

Chapter -2: Literature Review

2.1. Introduction

Biomass resources and their utilization offers a new prototype of research to the world energy sector that is currently facing a tremendous pressure due to the shortage of fossil fuel supply and reserve to fulfill the energy needs of the society [1]. Sustainable biomass production and their conversion into fuels and chemicals have recently received an increased attention due to their indirect land use and other effects associated with global food and energy markets. Since, a well-managed renewable biomass has the potential to contribute more substantially towards the development of a viable economy [2]. Further, there are numerous advantages of using biomass for energy recovery purpose, since it is an environmentally friendly fuel, abundantly available, low price in agricultural-based countries, and free from net carbon dioxide emission [3]. Among the various processes of producing energy from biomass, pyrolysis has become the most promising alternative route to convert biomass into heat/power generation, production of transportation fuels and chemical recovery [4]. It is a viable process for efficient and economic transformation of biomass into solid char, biooil and gaseous product. Usually, the biooil obtained from pyrolysis has the potential to use as a liquid fuel due to its ease of handling, storage, and transportation ability [5]. The unique composition of biooil makes it especially suitable for the extraction of value-added chemicals and materials that can replace petrochemicals [6–7]. The production of such chemicals from biomass enhances the economic viability of a society that depends on renewable.

Up till now, several biomass resources have been investigated as a suitable feedstock for recovery of fuels and chemicals through pyrolysis by a number of researchers. Since several decades, pyrolysis in its various forms has been investigated all over the world. Despite decades of study, the fundamental science of biomass pyrolysis is still lacking and detailed models capable of describing the chemistry are unavailable. Among various types of pyrolysis, exploration of a less complicated one has always been a better alternative. In this regard, slow pyrolysis process which is capable of providing all the three useful products (biooil, biochar and gases) along with its simpler operation and lower construction cost becomes the center of motivation. Further, the flexibility of regulating pyrolysis conditions to

Chapter -2: Literature Review

produce the desired proportions of liquid, solid and gas products could make the slow pyrolysis process more attractive from the economic point of view. Therefore, slow pyrolysis in a fixed-bed mode has been undertaken as a suitable option for the present study. A detailed survey of contemporary literature on slow pyrolysis of lignocellulosic bio-waste and aquatic biomass needs attention as it serves many compensations from both energy and environmental point of views.

2.2. Pyrolysis of lignocellulosic biomass

Lignocellulosic biomass is the most plentiful and inexpensive sustainable source of carbon that can be used as a feedstock for the production of renewable fuels and commodity chemical feedstocks [8]. Lignocellulosic materials are composed of biopolymers which consist of various types of cells, and the cell walls are built of cellulose, hemicelluloses and lignin. Therefore, the utilization of lignocellulosics as feedstock might faces problems due to their complex structure and the difficulty to separate their components in an economically feasible way. However, pyrolysis is one of the simplest and oldest technologies that have been used to convert lignocellulosic materials to another class of fuels and chemicals [9]. Some reported works on pyrolysis of lignocellulosic materials are discussed below:

Williams and Besler [10] investigated the slow pyrolysis of pinewood in a static batch reactor at a temperature range of 300–720 °C with a heating rate of 5–80 °C/min. Product yield and their characterization were determined in relation to temperature and heating rate. The results indicated that with an increase in pyrolysis temperature the char yield was reduced slightly whilst the oil and gas yields increased. There was a small effect of heating rate on product yield. FTIR spectroscopy and elemental analysis showed that biooils were highly oxygenated.

Sensoz et al. [11] conducted the pyrolysis experiments of rapeseed in a fixed bed reactor under the static atmosphere at a pyrolysis temperature of 500 °C and a heating rate of 40 °C/min. The particle size of rapeseed was varied in the range of 0.22–1.8 mm. Study revealed that oil and char yields were independent of particle size. Maximum oil yield of 46 wt.% was obtained with a particle size range of 0.85–1.8 mm. The calorific value of the biooil was found to be 38.4 MJ/kg. The results

Chapter -2: Literature Review

showed the potentiality of rapeseed as an important source of liquid hydrocarbon fuels.

Yorgun et al. [12] reported the pyrolytic conversion of sunflower extracted bagasse in fixed bed reactor from a temperature range of 400–700 °C with a heating rate of 7–40 °C/min. The effects of temperature, heating rate, particle size and atmosphere on the product yields and chemical compositions were investigated. The maximum oil yield of 23 wt.% was obtained in N₂ atmosphere at a pyrolysis temperature of 550 °C and a heating rate of 7 °C/min. The chemical characterization of biooil estimated that the feedstock has the potential to be used as a valuable source of fuel and chemical.

Ucar and Karagoz [13] carried out the slow pyrolysis experiments of pomegranate seeds at a temperature range of 400–800 °C. The effect of temperature on the product distribution was studied. The maximum liquid yields were obtained at the temperatures of 500 and 600 °C. The composition of gaseous products was found to be contained CO₂, CO, CH₄, hydrocarbons from C₂ to C₇ and H₂S. Phenols and alkyl-benzenes were prominent in biooils obtained at all tested temperatures. The total non-aromatic hydrocarbons were higher than that of aromatic hydrocarbons in water fractions for all pyrolysis temperatures. Biochar produced from pomegranate seeds was seemed to be carbon rich fuels with high bulk densities and calorific values.

Nayan et al. [14] conducted the pyrolysis of Karanja (*Pongamia glabra*) seeds in semi-batch mode at a temperature range of 450–550 °C with a heating rate of 20 °C/min. FTIR analysis of the liquid product indicates the presence of alkanes, alkenes, ketones, carboxylic acids and aromatics rings. GCMS demonstrated the presence of hydrocarbons between 14 and 31 carbon atoms in a chain. Study showed that physical properties of the pyrolysis liquid were close to a mixture of diesel and petrol.

Nayan et al. [15] reported the pyrolysis of neem seeds in a semi-batch reactor at a temperature range of 400–500 °C with a heating rate of 20 °C/min. The FTIR analysis showed the presence of alkanes, alkenes, ketones, carboxylic acids and amines. The main constituents of liquid products were found to be octadecanenitrile,

Chapter -2: Literature Review

oleanitrile, 9-octadecenoic acid methyl ester, stearic acid methyl ester. Thus, the obtained liquid product can be used as a source of valuable chemicals.

Moreover, the lignocellulosic bio-waste (stalks of wheat, corn, wood, agricultural waste, byproducts like seed covers, de-oiled cakes etc.) valorization has gained increasing prominence as it serves many advantages from both energy and environmental point of views. Production of biofuels from bio-waste by thermochemical conversion further helps to achieve the twin objectives of waste management and energy, and chemicals recovery. The present study aims at the establishing the possibility of utilizing unexploited seed covers for recovery of energy and chemicals. A few literatures have been reported on utilization of seed shell/cover from different fruits as feedstock for pyrolysis process. Some of them are discussed below:

2.2.1. Pyrolysis of seed covers

Das and Ganesh [16] reported the pyrolytic conversion of cashew nut shell in a packed bed vacuum pyrolysis unit. The detailed characterization of liquid product was carried out by using various techniques like ^1H NMR, ^{13}C NMR, FTIR, GC-MS. The properties of oil have been found to be near to that of petroleum fuels with a calorific value of 40 MJ/kg.

Tsai et al. [17] performed pyrolysis of coconut shell in a fixed-bed reactor to investigate the effect of pyrolysis temperature, heating rate and holding time on the yields of pyrolysis products and their chemical compositions. It was observed that the maximum pyrolysis liquid yield of 50 wt.% was achieved by employing higher pyrolysis temperature of $>500\text{ }^\circ\text{C}$, faster heating rate of $>200\text{ }^\circ\text{C}/\text{min}$, and longer holding time of $>2\text{ min}$.

Zabaniotou et al. [18] reported the pyrolysis of sunflower shells in a captive sample batch reactor in a temperature range from 300 to 600 $^\circ\text{C}$ under atmospheric pressure and helium (He) as a sweep gas. The maximum oil yield of about 21 wt.% was obtained at 400 $^\circ\text{C}$ and gas yield of around 53 wt.% was obtained at 500 $^\circ\text{C}$. A

Chapter -2: Literature Review

simple first-order kinetic model has been applied for the devolatilization of biomass. Kinetic constants were determined with values $E = 78.15 \text{ kJ/mol}$; $k_0 = 1.03 \times 10^3 \text{ s}^{-1}$.

Manurung et al. [19] investigated pyrolytic behaviors of *Jatropha curcas* L. nut shells. The experiments were carried out in a continuous bench scale rotating cone fast pyrolyzer at a temperature range of 470–490 °C in an atmospheric pressure. The non-optimized pyrolysis liquid yield of 50 wt.% was obtained along with char and gas yield of 23 wt.% and 17 wt.% respectively.

Duman et al. [20] reported the slow and fast pyrolysis of cherry seed shells in fixed and fluidized bed reactors respectively. They investigated the effects of reactor type and temperature on the yields and composition of products and observed maximum biooil yield of 44 wt.% at pyrolysis temperature of 500 °C. The study showed that liquid product obtained from slow pyrolysis can be used as fuel while fast pyrolysis oils provide scope for recovery of chemicals.

Abnisa et al. [21] carried out pyrolysis experiment of palm shell in a fluidized-bed reactor at a temperature range of 400–800 °C with varying flow rate of N₂ as carrier gas. The maximum liquid yield of 47 wt.% was observed at 500 °C with 2 L/min N₂ flow at 60 min reaction time. The characterization of biooil was further carried out by using FTIR and GCMS techniques.

Titiloye et al. [22] reported the potential use of *Parinari polyandra* fruit shell as feedstock for thermochemical conversion. The calorific value of the fruit shell was found to be 20.47 MJ/kg. Proximate, ultimate, and structural composition of the biomass indicates the suitability of the feedstock for biofuel production.

Önal et al. [23] reported the co-pyrolysis of almond shell with high density polyethylene polymer in a fixed bed reactor at a temperature of 500 °C to investigate the synergistic effects on the product yields and compositions. The liquid produced by co-pyrolysis had higher carbon and hydrogen contents, and lower oxygen content.

On the contrary, apart from lignocellulosic biomass, few researchers have explored the possibility of using microalgae species (non-lignocellulosic origin) as

Chapter -2: Literature Review

promising feedstock for biofuel production. Some of the reported works are discussed below:

2.2.2. Pyrolysis of microalgae biomass

Miao et al. [24] reported the fast pyrolysis of microalgae *Chlorella protothecoides* and *Microcystis aeruginosa* in a fluid bed reactor with a feed rate of 4 g/min. The biooil obtained had higher heating value of 29 MJ/kg, which was about 1.4 times more than that of biooil produced from wood. The saturated and polar fractions accounted for 1.14 and 31.17% of the biooils from microalgae on an average, which were higher than the wood derived biooil.

Chaiwong et al. [25] reported that biooil and biochar produced from *Spirulina Sp.* had maximum degradation temperature at 322 °C. The energy consumption ratio (ECR) of biooil and biochar was 0.49 and the net energy output was positive. The main compounds of the biooil were found to be heptadecane, toluene, ethylbenzene, and indole. The hydrocarbon groups were present in a range of heavy naphtha, kerosene and diesel.

Miao and Wu [26] reported an approach for increasing the biooil yield from fast pyrolysis by manipulating the metabolic pathway in microalgae through heterotrophic growth. The yield of biooil (57.9%) from heterotrophic *Chlorella protothecoides* cells was 3.4 times higher than autotrophic cells by fast pyrolysis. The biooil had much lower oxygen content, with a higher heating value (41 MJ/kg), lower density (0.92 kg/l) and lower viscosity (0.02 Pa) compared to the biooil from autotrophic cells and wood.

Ferreira et al. [27] reported the production of biooil from microalgae (*Chlorella vulgaris* and *Scenedesmus obliquus*) through pyrolysis in a fixed bed reactor with and without a catalyst. Both the microalgae showed significant differences in biooil yields in the range of 26–38 wt.% and 28–50 wt.% respectively. The use of carbonate catalysts increased the gas yield and decreased the biooil yield for both microalgae. The use of alkaline salt catalysts improved the quality of the obtained biooil with a net gain on the alkyl groups.

Chapter -2: Literature Review

Phukan et al. [28] reported that microalgae *Chlorella* sp. MP-1 exhibited several important attributes for futuristic study on renewable energy. With simple and inexpensive nutrient regime to culture, faster growth rate as compared to terrestrial energy crops, high biomass productivity, attractive biochemical profile and good energy content (18.59 MJ/kg), *Chlorella* sp. MP-1 offered a strong candidature as bioenergy feedstock.

2.3. Effects of pyrolysis parameters on product yields

There are many factors affecting the nature of products obtained during pyrolysis process. These factors can be divided into processing and non-processing parameters. Temperature and heating rate are two crucial parameters of pyrolysis process, also known as processing parameters. Based on these two parameters, the pyrolysis process can be classified into conventional and fast or flash pyrolysis. On the other hand, biomass composition is considered as the non-processing parameter of pyrolysis process. In this regard, the effect of pyrolysis temperature, heating rate and biomass composition on solid, liquid and gaseous product yield have been discussed as reported in various literatures.

2.3.1. Effect of Pyrolysis Temperature

Temperature plays a key role in determining the yield and composition of the pyrolysis products [10]. The yield of liquid product is found to be increased with increase in pyrolysis temperature up to 550 °C, followed by a decline with further rise in temperature indicating the start of secondary reactions. This trend was found to be followed by pyrolysis of various feedstocks like rapeseed [11], *Euphorbia rigida* [29], sunflower-oil cake [30], sunflower-pressed bagasse [31] etc. Usually, high pyrolysis temperature favors the production of pyrolysis gas, while biochar are prone to form at low pyrolysis temperature [32–35]. Moreover, the pyrolysis temperature has been reported to have no significant effect on water content in liquid product for the pyrolysis of biomass [12, 36]. The pyrolysis temperature has a remarkable effect on biooil composition [37]. Xiao et al. [38] reported that, the yield of semi-char and the contained organic functional groups(CO, CC, C–H, C–O and OH) decreases significantly with the increasing final temperature. The tar yield passes through a

Chapter -2: Literature Review

maximum at about 500 °C. The organic functional groups in tar were stable but the transmittance of these groups decreased with the increasing final temperature.

2.3.2. Effect of Heating Rate

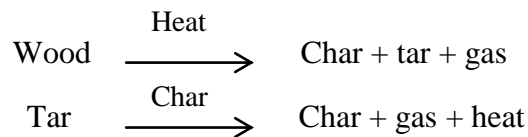
Heating rate is another important and significant parameter of biomass pyrolysis that shows prominent effects on the composition of the final product up to a certain extent. Generally high heating rate has been applied to obtain high yield of liquid product from biomass pyrolysis. For high yield of biochar and gas production low heating rate condition would be preferable [39]. Similar trends were observed for pyrolysis of straw and stalk of the rapeseed plant [40], wood powder [41], sugar cane bagasse [42], beech trunk bark [43], giant fennel (*Ferula orientalis* L.) stalks [44] and safflower seed press cake [45]. Low heating rate ensures that no thermal cracking of biomass takes place resulting in more biochar yield. High heating rate is likely to enhance the depolymerization of biomass into primary volatile components which at the end retard the biochar yield and further increases the gaseous and liquid yield. At high heating rate, the secondary pyrolysis reactions are dominant which aid to the formation of gaseous component. The effect of heating rate on the biochar yield is more noticeable and potent at lower temperatures [46–47].

2.3.3. Biomass composition

Biomass is generally a complex mixture of organic materials such as carbohydrates (hemicellulose, cellulose, and starch), lignin, fats, and proteins; along with smaller amounts of (organic and inorganic) extractives and minerals (inorganic compounds) [48]. Cellulose, hemicellulose, and lignin all have a different thermal decomposition behavior which could be attributed to their thermal and structural stability with lignin being the most stable of all structural components. These components are present in different proportions in different types of biomass which further influences the product distributions on pyrolysis [49]. On heating to pyrolysis temperatures the main components contribute towards the product yields can be summarized as follows: primary products of hemicellulose and cellulose decomposition are condensable vapors (hence liquid products) and gas. Lignin decomposes to liquid, gas and solid char products. Extractives contribute to liquid and

Chapter -2: Literature Review

gas products either through simple volatilization or decomposition. Minerals in general remain in the char in the form of ash [48]. Secondary pyrolysis reactions involve the decomposition products of primary reactions. The products of the primary reactions are mainly char and volatiles which further catalyze the secondary reactions. Such autocatalytic reactions are initiated when the hot volatile products come in physical contact with unpyrolysed biomass [50]. Autocatalytic secondary pyrolysis reactions are difficult to model since experimental information on the mechanism of these reactions and reaction rates is not available. In this regard, Lee et al. [51] suggested the following scheme for wood pyrolysis:



Yang et al. [52] reported the decomposition behavior of cellulose, hemicellulose and lignin. They have found that the pyrolysis of hemicellulose and cellulose occurred quickly (weight loss of hemicellulose mainly happened at 220–315 °C and that of cellulose at 315–400 °C) whereas, the lignin was more difficult to decompose (from 160 to 900 °C). Further, it was observed that the overall hemicellulose and lignin pyrolysis reactions are exothermic whereas the cellulose pyrolysis reactions are endothermic in nature. Ball et al. [53] reported that the charring process is highly exothermic whereas volatilization was endothermic in nature. Therefore, the endothermic cellulose pyrolysis reactions might be attributed to the quick devolatilization reactions, leaving very few solid residues. Burhenne et al. [54] reported that the lignin content of any biomass feedstock is the main controlling factor in pyrolysis process for industrial application. They found that the highest liquid product yield (i.e. 48 wt.%) and the lowest solid product yield of 32 wt.% was obtained from rape straw with a lignin content of 24 wt.% while the lowest liquid product yield of 41 wt.% and the highest solid product yield of 43 wt.% was produced by spruce wood pyrolysis that had a lignin content of 26 wt.%. Thus, it can be observed from the literature that final temperature to obtain maximum liquid product yield depends upon biomass components and that lignin contributes to the major portion of solid residues during lignocellulosic biomass pyrolysis process.

Chapter -2: Literature Review

2.4. Pyrolysis mechanism

Kan et al. [55] reported the complexity of biomass pyrolysis occurs from the difference in decomposition of biomass components with various reaction mechanisms and reaction rates which in turn depend on the thermal processing conditions and reactor designs. The interaction between hemicellulose and lignin promotes production of lignin-derived phenols while hinders the generation of hydrocarbons [56]. Lignin also significantly interacts with cellulose during pyrolysis as lignin hinders the polymerisation of levoglucosan from cellulose thus reducing biochar formation, while the cellulose-hemicellulose interaction has a lower effect on the formation and distribution of pyrolysis products [57]. During biomass pyrolysis, a large number of reactions take place in parallel and series, including dehydration, depolymerisation, isomerization, aromatization, decarboxylation, and charring [58]. It is generally accepted that the pyrolysis of biomass consists of three main stages: (i) initial evaporation of free moisture, (ii) primary decomposition followed by (iii) secondary reactions (oil cracking and repolymerisation) [59]. Vamvuka et al. [60] and Dauenhauer et al. [61] attempt to illustrate the pyrolysis process in a pictorial form so that the complexity of the pyrolysis process was well understood by the readers. Among the three major constituents of biomass, Velden et al. [62] reported the decomposition mechanism of cellulose illustrating the simplified reaction pathways of cellulose pyrolysis, which is the generally accepted Waterloo-mechanism.

2.5. Thermogravimetric analysis of biomass

Thermogravimetry analysis has proved to be a useful tool for elucidating the decomposition of various biomass materials. The temperature domains indicate the decomposition of various components present in a biomass. Kinetic study of biomass pyrolysis becomes useful for a better understanding of the physicochemical process and proper design of industrial pyrolysis units. Usually, two methods are highlighted in literatures viz. model-fitting as well as model-free methods. However, model-free methods are considered to be more suitable due to absence of some drawbacks that are associated with model-fitting techniques. Model-free methods are based on the principle that, at constant conversion, the reaction rate depends only on temperature.

Chapter -2: Literature Review

An overview of the published works on various models describing the kinetics of biomass pyrolysis is given below:

Antal and Várhegyi [63] reported the various works on thermogravimetric studies that carried out for pyrolysis of homogeneous cellulose sample (free of inorganic contaminants, with a well-defined degree of polymerization and crystallinity), at low to moderate heating rates. The process was endothermic with activation energy of 238 kJ/mol. Faix et al. [64] and Várhegyi et al. [65] reported the thermogravimetric analysis of lignocellulosic biomass at low to moderate heating rates. Decomposition of cellulose hemicellulose and lignin pyrolysis was evident from the DTG curve. A distinct DTG peak was observed for decomposition of cellulose whereas an attenuated shoulder can be attributed to lignin decomposition. Várhegyi et al. [65] revealed that there occurs an overlap in DTG curves due to presence of mineral matter in the biomass samples. However, several studies have been carried out to resolve the overlapping of the curves. Várhegyi et al. [66] and Di Blasi et al. [67] reported various pretreatment methods to separate merged peaks and able to displace reaction zones toward higher temperatures that decrease the yield of char production and increase peak reaction rates.

As reported by Basu [68], pyrolysis process is composed of three stages including drying, devolatilization, and carbonization. The study showed that drying or dehydration occurs within a temperature range of 30–150 °C. Devolatilization occurs due to release of volatiles from the decomposition of hemicellulose and cellulose contents between 150 °C and 400 °C. According to Vassilev et al. [69], cellulose is a long network of hydrogen bonds that established a link between the long chains to provide thermal stability and resistance. The cellulose devolatilization temperature is between 250–350 °C [70]. Carbonization and the char formation occur at above 400 °C. According to Pasangulapati et al. [71], the lignin is the higher precursor of char, about 50% yield, whereas the contribution of cellulose and hemicellulose are very low, 1% for cellulose and 7% for hemicellulose. Various studies have been focused on calculating activation energy of pyrolysis process by using different isoconversional methods (Friedman, Flynn–Wall–Ozawa and Kissinger–Akahira–Sunose methods) for different biomasses classified in fiber [72-74], wood [75-77],

Chapter -2: Literature Review

and woody shell residues [78-80]. From these studies, it can be concluded that the higher is activation energy, the higher is the biomass stability.

2.6. Statistical optimization

Nowadays biooil have many applications, especially as an alternative fuel or source of chemical recovery, therefore, it becomes crucial for researchers to concentrate on improving the quantity and quality of the product yield from biomass pyrolysis. The high yield of biooil depends on various parameters like temperature, particle size, heating rate, gas flow rate and the cooling method of the pyrolysis vapors. The optimal condition for the biooil production was obtained by testing the effect of various parameters on the pyrolysis. However, complex combination of various parameters creates difficulty to find the optimum parameter through experiments. In this regard, a statistical experimental design such as response surface methodology (RSM) was applied to figure out the best parameter combination with a minimum no of experiments [81]. Till now, a few studies have been reported on statistical optimization of experimental design using RSM. Some significant literature information is summarized below:

Kilic et al. [82] reported the optimum conditions for obtaining the highest yield of biooil from *Euphorbia rigida* by fast pyrolysis using response surface methodology (RSM) based on central composite design (CCD). The experiment was designed to optimize the pyrolysis parameters such as the reaction temperature, heating rate, and nitrogen gas flow rate. The most influential factor of the experiment was identified with the help of ANOVA test and an empirical model was established. The maximum biooil yield of 35.3% was obtained at optimum conditions of 600 °C reaction temperature, 200 °C/min heating rate, and 100 mL/min nitrogen flow rate.

Abnisa et al. [83] studied pyrolysis of palm shell waste to produce biooil. The effects of various pyrolysis parameters (include temperature, N₂ flow rate, feedstock particle size, and reaction time) were studied to identify the optimum condition for biooil production by using RSM based on CCD. A second-order polynomial equation explains the results adequately. R² value of 0.9337 indicates a sufficient adjustment of the model with the experimental data. The optimal biooil yield was found to be 46.4

Chapter -2: Literature Review

wt.% with conditions of 500 °C temperature, 2 L/min N₂ flow rate, with 2 mm particle size and 60 min of reaction time.

Isa et al. [84] investigated the thermogravimetric analysis of rice husk and determined the optimum condition for yield of biooil obtained through fixed-bed pyrolysis. Pyrolysis parameters temperature, heating rate, particle size, holding time, and gas flow rate was investigated to determine the optimum condition by employing CCD design matrix in response surface methodology. The optimum were found to be pyrolysis temperature of 473.37 °C, heating rate of 100 °C/min, particle size of 0.6 mm and holding time of 1 min.

Jamaluddin et al. [85] reported the pyrolysis of palm kernel shell (PKS) using microwave-assisted pyrolysis. Reaction time, mass of the sample and N₂ gas flow rate (mL/min) were considered to study the combined effects on product yield by using response surface methodology (RSM) based on central composite rotatable design (CCRD). Calorific value, fixed carbon content, volatile matters content and yield percentage were also analyzed by using CCRD. The predicted optimum conditions for the pyrolysis process was at 31.5 min for reaction time, 30g for sample mass and 100 mL/min for nitrogen gas flow rate, resulting in calorific value, fixed carbon content, volatile matters content and yield percentage of 29.9 MJ/ kg, 59.8 wt%, 36.4 wt% and 40.0 wt%, respectively.

Abnisa et al. [86] studied the co-pyrolysis of palm shell and polystyrene waste to obtain a high-grade of pyrolytic liquid that potentially could be used as a fuel. An optimization study using response surface methodology was carried out for three effective parameters: temperature, feed ratio, and reaction time. The maximum liquid yield of approximately 68.3% was obtained under optimum conditions, which were shown to be a temperature of 600 °C, a palm shell/polystyrene ratio of 40:60, and a reaction time of 45 min.

Jung et al. [87] reported the pyrolysis of lignin in a fixed-bed reactor. Biooil produced was systematically characterized by response surface methodology (RSM) to optimize operating variables such as temperature, heating rate, and loading mass. According to the mathematical model of RSM, the predicted maximum biooil yield of

Chapter -2: Literature Review

30.1% and the actual biooil yield of 29.3% were obtained under the optimum condition: 669 °C temperature, 15 °C/min heating rate, and 6.97g loading mass. The biooil produced in optimum condition found to have higher amount (43.2%) of 2-methoxyphenol.

2.7. Biooil

Biooil is the main product of the process of fast pyrolysis. It is a multi-component mixture of different size molecules obtained from the depolymerization and fragmentation of cellulose, hemicelluloses, and lignin. The chemistry of biooil is qualitatively well known, although detailed quantitative compositions are usually not available. As reported in many literatures, the dark brown liquid product has the efficiency to be burnt in standard or in slightly modified burners [88-92]. However, the use of biooil as fuel in boilers, diesel engines or gas turbines for heat and electricity generation is further limited by its high viscosity, high water and ash contents, low heating value, instability and high corrosiveness [93]. These undesirable properties are probably the most challenging and have so far limited the range of biooil applications [94]. Many publications have stated that different chemical compositions of biooil are responsible for different physical properties [95-98]. Since the biooil is a complex mixture of several hundreds of organic compounds, mainly including alcohols, acids, aldehydes, esters, ketones, phenols as well as lignin-derived oligomers [93]. Therefore, a thorough understanding of biooil becomes necessary pre-condition of research to clarify the reaction mechanism of biooil production, properties, and up-gradation techniques [99]. The main components of biooil are distributed as: water, 20–25%; water insoluble pyrolytic lignin, 25– 30%; organic acids, 5–12%; non-polar hydrocarbons, 5–10%; anhydrosugars, 5–10%; and other oxygenated compounds, 10–25%. The water content of biooils contributes to their low energy density, lowers the flame temperature of the oils, leads to ignition difficulties, and, when preheating the oil, can lead to premature evaporation of the oil and resultant injection difficulties [88].

Lu et al. [100] intensively reviewed the fuel properties of fast pyrolysis oils and discussed how these properties affect the utilization of biooil. Further, Huber et

Chapter -2: Literature Review

al. [101] reported the exact composition of the biooil is dependent upon the type and quality of the feedstock (including dirt and moisture content), organic nitrogen or protein content of the feedstock, heat transfer rate, time and temperature of vapors in the reaction, efficiency of the char removal system and the condensation equipment (to recover the volatile components from the non-condensable gas stream). Thus, characterization of biooil is beneficial to estimate the kind of up-gradation technique that needs to produce quality transportation fuels and chemicals.

2.8. Application of biooil

In order to explore the feasibility of biooil as a high-grade fuel, intensive research has been carried out for upgrading of biooil to higher value fuel hydrocarbons, including hydrogenation [102], hydrodeoxygenation [103], catalytic pyrolysis [104], catalytic cracking [105], steam reforming [106], molecular distillation [107], supercritical fluids [108], esterification [109] and emulsification [110]. Although these intensive efforts to upgrade biooils have resulted in considerable progress, there are still a number of technical barriers to overcome, such as catalyst deactivation, short lifetime of catalyst, low contents chemical recovery etc. [111-112]. Apart from these techniques, column chromatography has become the stimulating research area of the biooil up-gradation and chemical recovery from the biomass pyrolysis. This technique is economically feasible for separation of biooil to both fuels and value added chemicals [113]. In the present context, a few reviews regarding the column chromatographic separation of biooil derived from pyrolysis of different bio-wastes for extraction of alternative biofuels and value added chemicals have been presented below:

Inoue et al. [114] reported the production of oil by liquification of *Botryococcus braunii* green colonial microalga which produces and accumulates oily hydrocarbons called botryococcenes. The liquefied oil of *B. braunii* was fractionated into three fractions low molecular weight hydrocarbons, botryococcenes, and polar fractions by using liquid column chromatography. The maximum recovery (78%) of the botryococcenes was achieved at 200 °C with the use of catalyst.

Chapter -2: Literature Review

Peng et al. [115] in 2000, have shown that pyrolysis of the complete algae (chlorella) resulted in high oil yields, above 40% on dry biomass basis within a wide temperature range (300–500 °C). Thus, produced biooils are usually a mixture of oxygenated components such as alcohols, ethers, aldehydes, ketones, phenols, esters acids.

Horne and Williams [116] in 1996, reported the pyrolysis of mixed wood waste in a fluidized bed reactor at 400, 450, 500 and 550 °C. The liquid products were analyzed in detail to determine the concentration of environmentally hazardous polycyclic aromatic hydrocarbons (PAH) and potentially high-value oxygenated aromatic compounds. The gases evolved were CO₂, CO, and C₁-C₄ hydrocarbons. The liquids were homogeneous, low viscosity and highly oxygenated. Chemical fractionation of the liquids showed that only low quantities of hydrocarbons were present and the oxygenated and polar fractions were dominant. The liquids contained significant quantities of phenolic compounds and the yield of phenol and its alkylated derivatives was highest at 500 and 550 °C. These phenolic compounds could be removed from the pyrolysis liquids prior to their combustion, as they have a significant commercial value.

Putun et al. [117] investigated the fixed-bed pyrolysis of hazelnut shells to determine the yields and structural analysis of biooil. The effect of pyrolysis temperature was investigated on the product yields in presence of N₂ atmosphere. The maximum biooil yield of 23.1 wt.% was obtained at a temperature of 500 °C and a heating rate of 7 K/min. Biooil of the hazelnut shells was then fractionated using different solvents and each fraction contains 16% aliphatic, 37% aromatic, 27% ether (polar) and 20% methanol (more polar) sub-fractions. Consequently, the aliphatic and aromatic sub-fractions make up 53% and this seems to be more appropriate for the production of hydrocarbons and chemicals.

Sensoz and Can [118] in 2002, reported the pyrolysis of pine chips (*Pinus brutia Ten.*) in a fixed-bed reactor. The solid and liquid products were analyzed to determine their elemental composition and calorific values. Chemical fractionation of liquids showed that the oxygenated and polar fractions were dominant. The high

Chapter -2: Literature Review

concentration of phenolic compounds indicates the suitability of the oil as a source for value-added chemicals.

Uzun et al. [119] in 2007, investigated the effect of pyrolysis temperature on product distribution and composition obtained through fast pyrolysis of olive-oil residue. The liquid products obtained at various pyrolysis temperatures were subjected to column chromatography. The biooil obtained at 400 °C has 56% n-pentane soluble, the maximum solubility in n-pentane was achieved as 65% at 550 °C.

Singh et al. [120] in 2014, explored the pyrolysis of saal seed (*Shorea Robusta*) to liquid product at a temperature range of 400–625 °C and a heating rate of 20 °C/min. The FTIR analysis of biooil indicates the presence of various functional groups and GC–MS analysis showed the presence of hydrocarbons between 6 and 20 carbon atoms in a chain. The physical properties of the liquid product were close to that of petroleum fractions. The solid char can be used as an adsorbent as well as a solid fuel due to its high calorific value.

Varol et al. [121] in 2014, reported the thermal decomposition behavior of cottonseed via TGA/FT-IR/MS and characterization of liquid products from fast pyrolysis. Maximum oil yield of 49.5% was attained at 500 °C under N₂ flow rate of 200 cm³/min and a heating rate of 300 °C/min. The biooil pyrolyzed from cottonseed contains a high amount of oxygen. This unfavorable property was prevented by fractionating it into chemical classes (aliphatic, olefinic and polar) by column chromatography. Detailed characterization of biooil and its aliphatic sub-fraction show similarities with currently utilized transport fuels and can be considered as synthetic fuels.

2.9. Biochar

Biochar is a carbon dominant solid product which is obtained as a byproduct with the liquid fraction during pyrolysis of biomass. Till date, different types of biomass feedstocks have been used for the production of biochar ranging from agricultural wastes to woody resources and aquatic feedstocks etc. [122]. Biochar is an ancient material that has been widely used as a source of energy. Biochar can be

Chapter -2: Literature Review

burnt to supply heat, used as cooking material in home, used for water and gas purification, and used to bolster primarily soil fertility and crop production [123-124]. Furthermore, some salient features such as nitrate leaching [125], adsorption of inorganic and organic contaminants [126], and reduction of trace-gas emissions from soil and atmosphere [127] are witnessed in case of biochar. Bridgwater [128], reported that fresh biochar is pyrophoric in nature i.e. when exposed to air biochar has the tendency to combust spontaneously. Therefore, careful handling and storage is necessary. This property deteriorates with time due to oxidation of active sites on the char surface. Gaunt and Lehmann [129] in 2008, suggested a hypothesis that land application of biochar reduces greenhouse emissions to a greater extent than when the biochar is used to offset fossil fuel emissions.

2.10. Application of biochar

The novel interest in application of biochar has increased due to its beneficial effects in a number of different areas including waste recycling for bioenergy production [130], carbon sequestration [131], and improvements in the soil fertility, increases the soil microbial community [132-134], and decreases in nitrous oxide (N₂O) and methane (CH₄) emissions [135-137] etc. Recently, biochar has received increasing attention in wastewater treatment arena due to its adsorptive ability towards the various organic/inorganic contaminants [138]. The specific properties of biochar including surface area, porous structure, enriched surface functional groups and mineral components makes it possible to use as proper adsorbent to remove contaminants from aqueous solutions. Pintor et al. [139] investigated that surface chemical composition plays an important role in the adsorption property of biochar. The chemical characteristics of the biochar surface are closely associated to its chemical composition. So far, many studies have reported that biochar showed excellent ability to remove contaminants such as heavy metals, organic pollutants and other pollutants from aqueous solutions. In the present study, a detailed survey of existing literature on pollutant (both inorganic and organic) removal efficiency of biochar from wastewater has been summarized below:

Chapter -2: Literature Review

2.10.1. Biochar used for removal of heavy metal

Biochar has been widely used to remove toxic materials from aqueous solution. Many types of biomass-derived char have been investigated to remove heavy metals from aqueous solution such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co), zinc (Zn) etc. A comprehensive review on reported work related to adsorption characteristics of biochar exposed to various heavy metals are discussed below:

Inyang et al. [140] reported the removal efficiency of four heavy metals namely Pb, Cu, Ni, and Cd by using biochars derived from two anaerobically digested feedstocks such as dairy waste and whole sugar beet. Various studies have reported the removal of Cd from aqueous solution by using biochars produced from switch grass, peanut hull, manure, wood and bark [141-142]. Similarly, Lu et al. [143] studied sorption mechanism of Pb on a biochar derived from sewage sludge to estimate the possibility of removing heavy metals from acid solutions. Chen et al. [144] reported that biochar produced from wood or corn straw showed high removal efficiency of Cu (II) and Zn (II) from aqueous solutions. Adsorption isotherms were studied at different initial heavy metal concentrations ranging from 0.1 to 5.0 mM. Adsorption data were best fitted for Langmuir model ($R^2 > 0.998$) rather than the Freundlich model (R^2 were 0.86–0.94). Tong et al. [145] investigated the sorption ability of Cu from aqueous solution by using three straw derived biochars. Adsorption data were tested against Langmuir, Freundlich and Temkin equations. Among these isotherms, Langmuir model was found to be well fitted which was determined on the basis of the correlation coefficient. However, various studies showed better fits of adsorption data by biochar to Freundlich than Langmuir isotherm [143, 146-147]. These studies revealed the heterogeneous adsorption of metals on biochar surfaces.

It is being observed from the above discussion that a lot of research has been conducted for removal of Cu, Pb, Ni, Cd, Cr, and Zn. But a few works have published regarding the removal of Co metal from aqueous solution. Since, acute exposure to Co can induce nausea, vomiting and neurotoxicological symptoms such as headaches and changes in reflexes, while chronic exposure to cobalt may cause partial or complete loss of smell, gastrointestinal troubles and dilation of the heart [148].

Chapter -2: Literature Review

Therefore, the removal of Co ions from water is of great concern for conservation of environment as well as human health. In this regard, attempts have been made to find an adsorbent that can efficiently remove the Co metal from aqueous solution.

2.10.2. Biochar used for removal of organic pollutants

Biochar showed excellent ability to remove organic pollutants such as synthetic dyes, pesticides, herbicides, antibiotics etc. from aqueous solutions which have been witnessed from several literatures. These studies demonstrated that the biochar derived from biomass can serve as low-cost adsorbent for removal of organic pollutants from the water environment. An overview related to synthetic dye removal efficiency of biochar from aqueous solution is given below:

Hameed and Khaiary [149] investigated the feasibility of rice straw-derived biochar for removal of malachite green (MG) dye from aqueous solution. The isotherm parameters were estimated by non-linear regression analysis. The equilibrium process was described well by the Langmuir isotherm model. The study indicated that rice straw derived biochar was an attractive adsorbent for removing basic dye from aqueous solutions.

Qiu et al. [150] studied the removal efficacy of straw-based biochar and activated carbon against two dyes, reactive brilliant blue (KNR) and Rhodamine B (RB). The study showed that biochar (BC) was slightly more effective than activated carbon to adsorb RB due to the RB–BC electrostatic interactions and RB protonation at low pH. Due to its high surface area and proper microporous structure, BC was an effective adsorbent for both cationic and anionic dyes.

Mui et al. [151] reported that biochar was prepared from waste bamboo scaffolding for wastewater treatment against two acid dyes and one basic dye. The study revealed that bamboo char did not show very high adsorption capacities for two acid dyes (Acid Blue 25 and Acid Yellow 117) but exhibited significant uptake of Methylene Blue.

Xu et al. [152] explored that biochar produced from various straws such as canola straw, peanut straw, soybean straw, and rice hulls were used as adsorbent to

Chapter -2: Literature Review

test the removal efficiency of methyl violet dye. The study showed that adsorption capacity of biochar varied in the order of “canola straw char > peanut straw char > soybean straw char > rice hull char”. The study revealed that biochars have better dye removal efficiency from waters without any pre-treatment.

Ghani et al. [153] reported the adsorption study of methylene blue (MB) onto sawdust biochar formed by pyrolyzing the sawdust of rubber wood (*Hevea brasiliensis*). The experimental equilibrium data were analyzed using the isotherms of Langmuir, Freundlich, Tempkin. The Langmuir isotherm shows the best fitting of adsorption data with correlation coefficient (R^2) value of 0.999.

Sun et al. [154] stated that three biochars prepared from anaerobic digestion residue (BC-R), palm bark (BC-PB) and eucalyptus (BC-E) were used as sorbents for removal of cationic methylene blue dye (MB). Adsorption isotherm and kinetic studies were carried out to estimate the adsorption efficiency of respective biochars. Pseudo-second-order kinetics and Langmuir isotherm model were most suitable for describing the adsorption of MB onto the biochars.

Dawood et al. [155] established the Eucalyptus bark (EB) materials-based biochar as a suitable adsorbent for removal of Methylene Blue (MB) dye from aqueous solution. The study showed that equilibrium data were best represented by Langmuir isotherm model that gives a monolayer effective adsorption capacity of biochar. Thermodynamic parameters suggested that the adsorption was an endothermic, spontaneous and physical in nature. These results indicated EB biomass as good and cheap precursor for the production of an effective and environmental friendly biochar adsorbent.

Yang et al. [156] reported the removal efficiency of Congo red (CR) and Methylene blue (MB) dyes in an aqueous solution by using vermi compost derived biochar. Biochars, produced at 300, 500, and 700 °C were tested for their adsorption ability of dyes. The study established the fact that, biochar generated at the higher pyrolytic temperature displayed the higher ability to adsorb CR owing to its aromatic nature, and on the other hand cation exchange was the key factor that positively affects the adsorption of MB.

Chapter -2: Literature Review

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