CHAPTER 2

Literature review

Through decades the bio-energy generation from biomass through pyrolysis has been studied by many researchers. The study focuses mainly on the conversion of biomass to value added products and their utilization in different fields. Mostly, the studies have been done in packed bed system varying different parameters to establish optimum experimental conditions for the product yield. Literature review dealing with the pyrolysis of biomass to useful products and utilization of biochar for Cr(VI) removal in batch mode is reported in this chapter. This chapter includes detailed review on selection of biomass for pyrolysis, mechanism of biomass pyrolysis, effect of process parameters on pyrolysis product characteristics and adsorption of Cr(VI) using biochar.

2.1 Literature review on biomass selection

Biomass is defined as the complex bio-residue organic or non-organic solid products obtained from living or dead organisms which are available naturally. Key properties which a biomass should have for pyrolysis have been discussed in section 1.4.4. Based on these properties, the following section discusses some of the biomass used by many researchers for pyrolysis. **Table 2.1** shows the characteristics of some of the biomass which was taken as feedstock for pyrolysis by other researchers. Generally the higher energy content in solid fuels is found with higher carbon content. However, in reverse, high amount of MC and AC would lead to decrease of energy content in biomass.

Wang et al. (2008) performed the pyrolysis of sawdust using thermogravimetric analyzer to study the thermal degradation. Sawdust showed negligible AC, high VM suitable for bio-oil yield and moderate FC. The chemical composition showed 52.28 wt. % carbon and 9.06 wt. % hydrogen which is suitable for pyrolytic gases as it may produce high amount of hydrogen and methane gases. **Wongsiriamnuay and Tippayawong (2010)** investigated the physicochemical characteristics of a giant sensitive plant i.e. Mimosa for its use as feedstock for pyrolysis. Biomass had low MC and AC along with high VM. The FC for mimosa was comparatively higher (23.6 wt. %) as compare to the biomass used by many other researchers. High FC together with high lignin content (33.9 wt. %) suggests its utility in biochar production. The chemical composition of biomass showed carbon, hydrogen, nitrogen and oxygen content as 43.9, 6.0, 1.4 and 48.7 wt. %, respectively. The HHV for mimosa biomass was 17.5 MJ/kg. **Liang et al. (2014)** studied the organic properties of smooth cordgrass to find out its pyrolysis behaviour as well as its thermal decomposition mechanism. Results show that smooth cordgrass is a carbon and oxygen rich raw biomass material containing 6.2 % of hydrogen and trace amounts of nitrogen. The empirical formula of smooth cordgrass is $CH_{1.69}O_{0.84}N_{0.01}$. The HHV (on dry basis) of smooth cordgrass was calculated as 18.5 MJ/kg. The MC for the biomass was comparatively to higher to the biomass studied by many other researchers but the sufficient VM along with low AC makes it suitable for the pyrolysis. Compositional analysis showed smooth cordgrass consisted of cellulose, hemicellulose, and lignin, in addition to extractives, water, and mineral matter. It has high holocellulose (67.1 wt. % of total solids (TS)) and low lignin (9.6 wt. % of TS) contents.

In the year 2014, **Wu et al.** performed conventional and microwave-assisted pyrolysis with wood biomass under different rates to figure out the influence of each process on

the yield and quality of products. Wood biomass had lower MC and AC i.e. 6.4 and 1.2 wt. % respectively. In addition biomass had 74.8 wt. % VM along with 18.3 wt. % FC. The chemical composition of the biomass showed carbon, hydrogen, nitrogen and oxygen as 36.17, 6.30, 1.78 and 55.75 wt. %, respectively. Similarly, in the same year 2014, **Cepeliogullar and Putun**, checked the physicochemical characteristics of four different biomass (Cotton stalk, Hazelnut shells, Sunflower residues, *Euphorbia rigida*) for pyrolysis. The MC of all the biomass were in lower range whereas the AC varied in between 0.7 to 6.7 wt. %. All the biomass had sufficient amount of VM of which it was maximum for *Euphorbia rigida* (75.05 wt. %). **Liu and Han (2015)** performed pyrolysis experiments for the production of biochar with both woody (pine wood) and non-woody (coconut fibre). Both the biomass showed good proportion of VM in them however AC was comparatively higher in case of coconut fibre (8.05 wt. %). Also both the biomass had HHV of 19.23 and 19.83 MJ/kg, respectively. **Li et al. (2015)** investigated the physicochemical properties of rice straw and sawdust for their use in co-pyrolysis with bituminous coal. The biomass used was in the particle range of 0.180 – 0.250 mm. Both rice straw and sawdust had high VM calculated on dry basis. However, the AC for rice straw was 11.01 wt. % which is higher as it may cause agglomeration and sintering problem. The carbon content for rice straw and sawdust were 44.75 and 45.29 wt. % whereas the hydrogen content was 7.32 and 6.04 wt. %, respectively. Both these elements were in good proportion adding advantage for higher HHV. **Sellin et al. (2016)** investigated the characteristics of dried banana leaves before its oxidative pyrolysis in a fluidized bed reactor. The characteristics for banana leaves were similar to other biomasses discussed above however in addition it contained small amount of sulphur (0.95 wt. %). The VM for the biomass was 78.2 wt. % and HHV 17.1 MJ/kg. The results clarify the potential of dried banana leaves for generating fuel

products and chemical inputs from pyrolysis. **Motghare et al., (2015)** analyzed different biomasses (wheat straw, soybean waste etc.) in the region of Maharashtra (India) for their proximate, ultimate analysis and calorific value to assess their potential as fuel. It was observed that AC of these biomass species was quite low, while the VM content was high as compared to Indian coal. The heating value for wheat straw and soybean waste were calculated as 17.62 and 18.77 MJ/kg, respectively. The results suggested that these biomasses appear suitable as renewable and sustainable alternative sources to commonly used fossil fuels. **Singh et al. (2017)** compared the comprehensive characterization of five different lignocellulosic biomasses (*Impereta cylindrica*, *Eragrostis airoides*, *Typha angustifolia L.*, *Arundinella khasiana* Nees ex Steud, and *Echinochloa stagnina* (Retz.) P. Beauv) through proximate, ultimate and compositional analysis for bio energy production. The MC was found to be highest in *Typha angustifolia* (13.95 wt. %) and lowest in *Eragrostis airoides* (8.27 wt. %). AC was seen to be maximum in *Arundinella khasiana* (8.12 wt. %) and minimum in *Eragrostis airoides* (3.66 wt. %). The VM content for all five biomass samples were more than 80 wt. % with maximum in *Eragrostis airoides* (86.84 wt. %). The cellulose content were in comparable range with maximum in *Eragrostis airoides* (43.17 wt. %) and minimum in *Echinochloa stagnina* (24.90 wt. %). The five collected biomass species have great potential to produce biofuel in future which was indicated by the data derived from proximate, ultimate and compositional analysis.

Table 2.1 Literature on biomass selection criteria

Biomass	Physicochemical properties (Wt. %)									HHV (MJ/kg)	References
	MC	VM	AC	FC	C	H	N	S	O		
Wood biomass	6.4	74.8	1.2	17.6	36.17	6.30	1.78	-	55.75	-	Wu et al., (2014)
Cotton stalk	7.46	64.92	5.52	22.10	47.95	5.50	3.24	-	43.31	16.3	Cepeliogullar and Putun, (2014)
Hazelnut shells	10.94	68.98	0.71	19.36	56.37	5.62	5.96	-	32.05	21.4	Cepeliogullar and Putun, (2014)
Sunflower residues	6.05	65.26	9.34	19.35	47.91	5.27	8.65	-	38.17	16.9	Cepeliogullar and Putun, (2014)
Euphorbia rigida	3.02	75.05	6.72	15.21	54.17	5.70	1.3	-	38.3	19.8	Cepeliogullar and Putun, (2014)
Sawdust	-	92.85	0.99	6.16	45.29	6.04	3.46	3.12	41.10	-	Li et al., (2015)
Coconut fiber	-	80.85	8.05	11.10	47.75	5.61	0.90	0.23	45.51	19.23	Liu et al., (2015)
Pine wood	-	85.45	1.40	13.15	48.15	6.70	1.35	0.20	43.60	19.83	Liu et al., (2015)
Rice straw	-	80.89	11.01	8.10	44.75	7.32	3.78	0.61	32.52	-	Li et al., (2015)
Mimosa	1.6	71.1	23.6	3.7	43.9	6.0	1.4	-	48.7	17.5	Wongsiriamnuay,and Tippayawong, (2010)
Sawdust	5.05	81.46	0.76	13.49	52.28	9.06	0.11	0.2	38.35	-	Wang et al., (2008)
Smooth cordgrass	9.5	71.3	13.0	6.2	43.9	6.2	0.5	-	49.4	18.5	Liang et al., (2014)
Banana waste	7.8	78.2	11.4	15.6	43.5	6.2	0.86	0.95	42.3	17.1	Sellin et al. (2016)
Wheat straw	8.6	68.4	7.9	15.1	40.6	6.0	0.19	0.9	53.2	17.62	Motghare et al. (2015)
Soybean waste	5.8	70.5	4.7	19.0	43.8	6.3	1.4	0.8	48.5	18.77	Motghare et al. (2015)

2.2 Literature review on biomass degradation kinetics

The study of degradation kinetics of biomass is essential as it gives the knowledge of its thermal behaviour, reaction mechanism and also assesses biomass as feedstock for fuel or chemical production. Understanding of kinetic parameters and predominant chemical mechanism is necessary for the efficient design and optimization of the thermochemical processes for biofuel production. According to the recommendations provided by the kinetic committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermogravimetric analysis (TGA) has been proved to be a dynamic and effective approach to describe the thermal decomposition behavior and kinetics of biomass degradation (Vyazovkin et al., 2011). TGA measures the rate of weight loss of biomass as a function of temperature or time and the first derivative of mass loss curves obtained from TGA provides the maximum thermal decomposition rate. Two mathematical approaches, model fitting and iso-conversional methods (model free), are implied to evaluate the kinetic parameters (activation energy (E) and pre-exponential factor (A)) from the thermogravimetric data (Mishra and Mohanty, 2018). From model fitting method a single value of activation energy is obtained and it does not describe the changes in reaction mechanisms of the process with increasing conversion. However, iso-conversional models do not show any such drawback and activation energy is calculated with change in conversion. Hence, mostly these model-free methods have been used by many researchers to calculate the kinetic parameters.

Table 2.2 summarizes the degradation kinetics of some of biomasses used by researchers in their research work.

Yuan et al. (2015) compared the thermal degradation and kinetic characteristics of peanut shell with corncob. Major degradation for peanut shell was observed in the temperature range of 224 to 449 ˚C whereas for corncob it was 249 to 439 ˚C. The

maximum mass loss rate (DTG_{max}) for peanut shell and corncob occurred at 310 and 327 ˚C, respectively showing the decomposition of cellulose. However, a little dissimilarity was seen in the degradation profile of corncob. Along with a strong peak, a shoulder peak was observed in between 250 to 300 ˚C indicating the decomposition of hemicelluloses as well. Slight variation was observed in the average activation energy in their degradation. The average activation energy values obtained for pyrolysis of peanut shell and corncob by FWO were 253.9 and 258.98 kJ/mol and from KAS method were 244.29 and 249.25 kJ/mol, respectively. **Huang et al. (2016)** described the thermal decomposition of soybean straw at heating rates of 5, 10, 20, and 30 ˚C/min in three stages i.e. the degradation from 110 to 180 ˚C corresponds to removal of moisture and lighter volatiles whereas major degradation took place because of cellulose and hemicelluloses pyrolysis in the temperature range of 180 to 400 ˚C with DTG_{max} at 330 ˚C. Finally the third stage describes the degradation of lignin from 400 to 900 ˚C. He also explained that the increase in the heating rate contributes to the deceleration of thermal degradation processes towards high temperatures because of thermal lag. The pyrolysis of soyabean straw is a complex process as it involves different reactions and the average activation energy from KAS and FWO models were 154.15 and 156.22 kJ/mol, respectively.

The pyrolysis tests for cardoon stems and leaves were studied by **Damartzis et al.** in the year 2011 by non-isothermal thermogravimetric analyzer. The study revealed the thermal degradation of both the biomass started at around 200 ˚C followed by major mass loss upto 430 ˚C and its essential completion of the process by 500 ˚C with the evolution of secondary gases and formation of char. The increase in the heating rate increased the thermal degradation rate, shifted the onset of the devolatilization and peak temperatures to a higher value. A variance in the activation energy was observed during

computation with KAS and FWO models that implies pyrolysis proceeds through multi-step kinetics. The activation energy for the leaves was higher than the stems, showing the absence of lignin in the leaves in contrast to the stems.

The thermal degradation characteristic of smooth cordgrass was investigated by **Liang et al. (2014)** at heating rates of 5, 10, 20, and 40 ˚C/min. Around 72 – 74 wt. % of total volatiles were released in between 200 to 360 ˚C followed by slow weight loss until 700 ˚C. Heating rate had no major effect on total volatile yield however thermal-decomposition rate changed significantly with shift in DTG_{max} from 307.3 ˚C at 5 ˚C/min to 338.6 ˚C at 40 ˚C/min. Activation energy calculated from three iso-conversional models (Friedman, FWO and KAS) showed an increasing trend with conversion suggesting multi step kinetics for smooth cordgrass degradation.

Apple pomace biomass (residue produce after extraction of apple juice) was used by **Baray Guerrero et al. (2015)** for pyrolysis with the aim to utilize liquid and gaseous products for the production of valuable chemicals and hydrogen. Prior to pyrolysis, thermogravimetric study at heating rates 5, 10, 15 and 20 ˚C/min revealed major degradation occurred in between 220 to 600 ˚C with three peaks in DTG curve giving the evidence of hemicelluloses, cellulose and lignin degradation. The study described the dependence of activation energy on conversion as several reactions occurred in parallel. The average activation energies estimated from Friedman, FWO and KAS methods were 197.7, 213.0 and 201.7 kJ/mol, respectively.

Prosopis juliflora fuelwood was another useful biomass for bio-energy generation as studied by **Chandrasekaran et al. (2017).** Thermogravimetric study at six heating rates (2, 5, 10, 15, 20 and 25 ˚C/min) in argon atmosphere described maximum devolatilization in between 230 to 400 ˚C and the complete process was segregated into three stages, drying, devolatilization and char formation. The effect of heating rate on

TG and DTG curve was similar as described by other researchers. However, the activation energy for the biomass was little higher as compared to other biomasses. The average activation energy was 204, 203.2 and 219.3 kJ/mol using KAS, FWO and Friedman methods, respectively.

Mishra and Mohanty (2018) compared the thermal degradation characteristics of three biomass wastes Pine sawdust, Sal sawdust and areca nut husk. The study was performed in non-isothermal condition at 5 different heating rates in between (5 – 25 ˚C/min). Though the degradation profile was similar for all three biomasses and major degradation zone was 200 – 500 ˚C, However the release of volatiles was maximum for Pinus ponderosa. DTG thermograph of three waste biomass samples showed difference in their peak positions and height. It indicates the presence of organic and inorganic components and their distribution affected broadly due to the influence of thermal decomposition. Heating rate had almost similar effect as studied by other researchers however they assumed at lower heating rate, the temperature profile along the cross-section was linear whereas temperature profile has substantial difference from the inner core to the outer core along the cross-section of biomass at the higher heating rate. Kinetic study for the process revealed the dependence of activation energy on conversion and also the average activation energy calculated using iso-conversional models were in moderate range similar to other biomasses discussed above. The study concluded the potential of all three biomass for energy generation.

Thermal degradation of pine needle has been described by **Varma and Mondal (2015)** in four different zones with maximum degradation of 53 wt. % in the temperature range of 200 – 340 ˚C followed by 38 wt. % in the temperature range of 340 – 500 ˚C. Major degradation in this zone is mainly due to breaking of hemicelluloses and cellulose bonds. The temperature range for the kinetic study was 220–520 ˚C as beyond 520 ˚C.

Table 2.2 Literature review on biomass degradation kinetics

Biomass	Heating rate (˚C/min)	Major degradation-on range (˚C)	Model	Activation energy (kJ/mol)	Reference
Peanut shell	5, 10, 20	224 - 449	FWO	253.90	Yuan et al., 2015
			KAS	244.29	
Corncob	5, 10, 20	249 - 439	FWO	258.98	Yuan et al., 2015
			KAS	249.25	
Pine needle	5, 10, 20	200 - 520	FWO	79.13	Varma and Mondal, 2015
			KAS	70.97	
Soybean straw	5, 10, 20, 30	180 - 400	FWO	156.22	Huang et al., 2016
			KAS	154.15	
Cardoon leaves	5, 10, 20, 30	200 - 430	FWO	342.08	Damartzis et al., 2011
			KAS	350.17	
Cardoon stems	5, 10, 20, 30	200 - 430	FWO	241.50	Damartzis et al., 2011
			KAS	229.50	
Smooth cordgrass	5, 10, 20, 40	200 – 360	FWO	183.6	Liang et al., 2014
			KAS	183.4	
			Friedman	200.9	
Apple pomace	5, 10, 15, 20	220 - 600	FWO	213.0	Baray Guerrero et al. 2015
			KAS	201.7	
			Friedman	197.7	
Prosopis juliflora fuelwood	2, 5, 10, 15, 20, 25	230 - 400	FWO	203.2	Chandrasekaran et al. 2017
			KAS	204	
			Friedman	219.3	
Pine sawdust	5, 10, 15, 20, 25	200 - 500	FWO	179.29	Mishra and Mohanty, 2018
			KAS	171.66	
			Friedman	168.58	
Sal sawdust	5, 10, 15, 20, 25	200 - 500	FWO	156.58	Mishra and Mohanty, 2018
			KAS	148.44	
			Friedman	181.53	
Areca nut husk	5, 10, 15, 20, 25	200 - 500	FWO	179.47	Mishra and Mohanty, 2018
			KAS	171.24	
			Friedman	184.61	

degradation was very less. Average activation energy calculated from FWO and KAS models were 79.13 and 70.97 kJ/mol, which is much lower as compare to other biomasses. Reaction order for the process was calculated using Coast Redfern method and it was observed that for n = 9 the computed conversion was in good agreement with experimental conversion obtained from TG analysis. The study described pine needle has excellent potential for energy production through pyrolysis process.

2.3 Literature review on effect of process parameters on pyrolysis

Pyrolysis has been the most promising technique to produce bio-energy from decades. The chemical constituents of the biomass get converted to bio-energy when thermal energy is applied in inert atmosphere. The products from the pyrolysis are solid biochar, liquid bio-oil and pyrolytic gases. However the yield and characteristics of these products are entirely dependent on the process parameters. Some of these process parameters are temperature, heating rate, packed bed height, biomass particle size, sweeping gas flow rate etc. The process parameters play a very significant role in the pyrolysis of biomass as they not only control the pyrolysis product yield but also affect the product characteristics.

Temperature has the most significant role to play in pyrolysis process as it severely affects the product yield and their characteristics. Temperature provides necessary heat required to degrade the respective bonds in the biomass. Increase in the temperature increases the cracking reaction thereby increasing the conversion of biomass. The increase in the temperature has a positive effect on the bio-oil yield. It has been reported that the optimum temperature for maximum bio-oil yield generally lies in the temperature range of 450 – 550 ˚C (Guedes et al., 2018). However, it varies depending upon the biomass type and other process parameters as well. But at much higher temperature (above optimum bio-oil yield temperature), the reverse effect is observed

i.e. at higher temperature secondary reactions occurs leading to cracking of larger molecular weight hydrocarbon to smaller hydrocarbons which produces more gases and less bio-oil (Isahak et al., 2012). The biochar yield decreases continuously with increase in temperature because of the generation of more and more volatiles. **Heating rate** also plays a crucial role in biomass degradation process as it defines the type of pyrolysis i.e. slow, fast, intermediate or flash pyrolysis. High heating rate favours the quick degradation of biomass which produces more volatiles and less biochar. This leads to more production of bio-oil because of reduction in heat and mass transfer limitations along with inhibition of secondary reactions that causes repolymerization reactions (Akhtar and Amin, 2012). However, certain secondary reactions occur that produces more and more volatiles which on condensation enhances the bio-oil yield. In addition, the slower heating rate prevents the thermal cracking of biomass and thus produces more biochar.

Since biomass particles are poor conductor of heat thus it affects the heat transfer during pyrolysis and also affects the product distribution. **Particle size** of the biomass is one of the significant parameter that determines the rate with which heat is being provided to the biomass inner core. It has been investigated by various researchers that with increase in the biomass particle size the bio-oil yield decreases and biochar yield increases. Upon increment in the particle size, the space between the core and outer surface increases which increases the resistance for heat flow to the inner core. Also, the vapour produced has to travel longer distance which leads to additional secondary reactions that result into the increase in the biochar yield and reduction in bio-oil yield (Tripathi et al., 2016). During pyrolysis biomass is converted to significant amount of vapour that has to be condensed to get the bio-oil. **Vapour and gas residence time** refers to the time for staying vapour and gas in the reaction zone. Long residence time

in the reaction chamber increases the further secondary reactions like thermal cracking, repolymerization and recondensation of vapours that enhances the biochar yield and decreases the bio-oil yield. However, in case of short residence time there are incomplete secondary reactions and thus less biochar is produced (Guedes et al., 2018). Thus to reduce these secondary reactions for better bio-oil yield, these vapours has to be removed from the reaction chamber to the condensation zone. The most commonly used purging gas for pyrolysis is nitrogen as it is inert, easily available and also very cheap. The flow rate of the purging gas decides the vapour and gas residence time.

Pyrolysis can be performed in both either in fixed bed or moving bed reactors. Moving bed reactors are those where biomass particles are in moving mode i.e. not stationary like sprouted bed, rotary bed, fluidized bed, etc. whereas fixed bed reactors are those where there is no movement of particles. The heat transfer in case of moving bed pyrolysis process occurs by both solid-solid (conduction) and gas-solid (convection) interaction. However, in case of fixed bed reactors the mode of heat transfer is mainly conduction. The **composition of biomass** is another parameter that influences the pyrolysis process. The chemical composition of biomass includes hemicelluloses, cellulose, lignin and other extractives. The composition of biomass varies from one biomass to other; even the biomass of same origin may have dissimilar composition because of different soil or planting conditions (Omar et al., 2011). Thus, the product yield and their composition vary severely. High amount of cellulose and hemicelluloses in the biomass favours more of the bio-oil generation but high lignin content refers to more biochar yield after pyrolysis because lignin is quite stable and very difficult to degrade. The following section discusses the pyrolysis of some of the biomass performed at different parameters and also about the product yield and its characteristics by different researchers.

Aysu and Durak (2016) performed the pyrolysis of *Verbascum thapsus L.* in a fixed bed reactor of inner diameter 70 mm and length 200 mm. The study investigated the effect of temperature (400 – 550 ˚C) on pyrolysis product yield keeping heating rate N_2 flow rate fixed at 50 ˚C/min and 100 mL/min, respectively. A maximum 39.84 wt. % bio-oil yield was collected at 500 ˚C whereas biochar and pyrolytic gas yield were 25.86 and 34.30 wt. % respectively at the same temperature. The bio-oil obtained was a mixture of different organic compounds most of which were phenols and its derivatives. The bio-oil could be used as fuel in boilers or engines and biochar had higher HHV that can be used as solid fuel.

The pyrolysis of *Madhuca indica* for the production of biofuel and its characterization was performed by **Pradhan et al., (2016)**. The study reported the effect of temperature on pyrolysis yield at 30 mL/min nitrogen flow rate and at 20 ˚C/min constant heating rate in a semi batch reactor. Maximum 49 wt. % bio-oil yield was generated along with 18 wt. % biochar at the temperature of 525 ˚C. The HHV and pH for bio-oil was 39.02 MJ/kg and 4.8, respectively and this acidic nature of the bio-oil were due to the presence of organic acids as affirmed by GC-MS and NMR analysis. Along with acids, other components like alcohols, ketones, aldehydes, esters, amines, ethers, and nitriles were also present. The presence of these components makes bio-oil suitable source of chemical or as alternative fuel. The bio-char collected simultaneously at the same condition was also found suitable as solid fuel. The valuable fuel characteristics of bio-char includes, higher HHV of 26.035 MJ/kg and the molar ratio H/C and O/C of *Madhuca indica* bio-char lies within the range of coal.

Varma and Mondal (2018) studied the effect of temperature (350 – 650 ˚C), heating rate (10 and 50 ˚C/min), N_2 flow rate (50 – 200 mL/min) and particle size (0.25 – 1.7 mm) on pyrolysis of pine needle in a semi-batch reactor. Maximum bio-oil yield of

43.76 wt. % was attained at temperature of 550 ˚C at the heating rate of 50 ˚C/min, nitrogen flow rate of 100 mL/min for biomass particle size of $0.6 < d_p < 1$ mm. The physiochemical properties of the bio-oil revealed its density to be 1062 kg/m^3 at 15 ˚C whereas viscosity was 12.54 cSt at 40 ˚C which is quite higher in comparison to the conventional fuels. The low pH of bio-oil due to presence of organic acids, phenols and aldehydes showed its instability and corrosive nature. However, the HHV for bio-oil was 26.25 MJ/kg. The chemical composition of bio-oil as analyzed by FTIR and GC-MS marked the presence of different various hydrocarbons like organic acids, alcohols, aromatics etc that can be used as fuel in different industries after upgradation or as a feedstock for chemicals production. The biochar produced had high carbon content and HHV of 25.50 MJ/kg. It had porous surface that contained various nutrients which makes its utility as adsorbent or in soil amendment. The pyrolytic gases contained carbon monoxide and hydrogen that could be used as fuel or can be synthesized into liquid fuels.

In the study by **Mishra et al., (2020)** for samanea saman seed pyrolysis, the maximum bio-oil yield of 44.20 wt. % was collected at temperature 500 ˚C, heating rate 80 ˚C/min, particle size 0.5 mm and N_2 flow rate of 100 mL/min. the increased bio-oil yield at smallest particle size is due to the higher heat and mass transfer which showed complete conversion of biomass. The produced bio-oil had comparable properties as diesel fuel. Bio-oil had lower MC, high carbon content which increased the heating to 25.73 MJ/kg. But the higher viscosity and acidic nature discard its direct use as fuel. FTIR and GC-MS analysis showed the presence of hydrocarbons, acid, ether, ester, ketone, phenol, amide, nitrogenous compounds etc. These results concluded the utilization of bio-oil as domestic fuel or as a source for extraction of chemicals. Biochar properties were compared with coal and palm shell hydrochar. The biochar had

favourable physic-chemical properties to be used as solid fuel or as soil enhancer. The biochar had low BET surface area 8.20 m^2/g but had the possibility to be used as adsorbent. The increase in pyrolysis temperature increased the hydrocarbon content along with H$_2$ in the pyrolytic gas but decreased CO and CO$_2$ content because at higher temperature, the secondary cracking reaction occurs that produces more hydrocarbons and hydrogen gases.

Comparative study for the pyrolysis product yield for phumdi and para grass biomass was conducted by **Awasthi et al., (2019)**. The maximum bio-oil yield for phumdi and para grass biomass was 36.90 and 46.70 wt. %, respectively at temperature 450 ˚C. The chemical characteristics of both the bio-oil were studied via FTIR, GC-MS and NMR. The bio-oil contained around 14.53 wt. % furans where as furan was observed in the bio-oil from para grass. On the other hand, Para grass bio-oil had 25.31 wt. % aromatics whereas phumdi biomass had only 3.45 wt. %. Along with this other compounds such as ethers, esters, ketones, organic acids etc were also present in the bio-oil from both the biomass. These compounds are of industrial importance and can be used for the production of chemicals after their separation. Biochar from both the biomass had higher amount of organic carbon compared to raw biomass.

The effect of temperature (350 – 650 ˚C), heating rate (10 and 50 ˚C/min), N$_2$ flow rate (50 – 200 mL/min) and particle size (0.25 – 1.77 mm) on wood sawdust pyrolysis was investigated by **Varma et al. (2019).** The study revealed maximum bio-oil yield of 44.16 wt. % with high carbon and hydrogen content and no sulphur content. The water content, density and kinematic viscosity of the bio-oil was 22 wt. %, 1062 kg/m^3 and 16.53 cSt, respectively which is much higher as compare to commercial diesel and petrol. The presence of heavy residue content makes the bio-oil denser. The low HHV of the bio-oil was 27.82 MJ/kg which is quite low as compared to conventional fuels.

The chemical characteristics of the bio-oil revealed the presence of different chemical compounds like phenols, furfural, furan, cresol etc, organic acids, aliphatic and aromatics. The pyrolytic gas had the much amount of CO and H_2 that can be a good source for combustion or for the production of liquid hydrocarbons. The biochar collected was alkaline in nature and had the HHV of 22.03 MJ/kg. FESEM marked the pores and cracks on the biochar surface and EDX analysis confirmed the presence of valuable nutrients like N, Ca, Si, Al, Mg, etc. BET surface area for the biochar was 3.10 m^2/g which is low owing to the shrinkage of biochar at post-softening and swelling temperatures, resulting in reduction or closing the pores.

Oginni and Singh (2019) studied the pyrolysis characteristics of *Arundo donax* in a fixed-bed batch reactor of diameter of 22.86 cm and height 25.40 cm. The yield of biochar, bio-oil and pyrolytic gas were 30.12%, 45.62% and 24.26% respectively at temperature 500 ˚C, heating rate of 7 ˚C/min and N_2 purging rate of 2 l/min. the biochar collected was of alkaline nature having high carbon content and negligible BET surface area. The surface of the biochar collected was porous having HHV and electrical conductivity of 29.51 MJ/kg and 23.87 μs/cm. this low electrical conductivity suggested its application for soil amendment. The pyrolytic gas was the mixture of mainly CO, CO_2, CH_4, H_2 and N_2. The bio-oil collected was of highly acidic nature because of the presence of more organic acids. The density for the bio-oil was 1037.20 kg/m^3 and the viscosity of the bio-oil was analyzed in the temperature range of 20 to 80 ˚C. The result showed with increase in temperature the bio-oil has a greater tendency to flow easily. The flow activation energy for the bio-oil was estimated to be 11.45 kJ/mol.

Table 2.3 Literature review on effect of process parameters on pyrolysis

Biomass	Process parameters	Product yield (wt. %)	Reference
Verbascum thapsus L.	Temperature : 500 ˚C Heating rate : 50 ˚C/min N_2 flow rate : 100 mL/min	Bio-oil : 39.84 Biochar : 25.86 Pyrolytic gas : 34.30	Aysu and Durak, 2016.
Madhuca indica	Temperature : 525 ˚C Heating rate : 20 ˚C/min N_2 flow rate : 30 mL/min	Bio-oil : 49.00 Biochar : 18.00	Pradhan et al., 2016
Pine needle	Temperature : 500 ˚C Heating rate : 50 ˚C/min N_2 flow rate : 100 mL/min Particle size : $0.6 < d_p < 1$ (mm)	Bio-oil : 43.76 Biochar : 29.15 Pyrolytic gas : 27.09	Varma and Mondal, 2018
Samanea saman seed	Temperature : 550 ˚C Heating rate : 80 ˚C/min N_2 flow rate : 100 mL/min Holding time : 60 min.	Bio-oil : 44.20	Mishra et al., 2020
Phumdi biomass	Temperature : 450 ˚C N_2 flow rate : 40 mL/min Particle size : $250 < d_p < 500$ (μm)	Bio-oil : 36.90 Biochar : 38.90 Pyrolytic gas : 24.30	Awasthi et al., 2019.
Para grass	Temperature : 450 ˚C N_2 flow rate : 40 mL/min Particle size : $250 < d_p < 500$ (μm)	Bio-oil : 46.70 Biochar : 33.30 Pyrolytic gas : 20.00	Awasthi et al., 2019
Wood sawdust	Temperature : 500 ˚C Heating rate : 50 ˚C/min N_2 flow rate : 100 mL/min Particle size : $0.6 < d_p < 1$ (mm)	Bio-oil : 44.16	Varma et al., 2019
Arundo donax	Temperature : 500 ˚C Heating rate : 7 ˚C/min N_2 flow rate : 2 l/min	Bio-oil : 45.62 Biochar : 30.12 Pyrolytic gas : 24.26	Ogini and Singh, 2019

2.4 Literature on optimization of process parameters for pyrolysis using RSM

Although individual parameters significantly affects the yield of products from pyrolysis, but the combined effect of their interaction has also severe effect on the statistical optimization of the process. For sustainable engineering process design, a convenient optimization model is commonly applied as it offers a reasonable and less time-consuming method to analyze the effect of a design variable change on the production of products. Optimization of the process is necessary to get the maximum of desired product and minimum undesired product. Response surface methodology (RSM) is a statistical tool to examine the interaction between the various independent process variables by performing the least number of experimental runs. The objective of RSM is to develop an experimental design for the analysis of responses and bring out the optimized condition. The different methods of RSM include Doehlert matrix, central composite designs (CCD) and Box-Behnken design (BBD) (Kapur et al., 2016). BBD to some extent is more efficient than any other methods (Ferreira et al., 2007) since very few combinations of variables used for the determination of the response function (Muthukumar et al., 2003). The suitability of the model is confirmed by the desirability value, and a value closer to 1 suggests the best optimized condition. The following section describes the optimization of different process parameters to get the desired product yield by different researchers.

Mohammed et al. (2017) studied the maximized the bio-oil yield and minimized biochar and pyrolytic gas yield from Napier grass pyrolysis in a vertical fixed bed reactor using CCD. The optimum bio-oil yield was 50.57 wt. % at the optimum temperature 600 ˚C, heating rate 50 ˚C/min and N_2 flow rate of 5 l/min. The quadratic model was significant and the co-efficient of variation (R^2) for the bio-oil yield was

0.9936 whereas in case of biochar and pyrolytic gas yield the R^2 was 0.9927 and 0.9843, respectively.

The investigation for maximum H_2 generation and biochar yield from oil palm fibre has been reported **Hossain et al. (2017).** The pyrolysis process was optimized via CCD and the maximum H_2 and biochar yield were 6.42 g/kg and 37.45 wt. %, respectively at temperature 450 ˚C, N_2 flow rate of 950 mL/min and microwave power of 400 W. The actual vs. predicted results implied good agreement between experimental and predicted values for both H_2 and biochar yield. The model was found to be significant and the R^2 values for H_2 and biochar were 0.9786 and 0.9832, respectively.

The optimum pyrolysis condition for maximum bio-oil yield from brown Sal wood has been investigated by **Charusiri and Numcharoenpinij (2017)** through the use of BBD. The optimum condition for the process was temperature 540 ˚C, N_2 flow rate of 155 mL/min and biomass feed rate of 0.45 kg/h. the analysis of variance (ANOVA) for the bio-oil yield provided R^2, the coefficient value (CV) and the Predicted R^2 as 0.9871, 7.86 and 0.9686, respectively which suggests high precision and reliability of the experiment. The lack of fit for the process was insignificant and thus the regression model presents an excellent explanation of the correlation between the independent variables and the responses.

Dhanvanth et al. (2017) performed the optimization study to maximize the bio-oil production Mahua press seed cake via slow pyrolysis in a fixed bed batch reactor. Using BBD, 15 experiments were performed and the experimental results were in good agreement with predicted results. The optimum operating conditions provided bio–oil yield as high as 49.25 wt. %. The high F–value of 37.53 and low P–value of the predicted model for bio–oil yield established that the RSM model derived is significant.

The R^2 attained for the responses of the bio–oil and bio– char were 0.985 and 0.989 that justifies an excellent correlation between the independent variables.

The maximum bio-oil yield of 38.10 wt. % was achieved by **Saikia et al. (2018)** for perennial grass pyrolysis. The process was optimized via RSM through CCD and optimum temperature, heating rate and N_2 flow rate were 550 ˚C, 20 ˚C/min and 226 mL/min, respectively. The F and p value for the model was 45.91 and <0.0001 which describes its significance. Along with it, most of the interaction terms were also significant and the R^2 for the model was 0.9764.

Similarly the optimum condition for food waste bio-oil as obtained by **Kadlimatti et al. (2019)** was temperature 400 ˚C, N_2 flow rate 50 mL/min and residence time 30 min. The regression model with 95 % confidence level resulted in the high value of $R^2 =$ 95.4% with adjusted R^2 of 91.2 % indicated a very good or excellent ft of the data to the model. The high F value for the model suggested its significance.

Kumar et al. (2019) performed optimization study for Saccharum munja pyrolysis with only two variables i.e. temperature and retention time through CCD. The optimum temperature and retention time for the process were 525 ˚C and 60 min which yielded 46.00 wt. % bio-oil. The experimental and predicted yields were close to each other and also the ANOVA analysis confirmed significance of the model through very high F value and very low p value.

Table 2.4 Literature on optimization of process parameters for pyrolysis

Biomass	RSM model	Optimized condition	Response (optimized yield) (wt. %)	References
Napier grass	CCD	Temperature: 600 ˚C N_2 flow rate: 6 l/min Heating rate: 50 ˚C/min	Max. bio-oil: 51.94 Min. biochar- 20.06	Mohammed et al., 2017
Oil palm fiber	CCD	Temperature: 450 ˚C N_2 flow rate: 950 mL/min Microwave power: 400 W	Max. H_2: 6.42 g/kg Max. biochar: 37.45	Hossain et al., 2017
Brown salwood	BBD	Temperature: 540 ˚C Biomass feed rate: 0.45 kg/h N_2 flow rate: 155 mL/min	Max. bio-oil: 44.78	Charusiri and Numcharoenp inij, 2017
Mahua press seed cake	BBD	Temperature: 475 ˚C Retention time: 45 min N_2 flow rate: 0.3 l/min	Max. bio-oil: 49.25	Dhanavath et al., 2017
Perennial Grass	CCD	Temperature: 550 ˚C N_2 flow rate: 226 mL/min Heating rate: 20 ˚C/min	Max. bio-oil: 38.10	Saikia et al., 2018
Food waste	CCD	Temperature: 400 ˚C N_2 flow rate: 50 mL/min Residence time: 30 min	Max. bio-oil: 30.24	Kadlimatti et al., 2019
Saccharum munja	CCD	Temperature: 550 ˚C Retention time: 60 min	Max. bio-oil: 46.00	Kumar et al., 2019

*(RSM – Response surface methodology, CCD – Central composite design, BBD – Box-Behnken design, Max.- Maximum, Min. - Minimum)

2.5 Literature review on adsorption of Cr (VI) using biochar

The adsorptive removal of heavy metal ions from aqueous solutions, ground water and industrial effluent has been studied by many researchers through decades. The experimental investigation can be focused on either treating a single metal present in the solution or more than one metallic ion, as mostly the waste streams have one or more of such ions. The mode of contact for the adsorbent-adsorbate can be either in batch or fixed-bed arrangement. Batch operation is mainly done to establish the optimum experimental conditions for the adsorption. However, when there is a large volume of solution or industrial effluent to be treated, fixed-bed column is generally preferred. A literature dealing with the adsorption of Cr(VI) using biochar through batch mode of operation is reported in this chapter. This chapter includes detailed review on adsorbent characteristics and effect process parameters involved in the adsorption process by different researchers.

Adsorption is a surface phenomenon and adsorbent is defined as the material having active sites present on its surface that binds the heavy metal ions present in the solution and thus makes the system clean and free from ions. An effective adsorbent should have high surface to volume ratio and high adsorption capacity. The other characteristics like pore size distribution, pore volume, presence of various functional groups etc affect the adsorption capacity severely. Along with the characteristics of the adsorbent, process variables like pH of the solution, initial metal ion concentration, adsorbent dose, time and temperature also play a significant role in deciding the optimum condition for the maximum removal of Cr(VI). The following section describes the Cr(VI) removal study by various researchers.

Mohan et al., (2011) performed the comparative study for the Cr(VI) removal in batch mode using Oak wood and Oak bark biochar prepared via pyrolysis at 400 – 450 ˚C.

The BET surface area for oak wood and oak bark biochar were very less i.e. 2.73 and 1.88 m^2/g, respectively but the Cr(VI) removal efficiency was comparable to the activated carbon having BET surface area ~ 1000 m^2/g. Maximum Cr(VI) removal was achieved at pH 2, adsorbent dose 10 g/L and equilibrium time of 48 h. the adsorption capacities for oak wood and oak bark biochars were 3.03 and 4.61 mg/g at 25 ˚C. The process followed second order kinetics and sips isotherm fitted well to the experimental results with high R^2 value. Cr(VI) removal efficiency was maximum for oak bark biochar than oak wood biochar. In the adsorptive study of Cr (VI) by **Deveci and Kar, (2013)**, biochar was produced from the oily seeds of P. *terebinthus* L. via pyrolysis. The elemental analysis illustrated high amount of carbon, SEM images showed cracks and mesopores over the biochar surface and FTIR study revealed biochar has several functional groups that are capable of adsorbing Cr(VI). The adsorption studies were performed in the varying initial pH (1.5-7), contact time (5-900 min), adsorbent dose (0.2 – 5 g/L) and initial Cr (VI) ion concentration (5 – 75 mg/L). The study reported maximum adsorption capacity of 3.53 mg/g. The experimental data showed better alignment to pseudo second order kinetics and Langmuir isotherm.

In a similar approach of treating Cr (VI) rich aqueous solution **Tytłak et al., (2015)** prepared biochar from wheat straw and wicker by thermal decomposition. The FTIR characteristics of biochar revealed presence of several functional groups and SEM-EDX study confirmed porous structure with Cr ions present in the form of irregular island. The BET surface area for wheat straw biochar (26.3 m^2/g) was higher than wicker biochar (11.4 m^2/g). the maximum adsorption capacities for wheat straw biochar and wicker biochar were 24.6 and 23.6 mg/g respectively at pH 2. The Langmuir model had better fitting of adsorption isotherms and the process is well described by the pseudo second-order equation. The X-ray photoelectron spectroscopy (XPS) study described

the reduction of Cr (VI) to Cr (III) and Cr (III) ions were the most abundant chromium species on the biochar's surface after adsorption.

For adsorbing Cr (VI) ions from the aqueous solution, magnetic biochar was used by **Yang et al., (2017).** The magnetic biochar was prepared by mixing pinewood sawdust with iron salt by co-precipitation method and then it was pyrolyzed at 700 ˚C. The effects of adsorbent dose (0.4 – 2.8 g/L), solution pH (1-10), contact time (0 – 1440 min), initial Cr (VI) concentration (30 – 120 mg/L) and temperature (20 – 40 ˚C) were investigated in batch mode. The maximum adsorption capacity for the adsorbent was 42.7 mg/g. After adsorption, biochar surface became coarse as marked by SEM and EDX analysis confirmed the efficient adsorption of Cr on biochar surface. The reduction of Cr (VI) to Cr (III) was affirmed by XPS analysis. Pseudo second order kinetic model and Langmuir isotherm had the best fit to the experimental data with R^2 of 0.9996. In the adsorptive study of Cr (VI) by **Wang et al., (2016)**, biochar was prepared from pineapple-peel via pyrolysis at 750 ˚C. The pineapple-peel derived biochar had BET surface area of 323.80 m^2/g, SEM images showed cracks and porous structures over the biochar surface and the presence of different functional groups over the biochar surface was identified by FTIR. The adsorption study showed maximum Cr (VI) removal at pH 2, contact time 12 h, adsorbent dose 10 g/L and temperature 30 ˚C. The study reported maximum adsorption capacity of 7.44 mg/g. The experimental data showed better alignment to pseudo second order kinetics with R^2 of 0.999 and Langmuir isotherm R^2 of 0.988.

For the uptake of Cr (VI) from aqueous solutions, **Choudhary and Pal (2018)** prepared biochar from *Eucalyptus globulus* bark at 500 ˚C via pyrolysis. Surface characteristics of biochar revealed high BET surface area of 265 m^2/g and pore volume of 0.165 cm^3/g. the maximum efficiency of the adsorbent was observed at pH 2 and the equilibrium

time of 6 h. The isotherm study suggested both Langmuir and Temkin isotherms fit well to the experimental results and the maximum adsorption capacity based on Langmuir isotherm was 21.3 mg/g at 30 ˚C. The study reported intraparticle diffusion was not the rate limiting step rather the process is governed by film diffusion. The negative ΔG value confirmed the spontaneous nature of Cr (VI) adsorption, whereas positive ΔH and ΔS values indicated endothermic and physical nature of sorption and increasing randomness. The FTIR and XPS results designated dominance of carboxylic and phenolic surface functional groups in Cr (VI) sorption and reduction, respectively. For the uptake of Cr (VI) from aqueous solutions, **Chen et al., (2018)** prepared magnetic biochar from *Enteromorpha prolifera* at 600 ˚C. The SEM images affirmed highly porous structure along with crystal of magnetic material and FTIR analysis marked several functional groups over its surface. Modified biochar had the maximum adsorption capacity of 88.17 mg/g from Langmuir isotherm and a removal efficiency of 97.71 % for 100 mg/L of Cr (VI) was achieved with adsorbent dose of only 2 g/L. For the kinetic study, Elovich model fitted well to the experimental data as compared to first or second order kinetics. The study concluded electrostatic interaction might be the dominant mechanism for Cr (VI) adsorption by the magnetic biochar.

Shakya et al., 2019 discussed the Cr (VI) removal from aqueous solution using biochar derived from sweet lime peel at 450 ˚C. The study reported maximum adsorption capacity for the adsorbent to be 90.91 m^2/g at pH 2 and temperature 30 ˚C. Pseudo second order kinetics and Langmuir adsorption isotherm best explained the experimental data, suggesting monolayer adsorption as the prevailing mechanism. Chemical interaction, ion exchange and physical adsorption also contributed into Cr (VI) adsorption process. The regeneration and reusability of the adsorption was three times i.e. it had good removal efficiency for the three successive cycles.

Table 2.5 Literature review on adsorption of Cr (VI) using biochar

Adsorbent	pH	Temperature (˚C)	Equilibrium time (h)	Adsorbent dose (g/L)	Maximum adsorption capacity (mg/g)	Reference
Oak wood char	2	25	48	10	3.03	Mohan et al., 2011
Oak bark char	2	25	48	10	4.61	Mohan et al., 2011
P. *terebinthus* L. biochar	1.5	25	2	2	3.53	Deveci and Kar, 2013
Wheat straw biochar	2	25	21.5	4	24.6	Tytłak et al., 2015
Wheat wicker biochar	2	25	18	4	23.6	Tytłak et al., 2015
Pinewood sawdust magnetic biochar	2	30	3	1.6	42.7	Yang et al., 2017
Pineapple-peel- biochar	2	30	12	10	7.44	Wang et al., 2016
Eucalyptus bark biochar	2	30	6	2	21.3	Choudhary and Pal, 2018
Enteromorpha prolifera magnetic biochar	2	25	10	2	88.17	Chen et al., 2018
Sweet lime peel biochar	2	30	8	3	90.91	Shakya et al., 2019

According to the recent literatures reviewed, the first objective of the study i.e. kinetic and thermodynamic study of sagwan sawdust pyrolysis was executed as discussed in the next chapter.