Graphical Abstract



Pyrolyiss products

1	A critical review on biomass pyrolysis: Reaction mechanisms, process
2	modeling and potential challenges
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26 Abstract

27 Pyrolysis is a versatile technology for exploiting diversified feedstocks to produce a wide range of 28 products, including biochar, bio-oil, and syngas with high potential in diverse applications. The cardinal 29 motivation of pyrolysis research is to productively use diverse biomass to reduce adverse impacts on ecology 30 and enhance process economics. However, complex reactions of pyrolysis pose operational challenges. Thus, 31 the present review targets the reaction mechanisms and kinetics of pyrolysis to enhance the understanding for 32 better process control, improved performance, and product distribution. Pyrolysis mechanisms of the major 33 structural components of biomass, such as cellulose, lignin, and hemicellulose, as well as proteins, lipids, and 34 carbohydrates, are discussed in detail. Various modeling techniques and tools, viz., mathematical, kinetic, 35 computational fluid dynamic modeling, and machine learning algorithms, have been employed to better 36 understand the pyrolysis mechanisms and product distribution. In addition, the most critical challenges, namely 37 aerosol formation, tar formation and their removal mechanisms, that severely impact the pyrolysis process and 38 products are identified and reported. Thus, the present work critically discusses state-of-art biomass pyrolysis, 39 focusing on the reaction mechanism, modeling, and associated challenges to overcome, given that the pyrolysis 40 products and the process are enhanced.

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keywords: Pyrolysis, Mechanisms, Modeling, Lignocellulosic Biomass, Aquatic Biomass, aerosol and tar
 formation

44 1. Introduction

45 Clean energy technology banks on biomass owing to its abundance and carbon neutrality (Chio et al., 2019). 46 Biomass can be processed via thermochemical or biochemical conversion routes to generate heat and power. 47 High-value- chemicals derived from biomass have economic benefits and bio-fuels can substitute fossils (Leng 48 et al., 2022). The benefits of employing biomass as a feedstock for energy production are many, including 49 availability in abundance, economical, and being carbon neutral. The estimated global biomass reserves are ca. 50 5 billion tons, making them the fourth most abundantly available resource (Ansari et al., 2021). It is noteworthy 51 that identifying a suitable feedstock is crucial in deciding the conversion route. Structural composition classifies 52 biomass into lignocellulosic and aquatic biomass. Cellulose (37-50%), lignin (15-26%), and hemicellulose (22-53 32%) dominate lignocellulosic biomass composition (Hameed et al., 2019). Similarly, aquatic biomass is 54 composed of proteins (14-65%), carbohydrates (3-30%), and lipids (1-51%), depending on the specie (Su et al., 55 2022; Vuppaladadiyam et al., 2018).

56 The biorefinery concept is not new, and the feedstock type delineates biorefineries into four generations. The 57 first-generation biorefinery considered edible crops and animal fats to produce biofuels. Agricultural residues, 58 industrial waste, and municipal and household waste are used in second-generation biorefineries to avoid 59 problems their predecessor raises. The third generation considered photosynthetic aquatic organisms, such as 60 micro- and macro-algae, to produce biofuels and other upgraded products. Finally, the fourth-generation 61 biorefinery relies on the genetic modification of microorganisms to produce biofuels (Su et al., 2022). Major 62 biomass-to-energy conversion routes include physical, agrochemical, biochemical, and thermochemical routes 63 (Ansari et al., 2021; Ghodake et al., 2021). Pyrolysis, a thermochemical process, offers excellent control over 64 process parameters, resulting in low emissions of harmful gases. In addition, the scale-up of pyrolysis plants is 65 simple and convenient, unlike incineration plants (Uzakov et al., 2018). Although biomass pyrolysis has been 66 extensively studied, it is undeniable that biomass valorization remains challenging, given the complex nature of 67 biomass. In the last few decades, enormous interest has been in understanding pyrolysis mechanisms and 68 modeling owing to its potential for commercialization and profitability. In addition, the availability of inherent 69 metals in the biomass can profoundly impact the pyrolysis products. Investigating the catalytic impact on the 70 mechanism is vital in reactor design and process optimization. Despite the availability of biomass mechanism in 71 the literature, a majority is focusing on biomass as a whole and detailed mechanism on the individual 72 components is sparse and not comprehensive.

73 In view of process optimization, modeling and simulation of biomass pyrolysis are extremely important. The 74 models usually consider the reaction of individual structural components proceeding independently; thus, 75 biomass modeling is the superposition of these components. The inherent interactions between the structural 76 components are often neglected (Hameed et al., 2019). Modeling of biomass pyrolysis does not include the 77 influence of inorganic biomass species, resulting in deviations from the actual mechanism (Trendewicz et al., 78 2015). Recent reviews (Anca-Couce, 2016; Sharma et al., 2015) presented an excellent analysis of the 79 conversion rate, reactor models and mechanisms of biomass pyrolysis at molecular, particle and reactor levels. 80 The current work complements the available literature and critically discusses key topics not addressed in the 81 previous reviews. The role of structural components of biomass and secondary reactions on product formation 82 mechanisms has been critically discussed and summarised. The review is structured in four sections; section 1 83 offers basic information on pyrolysis, reaction mechanism and modeling. Section 2 provides an in-depth 84 discussion of the pyrolysis mechanism considering the type/nature of biomass. The overall reaction scheme and 85 each component's reaction mechanism have been summarised. Section 3 provides a detailed review of the 86 modeling of biomass pyrolysis, considering different modeling approaches. Section 4 presents a detailed 87 overview and in-depth discussion of the major challenges in biomass pyrolysis. Aerosol formation mechanisms 88 and their impact on bio-oil, tar formation and removal mechanisms and their impact on pyrolysis have been 89 critically summarised. Finally, section 5 provides information on the prospects in research and development.

90 2. Pyrolysis mechanisms

91 Understanding the biomass pyrolysis mechanisms improves reactor design and augments process 92 optimization. The thermal behavior of the macromolecular components in lignocellulosic and aquatic biomass 93 overlaps with one another. For instance, the pyrolysis of hemicellulose and carbohydrates occurs at 150-200°C, 94 whereas the decomposition of cellulose and proteins occurs at 200-350°C. Similarly, the pyrolytic 95 decomposition of lignin and lipids occurs in the temperature range of 200-450°C (Van de Velden et al., 2010). 96 Char formation results in an aromatic polycyclic structured solid residue (McGrath et al., 2003). Intramolecular 97 and intermolecular reorganizations favor char formation pathways and result in a high degree of thermal 98 stability of the residual char (Fu et al., 2010). Polycyclic structure in char involves the formation and orientation 99 of benzene with the evolution of water and non-condensable gases (NCGs) (Van de Velden et al., 2010). 100 Depolymerization involves in cleavage of bonds among the monomers of the biopolymers. The degree of 101 polymerization decreases until the newly formed molecules are converted into volatiles (Mamleev et al., 2009). 102 However, the condensable molecules are liquid-derived-monomers, dimers or trimers at ambient temperature 103 (Mullen and Boateng, 2011). Fragmentation involves breaking the covalent bonds in the monomer units,

104 producing NCGs and a wide range of small-chain organic compounds that are condensable at room temperature 105 (Collard and Blin, 2014). Pyrolysis temperature is a critical parameter that influences the yield and quality of the 106 desired product during pyrolysis. Generally, the pyrolysis temperature is chosen based on the desired product or 107 application. At low pyrolysis temperatures (<500°C), the yield of solid char is high, while at higher 108 temperatures (>700°C), the yield of char decreases. The char quality is also influenced by the pyrolysis 109 temperature, with higher temperatures resulting in higher ash content and lower fixed carbon content. The yield 110 and composition of liquid bio-oil strongly depend on the pyrolysis temperature. Low-temperature pyrolysis 111 (<500°C) typically results in high yields of bio-oil, while high-temperature pyrolysis (>700°C) produces less 112 bio-oil but with higher energy content and lower oxygen content. The bio-oil produced at higher temperatures 113 also has a higher heating value and is more stable. The pyrolysis temperature also influences the composition of 114 gaseous products such as hydrogen, methane, and carbon monoxide. The pathways involved in the primary 115 conversion mechanisms of biomass constituents are presented in Fig. 1. The unstable, volatile compounds of 116 primary reactions may enter secondary reactions, which include recondensation and cracking, and produce low 117 molecular weight (LMW) and high molecular weight (HMW) molecules. During cracking, LMW molecules are 118 formed due to the breakdown of chemical bonds in volatile compounds (Neves et al., 2011). Due to the 119 possibility of breaking a similar chemical bond in the volatiles or the polymer, the products obtained from 120 fragmentation and cracking reactions share similarities. High molecular weight (HMW) molecules are formed in 121 recondensation due to the combination of volatile compounds (Hosoya et al., 2007). Secondary char formation 122 can be attributed to inter-pore recombination (Neves et al., 2011; Wei et al., 2006). In addition, the secondary 123 mechanism can be catalyzed at the reactor surface (Collard and Blin, 2014).



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Fig. 1. Important routes in the primary mechanisms during the conversion of biomass (MW: molecular weight;
 M: monomer). Adapted from (Collard and Blin, 2014).

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3. Conversion mechanisms for constituents of biomass during pyrolysis

129 The primary reaction involves heating the biopolymers, and releasing volatile compounds through lysis and 130 reorientation of chemical bonds (Hosoya et al., 2007; Van de Velden et al., 2010). These volatiles are relatively 131 unstable and may undergo supplementary conversion via secondary reactions. The breakdown of the chemical

132 bonds follows three pathways: char formation, depolymerization and disintegration (Collard and Blin, 2014; 133 Elyounssi et al., 2012). Understanding biomass characteristics is crucial to defining pyrolysis parameters and the 134 final by-product characteristics and distribution. Fig. 2 presents the composition of different types of biomasses: 135 agricultural residues (rice husk, wheat straw, swine manure), forestry biomass (bamboo, beech wood), 136 municipal solid waste (sewage sludge) and industrial residues (sawdust, sugarcane bagasse and tires). The 137 critical moisture content of biomass is <10% for effective thermochemical conversion. Sewage sludge (SS) 138 often has a moisture content of ca. 80% depending on the previous treatment processes and requires a drying 139 step before pyrolysis, which can significantly increase the cost of the overall process. While materials like nut 140 shells, spruce wood, tires and wheat straw have high fixed carbon, typically above 20%, SS and animal manure 141 are low in fixed carbon and high in ash content due to high levels of inorganic elements such as phosphorus, 142 silicon and magnesium that are present in urine and feces (Magdziarz et al., 2016). Other metals, such as aluminum and iron, arise from metal salts used in wastewater treatment plants to precipitate phosphorus and 143 144 remove nitrogen. Nutshells have the highest lignin content, while the cellulose and hemicellulose percentages 145 are similar. By contrast, SS and animal manure displayed a high amount of cellulose (>50%), a smaller amount 146 of hemicellulose (~12%), and a lower lignin content than 8%.

147 3.1. Pyrolysis mechanism for individual components in lignocellulosic biomass

148 The composition of various lignocellulosic biomasses and other categories of wastes is shown in Fig. 2 149 and Fig. 3(a) summarises the cellulose pyrolysis. A set of reactions (R1-R4) are expected to happen during the 150 two-step cellulose pyrolysis process. After the depolymerization reaction (R1) and formation of intermediate 151 liquid compounds (ILC), competition arises between the fragmentation reaction (R2) and transglycosilation 152 reaction (R3). The products from reactions R3 and R4 are mainly LMWCs and levoglucosan (LGA), 153 respectively.(Anca-Couce, 2016) The products from primary pyrolysis may experience other secondary 154 reactions to produce char. Char production via reaction R4 ishighly debatable (Lin et al., 2009). The pathways 155 associated with the charring reactions (R5) result in the formation of H_2O , CO_2 and volatile PAHs. The increase 156 in the volatiles retention time and pressure, low temperatures and the availability of inorganics favor secondary 157 charring reactions (Yang et al., 2007), while reaction R6, which is the cracking of volatile compounds in the gas phase, results in CO production at temperatures above 500°C. Recently, a novel thin-film pyrolysis technique 158 159 was used to reveal the pathways of cellulose pyrolysis. Furan formation occurred directly from cellulose and no 160 intermediates (such as glucose) were detected. Glycosidic linkages undergo homolytic cleavage to form furan 161 and glycolaldehyde against ionic mechanisms. The study also emphasized the interconnection between intrapyran chemistry and the cleavage of glycosidic bonds (Mettler et al., 2012a). The literature regarding the 162 163 hemicellulose pyrolysis mechanism is limited, and xylan, a straight-chain polymer of xylose, is an auxiliary to 164 hemicellulose to explain the reaction mechanism of hemicellulose (Gao et al., 2020; Giudicianni et al., 2019; 165 Yang, H. et al., 2020; Zheng et al., 2019). Many remarkable differences exist along with considerable 166 similarities between cellulose and hemicellulose pyrolysis. For instance, hemicellulose pyrolysis starts 167 comparatively at low temperatures to yield more char and a lower quantity of sugars than cellulose (Balci et al., 168 1993; Orfão et al., 1999; Shafizadeh et al., 1972).

Patwardhan et al. (Patwardhan et al., 2011) demonstrated the difference between cellulose and
 hemicellulose pyrolysis reaction pathways (Fig. 3 (a). Alkali conditions increase the formation of char and CO₂

and decrease the yield of sugars, there is no noticeable influence on the yield of CO. Acetic acid, 1-hydroxy-2-

- 172 propanone, furfural, CO₂, CO and H₂O are a few important decomposition products from xylan (Wang, Shurong
- transmitted et al., 2013). O-acetyl groups connected to the primary xylan chain dissociates at low temperature to produce
- acetic acid (Peng and Wu, 2010). Lignin has a much-complicated structure, and its pyrolysis occurs in several
- 175 stages and over a wide range of temperatures (Vuppaladadiyam, 2019a; 2019b; 2019c). Initially, lignin softens 176 between 150-190°C, followed by dehydration at *ca*. 200°C. The cleavage of aliphatic side chains, α - and β -aryl-
- alkyl ether linkages, methoxyl groups and C-C linkages occur between 150-300, 300, 370-400 and 310-350°C,
- 178 respectively (Zhou et al., 2014).

179 Lignin pyrolysis produces phenolics, carbonyls, alcohols, water vapor and gases such as CO_2 and CO. 180 Methanol and methane are also the typical products of lignin pyrolysis. They are generated in high quantities 181 due to the scission of methoxyl groups. Volatile compounds of lignin pyrolysis are mainly released for two 182 reasons; (a) instability in the propyl chains and (b) instability within the linkages between monomer units and 183 aromatic rings (Collard and Blin, 2014). The release of volatiles is followed by char formation reactions to form 184 polycyclic aromatic structures (Liu et al., 2008). However, benzene rings are highly stable under an inert 185 atmosphere and tend to accumulate during the reaction (Mu et al., 2013). Inorganic biomass compounds also 186 catalyze the pyrolysis of lignin and influence the composition of pyrolysis products and mass loss rate. Higher 187 char formation of softwood at higher temperatures has been linked to the higher carbon content of softwood 188 lignin (Anca-Couce, 2016). The distinctive polymer structure of lignin resists thermal degradation. Lignin, 189 unlike cellulose, is not a linear polymer with repeating subunits but is composed of a wide range of monolignols 190 or chemically distinct subunits. The most common monolignols are p-hydroxyphenyl (H), guaiacyl (G) and 191 syringal (S) monolignols. These monolignols create radicals due to the existence of extracellular laccases or 192 peroxides and the radicals then form a wide variety of bonds (carbon-carbon or ether) with the growing lignin 193 polymer to form a complex, branched network (Weng et al., 2008).





Fig. 2. Composition of widely reported lignocellulosic biomass and other waste feedstocks (Aerts, 1997; Antal et al., 2000; Backreedy et al., 2005; Bhuiyan et al., 2018; Black et al., 2013; Demirbaş, 2005; Di Blasi et al., 2010; Dyjakon and Noszczyk, 2020; Garcia-Pèrez et al., 2002; Gulyurtlu et al., 2004; He et al., 2019; Lynd et al., 1999; M. Ebeling and M. Jenkins, 1985;
Pattanayak et al., 2020; Qu et al., 2011; Rabemanolontsoa and Saka, 2013; Sajdak et al., 2015; Singh et al., 2020; Taherzadeh et al., 1997; Uzun et al., 2010; Vuppaladadiyam, Arun K et al., 2019c; Ward et al., 2014; Yang et al., 2018; Yazdani et al., 2019; Zeng et al., 2015a; Zhao et al., 2018).



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Fig. 3. Schematics of (a) cellulose and (b) lignin pyrolysis

A simple reaction pathway suggested by Zhao et al. (Zhou et al., 2014) for lignin pyrolysis is presented in Fig. 3(b). Pyrolytic lignin is produced along with char and light condensable gases during primary pyrolysis, as shown in Fig. 3 (b). Post this, pyrolytic lignin further reacts to produce phenolic oligomers, phenolic monomers, char, and light condensable gases Kotake et al. (Kotake et al., 2014).

206 3.2. Pyrolysis mechanism for individual components in aquatic biomass

207 The biochemical composition of aquatic biomass, such as micro- and macroalgae, is complex, with 208 proteins, lipids, and carbohydrates as the three primary constituents. Each component contributes, albeit 209 unevenly, to the product formation. The composition of different algal species is presented in Fig. 4. The lipid 210 content in macroalgae is generally lower than in microalgae, varying between 0.1-11.5 and 1.4-51, respectively. 211 The volatile content of macroalgae reached a maximum of 77%, while the microalgae have a maximum of 212 89.4% on a dry ash-free basis. While microalgae seem promising for biogas and bio-oil production, macroalgae 213 appear suitable for biochar production owing to the lower volatile content (low carbon and hydrogen content in 214 general) and high ash content. No trend is noticed regarding the nitrogen, oxygen and sulfur content, and the 215 percentage of these three elements seems to be a characteristic of each algae species. However, apart from two 216 of the species listed in Fig. 4, algae's nitrogen content is usually less than 2.5%. Many research studies 217 considering model compounds have examined the reaction mechanisms and pathways followed by the primary compounds during pyrolysis (Bach and Chen, 2017a, b; Chiaramonti et al., 2017; Du et al., 2013; Wang et al., 218 219 2017b). For instance, Wang et al. (Wang et al., 2017a) explored the pyrolysis pathways of microalgae 220 Nannochloropsis sp. and explained that lipids adopted decarbonylation, decarboxylation and fragmentation. 221 While proteins followed deamination, decarboxylation, dimerization and fragmentation, carbohydrates followed 222 dehydrated and fragmentation reactions as major pathways during pyrolysis. Yang et al. (Yang et al., 2019) 223 compiled and summarized possible reaction mechanism pathways presented in Fig. 5.

Macroalgae

- 1 Cladophora glomerata
- 2 Enteromorpha clathrate
- Enteromorpha compressa 3
- Enteromorpha intestinalis 4
- Enteromorpha prolifera 5
- Gelidium floridanum 6
- Gracilaria gracilis 7
- Laminaria japonica 8
- 9 Laminaria digitata
- 10 Oedogonium intermedium
- 11 Sargassum linearifolium
- 12 Saccharina japonica
- 13 Ulva intestinalis
- 14 Ulva lactuca
- 15 Ulva prolifera

Microalgae

- 16 Chlamydomonas reinhardtii
- 17 Chlorella sp.
- 18 Chlorella sorokiniana
- 19 Chlorella vulgaris
- 20 Chlorella pyrenoidosa
- 21 Cladophora sp.
- 22 Dunaliella salina
- 23 Dunaliella tertiolecta
- 24 Euglena gracilis
- 25 Haematococcus pluvialis
- 26 Lyngbya sp. 27 Nannochloropsis sp.
- 28 Nannochloropsis oculata
- 29 Scenedesmus obliquus







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Nitrogen (wt. %)







228 229

224 225

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230 Aquatic biomass comprises amino acids, lipids, chlorophyll, glucose, and xylose. The lipids of the 231 biomass form olefins at a higher temperature. Amino acids at higher temperatures enter into the cyclization 232 reaction to form derivatives of pyrazole and indole (Fig. 6). Calvin cycle enhances the aquatic biomass to store 233 carbohydrates in the form of glucose isomers. Glucose undergoes thermal degradation between 180-220 °C to 234 produce hexane (C₆H₁₄) molecules. Xylose is an aldopentose that represents hemicellulose. The cracking of 235 hemicellulose at higher temperatures results in furfurals. The furans present in pyro-oil are actually from the 236 cracking of hemicellulose. In the algal cells, carbohydrates can be found in poly- and oligosaccharides. Glucose 237 is the commonly available monomer in most species of algae (Templeton et al., 2012). However, cellulose, 238 pectin and hemicellulose are also reported in the cell membrane of some microalgae, such as green algae. Other 239 forms, such as agar, alginic acid $(C_6H_8O_6)_n$, carrageenan, fucans, laminarin $(C_6H_{10}O_5)_n$, lipopolysaccharides, 240 mannitol ($C_6H_{14}O_6$), and peptidoglycan are also seen in algae biomass (Chen et al., 2013; Dawczynski et al., 241 2007). The carbohydrate pyrolysis is governed by hydrolysis, cracking and dehydration, producing 242 anhydrosugars and furfurals as their main products. The thermal behavior of algae carbohydrates and cellulose 243 are not similar. A few studies reported different forms of carbohydrates, such as alginic acid, fucoidan, 244 laminarin and mannitol, all of which adopted different degradation pathways (Anastasakis et al., 2011) and had different weight loss zones (Debiagi et al., 2017). For instance, mannitol and alginic acid exhibited a single 245 246 major weight loss region during pyrolysis, and fucoidan and laminarin showed two major weight loss regions 247 (Debiagi et al., 2017). Their intrinsic chemical structure influences the response of carbohydrates to 248 temperature. Pyrolysis of carbohydrates involves moisture removal, breaking the glycosidic bond, 249 rearrangement and ring scission resulting in deoxygenated olefins (Easton et al., 2018). Furans, pyrroles, 250 pyrazines (Harman-Ware et al., 2013; Saber et al., 2016) and polyaromatic hydrocarbons (PAHs) (Hong et al., 251 2017) are produced during the pyrolysis of carbohydrates at temperatures above 300°C. Additionally, at 252 temperatures above 500° C, the decomposition of saccharides results in CO₂ (Wang et al., 2007).

253 Lipids, long-chain hydrocarbons, act as structural components and energy storage molecules. They are 254 available in algae as glycolipids, phospholipids, triglycerides and fatty acids (Debiagi et al., 2017). During 255 pyrolysis, these compounds may initially undergo a cracking reaction to acyl chains from the glycerol backbone 256 to produce long-chain fatty acids (LCFAs) (Ahmed et al., 2018). Further, acids, alcohols, aldehydes, ketones 257 and short-chain hydrocarbons (SCHs) (like olefins) may be produced from LCFAs via decarboxylation, 258 decarbonization, deoxygenation, and/or cracking reactions (Yang et al., 2019). Finally, aromatic hydrocarbons 259 may be produced from SCHs via aromatization and cyclization reactions (Maher and Bressler, 2007). 260 Kebelmann et al. (Kebelmann et al., 2013) reported the formation of hydrocarbon compounds such as 1-261 nonadecene, heneicosane and heptadecane during the pyrolysis of Chlorella vulgaris. Pyrolysis of the protein in 262 algal biomass exhibits multistep and multiphase kinetics (Debiagi et al., 2017). Pyrolysis of protein-rich algal 263 biomass resulted in amides, amines, imidazoles, indoles, nitriles, polyheteroaromatics, pyrazines, pyrazoles, 264 pyridines, and pyrroles (Andrade et al., 2018; Harman-Ware et al., 2013). The formation of cyclic and linear 265 amides are unique. Intramolecular cyclization results in cyclic amides, whereas amino acids react with carboxylic acids to form linear amides. Hydrophobic protein fragments may be produced as the main products at 266 267 low temperatures. At high temperatures, gaseous products such as C₂H₆, NO and HCN can be linked to the 268 protein decomposition in the algal biomass (Lee et al., 2020). Gallois et al.(Gallois et al., 2007) reported the

- 269 pyrolysis mechanism for 20 amino acids and Choi et al.(Choi and Ko, 2011) noted that large quantities of N-
- 270 heterotrophic compounds were generated during the pyrolysis of amino acid monomers. Table 1 summarises the
- 271 reaction mechanism of different biomass components.



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Fig. 5. Possible pathways for aquatic biomass pyrolysis.

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Table 1. Summary of pyrolysis mechanisms for biomass components.

Component	Structure	Mechanism
Cellulose	linear homopolysaccharide of cellobiose m onomers	150–300 °C: Dehydration, Depolymerization. 300–390 °C: Depolymerization. 380–800 °C: Charring process
Hemicelluloses	heteropolysaccharides	 150–270 °C: Dehydration and breaking of less stable linkages. 270–350 °C: Depolymerization. 350–800 °C: Charring process
Lignin	complex three-dimensional amorphous polymer	150–420 °C: Conversion of the alkyl chains and rupture of some of the linkages between units 380–800 °C: Conversion of the short substituents of the aromatic rings and charring process
Proteins	Sequence of amino acids linked together to form a polypeptide chain	Cracking, Deamination and Cracking+Maillard
Lipids	Heterogeneous group of compounds, mainly composed of hydrocarbon chains	Decrboxylation, cracking, Decarbonylation and Deoxygenation
Carbohydrates	Include an aldehyde or ketone group and a hydroxyl group	Deoxygenation, Decarbonylation, Dehydration, Cracking and Cyclization

276 4. Mathematical modeling

277 Pyrolysis of biomass and other wastes can be assessed either by experimental means or by developing 278 suitable models. Pyrolysis modeling uses mathematical models to predict the yield and composition of the 279 various products formed during pyrolysis. The models typically incorporate detailed chemical kinetics and 280 thermodynamics to capture the complex reaction pathways and rate dependencies during pyrolysis. Pyrolysis 281 modeling has many applications, including process design and optimization, feedstock selection, and evaluating 282 the environmental and economic impacts of pyrolysis processes. Experimental investigations are crucial for the 283 accurate design and subsequent optimization of pyrolyzers. However, experimental studies are expensive and 284 time-consuming, and under extreme operational conditions, precise measurement becomes unmanageable 285 (Hameed et al., 2019; Sikarwar and Zhao, 2017). "Virtual" experiments using mathematical modeling can overcome such challenges.(Sharifzadeh et al., 2019) In general, the simulation of pyrolysis can be classified into 286 287 four classes, namely, (i) Thermodynamic modeling (TDM), (ii) Kinetic modeling (KM), (iii) Computational 288 Fluid Dynamics (CFD) modeling and (iv) Artificial Neural Network (ANN) modeling (Di Blasi, 2008; Sikarwar 289 et al., 2016). Significant studies related to the modeling of pyrolysis are shown in Table 2. The simplest model 290 is thermodynamic modeling (TDM), which is based on the supposition that reacting species inside the pyrolyzer 291 develop the product distribution that would be found if they reacted for an infinite time (Sikarwar et al., 2017), 292 assisting in deducing the pyrolysis products (Gan et al., 2018). TDMs demonstrate the thermodynamic limits for 293 defined operational conditions (Sikarwar and Zhao, 2016). However, the drawback of TDM is the considerable 294 deviation from real-life set-ups (Krutof and Hawboldt, 2020). Therefore, there are limited studies regarding the 295 development of thermodynamic models compared to CFD and KT models.

296 The KM approach overcomes the limitations of thermodynamic models to some extent. Kinetic models take 297 into account the hydrodynamics of the reactor coupled with the kinetics of reactions (Gan et al., 2018), which 298 aids in developing insights into reaction mechanisms and kinetics. KM encompasses a diverse range, from 299 single-step to intricate multiparameter models (Várhegyi et al., 1997). As this approach is complicated, a deep 300 and complete understanding of kinetics and reaction rate constants is not achieved. The evaluation of complex 301 multiphase flows experienced by a pyrolyzer can be approximated by applying CFD principles. With its 302 inherent potency, CFD modeling is widely used to assess biomass/waste pyrolysis (Xiong et al., 2017), and 303 employed for almost all types of pyrolyzers, but it remains complicated (Zhong et al., 2019). Artificial Neural 304 Network modeling is relatively new and is similar to machine learning. It is commonly employed to deduce the 305 non-linear connection between the input and output based on estimating random non-linear 306 functions.(Sunphorka et al., 2017) In addition, a mathematical narrative of the process is not needed to develop 307 the ANN model (Zhang et al., 2020). However, ANN modeling is impossible when the data is restricted, and the 308 inherent lack of an underlying physical model can lead to issues with model extrapolation.

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4.1. Thermodynamic modeling (TDM)

Gagliano et al.(Gagliano et al., 2018) developed two equilibrium models for slow pyrolysis (Pyro_2) and intermediate pyrolysis (Pyro_3). The authors generated the thermodynamic models in MATLAB and evaluated the gas composition and LHV of NCGs and bio-oil. Global and equilibrium chemical reactions govern the transformation of biomass to char, gases, and bio-oil, which formed the basis of these models. Hydrogen, methane, carbon dioxide, carbon monoxide, and water mole fractions were estimated, along with the amount of 315 bio-oil. The amount of char and the operational temperature was constant for both of these models. An 316 enhancement in the producer gas and LHV was noticed when the operating temperature was increased from 400 317 to 700°C. Plausible reasons can be the rise in combustibles and the increase in H_2 due to the thermal cracking of 318 gases and vapors. Comparing both models, the authors found that the Pyro_2 model was more precise than 319 Pyro_3 vis-à-vis bio-oil yield. When the modeling deductions were assessed concerning trial data, it was 320 reported that the estimates were within the permissible limits for diverse pyrolytic conditions. The 321 thermodynamic models can be employed to examine the thermodynamic limitations, which in turn can be used 322 to optimize the pyrolysis process.

323 A 100 kg/h banana (Musa spp.) waste was employed in developing an Aspen plus-based thermodynamic model 324 (Ighalo and Adeniyi, 2019). The authors assessed the product composition vis-à-vis temperature for diverse 325 types of banana wastes, which included pseudo-stem, banana peels, and banana leaves. Interestingly, pseudo-326 stem contributed more toward gas yield. It was reported that gas yields at the thermodynamic limit were similar 327 for all the feed materials at low temperatures (450 to 500°C). However, at higher temperatures (500 to 650°C), a 328 variation in the yield was noticed, with leaves producing the smallest quantity of gases. It also noted that leaves 329 produced less bio-oil and (quite obviously) a more significant amount of char. The proximate analysis indicated 330 that the pseudo-stem produced a higher fraction of volatiles. Consequently, it generated higher amounts of 331 producer gas and oil. Banana pseudo-stem was appropriate for oil generation, whereas banana leaves and peel 332 were suitable for char production.

333 In another investigation, physical and chemical characteristics coupled with vapor-liquid phase properties of fast pyrolysis bio-oil were assessed (Krutof and Hawboldt, 2020). Softwood residues-derived fast 334 335 pyrolysis bio-oil generated using a pilot-scale auger reactor at 450°C entered an advanced distillation curve 336 equipment under 5 kPa. The thermodynamic state points and vapor phase composition data were deduced using 337 an advanced distillation curve apparatus. VMGSimTM was used to develop a bio-oil model employing the 338 UNIQUAC equations of states. The authors deduced the vapor-liquid equilibrium and physicochemical 339 characteristics using a blend of H₂O, pyrolytic lignin, inert solids, and multiple organic components. The results 340 were then obtained using a reduced-pressure version of Windom and Bruno's advanced distillation curve (V-341 ADC) (Hameed et al., 2019). V-ADC enhanced the distillable fraction of bio-oil from 55 vol% (with ambient 342 conditions) to 72 vol%. It was done by restricting the polymerization at elevated temperatures. Thermodynamic 343 models of bio-oil enhance insights into bio-oil bulk and fraction characteristics, promoting its usage in multiple 344 end applications. Lee et al. (Lee et al., 2007) combined thermodynamic and kinetic simulations to evaluate the 345 product distribution obtained from palm oil waste pyrolysis. The authors employed the HSC Chemistry software 346 to provide a thermodynamic approach, whereas the Sandia PSR code was used for kinetic calculations. In 347 addition, the gas compositions were assessed by HSC computations which were then fed into the PSR code to 348 provide a more precise distribution of gaseous products. The authors reported a decrease in char with a rise in 349 gaseous species when the temperature was enhanced. By adding PSC code to a thermodynamic model, the 350 authors could predict C_2H_2 , C_2H_4 , C_2H_6 and C_3H_8 , which are formed at the expense of char and CH₄, mostly 351 between 200 to 700°C. Among the newly generated species, C_2H_2 formed the largest fraction with 12% and 352 C₂H₄ as 4.5% at 400°C. The conjunction of the thermodynamic and kinetic approach can enhance the precision 353 of gas composition values and aid in computing other gaseous species found in smaller fractions.

Table 2. A selection of pyrolysis modelling studies.

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Modeling	Tool	Approach	Line of study	Reference
type				
TD	MATLAB	Developing and solving non-linear equations	Composition and LHV of gases and amount of bio-oil	(Gagliano et al., 2018)
TD	ASPEN PLUS	-	Product composition w.r.t. temperature	(Ighalo and Adeniyi, 2019)
TD	VMGSim™	UNIQUAC equations of states	Physico-chemical and vapor-liquid phase properties of bio-oil	(Krutof and Hawboldt, 2020)
TD and KT	-	HSC Chemistry computation code and Sandia PSR code	Product composition and distribution	(Lee et al., 2007)
TD and KT	-	Flynn Wall Ozawa (FWO) model and Distributed activation energy Model (DAEM)	Feasibility of rice hull pyrolysis using limestone and eggshell catalysts	(Gan et al., 2018)
KT	-	Modelling study followed by experimental work for validation	Potential of glycerol pyrolysis to produce hydrogen	(Fantozzi et al., 2016)
KT	-	DAEM approach, model-free approach, and model-based method	Assessment of the influence of vulcanization on the fixed bed pyrolysis of rubber	(Liu et al., 2018)
KT	-	DAEM	Co-pyrolysis of chest-nutshell and polystyrene	(Özsin and Pütün, 2018)
KT	-	Sequential and coupling method (Coats- Redfern method and Kissinger method)	Relationship of activation energy (E_{α}) with conversion rate for cellulose, hemicellulose and lignin pyrolysis	(Wang et al., 2016)
CFD	FLUENT	multi-component and multi-step reaction model and Euler-Euler approach	Evaluation of pyrolytic product distribution, temperature distribution and flow regime in the reactor bed along with the effect of temperature, superficial gas velocity and bed height	(Ding et al., 2020)
CFD	-	Eulerian-Eulerian approach	Examination of heat transfer characteristics and hydrodynamics of conical spouted bed pyrolyzer	(Hooshdaran et al., 2017)
CFD	-	Chemical kinetics along with multiphase flow dynamics were employed for auger reactor with the inclusion of rotating reference frame	Development of a design tool to scale-up a fast pyrolysis plant	(Jalalifar et al., 2020)
CFD	-	Lumped kinetics approach with multi fluid model	Evaluation of synergistic impact of intra-particle heat conduction and particle shrinkage on biomass fast pyrolysis	(Zhong et al., 2019)
ANN	-	Levenberg-Marquardt pathway	Fuel production from plastic waste	(Abnisa et al., 2019)
ANN	-	Least Squares Support Vector Machine (LS-SVM)	Production of biochar from cattle manure	(Cao et al., 2016)
ANN	MATLAB	NFTOOL	Hydrogen generation from the pyrolysis of wastes such as olive husk, cotton cocoon shell and tea waste	(Karaci et al., 2016)
ANN	-	-	Evaluation of relation between biomass components and kinetic parameters such as activation energy, reaction order and pre- exponential factor in pyrolysis	(Sunphorka et al., 2017)

357 4.2. Kinetic (KT) modeling

358 Fantozzi et al.(2016) investigated the possibility of glycerol as a feedstock for pyrolysis to generate H₂, 359 which could either be employed for CHP or as a fuel in the transportation sector. The gaseous yield and H_2 360 fraction can be enhanced by applying optimal operating conditions. A higher yield of NCGs(70 wt%) and 361 enhanced process efficacy between 750 - 800°C. The H2 mole fraction ranged between 44 to 48 vol%. CFD 362 simulation provides more profound insights into glycerol pyrolysis. Gan et al., 2018) assessed the 363 kinetic and thermodynamic parameters for rice hull pyrolysis with limestone and eggshells. The FWO model 364 (Ozawa, 1992) and the DAEM (McCown and Harrison, 1982) were adopted, with variable temperatures ranging 365 from 50°C to 900°C. The FWO model considers the first-order reactions and is a single-step reaction model. 366 The DAEM considers the devolatilization of biomass, along with numerous first-order reactions. An average E_{α} for non-catalytic pyrolysis was noticed as 175.4 - 177.7 kJ/mol. Limestone as a catalyst reported decreased E_{α} of 367 368 123.3 - 132.5 kJ/mol, which reduced to 96.1 - 100.4 kJ/mol when eggshell was used as a catalyst. The FWO 369 model considers the first-order reactions and is a single-step reaction model. The average E_a for non-catalytic 370 pyrolysis ranges between 175.4 - 177.7 kJ/mol. Some researchers (Liu et al., 2018) conducted in-depth kinetic 371 modeling investigations to evaluate the impact of vulcanization on the fixed bed pyrolysis of natural-, 372 butadiene- and styrene butadiene-rubber. The distributed activation energy approach predictions were more 373 accurate than the model-based approach, suggesting that the cardinal rubber degradation followed a chain 374 reaction. The highest bio-oil generation was 90.82% for natural rubber at 430°C, whereas 90.61% for butadiene 375 rubber and 92.80% for styrene-butadiene rubber at 470°C. The vulcanized rubber, however, displayed a 376 different trend, where sulfur was released at lower temperatures.

377 On the other hand, gaseous species were increased at the expense of sulfur-containing oils at elevated 378 temperatures. Liu et al. (Liu et al., 2019) employed Rhus Typhina biomass to explore the E_{α} and frequency 379 factors of the pyrolysis process with the aid of the Friedman method. Thermal degradation rates were deduced 380 via a three pseudo-component DAEM, where the pseudo-components denoted hemicellulose, cellulose, lignin 381 and others respectively. A nonlinear dynamic optimization model was coupled with the DAEM to enhance the model's precision. Pseudo-components DAEM accurately deduced the biomass transformation and degradation 382 383 rate for 10, 20, and 30 K/min. The experimental data and model deductions were in line. Özsin and Pütün(Özsin 384 and Pütün, 2018) examined the co-pyrolysis behavior of chestnut shell and polystyrene and compared it with the 385 individual performances of both feedstocks. In order to carry out the kinetic investigation, a DAEM was 386 developed. The authors reported that the individual activation energies of polystyrene and chestnut shells as 387 208.9 kJ/mol and 175.2 kJ/mol, respectively. In contrast, the E_{α} for co-pyrolytic degradation was 191.6 kJ/mol. 388 The predictions via models agreed with the findings from Friedman and FWO iso-conversional methods.

Wang et al.(Wang et al., 2016) evaluated the kinetic models employing sequential and coupling methods and assessed the pyrolysis of cellulose, lignin, and hemicellulose, taking microcrystalline cellulose, beechwood xylan and organosolv lignin as the model compounds. The relationship of E_{α} to conversion rate was examined by applying the Isoconversional approach.(Kujirai and Akahira 1925) A one-step reaction model was used for cellulose, whereas a three-stage model for hemicellulose and a two-stage model for lignin was employed. The E_{α} for cellulose pyrolysis remained unaltered under different conversion rates, indicating that the complete process followed a common reaction pathway. The concept of a typical reaction pathway paved the 396 way for applying a single global reaction model to represent the devolatilization during cellulose pyrolysis. The 397 Coats-Redfern method (Coats and Redfern, 1964) and Kissinger (Elder, 1985) pathways were adopted to 398 produce the reaction model. Avrami-Erofeev nucleation model (Allnatt and Jacobs, 1968) explained cellulose 399 pyrolysis with an E_{α} of 119.2 kJ/mol. On the other hand, a reaction order model explained the pyrolysis of 400 hemicellulose, with the E_{α} of 93.6 kJ/mol in the first parallel reaction route and lignin with E_{α} of 114.6 kJ/mol. 401 The authors further demonstrated that cellulose pyrolysis is comparatively more straightforward vis-à-vis 402 hemicellulose and lignin pyrolysis, with parallel and successive reactions in the latter two, modeling their 403 pyrolysis very complicated. It can be deduced from the literature that while kinetic modeling is an essential tool 404 to enhance the understanding of the pyrolysis of different biomasses, incorporating transport mechanisms can 405 generate improved computational tools which can aid in the design and optimization of pyrolyzers. More 406 research is however needed to formulate and validate all-inclusive models.

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4.3. Computational Fluid Dynamics (CFD) Modeling

408 The biomass pyrolysis process is highly complicated, with thousands of chemical reactions (Sikarwar 409 and Zhao, 2017). Therefore, it is impossible to consider all the reactions while developing a CFD model. In real-410 life scenarios, appropriate and simplified reaction kinetics is required to depict feedstock devolatilization 411 followed by tar cracking (Xiong et al., 2018), and is crucial as the chemical reactions directly impact the 412 pyrolyzer's efficacy. In addition, any model should be computationally affordable. Many chemical reactions, 413 reactants and products are usually considered in all the reactor scale CFD models⁷⁶ and are known as lumped 414 global kinetics. However, comparatively complicated kinetics have also been employed in recent investigations 415 to depict biomass pyrolysis. Ding et al., 2020) developed a CFD model for fluidized bed pyrolysis of 416 solid waste to evaluate product distribution, temperature distribution and flow regime in the reactor bed and 417 assessed the impact of temperature, superficial gas velocity and bed height. Pyrolysis was defined by multi-418 component and multi-step reaction models, whereas multiphase flow was described by the Euler-Euler 419 approach. The feedstock was fed at a rate of 5 kg/h. User-defined functions in Fluent software characterized 420 heterogeneous reactions. It was reported that the feedstock has a trivial impact on gas temperature, which 421 became stable at 37.4 s.

422 Moreover, the mass flow rate of products fluctuated with pyrolysis time within $\pm 10\%$ of the average 423 values after achieving a steady fluidized state. In addition, it was also noticed that there was a periodic 424 fluctuation in the distribution of products in the bed. As the temperature increased, the tar fraction increased at 425 temperatures up to 500°C and then started reducing, whereas the gas fraction showed the opposite tendency. It 426 was noticed that secondary tar cracking was elevated above 500°C, leading to a reduction in tar amounts. 427 Superficial gas velocity harmed gas fraction, reducing the tar residence time and decreasing tar cracking. The 428 other impact of increased gas velocity was an enhancement in the product flow rate fluctuation, although the 429 char fraction was not influenced. The fluctuations in flow rates of pyrolytic products were also reported with 430 increasing bed height, with a negligible impact on product fractions. The authors found the temperature 431 distribution was similar, whereas product yields varied concerning experimental validation. Lu et al. (Lu et al., 432 2021) from NREL investigated the influence of biomass size and composition on fast pyrolysis using the CFD 433 model and step pyrolysis kinetics. The authors validated the model with two sets of experimental data. In 434 addition, the influence of biomass components on the yields of pyrolysis products was investigated using 435 sensitivity analysis. The authors also investigated the effect of particle size on heat transfer, hydrodynamics and product yields using a fluidized bed model by coupling chemical reactions with the CFD reactor model. It was 436 437 noticed that the impact of particle size on hydrodynamic behavior was similar in the reactor. With the progress 438 in pyrolysis, the biomass particle's density fell to 80-90% of their original density and the lighter particles began 439 to shift to the upper region of the bed. In addition, it was noticed that the larger particles needed longer 440 residence time because they have a slower heating rate and, thus, slow conversion. The simulation also indicated 441 that particle size significantly influenced the yields of pyrolysis products. An increase in bio-oil yield was 442 attributed to the extended residence time of the larger particle size.

- 443 Hoosdaran et al. (Hooshdaran et al., 2017) evaluated a conical spouted bed pyrolyzer's heat transfer 444 characteristics and hydrodynamics by generating a CFD model employing an Eulerian-Eulerian technique combined with the kinetic theory of granular flow. The study assessed the heat transfer coefficients, pressure 445 446 drop, particle velocity and solid volume fraction along with the influence of the specularity coefficient (ϕ), and 447 particle-wall restitution coefficient on heat transfer and hydrodynamics. The authors found a direct relationship between wall temperature, heat transfer coefficients, and pressure drop. However, the opposite trend was 448 449 noticed for the influence of φ on the bed pressure drop and wall-to-bed heat transfer coefficients. At lower φ , the 450 rate of fall for pressure-drop and heat transfer coefficient was higher, where the rate of decrease was more 451 important for the former than for the latter. The authors deduced that the pressure drop changed by 14%, while 452 the alteration in heat transfer coefficient was about 7% when φ was elevated from 0.01 to 0.15. In addition, an 453 inverse relationship between the restitution coefficient and pressure drop was established. A similar trend was 454 noticed for heat transfer performance. A decrease of 31% in pressure drop and 7.8% in heat transfer coefficient 455 was deduced when the restitution coefficient was increased by 80%. Jalalifar et al. (Jalalifar et al., 2020) developed a CFD model for pilot scale fast pyrolysis intending to use it as a design tool for scale-up. Chemical 456 457 kinetics and multiphase flow dynamics were employed for an auger reactor, where a rotating reference frame 458 was included to model the impact of the rotation of the auger. Feedstock flow rates varied from 1 to 4 kg/h, the 459 temperature ranged from 400 to 600°C and pressure varied from 0 to 50 kPa. In addition, the impact of N_2 was evaluated as a carrier gas with a flow rate ranging from 1 to 10 kg/h and the influence of the angular velocity of 460 461 the screw was assessed from 45 to 95 rpm. The study reported 500°C to be the optimal temperature for bio-oil 462 generation. It was also noticed that an elevation in bio-oil happens with the enhancement in feedstock flow rate 463 due to the decrease in vapor residence time which resulted in minimizing the reactions of the non-condensable 464 part in the vapor phase. In addition, an increase in bio-oil fraction was noticed when N₂ was fed because of reduced vapor residence time. The optimal value of rpm was reported as 70. The results were in good agreement 465 466 with experimental values.
- 467 CFD principles were applied by Zhong et al. (Zhong et al., 2019) to investigate the synergistic influence 468 of particle shrinkage and intra-particle heat conduction on the fast pyrolysis of biomass. A lumped kinetics 469 approach was adopted to assess fast pyrolysis, whereas a multi-fluid model was chosen to evaluate the 470 hydrodynamics. Four different cases with diverse particle shrinkage and intra-particle heat conduction 471 arrangements were considered and their efficacies vis-à-vis product yields were investigated. The authors 472 assessed the char characteristics, product distribution and the distribution of particle diameter and density. They 473 reported a decrease in tar fraction and an increase in char amounts when the impact of particle shrinkage and

- intra-particle heat conduction were considered. In addition, a trivial effect of intra-particle heat conduction was
 noticed, especially for small diameter (325 μm), which further weakened when the particle shrinkage effect was
 considered. The survey of CFD modeling studies emphatically reflects a need to improve modeling precision.
 Regarding multi-fluid modeling, the impact of sub-grid structures should be considered (Xiong et al., 2018;
 Xiong et al., 2017). Moreover, the modeling speed needs to be enhanced for discrete phase modeling as it is
 computationally intensive. More developments in applying CFD principles to develop deep insights can lead to
- 480 a better understanding of the pyrolysis process.

481 4.4. Artificial Neural Network (ANN) Modeling

482 Artificial Neural Networks (ANNs) are a programming concept built based on biological neural 483 networks in the human brain. A simple schematic of ANN with two hidden layers forward propagation network 484 is shown in Fig. 6. An ANN comprises nodes called artificial neurons. Depending on the complexity of the 485 model, neurons are organized in multiple layers, which are an input layer, an output layer and several hidden 486 layers (two hidden layers as shown in Fig. 6). ANNs are a widely accepted powerful tool to simulate highly non-487 linear processes. However, many researchers highlight the lack of interpretability and the black-box nature of 488 ANNs as major drawbacks (Li, J. et al., 2020; Pandey et al., 2016; Serrano and Castelló, 2020). It is to be noted 489 that the researchers have made substantial efforts to address these issues and improve their interpretability 490 (Ascher et al., 2022). The potential of ANN to model highly non-linear problems enhanced its reputation in 491 modeling complex thermochemical processes. ANNs are highlighted as universal function approximators, which 492 means that a neural network can be created to model any given function successfully [103].



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Fig. 6. An ANN model with two hidden layers. I and O represent perceptron's inputs and outputs, respectively.

496 Cao et al. (Cao et al., 2016) explored the possibility of obtaining biochar through the pyrolysis of cattle 497 manure. The authors combined Least Squares Support Vector Machine (LS-SVM) with the conventional ANN 498 model to perform the investigation. Thirty-three datasets from the lab-scale reactor were taken to develop the 499 model and predict the results. During the exploration, the value of R^2 was found to be 0.96 and 0.80, 500 respectively. The authors argued that the LS-SVM model was more precise and robust vis-à-vis the 501 conventional Neural Network Model. These studies can pave the way for further research employing similar 502 approaches for other types of waste. Non-recycled plastic waste is a growing problem in almost all nations. 503 Using pyrolysis to transform plastic waste into usable fuel was evaluated by some researchers by developing the 504 ANN model. These researchers assessed the data about fuel generation from plastic waste through the 505 Levenberg-Marquardt pathway (Abnisa et al., 2019). The lowest mean square error (MSE) formed the basis to 506 designate the optimum number of concealed neurons. In order to ensure precision and reliability, statistical 507 evaluation and graphical presentation were employed to examine the model. The optimal solution aims to report 508 the best fit of MSE between output (from the dataset, product yield) and feed-forward neural network (FANN) 509 prediction. The drawback of the FANN system is the limitation in restricting the training and validation errors. 510 Early stopping method can be used to overcome the over-fit or under-fit issues with FANN, thereby improving 511 performance of FANN. The regression analysis revealed that the values for training and validation datasets were 512 above 0.9. In addition, the mean square error values for both datasets were negligible $(2.6419 \times 10^{-4} \text{ and}$ 513 0.1114). The values of tar, oil and gas acquired from the developed ANN model were examined via a ternary 514 graph and in close agreement with the published literature. This clearly shows that the pyrolytic products can be 515 precisely and reliably evaluated from the ANN modeling approach.

516 Karaci et al.[106] developed a rigorous ANN model to examine hydrogen generation from the 517 pyrolysis of wastes such as olive husk, cotton cocoon shell and tea waste. The authors employed the Neural Net 518 Fitting tool in MATLAB to perform the computations and made the model more rigorous by including a wide 519 number of parameters: quantity of biomass, biomass diversity, and different types of catalysts (ZnCl₂, NaCO₃ 520 and K₂CO₃). The study reported a trivial deviation in hydrogen ratio when the mean square error was 521 considered. The authors noticed that the optimal model was produced for olive husk waste at 700°C with 10% 522 ZnCl₂. It has been posited that such ANN models can save a huge amount of time needed for experimental work 523 and reduce labor. In addition, they can be a crucial aid for waste managers, planners, and research workers. Care 524 must always be taken when extrapolating beyond the "trained" regimes of such models, though, in fairness, they 525 can sometimes elucidate pathways not considered by human workers. Thus, for example, AlphaGo, a computer-526 based program that integrates deep neural networks with an advanced search tree, can be considered an example 527 of the potential "intuitive leaps" possible using artificial intelligence (AI). During the initial stages, AlphaGo 528 was made to play against itself many times and could learn from its mistakes. Over time, AlphaGo became 529 stronger and better at learning and decision-making. However, two moves, move 37 and move 78, are 530 recognized as pointers to how AI can go beyond current thinking and influence major aspects of the world, such 531 as health care and software designs. In a game between AlphaGo and Lee Sedol (the world champion) in March 532 2016, the machine made a move, move 37, which goes beyond what was achieved by human intuition in the 533 3000 years of history of the Chinese game GO. In response, Lee Sedol's move 78 was described as "God's 534 touch" by the GO gaming community. In other words, the machine-human interaction during the game 535 empowered the human brain to realize a part of previously unnoticed reality (DeepMind, 2020). Not just 536 empowering the human brain, AI provides an opportunity to enhance the coding process further to provide a 537 better experience from simple tasks (games) to highly complicated and complex tasks (health care).

Some researchers (Zhang et al., 2020) developed an ANN model to deduce higher heating value (HV)
of producer gas generated via sludge pyrolysis. Multiple parameters were evaluated, such as sludge type, the
moisture content in sludge, pyrolytic temperature, catalyst type, and catalyst amount. ANN model with a

541 regression coefficient and a model F value of 0.9501 and 19.87 reported goodness of fit. It can be inferred that 542 the model best describes the behavior of the neurons in the hidden layer and the initial value of weights (and 543 bias) on the MSE of the model. The training was automatically stopped after 19 epochs when the network gave 544 the minimum MSE. At the optimal conditions, a three-layer topology network was obtained with eight neurons 545 in the input layer, 15 neurons in the hidden layer, and one neuron in the output layer. A correlation coefficient of 546 0.97 and mean square error of 14.62 was found while forecasting the HV of sludge pyrolysis-derived producer 547 gas. The authors found pyrolytic temperature and sludge moisture as the most crucial parameters influencing the 548 HV of producer gas among all the inputs. They reported the maximum value obtained for HV as 1833.5 kJ/m³N 549 at 895°C with the moisture of 45.63 wt%. They compared the developed model with multiple linear and 550 principal component regression and found it more precise when compared to the latter two approaches.

551 ANN models can be applied for estimating the kinetic parameters of biomass pyrolysis with cellulose, 552 hemicellulose and lignin as inputs. The critical step of development includes the diversity of biomass 553 composition and type. TGA, kinetic data can be employed to calculate the input data. Datasets from around 150 554 TGA experiments of different biomass compositions were taken to examine the network. They reported a non-555 linear relation between biomass constituents and output parameters. They also argued that the relationship 556 between biomass constituents and kinetic parameters could be accurately forecasted with $R^2 > 0.9$. They adopted 557 30 neurons for reaction order, 17 neurons for E_{α} and 20 neurons for pre-exponential factor post-optimization 558 with a mean standard error of 0.001. They assessed their results via contour plots and determined that the 559 maximum values of all three kinetic parameters are required by cellulose. These plots also reflected the non-560 linearity and intricacy of the system. Kasmuri et al. (Kasmuri et al., 2019) conducted an interesting analysis to 561 employ pyrolysis for methanol generation to develop a control system using MATLAB. Model reference control 562 in a dynamic study of nonlinear methanol synthesis vis-à-vis process design and control parameters were used to 563 sustain high methanol generation with set point constant values at optimal operational conditions from 564 experimental investigations. They found the reaction temperature, time and N_2 flow to be the vital variables that 565 significantly impacted the process. The maximum yield of ethanol was reported to be 3.09 wt.% with a mean 566 squared error of 0.2617. The nonlinearity of regulating input temperature to the linearity of the measured output 567 of bio-methanol yield was accomplished in this study (Yoon et al., 2019).

568 In recent years, ANN models have become an influential tool for evaluating different dimensions of 569 pyrolysis processes. These models can save a considerable amount of labor and time needed for the 570 experimental work. More importantly, they aid in cost-cutting. Based on this literature survey, it is concluded 571 that combining two or more approaches, such as LS-SVM, fuzzy logic, quantum models, etc., with traditional 572 ANN models enhances the accuracy and reliability of the prediction. Therefore, more research is needed on 573 integrating approaches for diverse scenarios. Modeling approaches have been extensively used to understand the 574 biomass pyrolysis process (Ciesielski et al., 2018). Modeling studies are reported for atomic-scale phenomena 575 (Burnham et al., 2015; Krumm et al., 2016) Meso/Particle-scale phenomena (Ciesielski et al., 2017; Di Blasi, 576 2002a), and the reactor scale (Eri et al., 2017; Lee et al., 2017). Atomic-scale models could consider about 25 577 chemical species for modeling biomass pyrolysis. The model developed by Ranzi et al., employed a categorical 578 reactant and product lumping scheme, which included 25 chemical species (Ranzi et al., 2017). The atomistic 579 and sub-atomistic models provide details that assist in understanding the fundamental reactions of biomass

580 pyrolysis. The limitation of atomistic and sub-atomistic models is their link to the physical process, time scale 581 and incomplete product speciation. The single-particle models are computationally fast and simple for particle-582 scale modeling, but their inability to represent anisotropy, the basic characteristic of biomass particles, is their 583 major disadvantage. However, two- and three-dimensional models consider anisotropy and allow the vapor 584 fields within the particles. The reactor-scale modeling, for example, the CFD approach, although there has been 585 substantial progress in this area, even the most sophisticated modeling approaches consider simple global 586 pyrolysis schemes, assume oversimplified biomass particle geometries (in case of a Lagrangian approach) and 587 employs models that were developed for other materials with different properties. Though substantial research 588 has been done using modeling to understand the pyrolysis process, it is still possible to develop kinetic 589 mechanisms that de-couple transport phenomena with reaction kinetics and facilitate their applicability to new 590 systems. In addition, alongside maintaining computational manageability, future work needs to focus on 591 including chemical speciation that enables predicting product composition.

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593 5. Challenges in the pyrolysis process

594 Pyrolysis technologies are generally tested at laboratory and pilot scales. Scaling up to commercial production 595 can be challenging owing to the complexity of the heat transfer quality and quantity of the feedstock. Biomass 596 feedstocks are regularly heterogeneous in composition with huge differences in moisture content, particle size, 597 and chemical composition leading to non-uniform heating and reaction rates during pyrolysis, affecting the yield 598 and quality of the products. The following section throws light on the challenges associated with thermal 599 cracking.

600 5.1. Aerosol formation during the pyrolysis process

601 Lignocellulosic biomass, with porous and microstructure structural compounds, under pyrolytic 602 conditions produce a short-lived intermediate liquid phase which furthers breakdown to volatiles and permanent 603 gases and releases aerosols. The inevitable aerosol emissions during pyrolysis can severely impact the 604 downstream processes. The first-ever experiment of biomass pyrolysis done in a micropyrolyzer revealed that 605 the feed, before final decomposition, is converted into a short-lived intermediate (liquid phase) accompanied by 606 multiple pyrolysis reactions (Ansari et al., 2021). Aerosols formed during the pyrolysis process can be grouped 607 as primary or secondary. Three mechanisms are responsible for the formation of primary aerosols during the 608 pyrolysis process; (i) intermediate liquid (IL) mechanism, in which biomass forms an IL during the thermal 609 decomposition and within the liquid phase, reactions such as dehydration, depolymerization and rearrangement 610 occur before the products are converted to gas, char or aerosols (Teixeira et al., 2016). (ii) Vapor-bubble 611 collapse mechanism, within which the molten IL vapor-bubbles are produced, is followed by a collapse to form 612 a liquid jet and droplets of liquid aerosol (Iisa et al., 2019). (iii) Film-aerosol generation occurs due to the shear 613 thinning of bubbles, and the aerosols formed via this mechanism generate smaller aerosol droplets compared to 614 the vapor-bubble collapse mechanism (Teixeira et al., 2016). However, it is possible to trap the aerosols inside a 615 solid matrix after ejection and, as a consequence of the collision, the particle size of the aerosols may increase 616 (Pecha et al., 2019). Secondary aerosols can be formed due to secondary condensation reactions during the rapid 617 cooling of pyrolysis vapors (Winkelmann et al., 2018).

618 Even though secondary aerosols have been reported for an extended time, the existence of primary 619 aerosols in biomass pyrolysis is recently reported. Very few studies characterized the size distribution of 620 primary aerosols at the laboratory scale. Consequently, little is known about aerosols' composition, size 621 distribution and capacity to transport the impurities (such as inorganics) from biomass to the final products (bio-622 oil) (Teixeira et al., 2016). Teixeira et al.(Teixeira et al., 2011) proposed a 'reactive boiling ejection' 623 mechanism, which suggests that the primary aerosols are spontaneously generated from biomass (cellulose) 624 pyrolysis. A high-speed photography technique was used to record the release of primary aerosols from molten 625 cellulose. The aerosols were released in the form of liquid jet as the bubble collapsed, as shown in Fig. 7. The 626 authors reported that after 100 ms, particles are fully molten and adopt a hemispherical shape (Fig. 7B). 627 Spontaneous ejection of aerosol occurs (107 ms), and a trace of the ejected particle is visible at 108 ms (Fig. 628 7C). The ejected particle appears to slow down after one ms (Fig. 7D) and the molten droplet is converted to 629 gases, aerosols and vapors, leaving a clean surface (Fig. 4 E). The aerosol droplets were noticed to have a 630 number-based mode diameter of ca. 0.8 mm and a size smaller than 3 μ m. In addition, the authors reported that, 631 based on the aerosol composition, the aerosols were formed via the ejection mechanism and not because of 632 secondary reactions.



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Fig. 7. Stages of ejection of aerosols from microcrystalline cellulose particle. Source: Adapted from (Teixeira et al., 2011).

637 In another study aimed at understanding the impact of aerosols on the origin and fate of inorganic 638 particles based on product fractionation, the authors reported that ca. 3% of initial feed was transported to the 639 gas phase as primary aerosols (Teixeira et al., 2016). Fig. 8 shows the high-speed imaging of cellulose pyrolysis 640 on a 500 °C aluminum nitride surface. Fig. 8-A shows the sequential frames explaining the solid cellulose 641 particle (0 ms) forming a liquid particle/surface interaction (1183 ms), followed by a four-phase stage (1350 ms) 642 which has a solid cellulose cap (@1, 1350 ms), solid/liquid interface (@2, 1350 ms), liquid intermediate at the 643 bottom of the particle (@3, 1350 ms) and reflection (@4, 1350 ms). Fig. 8-B shows more than 40 large primary 644 aerosols, highlighted in red with varying intensity, ejected from the liquid intermediate cellulose in 1 ms. It is reported that *ca.* 30% of bio-oil originates from particulates and aerosols (Radlein et al., 1987) and more than 60
wt.% of inorganic content in the bio-oil is linked to aerosols (Jendoubi et al., 2011).

647 The boiling ejection mechanism can serve as a tool to address the challenge of aerosol generation. 648 However, there could be numerous other possible mechanisms and the information on whether these alternative 649 mechanisms occur in the IL phase is unknown.(Mettler et al., 2012b) Soot is an aerosol product produced due to 650 the incomplete combustion of biomass. Unfortunately, the soot formation mechanisms from biomass fuel are not 651 well understood either (Li et al., 2018). During biomass pyrolysis, macro-molecule cracking results in HMW 652 compounds, such as saccharides, phenols, ketones and aromatics. It is worth stressing that the pathway from 653 these HMW compounds to nascent soot production is very complex and more challenging to explain than that 654 arising from small molecules.(Wang, X. et al., 2018) Considering that high levels of volatiles are produced 655 during biomass pyrolysis, the secondary reactions of hydrocarbons in volatiles are expected to trigger soot 656 formation. There are three main routes for soot formation, namely (i) small hydrocarbon mechanism based on 657 hydrogen abstraction carbon addition (HACA), (ii) generation of aromatic rings via dimerization of two 658 resonance stabilized cyclopentadienyl radicals and (iii) direct condensation and transformation of aromatic rings 659 (Fletcher et al., 1997; Richter and Howard, 2000). However, it is still unknown as to which pathway is dominant 660 in biomass pyrolysis.



661

Fig. 8. High-speed imaging of cellulose pyrolyzing on a 500 °C aluminium nitride surface. (A) Sequence
indicating the transformation of solid particle to liquid, bubble and vapor. (B) Aerosols observed during one ms
within the detection limits. Scale bars = 100 μm.

665

666 5.2. Tar formation and removal

667 Tar is used as a collective term for all the organic compounds with a molecular weight greater than 668 benzene but does not include char and soot. Currently, there are numerous definitions of tar available in the 669 literature depending on the field of research, however, no commonly accepted definition is agreed on (Gredinger 670 et al., 2018). According to standard DIN CEN/TS 15439(GIS, 2013), tar is a "generic (unspecific) term for

- 671 entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C_1 to C_6)". The
- total quantity and composition of tar can be determined using a solid phase adsorption method to perform tar
- 673 measurement. In general, tar is classified into five categories, namely (Sikarwar et al., 2016), (i) GC
- undetectable tars, (ii) heterocyclic components (for example, C₆H₆O, C₇H₈O, etc.), (iii) Aromatic compounds
- 675 (C₇H₈, C₈H₈, etc.), (iv) Light poly-aromatic hydrocarbons (C₁₀H₈, C14H₁₀, etc.) and (v) Heavy poly-aromatic
- 676 hydrocarbons ($C_{16}H_{10}$, $C_{24}H_{12}$, etc.).
- 677 In another classification of tar vis-à-vis pyrolyzers and gasifiers, researchers (Evans and Milne, 1997) have678 categorized them into the four groups below:
- i. Primary tars these originate from the cellulose, hemicellulose and lignin fractions in the biomass.
- 680 ii. Secondary tars originate from the conversion of primary tars and mostly contain phenolics and681 olefins.
- 682 iii. Alkyl tertiary tars cardinally contain methyl derivatives of aromatics such as xylene.
- 683 iv. Condensed tertiary tars poly-aromatic hydrocarbons.

The stability of the bio-oil is severely affected by the polymerization reaction of tar components at ambient conditions. Tar can chemically bind with the porous activated carbon irreversibly, thereby preventing desorption. The above challenges necessitate the removal of tar from the pyro-oil. Several pathways have been suggested as a result of extensive research in the field of tar cracking. These methods are widely employed and are partially effective. In general, tar destruction can be classified into five strategies: self-modification methods, mechanism methods, thermal cracking, plasma cracking and catalytic cracking (Sikarwar et al., 2016).

690

691 5.2.1. Self-modification method

692 As the name suggests, this route involves altering operational variables such as temperature, pressure, 693 heating rate, residence time, etc., to modify the tar produced during the thermochemical process. Sadakata et 694 al.(Sadakata et al., 1987) conducted a study to evaluate the pyrolysis of wood-derived lignin and holocellulose 695 in an electric furnace in the range of 400 to 900 °C with a heating rate of more than 1000°C/min. The authors 696 reported the production of ca. 10% of tar from holocellulose at 400°C, which fell rapidly, with further increase 697 in temperature, to ca. 1% at 700°C. In addition, the maximum amount of tar was seen at 500°C for lignin, 698 followed by a decrease when the temperature was further raised. The authors concluded that pyrolysis of lignin 699 and holocellulose should be conducted above 700°C to ensure the minimum tar yield. In another investigation 700 conducted by Fagbemi et al. (Fagbemi et al., 2001), it was observed that temperature has a crucial impact on tar 701 destruction. Tar quantities were found to increase up to 600°C and then reduce with further increase in 702 temperature, which suggested the existence and enhancement of secondary tar reactions beyond 600 °C as the 703 underlying reason for tar reduction.

704

705 5.2.2. Mechanism method

For the thermochemical treatment of rice husk, a venturi scrubber displayed an efficiency between 51 to

710 91% for tar capture.(Hasler et al., 1997) The cardinal drawback of this system was the generation of huge 711 amounts of wastewater which represented a disposal problem. A novel oil-based tar capture system devised by 712 the Energy Research Center of the Netherlands known as OLGA (oil-based gas washer in Dutch)(Boerrigter et 713 al., 2005) reported an impressive removal of 99% for phenol and 97% for heterocyclic tars. Other advantages of 714 ESP were the lack of fouling of ESP plates and insensitivity to voltage and residence times. In an interesting 715 study, Hasler et al. (Hasler et al., 1997) noted the potential of a bed filter made up of activated carbon in tar 716 removal. The phenols and high-boiling hydrocarbons were reported to be effectively captured by the carbon 717 filter, which was placed near the fabric filter. However, major challenges include cleaning tar from the filter 718 surface and the eventual plugging of such systems.

719

720 5.2.3. Thermal cracking

721 The application of heat to crack tars is called thermal cracking. Di Blasi (Di Blasi, 2002b) studied the 722 effect of feedstock particle size on tar generation and varied the heating rate from 177 to 182°C/s for a reactor 723 temperature of 527°C. The particle size ranged from 0.1 to 6 mm, and woody biomass was the feedstock. The 724 intra-particle reactions of tar cracking did not occur when small particles were used, effectively offering zero residence time of tars within the particles to convert volatiles. Consequently, there was a generation of high 725 726 amounts of tar (~80%). On the other hand, when large particles of size 5 mm were examined at the temperature 727 of 527°C, high degradation of tars was noticed. Brandt et al. (Brandt and Henriksen, 2000) used a pure 728 aluminum oxide reactor to investigate the impact of temperature on tar cracking. Out of the four sets of 729 measurements, one set was related to the gas from pyrolysis units and one set was from the updraft gasifier. The 730 residence time for these experiments was 0.5 s. Here, a significant tar degradation (130 mg/kg dry feedstock as 731 compared to the initial value of more than 1000 mg/kg dry feedstock) occurred for a residence time of 0.5 s at a 732 temperature of 1250°C or higher. Gas from the updraft gasifier was found to have a tar content of 32 mg/kg dry 733 feedstock, after treatment at 1290°C, compared to the previous value of more than 1000 mg/kg dry feedstock. 734 These studies certainly reflect the significance of particle size and how heat is used to crack tar.

735

736 5.2.4. Plasma cracking

737 Corona discharges were employed in some investigations to assess their influence on tar cracking. Nair 738 et al. (Nair et al., 2004) applied corona discharge for about 3 min to decompose naphthalene. At 400°C with an 739 energy density of 40 J/L, 50% of the naphthalene was destroyed. Tar cracking was due to reactive species 740 generated by high-energy electrons (Sikarwar et al., 2020). The authors argued that an elevation in gas 741 temperature would enhance the oxidation kinetics coupled with primary O radical yield. Heesch et al.(Van 742 Heesch et al., 2000) evaluated the reliability of a plasma system for a gasifier (with wood as the feedstock). 743 They demonstrated a removal efficiency of 72 to 95% for dust, 68% for heavy tar and 50% for light tar. In a 744 study by Pemen et al. (Pemen et al., 2002), gliding arc technology was examined for tar destruction with variable 745 energy density. The temperature range applied for the experimental work was from 400 to 800°C. The study 746 reported a slight enhancement in tar destruction when the energy density was raised. However, a significant and 747 continuous tar decomposition was noticed with rising temperature in the reactor. 748

749 5.2.5. Catalytic cracking

750 Catalytic tar decomposition has become one of the well-studied pathways for tar cracking in recent years. 751 Diverse range of catalysts (Ni, Olivine, Dolomite, Zeolites, Ceramic, Carbon-based, etc.) have been 752 investigated. Catalytic tar cracking occurs in both in-situ and secondary tar cracking (Gil et al., 1999). Under in-753 situ tar cracking, a catalyst is employed inside the pyrolyzer/reactor. In contrast, the secondary tar cracking 754 method uses a secondary reactor, where tar in the producer gas is treated in the presence of a catalyst (Sikarwar 755 et al., 2016). The tar decomposition reactions are often kinetically limited; therefore, the reaction rate is 756 improved by increasing the temperature or using a catalyst. However, a catalyst can enhance the reaction rate 757 only where a reaction is thermodynamically favorable and becomes increasingly unimportant at higher 758 temperatures (Zeng et al., 2020). All the significant reactions normally considered in tar degradation are 759 described in Table 3. Simell et al. (Simell et al., 1997) conducted an in-depth study, used toluene as the model 760 compound for tar and suggested a series of tar cracking reactions (R1 to R8) and equilibrium reactions (R9 to 761 R14) (Table 2). Toluene is taken as a generic depiction of tar in all the reactions. The authors suggested that 762 Group VIII metals catalyzed the reforming reactions (R1 and R6).(Rönkkönen et al., 2010) It was inferred that 763 Fe present in ilmenite, coupled with CO_2 and H_2O in producer gas, catalysed reactions R1 and R6 and shown by the authors that at 830 °C and above, R6 is more favoured than R1 on the grounds of thermodynamics. However, 764 R12, R13 and R14 were favoured below 650 °C. Moreover, R8 is increased at elevated temperatures. In 765 766 addition, R9 was found to be catalyzed by Fe-based catalysts (Uddin et al., 2008).

767

Table 3. Significant reactions associated with tar cracking (Shen and Yoshikawa, 2013; Simell et al., 1997).

S. No.	Chemical reaction	Name of the reaction
R1	$C_nH_m^* + nH_2O \rightarrow nCO + (n+0.5m)H_2$	Steam reforming
R2	$C_nH_m + xH_2O \rightarrow C_xH_y + qCO + pH_2$	Steam dealkylation
R3	$C_nH_m \rightarrow C + C_xH_y + gas$	Thermal cracking
R4	$C_nH_m + (2n - (m/2))H_2 \rightarrow nCH_4$	Hydro cracking
R5	$C_nH_m + xH_2 \longrightarrow C_xH_y + qCH_4$	Hydro dealkylation
R6	$C_nH_m + nCO_2 \rightarrow 2nCO + 0.5mH_2$	Dry reforming
R7	$C_nH_{2n+2} \longrightarrow C_{n\text{-}1}H_{2(n\text{-}1)} + CH_4$	Cracking
R8	$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$	Carbon formation
R9	$CO + H_2O \rightarrow H_2 + CO_2$	Water gas shift
R10	$CO + 3H_2 \rightarrow CH_4 + H_2O$	Methanation 1
R11	$2H_2 + C \rightarrow CH_4$	Methanation 2
R12	$CO + H_2 \longrightarrow H_2O + C$	Water gas 1
R13	$CO_2 + 2H_2 \rightarrow 2H_2O + C$	Water gas 2
R14	$C + CO_2 \rightarrow 2CO$	Boudouard

 $*C_nH_m = Tars$

769

770 5. Future recommendations

Based on the research carried out in this review, several longstanding challenges are associated with
 biomass pyrolysis. Though cellulose can offer an approximate approach to elucidate the pyrolysis mechanism, it

773 is essential to develop model components that represent actual biomass, including cellulose, lignin, and 774 hemicellulose/ proteins, carbohydrates, and lipids. Further investigations on the fundamental mechanisms are 775 necessary to develop a methodology to optimize the pyrolysis process at the industrial level. Even though 776 different reactor designs have been tested to maximize the bio-oil yields, establishing the design on commercial 777 reactors for the pyrolysis of biomass at an industrial scale is challenging due to techno-economic reasons. 778 Further research is necessary for developing a pyrolyzer with features such as being suitable for a wide range of 779 feedstock, high heat transfer efficiency, low dependency on feedstock characteristics (i.e., moisture, particle 780 size) and high processing capacity for commercial application. Molecular studies on pyrolysis chemistry require 781 immediate attention. Pyrans and furan formation during cellulose pyrolysis can be explored to elucidate a 782 plausible mechanism. Determining the properties of intermediate liquids requires faster response (<1 ms) analytics, necessitating techniques capable of collecting and rendering inert to further reaction of intermediate 783 784 liquids in a short time. Challenges in the scale-up of pyrolysis technology restrict the commercialization of 785 biomass pyrolysis. Technical challenges, such as developing fundamental descriptions for elementary reaction 786 mechanisms that would facilitate the optimization of the process, should be addressed.

787 Popular reaction models consider a component of biomass rather than biomass. Research needs to be 788 focussed on developing a robust model considering whole biomass, including the major structural components 789 and other components (including inorganic species and extractives). The availability of data for model 790 development remains a significant challenge. Developing new models can improve the prediction accuracy and 791 generalization capacity related to the data type. For instance, modeling the process in a particular type of reactor 792 generates highly accurate data when the experimental/training data corresponds to the particular type of reactor. 793 This indicates that the model applies to a narrow range of training data. Efforts are recommended in developing 794 diverse models with low but satisfactory prediction accuracy. Therefore, more efforts are needed to generate 795 valid and legitimate data by considering a wide range of parameters. Future research is recommended to 796 illuminate the black box of ANN algorithms to enhance the interpretability of the results. Improving the 797 interpretability of the ANN models can help to understand the fundamental mechanisms of the pyrolysis process 798 from the network prediction. The solid-state models reported in the literature mainly considered TGA data, so 799 these models cannot adequately fit the short induction period during the pyrolysis process. It is to be noted that 800 only a limited number of studies considered multiple parallel reaction models, and data in this segment is sparse. 801 The kinetic models that use thermodynamic equilibrium equations often neglect the information about heat and 802 mass transfer phenomena. Further research is to be carried out in developing models that include these aspects. 803 A very urgent research direction for developing CFD modeling is improving model accuracy. Also, little is 804 known about aerosol formation and its chemistry during biomass pyrolysis. Most information regarding the 805 formation of primary aerosols is confined to the bubble ejection mechanism. Research must be directed towards 806 identifying the potential alternative aerosol formation mechanisms, which would require detailed information 807 about the properties of intermediate liquid species. In addition, a complete understanding of generation 808 mechanisms and the process through which the aerosols escape the microstructures of biomass is necessary to 809 address the challenge of aerosol generation.

810 Conclusions

811 Conversion technologies such as pyrolysis can utilize a wide range of biomass to generate valuable 812 products such as bio-oil, char, and pyrolysis gases. A deeper understanding of the pyrolysis mechanisms and 813 modeling is necessary for its optimization and cost reduction. A detailed description of the mechanism involved 814 in the conversion of polymers constituting the biomass, this review provides a comprehensive overview on the 815 pyrolysis mechanisms of structural components of lignocellulosic as well as aquatic biomass. It can be 816 concluded that each modeling approach's characteristics are unique under different operating conditions and 817 specific materials. At present, the mechanical models are mostly based on model compounds such as protein, 818 lipids and carbohydrates or lignin, cellulose and hemicellulose. However, more attention is needed in 819 developing robust models that consider the inorganics and extractives and represent the whole biomass. A 820 deeper understanding of pyrolysis is necessary to optimize, scale up, and reduce costs. Understanding aerosol 821 chemistry could minimize the impurities in bio-oil. Higher temperatures and longer residence time during 822 thermal cracking can minimize tar formation.

823 Author Contributions

Arun K. Vuppaladadiyam, and Shao-Yuan Leu conceived the idea and designed the manuscript; Arun K.
Vuppaladadiyam and Sai Sree Varsha wrote the manuscripts and took the contributions of Vineet Singh
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gave valuable suggestion and critically evaluated the manuscript many times that improved the quality of the
manuscript. Arun K. Vuppaladadiyam and Sai Sree Varsha share equal authorship. All the authors have agreed
to submit this manuscript to the Journal of Energy Institute.

830 Abbreviations

831 AI artificial intelligence; ANN artificial neural network; CFD computational fluid dynamics; DAEM distributed

activation energy model; FANN feed-forward neural network; FWO Flynn Wall Ozawa; HMW high molecular
weight; ILC intermediate liquid; KM kinetic modeling; LCFAs long-chain fatty acids; LHV lower heating

value; LMW low molecular weight; compounds; LS-SVM least squares support vector machine; MSE mean

- square error; NCGs non-condensable gases; SS Sewage sludge; TDM thermodynamic modeling;
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Highlights

- Biomass pyrolysis mechanisms concerning feedstock type are critically discussed
- Pyrolysis mechanisms play a major role in deciding the quality of end products
- Recent advancements in modeling ease the understanding of pyrolysis mechanisms
- Aerosol formation during pyrolysis severely impacts the quality of bio-oil