

CHAPTER 2

Literature review and objectives

This chapter is dedicated to the literature review of biomass pyrolysis. A thorough literature review is pre-requisite for carrying out any study. Various aspects related to the biomass pyrolysis such as physicochemical properties, its thermal degradation kinetics, influence of variation in operating parameters on biomass pyrolysis and catalytic pyrolysis were studied. So, this chapter has been divided into four sections: (1) literature review on physicochemical properties of different biomass, (2) review of thermal degradation kinetics of biomass in the available literature, (3) detailed review of effect of process parameter variation on the product yield distribution of pyrolysis, and (4) literature related to catalytic pyrolysis was reviewed in this part. In this way this chapter paved the way for deciding the objective and direction for this study.

2.1 Literature review

2.1.1 Literature review on physicochemical properties of biomass

Lignocellulosic biomass is the most abundant, renewable, sustainable, and carbon neutral feedstock for the production of bio-energy, bio-fuels and high value bio-products. A profound knowledge about physicochemical characteristics of biomass is important for selection of biomass conversion process. This section is intended to present a review of physicochemical properties including proximate, ultimate and HHV analysis of various biomass reported in the literature. Physicochemical properties of different biomass are presented in Table 2.1.

Mishra and Mohanty (2018) studied sal sawdust for its physicochemical properties and reported that it possessed high VM (76.03 wt. %), low MC (8.88 wt. %) and AC (1.14 wt. %) along with high carbon, hydrogen, nitrogen and oxygen content as 49.83, 6.01, 0.58 and 43.56 wt. %. All these properties and HHV (18.2 MJ/kg) make sal sawdust a potential candidate for pyrolysis. Properties of pine sawdust were evaluated by Laougé and Merdun (2021) and reported that MC, VM, AC and FC were 5.9, 77.8, 0.79, 15.55 wt. %, respectively whereas carbon, hydrogen, nitrogen and oxygen was found to be 46.82, 6.04, 0.14 and 46.98 wt. %, respectively and HHV was 18.59 MJ/kg. In the same year, Rathore et al. (2021) carried out pyrolysis of wheat straw and announced its elemental composition to be 42.4 wt. % carbon, 6.01 wt. % hydrogen, 0.5 wt.% nitrogen, 41.1 wt.% oxygen along with 16.1 MJ/kg of HHV and 4.41, 81, 6.77 and 8.13 wt. % of MC, VM, AC and FC, respectively.

Gupta et al. (2019) evaluated physicochemical characteristics of teak sawdust prior to carrying out its pyrolysis and announced that teak sawdust consisted of 3.87, 78.17, 3.45, 14.43 wt. % MC, VM, AC, FC, respectively and its elemental composition was 5.93, 43.87, 1.03 and 49.17 wt. % hydrogen, oxygen, nitrogen and carbon, respectively. 17.73 MJ/kg of HHV was exhibited by teak sawdust. Proximate, ultimate and HHV findings of teak sawdust revealed its suitability towards energy production. Similarly, Ahmad et al. (2021) investigated Maple Leaf Waste and reported 6.28, 81.2, 6.12, 6.4 wt. % of MC, VM, AC, FC and carbon, hydrogen, nitrogen, oxygen in its elemental composition as 49.4, 4.32, 1.98, 44.14 wt. %, respectively. Its HHV value was 16.32 MJ/kg.

Similarly, physiochemical properties were reported for various biomass feedstocks such as pine needle (Gupta and Mondal, 2021), Corn Stover (Mathanker et al., 2020), *Acacia nilotica* wood (Singh et al., 2020), Paulownia wood (Yorgun and Yıldız, 2015) and

Sugarcane bagasse (El-Sayed and Mostafa, 2014) etc. It was observed that biomass containing high VM, low MC and AC are desirable for pyrolysis. High VM results in high bio-oil yield which is the main desired pyrolytic product. Presence of ash in feedstock decreases its heating value thus, low AC is a favorable trait of biomass. MC should also be low in feedstock. In biomass low nitrogen and sulfur indicate less NO_x and SO_x emissions during thermochemical conversion. The heating value of the fuel is directly related to the carbon content; high content of carbon leads to more heating value of the fuel therefore high portion of carbon in biomass is a desirable characteristic of feedstock for pyrolysis. So, it is essential to evaluate the physicochemical properties of biomass prior to their application for bio-energy generation as they are the key parameters that influence quality and quantity of the resultant products.

Table 2.1. Literature review on physicochemical characterization of different biomass

Biomass	MC (wt.%)	VM (wt.%)	AC (wt.%)	FC (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	HHV (MJ/kg)	References
Sal sawdust	8.88	76.03	1.14	14.09	49.83	6.01	0.58	43.56	18.2	Mishra and Mohanty, 2018
Pine sawdust	5.9	77.8	0.79	15.55	46.82	6.04	0.14	46.98	18.59	Laougé and Merdun, 2021
Teak sawdust	3.87	78.17	3.45	14.43	49.17	5.93	1.03	43.87	17.73	Gupta et al., 2019
<i>Acacia nilotica</i>	6.46	79.08	0.78	13.68	43.69	7.54	0.47	48.3	18.66	Singh et al., 2020
Wheat straw	4.41	81	6.77	8.13	42.4	6.01	0.5	41.1	16.1	Rathore et al., 2021

Sugarcane bagasse	4.99	73.5	2.34	2.41	41.98	6.04	0.53	48.87	17.44	El-Sayed and Mostafa, 2014
Bamboo sawdust	10.1	74.9	5.8	9.2	46.73	5.91	0	47.36	20.43	Alam et al., 2020
Paulownia wood	6.5	71.8	1.06	20.64	44.73	6.12	0.87	48.28	20.7	Yorgun and Yıldız, 2015
Eucalyptus	10.7	76.1	4.2	19.7	38.7	4.5	0.3	54.9	15.7	Pidtasang et al., 2013
Corn Stover	5.4	70.9	6.96	16.7	43.5	5.84	0.56	49.9	14.1	Mathanker et al., 2020
Maple Leaf Waste	6.28	81.2	6.12	6.4	49.4	4.32	1.98	44.14	16.32	Ahmad et al., 2021
Pine needle	3.1	68.45	3.5	24.95	47.51	7.01	0.45	44.98	19.47	Gupta and Mondal, 2021

2.1.2 Literature review on kinetics of thermal degradation of various biomass

The knowledge of thermal decomposition kinetics of biomass is important as it facilitates in understanding of thermal degradation characteristics and reaction mechanism associated with it. As per the recommendations of ICTAC (International Confederation of Thermal Analysis and Calorimetry), thermogravimetric analysis (TGA) is an efficient tool to evaluate thermal degradation behavior and biomass decomposition kinetics (Vyazovkin et al., 2011). In TGA rate of loss of biomass weight is measured as a function of time or temperature. Further, first order derivative of weight loss plots is secured from TGA and it gives rate of maximum thermal degradation of biomass. Model-fitting and model-free (iso-conversional models) are the two alternative ways to calculate

kinetic parameters including activation energy (E) and frequency factor or pre-exponential factor (A) by employing TGA data. Model-fitting methods give a single value of activation energy for whole conversion range. Whereas model-free iso-conversional methods do not pose any such limitations and activation energy can be evaluated with change in the degree of conversion. Therefore, in the recent past mostly iso-conversional models have been employed for kinetic evaluations of thermal degradation. In Table 2.2 iso-conversional model used and activation energy obtained from them is presented in tabular manner.

Mishra and Mohanty (2018) reported TGA study of sal and pine sawdust. Both were carried out in inert N₂ atmosphere (at 50 mL/min flow rate) and at five distinct heating rates of 5, 10, 15, 20 and 25 °C/min. Majority of mass loss was noticed in the temperature range of 200-500 °C indicating most of degradation of biomass in this range. DTG curves exhibited different peaks with different heights due to difference in their organic and inorganic compositions. Average activation energy from Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) model came out to be 148.44, 156.58 and 171.66, 179.29 kJ/mol for sal and pine sawdust, respectively.

Rasool et al. (2018) conducted TGA experiments at 10, 25, 50, 100 °C/min of heating rates with 200 mL/min N₂ flow rate for deodar sawdust. TG and DTG graphs secured at various heating rates displayed similar pattern because thermal degradation reaction mechanism is independent of applied heating rates. Activation energy of 179.20 and 180.60 kJ/mol was found for KAS and FWO models, respectively.

Singh et al. (2020) performed TGA study of *Accacia nilotica* at 20 mL/min N₂ flow rate and at three heating rates (5, 10 and 15 °C/min) and reported 211.49, 221.58 and 211.89 kJ/mol activation energy for KAS, FWO and Starink models, respectively. TG/DTG

curves secured at various heating rates confirmed its degradation in three distinct zones associated with moisture removal, hemicellulose and cellulose decomposition and finally lignin decomposition.

TGA for dahlia flower was studied by Mishra et al. (2020) in temperature range of 25-900 °C at three distinct heating rates of 5, 10, 20 °C/min while N₂ gas was purged at a flow rate of 40 mL/min. Decomposition of biomass occurred in three main stages; 30–50 °C (moisture and light volatile removal), 150–500 °C (this second stage is due to devolatilization and degradation of the majority of hemicellulose and cellulose content of biomass thus, it showed maximum mass loss) and above 500 °C temperature (mainly due to lignin decomposition). TGA findings showed around 3 wt.% biomass decomposed in the first stage, during second stage approximately 56 wt. % mass loss occurred while around 6 wt. % loss of mass was registered for the third stage. DTG plots also affirmed three staged degradation of dahlia flower. At 68 °C first peak of DTG was noticed associated with moisture removal, peaks at 256 °C and 314 °C were observed owing to the fact that hemicellulosic and cellulosic parts of biomass decomposed in this stage, respectively. No peak was observed for lignin degradation as its degradation rate was very slow. Activation energy was found to be 220.12, 229.81 kJ/mol for KAS and FWO models, respectively.

Gupta and Mondal (2019a) discussed thermal decomposition behaviour displayed during pyrolysis of maize cob via TGA study. Highest mass loss took place in 200-600 °C. Activation energy for KAS, FWO and Starink models were reported to be 185.39, 186.06 and 185.80 kJ/mol, respectively. TGA experiments were conducted in inert ambience generated by purging N₂ at 60 mL/min and 5, 10, and 20 °C/min of heating rates. DTG plots revealed that in 220-315 °C hemicellulose degraded as a peak was noted in this

temperature range and peak occurring between 314-400 °C was due to cellulose decomposition.

Pine needle thermal decomposition behavior was analysed by Gupta and Mondal (2021) under 200 mL/min N₂ flow at heating rates of 10, 20, 30, 40 °C/min. TG curve disclosed that major mass loss happened in the temperature range of 200-432 °C and DTG curve displayed peak at 339 °C indicating highest rate of mass loss in feedstock. 121.36 and 125.60 kJ/mol of activation energy was calculated for KAS and FWO model, respectively.

Thermal degradation study of several other biomass such as bamboo dust, *Zea mays*, black gram straw and wheat straw also revealed similar results associated with their degradation (Mallick et al., 2018; Rony et al., 2019; Gajera and Panwar, 2019 and Rathore et al., 2021). Evaluation of thermal decomposition behaviour of all biomass materials inferred three stage decomposition owing to the fact that first, second and third stages are related to moisture and light volatile removal, cellulose and hemicellulose devolatilization and finally lignin decomposition. Activation energy gives information about energy requirement for pyrolysis process. So, lower value of activation energy is a desired trait for selection of biomass.

A profound knowledge about the physicochemical characteristics of lignocellulosic biomass is important for selection of feedstock for pyrolysis because pyrolytic product yield distribution and their properties are greatly dependent on the biomass properties.

Table 2.2. Literature review on kinetics of thermal degradation of various biomass

Biomass	Sweeping gas, flow rate (mL/min)	Heating rate (°C/min)	Model	Average E (kJ/mol)	References
Sal sawdust	N ₂ , 50	5, 10, 15, 20, 25	KAS	148.44	Mishra and Mohanty, 2018
			FWO	156.58	
Pine sawdust	N ₂ , 50	5, 10, 15, 20, 25	KAS	171.66	Mishra and Mohanty, 2018
			FWO	179.29	
Deodar sawdust	N ₂ , 200	10, 25, 50, 100	KAS	179.20	Rasool et al., 2018
			FWO	180.60	
<i>Accacia nilotica</i>	N ₂ , 20	5, 10, 15	KAS	211.49	Singh et al., 2020
			FWO	221.58	
			Starink	211.89	
Dahlia flower	N ₂ , 40	5, 10, 20	KAS	220.12	Mishra et al., 2020
			FWO	229.81	
Pine needle	N ₂ , 200	10, 20, 30, 40	KAS	121.36	Gupta and Mondal, 2021
			FWO	125.60	
<i>Zea mays</i>	N ₂ , 100	10, 20, 30, 40	KAS	181.66	Rony et al., 2019
			FWO	191.57	
Bamboo dust	N ₂ , 50	10, 15, 20, 30	KAS	189.43	Mallick et al., 2018
			FWO	188.74	
Maize cob	N ₂ , 60	5, 10, 20	KAS	185.39	Gupta and

			FWO	186.06	Mondal, 2019a
			Starink	185.80	
Black gram straw	N ₂ , 50	20, 30, 40	KAS	172.8	Gajera and Panwar, 2019
			FWO	172.96	
			Starink	172.54	
Wheat straw	N ₂ , 80	20, 30, 40	KAS	181.85	Rathore et al., 2021
			FWO	179.33	
			Starink	178.31	

2.1.3 Literature review on influence of process parameter variation on pyrolysis of various biomass

Pyrolytic product yield distribution and their quality is highly dependent upon the process parameters at which pyrolysis is conducted. To attain maximum yield of desired pyrolytic product (bio-oil, bio-char or pyrolytic gases), selection of favorable process parameters is important. Main process parameters which influence pyrolysis products are temperature, sweeping gas flow rate, bed height, particle size of feedstock, heating rate and pyrolysis time. Studies related to biomass pyrolysis in the recent past have shown that yield and properties of pyrolysis process are influenced by variation of operating process parameters. In Table 2.3, literature review on influence of process parameter variation on pyrolytic product yield of various biomass has been presented.

Gupta and Mondal (2019b) discussed the bio-energy generation from sagwan sawdust via pyrolysis by varying temperature, sweeping gas flow rate, particle size and maximum bio-oil yield was observed to be 48.71 wt.% with 25.56 wt.% bio-char yield at a temperature

of 639.45 °C, N₂ flow rate 181.59 mL per minute and particle size of 0.25mm. In the same year, Gupta et al. (2019) carried study on process parameter variation for pyrolysis of teak sawdust to determine the yield and main characteristics of solid, liquid and gaseous products. The maximum bio-oil and bio-char yield were observed at 600 °C as 48.8 wt.% and 27.4 wt.%, respectively, with pyrolytic gases 23.8 wt.%. With the increase in temperature from 400 to 700°C the biochar yield decreased from 37.42 to 26.45 wt.%. Bio-oil yield increased from 42.24 wt.% at 400 °C to 48.8 wt.% at 600°C, and then it decreased to 47.25 wt.% at 700 °C. The pyrolytic gas yield increased from 20.34 to 26.3 wt.% with increase in temperature. With the increase in flow rate of sweeping gas there was slight decrease in bio-oil and bio-char yield. Bio-oil yield decreased to 45.78 from 48.80 wt.% and biochar yield decreased to 24.27 from 27.40 wt.%. Pyrolytic gas yield increased from 23.80 to 29.95 wt.% as the sweeping gas flow rate increased from 150 to 250 mL/min. Particle size has not such major effect on product yield in the study. With the increase in particle size bio-char yield was increased while bio-oil and pyrolytic gas showed a decrease in yield.

Verma and Mondal (2017) explored the effect of process parameters on product yields of sugarcane bagasse and reported that maximum yield of bio-oil (45.23 wt.%) was obtained at a temperature of 500 °C, 100 mL/min N₂ flow rate, particles of 0.5-0.6 mm size range, 100 °C/min heating rate. Biswas et al. (2017) compared pyrolysis behaviors of four agricultural residues namely, corn cob (47.3 wt.%), rice husk (38.1 wt.%), rice straw (28.4 wt.%) and wheat straw (36.7 wt. %). Maximum bio-oil yield for corn cob, rice husk, rice straw and wheat straw were attained at 450, 450, 400 and 400 °C, respectively. For this study a 280 mm long reactor of 34 mm internal diameter was employed and pyrolysis time of 1 h was used for all the experimental runs.

With an aim of inspecting impact of pyrolysis operating process parameters for deodar sawdust Varma et al. (2019) hovered N₂ flow rate from 50-200 mL/min, heating rate between 10-50 °C/min, 350-600 °C temperature along with particles of 0.25-1.7 mm size range. Outcomes demonstrated that bio-oil yield increased till 500 °C and after attaining a maximum value (44.16 wt.%) it started to show a decreasing pattern meanwhile bio-char yield decreased with increasing temperature and gaseous yield increased monotonically with increase in reaction temperature. With increase in flow rate of N₂ yield of bio-oil improved but it declined after reaching maximum value whereas bio-char yield exhibited decreasing trend and gaseous products showed increasing trend in yield as N₂ flow rate was increased. Bio-oil yield did not show any significant variation with change in particle size. Temperature of 500 °C, 100 mL/min N₂ flow rate, 50 °C/min heating rate and particles of size 0.6-1.0 mm produced maximum 44.16 wt.% of bio-oil.

Al-Layla et al. (2021) conducted a study of effect of process parameters on pyrolysis of milk thistle seeds. Pyrolysis experiments were carried out to explore the influence of the pyrolysis temperature (350–600 °C), rate of heating (10, 15, 20, 25 and 30 °C/min), feedstock particle size (0.84, 0.595, 0.40, 0.25, 0.21 and 0.177 mm), and pyrolysis time (20, 40, 60, 80, 100 and 120 min) on the yields of pyrolytic products. The maximum yield of bio-oil (49.55 wt.%) was obtained at 475 °C temperature, 20 °C/min heating rate, 0.25 mm sized particle and 60 min duration.

Among all the parameters temperature has most significant effect of pyrolysis product yield distribution. High sweeping gas flow rates decrease bio-oil, bio-char yield but favors formation of pyrolytic gases. Particle size does not show any appreciable influence on products of pyrolysis.

Table 2.3. Literature review on influence of process parameter variation on pyrolysis of various biomass

Name of Biomass	Process conditions				Product yield (wt. %)			References
	Temp (°C)	N ₂ flow rate (mL/min)	Particle size (mm)	Heating rate (°C/min)	Bio-oil	Bio-char	Gas	
Sagwan sawdust	639.45	181.59	0.25	-	48.71	25.56	25.73	Gupta and Mondal, 2019b
Sugarcane bagasse	500	100	0.5-0.6	100	45.23	-	-	Varma and Mondal, 2017
Rapeseed cake	500	30	2	5	58.59	-	-	Ucar and Ozkan, 2008
Dry sewage sludge	487.5	4500	0.6	5	35.7	28.7	23.5	Arazo et al., 2017
Rice husk	550,	3	0.1-0.2	20	53.81	37.64	8.55	Zhao and Li, 2016
Rice straw	600	1500	-	10	40.1	25	34.9	Park et al., 2014
Teak sawdust	600,	150	0.18-0.25	-	48.8	27.4	23.8	Gupta et al., 2019
Deodar sawdust	500	100	0.6-1	50	44.16	-	-	Varma et al., 2019
Corn cob	450	50	0.5 - 2	20	47.3	28.7	24	Biswas et al., 2017

Rice husk	450	50	0.5 – 2	20	38.1	35	26.9	Biswas et al., 2017
Rice straw	400	50	0.5 – 2	20	28.4	33.5	38.1	Biswas et al., 2017
Wheat straw	400	50	0.5 - 2	20	36.7	34.4	28.9	Biswas et al., 2017
Milk thistle seeds	475	-	0.25	20	49.5	-	-	Al-Layla et al., 2021

2.1.4 Literature review on different types of catalysts used for pyrolysis

Pyrolytic bio-oil has several drawbacks like high water and acid content along with high portion of oxygenated compounds which reduce its heating value, create problems for its storage and high-value applications. Catalytic pyrolysis has emerged as a promising method for enhancement of bio-oil quality. In addition to this, for some cases catalyst can also bring down energy requirement for pyrolysis (Yildiz et al., 2016). Upgradation of bio-oil is necessary for selective production of high value-added chemical compounds (phenols, sugars, hydrocarbons, furans, etc.), specific chemicals (such as phenols), enhancement in yield of compounds of transportation fuel (like olefins, aromatics) to make it suitable for blending with them, reduction in acidic and oxygenated compounds, improvement in the chemical and physical properties, etc. Table 2.4 illustrates the literature survey on different types of catalysts used for pyrolysis.

Kim et al. (2014) performed catalytic pyrolysis of yellow poplar wood using palladium on carbon (Pd/C) as a catalyst because of its high efficiency towards deoxygenation. Experiments were performed at various reaction times, temperature ranges and catalyst

loadings in the reactor and concluded that reduction in water content and less acidic nature was obtained for catalytic bio-oil in comparison with crude bio-oil. Study conducted by Rahman et al. (2020) for evaluating catalytic effect of ZSM-5 catalyst on pyrolysis of pinewood sawdust revealed that yield of aromatics increased upon introduction of ZSM-5.

Wang et al. (2018b) compared the catalytic effects imparted by Cu/C, Pd/C, Pd–Ag and HZSM-5 during catalytic pyrolysis of larch sawdust and announced that all four catalysts decreased the temperature of the maximum weight loss rate of larch, enhanced phenols formation during the pyrolysis of larch sawdust, and increased total phenolic compounds in the bio-oils. Ansari and Gaikar (2019) reported that formation of more deoxygenated products and hydrocarbons in catalytic bio-oil was promoted by Fe catalyst for napier grass' catalytic pyrolysis.

Huang et al. (2021) executed catalytic pyrolysis of Chinese Herb residue by employing Ni-Fe, Ni-Cu and Ni-Co as the catalysts and found that catalysts reduced activation energy for the pyrolysis. Catalyst addition promoted oil and char but suppressed gas yield. However, H₂ proportion enhanced in gas. Co catalyst favoured phenols and reduction in esters, acids and ketones in bio-oil. In the same year, Zhu et al. (2021) reported catalytic effects of ZSM-5, KOH, mixing of ZSM-5-KOH catalysts for catalytic pyrolysis of orange peel and announced that yield and HHV of all catalytic bio-oils increased as compared to that of non-catalytic bio-oil and ZSM-5-KOH resulted in highest bio-oil yield. Aliphatic and phenolic compounds were dominant in catalytic bio-oils.

Pb, Cu, and Zn-containing cow manure biochar catalysts were utilized in catalytic pyrolysis of wheat straw by Zeng et al. (2022) and heavy metals (especially Pb) loaded

catalyst increased production of phenolics and oxygenated compounds were decreased. Study conducted by Lin and Cheng (2022) for catalytic pyrolysis of crofton weed using ZnO and Na₂CO₃ resulted in increased bio-oil yield, production of alkane improved and carboxylic acid reduced as a result of catalyst introduction. In the very same year, a study on pinyon juniper, pine, and forest thinning waste and red mud was reported by Santosa et al. (2022) which showed enhancement in production of stable and less oxygenated bio-oil due to catalytic effect of red mud. Liu et al. (2022) investigated catalytic effect of Fe/activated char (activated char supported Fe) for catalytic pyrolysis of pine wood and reported that production of aromatic hydrocarbons was improved due to Fe/activated char catalyst.

Table 2.4. Literature review on different types of catalysts used for pyrolysis

Biomass	Catalyst	Key findings	References
Poplar wood	Pd/C	Reduction in water content and less acidic nature was obtained for catalytic bio-oil in comparison with crude bio-oil.	Kim et al., 2014
Pinewood Sawdust	ZSM-5	The yield of aromatics increased upon introduction of ZSM-5.	Rahman et al., 2020
Sawdust	5%Zn/ZSM-5	Zn/ZSM-5 enhanced quality and quantity of liquid products.	He et al., 2016
Radiata pine sawdust	Ga/HZSM-5	Ga/HZSM-5 exhibited selectivity towards the production of aromatics	Park et al., 2007
Coffee Grounds	NiCu/ γ -Al ₂ O ₃	More homogeneous distribution of organic compounds in the catalytic bio-oil.	Kan et al., 2014
Larch sawdust	Cu/C, Pd/C, Pd–Ag and HZSM-5	All four catalysts decreased the temperature of the maximum weight loss rate of larch, enhanced phenols	Wang et al., (2018b)

		formation during the pyrolysis of larch sawdust, and increased total phenolic compounds in the bio-oils.	
Napier grass	Fe	Fe promoted formation of more deoxygenated products and hydrocarbons in catalytic bio-oil.	Ansari and Gaikar, 2019
Wheat straw	Pb, Cu, and Zn-containing cow manure biochar catalysts	heavy metals (especially Pb) loaded catalyst increased production of phenolics and oxygenated compounds were decreased.	Zeng et al., 2022
Crofton weed	ZnO and Na ₂ CO ₃	Increased bio-oil yield, production of alkane improved and carboxylic acid reduced.	Lin and Cheng, 2022
Chinese Herb residue	Ni-Fe, Ni-Cu and Ni-Co	Catalysts reduced activation energy for the pyrolysis. Catalyst addition promoted oil and char but suppressed gas yield. However, H ₂ proportion enhanced in gas. Co catalyst favoured phenols and reduction in esters, acids and ketones in bio-oil.	Huang et al., 2021
Pinyon juniper, pine, and forest thinning waste	Red mud	Promoted production of stable and less oxygenated bio-oil.	Santosa et al., 2022
Orange peel	ZSM-5, KOH, Mixing of ZSM-5-	Yield and HHV of all catalytic bio-oils increased as compared to that of non-catalytic bio-oil and ZSM-5-KOH resulted in highest bio-oil yield.	Zhu et al., 2021

	KOH	Aliphatic and phenolic compounds were dominant in catalytic bio-oils.	
Pine wood	Fe/activated char	Fe/activated char catalysts promoted the production of aromatic hydrocarbons.	Liu et al., 2022

From this literature review it was observed that a careful selection of biomass material (based up on its physicochemical properties), process parameters of pyrolysis, catalyst type and biomass-to-catalyst ratio is essential for obtaining robust results.

2.2 Research gap

From literature survey related to pyrolysis of biomass it was observed that there are several research gaps present in this field such as:

- Kinetics and thermodynamic study of *Melia azedarach* sawdust is not present in the available literature.
- No study has been reported about *Melia azedarach* sawdust pyrolysis.
- Effect of process parameters' variation on the pyrolysis products yield distribution and speciation analysis has not been reported yet.
- Use of heavy metal present in wastewater as catalyst for catalytic pyrolysis of *Melia azedarach* sawdust has not been explored.
- Comparative study of non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust products using various characterization techniques is not available in the related literature.

2.3 Objectives of this study

Based on the literature review and research gap, the objectives of the present study can be summarized as follows:

- To study the physicochemical properties, thermo-kinetic parameters, and reaction mechanism for thermal degradation of *Melia azedarach* sawdust by employing thermogravimetric analysis.
- To study the effect of variation in operating parameters (temperature, nitrogen flow rate, bed height, particle size, heating rate and pyrolysis time) on yield of *Melia azedarach* sawdust pyrolysis products and to carry out in line characterization of these products.
- To use heavy metal (Cu) as a catalyst and carry out non-catalytic and catalytic pyrolysis of *Melia azedarach* sawdust. Also, to carry out in-depth characterization of bio-oil and bio-char by standard characterization techniques.