size particle yield of bio-oil and volatile gases is more while large size impedes the heat transfer resulting high char formation [Varma & Mondal, 2017 and Encinar et al., 2000].

3.3 Temperature

Bio oil yield is also varies significantly with the pyrolysis temperature. To enhance the quality of bio-oil it is important to consider the optimum temperature for pyrolysis as it can be seen from Table 1 that reaction temperature influences the product distribution. For example maximum oil yields of 44 % and 45 % for the pyrolysis of tamarind seed occur at 400 °C [Kader et al., 2013] and safflower seed at 500 °C [Beis et al., 2002], respectively. Thereafter, if temperature is further increased, this results in decomposition of oil into gases due to secondary reactions.

Table 1 Product distribution of biomass at various temperature ranges

Biomass	Temperature (°C)	Variation in product distribution
Palm oil waste [Kan et al., 2016]	400-550	Bio oil yield reaches at its peak value
	550- 600	Oil yield decline
	600-700	The char and bio-oils are transformed in to gas due to the dominant secondary reactions. The aliphatic, aromatic and polar fractions in the bio- oils improve.
	> 700	Increase the carbon content due to decarboxylation and dehydration reactions
Kernel cake and cassava pulp [Weerachanchai et al., 2011]	< 150	Char formation does not start
	150-300	Char formation takes place
	300-500	Char yield decreases sharply with increase in gaseous product
	500-800	Slow decrease in char formation as well decrease in liquid product due to devolatilization of cellulosic and hemi cellulosic material
	> 800	Char formation approaches a constant value
Hazelnut husk [Ceylan & Topçu, 2014]	< 122	Dehydration process
	122-550	Pyrolytic cracking, hemicelluloses, cellulose and lignin are decompose and a high amount of volatile matter formation occurs
	> 550	Endothermic decomposition of the lignin.
Wood [Bridgwater et al., 1999]	450-500	Gas yield increases from 8 % - 10 % Organic yield reaches at peak value of 64 %
	500-600	Gas yield increases from 10 % - 30 % Organic yield decreases to 47 % Char yield continuously decreases from 24 % to 10 % throughout temperature range 450-600 °C and constant afterward.
Babool seed	400-700	Char yield decreases from 21 % to 12 % due to the decompose of

[Garg et al., 2016]		char materials at higher temperature Gas yield increases from 32 % to 48 % Liquid yield increases initially from 47 % to 49 % (500 °C) and thereafter decreases
Sugarcane bagasse	350-500	At heating rate = 10 °C/min, bio-oil yield increases to 42.29 % from 29.41 %
[Varma & Mondal, 2017]	500-650	At heating rate = 50 °C/min, bio-oil yield increases to 45.23 % from 31.25 % At heating rate = 10 °C/min, bio-oil yield decreases to 38.82 % At heating rate = 50 °C/min, bio-oil yield decreases to 40.39 %

3.4 Heating rate

Heating rate of pyrolysis process is also an important parameter which affects the pyrolysis performance. Pyrolysis of biomass can be categorized based on heating rate along with reaction temperature as slow, fast and flash. (i) charcoal- low heating rate, low temperature; (ii) liquid- high heating rate, short retention time; (iii) fuel gas- high heating rate, large retention time required for maximization of desired product yield [Feng & Lin, 2017 and Balat et al., 2009]. Varma & Modal, 2017 reported that bio oil yield of sugarcane bagasse increases with the increase in heating rate. At pyrolysis temperature of 500 °C for different heating rate of 10 °C/min and 50 °C/min, the bio oil yield increases from 42.34 to 45.53 % and char yield decreases from 31.8 to 29.8%, respectively. Similarly, Demiral et al., 2012 also observed the increase in bio oil yield of corncob with heating rate. For different heating rate of 7 °C/min and 50 °C/min, the bio oil yield increases from 21.05 to 25.12 %, respectively at 500 °C of pyrolysis temperature. Senoz et al., 2006 observed that at 50 °C/min, the yield of bio-oil was about 3.4–8.4 % higher than the lower heating rate of 10 °C/min. It is reported that faster heating rate maximize the bio-oil yield [Chiaromonti et al., 2007] and char formation favoured by lower heating rate [Uzun et al., 2009].

3.5 Vapour residence time

The yield of bio oil also differs with the vapour residence time. The low residence time favours the high yield of bio oil and high residence time produces high gas during the pyrolysis thus the oil yield reduces. Shorter residence time minimizes the secondary reaction which results high bio-oil

formation [Dhyani & Bhaskar, 2017]. Reduction in bio oil yield at high residence time is obtained due to secondary cracking (>500 °C) and condensation reaction (> 400 °C) [Bridgwater et al., 1999]. [Scott et al., 1999] performed pyrolysis of raw sorghum at 525 °C and found that when vapour residence time change from 0.2 to 0.9 s, the reduction in yield of bio-oil is observed from 75 % to 57 %, respectively. Similar decrease in yield of bio oil is reported with the increase in residence time in case of sweet gum wood [Boroson et al., 1989].

3.6 Reaction atmosphere

Pyrolysis of biomass is generally performed under inert atmosphere because devolatilization rate in deoxidizing atmosphere found more to that of oxidative degradation [Oladeji et al., 2015]. According to study on corncob [Zhang et al., 2011] obtained total liquid yield under CO, N₂, CO₂, CH₄ and H₂ atmospheres are found 49.6 %, 57.1 %, 55.3 %, 58.7 % and 56.4 % respectively. This can be arranged in descending order of liquid yield CH₄ > N₂ > H₂ > CO₂ > CO. CH₄ has highest yield among all this gases but the gases containing carbon (i.e. CH₄, CO₂ and CO) provides favorable condition for deposition of polymerizing compound on reactor bed which is undesirable. Thus, second option of N₂ is found best suitable. Several other authors also conducted the pyrolysis process under nitrogen environment [Varma & Modal, 2017, Nanda et al., 2014]. Table 2 shows the influence of reaction atmosphere on pyrolysis product. Table 3 presents the optimum parameters such as heating rate, reaction temperature, particle size and sweeping gas flow rate as well as the yield of pyrolysis process of different biomass.

Table 2 Influence of reaction atmosphere on pyrolysis product

Atmosphere	Influence
Steam Pyrolysis [Putun et al., 2008]	Steam can weakly oxidise the biomass Increases yield of organic oxygenated product Prevent secondary cracking reaction
N ₂ , CO ₂ , CO, CH ₄ and H ₂ atmospheres [Zhang et al., 2011]	CH ₄ gives highest yield of bio-oil = 58.7 % CO gives lowest yield of bio-oil = 49.6 % CO and CO ₂ gives lower methoxy and larger monofunctional phenols containing

	compound			
CO ₂ and H ₂ atmosphere [Guizani et al., 2014]	Bio-oils reach the highest value (HHV) of 24.4 MJ/kg O ₂ to H ₂ O conversion are more Char produce has high surface area			
N ₂ [Saikia et al., 2015]	Volatile vapors are removed quickly at high flow rate of N ₂ Minimizes thermal cracking and formation of light gases to maximize bio-oil yield. Hot pyrolysis vapors quenched rapidly			
N ₂ [Varma & Mondal, 2017]	N₂ flow rate, cm³/min	bio-oil yield	Char yield	gas yield
	50-100	39.53-44.95 %	-	-
	200	41.89 %	-	-
	50-200		33.63-26.92 %	26.84-31.19 %

Table 3 Optimum parameters for pyrolysis of different biomass

Biomass	Optimum Parameters	Yield in wt%
Live and Dead fuels [Amini et al., 2019]	HR= 30 °C/min N ₂ flow rate=100 ml/min	Oil =51.5 % at 500 °C Char =35.5 % at 400 °C Gas =40.0 % at 800 °C
Corn cob [Khuenkaeo & Tippayawong, 2019]	T=500 °C N ₂ flow rate=5 L/min particle size= 8-10 mm	Oil =72 %
Coconut shells [Khuenkaeo & Tippayawong, 2019]	T=500 °C N ₂ flow rate=5 L/min particle size= 8-10 mm	Oil =50 %
Bamboo residue [Khuenkaeo & Tippayawong, 2019]	T=500 °C N ₂ flow rate=5 L/min particle size= 8-10 mm	Oil =45 %
Pine needle [Varma & Mondal, 2018]	T = 550 °C HR = 50 °C/min N ₂ flow rate = 100 ml/min	Oil =43.8 %
Sugarcane [Varma & Mondal, 2017]	T = 500 °C HR = 50 °C/min N ₂ flow rate = 100 ml/min Particle size =0.5-0.6 mm	Oil =45.23 %
Babool seed [Garg et al., 2016]	T = 500 °C N ₂ flow rate = 100 ml/min Particle size =upto 0.4 mm	Liquid =49 % Oil =38.3 %
Microalgae (Senedesmus Dimorphus) [Bordoloi et al., 2016]	T = 500 °C HR = 40 °C/min N ₂ flow rate = 100 ml/min	Oil =36.6 %
Hornbeam (Carpinus Betulus L.) [Morali & Sensoz, 2016]	T = 550 °C HR = 30 °C/min N ₂ flow rate = 100 ml/min	Oil =35.2 %
Wood [Mahmood et al., 2016]	T = 675 °C HR = 10 °C/min	Oil =52 %
Sewage sludge [Mahmood et al., 2016]	T = 675 °C HR = 10 °C/min	Oil =36 %
Newspaper [Mahmood et al., 2016]	T = 675 °C HR = 10 °C/min	Oil =68 %
Bamboo [Chen et al., 2015]	T = 500 °C HR = 10 °C/min N ₂ flow rate = 70 ml/min	Oil =36.5 %
Jatropha curcas cake [Majhi et al., 2015]	T = 550 °C HR = 5 °C/min N ₂ flow rate = 100 ml/min	Oil =45 %

Ferula orientalis L. [Aysu & Kucuk, 2014]	T = 500 ^o C HR = 50 ^o C/min N ₂ flow rate = 100 ml/min	Liquid = 45.2 %
Karanja seed [Shadangi & Mohanty, 2014]	T = 550 ^o C N ₂ flow rate = 50 ml/min	Oil =55.1 %
Blue green algae blooms [Hu et al., 2013]	T = 500 ^o C N ₂ flow rate = 100 ml/min	Oil =54.9 %
Corn cob [Demiral et al., 2012]	T = 500 ^o C HR = 40 ^o C/min N ₂ flow rate = 100 ml/min	Oil =26.4 %
Wheat straw [Ding et al., 2012]	T =400 ^o C RT =1 s	Liquid =46 % Char =47 % Gas =7 %
Single pass corn stover [Shah et al., 2012]	T =500 ^o C RT =1.5 s	Liquid =55 % Char =25.5 % Gas =16.2 %
Switchgrass (Panicum Virgantum) [Imam & Capareda, 2012]	T = 600 ^o C HR = 6 ^o C/min	Liquid =37 % Char =25 % Gas =26 %
Groundnut DOC [Agrawalla et al., 2011]	T= 450 ^o C HR= 20 ^o C/min	Oil= 50 %
Palm Shell [Abnisa et al., 2011]	T = 500 ^o C N ₂ flow rate = 2000 ml/min	Oil =47.3 %
Tea waste [Uzun et al., 2010]	T = 500 ^o C HR = 300 ^o C/min N ₂ flow rate = 200 ml/min	Oil =29.6 %
Hardwood shaving [Agblevor et al., 2010]	T =500 ^o C, fast HR RT < 5 s	Liquid =63.3 % Char =12.7 % Gas =24 %
Apricot pulps [Ozbay et al., 2008]	T = 550 ^o C HR = 5 ^o C/min N ₂ flow rate = 100 ml/min	Oil =23.3 %
Palm Shell [Yang et al., 2006b]	T =600 ^o C HR =10 ^o C/min Particle size < 1 mm	Liquid =57.66 % Char =28.57 % Gas =13.77 %
Soybean (Glycine Max L.) [Sensoz & Kaynar, 2006]	T =400 ^o C HR =50 ^o C/min	Liquid =25.81 % Char =23.56 %
Hazelnut bagasse [Demiral & Şensöz, 2006]	T =500 ^o C HR =10 ^o C/min Particle size =0.425-0.6 mm	Liquid =33.2 % Char =27.9 % Gas =29 %
Cotton stalk [Pütün et al., 2005]	T =550 ^o C HR =7 ^o C/min Particle size =0.85-1.8 mm	Liquid =23.8 % Char =27.1 % Gas =28.6 %
Rapeseed [Onay & Koçkar, 2004]	T= 550 ^o C HR = 30 ^o C/min No sweeping gas Particle size =0.85-1.25 mm	Liquid =49 % Char =16 % Gas =29 %
Silvergrass (Miscanthus X Gigantens) [Yorgun & Simsek, 2003]	T=550 ^o C HR=50 ^o C/min 0.425 < particle size > 0.6 mm	Oil =23.92 %
Safflower seed [Beis et al., 2002]	T =500 ^o C HR =5 ^o C/min Sweeping flow rate =100 ml/min 0.425 < particle size > 1.25 mm	Oil =44 %

Liquid means including water in oil; **HR** –Heating Rate; **T** –Temperature; **RT** –Residence time of vapour

4. CONCLUSION

Pyrolysis is an effective sustainable process due to its clean, abundant and carbon neutral characteristics. It has also a capability to fulfil the world energy requirements. Since, the performance of pyrolysis process depends on several parameters, thus the presents review study provides insight about the mechanisms of biomass pyrolysis as well as the optimum process parameters. Following notes can be useful to promote future researcher for further research on this volatile topic:

- Hemicellulose and cellulose containing biomass is preferred if it is aim to produce bio-oil and lignin for char.
- Particle size should be taken as smaller for higher bio-oil yield and larger for char yield.
- Increasing temperature of the reaction results bio-oil yield passes through maximum, char yield decreases continuously and gaseous product yield increases gradually. So, an optimum temperature is preferred in order to maximize oil yield.
- Liquid yield can be maximizing by maintaining high heating rate, moderate optimum temperature and short residence time.
- Slow heating rate along with high residence time but low temperature favours bio-char yield.
- Larger residence time at high heating rate and high temperature should be avoided for any gaseous component to be present in product stream.
- An inert atmosphere should be maintained by sweeping gas, in which nitrogen is commonly preferred for pyrolysis. It has similar effect as temperature on product distribution, i.e. an optimal inert gas flow rate for bio-oil yield.

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