

## **Chapter 2**

### **Literature review and objectives**

In this chapter literature review related to the torrefaction of biomass, optimization of torrefaction process for high grade torrefied biomass, pyrolysis of raw and torrefied biomass, and optimization of process parameters such as temperature, retention time, heating rate, sweeping gas flow rate, particle size, etc. have been discussed. Finally, the literature related to application of biochar from pyrolysis of raw biomass towards removal of methylene blue dye from aqueous solution has been systematically discussed. This chapter-2 has been divided into three parts: (1) literature review on torrefaction of biomass and optimization of torrefaction process, (2) literature review on pyrolysis of raw and torrefied biomass and optimization of process parameters, (3) literature review on application of biochar from pyrolysis of biomass for removal of aqueous methylene blue. Based on the literature review objectives of present research work have been decided.

### **2.1 Literature review**

#### **2.1.1 Torrefaction of biomass and optimization of torrefaction process**

##### **2.1.1.1 Torrefaction of biomass**

Torrefaction is thermochemical pretreatment process that occurs in the temperature range of 200 to 300 °C in an oxygen free environment at atmospheric pressure (Niu et al., 2019). Torrefaction can alleviate the undesired characteristics of biomass such higher moisture content, lower energy density and HHV, lower fixed carbon, hydrophobicity, higher grinding energy (Chen & Kuo, 2011).

**2.1.1.1.1 Effect of torrefaction on proximate and ultimate analysis of biomass**

The effect of torrefaction on proximate and ultimate analysis of various biomasses has been mentioned in Table 2.1. The proximate analysis of torrefied biomass at different torrefaction condition revealed the significant decrease in volatile matter and at the same time increase in fixed carbon content and ash content was observed due to torrefaction. The ultimate analysis demonstrates the higher carbon content and lower oxygen and hydrogen content in torrefied biomass as compared to the raw biomass. Also, the trend in results of proximate and ultimate analysis intensifies with increase in severity of torrefaction process (increase in process temperature and retention time). The cleavage of oxygen containing functional groups present in biomass consequently release of light volatile matter during torrefaction is responsible for change in results of proximate and ultimate analysis (Wannapeera et al., 2011b). The decrease in volatile matter during torrefaction is the result of catalytic effect of inorganic minerals present on biomass (Sadaka & Negi, 2009). The higher carbon content in torrefied biomass as compared to oxygen and hydrogen depicts the higher energy value of torrefied biomass as compared to raw biomass (Couhert et al., 2009). The increase in energy value of torrefied biomass makes it suitable for biofuel production. The ash content of torrefied biomass is higher than raw biomass; however, increase in ash content is lower than the increase in fixed carbon content. The ash content is the inherent characteristics of biomass selected for torrefaction. Thus, the ash content of biomass has relative effect on the obtained torrefied products (Bridgeman et al., 2008). The increase in ash content on torrefied can results in accumulation of metallic minerals which may act as catalyst during pyrolysis of torrefied biomass (Yildiz et al., 2015). The

elemental analysis also revealed that the atomic ratios H/C and O/C of torrefied biomass are lower than raw biomass. The decrease in these ratios facilitates the application of torrefied for biofuel production.

**Table 2.1** Effect of torrefaction on proximate and ultimate analysis of biomass

Biomass	Proximate analysis			Ultimate analysis				References
	VM (wt%)	FC (wt%)	AC (wt%)	C (wt%)	H (wt%)	O (wt%)	N (wt%)	
Beech wood (raw) *PS =50-500 $\mu$ m	84.20	15.50	0.30	47.20	6.00	45.20	0.40	(Couhert et al., 2009)
Torrefaction at T (240 $^{\circ}$ C) RT (1 h) PS = 50-500 $\mu$ m	80.60	19.20	0.35	51.70	5.40	42.90	0.00	
Torrefaction at T (260 $^{\circ}$ C) RT (1 h) PS = 50-500 $\mu$ m	75.70	24.20	0.40	54.40	5.20	40.40	0.00	
Leucaena (raw) PS < 75 $\mu$ m	86.10	13.10	0.80	50.10	7.40	41.80	0.70	(Wannapeera et al., 2011b)
Torrefaction at T (200 $^{\circ}$ C) RT (0.5 h) PS < 75 $\mu$ m	85.30	14.00	0.70	51.70	7.10	40.50	0.70	
Torrefaction at T (225 $^{\circ}$ C) RT (0.5 h) PS < 75 $\mu$ m	84.30	14.90	0.80	52.40	7.10	39.80	0.70	
Torrefaction at T (250 $^{\circ}$ C) RT (0.5 h) PS < 75 $\mu$ m	82.20	16.90	0.90	53.00	6.40	39.90	0.70	
Torrefaction at T (275 $^{\circ}$ C) RT (0.5 h) PS < 75 $\mu$ m	73.80	24.90	1.30	57.20	5.50	36.50	0.80	
Willow (raw) PS = NR	87.60	10.70	1.70	47.20	6.10	44.80	0.34	(Bridgeman et al., 2008)
Torrefaction at T (230 $^{\circ}$ C) RT (0.5 h) PS = **NR	82.10	16.10	1.80	50.70	6.20	39.50	0.20	

Torrefaction at T (250 °C) RT (0.5 h) PS = NR	79.80	18.40	1.90	51.70	6.10	38.70	0.20	
Torrefaction at T (270 °C) RT (0.5 h) PS = NR	79.30	18.60	2.10	53.40	6.10	37.20	0.20	
Torrefaction at T (290 °C) RT (0.5 h) PS = NR*	77.20	20.50	2.30	54.70	6.00	36.40	0.10	
Pine (raw) PS= 20.94-70.59 mm (length)	85.98	13.76	0.27	47.20	6.64	45.76	0.17	(Phanphanich & Mani, 2011)
Torrefaction at T (225 °C) RT (0.5 h) PS= 20.94-70.59 mm (length)	84.78	14.95	0.27	49.47	6.07	44.03	0.15	
Torrefaction at Temp (250 °C) RT (0.5 h) PS= 20.94-70.59 mm (length)	82.52	17.24	0.25	51.46	5.86	42.02	0.14	
Torrefaction at T (275 °C) RT (0.5 h) PS= 20.94-70.59 mm (length)	76.40	23.26	0.35	54.91	6.20	38.17	0.20	
Torrefaction at T (300 °C) RT (0.5 h) PS= 20.94-70.59 mm (length)	58.72	40.85	0.43	63.67	5.58	29.99	0.20	
Sawdust (raw) PS= 20-30 mesh	73.15	13.02	0.38	40.85	6.17	39.07	0.03	
Torrefaction at (230 °C) RT (0.5 h) PS= 20-30 mesh	69.10	19.84	8.62	45.92	5.20	37.01	0.53	
Torrefaction at T (250 °C) RT (0.5 h) PS= 20-30 mesh	64.79	23.74	9.21	47.16	5.01	0.55	35.52	
Torrefaction at T (270 °C) RT (0.5 h) PS= 20-30 mesh	57.07	30.15	10.63	50.67	4.77	30.81	0.65	
Torrefaction at (290 °C), RT (0.5 h)	49.68	35.71	12.54	52.22	4.41	27.72	0.71	

PS= 20-30 mesh								
Read canary grass (raw) PS = NR	82.50	12.10	5.50	48.60	6.80	37.30	0.30	(Bridgeman et al., 2008)
Torrefaction at T (250 °C) RT (0.5 h) PS = NR	80.30	13.30	6.40	50.30	6.30	37.00	-	
Torrefaction at T (270 °C) RT (0.5 h) PS = NR	76.60	16.10	7.30	52.20	6.00	37.30	0.10	
Torrefaction at (290 °C) RT (0.5 h) PS = NR	70.50	21.30	8.30	54.30	6.10	45.20	0.10	
Wheat straw (raw) PS = NR	76.40	17.30	6.30	47.30	6.80	37.70	0.80	(Bridgeman et al., 2008)
Torrefaction at T (250 °C) RT (0.5 h) PS = NR	77.00	15.60	7.40	49.60	6.10	35.60	0.90	
Torrefaction at T (270 °C) RT (0.5 h) PS = NR	65.20	26.50	8.40	51.90	5.90	33.20	0.80	
Torrefaction at T (290 °C) RT (0.5 h) PS = NR	51.80	38.00	10.20	56.40	5.60	27.60	1.00	
Miscanthus (raw) PS < 4 mm and PS > 10 mm	78.4	12.9	1.3	49.3	6.4	44.3	0.00	(Bridgeman et al., 2010a)
Torrefaction at T (290 °C) RT (10min) PS < 4 mm and PS > 10 mm	63.8	32.6	1.4	55.8	5.8	38.4	0.00	
Torrefaction at T (240 °C) RT (1 h) PS < 4 mm and PS > 10 mm	76.4	20.0	1.3	53.7	6.0	40.3	0.00	
Torrefaction at T (240 °C) RT (10min) PS < 4 mm and PS > 10 mm	81.3	15.0	1.2	50.6	6.0	43.4	0.00	
Torrefaction at T (290 °C) RT (1 h)	60.00	35.50	1.90	63.4	5.70	30.90	0.00	

PS < 4 mm and PS > 10 mm								
Eucalyptus (raw) PS < 5 mm	84.00	-	0.70	49.00	6.10	44.60	0.20	(Arias et al., 2008a)
Torrefaction at T (240 °C) RT (0 h) PS < 5 mm	80.50	-	0.50	49.20	6.20	44.30	0.20	
Torrefaction at T (240 °C) RT (0.25 h) PS < 5 mm	78.70	-	0.50	51.20	5.90	42.70	0.10	
Torrefaction at T (240 °C) RT (0.5 h) PS < 5 mm	75.40	-	0.70	53.10	6.10	40.60	0.10	
Torrefaction at T (240 °C) RT (1 h) PS < 5 mm	74.50	-	1.00	53.00	5.90	40.90	0.10	
Torrefaction at T (240 °C) RT (2 h) PS < 5 mm	73.30	-	0.90	54.20	5.90	39.70	0.10	
Torrefaction at T (240 °C) RT (3 h) PS < 5 mm	74.10	-	1.00	53.80	6.00	40.00	0.10	

\*PS: Particle size, \*\*NR: not reported

### 2.1.1.1.2 Effect of torrefaction on mass yield, energy yield and higher heating value of biomass

The mass yield, energy yield, and higher heating value are the crucial indicator of biomass for its practical evaluation during thermochemical conversion process (Dai et al., 2019).

The mass and energy yield can be calculated by using Eqs. (1) and (2) (Bridgeman et al., 2010a; Yan et al., 2009). The mass yield, energy yield, and higher heating value of different biomass are mentioned in Table 2.2. It was observed that mass yield decreases with increase in temperature and retention time during torrefaction process. The

decomposition of volatile matter in liquid and gaseous products at higher temperature and retention time is responsible for decrease in mass yield (Chew & Doshi, 2011; Dai et al., 2019). The major decomposition of hemicellulose takes place during torrefaction (Arias et al., 2008a). Thus, it was also observed that, the mass yield of herbaceous biomass is lower than the woody biomass during torrefaction due to higher hemicellulose content in herbaceous biomass (Bridgeman et al., 2008; Prins et al., 2006b). The increase in temperature and retention time during torrefaction causes increase in higher heating value of torrefied biomass. The increase in carbon content and decrease in oxygen content as a result of torrefaction is accountable for increase in higher heating value of torrefied biomass since, C-C bond has higher energy content as compared to C-H or C-O bonds (Phanphanich & Mani, 2011). The energy yield being a function of mass yield, HHV of torrefied and raw biomass signifies the amount of energy lost during torrefaction. The wide variation in energy yield of herbaceous biomass was observed due to large variation in volatile matter and hemicellulose content (Deng et al., 2009b). It was also observed that temperature has more pronounced effect on energy yield as compared to retention time. Thus, lower or higher temperature range along with shorter retention time can minimize the loss of energy through torrefaction (Chew & Doshi, 2011).

$$\text{Mass yield} = \frac{\text{Mass}_{\text{torrefied biomass}}}{\text{Mass}_{\text{raw biomass}}} \times 100 \quad (1.1)$$

$$\text{Energy yield} = \text{Mass yield} \times \frac{\text{HHV}_{\text{torrefied biomass}}}{\text{HHV}_{\text{raw biomass}}} \quad (1.2)$$

Phanphanich et al. (Phanphanich & Mani, 2011) investigated the mass and energy yield of pine chips and logging residues in the temperature range of 225-300 °C at a retention time of 0.5 h and reported that the mass yield varies in the range of 52-89%, while energy yield

varies in the range of 71-94%. Pimchuai et al. (Pimchuai et al., 2010) performed the torrefaction of water hyacinth, peanut husk, rice husk and bagasse in the temperature range of 250-300 °C and retention time in the range of 1-2 h. They reported that mass and energy yield fell in the range of 41-79% and 55-98%, respectively. The mass and energy yield and HHV of torrefied biomass depends on types of biomass, temperature, retention time and types of process reactor (Niu et al., 2019).

**Table 2.2** Effect of torrefaction on mass yield, energy yield and higher heating value of biomass

Biomass	Torrefaction condition	Mass yield (%)	Energy yield (wt%)	HHV (MJ/kg)	References
Leucaena	T (200 °C) RT (0.5 h) *PS < 75 µm	91.0	94.1	21.0	(Wannapeera et al., 2011b)
	T (225 °C) RT (0.5 h) PS < 75 µm	86.5	90.3	21.2	
	T (250 °C) RT (0.5 h) PS < 75 µm	73.0	76.2	21.2	
	T (275 °C) RT (0.5 h) PS < 75 µm	54.5	61.2	22.0	
Pine	T (230 °C) RT (1.0 h) PS = **NR	92.4	96.5	18.0	(Pach et al., 2002)
	T (250 °C) RT (1.0 h) PS = NR	88.2	94.3	18.5	
	T (280 °C) RT (1.0 h) PS = NR	78.1	93.9	20.8	
Willow	T (230 °C) RT (0.5 h)	95.1	96.0	20.2	(Bridgeman et al., 2008)



	PS = NR				
	T (250 °C) RT (0.5 h) PS = NR	89.6	92.2	20.6	
	T (270 °C) RT (0.5 h) PS = NR	79.8	85.3	21.4	
	T (290 °C) RT (0.5 h) PS = NR	72.0	78.8	21.9	
Wood briquette	T (220 °C) RT (0.5 h) PS = NR	94.0	95.9	20.4	(Felfli et al., 2005a)
	T (250 °C) RT (0.5 h) PS = NR	74.0	78.3	21.2	
	T (270 °C) RT (0.5 h) PS = NR	56.0	63.7	22.7	
Sugarcane bagasse	T (230 °C) RT (1.0 h) PS = NR	87.5	96.4	17.0	(Pach et al., 2002)
	T (250 °C) RT (1.0 h) PS = NR	78.9	92.0	18.0	
	T (280 °C) RT (1.0 h) PS = NR	68.6	82.9	18.7	
Cotton stalk	T (200 °C) RT (0.5 h) PS = 25 mm	63.8	83.4	23.9	(Wang et al., 2011)
	T (250 °C) RT (0.5 h) PS = 25 mm	33.8	45.3	24.5	
	T (300 °C) RT (0.5 h) PS = 25 mm	30.0	41.0	25.0	
Sawdust	T (250 °C) RT (1.0 h) PS = NR	67.2	72.4	19.5	(Pimchuai et al., 2010)
	T (270 °C) RT (1.0 h) PS = NR	59.5	67.1	20.4	
	T (300 °C) RT (1.0 h) PS = NR	42.0	55.1	23.8	

Wheat straw	T (200 °C) RT (0.5 h) PS = 25 mm	47.56	56.0	19.8	(Wang et al., 2011)
	T (250 °C) RT (0.5 h) PS = 25 mm	41.24	51.0	20.8	
	T (300 °C) RT (0.5 h) PS = 25 mm	31.61	40.6	21.6	
Rice straw	T (200 °C) RT (0.5 h) PS = 25 mm	59.8	59.9	17.1	(Deng et al., 2009b)
	T (250 °C) RT (0.5 h) PS = 25 mm	40.3	42.4	18.0	
	T (300 °C) RT (0.5 h) PS = 25 mm	36.5	39.9	18.6	
Reed canary grass	T (250 °C) RT (0.5 h) PS = NR	83.0	85.1	20.0	(Bridgeman et al., 2008)
	T (270 °C) RT (0.5 h) PS = NR	72.0	76.8	20.8	
	T (290 °C) RT (0.5 h) PS = NR	61.5	68.7	21.8	

\*PS: Particle size, \*\*NR: not reported

### 2.1.1.1.3 Effect of torrefaction on grindability and moisture absorption capacity of biomass

As a result of torrefaction, the fibrous structure of biomass is broken and smaller and spherical size particle are obtained which enhances the flow characteristics of biomass (Arias et al., 2008a; Wang et al., 2011). Thus, torrefaction makes the biomass brittle which enhances its grinding properties and lower the grinding energy as a result smaller particle size distribution are obtained (Deng et al., 2009b; Repellin et al., 2010). The grinding

energy of torrefied biomass was noted to 10-20% lower than the raw biomass, and this grinding energy can be compared with grinding energy of coal (Ciolkosz & Wallace, 2011; Phanphanich & Mani, 2011). Hence, torrefaction facilitate grindability and flowability of biomass. Repellin et al. (Repellin et al., 2010) performed the grinding of spruce and beech at different torrefaction temperature (180-280 °C for beech and 160-280 °C for spruce) and retention time (5-60 min for beech and 5 min for spruce) using ultra centrifugal mill (Retsch ZM1) coupled with 0.5 mm grid and found that grinding energy decreased with increase in temperature and retention time. However, small decrease in grinding energy was noted when retention time increased beyond 20 min. Bridgeman et al. (Bridgeman et al., 2010a) confirmed that temperature during torrefaction had most significant impact on grindability of torrefied biomass followed by retention time and particle size. Mani et al. (Mani et al., 2004) confirmed that higher moisture content in torrefied biomass increased its grinding energy due to more shear strength. Wang et al. (Wang et al., 2011) investigated the grinding energy for cotton stalk and wheat straw and reported that beyond 250 °C, temperature had almost no significance on grinding energy.

The hygroscopic characteristics of biomass is highly depends on the composition (cellulose, hemicellulose and lignin content) of biomass (Niu et al., 2019). Among the composition of biomass, hemicellulose has the strongest affinity toward water absorption while, lignin has the least affinity towards water (Björk & Rasmuson, 1995). Due to torrefaction, the decomposition of majority of hemicellulose along with reduction in H/C and O/C ratios, the torrefied biomass has hydrophobic characteristics as compared to raw biomass. The cleavage of hydroxyl bonds associated with hemicellulose is mainly accountable for hydrophobic characteristics of torrefied biomass (Kanwal et al., 2019;

Phanphanich & Mani, 2011). The hydrophobic nature of torrefied biomass facilitates its transport and storage without bacterial deterioration like raw biomass (Yan et al., 2009). The water absorption capacity of biomass decreases with increase in temperature during torrefaction (Pimchuai et al., 2010). Ciolkosz et al. (Ciolkosz & Wallace, 2011) summarized the mechanism of hydrophobic characteristics of biomass due to torrefaction. They reported that decomposition of hemicellulose during torrefaction leads to unbind the cellulose and lignin. This causes discharge of water molecules present in cell wall. The decomposition of hemicellulose brings the brittle characteristics in cellulose and lignin. The breakdown of hydroxyl groups present in hemicellulose decreases the tendency of formation of hydrogen bond with water molecules. Non-polar molecules are formed as a result of hemicellulose decomposition. The hydrophobic characteristics of biomass can be estimated by using Equilibrium Moisture Content (ECM) as proposed by Acharjee et al. (Acharjee et al., 2011) and Yan et al. (Yan et al., 2009). The torrefied biomass having lower ECM has lower risk of biological degradation as compared to torrefied biomass with higher ECM (Yan et al., 2009). Thus, it can be concluded that torrefaction significantly reduced the grinding energy and moisture absorption capacity of native biomass. The reduction in grinding energy of biomass due to torrefaction increased the energy efficiency of process and reduction in moisture absorption capacity can lead to lower bacterial degradation resulting in longer storage of native biomass.

### **2.1.1.2 Optimization of torrefaction process**

The torrefaction process depends on temperature, retention time, heating rate, type of biomass, process reactor system, particle size, etc. Among these parameters temperature and retention time has most significant impact on torrefaction process (Asadullah et al.,

2014). Also, the torrefaction process is generally used as a pretreatment process to upgrade the quality of native biomass; hence yield of upgraded biomass (torrefied biomass) with enhanced properties is the desired output from torrefaction. However, the yield and quality of torrefied biomass shows opposite trend during torrefaction process. With increase in temperature and retention time the quality of torrefied biomass (HHV, fixed carbon, H/C and O/C ratios) enhances while, yield of torrefied biomass decreases (Singh et al., 2019b). Thus, it is of prime importance to find a balance between quality and quantity of torrefied biomass. The process outcomes such as mass and energy yield are very sensitive to temperature and retention time. A small variation in temperature and retention time can cause significant variation in mass and energy yield (Koukios, 1993). The desired value of process parameters can be established through optimization of process parameters. Asadullah et al. (Asadullah et al., 2014) carried out the torrefaction of palm kernel shell between 200-350 °C, retention time 10-60 min and sweeping gas flow between 100-1000 mL/min. They reported the optimum condition of torrefaction for maximum yield (73%) and HHV (24.5 MJ/kg) of torrefied biomass at 300 °C, retention time (20 min) and sweeping gas flow rate (300 mL/min). Buratti et al. (Buratti et al., 2018) investigated the torrefaction of coffee chaff and spent coffee ground between 220-300 °C, retention time 20-60 min and heating rate between 5-25 °C/min and optimize the weight loss and HHV using response surface methodology. The optimum value for coffee chaff was found at 271.7 °C, retention time (20 min) and heating rate (5 °C/min) and for spent coffee ground the optimum value was found at 256 °C, retention time (20 min) and heating rate (25 °C/min). Table 2.3 represents the optimization of torrefaction process for different biomass.

Table 2.3 Optimization of process parameters for torrefaction of different biomass

Biomass	Independent Variable	Dependent variable	Optimization Tool	Optimum condition	Optimum Value of dependent variable	References
Palm kernel shell	T (200-350 °C), RT (10-60 min) SGF (100-1000mL/min)	Solid yield HHV	-	T (300 °C), RT (20 min), SGF (300 mL/min)	Solid yield (73%), HHV (24.5 MJ/kg)	(Asadullah et al., 2014)
Greenhouse crop residue	T (200-300 °C), RT (15-60 min)	Energy# yield	ANFIS modeling	T(263 °C), RT (15 min)	-	(Iáñez-Rodríguez et al., 2017)
Coffee Chaff	T (220-300 °C), RT (20-60 min) HR (5-25 °C/min)	Weight loss and Heating value	RSM based BBD	T(271.7 °C), RT (20 min), HR (5 °C/min)	Weight loss (28.7%), HHV (23.60 MJ/kg)	(Buratti et al., 2018)
Spent coffee ground	T (220-300 °C), RT (20-60 min) HR (5-25 °C/min)	Weight loss and Heating value	RSM based BBD	T (256.7 °C), RT (20 min) HR (25 °C/min)	Weight loss (21.6%), HHV (28.18 MJ/kg)	(Buratti et al., 2018)
Empty fruit bunch	T (200-300 °C), RT (15-60 min)	HHV yield	RSM	T (230 °C), RT (40 min)	121.1%	(Chin et al., 2013)
Oil palm trunk	T (200-300 °C), RT (15-60 min)	HHV yield	RSM	T(300 °C), RT (45 min)	109.2%	(Chin et al., 2013)
<i>Acacia spp.</i>	T (200-300 °C), RT (15-60 min)	HHV yield	RSM	T (260 °C), RT (30 min)	131.4%	(Chin et al., 2013)
<i>Macaranga spp.</i>	T (200-300 °C), RT (15-60 min)	HHV yield	RSM	T (280 °C), RT (45 min)	131.0%	(Chin et al., 2013)
Cotton stalk	T (260-320 °C), RT (10-60 min) BD (125-175 kg/m <sup>3</sup> )	HHV and carbon content	RSM based BBD	T (305 °C), RT (32 min) BD (158 kg/m <sup>3</sup> )	HHV (19.7 MJ/kg), Carbon content (64%)	(Kutlu & Kocar, 2018)
Rice straw	T (210-290 °C), RT (20-60 min)	Energy yield	RSM based CCD	T (210 °C), RT (20	91.3%	(Nam & Capareda, 2015)

				min)		
Cotton stalk	T (210-290 °C), RT (20-60 min)	Energy yield	RSM based CCD	T (210 °C), RT (20 min)	99.4%	(Nam & Capareda, 2015)

# the definition of energy yield has been defined in section 2.1.1.1.2 (Eq. 1.2)

## 2.1.2 Pyrolysis of raw and torrefied biomass and optimization of process parameters

### 2.1.2.1 Pyrolysis of raw biomass and optimization of process parameters

Pyrolysis is a process that can potentially be used to harness energy and various chemicals from biomass (Akhtar & Amin, 2012). The pyrolysis is a thermochemical conversion process which can convert the biomass into solid, liquid, and gaseous products in an inert atmosphere depending upon the process parameters such as temperature, heating rate and retention time. The amount of solid, liquid and gaseous products from pyrolysis depends on the process parameters (Akhtar & Amin, 2012). Generally the pyrolysis process takes place between 500-800 °C (Akhtar & Amin, 2012). Depending upon the process parameters, the pyrolysis can be classified as slow pyrolysis, fast pyrolysis, and flash pyrolysis (Dai et al., 2019). The flash pyrolysis is characterized by higher heating rate ( $> 1000$  °C/s) and lower retention time ( $< 0.5$  s) (Bahng et al., 2009). The flash pyrolysis process requires an experimental set-up equipped with high quality equipment for the control of process. In this regard, slow and fast pyrolysis has gathered huge attention for production of biochar and bio-oil from biomass (Dai et al., 2019). The slow pyrolysis is characterized by low heating

rate (0.1-1 °C/s) and longer retention time (300-550 s). While, fast pyrolysis generally occurs between heating rate of 10-200 °C/s, and retention time between 0.5-10 s (Ben & Ragauskas, 2013; Guedes et al., 2018; Jahirul et al., 2012). Biochar and bio-oil has been considered as the main product from slow and fast pyrolysis, respectively (Guedes et al., 2018). During pyrolysis process biomass went through primary and secondary cracking reactions through heat and mass transfer. The primary reactions during pyrolysis consist of degradation of hemicellulose, cellulose and lignin content of biomass.. The primary products and intermediates are the major products during primary reactions. The intermediates formed during primary reactions are further cracked during secondary reaction of pyrolysis. The primary reactions during pyrolysis follow the dehydration and charring mechanism; while, secondary reactions follows the volatilization and degradation of intermediates (Akhtar & Amin, 2012; Zaror & Pyle, 1982). The yield of bio-oil during pyrolysis of biomass is governed by many factors such as process temperature, retention time, heating rate, sweeping gas flow rate, particle size of feedstock, minerals present in biomass, initial moisture content of biomass and composition of feedstocks (Akhtar & Amin, 2012). Tsai et al. (Tsai et al., 2007) investigated the pyrolysis of rice husk and reported that the yield of bio-oil increased from 11.26 wt% to 35.92 wt%, once the temperature increased from 400 to 500 °C. However, the yield of bio-oil increased with lower rate to 40 wt% at a temperature of 800 °C. Lazzari et al. (Lazzari et al., 2016) performed the mango seed pyrolysis in the temperature range of 450 to 650 °C. The maximum yield of bio-oil (38.8 wt %) was obtained at 650 °C. Jung et al. (Jung et al., 2008) investigated the pyrolysis of saw dust from bamboo and reported that the yield of bio-oil increased from 56% to 72% , once the temperature increased from 350 to 405 °C.



On further increase in temperature up to 510 °C, the yield of bio-oil decreased to 61%. With increase in temperature during pyrolysis, the bio-oil yield increased up to maximum value and after that bio-oil yield decreased due to secondary cracking of volatiles at higher temperature (Isahak et al., 2012). Ates et al. (Ateş et al., 2004) investigated the pyrolysis of sesame stalk and varied the heating rate from 100-700 °C/min. they observed that maximum yield of bio-oil was obtained at a heating rate of 500 °C/min. Tsai et al. (Tsai et al., 2007) varied the heating rate form 100-500 °C/min during pyrolysis of rice husk in a fixed bed reactor. They reported that maximum bio-oil yield was obtained at a heating rate of 200 °C/min and further increase in heating rate has negligible impact on bio-oil yield. Morali et al. (Morali & Şensöz, 2015) carried out the pyrolysis of hornbean shell and varied the heating rate from 7-50 °C/min. They observed that the variation in yield of bio-oil was almost negligible and effect of heating rate on pyrolysis was minimal in the tested conditions of pyrolysis.

**Table 2.4** Optimization of process parameters for pyrolysis of different biomass

Biomass	Desired outcomes	Optimum condition	Optimization tool	References
Napier grass	Bio-oil yield (50.57 wt%)	T: 600 °C, HR; 50 °C/min, SGF: 5 L/min	RSM based CCD	(Mohammed et al., 2017c)
Oil Palm Fiber	Bio-oil yield (50.57 wt%)	T: 536.5 °C, RT: 23.88 min, AC loading: 86.21 g	RSM based CCD	(Abas et al., 2018)
Bambara groundnut	Bio-oil yield (36.49 wt%)	T: 600 °C, HR: 50 °C/min, SGF: 11 L/min	RSM based CCD	(Mohammed et al., 2017b)
Sagwan sawdust	Bio-oil yield (48.70 wt%)	T: 640 °C, SGF: 180 mL/min, Bed height: 8 cm	RSM based BBD	(Gupta & Mondal, 2019)

Food waste	Bio-oil yield (30.24 wt%)	T: 400 °C, RT: 30 min, SGF: 50 mL/min	RSM based CCD	(Kadlimatti et al., 2019)
Perennial grass	Bio-oil yield (38.1 wt%)	T: 550 °C, HR: 20 °C/min, SGF: 226 mL/min	RSM based CCD	(Saikia et al., 2018)
Neem press seed cake	Bio-oil yield (52.1 wt%)	T: 512.5 °C, RT: 60 min, SGF: 0.5 L/min	RSM based BBD	(Dhanavath et al., 2019)
Pine needles	Bio-oil yield (27.6 wt%)	T: 547 °C, HR: 50 °C/min, VCT: 15 °C, SGF: 1.85 L/min	RSM based CCD	(Mandal et al., 2018)
<i>Euphorbia rigida</i>	Bio-oil yield (35.3 wt%)	T: 600 °C, HR: 200 °C/min, SGF: 100 mL/min	RSM based CCD	(Kılıç et al., 2014)
Pearl Millet	Bio-oil yield (48.27 wt%)	T: 400 °C, SGF: 200 mL/min, PS:1.5 mm	RSM based CCD	(Boubacar Laougé et al., 2020)
<i>Sida cordifolia L.</i>	Bio-oil yield (48 wt%)	T: 400 °C, SGF: 200 mL/min, PS:1.5 mm	RSM based CCD	(Boubacar Laougé et al., 2020)
Rice husk	Biochar yield (37.71 wt%)	T: 300 °C, HR: 20 °C/min, RT: 5400 s, BL: 500 g	Taguchi method	(Vieira et al., 2020)
Rice husk	HHV of biochar (23.41 MJ/kg)	T: 500 °C, HR: 10 °C/min, RT: 5400 s, BL: 125 g	Taguchi method	(Vieira et al., 2020)
Rice husk	Fixed carbon of biochar (60.10 wt%)	T: 500 °C, HR: 5 °C/min, RT: 7200 s, BL: 500 g	Taguchi method	(Vieira et al., 2020)
Palm fruit empty bunch	Bio-oil yield (45.29 wt%)	T: 628.2 °C, SGF: 0.259 L/min	Central rotational compound design	(Ferreira et al., 2020)
Poplar saw dust	Bio-oil yield (30.45 wt%)	T: 528.44 °C, HR: 750	RSM based CCD	(Ates & Erginel, 2016)

	wt%)	°C/min, Pressure: 1 bar		
Oil palm trunk	Bio-oil yield (42.05 wt%)	T: 446.11 °C, RT: 119.98 min, moisture content: 9.26%	RSM based BBD	(Oramahi et al., 2015)
Waste mixture (10% pine, 10% scrap tyres, 80% recycled plastic)	Bio-oil yield (54.9 wt%)	T: 426 °C, RT: 28 min, Pressure: 0.2 MPa	RSM (experimental factorial design)	(Pinto et al., 2013)
Coffee silverskin	Organic phase yield (15.2 wt%)	T: 560 °C, SGF: 49 mL/min	RSM based CCD	(Polidoro et al., 2018)
Salwood	Bio-oil yield (44.78 wt%)	T: 540 °C, SGF: 155 cm <sup>3</sup> /min, Feed rate: 0.45 kg/h	RSM based BBD	(Charusiri & Numcharoenpinij, 2017)
Sugarcane bagasse	Bio-oil yield (53.4 wt%)	T: 560 °C, RT: 77 s, Particle size: 0.5 to 0.85 mm	Simplex method	(Vecino Mantilla et al., 2014)
Palm Empty fruit bunch	Bio-oil yield (48.4 wt%)	T: 540 °C, RT: 31 s, Particle size: less than 0.5 mm	Simplex method	(Vecino Mantilla et al., 2014)
<i>Cascabela thevetia</i> seed	Bio-oil yield (45.26 wt%)	T: 525 °C, HR: 75 °C/min, SGF: 75 mL/min	RSM based CCD	(Mishra et al., 2020)

### 2.1.2.2 Pyrolysis of torrefied biomass

#### 2.1.2.2.1 Effect of torrefaction on kinetics of biomass during pyrolysis

The torrefaction process can alter the kinetic parameters resulting in change in rate of heat and mass transfer due to decomposition of biomass during torrefaction. The torrefied

biomass displayed the better behavior than raw biomass due to lower moisture content, H/C and O/C ratios and fractured and brittle structure (Dai et al., 2019). Since, the torrefaction as a pretreatment process can alleviate the undesired characteristics of raw biomass such as higher moisture content, lower energy density, higher oxygen content, higher grinding energy and tendency to absorb the moisture, added energy provided during torrefaction can offset due to enhanced characteristics of raw biomass (Dai et al., 2019). Ren et al. (Ren et al., 2013a) and Martin-Lara et al. (Martín-Lara et al., 2017) performed the TGA analysis of raw and torrefied biomass to investigate the pyrolysis characteristics. They reported that activation energy for pyrolysis of torrefied biomass was lower as compared to raw biomass due to decomposition of biomass during torrefaction. Martin-Lara et al. (Martín-Lara et al., 2017) also reported that for torrefied biomass obtained at mild torrefaction condition, the first order, single kinetic model was followed however, for severe torrefaction condition multi step kinetic model was followed. Hu et al. (Hu et al., 2018) performed the pyrolysis of raw and pellets from torrefied corn stalk. They observed that considerable amount of volatiles were lowered and rate of decomposition of biomass had increased due to torrefaction. Ru et al. (Ru et al., 2015) reported that the activation energy of hemicellulose and cellulose significantly reduced due to torrefaction, while for lignin, slight change in activation energy was observed. This showed that with increase in temperature during torrefaction, contribution of hemicellulose and cellulose decreased while contribution of lignin increased during decomposition of torrefied biomass during pyrolysis.

**2.1.2.2.2 Effect of torrefaction on product distribution during pyrolysis of biomass**

The integrated torrefaction-pyrolysis process can be a promising route for upgradation of quality of bio-oil obtained from pyrolysis of biomass. However, yield of bio-oil from pyrolysis of torrefied biomass is lower than the raw biomass because lighter component of biomass has already been converted into gaseous and liquid condensate (water, CO<sub>2</sub>, CO, acids, etc.) during torrefaction process (Boateng & Mullen, 2013a; Chen et al., 2016c; Prins et al., 2006a). Table 2.5 represents the effect of torrefaction on quality of bio-oil obtained from pyrolysis of torrefied biomass. Boateng et al. (Boateng & Mullen, 2013a) performed the pyrolysis of torrefied biomass and reported that yield of bio-oil decreased and biochar yield increased however, quality of bio-oil has increased due to lower acidic content and higher energy content. Ukaew et al. (Ukaew et al., 2018) performed torrefaction of rice straw in the temperature range of 225-275 °C and retention time of 30 min followed by pyrolysis of torrefied rice straw. They reported that bio-oil yield decreased by quarter as compared to raw rice straw. However, bio-oil from pyrolysis of torrefied rice straw has lower water content, oxygenated and acids compounds as compared to raw rice straw. Pyrolysis of torrefied biomass favors the cross-linking reaction resulting in higher char yield and lower bio-oil yield (Wannapeera et al., 2011b). Zeng et al. (Zheng et al., 2013) performed the pyrolysis of raw and torrefied corncob and analyzed the composition of bio-oil by employing GC-MS analyzer. They reported that the bio-oil from pyrolysis of torrefied corncob has lower yield, acidic, furfural and aldehydes derivative compounds as compared to bio-oil from raw corncob. The higher heating value and pH of bio-oil were improved after torrefaction. They reported that intense devolatilization, cross-linking

reactions and charring of torrefied corncob was mainly accountable for decrease in yield of bio-oil. Xin et al. (Xin et al., 2018) performed the torrefaction of herbaceous residue having high moisture content between temperature 210-280 °C and retention time of 60 min followed by pyrolysis of torrefied herbaceous residue. They reported that torrefaction reduces the oxygen and acids derived compound in the bio-oil. Chen et al. (Chen et al., 2017) reported that torrefaction as a pretreatment can significantly reduce the acidic compounds and increase the phenol derivative compounds in the bio-oil from pyrolysis of torrefied biomass. Thus, it can be concluded that the yield of bio-oil from pyrolysis of torrefied biomass is lower as compared to pyrolysis of native biomass. However, the quality of bio-oil has improved due to torrefaction supporting the feasibility of integrated torrefaction-pyrolysis process for production of high quality bio-oil.

**Table 2.5** Effect of torrefaction on quality of bio-oil obtained from pyrolysis of torrefied biomass

Biomass	Torrefaction condition	Pyrolysis condition	Important findings*	References
Areca nut husk	T; 200-300 °C, HR; 10 °C/min, RT; 30 min	T; 300-600 °C, HR; 40 °C/min	The bio-oil yield decreased from 32 to 21 %, O/C ratio of bio-oil decreased from 0.36 to 0.28	(Gogoi et al., 2017)
Loblolly pine	T; 273-330 °C, RT; 2.5 min	T; 500 °C, Fr; 150 g/h	O/C ratio of bio-oil decreased from 0.63 to 0.31, while, HHV of bio-oil increased from 20 to 26.3 MJ/kg	(Meng et al., 2012)
Cotton stalk	T; 220-280 °C, RT; 30 min	T; 500 °C	Acid and furan content of bio-oil decreased, while, phenolic and ketone derivatives increased from 0.53-8.25, 0.59-6.41 %, respectively.	(Chen et al., 2015a)
Rice straw	T; 225-275 °C,	T; 450-500 °C,	Oxygenated, acid, aldehydes,	(Zheng et

	RT; 30 min	HR; 1000 °C/sec	ketones, and sugar derivative compounds as well as water content of bio-oil decreased	al., 2012)
Yunnan pine	T; 210-300 °C, RT; 30 min	T; 500 °C	The bio-oil yield decreased from 37 to 20 %, phenolic and hydrocarbon derivatives increased, while, acid, aldehydes and ketone derivative compounds decreased	(Zheng et al., 2017)
Rice straw	T; 240 °C, RT; 60 min	T; 550 °C	Phenolic compounds increased from 28 to 42 %, while, acid, aldehydes, ketone and furan derivative compounds decreased	(Dong et al., 2018)
Corn cob	T; 210-300 °C, RT; 20-60 min	T; 600 °C, HR; 20000 K/sec (catalytic pyrolysis)	The yield of bio-oil increased to 82 % from 51 %, aromatic compounds increased	(Zheng et al., 2014)
Corn stalk	T; 200-290 °C, RT; 30 min	T; 550 °C	Bio-oil yield decreased as compared to raw biomass	(Wang et al., 2018b)
Herbaceous residue	T; 210-280 °C, RT; 60 min	T; 600 °C, HR; 50 °C/min	Phenol, acid, ketone, ester and furan derivative compounds are the main components of bio-oil and collectively contribute 72.1 % of total compounds detected.	(Xin et al., 2018)

\*important findings are mentioned with respect to the pyrolysis of raw biomass at similar pyrolysis conditions

### 2.1.3 Application of biochar from pyrolysis of biomass for removal of aqueous methylene blue

The removal of methylene blue (MB) dye from real or synthetic wastewater using adsorption process has gathered huge attention in recent years due to simple operation, utilization of abundant and low cost adsorbent as well as high removal efficiency towards

MB removal (Santoso et al., 2020). In addition, adsorption process inhibit the generation of secondary pollutant which can generated via degradation or oxidation of MB dye (Katheresan et al., 2018; Salleh et al., 2011). Biochar obtained from pyrolysis of biomass or biomass waste can act as an adsorbent for removal of MB from wastewater (Santoso et al., 2020). The biochar derived from biomass can have similar properties to activated carbon. Hagemann et al. (Hagemann et al., 2018) discussed the two carbon based pyrogenic materials biochar and activated carbon that possess similar preparation technique, terminology and their applications. Biochar was used as a soil amendment agent in agriculture however; recently it has got more attention as an adsorbent towards wastewater treatment (Hagemann et al., 2018). Sun et al. (Sun et al., 2013) used three feedstocks namely, eucalyptus, palm bark, and anaerobic digestion residue for preparation of biochar from pyrolysis at 400 °C. They reported the adsorption capacity of 2.0, 2.95, and 9.77 mg/g for eucalyptus, palm bark, and anaerobic digestion residue, respectively towards MB removal. Ahmed et al. (Ahmed et al., 2019) reported the adsorption capacity of 512.67 mg/g towards MB removal for biochar derived from seaweed by performing pyrolysis process at 800 °C. Ji et al. (Ji et al., 2019) reported the adsorption capacity of 78.6 mg/g towards MB removal for biochar derived from fallen leaf by performing pyrolysis process at 500 °C. Table 2.6 represents the application of biochar derived from pyrolysis of different biomass. The large number of functional groups associated with biochar, porous structure and high surface area of biochar are accountable for removal of MB from wastewater (Que et al., 2018). Thus, with increase in the scope of integrated torrefaction-pyrolysis process, it is imperative to check the efficacy of biochar from pyrolysis of



torrefied biomass towards aqueous methylene blue removal. It might offset the extra energy provided during torrefaction during integrated torrefaction-pyrolysis process.

**Table 2.6** Application of biochar from pyrolysis raw biomass towards aqueous methylene blue removal

Feedstock	Pyrolysis condition	Duration of experiment (min)	Adsorbent dose (g/L)	Initial Conc. (mg/L)	pH	Adsorption capacity (mg/g)	Ref.
Eucalyptus sawdust	T: 400 °C, RT: 30 min	240	8	15	NR	0.957	(Sun et al., 2013)
Palm bark	T: 400 °C, RT: 30 min	240	8	15	NR	1.217	(Sun et al., 2013)
Municipal solid waste	T: 400-500 °C, RT: 30 min	240	2	50	6.5	21.83	(Sumalino g et al., 2018)
Tea waste mixed with sewage sludge	T: 300 °C, RT: 2 h	1440	NR	100	-	8.945	(Fan et al., 2016)
Mixed municipal discard material	T: 400 °C, RT: 30 min	360	5	10	5	1.798	(Hoslett et al., 2020)
Mixed municipal discard material	T: 400 °C, RT: 30 min	360	5	25	5	2.732	(Hoslett et al., 2020)
Mixed municipal discard material	T: 400 °C, RT: 30 min	360	5	50	5	2.960	(Hoslett et al., 2020)
Mixed municipal discard material	T: 400 °C, RT: 30 min	360	5	75	5	5.018	(Hoslett et al., 2020)
Mixed municipal discard	T: 400 °C, RT: 30 min	360	5	100	5	7.254	(Hoslett et al., 2020)

material	min						
Eucalyptus Sheathiana bark	T: 500 °C, RT: 2 h	150	10	100	11.3	104.2	(Dawood et al., 2016)
Wheat straw	T: 550 °C, RT: 5 min	50	-	100	8-9	12.03	(Liu et al., 2012)

NR: not reported

## 2.2 Objectives

The detailed literature review showed that torrefaction has been successfully employed as a pretreatment process to upgrade the quality of raw biomass. However, work related to the optimization of process parameters for maximum energy yield and higher heating value of torrefied biomass considering both at the same time has scarcely reported. Also, little attention has been given to the effect of heating rate on torrefaction process. The in-depth analysis of kinetics and solid reaction mechanism during pyrolysis of torrefied biomass has been scarcely reported. The literature review showed that pyrolysis of raw and optimization process parameters for maximum bio-oil yield have been extensively reported. However, pyrolysis of torrefied biomass has been scarcely reported. The optimization of process parameters for maximum bio-oil yield from pyrolysis of torrefied biomass has not been reported yet. The biochar from pyrolysis of raw biomass has been extensively used as an adsorbent for removal of methylene blue dye from wastewater. However efficacy of biochar from pyrolysis of torrefied biomass towards methylene blue dye removal has not been tested. In order to fulfill the above mentioned research gaps, the present thesis has the following objectives:

- ❖ Pretreatment of raw *Acacia nilotica* using torrefaction and investigation of fuel and flow properties to check the suitability of torrefied *Acacia nilotica* for pyrolysis process
- ❖ Investigation of kinetic and thermodynamic parameters and solid reaction mechanism of pyrolysis of torrefied *Acacia nilotica* using thermogravimetric analysis
- ❖ Optimization of process parameters (temperature, retention time and heating rate) for torrefaction of *Acacia nilotica* for maximum energy yield and higher heating value using response surface methodology
- ❖ The pyrolysis of torrefied *Acacia nilotica* obtained at optimum condition of torrefaction and optimization of process parameters (temperature, heating rate, retention time and sweeping gas flow rate) for maximum yield of pyrolysis oil using response surface methodology. Also, the comparative study of products obtained from pyrolysis of raw and torrefied *Acacia nilotica* at optimum condition of pyrolysis
- ❖ Application and comparative study of biochar obtained from pyrolysis of raw and torrefied *Acacia nilotica* at optimum condition of pyrolysis towards removal of aqueous methylene blue dye