Chapter 3

Literature Survey and Research Objective

Abstract

Agro-wastes and several virgin biomasses are abundantly available globally and have the potential to be used as a feedstock for pyrolysis and gasification. Before carrying out large scale pyrolysis of a given biomass one is required to know the amount of combustible and non-combustible components (moisture, ash, fixed carbon and volatile matter) present, its elemental composition (C, H, N, O, S), percentage of cellulose, ligno-cellulose and lignin in it and its calorific value. The ranges of the value of these parameters depend upon the nature of biomass such as woody or non-woody biomass. For non-woody biomass of agricultural origin the variation in these values is not wide. The thermal degradation behavior of a biomass is investigated using a TGA/DTG/DSC unit. The thermal degradation profiles thus obtained are analyzed using appropriate kinetic models. Various iso-conversional model free methods and model based methods are used for this purpose. Laboratory scale fixed-bed batch pyrolyser has been widely used for evaluating the yields of bio-oil, biochar and gas. Nature of biomass, heating rate and temperature range used control the yields of gaseous, liquid and solid products.

3. Biomass and its pyrolysis

Pyrolysis is one of the simplest technologies among thermal conversion processes to convert biomass or waste biomass into biofuels and other value added chemicals. It is also used for upgrading the biomass in to wood charcoal or biochar as a solid fuel and there are several large-scale facilities in operation globally. Pyrolysis process is carried out in the total or partial absence of oxygen in the temperature range of 350- 700°C at the ambient pressure. The product of pyrolysis is obtained in the form of solid (biochar), liquid (bio-oil) and stable gases such as hydrogen, methane, carbon monoxide (CO) carbon dioxide (CO_2) and some other gaseous hydrocarbons. Based on the operating conditions, the pyrolysis processes can be classified as slow, intermediate and fast pyrolysis that produces different type of products. Biochar is the main product during slow pyrolysis while bio-oil with improved quality is the primary product during fast pyrolysis. The bio-oil is further upgraded and used as transportation fuel and the non-condensable gases can be used for domestic heating or upgraded to be used as syngas. Pyrolysis is used in developing countries to produce wood charcoal and meet domestic heat requirements (Ong et al., 2019; Toro et al., 2021)

3.1 Biomass and their sources

Biomass, a renewable energy source, is a biological material derived from living, or recently living biological species- plants and organisms, most often referring to plants or plant-derived materials. Depending upon its source, the biomass can be grouped into several categories. The main sources are discussed briefly below (Tursi et al., 2019):

Wood and woody biomass: Wood and other woody parts of coniferous or deciduous; angiosperms or gymnosperms; stems, branches, foliage, bark, chips, sawdust and other sawmill wastes and their modified forms (lumps, pellets, briquettes); and others forms of woody species.

Herbaceous biomass : This category includes grasses and flowers (alfalfa, arundo, bamboo, banana, brassica, cane, cynara, miscanthus, switch grass, timothy, others); straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat, others); other residues (fruits, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, cakes, etc.).

Aquatic biomass: All large and small marine or freshwater plants such as algae; macroalgae (blue, green, blue-green, brown, red) or microalgae; seaweeds; kelp; lake weed; water hyacinth, etc.

Animal and human waste biomass: This type of biomass is derived from various types of animals and includes bones, meat-bone meal; various manures, etc.

3.2 Availability of biomass resources in India

A huge amount of agricultural waste biomass is available globally. India being primarily an agrarian country produces huge volume of agricultural wastes in different forms such as energy crops, agro-industrial wastes, agricultural wastes, municipal solid wastes and forest wastes. The globally available biomass that can be used for energy production can be represented as shown in Fig. 3.1:

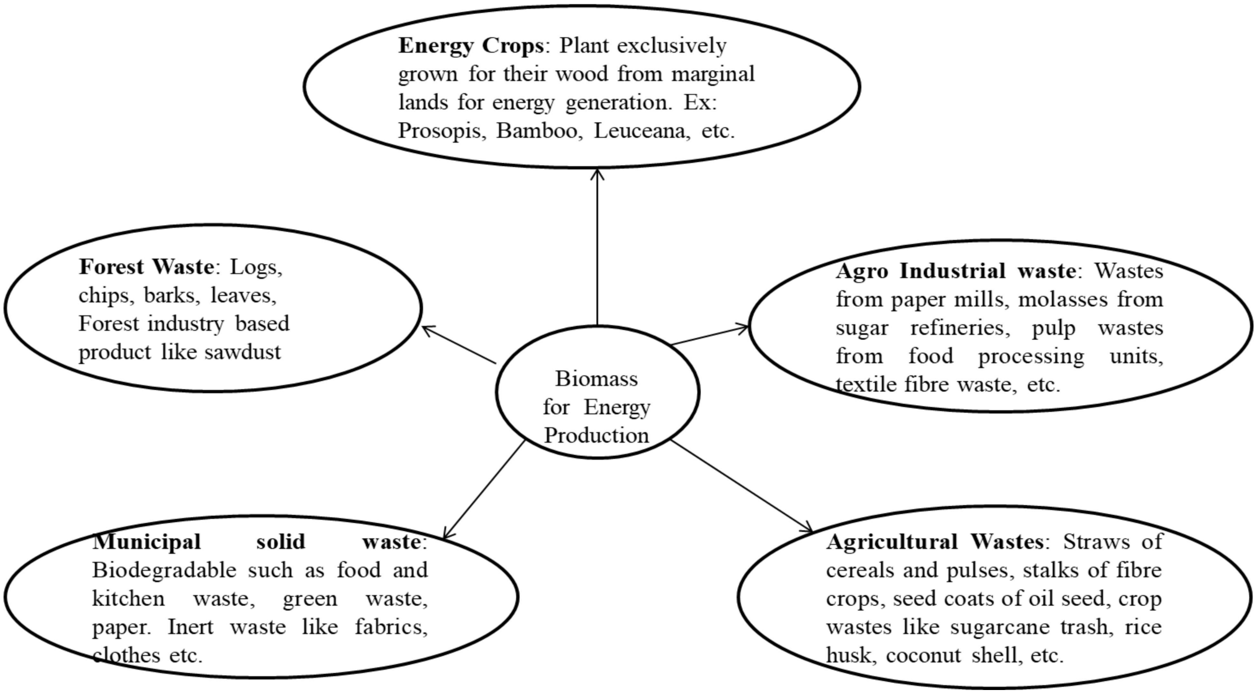

Fig. 3.1 Various biomass types useful for energy production

3.3 Why agricultural waste?

India is an agrarian country and its agricultural production has increased considerably during past few decades. Consequently the amount of agricultural waste in India has also increased enormously. This huge amount of biomass can be used energy production and obtaining several value added-products.

All the organic materials obtained as the by-product from the harvesting of agricultural crops and post-harvesting of cereals and grains are named as agricultural residue. The agricultural residues can be classified as primary and secondary residues. Residues which are acquired in the field at the time of harvesting are field-based or primary residue and those that are produced during processing are classified as secondary residues. Rice straw, sugar cane tops, and so on are primary residues while rice husk, bagasse, de-oiled cakes are secondary residues. Primary residues are also utilized as cattle feed while secondary residues are can be used energy source.

In light of study and information assortment, residue and their amount accessible in India are summarized in Table 3.1. It is estimated that, 686 MT of gross agricultural residue is available in India on annual basis from 39 crop residues generated from 26 different crops being produced in the country. Out of this, 545 MT is contributed by cereals, oil-seeds, pulses and sugarcane crops; 61 MT by horticultural crops (coconut, banana and areca nut) and 80 MT by others (cotton and jute). The cereals contribute the highest amount 368 MT (54%) followed by sugarcane 111 MT (16%). At the individual crop level, rice contributes the highest amount (154 MT) of gross residues followed by wheat (131 MT).

Table 3.1 Different types of crops and their residues produced in India: Production ratio and higher heating value (Hiloidhari et al., 2014)

Crop group	Crop	Residue	RPR (Residue Production Ratio)	Higher Heating Value, MJ/kg
Cereal	Rice	Straw	1.5	15.54
		Husk	0.2	15.54
	Wheat	Stalk	1.5	17.15
		Pod	0.3	17.39
	Maize	Cob	0.3	17.39
		Stalk	2	16.67
	Bajra	Cob	0.33	17.39
		Husk	0.3	17.48

		Stalk	2	18.16
	Barley	Straw	1.3	18.16
	Small millet	Straw	1.2	18.16
	Ragi	Straw	1.3	18.16
	Jowar	Cob	0.5	17.39
		Husk	0.2	17.48
		Stalk	1.7	18.16
Oilseeds	Mustard and Rapeseed	Stalk	1.8	17
	Sesame	Stalk	1.2	14.35
	Linseed	Stalk	1.47	14.35
	Niger	Stalk	1	14.35
	Safflower	Stalk	3	13.9
	Soybean	Stalk	1.7	16.99
	Groundnut	Shell	0.3	15.56
		Stalk	2	14.4
	Sunflower	Stalk	3	17.53
Pulses	Tur (arhar)	Stalk	2.5	18.58
	Lentil	Stalk	1.8	14.65
	Gaur	Stalk	2	16.02
	Gram	Stalk	1.1	16.02
Sugarcane	Sugar cane	Bagasse	0.33	20
		Top and leaves	0.05	20
Horticulture	Banana	Peel	3	17.4
	Coconut	Frond	4	10
		Husk	0.53	19.4

Others	Cotton	Stalk	3.8	17.4
		Husk	1.1	16.7
		Boll shell	1.1	18.3
	Jute	Stalk	2	19.7

The residue generated from crops like sugar cane, wheat, paddy etc. are left in the fields after the harvesting of crops. Normally most of these are burnt in the field, and there is little proper and scientific use of this large residue. Figure 3.2 shows the burning of different crop residues in the field. Further, burning of this waste in the field, releases carbon monoxide, carbon dioxide, oxides of sulphur, oxides of nitrogen and particulate matter as flyash, and affects soil fertility by reducing the microbial diversity (Pasakorn, 2018; Sindhu et al., 2016).

Fig. 3.2 burning of crop residues in field after harvesting of crops

3.4 Thermo-chemical characterization of biomass

Thermo-chemical characterization is one of the most important steps for deciding about the thermal conversion of a given biomass for producing value added products or chemicals. The levels of these parameters indicate the suitability of a biomass for further investigation for conversion using an appropriate thermal-conversion technique. All workers who are interested in carrying out R&D activity in the area of thermal conversion of biomass conventionally report data on these characteristics of biomasses. A large volume of published information is available on the proximate analysis parameters, elemental composition (C, H, N, S and O) and biological components of various types of biomasses such as wood and wood waste, agro-industrial waste, agricultural waste, oil crops and other agricultural wastes, non-woody biomass such as grasses, aquatic plants and algae, animal wastes, municipal solid wastes and shrub species. A comprehensive summary of the available published information is given in Table 3.2.

Table 3.2 Physicochemical characteristics of various biomasses reported in the literature

Sl. No.	Biomass feedstock	VM	FC	Ash	MC	CL	HEL	LIG	C	H	N	O	S	References
1	**Wood and Wood waste**													
1	Alfalfa stems (at early bud)	69.6	16.9	8.3	5.3	-	-	-	39.9	5.5	2.3	38.8	0.2	Boateng et al., 2008
2	Aspens	80.4	11.0	0.4	8.2	60.7	19.1	14.8	45.8	5.2	0.4	39.9	0.01	Shen et al., 2009
3	Australian oil	81.9	17.6	0.5	-	-	-	-	48.4	6.3	0.1	45.2	-	Shen et al., 2009
4	Bamboo sawdust	74.9	9.2	5.8	10.13	-	-	-	46.73	5.91	0.0	47.36	-	Alam et al., 2020
5	Bambusa Multiplex	73.56	14.51	2.44	9.49	-	-	-	46.75	6.17	0.48	36.49	0.01	Zhao et al., 2019
6	Black bamboo	75.31	13.53	2.67	8.49	-	-	-	42.39	5.71	0.55	39.52	0.01	Zhao et al., 2019
7	Beech wood	82.5	17.0	0.5	0.5	50.5	28.4	20.6	52.3	6.1	0.5	41.0	-	Demirbas et al., 2007
8	Birch	74.4	13.5	0.8	11.4	56.5	24.8	12.2	44.4	3.5	0.3	36.7	-	Shen et al., 2009
9	Cardoon leaves	59.5	10.9	29.6	-	-	-	-	34.1	4.9	1.4	29.8	0.20	Damartzis et al., 2011
10	Cardoon stems	77.7	14.7	7.6	-	-	-	-	41.6	6.1	0.8	43.8	0.05	Damartzis et al., 2011

11	Eucalyptus leaves	77.73	12.12	5.89	4.26	17.93	11.28	9.25	47.71	4.85	3.49	43.37	0.45	Chen et al., 2015
12	Eucalyptus bark	69.89	14.85	4.37	10.89	27.48	12.90	32.09	41.82	5.01	0.28	52.76	0.07	Chen et al., 2015
13	Eucalyptus sawdust	74.38	18.79	0.81	6.12	33.89	24.74	20.77	49.75	5.77	0.17	44.26	0.03	Chen et al., 2015
14	Holm oak	80.8	7.4	2.3	9.5	37.9	25.9	27.8	48.0	5.9	0.5	45.6	0.02	López et al., 2013
15	Mallee bark	69.5	24.1	6.4	-	26.3	18.6	24.7	48.5	5.5	0.3	45.4	0.1	Min et al., 2013
16	Mallee leaf	74.6	21.7	3.7	-	15.4	17.3	25.1	59.3	6.8	1.3	32.4	0.2	Min et al., 2013
17	Moso bamboo	74.81	13.96	2.56	8.67	-	-	-	44.87	5.73	0.71	38.32	0.01	Zhao et al., 2019
18	Oak wood	76.8	14.2	0.2	8.8	53.9	28.9	9.4	45.4	5.0	0.3	41.3	0.01	Shen et al., 2009
19	Palm fibre	-	-	4.46	16.14	36.69	30.51	32.80	45.61	6.05	1.21	36.31	-	Ly et al., 2013
20	Paulownia wood	-	-	-	-	25.7	65.4	8.9	47.6	7.3	0.94	-	0.14	Díaz et al., 2013
21	Pine wood	71.5	15.3	0.3	12.9	52.1	15.4	27.5	41.9	4.5	0.2	40.2	-	Shen et al., 2009
22	Pine cone	77.8	-	0.9	9.6	32.7	37.6	24.9	42.6	5.6	0.8	51.0	0.1	Brebu et al., 2010
23	Pine sawdust	77.7	16.9	0.3	5.0	43.8	25.2	26.4	50.3	6.7	0.2	42.7	0.2	Desisto et al., 2010., Wei et al., 2006

24	Pinyon pine	79.15	14.5	0.44	5.91	-	-	-	48.40	6.18	0.08	45.38	-	Jeguirim et al., 2014
25	Poplar wood sawdust (Raw)	75.54	11.15	3.7	9.6	44.75	16.73	30.72	45.5	6.26	1.04	47.2	-	Gu et al., 2014
26	Pyrenean oak	80.5	6.0	2.4	11.1	33.9	25.5	31.2	48.5	5.9	0.5	45.1	0.01	López et al., 2013
27	Sal sawdust	76.03	14.09	1.14	8.88	52.36	14.59	11.18	49.83	6.01	0.58	43.56	-	Mishra et al., 2018
28	Silver fir	78.7	6.5	0.4	14.4	52.1	15.0	29.9	51.2	6.4	0.2	42.2	-	López et al., 2013
29	Softwood	-	-	0.5	13.5	51.6	9.2	30.6	48.8	5.6	0.0	45.6	-	Tröger et al., 2013
30	Stone pine	82.1	7.4	0.7	9.8	41.0	21.0	31.2	50.4	6.0	0.3	43.3	0.01	López et al., 2013
31	Subabul wood	85.6	-	0.9	-	39.8	24.0	24.7	48.2	5.9	0.0	45.1	-	Raveendran et al., 1995
2	**Agro-industrial waste**													
32	Apricot pulp	71.9	13.0	4.7	10.3	-	-	-	51.4	5.7	2.5	40.2	-	Özbay et al., 2008
33	Apple pomace	81.32	6.41	3.40	8.87	47.49	27.77	24.72	47.98	6.65	0.78	37.44	-	Guerrero et al., 2014

34	Coffee husk briquettes	77.06	19.36	3.55	9.06	47.29		27.14	46.41	6.33	2.66	44.51	0.09	Setter et al., 2020
35	Coffee ground	77.5	19.8	1.4	1.3	-	-	33.3	54.6	6.6	3.9	34.8	0	Bok et al., 2012
36	Cotton gin residue	88.0	5.4	-	-	82.8	17.1	0.1	42.7	6.0	0.1	49.5	-	Raveendran et al., 1995., Vassilev et al., 2012
37	Cotton stalks	73.0	16.0	5.0	6.0	32	22.5	39.8	46.3	5.1	1.5	42.5	0.1	Xianjun et al., 2015
38	Defective coffee beans	69.18	21.16	3.14	6.5	28.83	6.05	3.41	45.95	6.62	2.38	45.02	-	Santos et al., 2020
39	Empty palm fruit bunches	76.4	11.6	4.6	7.4	59.7	22.1	18.2	51.8	7.0	0.7	40.3	0.2	Kim et al., 2013
40	Exhausted coffee residue	79.5	8.2	0.7	11.5	47.2	39.4	52.5	6.9	3.5	34.8	0.1	-	Tsai et al., 2012
41	Grape waste	62.5	20.7	5.3	11.5	-	-	-	47.2	6.3	2.4	38.6	0.1	Celma et al., 2007
42	Groundnut shell	64.63	29.45	5.91	8.0	-	-	-	42.02	5.8	1.88	50.28	0.0	Collins et al., 2018
43	Jatropha seed shell cake	79.8	14.1	3.4	2.7	36.6	4.8	39.6	50.5	6.2	2.3	39.4	-	Kim et al., 2013
44	Palm fibre	75.9	12.4	5.3	6.6	-	-	-	50.3	7.1	0.4	36.3	0.6	Yang et al., 2004

45	Palm kernel shell	71.3	17.8	4.9	5.9	30.6	30.6	20.4	44.6	6.5	2.9	40.2	<0.1	Kim et al., 2013
46	Palm mesocarp fibres	82.0	10.2	2.1	5.7	37.5	34.6	27.9	54.5	7.0	0.8	35.5	-	Ly et al., 2013
47	Peach pulp	70.2	18.0	2.4	9.3	-	-	-	45.6	6.9	0.9	46.5	-	Özbay et al., 2008
48	Tobacco waste	65.4	1.4	17.0	16.2	30.3	13.0	20.4	40.91	6.38	2.49	49.96	0.26	Cardoso et al., 2011
49	Wet distiller grain	24.6	-	1.9	68.3	-	-	-	49.9	7.3	5.3	36.5	1.0	Wang et al., 2011
3	**Agricultural wastes**													
50	Areca nut husk	74.05	15.55	2.48	7.43	48.98	16.81	13.27	48.80	5.79	1.95	43.45	0.1	Mishra et al., 2018
51	Arhar stalk	77.33	16.33	1.67	4.67	24.0	18.0	19.0	36.19	3.64	0.42	59.35	-	Kumar et al., 2019
52	Banana peels	66.79	20.55	4.13	8.53	-	-	-	45.43	5.67	2.31	36.40	0.35	Tahir et al., 2019
53	Banana trunk	74.33	7.33	11.67	6.67	25.0	25.0	15.0	33.09	2.94	0.94	63.03	-	Kumar et al., 2019
54	Barley straw	80.3	4.8	9.8	6.9	-	-	-	41.4	6.2	0.6	51.7	0.01	Naik et al., 2010
55	Cashew nut shell	69.3	19.3	1.0	10.4	41.3	18.6	40.1	48.7	6.9	0.4	42.9	-	Das et al., 2003

56	Cherry seed shells	76.1	17.0	0.8	6.1	27.2	31.9	36.9	48.9	6.3	3.1	41.6	0.1	Duman et al., 2011
57	Cherry stones	75.64	19.16	0.42	4.78	26.96	26.88	42.16	51.11	7.18	3.08	38.62	-	Özsin et al., 2017
58	Chestnut shells	65.55	23.08	1.20	10.17	31.61	22.64	42.69	48.14	5.47	0.6	45.79	-	Özsin et al., 2017
59	Coconut shells	80.2	22.0	0.7	4.4	40.3	27.8	31.9	50.2	5.7	0.0	43.4	0.1	Raveendran et al., 1995., Werther et al., 2000
60	Corn cob	77.1	12.9	1.9	8.1	41.0	46.0	-	46.4	5.4	1.0	45.2	-	Jeguirim et al., 2014
61	Corn straw	75.0	9.7	6.1	9.2	4.8	24.4	9.0	42.7	5.6	1.5	49.2	<0.1	Titiloye et al., 2013
62	Flax straw	80.3	8.8	3.0	7.9	-	-	-	45.2	6.3	1.0	-	1.2	Tushar et al., 2010
63	Grape bagasse	68.4	20.7	4.7	6.2	28.6	-	41.9	46.6	6.3	1.7	45.5	-	Demiral et al., 2011
64	Hazelnut bagasse	68.2	15.3	6.7	-	-	-	-	43.8	6.3	7.9	41.9	-	Demiral et al., 2008
65	Hazelnut shell	68.98	19.36	0.711	10.94	47.13	25.48	23.46	56.37	5.62	5.96	32.05	-	Çepeliogullar et al., 2013
66	Legume straw	73.7	14.8	1.6	9.8	28.1	34.1	34.0	43.3	5.6	0.6	50.4	0.1	Li et al., 2004

67	Laurel extraction residues	69.2	10.3	10.5	9.9	22.8	44.0	27.6	48.9	6.4	3.0	41.6	-	Ertaş et al., 2010
68	Litchi peels	75.53	15.42	3.30	5.75	-	-	-	47.39	6.32	0.81	36.81	0.019	Liu et al., 2020
69	Maize cob	77.85	17.46	2.81	1.88	-	-	-	45.27	5.97	1.09	47.67	-	Gupta et al., 2019
70	Maize stalk	71.9	12.1	8.3	7.6	-	-	-	49.1	6.1	0.7	43.7	-	Zheng et al., 2008
71	Mango peels	78.78	18.54	2.82	-	-	-	-	47.31	5.77	< 0.1	35.78	< 0.1	Arenas et al., 2019
72	Millet husks	80.7	-	18.1	-	33.3	26.9	14.0	42.7	6.0	0.1	33.0	-	Raveendran et al., 1995
73	Musa balbisiana	74.48	21.87	2.16	-	-	-	-	47.37	6.41	2.87	42.09	1.04	Sriram et al., 2018
74	Oat straw	75.9	0.1	17.3	6.7	31.6	49.6	16.6	48.5	6.0	0.4	45.1	-	Ates et al., 2008
75	Olive bagasse	67.2	21.6	4.4	6.8	-	-	-	53.4	7.5	1.7	37.4	-	Demiral et al., 2008
76	Olive husk	64.8	15.9	7.2	-	25.0	24.6	50.4	47.2	5.6	0.8	35.4	0.2	Vassilev et al., 2012., Celma et al., 2007
77	Orange peels	79.02	17.54	3.43	-	-	-	-	46.04	5.54	0.65	36.89	< 0.1	Arenas et al., 2019

78	Palm shell	73.7	18.4	2.2	5.7	-	-	-	53.8	7.2	0.0	36.3	0.5	Yang et al., 2004
79	Parinari fruit shell	78.2	14.5	4.7	2.7	45.4	6.4	30.1	48.0	5.8	2.1	43.5	0.1	Titiloye et al., 2013
80	Parthenium bagasse	79.1	14.8	3.2	3.1	23.0	25.8	30.0	53.5	6.2	0.6	33.4	0.2	Boateng et al., 2009
81	Pea waste	71.6	20.9	7.5	6.45	-	-	-	40.15	5.60	2.90	48.65	< 0.1	Müsellim et al., 2018
82	Peanut crust	72.4	13.2	8.5	5.8	36.5	13.1	24.7	43.8	5.7	1.8	34.0	0.4	Sattar et al., 2020
83	Pearl millet	61.29	0.59	34.51	3.61	48.93	3.16	15.75	43.66	6.30	0.45	49.54	0.06	Laougé et al., 2020
84	Pineapple peels	75.38	19.61	5.21	-	-	-	-	45.79	5.31	< 0.1	33.58	< 0.1	Arenas et al., 2019
85	Potato starch	81.52	6.35	0.18	11.95	-	-	-	39.07	5.54	0.18	42.92	0.16	Meng et al., 2019
86	Quinoa biomass	71.8	-	14.08	7.2	38.70	35.86	18.51	43.80	5.26	0.58	44.15	0.06	Bermejo et al.,2020
87	Quinoa husk	73.3	-	6.79	7.0	31.69	32.60	21.52	41.10	5.39	2.16	39.43	0.26	Bermejo et al.,2020
88	Rape straw	72.50	17.28	5.14	5.08	17.24	24.08	27.64	44.39	6.47	0.54	48.24	0.36	Chen et al., 2017
89	Rice	80.42	16.72	2.86	-	-	-	-	44.28	7.85	1.24	42.99	0.78	Ming et al., 2020
90	Rice hull	58.55	-	12.78	5.92	36.23	18.12	24.65	39.65	5.21	1.02	53.92	0.02	Gan et al., 2018

91	Rice husk	60.6	15.0	12.4	12.1	43.8	31.6	24.6	45.5	4.5	0.5	36.1	0.1	Gu et al., 2013
92	Rice straw	62.4	14.9	15.4	7.2	60.3	20.4	14.1	44.8	5.1	0.9	49.2	0.6	Titiloye et al., 2013., Putun et al., 2004
93	Soaked rice husk	70.5	14.3	13.2	2.0	-	-	-	41.3	5.1	0.4	38.0	0.02	Gu et al., 2013
94	Sorghum bagasse	81.0	1.9	9.5	7.6	41.0	24.0	10.0	68.33	8.64	0.08	22.81	0.14	Cardoso et al., 2011
95	Sugarcane bagasse	79.6	8.1	4.3	16.1	42.7	33.1	24.2	58.1	6.1	0.7	34.5	0.2	Vassilev et al., 2012., Titiloye et al., 2013
96	Sugarcane leaves	77.33	10.67	3.38	5.67	44.00	42.00	17.00	76.83	8.19	0.59	14.39	0.0	Kumar et al., 2019
97	Sunflower stalks	-	-	14.4	12.4	33.0	18.0	23.0	49.9	6.3	0.9	42.9	-	Tröger et al., 2013
98	Sunflower-extracted bagasse	78.4	10.5	6.1	5.0	-	-	-	53.2	7.1	8.0	31.7	-	Yorgun et al., 2001
99	Tobacco stalk	65.5	16.0	9.9	8.5	21.3	32.9	30.2	39.6	4.9	3.2	52.3	0.1	Wei et al., 2006
100	Tomato peel	78.12	12.34	4.87	4.67	-	-	-	55.0	7.9	2.8	34.0	0.3	Prasad et al., 2020
101	Vine shoots	-	-	-	-	14.2	72.5	13.3	48.2	6.9	1.0	-	0.07	Díaz et al.,..

102	Walnut shells	76.45	15.99	0.58	6.98	32.19	26.20	36.89	47.52	6.71	0.21	45.56	-	Özsin et al., 2017
103	Wheat bran	64.66	23.87	3.69	7.78	20.36	38.56	20.24	42.20	7.89	3.64	45.42	0.85	Chen et al., 2017
104	Wheat straw	80.98	7.52	4.09	7.41	35	36.0	18.0	48.24	5.64	0.56	45.55	-	Kumar et al., 2019
105	Wheat straw	74.2	13.0	6.9	5.9	31.2	45.2	18.1	52.9	6.3	0.4	40.4	-	Ates et al., 2008
4	**Seed and seed cakes**													
106	Black cumin seed cake	70.9	19.2	4.8	-	37.1	10.4	26.7	51.2	7.9	5.3	35.1	0.5	Şen et al., 2011
107	Cherry seed (kernel + shell)	77.6	15.7	1.2	5.5	32.1	28.6	29.1	52.5	7.6	4.5	35.3	0.1	Duman et al., 2011
108	Cotton seed cake	79.3	9.7	5.2	5.8	27.6	-	-	52.0	5.9	1.3	40.8	-	Putun et al., 2006
109	Date palm seed	76.6	7.7	10.8	4.9	20	55	23	45.3	5.6	1.0	47.2	0.8	Sait et al., 2012
110	Grape seeds	67.31	22.47	2.55	7.67	13.83	18.71	49.23	51.51	6.39	1.77	40.33	-	Özsin et al., 2017
111	Guarana seed residue	78.34	16.06	5.59	-	7.82	59.37	13.49	41.55	6.44	1.51	44.91	-	Lopes et al., 2018
112	Jatropha cake	72.5	10.9	6.5	10.0	-	-	-	44.4	6.2	4.3	44.5	0.5	Titiloye et al., 2013
113	Jatropha seed cake	43.6	4.4	-	8.1	-	-	-	49.3	6.1	3.4	-	-	Murata et al., 2011

114	Linseed seed	77.0	10.7	5.6	6.7	14.1	-	-	61.0	8.5	2.3	28.2	-	Acikgoz et al., 2009
115	Melon seed husk	79.52	18.99	1.50	7.53	-	-	-	51.80	6.67	0.85	40.28	0.40	Nyakuma et al.,..
116	Moringa cakes	75.1	8.3	6.3	10.4	17.9	1.9	24.9	45.6	6.5	6.5	41.5	-	Titiloye et al., 2013
117	Neem seed	71.0	8.1	4.9	16.0				38.4	8.3	7.5	45.1	0.7	Nayan et al., 2013
118	Pomegranate seed	78.7	14.1	1.8	5.4	26.9	25.5	39.7	49.7	7.5	4.0	38.1	0.7	Uçar et al., 2009
119	Rapeseed residue	81.7	7.9	5.5	4.9	-	-	-	62.1	9.1	3.9	24.9	-	Onay et al., 2006
120	Safflower seed	80.8	11.3	2.2	5.7	27.2	18.6	28.9	60.5	9.1	3.1	27.4	-	Onay et al., 2007
121	Safflower seed cake	83.0	14.0	3.0	6.0	40.0	16.0	26.7	49.5	6.9	3.0	40.6	-	Sensoz et al., 2008
122	Soybean cake	71.6	14.4	5.6	8.4	-	-	-	55.9	6.6	9.3	28.3	-	Uzun et al., 2006
5	**Oil crop and other Agricultural wastes**													
123	Canola residue	81.85	13.32	4.82	6.88	-	-	-	50.22	5.41	3.18	41.19	-	Tahir et al., 2019
124	Castor residue	74.30	9.16	5.40	11.16	38.42	22.40	20.20	43.59	5.56	4.69	46.16	-	Kaur et al., 2018
125	Cocoa pod	68.5	10.4	10.8	10.3	-	-	-	43.9	4.9	2.2	47.3	0.8	Titiloye et al., 2013

126	Coconut coirs	82.8	-	0.9		52.2	28.4	19.4	47.6	5.7	0.0	43.4	-	Raveendranet al., 1995., Vassilevet al., 2012
127	Coconut coir pith	73.3	-	7.1	-	38.1	20.3	41.6	44.0	4.7	0.7	40.4	-	Raveendran et al., 1995., Vassilev et al., 2012
128	Corn stover	64.5	-	7.3	9.4	40.7	26.6	26.0	51.9	5.5	0.8	41.5	0.3	Vassilev et al., 2012., Wang et al., 2011
129	Corn cob	80.7	7.6	2.1	6.3	31.7	31.7	3.4	42.9	6.4	0.6	45.5	0.3	Titiloye et al., 2013
130	Empty fruit bunch	75.61	16.42	5.36	2.88	26.6	26.9	25.4	46.83	6.28	0.66	45.99	0.24	Yiin et al., 2018
131	Olive kernel	73.1	19.8	7.1	-	-	-	-	49	6.7	2.0	34.8	0.3	Sfakiotakis et al., 2018
132	Olive-oil residue	68.8	17.3	5.1	8.8	23.2	35.6	34.9	49.1	5.6	1.1	44.2	-	Uzun et al., 2007
133	Olive residue/waste	70.4	15.3	3.7	10.6	56.0	-	-	44.8	5.1	0.9	49.2	-	Pütün et al., 2005
134	Olive stone	-	-	-	-	25.7	50.5	23.8	49.9	6.1	0.51	-	-	Díaz et al., 2013
135	Palm empty fruit bunch	79.7	8.7	3.0	8.8	-	-	-	48.8	7.3	0	40.2	-	Kim et al., 2013

136	Palm oil	97.32	0.0	2.68	-	-	-	-	76.92	11.88	0.22	10.74	0.24	Qiao et al., 2019
137	Peach stones	72.42	19.84	0.86	6.88	29.50	25.10	39.26	49.28	6.65	0.34	43.73	-	Özsin et al., 2017
138	E. rigida	75.05	15.21	6.72	3.02	19.17	29.50	37.92	54.17	5.70	1.30	38.30	-	Çepeliogullar et al., 2013
139	Soybean straw	75.5	19.8	4.7	1.8	-	-	-	47.8	6.9	1.0	44.3	0.1	Huang et al., 2016
6	**Non woody/Grass**													
140	Bermuda grass	-	-	-	-	37.3	53.2	9.5	-	-	-	-	-	Vassilev et al., 2012
141	Elephant grass	-	-	-	-	31.5	34.3	34.2	-	-	-	-	-	Vassilev et al., 2012
142	Miscanthus	72.9	25.0	2.0	5.7	40.8	29.6	21.9	46.0	6.0	0.5	47.5	-	Cortés et al., 2015
143	Miscanthus-acid hydrolysis residue	42.7	54.5	2.8	3.5	-	-	91.2	65.1	4.5	0.4	28.9	0.2	Cortés et al., 2015
144	Para grass (*Urochloa mutica*)	79.45	-	9.32	7.23	-	-	-	44.73	6.88	0.98	46.84	0.24	Ahmad et al., 2017
145	Reed canary grass	74.9	15.8	3.6	5.7	42.9	28.3	9.4	44.9	6.1	<0.04	39.1	-	Bridgeman et al., 2007

146	Saccharum munja	80.7	10.91	3.89	4.5	35.10	38.90	17.70	63.29	7.84	2.34	27.19	-	Kumar et al., 2019
147	Switchgrass	72.6	16.4	3.1	7.9	39.0	31.9	10.2	44.8	5.7	0.2	38.2	-	Bridgeman et al., 2007
148	Timothy grass	77.9	16.0	1.1	5.0	38.0	33.1	28.9	42.4	6.0	1.0	50.4	0.2	Naik et al., 2010., Vassilev et al., 2012
7	**Aquatic plants and algae**													
149	*C. humicola*	55.6	14.18	26.8	3.42	-	-	-	33.16	5.58	4.8	27.54	2.42	Kirtania et al., 2013
150	*C. pilulifera*	32.2	18.4	38.6	10.5	-	-	-	-	-	-	-	-	Li et al., 2011
151	*Microalgae chlorella*	72.2	15.1	5.9	6.8	9.5	47.5	7.1	6.7	38.6	-	-		Phukan et al., 2011
152	*Polysiphonia elongata*	48.2	12.8	27.45	11.55	-	-	-	35.81	5.93	6.86	51.40	-	Ceylan et al., 2014
153	*Potamogeton crispus*	8.8	60.3	26.3	6.1	-	-	-	-	-	-	-	-	Li et al., 2012
154	*P.telfairiae Harv*	30.6	24.3	33.2	11.7	-	-	-	-	-	-	-	-	Li et al., 2011
155	*P. yezoensis*	36.8	22.1	31.3	9.2	-	-	-	-	-	-	-	-	Li et al., 2011

156	*Reeds*	72.12	13.52	8.47	5.89	43.05	30.68	20.34	42.78	5.17	1.33	50.51	0.21	Li et al., 2019
157	*Saccharina japonica*	68.79	4.1	20.21	6.90	-	-	-	32.89	6.17	0.93	60.01	-	Kim et al., 2012
158	*Sagarssum sp.*	44.5	9.34	36.82	9.34	-	-	-	26.70	4.23	1.35	67.53	0.19	Kim et al., 2013
159	*Sargassum thunbergii*	9.7	55.7	30.8	3.5	-	-	-	-	-	-	-	-	Li et al., 2012
160	*S. patens (marine brown algae)*	55.5	12.4	17.8	14.4	-	-	-	40.2	5.2	2.0	33.9	0.9	Li et al., 2012
161	*T. suecica*	54.0	20.0	20.0	6.0	-	-	-	24.09	3.64	4.12	67.54	0.61	Kim et al., 2014
162	*Typha latifolia*	71.0	19.5	-	-	-	-	-	44.00	6.09	2.45	32.34	0.34	Ahmad et al., 2017
163	*Ulva prolifera*	57.87	7.77	24.46	9.92	-	-	-	37.44	7.01	1.87	50.8	2.88	Ceylan et al., 2015
164	*Wolffia arrhiza*	72.6	-	10.4	4.76	-	-	-	35.55	6.36	5.25	35.87	1.16	Ahmad et al., 2018
8	**Animal waste**													
165	Cattle manure	53.1	4.6	42.3	24.6	32.7	24.5	42.8	21.9	3.6	2.3	20.8	1.1	Vassilev et al., 2012., Wang et al., 2011
166	Horse manure	70.4	11.0	10.5	8.2	6.3	23.8	56.0	43.3	5.9	0.9	49.2	0.8	Chong et al.,

														2019
167	Pork	83.59	12.56	3.76	-	-	-	-	43.56	8.12	9.75	33.85	0.96	Ming et al., 2020
168	Rice	80.42	16.72	2.86	-	-	-	-	44.28	7.85	1.24	42.99	0.78	Ming et al., 2020
9	**Municipal solid waste**													
169	Corrugated cardboard	-	13.1	4.0	-	-	-	13.2	43.24	5.8	0.12	-	-	Sotoudehnia et al., 2020
170	Incense sticks	65.98	13.12	14.82	6.08	-	-	-	35.63	4.51	0.32	38.62	0.023	Wen et al., 2019
171	Kitchen garbage	63.5	8.8	27.8	-	-	-	-	-	4.4	2.3	5.3	0.6	Luo et al., 2010
172	Paper	-	-	-	-	92.5	0.0	7.5	-	-	-	-	-	Vassilev et al., 2012
173	Paper (newspaper)	-	-	-	-	45.6	31.3	23.1	-	-	-	-	-	Vassilev et al., 2012
174	Paper (waste pulps)	-	-	-	-	74.3	17.1	8.6	-	-	-	-	-	Vassilev et al., 2012
175	Plastic	100	0	0	-	-	-	-	-	86.1	13.0	-	0.9	Luo et al., 2010
176	Polystyrene	97.71	0.45	0.98	0.86	-	-	-	90.34	9.06	0.29	0.31	-	Özsin et al., 2017
177	Refuse-derived fuel	-	-	-	-	60.0	20.0	20.0	-	-	-	-	-	Vassilev et al., 2012
178	Sewage sludge	44.6	4.3	44.6	6.5	-	-	-	40.4	6.2	6.7	45.7	1.0	Naqvi et al., 2019

179	Solid leather waste	64.5	10.15	11.36	13.99	-	-	-	34.25	6.10	12.36	35.54	2.23	Guan et al., 2019
10	**Shrub species**													
180	Parthenium argentatum	72.7	12.2	12.5	2.6	-	-	-	45.9	5.1	1.3	32.0	0.6	Boateng et al., 2009
181	Jerusalem artichoke stalk	67.4	13.5	3.34	15.76	63.63	16.56	7.44	45.36	6.11	0.75	47.26	0.52	Li et al., 2019

Note- VM- Volatile matter, FC- Fixed carbon, MC-moisture content, CL-Cellulose content, HEL- Hemicellulose content, LIG-Lignin, C-Carbon, H-Hydrogen, N-Nitrogen, S-Sulfur, O-Oxygen

From Table 3.2 it is seen that values of moisture content, fixed carbon, volatile matter and ash content have varied in the range 0.5 to 16.20, 1.9 to 60.0, 24.66 to 97.30, 0.98 to 44.60, respectively. Similarly the elemental composition has varied as- hydrogen: 3.5 to 86.0%, carbon: 35.63 to 90.34%, nitrogen: 0 to 4.69%, oxygen: 0.31 to 67.56% and sulfur: 0.0 to 2.88%. It is interesting to note that barring a few types of biomasses most have extremely low nitrogen content and Sulfur content.

3.5 Kinetic analysis of thermal degradation of biomass

To convert the abundantly available biomass through pyrolysis to liquid product (bio-oil), syngas and solid (biochar) efficiently it is essential to know the kinetics of thermal decomposition process and the nature of degradation products. Kinetics of pyrolysis plays an important role in the design of pyrolyser (Dhyani et al., 2017; Huang et al., 2011; Mishra and Bhaskar, 2014). The relevant kinetic parameters include activation energy, pre-exponential factor, and reaction order. Thermo-gravimetric and differential thermo-gravimetric analyses (TGA and DTG) are the basic methods used for investigating the thermal decomposition (Ali et al., 2017; Maurya et al., 2016). The TGA analysis can be carried out in two ways- non-isothermal and isothermal. Non-isothermal TGA is extensively used as it is less time consuming. There are two important methods of analyzing the TGA data model-fitting and model free (iso-conversional) methods. Iso-conversional methods are frequently used because these are simple and accurate. The available published information on the kinetic analysis of thermal degradation process is summarized in Table 3.3.

Table 3.3 Kinetic analysis data of different type of biomasses using various kinetic models

S.No.	Biomass	Temperature range (°C or K)	Heating rate (°C or K /min)	Kinetic Models	Average activation energy (kJ/mol)	Pre-exponential factor (min^{-1} or s^{-1})	Higher heating values (HHV) (MJ/ kg)	References
1	Dahlia flowers	25°C to 900°C	5,10 and 20°C/min	KAS, FWO FM, DAEM.	220.12, 229.81, 222.57, 232.78	1.68983×10^{16} min^{-1}, $5.93952\times10^{20}min^{-1}$, $6.30444\times10^{18}min^{-1}$, $7.71732\times10^{16}min^{-1}$	16.52 ± 1.2	Mishra et al., 2020
2	Coffee husk briquettes	Room temperature to 1173K	5,10,15 and 20 K/ min	FM,FWO	233.20, 180.50	-	18.5	Setter et al.,2020
3	Pearl millet	Ambient to 950°C	10, 20, 30, 40,and 50°C/min	FWO, KAS	**Pyrolysis-** 89.63, 83.89 **Combustion-** 57.27, 49.47	**Pyrolysis-**8 to 20.93×10^{8} s^{-1}**,** 4 to 3.30×10^{5} s^{-} **Combustion-**1 to 13.16×10^{8} s^{-1}**,** 0 to 37.3×10^{3} s^{-1}	17.53	Boubacar et al.,2020
4	Corrugated cardboard	30°C to 900°C	5,10,15, 20 and 25°C/min	-	260.44	-	18±0.9	Sotoudehniet al.,2020
5	Pork and Rice husk	30 °C to800 °C	30, 60 and 90°C/min	FM, FWO, KAS	167.54, 170.04, 159.73 and 222.29, 213.14, 203.20	1.153×1016 s^{-1}, 3.081×1014 s^{-1}, 3.172×1013 s^{-1} 1.160×1026 s^{-1},	19.574 18.039	Ming et al., 2020

						1.719×1021 s^{-1}, 2.087×1020 s^{-1}		
6	Tomato peel	Ambient to 1000°C	5,10,15, 20 and 25°C/min	Kissinger, KAS, FWO	112.7, 113.85, 234.27	-	22.50	Prasad et al.,2020
7	Defectivecoffee beans	298.15 to 898.15 K	5,10,15, 20, 25 and 30 K/min	FWO, KAS, FM	**Air-**180.38, 179.75,144.66 **N_2-** 144.3,141.92,151.15	**Air-** 10-33 to 1028 s^{-1}, 10-34 to 1027 s^{-1}, 10-57 to 1034 s^{-1} **N_2-** 10^7 to 10^{13} s^{-1},10^7 to 10^{13} s^{-1}, 106 to 1013 s^{-1}	19.39	Santos et al.,2020
8	Quinoa biomass, Quinoa husk	Ambient to 1000K	10,20 and 40 K/min	-	-	-	16.29 and 17.33	Bermejo et al.,2020
9	Litchi peels	Room temperature to 800°C	10,20,25 and 30°C/min	FWO, KAS	176.4	-	19.12	Liu et al.,2020
10	Bamboo sawdust, Low density polyethylene	30°C to 900°C	5, 10 and 20 °C/min	KAS, FWO, FM	265, 265, 353 207, 230, 175	-	17.04	Alam et al.,2020
11	Rice husk, Corn cobs, Peanut crust, Khushab coal	Room temperature to 950°C	10,20 and 30°C/min	Arrhenius, Coats-Redfern	Arrhenius Model N_2- 102.55,117.93,104.3, 67.79	Arrhenius Model (s^{-1}) N_2- 1.79×10^9, 1.66×10^{10}, 9.25×10^8, 35.6 Air- 4.67×10^{12},	14.5, 17.1 18.3 and 24.3	Sattar et al.,2020

					Air- 131.61,152.31, 112.21, 55.64 Coats-Redfern Model N_2- 80.85, 104.01, 85.28, 59.50 Air- 97.19, 111.5, 91.68, 79.8	2.96×10^{16} ,1.6×10^{10}, 1.96×10^{2} Coats-Redfern Model (s^{-1}) N_2- 9.67×10^{4},5.66×10^{7},1.99×10^{4}, 7.9 Air- 3.3×10^{6},1.3×10^{9},2.01×10^{6}, 43.36		
12	Cherry seed, Poly vinyl chloride (PVC)	25°C to 1000°C	5, 10, 20 and 40 °C /min	FM, FWO, Vyazovkin, DAEM	274.6, 268.5, 266.6, 272.2 and 151.5, 161, 144.7, 159.1	-	-	Özsin et al., 2019
13	Straw, Sawdust, Cellulose	Room temperature to 800°C	20, 30, 40 and 50 °C/min	FWO,KAS, Starink, DAEM	193.3 , 141.05 and 145.65	-	-	Yang et al., 2019
14	Pineapple peels, Orange peels, Mango peels, Rice husk, Pine wood	Room temperature to 700°C	5, 10 and 20°C/min	KAS,FWO, Starink, Vyazovkin, FM, DAEM	185 , 275 , 250 , 170, 180	-	19.02, 18.57, 18.36, 15.30 , 20.37	Arenas et al., 2019
15	Jerusalem	Room	100, 300	FWO,	255, 225.4	**DAEM-** 5.68×10^{25} s^{-}	15.69	Li et al.,

	artichoke stalk Reeds	temperature to 1000°C	and 500 °C/min	DAEM	238.2, 226.6	^{1} **DAEM-** 3.99×10^{20} s^{-1}	16.16	2019
16	Palm oil	30°C to 900°C	50°C/min	Coats-Redfern	275.257	4.252×10^{20} s^{-1}	40.92	Qiao et al., 2019
17	Sewage sludge	25°C to 800°C	5,10 and 20°C/min	Coats-Redfern	-	-	11.5	Naqvi et al., 2019
18	Potato starch, Lignite coal	Ambient to 950°C	10,20 and 40°C/min	KAS	183, 253	-	15.92 18.79	Meng et al.,2019
19	Banana peel	Ambient to 800°C	10, 20, 30 and 40°C/min	FM, KAS, FWO	94±17, 94± 11, 94±2	-	18.87	Tahir et al., 2019
20	Solid leather wastes	30°C to 800°C	5, 10, 15 and 20°C/min	FWO, KAS, Kissinger	391.79, 348.77, 174.09	**FWO and KAS-**10^{19} to 10^{52} s^{-1}, **Kissinger**1.11×10^{15} s^{-1}	14.15	Guan et al., 2019
21	Mosobamboo, Bambusa, Multiplex Black bamboo	30°C to 900°C	10, 40 and 70°C/min	DAEM	201.59 220.49 224.47	1.67×10^{7} to 8×10^{11} min^{-1} 2.7×10^{8} to 5.41×10^{21} min^{-1} 6.79×10^{8} to 5.84×10^{15} min^{-1}	-	Zhao et al., 2019
22	Horse manure	Room temperatu	1, 2, 5 and	FWO,KAS,	199.3, 200.2, 194.6, 149	9.31×0^{18} s^{-1}, 1.8×10^{19} s^{-1},	-	Chong et al., 2019

		re to 900ºC	10ºC/min	FM, Kissinger		3.6×1020 s-1, 3.3×1012 s-1		
23	Incense sticks	30ºC to 900 ºC	5, 10, 15, 20 and 25ºC/min	FWO, KAS, Starink, FM, Horowitz-Metzger	**N_2-** 159.47, 162.48, 162.81, 200 **CO_2-** 130.51, 126.08, 126.63, 145.94	-	12.924	Wen et al., 2019
24	Sugarcane leaves(*Saccharum officinarum* L)	30ºC to 1000ºC	5, 10, 15, 20, 30 and 40ºC/min	Vyazovkin V.AIC, FM, FWO, KAS, Starink, Tang,	215.11, 214.89, 239.58, 226.97, 226.75, 226.94, 226.91	**MLR-** 5.2 to 2.8×10^4 min^{-1}	18.08	Kumar et al., 2019
25	Maize cob	Ambient to 900ºC	5, 10 and 20 ºC/min	FM, FWO, KAS, Starink	197.63, 186.06, 185.39, 185.80	**KAS-** 2.72×10^6 to 1.77×10^{20} s^{-1} **FM-** 1.24×10^5 to 2.76×10^{23} s^{-1}	15.27	Gupta et al., 2019
26	Rice hull, Rice hull-Limestone, Rice hull-Eggshells	323 K to 1173 K	10, 20, 50 and 100 K/min	FWO, DAEM	177.7, 175.4 7.991×10^{16}, 2.939×10^{17} min^{-1} 132.5, 123.3	4.148×10^{12}, 5.803×10^{11} min^{-1} 100.4, 96.1 1.948×10^9, 2.033×10^{10} min^{-1}	-	Gan et al., 2018
27	*Chlorella vulgaris*,	Room temperatu	20, 30, 40 and	FWO, KAS	206.67, 198.94 237.00, 230.92	-	22.82±0.044,	Chen et al., 2018

	Kitchen waste	re to 900°C	50°C/min			18.74±0.040	
28	Rice husk	323 K to 1173K	10, 20, 30 and 50 K/min	Coatsredfern, FM, KAS, FWO,	60.15,190.8, 183.9, 185.7	2.539×10^{4} min^{-1} 1.36×10^{16}min^{-1} 9.81×10^{16}min^{-1} 1.31×10^{17}min^{-1}	15.49	Loy et al., 2018
29	*Wolffia arrhiza*	50°C to 800°C	10, 30 and 50 °C/min	KAS, FWO	168.35,170.37	1.14×10^{10} to 4.46×10^{14} s^{-1} 1.04×10^{10} to 9.59×10^{13} s^{-1}	17.77	Ahmad et al., 2018
30	Empty fruit bunch	40°C to 600°C	10°C/min	Coats-Redfern	-	-	19.64	Yiin et al., 2018
31	Guarana seed residue	25±2°C to 899.15± 0.36 °C	5, 10 and 15°C/min	Vyazovkin	Inert atm. 161.98±8.29 O_2 atm.- 142.70±7.31	-	17.58±0.03	Lopes et al., 2018
32	Castor residue	Room to 900°C	5, 10, 15, 20, 30 and 40 °C/min	FWO, KAS	167.10, 165.86	3.06×10^{8} to 6.26×10^{18} s^{-1} 7.68×10^{7} to 7.92×10^{18} s^{-1}	14.43	Kaur et al., 2018
33	Melon seed husk	Room to 800°C	5, 10 and 20 °C/min	Kissinger, FWO	161.26, 192.96	2.08×10^{10} min^{-1} 2.86×10^{26} min^{-1}	21.78	Nyakuma et al., 2018
34	Yiluo coal, Fermented cornstalk	Ambient to 900°C	5, 15 and 25 °C/min	KAS, FWO	304.56, 303.97 223.92, 225.96	8.82×10^{20} s^{-1} 6.32×1019 s-1	-	He et al., 2018
35	*Musa*	35°C to	5, 10	KAS,	137.94, 136.76,	KAS and FWO-	16.35	Sriram et al.,

	balbisiana	900°C	and 20 °C/min	FWO, FM	133.36	10^2 to 10^{26} min^{-1}		2018
36	Coffee ground residues	Room Temp. to 500°C	5, 10, 15, 25, 50 and 100°C/min	KAS, FWO	Cellulose -214, Hemi cellulose -241 lignin -266	-	23.4	Fermoso et al., 2018
37	Groundnut shell	383 K to 1223 K	10, 20 and 30 K/min	Single reaction, Series reaction, DAEM	-	-	20.2	Collins et al., 2018
38	Pea waste	Room Temp. to 800°C	10, 20, 30 and 40 °C/min	KAS, FWO, Starink, Vyazkovin	212.71, 211.55, 212.94, 212.93	3.34×10^{16} to 1.23×10^{28} s^{-1}	18.42	Müsellim et al., 2018
39	Pine sawdust Sal sawdust and Areca nut husk	25°C to 900°C	5, 10, 15, 20 and 25 °C/min	KAS,FWO, FM,DAEM,	171.66, 179.29, 168.58, 206.62 and 148.44, 156.58, 181.53, 171.63 and 171.24, 179.47, 184.61, 160.45,	**DAEM-** 1.13×10^{12} to 1.02×10^{13} min^{-1} **DAEM-** 25,672,210,682 to 5,028,404,917 min^{-1} **DAEM-**, 33,236,984,933 to 615,862,053.6 min^{-1}	18.44±09, 18.20±09, 18.21±09	Mishra et al., 2018
40	Olive kernel, Municipal solid waste,	40°C to 850°C	5, 10, 20, 30 and	Modified IPR	-	-	20.6 , 15.6 and 14.8	Sfakiotakis et al., 2018

	Sewage sludge		40 °C/min					
41	Chestnut, shells, Cherrystones, Grape seeds	25°C to 1000°C	5, 10, 20 and 40 °C/min	FM, KAS, FWO and Starink	170.3, 175.2, 175.9, 175.5 and 274.6, 272.2, 268.5, 272.2 and 184.2, 186.6, 187.3, 186.9	-	-	Özsin et al., 2017
42	Walnut shell, Peach stones, Polystyrene	25°C to 1000°C	5, 10, 20 and 40°C/min	Kissinger, FM, FWO, KAS, Starink, Vyazovkin	168, 155.3 157.6, 159.2, 158, 153.3 and 188, 146.4, 147.8, 150.1 148.3, 143.5 and 193, 208.6, 209, 210.8 209.4, 204	2.27×10^{14} min^{-1}, 6.65×10^{14} min^{-1}, 6.99×10^{13} min^{-1}	17.836,18.379, 43.576	Özsin et al., 2017
43	Rape straw, Wheat bran	Room temperature to 1073K	10, 20 and 30 K/min	Starink	98.93 and 96.85	6.902×10^{5} s^{-1}, 3.447×10^{6} s^{-1}	-	Chen et al., 2017
44	*Typha latifolia*	Ambient to 1275K	10, 30 and 50 K/min	FWO, KAS	184.58, 182.67	5.53×10^{10} to 3.02×10^{15} s^{-1}, 7.61×10^{9} to 7.93×10^{15} s^{-1}	18.32	Ahmad et al., 2017
45	Cattle manure	Room to 800°C	10, 20, 30,	FM, FWO,	195.49, 182.05, 181.45, 181.22	-	-	Yuan et al., 2017

			40 ,60, 80 °C/min	KAS, Starink				
46	Soybean straw	Room to 1173K	5, 10, 20 and 30 K/min	KAS, FWO	154.15, 156.22	4.26×10^{13} to 5.78×10^{15} min^{-1}, 4.89×10^{13} to 1.09×10^{16} min^{-1}	-	Huang et al., 2016
47	Pine wood	-	-	Single step first order	21.305	18.9×10^{3} s^{-1}	20.58±0.12	Johansen et al., 2016
48	Agricultural residue (cotton, wheat, rice, corn)	Room to 700°C	10, 20 and 30 °C/min	CK-TPR	221.7	10^{11} to 10^{16} s^{-1}	-	Wang et al., 2016
49	Sawdust	Room temperature to 800°C	140, 160, 180 and 200 °C/min	KAS, FWO	**O_2-** 75.56, 82.05 **N_2-** 81.38, 87.96	-	16.37	Jaroenkhasemmeesuk et al., 2016
50	Para grass (*Urochloa mutica*)	Room temperature to 1000°C	10, 30 and 50 °C/min	KAS, FWO	163, 175	1.42×10^{7} to 2.9313×10^{18} s^{-1}, 2.55×10^{8} to 2.26×10^{19} s^{-1}	15.04	Ahmad et al., 2016
51	Rice straw	298K to 973K	5, 10 and 15 K/min	FWO, KAS, Kissinger	192.66, 193.60, 172.62	1.287×10^{22} min^{-1}, 6.887×10^{15} min^{-1}, 1.456×10^{11} min^{-1}	-	Kongkaew et al., 2015
52	Empty fruit	30°C to	10, 20,		77.475	62.2 to 1.50×10^{11}	_	Ninduangdee et

	bunch Palm kernel shell	900°C	30 and 40 °C/min	Coats-Redfern	84.475	min^{-1} 0.835 to 6.0×10^{12} min^{-1}		al., 2015
53	Miscanthus, Miscanthus acid, hydrolysis residue	50°C to 900°C	2.5, 5, 10, 17 and 25 °C/min	KAS,FWO, Vyazovkin	142.5 , 288	5.6×10^{10} to 3.9×10^{13} min^{-1} 2.1×10^{16} to 7.7×10^{25} min^{-1}	18.17 , 25.65	Cortés et al., 2015
54	Cotton stalk, Corn straw	Ambient to 1173K	20 K/min	Two dimensional diffusion model	83.45 , 54.5	1.69×10^{4} min^{-1} 3.5×10^{3} min^{-1}	-	Xianjun et al., 2015
55	Eucalyptus leaves, Eucalyptus bark, Eucalyptus sawdust	Room to 800°C	10 and 40 °C/min	Continuous DAEM , Modified discrete DAEM	141.15, 215.65 149.21, 264.76 175.79, 150.66	1.15×10^{10} s^{-1} , 4.84×10^{13}-6.12×10^{22} s^{-1} 4.34×10^{10} s^{-1} , 1.91×10^{12}-4.51×10^{25} s^{-1} 7.44×1012 s-1 , 63.43-4.36×10^{11} s^{-1}	-	Chen et al., 2015
56	*Ulva prolifera*	Ambient to 1000°C	5, 10 and 20 °C/min	DAEM	141.34±8.71	1.52×10^{12} to 4.36×10^{15} s^{-1}	16.54	Ceylan et al., 2015
57	Pine wood Olive kernel Thistle flower Corncob	50°C to 1000°C	10,13, 16, 19, 22,25,	DAEM	165.0, 162.2, 154.5 183.5	1.6×1012 s-1 4.1×1012 s-1 2.8×1011 s-1 2.3×1014 s-1	-	Verdugo et al.,2015

			30, 35and 40 K/min					
58	*Chlorella sp.*, *T. suecica*	Ambient to 600^{o}C	5, 10 and 15 ^{o}C/min	FWO, KAS	298.42, 301.70 99.69, 94.77	1.81×10^{21} to 2.1×10^{30}min^{-1}, 2.91×10^{16} to2.83×10^{23} min^{-1} 3751.83 to 1.51×10^{14}min^{-1}, 1043.14 to 1.59×10^{8} min^{-1}	-	Kassim et al., 2014
59	Pinyon pine	20^{o}C to 900^{o}C	5, 10, 15 and 20 ^{o}C/min	Differential method	102.1	**Pure N_2-** 1.92×10^{7} min^{-1}	18.94	Kim et al., 2014
60	Palm kernel shells, Palm mesocarp fibers, Coffee husk, Corn cob, Peanut shell	Room temperature to 900^{o}C	5 K/min	Diffusion and chemical reaction mechanism	-	-	19.5 , 22.7 16.3, 16.1, 18.1	Jeguirim et al., 2014
61	Corn cob, Tree root, Bagasse	Room temperature to 850^{o}C	20^{o}C/min	DAEM	164.475 , 181.6 174,75	-	-	Meng et al., 2013
62	Palm fiber	30^{o}C to 800^{o}C	5, 10, 15 and 20 ^{o}C/min	Differential method	440.85	0.0015 to 0.1202 min^{-1}	18.08	Ly et al., 2013

63	C. *humicola* *Yallourn* coal	Ambient to 1000ºC	5, 10 and 20 K/min	DAEM	189.99 , 219.94	2.4359×10^{16} s^{-1} 1.649×10^{16} s^{-1}	13.6, 25.9	Kirtania et al., 2013
64	*Sagarssum sp.*	30ºC to 800ºC	5, 10, 15 and 20 ºC/min	Lumped kinetic model	344.55	1015-1042 s-1	10.10	Kim et al., 2013
67	Corn straw, Rice husk	298K to 1073K	5, 10, 20 and 40 K/min	Starink method	129 79	-	-	Gai et al., 2013
68	*Sargassum thunbergii*, *Potamogeton crispus*	Ambient to 800ºC	10, 30 and 50 ºC/min	FWO, KAS, Popescu	185.4, 185.6, 196.8 145.3, 143.2, 131.7	-	-	Li et al., 2012
69	Pinewood sawdust	Room Temperature to 800ºC	15ºC/min	-	-	-	19.8	Amutioet al., 2012
70	Poplar wood	298K to 973K	2,5, 10 and 15K/min	Kissinger, FWO, KAS	153.92, 158.58, 157.27	2.14×10^{12} min^{-1} 7.96×10^{13} min^{-1}, 1.69×10^{13} min^{-1}	-	Slopiecka et al. 2012
71	*Saccharina japonica*	30ºC to 800ºC	10, 15 and 20 ºC/min	Lumped kinetic model	181.66	107-1022 s^{-1}	12.11	Kim et al., 2012
72	Corn cobs, Sugarcane bagasse	Room temperature to 700ºC	10, 20, 30, 40 and 50 ºC/min	FM	102.5 , 197.5	-	17.2 , 17.5	Aboyade et al., 2011
73	Tobacco	373K to	5, 10,	Ozawa,	103.94, 135.95	-	-	Cardoso et al.,

	waste, Sorghum bagasse	1173K	15, 20 and 25 K/min	Starink	120.01, 148.91		2011
74	Cardoon leaves, Cardoon stems	25ºC to 850ºC	5, 10, 20 and 30 ºC/min	KAS, FWO	350.07, 242.01 and 224.51, 229.70	2.94×10^{31} to 4.23×10^{31} s^{-1} , 6.46×10^{28} to 9.44×10^{28} s^{-1} 1.4×10^{19} to 2.3×10^{19} s^{-1} , 4.27×10^{17} to 6.51×10^{17} s^{-1}	17.9 21.5	Damartzis et al., 2011
75	Olive residue Sugarcane bagasse	300K to 900K	2, 10, 20 and 50 K/min	FWO, Vyazovkin	178.25, 188.5 199.5, 210	-	-	Ounas et al., 2011

3.6 Pyrolysis of biomass

Using the basic information obtained through TG/DTG analyses several workers have investigated the pyrolysis behavior of some biomasses in laboratory scale fixed and fluidized bed units. The operating conditions and results of available published work on batch pyrolysis studies are summarized in Table 3.4 and discussed below.

Biswas et al (2018) studied the pyrolysis of rice straw using a fixed bed reactor under CO_2 atmosphere at temperatures ranging from 300 to 450°C to study the effect of CO_2 and temperature. The maximum oil yield (34.5 wt. %) was obtained at 400°C. They found that the yield of solid residue decreased while that of the gas increased with temperature from 300 to 450°C. The results showed that both the temperature and reaction atmosphere had an influence on the product distribution and nature of the products. The main compounds observed in the bio-oil were phenol, 2-ethyl-phenol, 2-methyl-Phenol, 2-methoxy-phenol, 2-methoxy-4-vinylphenol, 2, 6-dimethoxy-Phenol. Liquid product obtained from pyrolysis of rice straw showed high proton percentage from region 1.5-3.0 ppm; around 31-34.5% of protons resonate in this region indicating that the liquid products have high aliphatic proton content. Bio-oil produced at 400°Cindicated the higher proton percentage of 34.5% in this region (1.5-3.0 ppm), higher than the other conditions.

Biswas et al (2017) studied the pyrolysis of conventional biomass in fixed bed reactor at different temperatures of 300, 350, 400 and 450°C. Agricultural residues such as corn cob, wheat straw, rice straw and rice husk showed that the optimum temperatures for these residues are 450, 400, 400 and 450°C respectively. The maximum bio-oil yield in case of corn cob, wheat straw, rice straw and rice husk were obtained as 47.3, 36.7, 28.4 and 38.1

wt%, respectively. The effects of pyrolysis temperature and biomass type on the yield and composition of pyrolysis products were investigated. All bio-oil contents were mainly composed of oxygenated hydrocarbons. The higher percentages of phenolic compounds were observed in the corncob bio-oil than other bio-oil.

Park et al (2014) studied the slow pyrolysis of rice straw in the temperature range of 300–700ºC to characterize the yields and detailed composition of bio-char, bio-oil and non-condensable gases. Bio-char was analyzed for pH, microscopic surface area and pore volume distribution. Although the mass yield for the organic fraction was only about 25% above 500ºC, biochar was the primary product of pyrolysis containing 40% of energy and 45% of carbon from the straw. The utilization of by-products (bio-oil and gases) as energy resources is essential, since the sum of energy yield was about 60%. The gases could be burned to produce the heat for an auto-thermal pyrolysis process, but the heat balance was significantly influenced by the moisture content of the raw material.

Balagurumurthy et al (2015) studied the pyrolysis of rice straw under hydrogen atmosphere at 300, 350, 400 and 450ºC and pressures of 1, 10, 20, 30 and 40bar and in nitrogen atmosphere, experiments have been carried out at the same temperatures. It has been observed that the optimum process conditions for hydro pyrolysis are 400ºC and 30 bar pressure and for slow pyrolysis, the optimum temperature is 400ºC. The bio-oil has been characterized using GC–MS, ^{1}H NMR and FT-IR and bio-char using FT-IR, SEM and XRD. The bio-oil yield under hydrogen pressure was observed to be 12.8 wt. % (400ºC and 30 bar) and yield under nitrogen atmosphere was found to be 31 wt. % (400 ºC). From the product characterization, it was found that the distribution of products is different for hydrogen and nitrogen environments due to differences in the decomposition reaction mechanism. Table 3.4 summarizes the available published information on batch pyrolysis of biomass. Nature of biomass, type of pyrolysis operating condition and observed optimum temperature and yield are listed in the table.

Table 3.4 Various operating parameters of biomass pyrolysis

Biomass	Reactor	Operating condition of pyrolysis	Optimum condition of temperature (°C)	Optimum product yield (wt.%)	References
Rice straw	Fixed bed reactor	Temperature range, 300-450°C, under CO_2 environment	400	34.50	Biswas et al (2018)
Corn cob, Wheat straw, Rice straw and Rice husk	Fixed bed reactor	Temperatures 300, 350, 400 and 450°C	450, 400, 400 and 450	47.3, 36.7, 28.4 and 38.1	Biswas et al (2017)
Rice straw	Fixed bed reactor	Temperature range, 300‑700°C	500	25%	Park et al., 2014
Rice straw	Fixed bed reactor	Under hydrogen and nitrogen atmosphere at 300, 350, 400 and 450°C and pressures of 1, 10, 20, 30 and 40bar	400 and 30 bar pressure	Hydrogen 12.8 wt. % (400°C and 30 bar) and yield under nitrogen atmosphere 31 wt. % (400°C)	Balagurumurthy et al (2015)
Glycerol	Rotary kiln reactor	600°C	600	40wt.%	Bartocci et al (2018)
Acid treated peanut shell	Fixed bed reactor	400, 500 and 600°C	500	42 and 33wt.%	Messina et al (2017)
Cassia siamea seed	Fixed bed	temperature range of	550	50.21%	Chatterjee et al (2018)

	reactor	450°C and 575°C at a heating rate of 50°C min^{-1}.using nitrogen gas at a flow rate of 40 mLmin^{-1}			
Mesuaferrea seed cover (MFSC) and *Pongamia glabra* seed cover (PGSC)	Fixed bed reactor	temperature range of 350‑650ºC	550at heating rate of 40ºC/min	28.5 wt.% and 29.6 wt.% for PGSC and MFSC respectively	Bordoloi et al (2015)
Rapeseed oil cake	Fixed bed reactor	Particle size range ≤0.5 mm, 500°C and 100 mL/min (N_2) carrier gas flow rate.	500	38.7%	David et al (2018)
Cherry pulp	Fixed bed tubular reactor at	Five different temperatures (400, 500,550, 600 and 700ºC) and three different heating rates (10, 100 and 200ºC/min)	400 heating rate of 10ºC/min, nitrogen flow rate of 100 cm^3/min, mean particle size of 1.18 mm	Char yield was31.25%	Pehlivan et al (2017)
Neem seeds (*Azadirachta Indica*)	Semi-batch reactor	temperature range of 400‑500ºC and at a heating rate of 20ºC/min	475	Bio-oil 38%	Nayan et al (2013)
Non-edible seed Neem (*Azadirachta indica*)	Fixed bed reactor	optimum conditions (500°C temperature, 80°Cmin^{-1} heating rate, 0.5 mm particle size and 80 mL min^{-1} nitrogen gas flow rate)	-	Liquid yield 49.53 wt. %	Mishra et al (2018)

3.7 Operating parameters of biomass pyrolysis for bio-oil yield

Various parameters such as temperature, heating rate, inert gas flow rate, biomass particle size etc. which affect the bio-oil yield. Several workers have studied the effects of these parameters on product yield. These are briefly discussed below.

3.7.1 Pyrolysis temperature

Temperature is one of the most important and necessary parameters for pyrolysis. It provides the required heat energy for thermal decomposition of component of biomass. The pyrolysis process becomes more efficient with increase in temperature because the extra energy is available for breaking the bonds of the constituents of biomass. In general it is reported by various researchers that the temperature to obtain higher liquid yields ranges from 450°C-550°C, on the other hand these range of temperature is no longer for each biomasses used.

Tsai et al (2007) reported that the yield of bio-oil from rice husk pyrolysis increased from 11.26% to 35.92% when the temperature was increased from 400°C to 500°C. However, the yield still increased with temperature at a slow rate and reached up to 40% at 800°C. Lazzari et al. (2016) studied the pyrolysis of mango seed almond in the temperature range of 450°C to 650°C. The maximum bio-oil yield (38.8%) was found to be at higher temperature of 650°C. Though most workers have reported that increase in bio-oil yield with increasing temperature, however some have reported that beyond on optimum temperature the yield decreases as secondary reaction lead to increased gas formation.

3.7.2 Effect of heating rate

Tsai et al (2007) studying the pyrolysis of rice husk in the fixed bed reactor, changed the heating rate from 100°C/min to 500°C/min and the oil yield reached its maximum at the heating rate of 200°C/min and remained constant at higher rates. Putun et al. (2007) compared the product distributions of bio-oil from tobacco residues in the fixed bed reactor. The maximum oil yield was 27% with the heating rate of 7ºC/min. Increasing heating rate up to 300ºC/min caused 10% increase in the bio-oil yields. Sensoz et al (2006) in the lower heating rate of 10 ºC/min, the bio-oil yields were about 3.4–8.4% higher than those at 50ºC/min for the olive bagasse pyrolysis in the fixed bed reactor. These results showed that the effect of the heating rate on the pyrolysis process depends on other parameters of the process. Uzun et al. (2006) obtained an accentuated reduction of the water content in the bio-oil with the increase in the heating rate, obtaining a better quality bio-oil. Fast heating probably inhibits secondary dehydration reactions causing a reduction in water content in the bio-oil. The oxygen content in the pyrolysis liquid product is also reduced at higher heating rates.

3.7.3 Effect of carrier gas flow rate

Flow rate of inert gas during the pyrolysis of biomass is important parameters which affects the yield of the bio-oil and other products of pyrolysis. It alters the residence time of vapor formed inside the reactor during pyrolysis, affecting the vapors start secondary reactions of thermal cracking, depolymerization, and condensation of the char residue, which leads to a decrease in bio-oil yield (Akhtar et al., 2012). A higher inert gas flow in the process leads to a shorter vapor residence time in the hot pyrolysis zone, which resist the formation of secondary reaction and consequently increase in bio-oil yield. Pattiya et al. (2012) observed a higher in liquid yield with increasing gas flow from 1L/min to 1.5L/min, but an increase to 3L/min did not affect the yield. Islam et al. (2010) studied the effect of vapor residence time in the sugarcane bagasse pyrolysis in fixed bed reactor and observed that increase of vapor residence time from 5s to 20s decreases the liquid and char yields while the gas yield increases. Several studies that analyzed the effect of N_2 flow in the pyrolysis showed that the increase in the flow of inert gas causes an improvement in the bio-oil yield. However, a very high gas flow reduces the liquid yield due to complete condensation of the vapors, which increases the gas yield in the process and, besides that, part of the biomass can also be swept out of the reactor before pyrolysis is completed (Biradar et al., 2014).

3.7.4 Effect of particle size

Heat transfer during pyrolysis is slow because the biomass is a poor conductor of heat. Thus, particle size influences the bio-oil yield produced, and it is critical in minimizing heat transfer problems in the process (Akhtar et al., 2012). Abnisa et al. (2011) observed an opposite effect in palm shell pyrolysis, where increasing particle size from 0.5 mm to 2 mm caused an increase in liquid production of 69.6 wt.%. Garg et al. (2016) reported that a reduction in the liquid yield was observed with increase in particle size of babool seeds in fixed bed reactor. The maximum bio-oil yield (~32%) was obtained with particle diameter < 0.4 mm. In general, smaller particles are preferred for pyrolysis due to their faster and uniform heating. However, microscopic particles can reduce the liquid yield in the pyrolysis because the decomposition of the biomass occurs very quickly with sufficient time for secondary reaction between vapor products and consequently increase in the gas yields and a decrease in the liquid and char yield (Ishlam et al., 2010). Also, a very fine particle can be removed from the reaction zone before the completion of the process (Pattiya et al., 2012).

3.7.5 Effect of the reaction time

Reaction time also influences the product distribution of the pyrolysis process. Reaction time of the pyrolysis process is the time where the process is continued at constant desired temperature. In batch (fixed bed reactor) pyrolysis process the reaction time should be sufficient in order to achieve the desired product. With longer reaction time, secondary reactions of pyrolysis vapors such as carbonization, gasification and thermal cracking cause a lower bio-oils production (Bartoli et al., 2016). In Açıkalın et al. (2014) pyrolyzed pistachio shell at holding time of 10 to 50 min. The liquid product yield was slightly affected by the reaction times ranging from 10 min (52.96%) to 20 min (53.08%). Further increments of reaction time resulted in a continuous decrease, and the liquid yield dropped to 50.13% in 50 min. Abnisa et al. (2011) conducted experiments at reaction time ranging from 30 to 150min. The bio-oil yield increased continuously with reaction times from 30 min to 60 min, and after 60 min the liquid yield remained continuous. However, the longer the reaction time, the higher the cost of the process.

3.8 Process Optimization using RSM software

Converting biomass into bio-oil makes it more efficient in many applications. Therefore, optimization by maximizing the desired product quality and quantity is an important issue for engineers while paying attention to minimizing costs and environmental concerns. In most of the earlier reported batch and continuous mode studies, effect of individual parameters has been reported while maintaining other process parameters constant at unspecified levels. This approach does not depict the combined effect of all process parameters. It is also time consuming and requires a number of experiments to determine optimum levels, which may be unreliable. These limitations of a classical method can be eliminated by optimizing all the process parameters collectively by statistical experimental design such as response surface methodology (RSM). The most important aspect in this optimization study is to gain the highest amount (quantity) of bio-oil by pyrolysis process.

Abnisa et al (2011) studied that pyrolysis of palm shell waste to produces bio-oil. The effects of several parameters on the pyrolysis efficiency were tested to identify the optimal bio-oil production conditions. The tested parameters include temperature, N_2 flow rate, feedstock particle size, and reaction time. The experiments were conducted using a fixed-bed reactor. The efficient response surface methodology (RSM), with a central composite design (CCD), were used for modeling and optimization the process parameters. The results showed that the second-order polynomial equation explains adequately the non-linear nature of the modeled response. An R^2 value of 0.9337 indicated a sufficient adjustment of the model with the experimental data. The optimal conditions were found to be at the temperature of 500°C, N_2 flow rate of 2L/min, particle size of 2 mm and reaction time of 60 min and yield of bio-oil was approximately obtained 46.4 wt %.

Kılıc et al (2014) optimized the experimental conditions for obtaining the highest bio-oil yield from *Euphorbia rigida (E. rigida)* by fast pyrolysis using response surface methodology (RSM) based on the central composite design (CCD). Experimental design was applied to optimize the reaction temperature, heating rate, and nitrogen gas flow rate which are the important parameters effecting the pyrolysis process. From the analysis of variance (ANOVA), the most influential factor of each experimental design response was identified and an empirical model in terms of factors was derived. The optimum conditions were found to be at reaction temperature of 600°C, heating rate of 200°C/min, and nitrogen flow rate of 100mL/min. Maximum bio-oil yield was obtained as 35.3% under optimum conditions.

Pinto et al (2013) studied the influence of experimental conditions on product yields formed by waste mixtures pyrolysis, using response surface methodology (RSM). Experiment Factorial Design was used for the optimization of reaction time, temperature and initial pressure to maximize the yield and composition of liquid products for the waste mixture studied. According to the model, the production of total pyrolysis liquids (including those obtained by solvent extraction) was maximized when the following conditions were used: reaction temperature of 350°C, reaction time of 30 min and initial pressure of 0.2 MPa, leading to liquid yield of 91.3% (w/w).

3.9 Products of biomass pyrolysis

3.9.1 Liquid product (Bio-oil)

The liquid fraction of biomass pyrolysis is termed as bio-oil or bio-crude. It is a multi-component mixture of water and different size molecules derived from depolymerization and fragmentation of the three main component of biomass such as cellulose, hemicellulose and lignin.Cellulose is the largest component of lignocellulosic materials, followed by hemicellulose and lignin. Cellulose usually exists as long thread like fibres called micro fibrils. This nature of bonding allows the micro fibril structure to develop strong inter-molecular and intra-molecular hydrogen bonding. Micro fibrils are usually embedded on a matrix that contains hemicelluloses and lignin. Hemicellulose is a branched polysaccharide comprises of different sugar monomers such as glucose, xylose, mannose, galactose and arabinose and uronic acids. Unlike cellulose, they do not form micro fibrils. But, they can form hydrogen bonds with the cellulose and lignin and hence they are referred as “cross linking glucans”. Lignin is the cementing material that provides elasticity and mechanical strength to the wood. It is a phenolic macromolecule with a high degree of cross linking between the phenyl propane units.

This cross linking makes lignin more thermally stable than hemicellulose. Lignin can be regarded as a group of amorphous, high molecular-weight, chemically related compounds. Various compounds are formed from cellulose, hemicellulose and lignin during pyrolysis. For example, guaiacols and syringols are formed from the lignin fraction, whereas the miscellaneous oxygenates, sugars, and furans form from the cellulose and hemicellulose biomass fraction. The esters, acids, alcohols, ketones, and aldehydes probably form from the decomposition of the miscellaneous oxygenates, sugars, and furan. Therefore the elemental composition of bio-oil and petroleum derived fuel is different.

3.9.2 Water

The water content of bio-oil is as high as 15–30 wt.%, which is derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. Most of the water in pyrolytic oil formed from the decomposition of cellulose and hemicellulose; however some additional water is formed from lignin decomposition. Formation of water could be attributed to the dehydration of lignin aliphatic hydroxyl groups. The presence of water content has both negative and positive effects on the bio-oil properties. The water content lowers the heating value and flame temperature; on the contrary, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine.

3.9.3 Oxygen

The oxygen content of bio-oils is usually 35–40%, distributed in more than 300 compounds depending on the resource of biomass and severity of the pyrolytic processes (temperature, residence time and heating rate). The presence of oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content cause the lowering of energy density (heating value) than the conventional fuel by 50% and due to large amounts of oxygenated components present, the oil has a polar nature and does not mix readily with hydrocarbons.

3.9.4 Acidity

Bio-oils comprise substantial amounts of carboxylic acids, such as acetic and formic acids, which lead to low pH values of 2–3. Acidity makes bio-oil very corrosive to common construction materials and extremely severe at elevated temperature, which imposes more requirements on construction materials of the vessels and the upgrading process before using bio-oil in transport fuels.

3.9.5 Heating value

The properties of bio-oils depend on factors, such as biomass feedstock, production processes, reaction conditions and collecting efficiency. Usually the bio-oils from oil plants have a higher heating value compared with those of straw, wood or agricultural residues. Das et al (2014) conducted pyrolysis experiments on a sample of cashew nut shell and obtained bio-oil with a heating value of 40 MJ/kg and a maximum yield of 40%. Lu et al (2015) produced bio-oil from rice husk with a heating value of 16.5 MJ/kg.

3.9.6 Ash

The presence of ash in bio-oil can cause erosion, corrosion and knocking problems in the engines and the valves and even deterioration when the ash content is higher than 0.1 wt.%. However, alkali metals are problematic components of the ash. More specifically, sodium, potassium and vanadium are responsible for high temperature corrosion and deposition, while calcium is responsible for hard deposits. Acid washing of biomass feedstock prior to pyrolysis can decrease the ash content and result in a better quality bio-oil. For example Abdullah et al (2013) conducted pyrolysis experiment on empty fruit branches and observed that the bio-oil yield can be increased from 50 wt. % to 72 wt. % by washing pretreatment. Eom et al (2017) reported that the demineralization of biomass increases the maximum degradation rates of biomass. They conducted experiments with poplar wood powder which were treated with distilled water, tap water, HCl and HF and found that the maximum degradation rates for washed biomass increased in the order HCl treated biomass (1.55%/°C) > Deionized H_2O treated biomass (1.23%/°C) > Tap H_2O-treated biomass (1.19%/°C) > HF-treated biomass (1.15%/°C).

3.9.7 Gases

Thermal decomposition of biomass produces both condensable and non-condensable gases (primary gas). The vapors which are made of heavier molecules, condense upon cooling, produces the liquid part of pyrolysis. The non-condensable gas mixture contains lower molecular weight gases for example carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene, minor amounts of higher gaseous organics and water vapor. It is reported in the literature that CO_2 releasing is mainly caused by primary pyrolysis, while CO and CH_4 released during secondary pyrolysis. The hemicellulose shows higher CO and CO_2 while higher CH_4 release is from lignin.

3.9.8 Solid product (Char)

The solid product of pyrolysis is termed as char. It is another important product of pyrolysis process. The char can be used within the process to provide the process heat requirements by combustion. The fresh char is pyrophoric i.e. it spontaneously combusts when exposed to air so careful handling and storage is required. This property deteriorates with time due to oxidation of active sites on the char surface.

3.10. Catalytic pyrolysis

Liquid upgraded bio-oils derived from biomass sources are an attractive substitute for fossil derived fuels (Wildschut et al., 2010). Pyrolysis is an effective technology for the conversion of biomass into liquid bio-oil. Pyrolysis involves the rapid heating of biomass to the temperature range of 400-600°C in an oxygen-free atmosphere (Cheng et al., 2015). Bio-oil cannot be used directly as a transportation fuel for high-speed combustion engines due to the high oxygen content (35‐ 40 wt% dry basis), high water content (up to 30 wt%) and the presence of corrosive organic acids compounds (up to 10 wt%) Fisk et al (2009). Bio-oil upgrading is required before it can be used as fuel (upgraded bio-oil). The upgraded bio-oil (biofuel) is defined as bio-oil with higher quality (lower water content, improved pH and carbon content, higher heating value and improved hydrocarbons content).

Cheng et al (2017) studied the up gradation of bio-oil using catalyst. Non-sulfide catalysts are effective in bio-oil hydrodeoxygenation due to low cost and high activity. Ni-Zn/Al_2O_3 catalysts were first used to selectively produce upgraded bio-oil through bio-oil hydrodeoxygenation. Upgrading of pine sawdust bio-oil to upgraded hydrocarbon bio-oil was performed using a series of Ni and/or Zn loaded Al_2O_3 catalysts. The crystalline structure of Al_2O_3 was maintained after Ni and/or Zn loading, but BET surface area and total pore volume of Ni-Zn/Al_2O_3 catalysts decreased significantly compared to Al_2O_3 support. Bimetallic Ni-Zn/Al_2O_3 catalysts were more effective than monometallic Ni/Al_2O_3 or Zn/Al_2O_3 catalyst. Bimetallic 15%Ni-5% Zn/Al_2O_3 catalyst generated the highest upgraded bio-oil yield of 44.64 wt% and produced the upgraded bio-oil with the highest hydrocarbon content of 50.12%. Physicochemical properties of upgraded bio-oils including heating value, water content and pH were significantly improved in comparison with raw bio-oil.

Messina et al (2017) studied the in-situ catalytic pyrolysis of peanut (*Arachis hypogaea*) shells using modified clinoptilolite. Two solid catalysts obtained from natural clinoptilolite were used: one which retained most of the native cations and another one subjected to ion exchange treatment to develop Brønsted acid sites. These catalysts were characterized using different techniques, such as scanning electron microscopy with X-ray microanalysis, Fourier transform infrared spectroscopy by pyridine adsorption, and nitrogen sorptometry. Assays in a bench scale installation based on a fixed bed reactor were conducted at 500°C and the yields of the three kinds of pyrolysis products (bio-oil, bio-char and gases) were determined. Both catalysts reduced the oxygen content of the bio-oil and improved its high heating value. On the other hand, catalytic pyrolysis caused a slight reduction in bio-oil production at the expense of an increase in gases generation. The catalyst subjected to ion-exchange performed better than the native form as less water was generated in the catalytic cracking.

Mishra et al (2018) studied the thermo-catalytic pyrolysis of non-edible neem seed. The physiochemical characterization confirmed the seed's bioenergy potential. Thermal and catalytic pyrolysis were carried out at optimum conditions (500°C temperature, 80°Cmin^{-1} heating rate, 0.5mm particle size and 8 mL min^{-1} nitrogen gas flow rate) which produced maximum liquid yield (49.53 wt. % at thermal and 54.06 wt. % and 52.08 wt. % for K_2CO_3 and Zeolite respectively at biomass/catalyst ratio 8:1). The comparative study of thermal and catalytic pyrolytic liquid confirmed that the yield as well as fuel properties of the pyrolytic liquid were enhanced with the use of catalysts. It was also noticed that the energy content of gases increased with increasing pyrolysis temperature. Further, with increase in pyrolysis temperature, the amounts of hydrogen and hydrocarbons increased significantly, but at the same time, the formation of carbon dioxide reduced.

Cheng et al (2017) used non-sulfide Fe-Co/SiO_2 catalysts to upgrade bio-oil using hydrodeoxygenation (HDO) process. A series of Fe-Co/SiO_2 catalysts with different Fe/Co mole ratios were prepared, characterized and evaluated. The Fe and/or Co loading did not change SiO_2 crystalline structure. The Fe and/or Co increased the amount and strength of Fe-Co/SiO_2 catalyst acidity. Physicochemical properties of upgraded bio-oils produced using Fe-Co/SiO_2 catalysts such as water content, total acid number, viscosity and higher heating values improved in comparison to non-catalytically produced bio-oil. Bimetallic Fe-Co/SiO_2 catalysts resulted in better HDO performance than monometallic Fe/SiO_2 or Co/SiO_2 catalysts. This was due to the synergistic effect of Fe and Co happening on the

SiO_2 support. Fe-Co/SiO_2 catalyst having medium amount of acidity was more effective for bio-oil upgrading. The highest hydrocarbons content produced using Fe-Co/SiO_2 catalyst was 22.44%. The mechanism of bio-oil HDO on Fe-Co/SiO_2 catalysts is also proposed.

From the available published information summarized in Tables 3.2 to 3.3 and discussed above it is seen that a considerable volume of basic information generated through TG, DTG and DSC analysis of various types of biomasses as well as non-biological carbonaceous materials is available in the literature. The pyrolysis of biomass in lab-scale or pilot scale units is relatively less studied, though it is of immense importance for generating requisite data on the effect of various operating parameters such as biomass particle size and rate of its feeding in the pyrolyser, residence time of biomass in the pyrolyser, heating rate and temperature range, and rate of removal of pyrolysis products.

It is also interesting to note that in spite of India being an oil importing country and its focus on harnessing energy from renewable resources is more or less limited to the use of rice husk and bagasse as fuel in place of coal in sugar mills, distilleries and some other industries. The use of agro-waste biomass like stalk and straw biomass is largely being promoted through the low level technology like briquetting. A large volume of stalk and straw and other similar biomasses is being burnt in fields leading to air pollution and loss of soil fertility and destruction of soil microbial population. It is seen from the literature review that since 1978 Indian researchers also have started work in the area of biomass gasification, pyrolysis and torrefaction and research results on the thermal degradation behavior of agro-waste biomasses like wheat straw, rice husk, maize, bajra stalk, cotton, coconut etc. are available in the literature. But the potential of several of such waste biomass, though available in large amount, is yet to be assessed. The present work has been planned to fill this knowledge gap.

3.11 Objectives of Present Work

Based on the critical assessment of the available literature and information pertaining to the availability of agricultural and industrial waste biomasses and the research gap in the area, following objectives have been set for the present work:

1. Physicochemical characterization of selected biomass such as arhar stalk (AS), banana trunk (BT), rice husk (RH), rice straw (RS), wheat straw (WS), sugar cane bagasse (SB), sugar cane leaves (SCL), peanut shell (PS) and paper mill waste (PMW) for assessing their possible use as a feedstock for pyrolysis and production of value added products,
2. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of various biomasses and analysis of the resultant data using model free iso-conversional as well as model fitting methods,
3. Pyrolysis of selected biomass in a lab-scale fixed bed tubular reactor and collection of products and their characterization,
4. Study the effects of various operating parameters on the pyrolytic products yields (liquid, char, and gases),
5. Optimization of various parameters of pyrolysis process using the response surface methodology (RSM) of Design Expert Software Version 11 (Stat Ease, USA),
6. Study of the influence of heterogeneous catalyst on the kinetic parameters, and
7. Physicochemical characterization of biochar obtained from through the batch pyrolysis of selected biomasses.