

Waste Tyre Gasification Processes: A Bibliometric Analysis and Comprehensive Review

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Highlights

- A bibliometric analysis of all known works on waste tyre gasification was investigated.
- Models that could simulate carbon nanomaterials production from waste tyre gasification need to be investigated.
- Polygeneration of products from gasification would make the process more effective.
- The application of artificial intelligence in waste tyre gasification could be considered in future works.
- Bibliometric analysis of works on waste tyre gasification
- Simulation of carbon nanomaterials from this process needs investigation.
- Polygeneration of products would make the process more effective.
- AI application could be considered in future works.

23 **Table of Contents**

24

25	Highlights.....	1
26	Table of Contents.....	2
27	Abstract.....	3
28	1.0. Introduction.....	4
29	2.0. Bibliometric Analysis	6
30	3.0. Literature Review.....	9
31	3.1. Waste Tyre Gasification Overview.....	9
32	3.1.1. Waste tyre Gasification Modes.....	12
33	3.1.2. Waste Tyre Gasification Reactors	14
34	3.2. Waste Tyre Gasification Targeted at Gaseous Product Production.....	19
35	3.2.1. Waste Tyre Gasification Targeted at Syngas Production	24
36	3.2.2. Waste Tyre Gasification Targeted at Hydrogen Production.....	31
37	3.3. Waste Tyre Gasification Targeted at High Valued Carbon Production	38
38	3.4. Waste Tyre Gasification Targeted at Other Products along with Energy Production ..	45
39	3.5. Modelling Waste Tyre Gasification Process.....	52
40	3.5.1. Kinetic Model	53
41	3.5.2. Thermodynamic Equilibrium Model (TEM)	61
42	3.5.3. Other Models Employed in Waste Gasification	65
43	4.0. Research Gaps and Recommendations for Future Works	65
44	5.0. Conclusion	67
45	Declaration of Conflict of Interest	69
46	Acknowledgements.....	69
47	References.....	69

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49 **Abstract**

50 Waste tyres are a significant environmental problem due to their large volume and the difficulty
51 of disposing of them safely. Waste tyre gasification is one of the key thermochemical routes
52 for converting waste tyres into valuable products such as gaseous fuels and/or solid fuels. In
53 this review, a bibliometric analysis of all works on waste tyre gasification from its onset was
54 investigated. We provide an overview of the current state of the art in waste tyre gasification
55 processes, including the types of reactors, gasification modes, and gasification products. The
56 modelling aspect of waste tyre gasification was also investigated as well as its shortcomings.
57 We also discuss the challenges and opportunities associated with the co-production of gaseous
58 products (syngas and hydrogen) and solid carbon products, polygeneration of multiple
59 products, and identify areas for further research. Our review demonstrates that gasification of
60 waste tyres is a viable option for the production of energy and valuable by-products, but more
61 research is needed to optimize the process and improve its economic feasibility. More research
62 is also required in modelling and optimization of other products such as carbon nanomaterials.
63 In addition, the investigation of the life cycle assessment (LCA) of waste tyre gasification is
64 vital as this can ease the adoption of waste tyre gasification technology in developing nations.

65 **Keywords:** *Waste Tyres; Hydrogen; Activated Carbon; Carbon Nanomaterials;*
66 *Polygeneration.*

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70 **1.0. Introduction**

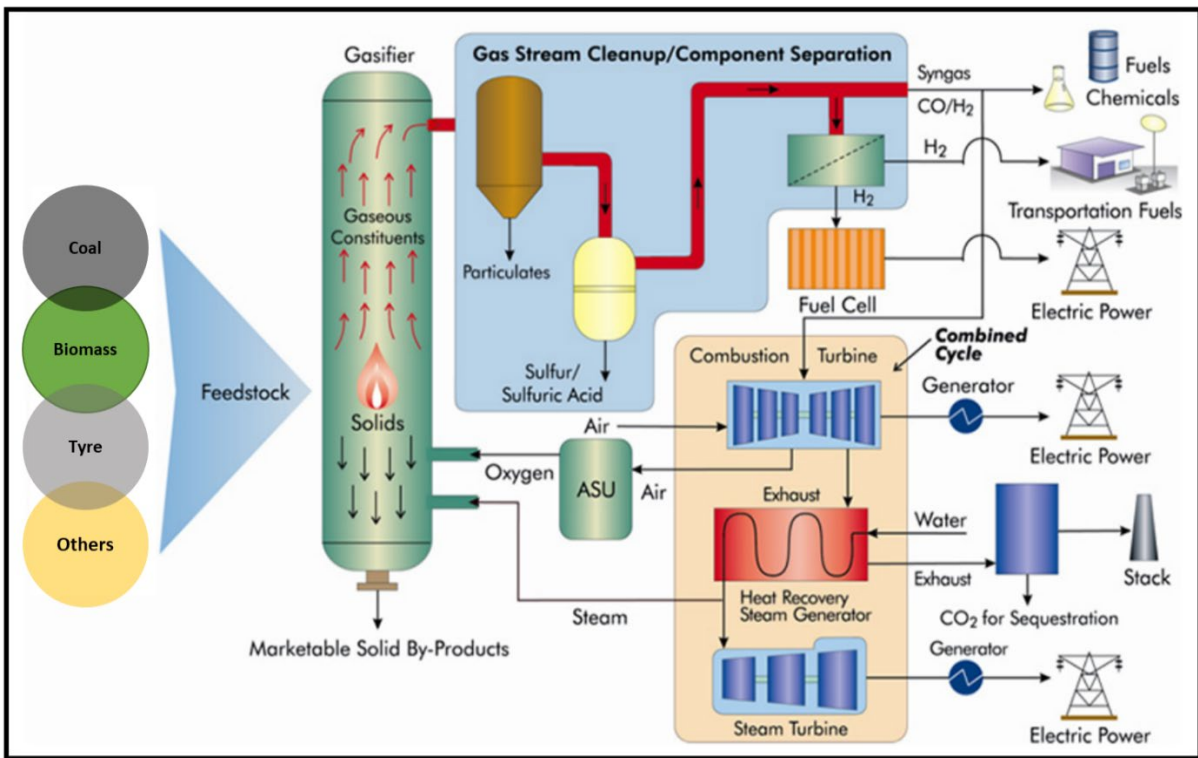
71 Biomass wastes are considered to be an underutilized energy source that currently
72 supplies around 10% of global energy and has the ability to supply well over 25% of global
73 energy demand by 2035 [1-3]. This vast volume of biomass wastes combined with other solid
74 wastes (including waste tyres) has enormous potential for conversion to energy [4-6]. By 2050,
75 the population of the world is projected to exceed 9 billion while the number of automobiles is
76 estimated to be around 2.4 billion [7]. Likewise, close to 17 million tons per annum of waste
77 tyres—more than 1.4 billion in number—are produced by various sources related to
78 transportation, meanwhile, only 10% of these waste tyres are being recycled globally [8-10].
79 With the current waste tyre recycling rate, these figures indicate that there will be a significant
80 amount of waste tyres lying around if no proper action is taken. Tyres typically last between
81 three and six years, and after that time they are either recycled or rethreaded, or they are
82 disposed of in a landfill [11, 12]. Waste tyre management has been a major challenge because
83 the dumping of these tyres in landfills is no longer permitted in most developing countries
84 because of their chemical and biological resistance to degradation [12-15]. In the past, the
85 common practice was to dispose of these tyres in landfills, where they would take up space and
86 pose environmental risks [11, 16-18]. Tyres generally have a complex chemical makeup and
87 are therefore difficult to decompose; it will take more than a century for them to decompose in
88 a landfill [19]. The non-biodegradable and non-decomposable parts of waste tyres produce
89 hazardous substances, solid waste, particulate matter, heavy metals, and pyrolytic oils that
90 contain polycyclic aromatic hydrocarbons (PAHs) when they are disposed of in landfills or
91 burned. These substances can also have a negative impact on the environment and human
92 health [20]. An average passenger car tyre is known to weigh 7-10 kg with a calorific value
93 between 30-45 MJ/kg which is greater than biomass and coal of equal weight [21, 22]. Over
94 40% of waste tyres are discarded worldwide without putting into considerable use hence, waste

95 tyres must be disposed of properly to minimize their influence on the environment [23, 24].
96 However, as the awareness of the negative impact of landfill waste has grown, there has been
97 a shift towards exploring alternative ways to manage waste tyres [25, 26]. As a compromise
98 reached through the 2018 EU Landfill Directive, the European Environmental Agency set an
99 aim to reduce the amount of solid waste being discarded (including waste tyres) to 10% of the
100 total by 2035 [27].

101 One of the processes that is used in the recovery of energy from solid wastes such as
102 biomass, waste tyres, and coal. is gasification. The capability of the gaseous products to be
103 stored, transported, and supplied to boilers and combustors makes waste tyre gasification
104 appealing [15]. The production of high-quality syngas from steam gasification is a possibility.
105 Standard gasification systems, on the other hand, necessitate high temperatures to degrade the
106 feedstock and to initiate reforming processes, both of which could reduce the efficiency of the
107 process [28]. One of the main advantages of gasification is its versatility in terms of feedstock
108 [29]. Unlike traditional incineration methods, which require a uniform and consistent fuel
109 source, gasification can process a wide range of feedstocks, including solid waste (which
110 includes waste tyres), biomass, and even coal as shown in **Fig. 1** [15, 30]. This flexibility allows
111 gasification plants to operate in a more stable and reliable manner, as they can adjust their
112 feedstock sources depending on availability and price [31, 32]. Waste tyres have been known
113 to have a high sulphur content (1-5wt.%) when compared to other solid wastes which mostly
114 come from vulcanization process [33-35]. This often leads to the formation of sulphur
115 compounds, hence, proper cleaning must be carried out after the gasification process .

116 Authors such as Oboirien & North [36] and Labaki & Jeguirim [37] have published
117 review articles on waste tyre gasification, however, no comprehensive review on waste tyre
118 gasification works from 2018 till present has been made. In addition, to the best of the authors'

119 knowledge, a bibliometric analysis that investigates all works on waste tyre gasification has
120 not been made available. Hence, this work combined a detailed bibliometric analysis with a
121 comprehensive review on the status of waste tyre gasification as well as recommendations for
122 future works.



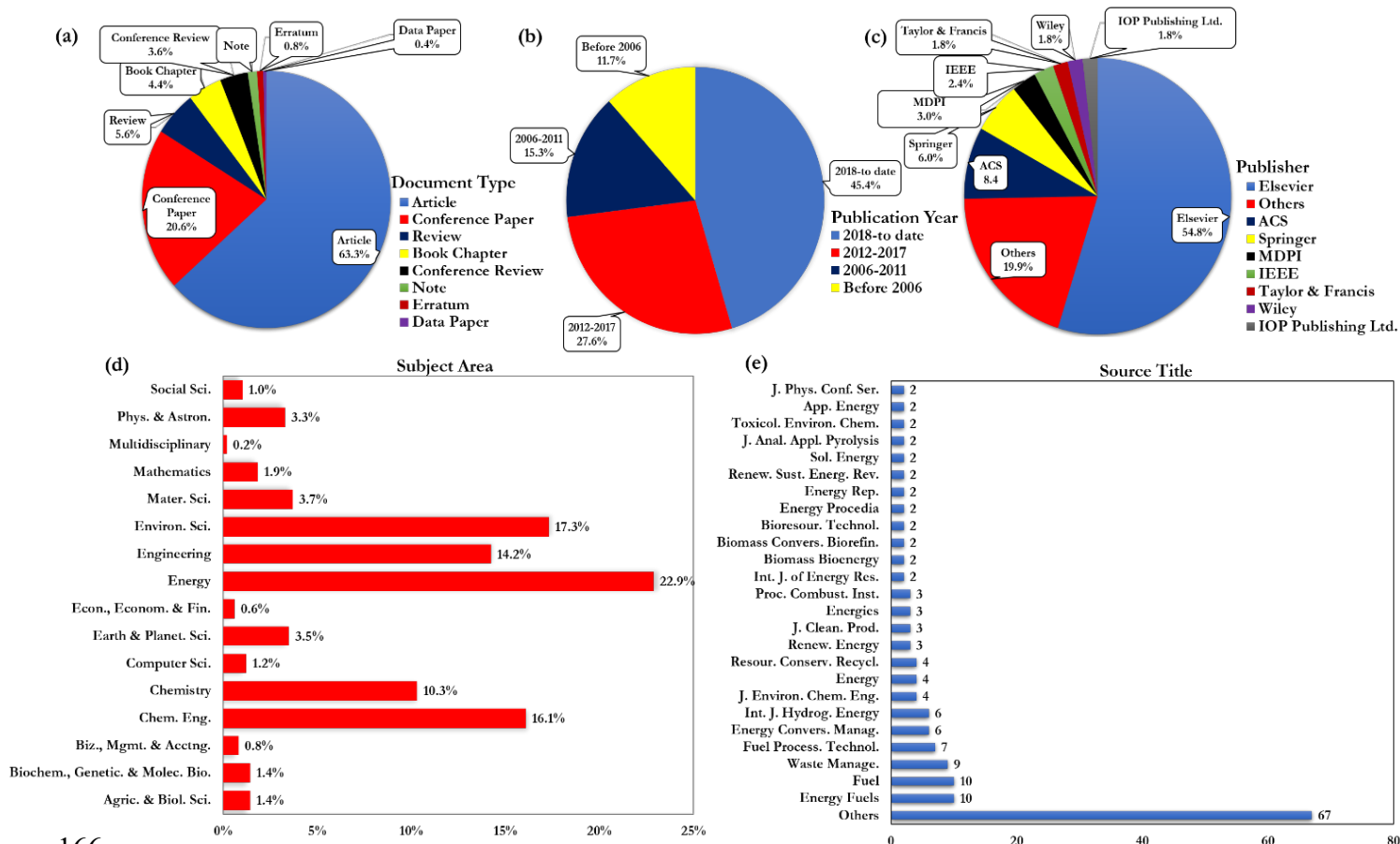
123
124 **Fig. 1.** A conceptual illustration of a gasification process showing the various kinds of products
125 that can be produced as well as the feed flexibility (Image obtained with permission from
126 National Energy Technology Laboratory [30]).

127 2.0. Bibliometric Analysis

128 The present study leveraged the bibliometric analysis technique to accomplish one of
129 the goals of this review which is to quantitatively visualize data on waste tyre gasification. This
130 approach is appropriate for reviews since it highlights and analyses waste tyre gasification
131 research growth over the years using bibliographic data. The most commonly employed
132 research article databases are Scopus, Google Scholar, and Web of Science, however, due to a

147 **Fig. 3.** shows the breakdown of waste tyre gasification publications in terms of metrics
148 such as the document type, year of publication, publisher, main subject areas, and the
149 publication source title. The document type breakdown shows 63% of the total articles were
150 journal articles, 21% were conference papers, and 6% were review articles while the remaining
151 10% were book chapters, conference reviews, notes, data papers and erratum as shown in **Fig.**
152 **3a.** The breakdown of the waste tyre gasification also shows that 2018 to date has the highest
153 number of researchers who have worked on the topic. A total of 73 articles representing 45%
154 of all the works on waste tyre gasification fall within the last 5 years. From 2012-2017
155 represents 28% of all works on waste tyre gasification, while before 2011 only 22% of the total
156 works on waste tyre gasification as shown in **Fig. 3b.** Considering the interest shown in waste
157 tyre gasification in recent years shows that it is still a technology at its development stage
158 worldwide. The top publishers for waste tyre gasification articles were Elsevier (55%), ACS
159 (8%), Springer (6%), MDPI (3%) and IEEE (2%) as shown in **Fig.3c.** **Fig. 3d** shows that
160 Energy (23%), Environmental science (17%), Chemical Engineering (16%), Engineering
161 (14%), and Chemistry (10%) are the top subject areas in waste tyre gasification. Meanwhile,
162 the top journal titles in waste tyre gasification were Energy & Fuels (10%), Fuel (10%), Waste
163 Management (9%), Fuel Processing Technology (7%), Energy Conversion and Management
164 (6%) and International Journal of Hydrogen Energy (6%).

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167 **Fig. 3.** Breakdown of waste tyre gasification publications in terms of (a) Document Type (b)

168 Publication Year (c) Publisher (d) Subject Area (e) Source Title.

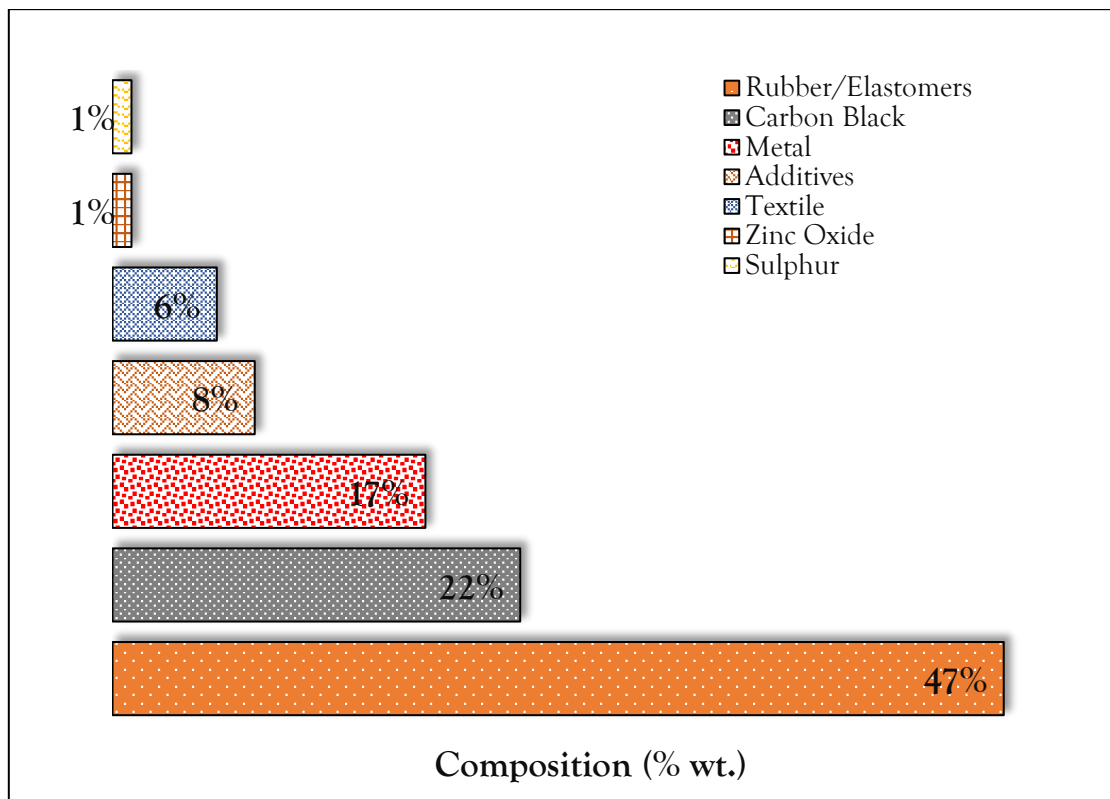
169 **3.0. Literature Review**

170 **3.1. Waste Tyre Overview**

171 Just like new tyre, waste/used/scrap tyres are made up of a variety of materials,
 172 including elastomers made of natural rubber (NR), synthetic rubber (SBR), cis-polyisoprene
 173 (SR), carbon black, zinc oxide (ZnO), sulphur, textiles and additives as shown in **Fig 4.** [23].
 174 With ZnO acting as an activator and carbon black as a compound, raw rubber with a sulphur
 175 content of 1-3wt.% is vulcanized to create a cross-link for hardening, enhancing the rubber's
 176 elasticity, conductivity, support, as well as thermal and abrasion resistance [20]. During the
 177 production process, other components such as steel cables, sulphur, textiles, ZnO, rubber
 178 extender oils, and carbon black are combined [20]. Generally, tyres need an appropriate

179 composition of carbon blacks with varying particle sizes to achieve the expected performance.
 180 The carbon black structure helps the rubber's continuous elongation stress and modulus. The
 181 more wear resistance and effective reinforcing there is, the smaller the carbon black particle
 182 size [39]. Waste tyre-derived fuel (WtDF) is produced by treating and removing the heavier
 183 components from it, followed by shredding, grinding, and sifting the waste tyres into various
 184 particle sizes. Compared to municipal solid wastes (MSW), coal, or biomass, the moisture
 185 content (MC) and ash content in waste tyres are low, while the fixed carbon content is higher
 186 [20]. This makes the calorific values (CV) of waste tyres (35-45MJ/kg) higher than those of
 187 various coal samples (13.5-33 MJ/kg) [40, 41], plastics (24-44MJ/kg) [42], refuse derived fuel
 188 (RDF) (30.42MJ/kg)[43] and a variety of biomass (15-22 MJ/kg) [44]. The high CV of waste
 189 tyre samples makes aids in for the potential energy recovery from waste into hydrogen, syngas,
 190 and liquid feedstock [45].

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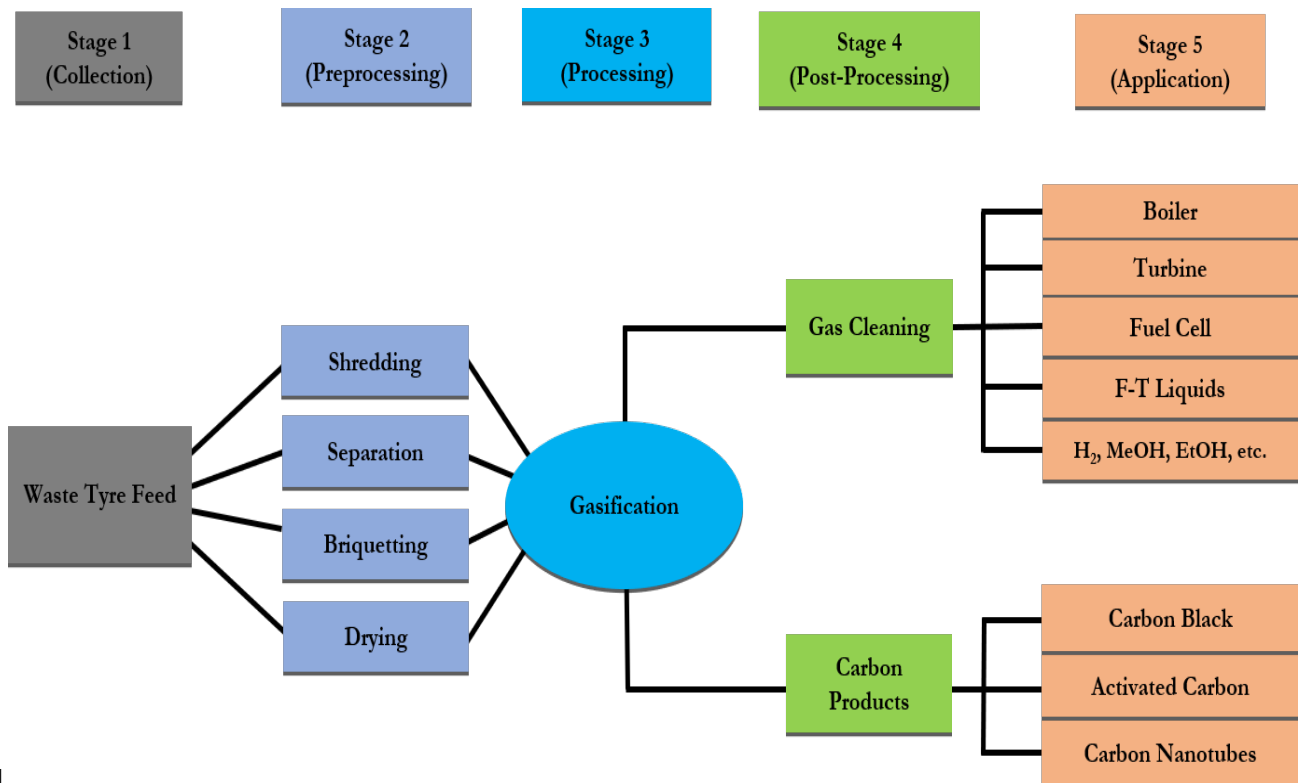
Fig. 4. Average tyre composition [46].

194 3.2. Waste Tyre Gasification Overview

195 Waste tyre gasification as an alternate source of renewable energy has been regarded
196 as a viable thermal conversion alternative process to pyrolysis as well as combustion. In
197 comparison to biochemical routes, thermochemical gasification processes appear to be a better
198 process for energy extraction from syngas [47, 48]. Waste tyre gasification is also a promising
199 technology for converting waste tyres into other by-products such as chemicals and carbon
200 products [23]. Depending on the gasification conditions, product gases from gasification
201 process can yield as high as 40 MJ/Nm³ [49]. The composition of the product gases as well as
202 their heating values depend on the selected gasification agent. ~~Air gasification also produces~~
203 ~~large concentrations of nitrogen in the dry gas mixtures with lower heating values (LHV)~~
204 ~~between 4 MJ/Nm³ and 5 MJ/Nm³, whereas steam and steam-air mixture can yield more~~
205 ~~hydrogen with LHV ranging between 7 MJ/Nm³ and 13 MJ/Nm³ [50].~~ Insights on the different
206 waste tyre gasification agents as well as their ratios on waste tyre gasification are further
207 explained in subsection 3.1.3.2. Waste tyre gasification process can be broken down into 5
208 stages which include: the collection stage, pre-processing stage, processing, post-processing
209 and the application stage as shown in **Fig. 5**. The final stages show that waste tyres gasification
210 has been employed in the production and co-production of several products. In order to improve
211 syngas and hydrogen production, waste tyres have been co-gasified with other feedstocks such
212 as coal, rubber, plastic and biomass such as acacia, pine, sawdust, and bamboo [34, 41, 43, 51,
213 52]. In waste tyre gasification processes, gasifier operating conditions (pressure and
214 temperature) are very important. Any increase in the gasifier operating pressure will result in
215 higher syngas (H₂ and CO) yield and higher lower heating value (LHV) [18]. Meanwhile, an
216 increase in the operating temperature will increase the syngas production rate and reduce the
217 char yield [53]. At temperatures above 1000°C, the production of hydrogen is favoured at the
218 expense of methane [18, 54]. Waste tyre gasification can achieve a thermal efficiency of up to

219 90%_{LHV} [55, 56]. More insights on the operational parameters that can influence waste tyre
 220 gasification can be found in section 3.1.3. Some of the studies that employed waste tyre
 221 gasification and co-gasification which produces key products and are discussed in subsequent
 222 sections.

223



224

225 **Fig. 5.** Stages involved in a complete waste tyre gasification process [15].

226 *3.2.1. Waste tyre Gasification Modes*

227 Currently, there are four modes of waste tyre gasification processes that have been
 228 employed to date. They include common/conventional gasification [34, 51, 56-63], plasma
 229 gasification [64-70], hydrothermal gasification [8, 71], and solar-assisted gasification [72-75].
 230 Each of the aforementioned waste tyre gasification modes is described in the subsequent
 231 section.

232 3.2.1.1. Conventional Gasification of Waste Tyres

233 Conventional gasification of waste tyres requires the use of gasifiers (fixed bed,
234 fluidized bed, rotary kiln, and entrained flow gasifier) and gasifying agents to breakdown tyres
235 into the desired products. The mode of operation of the conventional gasifiers is discussed in
236 section 3.1.2. By using air or oxygen, the required heat needed to breakdown the organic
237 portions of waste tyres is generated by the partial oxidation of the waste tyre feed [36].

238 3.2.1.2. Hydrothermal Gasification of Waste Tyres

239 Hydrothermal gasification of waste tyres is the gasification of tyres using
240 supercritical or subcritical water [76]. This mode of waste tyre gasification process does not
241 require any pre-drying, which results in significantly less tar and char being produced than
242 typical gasification and pyrolysis procedures [8]. The complete miscibility of supercritical
243 water with gas means that all reactions are carried out in homogeneous media which speeds up
244 the heat and mass transfer process [77]. Hydrothermal gasification technology is also beneficial
245 to the destruction of the polymer structures in waste tyres [8]. In addition, water serves as both
246 a solvent and a reactant to improve the yield of hydrogen gas, which might considerably
247 encourage the use of this gasification technology. This type of gasification is a promising
248 technology recently employed to gasify waste tyres and this process can be environmentally-
249 friendly for the conversion of waste tyres to hydrogen-rich syngas or hydrogen [8, 78].

250 3.2.1.3. Plasma Gasification of Waste Tyres

251 In this mode of waste tyre gasification, tyres are broken down into syngas and vitrified
252 slag [36]. While conventional and hydrothermal are usually carried out in the common gasifiers
253 (fixed bed, fluidized bed, rotary kiln, and entrained flow gasifier), plasma gasification is done
254 in an electric arc or plasma torch furnace [65, 66]. A working gas must flow between the two
255 electrodes in order to form the thermal plasma, which is done by transferring a strong electric
256 current between them [79]. Plasma gasification of waste tyres requires higher temperatures

257 than those used in conventional gasification. Regardless of the reactor architecture, the majority
258 of studies on the conventional mode of gasification of tyres have been conducted below 1000°C
259 while plasma can be carried out as high as 1800°C [36, 70, 79]. A major drawback of the plasma
260 gasification process is the high concentration of N₂ in the syngas stream [67].

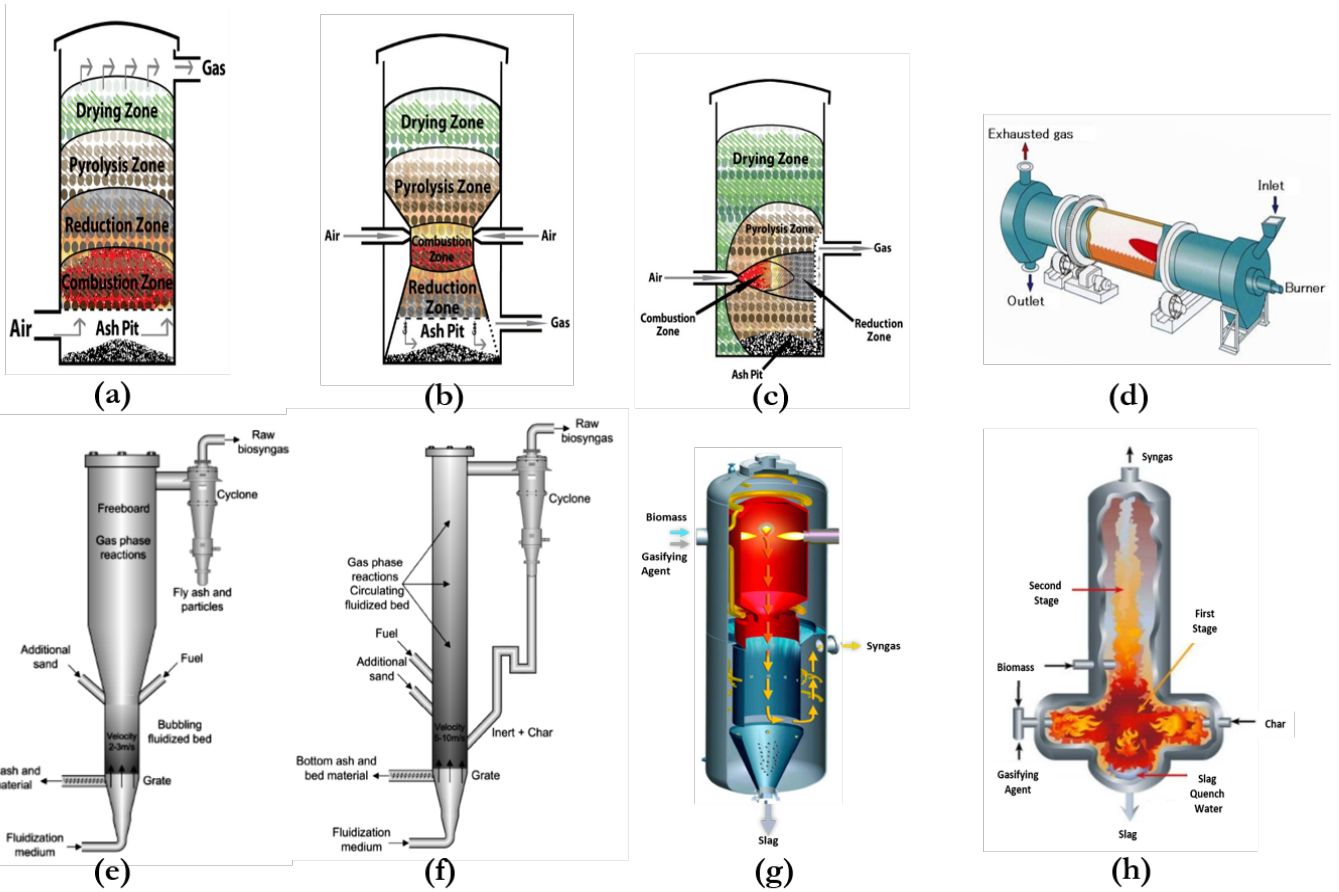
261 3.2.1.4. *Solar-assisted Gasification of Waste Tyres*

262 This mode of waste tyre gasification requires concentrated solar energy as the heat
263 source [74]. Higher gasification temperatures (above 1100°C) are possible without the use of
264 an oxygen-blown furnace, which leads to much faster reaction kinetics and better-quality
265 syngas with low or no tar content [72]. The need for expensive downstream gas cleaning and
266 separation is reduced because the contamination of syngas via combustion is prevented [72,
267 73]. Since, solar-assisted waste tyre gasification requires only steam, an upstream air separation
268 unit (ASU) is not required and this also brings down the operating cost [80]. In addition, the
269 process makes it possible to process virtually any kind of carbonaceous feedstock, maximizing
270 the use of the available resources [73, 81].

271 3.2.2. *Waste Tyre Gasification Reactors*

272 Waste tyre gasification reactors (see **Fig. 6**) can be divided into three categories: fixed
273 bed (which could be updraft, downdraft or cross draft), fluidized bed (which could be bubbling
274 or circulation), and entrained flow reactor (which could be top-fed or side-fed) [6, 55, 82]. In
275 addition to these three, rotary kilns and plasma reactors have also been employed to gasify
276 waste tyres [79, 83]. The choice of reactor depends on the operation size, the properties of the
277 waste tyre feed, and the intended application of the syngas [84]. All of these reactors have
278 advantages and downsides as summarized in **Table 1**. Due to the relatively lower cost of a
279 fixed bed gasifier, most recent studies [34, 35, 55, 58, 61, 85-89] have employed this reactor
280 at all scales. In addition, rotary kilns have been explored mainly at pilot scale [83, 90, 91] while
281 fluidized bed have been applied at lab scale [60, 90]. Ma *et al.* [65] and Larionov *et al.* [64]

282 explored plasma torches and electric arc approaches to gasify waste tyres. The Larionov *et al.*
283 [64] result showed that hydrogen-rich syngas (with a composition of up to 54 vol.% H) were
284 produced from this process. In addition, the CH₄, CO and CO₂ also ranged between 7-26 vol.%,
285 20-36 vol.% and 12-18 vol.% respectively. Ma *et al.* [65] also produced a hydrogen-rich syngas
286 and also reported carbon conversion rate up to 99%, and 94%_{HHV} energy recovery. Even
287 though the electric arc system has not been commercialized, it has also been proven to co-
288 produce carbon nanomaterials along with the syngas. Most studies of the commercial scale
289 applications in recent years have been based on techno-economic analytical adaptation of these
290 reactors. For example, a commercial scale fluidized bed gasifier system would cost over \$10
291 million for a 5.4 ton/hr plant [86] while a rotary kiln system can cost as much as \$279 million
292 for a 90 ton/hr plant [92]. The intricate and complicated nature of the technology, together with
293 the requirement for cutting-edge pollution control systems, contribute to the high capital cost
294 of gasification plants. The majority of the time, these costs do not include the price of tar
295 cracking, waste tyre pretreatment, ash handling, or syngas cleaning [92, 93]. Additionally,
296 because of this cost, waste tyre gasification may find it challenging to compete with other waste
297 management techniques (such pyrolysis), especially in areas with limited financial resources.



298

299 **Fig. 6.** Diagrammatic representation of different waste tyre gasification reactors (a) Updraft
 300 fixed bed (b) Downdraft fixed bed (c) Cross draft fixed bed (d) Rotary kiln (e) Bubbling
 301 fluidized bed (f) Circulation fluidized bed (g) Top-fed entrained flow reactor (h) Side-fed
 302 entrained flow reactor (Images reproduced with permission from [94-97]).

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Table 1. Properties of different types of waste tyre gasifiers [98-100].

Gasifier	Pros	Cons
<i>Updraft</i>	1. Very Simple and less expensive.	1. High tar production.
<i>Fixed Bed</i>	2. Low exit gas temperature.	2. Potential channelling.
<i>Gasifier</i>	3. High carbon conversion ratio.	3. Clinkering.
	4. Clean gas.	4. Small feed size.
	5. High thermal efficiency.	5. Bridging potential.
	6. Operates well under pressure.	6. Low syngas production.
	7. Ability to handle high humidity materials.	7. Low specific capacity.
	8. Reduced ash and dust entrainment.	
<i>Downdraft</i>	1. Simple construction.	1. Minimum feed size.
<i>Fixed Bed</i>	2. Low tar production.	2. Bridging and clinkering potential.
<i>Gasifier</i>	3. High carbon conversion ratio.	3. Requires feed with low moisture.
	4. Limited ash and dust entrainment.	4. Limited scale up capacity.
	5. High solid hold time.	
	6. Very reliable.	
<i>Rotary Kiln</i>	1. Operates at very high temperature.	1. Difficult to operate under pressure.
<i>Gasifier</i>	2. Not prone to overheating and chemical attacks.	2. High production of tar and dust.
	3. Can resist high impact and thermal shocks.	3. High cost of maintenance.
	4. Less tar formation.	4. Low flexibility.
	5. Sensitivity to changes in feed size, composition and humidity is low.	5. Low thermal efficiency.
	6. High carbon conversion ratio.	6. Low heat exchange capacity.
	7. Low cost of investment.	7. High refractory consumption.
	8. Simple construction and very reliable.	
<i>Bubbling</i>	1. Flexible feed rate and composition.	1. High product gas temperature.
<i>Fluidized</i>	2. High ash fuel.	2. Ash and dust dragging.

<i>Bed</i>	3. Easy temperature control.	3. High carbon content in fly ash.	
<i>Gasifier</i>	4. Ability to handle different kinds of feed.	4. High cost of maintenance.	
	5. Ideal for fuels with high reactivity.	5. High investment cost.	
	6. Low level tar in syngas.	6. Pre-treatment is needed when used for	
	7. Good scalability.	co-gasification operation.	
	8. Adaptable to catalyst usage.		
	9. High carbon conversion ratio.		
	10. High gas-solid contact and mixing.		
	11. High heat capacity.		
	<i>Circulating</i>	1. High operating temperature.	1. Problems of corrosion and attrition.
	<i>Fluidized</i>	2. Flexible process.	2. Poor operational control.
	<i>Bed</i>	3. Low tar production.	3. High cost of operation.
<i>Gasifier</i>	4. Low residence time.	4. Low solid-gas contact.	
	5. Good scalability.	5. Require feed size reduction.	
	6. High carbon conversion.		
<i>Entrained</i>	1. Very low in tar and CO ₂ .	1. Low methane formation.	
<i>Flow</i>	2. Flexible to feedstock.	2. Requires very small feed size.	
<i>Gasifiers</i>	3. High exit tar temperature.	3. Ash slagging.	
	4. High temperature slagging operation.	4. Complex control of operation.	
	5. Uniform reactor temperature.	5. High cost of maintenance.	
	6. No scale-up problem.	6. Heat recovery is required to improve	
	7. Excellent Process parameter control.	efficiency.	
	8. Short hold time.	7. Requires large amount of oxidant.	
	9. High carbon conversion.	8. Efficiency of the cold gas is low.	
		9. Components have short lifespan.	

311 3.2.3. *Waste Tyre Gasification Operational Parameters*

312 The description of the operational requirements for gasifiers is a necessary step in the
313 waste tyre gasification process. Research has been conducted on a number of parameters that
314 impact several performance metrics such as product yield, energy efficiency, cold gas
315 efficiency, syngas efficiency, and product gas quality [101]. These parameters are categorized
316 into four categories: feed characteristics, gasifying agent, gasifier operating condition and
317 catalyst. The following subsections provide insights on the parameters that can influence waste
318 tyre gasification process.

319 3.2.3.1. *Feed Characteristics*

320 One of the feed characteristics that can affect the final composition of the produced gas
321 during the waste tyre gasification process is its moisture content [55, 86]. The amount of water
322 present in waste tyre sample, expressed as a percentage of its total mass, is known as its
323 moisture content [102]. As a result, adding additional moisture will produce more water
324 reactants, which will lower the GT and enhance the WGS reaction [102]. As energy is required
325 for moisture vaporization and vapour superheating, moisture has a significant impact on
326 recoverable energy [103]. In waste tyre gasification, the FMC was found to have no impact on
327 other gasification parameters in the gasification reactors, however, the authors observed a rise
328 in CO₂ and hydrocarbons and a decrease in other syngas components as the moisture level
329 increased [86]. In addition, the FMC in waste tyres should not be confused with concept of
330 hydrothermal gasification (see subsection 3.1.1.2). Another key parameter influencing the rate
331 and efficiency of char production during the waste tyre gasification process—which is mostly
332 dependent on the gasifier diameter—is the size of the waste tyre particles [104, 105]. While
333 Kandasamy & Gökalp [106] concluded that an FPS between 0.5-10mm does not have
334 significant effect on the output of the tyre gasification process, some authors [104, 107] proved
335 this does not apply to all scenarios. Straka & Bučko [107] studied the effect of FPS for particles

336 sizes between 3-40 mm, the authors found that an FPS less than 20 mm is required to optimize
337 waste tyre gasification and co-gasification processes. Leung & Wang [104] also explored how
338 different gasification parameters in a fluidized bed reactor were affected by the FPS. FPS
339 between 0.4 and 2.1 mm were examined by the authors and it was found that the smaller
340 particles had higher reactivity because they dispersed more readily inside the reactor than the
341 bigger ones. The authors concluded that when FPS above 1mm is employed, the gasification
342 process becomes ineffective to the secondary reaction temperature and bed temperature.
343 However, when FPS below 1mm was employed, the reaction temperature falls while the
344 product gas yield, char yield, oil yield, volatile release ratio, energy recovery ratio, and gas
345 heating value increase [104]. Song *et al.* [108] also concluded from their study that smaller
346 FPS improved the syngas yield and syngas LHV. Furthermore, other characteristics such as the
347 volatile matter (VM), ash, fixed carbon (FC), heating value, sulphur, atomic (H/C), atomic O/C
348 ratios, etc have also been established to influence waste tyre gasification process in their
349 respective ways [11, 64, 108].

350 3.2.3.2. Gasification Agents (GAs) and their Ratios

351 Oxygen, air, steam, CO₂ as well as their combinations are the gasification agents that
352 have been employed in previous studies [34, 58, 60, 61, 65, 85-87, 108] on waste tyre
353 gasification on both lab-scale and commercial-scale. However, the choice of these agents is
354 dependent upon the energy output and desired composition of the product gas stream. Through
355 the exothermic process of gasification with air, hydrocarbons and minimal hydrogen gas are
356 produced along with low heating value gas that is rich in CO [101]. Air gasification also
357 produces large concentrations of nitrogen in the dry gas mixtures with LHV between 4 MJ/Nm³
358 and 5 MJ/Nm³, whereas steam and steam+air mixture can yield more hydrogen with LHV
359 ranging between 7 MJ/Nm³ and 13 MJ/Nm³ [50]. In addition, gasification using steam is an
360 endothermic process that yields a gas with a higher heating value with hydrogen composition

361 [101]. Gasifying waste tyres with steam+CO₂ have been observed to have a higher char
362 reactivity and cold gas efficiency when compare with steam only process [87]. Karatas *et al.*
363 [109] employed different GA combinations (steam, air+steam, and air+CO₂) in their study. The
364 findings shows that steam>Air+CO₂>Air+steam have the highest syngas yield and LHV
365 respectively. Gasification with steam and its combination with other GAs have been frequently
366 chosen to improve the quality of producer gas because it increases the hydrogen concentration.

367 The equivalence ratio (ER) and steam to fuel ratio (SFR) are two most important
368 parameters investigated in relation to the GA employed during waste tyre gasification. In the
369 waste tyre gasification process where air or oxygen is used as the GA, the ER is defined as the
370 ratio of the theoretical to the actual air requirement [86]. Given that gasification is predicated
371 on attaining the partial combustion of the waste tyre samples, only a portion of this ratio is
372 often employed. Theoretically, the oxygen demand needed to achieve the combustion of waste
373 tyres depends on their contents [101]. The ER has been proven to have a significant effect on
374 the performance of the gasification reactor. In addition, ER directly affects the thermal
375 efficiency of the process, gas quality, as well as the bed temperature [86]. The SFR, which
376 measures the amount of steam fed per mole of fuel, has a significant influence on the system's
377 energy input as well as the composition of the final syngas stream [110]. Although the
378 production of methane and solid carbon is encouraged by a lower SFR value, the carbon and
379 methane present are ultimately converted to CO and hydrogen as more steam is delivered [101].
380 In addition, similar to the FMC, the introduction of more steam will also produce more water
381 reactants, which will lower the GT and enhance the WGS reaction [55].

382 3.2.3.3. *Gasification Conditions*

383 The most significant impact on the overall efficiency of the waste tyre gasification
384 process appears to be the temperature at which the gasifier is operated [101]. Reaction rate and
385 product composition are impacted by gasification temperature (GT). The impact of the GT on

386 the gasification of waste tyres has been investigated in various studies [34, 35, 60, 85-88, 106,
387 108]. Temperature changes in a gasifier have the ability to modify the equilibrium point of any
388 gasification reaction, as these reactions are typically reversible [111]. Change in the GT during
389 the gasification of have a notable impact on the shares of different fractions and the
390 composition of the resulting syngas [33]. These changes also affect the quality of the gas
391 produced and the parameters that describe the process' efficiency [33]. Raman *et al.* [112]
392 observed that while the char yield remained constant, raising the GT increased the yield of
393 product gas and decreased the yield of liquid. The process of gasifying waste tyres is also
394 significantly influenced by the gasification pressure (GP). A few studies [58, 113] have looked
395 into the significance of GP and found that as the pressure goes up, so do the syngas's HHV,
396 composition, and yield. The number of active sites on the surface of the waste tire sample has
397 been connected to an increase in the GP, which has also been found to promote heterogeneous
398 gas-solid interactions. Furthermore, an increase in the GP has been found to boost the
399 production rate and yield of CO. Due to the fact that homogeneous processes also occur in the
400 gas phase, the impact of pressure on hydrogen was ambiguous [4, 33]. Another significant
401 parameter influencing waste tyre gasification process is the heating rate (HR). Due to the limits
402 of heat transfer, thermogravimetric curves move toward higher temperatures with increasing
403 HR. When heating at a rate of 3K/min, Czernski *et al.* [114] found that the maximum conversion
404 rate was around 1313K. However, when HR was increased to 15K/min, the conversion rate
405 improved by ~5%. Song *et al.* [108] also observed that the HR employed in waste tyre
406 gasification is proportional to the mass loss in the process. The residence time (RT) of the waste
407 tyre char is another important component to take into account in waste tyre gasification in order
408 to enhance syngas production. A study by Molino *et al.* [83] examined the impact of RT on
409 waste tyre gasification. Investigated were six experimental studies with gasification residence
410 periods ranging from 60 to 360 minutes. At the conclusion of the experiment, it was found that

411 the waste tyre gasification process produced more syngas and a higher burn-off value the longer
412 the char RT.

413 3.2.3.4. *Catalyst*

414 Catalyst action will expedite the waste tyre gasification process because it is imperative
415 that the reaction rate be increased [52]. Waste tyre gasification procedures have been studied
416 using catalysts such $\text{MgCa}(\text{CO}_3)_2$, NiO, CaO, Ni/Al₂O₃, Ni/SiO₂-Al₂O₃, Ni-Mg-Al, Ni/Ce,
417 Co/Al₂O₃ amongst several others. Previous research [8] emphasized that syngas yield is
418 increased by both homogeneous and heterogeneous catalysts by accelerating the WGS reaction
419 and the cracking reaction. Some authors [8, 89, 115, 116] also came to the conclusion that
420 catalysts were necessary in order to maximize the production of hydrogen gas from waste tyre
421 gasification, after these Nickel-based catalysts were utilized to increase the production of
422 hydrogen. Elbaba *et al.* [117] have investigated the viability of gasifying waste tyres in a steam
423 atmosphere using a Ni-Mg-Al catalyst. The findings demonstrate that better solid and gas
424 fraction yields were achieved at the price of lower liquid product yields when compared to the
425 process performed without the inclusion of a catalyst. In addition, catalysts have also been
426 reported to reduce the energy recovered from waste tyre gasification process [36]. Zhang *et al.*
427 [89] also observed that the primary adverse reaction resulting from the application of catalyst
428 is its deactivation from the char surface.

429 **3.3. Waste Tyre Gasification Targeted at Gaseous Product Production**

430 Waste tyre gasification can produce a variety of gases including syngas, hydrogen,
431 methane and other volatile organic compounds (VOCs). Syngas (which comprise mainly
432 carbon monoxide (CO) and hydrogen gas) have been used as fuel in internal combustion
433 engines, gas turbines, and boilers [109, 118]. Methane and VOCs have been used as fuel in
434 boilers and also as a feedstock for the production of other chemicals. Hydrogen has been used
435 as a fuel in fuel cells or as a chemical feedstock [55]. Waste tyre gasification and co-gasification

436 process(es) to produce syngas/hydrogen have been investigated using direct gasification [8, 34,
437 41, 51, 52, 55, 56, 59-61, 63, 71, 85, 86, 88, 91, 102, 108, 119-122], a combination of steam
438 gasification and catalytic reforming [115] and catalytic pyrolysis–gasification [89, 117, 123].
439 This section will investigate recent studies on the use of gasification for the production of
440 hydrogen and syngas production from waste tyres. These studies [8, 34, 41, 51, 52, 55, 56, 59-
441 61, 63, 71, 85, 86, 88, 91, 102, 108, 119-122] have found that various gasification technologies,
442 including catalytic, plasma-assisted, and entrained-flow gasification, are able to efficiently
443 convert waste tyres into syngas/hydrogen with high yields. The use of catalysts in the process
444 has also been found to improve the process efficiency and hydrogen yield [124]. However,
445 more research is needed to optimize the process conditions and to investigate the longevity and
446 stability of catalysts under prolonged use.

447 *3.3.1. Waste Tyre Gasification Targeted at Syngas Production*

448 As mentioned earlier, the syngas produced from waste tyre gasification process could
449 be used to power gas turbines, and fuel cells [109, 118]. The quality of syngas produced in
450 terms of the presence of tars, metals, sulphurous compounds, heating value (LHV), carbon
451 conversion, and efficiency (%LHV) is a significant consideration in waste tyre gasification. Gas
452 turbine and fuel cell applications for heat and electricity generation require a very high syngas
453 quality [125]. Presently, varieties of technological alternatives have been put up as a way to
454 trap corrosive gases that may hinder syngas quality [126]. Conventional technologies are
455 largely multistep and complex so they need a very large land space with high capital cost [127,
456 128]. The process also suffers from a variety of operational challenges including equipment
457 corrosion and fouling, solvent losses, liquid channelling, floods, and unusual foaming. The ash
458 produced after gasification is quite different from that of incineration; while that of incinerator
459 is considered safe for usage as substitute cover in dumping grounds, there have been concerns
460 about its usage in commercial products [129]. However, in high-temperature gasification, the

461 ash flows in molten form from the reactor where it is quenched and forms a glassy, non-
462 leachable slag that could be used in industrial operations such as cement making, roofing
463 shingles, asphalt filling, and sand blasting [129]. The findings of some authors who have
464 worked on syngas production from waste tyre gasification in recent years are presented in
465 **Table 2.**

Table 2. Summary of some recent studies on gasification of waste tyres targeted at syngas production.

Author(s)	Work	Gasifier Type & Scale	Waste Tyre Characteristics	GA(s), SFR & ER	Gasification Condition(s)	Catalyst	Deductions
1. Czernski <i>et al.</i> (2023) [34]	Study on steam co-gasification of waste tyre char and sewage sludge	Type: Fixed Bed Gasifier Scale: Lab Scale	Type: Waste Tyre Char FPS: NR <i>Proximate Analysis (wt.%)</i> MC: 1.1; FC: 75.4 VM: 2.2; Ash: 21.3 <i>Heating Value</i> HHV: 26.21 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 74.6; H: 0.77; N: NR S: 2.87; O: NR	GA: Steam SFR: 0.6 ER: NE	GT: 800-900°C GP: 1 MPa HR: NE RT: NR	SiO ₂ and P ₂ O ₅ from the sewage sludge ash	The authors employed steam gasification to evaluate the effect of feed ratio on syngas production. Two waste tyre char to sewage ratios (90:10 and 67:33) were employed at different GTs (800-900°C) at 1 MPa. Their results show that at high temperatures (900°C), the 90:10 blend ratio improves both CO and CH ₄ composition and reduces CO ₂ and H ₂ composition in the syngas stream. The authors concluded that the combination of waste tyre char and sewage sludge reduced both the activation energy and pre-exponential factor of waste tyre gasification process significantly.
2. Spiewak <i>et al.</i> (2023) [58]	Influence of pressure and sunflower husks ash as catalyst on tyre-char steam gasification	Type: Fixed Bed Gasifier Scale: Lab Scale	Type: Waste Tyre Char FPS: 100µm-2mm <i>Proximate Analysis (wt.%)</i> MC: 1.1; FC: 75.4 VM: 2.2; Ash: 21.3 <i>Heating Value</i> HHV: 26.21 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 74.64; H: 0.77; N: NR S: 2.87; O: NR	GA: Steam SFR: 0.6 ER: NE	GT: 800-1000°C GP: 0.5 MPa & 1 MPa HR: NE RT: NR	Sunflower husk ash (SHA)	The authors employed different SHA catalyst compositions (0-15 wt.%) in the production of syngas from waste tyre gasification. In addition to this, the experiment was also performed at different GTs (800-1000°C) and pressures (0.5 MPa and 1 MPa). Results from the study show that at low temperatures (<850°C) the effects of pressure and catalyst on the CO/H ₂ ratios in the syngas stream were more pronounced. The carbon conversion reaction during steam gasification demonstrated that the catalyst addition decreased activation energy (E _a) and pre-exponential factor (A). In addition, the results indicated that steam gasification at low temperatures at 1 MPa, and 15 wt.% SHA is the best combination for obtaining hydrogen-rich syngas.

3. Larionov <i>et al.</i> (2023) [64]	Electric arc gasification of pyrolysis oil with the production of hydrogen-enriched synthesis gas and carbon nanomaterial	Type: Electric Arc Scale: Lab Scale	Type: Waste Tyre Oil FPS: NA <i>Proximate Analysis (wt.%)</i> MC: NR; FC: NR; VM: NR; Ash: Trace <i>Heating Value</i> HHV: 43.3 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 86.2; H: 11.0; N: 0.6 S: 0.8; O: 1.4	GA: Air SFR: NE ER: NR	GT: NA GP: 1 atm HR: 10°C/min RT: NR	NE	The authors employed waste tyre pyrolysis oil to produce syngas through waste tyre gasification using a 74-voltage laboratory-scale DC arc reactor. This process was validated by employing petroleum and pyrolysis oil from other samples such as sludge and wood. The result showed that hydrogen-rich syngas (with a composition of up to 54 vol.% H) were produced from this process. In addition, the CH ₄ , CO and CO ₂ also ranged between 7-26 vol.%, 20-36 vol.% and 12-18 vol.% respectively.
4. Serrano <i>et al.</i> (2022) [60]	Waste tyres valorization through gasification in a bubbling fluidized bed: An exhaustive gas composition analysis	Type: Bubbling Fluidized Bed Gasifier Scale: Lab Scale	Type: Raw Waste Tyre FPS: 150-600µm <i>Proximate Analysis^{db} (wt.%)</i> MC: 1.19; FC ^a : 25.19; VM: 64.76; Ash: 8.86 <i>Heating Value</i> HHV: 35.11 MJ/kg ^{ar} <i>Ultimate Analysis (wt.%)</i> C: 74.75; H: 5.46; N: 0.71 S: 1.15; O ^a : 8.96	GA: Air & Air+Steam SFR: 0.39 ER: 0.13-0.33	GT: 700°C & 850°C GP: 1 atm HR: NE RT: NR	NE	The authors investigated the effect of GT (700°C and 800°C), ER (0.13-0.33) and SFR (0.39) on syngas production from waste tyre gasification. The results from the at high temperature and low ER, the production of H ₂ and light hydrocarbons were favoured while cold gas efficiency (CGE), lower heating value LHV, and carbon conversion were not favoured. In addition, the authors concluded that the steam-gasified system produced higher H ₂ , lower CO, and higher syngas LHV than the air only-gasified system.
5. Song <i>et al.</i> (2021) [108]	Utilization of waste tyre powder for gaseous fuel generation via CO ₂ gasification using waste	Type: Entrained Bed Gasifier Scale: Lab Scale	Type: Raw Waste Tyre FPS: 80-300 mesh <i>Proximate Analysis (wt.%)</i> MC: 0.95; FC ^a : 30.66; VM: 62.17; Ash: 7.17 <i>Heating Value</i> HHV: 21.16 MJ/kg	GA: CO ₂ SFR: NE ER: NE CO ₂ FR: NR	GT: 300-1400°C GP: 1 atm HR: 5-20°C/min RT: NR	NE	The authors employed furnace waste heat to gasify waste tyre powder in the presence of CO₂. The gasification process was monitored in a thermogravimetry mass spectrometry (TGMS) system. In addition to the kinetic analysis investigated in the study, the effects of temperature, FPS, CO ₂ :CO ratio in the process were also studied. From the TGMS system, at temperatures from 300-500°C, the main syngas

	heat in converter vaporization cooling flue		<i>Ultimate Analysis (wt.%)</i> C: 79.41; H: 7.25; N: 0.77 S: 1.75; O ^a : 3.65				components were CO, H ₂ , CH ₄ , H ₂ O, and C ₂ H ₆ . In addition, the activation energy from the process was found to be 144.5 kJ/mol while the LHV at 500°C was 10.27 MJ/Nm ³ . The authors concluded that FPS and GT greatly affect syngas production and LHV.
6. Carmo-Calado <i>et al.</i> (2020) [35]	Co-combustion of waste tyres and plastic-rubber wastes with biomass technical and environmental analysis	Type: Fixed Bed Gasifier Scale: Pilot Scale	Type: Raw Waste Tyre FPS: 1-4cm <i>Proximate Analysis (wt.%)</i> MC: 0.8; FC: 29.6; VM: 64.5; Ash: 5.1 <i>Heating Value</i> HHV: 38.6 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 75.5; H: 0.7; N: 0 S: 5.6; O: 13.1	GA: Air SFR: NE ER: 0.28-0.41	GT: 790-900°C GP: NR HR: NE RT: NR	NE	The authors performed co-combustion and co-gasification tests using waste tyres with plastic, rubber and acacia, however, the key gasification test is waste tyre co-gasified with acacia. The experiment was performed in a downdraft fixed bed reactor at different GTs, ERs, and feed ratios. The obtained results indicate that the best syngas composition and LHV values were obtained at waste tyre/acacia blend ratios of 80:20 and 40:60 respectively. At these ratios, the syngas LHV were 3.64 MJ/m ³ and 3.14 MJ/m ³ respectively. In addition, the optimum GT and ER at these blend ratios were 800°C and ER of 0.31 respectively.
7. Wang <i>et al.</i> (2019) [85]	Co-gasification characteristics of waste tyre and pine bark mixtures in CO ₂ atmosphere	Type: Semi-Batch Fixed Bed Gasifier Scale: Lab Scale	Type: Raw Waste Tyre FPS: 140 mesh <i>Proximate Analysis (wt.%)</i> MC: 0.69; FC: 27.88; VM: 62.58; Ash: 8.92 <i>Heating Value</i> HHV: NR <i>Ultimate Analysis (wt.%)</i> C: 74.75; H: 5.46; N: 0.71 S: 1.15; O: 8.96	GA: CO ₂ SFR: NE ER: NE CO ₂ FR: NR	GT: 800°C & 900°C GP: NR HR: NE RT: NE	NE	The authors co-gasified waste tyres and pine bark in a fixed bed reactor at different GTs (800°C and 900°C) and blend ratios in a CO ₂ atmosphere. The results obtained from the co-gasification process showed that an increase in pine bark ratio increased the flowrate peak of H ₂ , CO, and total syngas, but decreased the flow rate peak of the hydrocarbon components (C _m H _n) at the two GTs. At the same blend ratios, the overall yield of the syngas was higher at 900°C than at 800°C. In addition, the authors concluded that co-gasification of waste tyres and pine bark with a blend ratio of 75:25 at 900°C has a higher energy recovery efficiency. At the same

							condition and different blend ratios, the reverse was the case.
8. Zang <i>et al.</i> (2019) [86]	Modeling and economic analysis of waste tyre gasification in fluidized and fixed bed gasifiers	Type: Downdraft Fixed Bed Gasifier and Fluidized Bed Gasifier Scale: ^{fixb} Pilot Scale and ^{fib} Commercial Scale	Type: Raw Waste Tyre FPS: 2mm ^{fib} & 20mm ^{fixb} <i>Proximate Analysis (wt.%)</i> MC: 0.9; FC: 27.04; VM: 66.3; Ash: 6.66 <i>Heating Value</i> LHV: 37.1 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 81.74; H: 7.06; N: 0.30 S: 1.82; O: 2.42	GA: Air+Steam SFR: NR ER: 0.22-0.50	GT: 850°C GP: 1 atm HR: NE RT: NE	NE	The authors studied syngas production from waste tyre gasification and co-gasification (with wood) in two gasification reactors namely: fixed bed and fluidized bed. The authors' objective was to find the most efficient and economic pathway to achieve the best production routes by comparing the performance of both gasifiers in a co-gasification process. To simulate the fixed bed and fluidized bed production routes, the authors employed a one-dimensional kinetic model and a semi-empirical model respectively. The effect of parameters such as waste tyre-to-wood ratio, ER, and MC (0.9-30%) were also investigated. The obtained result shows that waste tyre-wood mixture has higher syngas efficiency in both reactors however, the energy output from 100% waste tyre is greater. In addition, an ER of 0.3 produced the best gasification result. The authors also concluded that plant capacity is an important factor in determining the best reactor to employ in waste tyre gasification
9. Policella <i>et al.</i> (2019) [87]	Characteristics of syngas from pyrolysis and CO ₂ -assisted gasification of waste tyres	Type: Semi-Batch Fixed Bed Gasifier Scale: Lab Scale	Type: Raw Waste Tyre FPS: 100µm <i>Proximate Analysis (wt.%)</i> MC: 0 ; FC: 26.2; VM: 66.5; Ash: 7.3 <i>Heating Value</i> LHV: 35.93 MJ/kg <i>Ultimate Analysis^{daf} (wt.%)</i>	GA: CO ₂ SFR: NE ER: NE CO ₂ FR: NR	GT: 700-1000°C GP: 1 atm HR: NE RT: ~21s	NE	The authors compared the quality of syngas produced from waste tyre gasification to syngas produced from waste tyre pyrolysis in a lab-scale experiment. The pyrolysis experiment was performed from 400-900°C while the gasification was performed from 700-1000°C in the presence of CO ₂ . The result obtained shows that waste tyre gasification carried out at 800°C produced CO which is 3.3 times more than that produced by pyrolysis at 900°C. In addition, the CO produced from waste tyre gasification at

			C: 89.5; H: 7.3; N: 0.3 S: 1.9; O: 0.9				1000°C is 150% higher than CO produced at 900°C. The authors concluded that the GT greatly influences the overall syngas yield, quality and energy content.
10. Škrbić <i>et al.</i> (2018) [90]	Differentiation of syngases produced by steam gasification of mono- and mixed sources feedstock: A chemometric approach	Type Bubbling Fluidized Bed Gasifier and Rotary kiln Scale: Lab Scale and Pilot Scale	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis (wt.%)</i> MC: NR; FC: NR; VM: NR; Ash: NR <i>Heating Value</i> HHV: NR <i>Ultimate Analysis (wt.%)</i> C: NR; H: NR; N: NR S: NR; O: NR	GA: Steam SFR:0.32-1.15 ER: NE	GT: 700-1000°C GP: NR HR: NE RT: NE	NE	The authors employed principal component analysis (PCA) to select the best feedstock type, operation parameters, and gasifier type that would achieve the maximum syngas quality in waste tyre gasification and co-gasification process. The result from their experiment shows that the syngas quality in terms of CH ₄ , H ₂ /CO and H ₂ +CO, and CO ₂ content from the co-gasification process were better than the single-fed process. In addition, they concluded that the coal+waste tyre mixtures produced the best result with higher H ₂ , H ₂ /CO and H ₂ +CO.

467 NE–Not Employed; NR–Not Reported; ^{ar}–As Received; ^{db}–Dry Basis; ^{daf}–Dry Ash-Free; ^a–By Difference; ^{fixb}–Fixed Bed; ^{flb}–Fluidized Bed; ^v–Vapour RT;
468 CO₂FR–CO₂ to Fuel Ratio.
469

470 Collectively, the studies summarized in **Table 2** show that performance is significantly
471 impacted by many parameters such as temperature, pressure, gasification agent (air/steam) and
472 particle size. Furthermore, co-gasifying tyres with coal, biomass or other wastes like sewage
473 sludge results in syngas blends that contain larger amounts of H₂ and CO than just waste tyre
474 alone. In addition, co-gasification of waste tyres (at certain conditions) has been established to
475 have higher efficiencies than tyres alone [34, 85]. Co-gasification of waste tyres with wood has
476 been shown to have less syngas efficiency [86]. However, it has not yet been well-determined
477 yet how co-gasification could affect the co-production of carbon products from waste tyre
478 gasification process. Authors such as Czerski *et al.* [34] and Spiewak *et al.* [58] emphasized
479 that catalyst play a vital role to achieve a high waste tyre char reactivity. Both authors also
480 concluded that at temperatures below 850°C, the effect of pressure and catalyst on waste tyre
481 gasification is more pronounced.

482 3.3.2. Waste Tyre Gasification Targeted at Hydrogen Production

483 The necessity for developing clean and renewable energy sources is enormous and
484 growing as a result of current environmental pollution and its associated greenhouse impacts.
485 It is consequently of great relevance that the hydrogen gas produced via waste tyre gasification
486 has a high caloric value [91, 130]. Hydrogen has a higher heating value (HHV) of ~142 MJ/kg
487 at 25°C and an LHV of ~120 MJ/kg at the same temperature [131, 132]. Compared to most
488 fuels, which have a value of ~44 MJ/kg at 25°C, this number is substantially greater, however,
489 it has one-quarter the energy density on a volumetric basis when compared to gasoline [132].
490 Hydrogen is a secondary energy source that could be produced from waste tyre
491 gasification [133-136] in addition to more traditional routes such as the electrolysis of water,
492 photolysis of water using solar energy, and thermochemical conversion of methane (such as
493 steam reforming) amongst several others [130]. Hydrogen production through gasification
494 process is also proven to be very fast and also has a high energy efficiency (47-69% LHV) [132,

495 137-139]. However, hydrogen production is largely influenced by the operational parameters,
496 such as the gasification feedstock characteristics, reaction temperature, catalyst, steam-to-feed
497 ratio, as well as ER [140, 141]. The findings of some authors who have worked on hydrogen
498 production from waste tyre gasification in recent years are presented in **Table 3**.

Table 3. Summary of some recent studies on gasification of waste tyres targeted at hydrogen production.

Author(s)	Work	Gasifier Type & Scale	Waste Tyre Characteristics	GA(s), SFR & ER	Gasification Condition(s)	Catalyst	Deductions
1. Ma <i>et al.</i> (2023) [65]	Thermodynamic analysis of a carbon capture hydrogen production process for end-of-life tyres using plasma gasification	Type: Plasma Torch Scale: Commercial Scale	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis^{db} (wt.%)</i> MC: 0.8 ; FC: 33.5; VM: 61.3; Ash: 5.2 <i>Heating Value</i> HHV: 38.6 MJ/kg <i>Ultimate Analysis^{db} (wt.%)</i> C: 84.1; H: 7.3; N: 0.3 S: 2.3; O: 0.8	GA: Oxygen+Air and Steam+Air SFR:0.1-1.1 ER: 0.1	GT: 1500-2500°C GP: 1 atm HR: NE RT: NE	NE	The authors employed plasma gasification to produce H ₂ from waste tyres. The effect of combinations of GAs (Oxygen+Air and Steam+Air) was studied to check for the best condition for H ₂ production. The result from the experiment shows that the Steam+Air combination produced the highest H ₂ (969 kmol/hr) along with the best carbon conversion rate (99%), energy recovery (94% _{HHV}), and exergy efficiency (80% _{HHV}).
2. Al-Qadri <i>et al.</i> (2022) [91]	Technoeconomic feasibility of hydrogen production from waste tyres with the control of CO ₂ emissions	Type: Rotary Kiln Scale: Commercial Scale	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis (wt.%)</i> MC: 0 ; FC: 25.5; VM: 67.7; Ash: 6.8 <i>Heating Value</i> LHV: 33.96 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 77.3; H: 6.2; N: 0.6 S: 1.8; O: 7.3	GA: Steam SFR: 2 ER: NE	GT: 1000°C GP: 1 bar HR: NE RT: NE	NE	The authors investigated H ₂ production through two production routes. The first route involved three key processes (steam gasification, WGS and acid gas removal (AGR)). The second route used the first route but the integrated the gasification process with natural gas reforming. The result from their experiment shows that the second route has 28% higher H ₂ production, 7% higher purity and 26% less CO ₂ emission when compared to the first production route. However, the production cost of H ₂ from the

3. Santasnachok & Nakyai (2022) [61]	Exergetic and environmental assessments of hydrogen production via waste tyre gasification with co-feeding of CO ₂ recycled	Type: Downdraft Fixed Bed Gasifier Scale: Pilot Scale	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis^{db}(wt.%)</i> MC: 1.5; FC: 30; VM: 55; Ash: 13.5 <i>Heating Value</i> HHV: 36.5 MJ/kg <i>Ultimate Analysis^{db}(wt.%)</i> C: 75; H: 7.0; N: 0.3 S: 4.5; O: 2.7	GA: Air, Air+Steam, Air+Steam +CO ₂ SFR:0.5-2.5 ER: 0.35 & 0.38 CO ₂ FR:0-3.5	GT: 500-1000°C NE GP: 1 atm HR: NE RT: NE	second route was more than the first production route. The authors studied H ₂ production from waste tyre gasification through a computer-aided simulation using different combinations of air, steam and CO ₂ as the GAs at 800°C. Three experiments were carried out and all were done in the presence of air (i.e., Air+Tyre, Air+Steam+Tyre, and Air+Steam+CO ₂ +Tyre). The effect of gasification agent-to-fuel ratio on H ₂ production as well as energy and exergy analysis were investigated in the process. The result from the experiment shows that the highest H ₂ yield was obtained from the GA-to-waste tyre ratios of 2 and 0.1 for steam and CO ₂ respectively. The energy and exergy efficiencies from the process with the highest H ₂ yield were found to be 59.6% _{HHV} and 49.4% _{LHV} , respectively. In addition, to estimate the greenhouse gas emission from the process, a CO ₂ emission intensity test was also carried out and the authors established that the air+steam mixture has the lowest CO ₂ emission when compared to the other two.
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4. Marzoughi <i>et al.</i> (2021) [88]	Environmental and thermodynamic performance assessment of biomass gasification process for hydrogen production in a downdraft gasifier	Type: Downdraft Fixed Bed Gasifier Scale: Commercial Sclae	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis (wt.%)</i> MC: 0-40%; FC: 27.04; VM: 66.3; Ash: 6.66 <i>Heating Value</i> LHV: 38.65 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 81.74; H: 7.06; N: 0.3 S: 1.82; O: 2.42	GA: Air, Steam, Air+Steam SFR: 0-1.5 ER: 0-0.4	GT: 800-1500°C NE GP: 1 atm HR: NE RT: NE	The authors investigated the effects of feed ratio, ER gasification inlet temperature, and MC (0-40%) in gasification experiments using different feedstock including waste tyres. Different combinations of gasification agents were employed in the process. The result from the experiment shows that steam gasification produced the highest H ₂ yield and LHV when compared to air/steam and air-only GAs. The authors emphasized that the steam-feed ratio and gasification inlet temperature favours H ₂ production. The authors emphasized from an environmental view, feed with high carbon such as plastic and waste tyre tend to emit more CO ₂ (80-200 kg CO ₂ -e/hr) than other feeds (manure, MSW, paper, sawdust, wood and pine wood) investigated (< 94 kg CO ₂ -e/hr).
5. Hasan & Dincer <i>et al.</i> (2019a) [134]	Comparative assessment of various gasification fuels with waste tyres for hydrogen production	Type: Entrained flow Gasifier Scale: Lab Scale	Type: Raw Waste Tyre FPS: NR <i>Proximate Analysis (wt.%)</i> MC: 1.5; FC: 30; VM: 55; Ash: 13.5 <i>Heating Value</i> LHV: 36.5 MJ/kg	GA: Steam & Oxygen SFR: 0.17-1.7 ER: NR	GT: 1460°C NE GP: 2.4 MPa HR: NE RT: NE	The authors investigated H ₂ production through gasification in an integrated gasification combined cycle (IGCC) via computer-aided simulation using three different feeds including waste tyres. After the gasification process, the authors employed a WGS membrane reactor to simulate H ₂ production to obtain

			<p><i>Ultimate Analysis (wt.%)</i> C: 75; H: 7; N: 0.3 S: 1.5; O: 2.7</p>				<p>a 98% H₂ conversion rate. From the result obtained from the process, the authors found that the H₂ production rate to waste tyre ratio was found to be 0.16 and better than coal with an average of 0.14. This rate was achieved at SFR of 0.25 and oxygen rates to feed ratio of 0.88. In addition, the waste tyre-to-H₂ production route has energy and exergy efficiencies of 55%_{LHV} and 52%_{LHV} respectively.</p>
6. Nanda <i>et al.</i> (2019) [8]	Catalytic subcritical and supercritical water gasification as a resource recovery approach from waste tyres for hydrogen-rich syngas production	Type: Tubular Batch Reactor Scale: Lab Scale	Type: Raw Waste Tyre FPS: <2mm <i>Proximate Analysis (wt.%)</i> MC: 1.21; FC: 28.8; VM: 65.1; Ash: 4.9 <i>Heating Value</i> HHV: 29.5 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 67.9; H: 6.6; N: 1.9 S: 1.28; O: 17.4	GA: NE SFR: NE ER: NE	GT: 325-625°C GP: 21 MPa & 23 MPa HR: 15°C/min RT: NE	Ni/SiO ₂ -Al ₂ O ₃ , Ru/Al ₂ O ₃ , Ba(OH) ₂ , Ca(OH) ₂ , Mg(OH) ₂	The authors studied hydrothermal waste tyre gasification in catalytic subcritical and supercritical conditions. Process parameters such as GT, reaction time and feed concentration and catalyst were optimized to achieve maximum syngas production. The result from their experiment shows that the best condition for H ₂ -rich syngas production was at 625°C, 60 mins and 5wt.% respectively. At this condition, a syngas and H ₂ yield of 34 mmol/g and 14.4 mmol/g respectively with a 43% carbon conversion efficiency. In addition, the application of Ni/SiO ₂ -Al ₂ O ₃ catalyst to the process improved H ₂ production the most when compared

500

	to other catalyst and no-catalyst scenarios.
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NE – Not Employed; NR – Not Reported; ^{db} – Dry Basis; CO₂FR – CO₂ to Fuel Ratio.

501 The overall evaluation of the works presented in **Table 3** shows that waste tyre
502 gasification for hydrogen production is a promising technology with various advantages, but
503 still, a lot of work needs to be done to make the process more efficient, cost-effective and
504 environmentally friendly. One suggestion includes a clear objective of the desired product (i.e.,
505 direct production of clean hydrogen fuel). Most of the hydrogen produced from previous
506 studies is considered dirty until it is properly cleaned. The clean-up process could be expensive.
507 As mentioned earlier, clean hydrogen production is largely influenced by the operational
508 parameters such as properties of the waste tyre feed, gasification reaction temperature, catalyst,
509 ER and gasification agents. In conclusion, the production of hydrogen from waste tyres is a
510 complex process and the optimization of process conditions is vital to achieve the desired
511 results which is an affordable alternative to fossil fuel.

512 **3.4. Waste Tyre Gasification Targeted at High Valued Carbon Production**

513 Since the beginning of waste tyre gasification, the formation of solid products has been
514 dominated by the production of syngas/hydrogen as the primary goal of the process. Most
515 authors who have worked on waste tyre gasification either presume a 100% carbon conversion,
516 which is not always the case, or they discard the chars that are left over after gasification
517 experiments [55]. Activated carbon (AC), carbon black, char, and carbon nanomaterials are
518 some of the high-valued carbon products that could be produced through gasification of waste
519 tyres. Some studies [55, 64, 83, 86, 89, 104, 142-145] have been able to report the production
520 of these solid products obtained from waste tyre gasification. Some of these studies have also
521 proposed that carbon products derived from waste tyre gasification carbon activation have a
522 particle surface area of around 1000 m²/g which is an equivalence of a medium-to-high quality
523 AC which can be used for several applications [55, 83]. Some studies [86, 144, 145] show that
524 char obtained from gasification could be utilized in direct carbon fuel cells, as catalyst, in soil
525 amendment, or in water treatment. Raman *et al.* (1981) [49] were one of the first authors to

526 investigate the gasification of waste tyres and were also the first to confirm the presence of
527 solid product (char) in a waste tyre gasification experiment. The authors performed the
528 experiment from 627-787°C and the resulting product had a gas composition between 20 wt.%
529 to 52 wt.%, liquid composition from 51 wt.% to 17 wt.% and solid char yield 29 wt.% to 25
530 wt.%.

531 Leung & Wang [104] reported that after gasifying waste tyre powder from 350-900°C,
532 the experiment yielded a char product within 24 wt.% to 37 wt.% from the process. The authors
533 also highlighted the importance of parameters such as the ER, waste tyre feed rate and particle
534 size in both solid char and syngas production. Gonzalez *et al.* [143] also reported the production
535 of solid carbon (activated carbon) from waste tyre gasification in a two-stage activation
536 procedure. In the first process, pyrolysis was carried out at 800°C in the presence of N₂ while
537 the second process employed using steam and/or CO₂ as activation agents at different activation
538 temperatures (750-900°C) and activation times (1-3 hrs). The authors employed carbon burn-
539 off as the performance metrics of the experiment and the results from their experiment show
540 that steam/N₂ and steam/CO₂ mixtures produced AC with a surface area of 1317 m²/g and 496
541 m²/g respectively. The authors conclude that the characteristics of AC depend on the degree of
542 char activation, porosity of the char, surface area, the nature of the activating agent as well as
543 the process temperature. Other authors that have worked on solid carbon production from waste
544 tyre gasification in recent years are presented in **Table 4**.

Table 4. Summary of some recent studies on gasification of waste tyres targeted at carbon product production.

Author(s)	Work	Gasifier Type & Scale	Waste Tyre Characteristics	GA(s), SFR & ER	Gasification Condition(s)	Catalyst	Deductions
1. Larionov <i>et al.</i> (2023) [64]	Electric arc gasification of pyrolysis oil with the production of hydrogen-enriched synthesis gas and carbon nanomaterial	Type: Electric Arc Scale: Lab Scale	Type: Waste Tyre Oil FPS: NA <i>Proximate Analysis (wt.%)</i> MC: NR; FC: NR; VM: NR; Ash: Trace <i>Heating Value</i> HHV: 43.3 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 86.2; H: 11.0; N: 0.6 S: 0.8; O: 1.4	GA: Air SFR: NE ER: NR	GT: NA GP: 1 atm HR: 10°C/min RT: NR	NE	The authors co-produced CNT and syngas using a novel approach using different feedstock which are waste tyres, oil sludge, wood waste and petroleum. The experiment was carried out in a 74V vacuum-free lab-scale DC arc reactor. The carbon produced from the four samples was characterized and the result from the experiments shows that a graphite-like carbon nanomaterial (CNM) is very close to carbon black. In addition, the CNM produced from waste tyres has a specific surface area of 64.1 m ² /g and a porosity of 0.17 cm ³ /g. The SEM analysis also confirmed that the structure of nanosized carbon particles was arranged in arrays in the forms of inhomogeneous agglomerated structures which differ from the typical spherical-shaped carbon black.
2. Semaan <i>et al.</i> (2022) [145]	Pilot scale pyro-gasification of biomass and waste: char characterization	Type: Fixed Bed Gasifier	Type: Waste Tyre Char FPS: <10mm <i>Proximate Analysis^{db} (wt.%)</i>	GA: Air SFR: NE ER: NR	GT: NA GP: 1 atm HR: 10°C/min RT: NR	NR	The authors performed pyro-gasification experiments with different feedstocks (sawdust, waste wood, grape pomace,

		Scale: Pilot Scale	MC: 0.575; FC: NR; VM: NR; Ash: 35 <i>Heating Value</i> HHV: NR <i>Ultimate Analysis (wt.%)</i> C: 62.4; H: 0.7; N: 0.11 S: 2.0; O: 1.9				miscanthus wood, waste tyres, MSW, and industrial refuse-derived fuel (RDF)). The char produced from the process was characterized using different property domains which include physicochemical properties, texture and morphology, and surface chemistry and structure. The obtained results from the process show that waste tyre char has a surface area of 73 m ² /g and a skeletal density of 2.06 g/cm ³ . The authors concluded that waste tyre char was the least reactive when compared to other feed samples.
2. Fajimi <i>et al.</i> (2021) [55]	Simulation studies on the co-production of syngas and activated carbon from waste tyre gasification using different reactor configurations	Type: Dwindraft Fixed Bed Gasifier, Fluidized Bed Gasifier and Rotary kiln Scale: Pilot Scale and Commercial Scale	Type: Waste Tyre FPS: 2-20mm <i>Proximate Analysis (wt.%)</i> MC: 0.9; FC: 27.04; VM: 66.3; Ash: 6.66 <i>Heating Value</i> LHV: 37.1 MJ/kg <i>Ultimate Analysis (wt.%)</i> C: 81.74; H: 7.06; N: 0.30 S: 1.82; O: 2.42	GA: Air+Steam SFR: 0.1-0.25 ER: 0.18-0.38	GT: 850°C GP: 1 atm HR: NE RT: NE	NE	The authors employed three gasification reactors in the production of syngas along with activated carbon (AC) from waste tyre gasification via computer-aided simulation. The gasification reactors include fixed bed reactor, fluidized bed reactor, and rotary kiln reactor. In order to simulate these reactors a single-stage steam gasification (at 800°C) and char activation (at 900°C) was employed. In addition, an air-steam mixture was employed in the gasification process while N ₂

							<p>and steam were employed to activate the char. The effect of operational parameters such as ER and SFR were also investigated. The AC produced was characterized using the Brunauer-Emmett-Teller (BET) analysis. The result from this process shows that AC produced with a fixed bed gasifier had the highest BET surface area (698.6 m²/g). The rotary kiln and the fluidized bed other the other had AC with BET surface areas of 661.7 m²/g and 432.5 m²/g respectively. In addition, the authors concluded that the best condition to achieve maximum AC production is ER of 0.3 and SFR of 0.25.</p>
3. Molino <i>et al.</i> (2018) [83]	Waste tyre recycling process for production of steam activated carbon in a pilot plant	Type: Rotary Kiln Scale: Pilot Scale	Type: Waste Tyre FPS: 1-2cm <i>Proximate Analysis^{db} (wt.%)</i> MC: 0.8; FC: 33.5; VM: 61.3; Ash: 5.2 <i>Heating Value</i> HHV: 38.6 MJ/kg <i>Ultimate Analysis^{db} (wt.%)</i> C: 84.1; H: 7.3; N: 0.3	GA: Steam SFR: 1 ER: NE	GT: 850°C GP: NR HR: NR RT: 0-6 hrs	NE	The authors performed a double-stage steam gasification (at 850°C) and steam activation (at 920°C) of waste tyre gasification in a pilot-scale rotary kiln reactor. The authors also investigated the best hold time for the char activation stage to ensure the production of the best AC quality. The authors employed a steam-to-waste tyre ratio of 1, an activation steam-to-char ratio of 2, a mean

			S: 2.3; ^a O: 0.8				residence time of 6mins and an activation N ₂ flow rate of 1 Nm ³ /hr. From the result obtained, the AC produced from the process has a surface area of 786 m ² /g and a carbon burn-off value of 78%. The authors concluded that the best hold time for producing high-quality AC is three hours.
4. Zhang <i>et al.</i> (2015) [89]	Pyrolysis-Catalytic Reforming/Gasification of Waste Tyres for Production of Carbon Nanotubes and Hydrogen	Type: Two-Stage Fixed Bed Gasifier Scale: Lab Scale	Type: Waste Tyre FPS: ~6mm <i>Proximate Analysis (wt.%)</i> MC: 0.82; FC: 32.31; VM: 62.7; Ash: 4.17 <i>Heating Value</i> HHV: NR <i>Ultimate Analysis (wt.%)</i> C: 81.2; H: 7.2; N: 0.8 S: 2.1; O ^a : 8.7	GA: Steam SFR: NE ER: NE	GT: 800°C GP: NR HR: 40°C/min RT: NR	Co/Al ₂ O ₃ , Cu/Al ₂ O ₃ , Fe/Al ₂ O ₃ , and Ni/Al ₂ O ₃	The authors co-produced carbon nanotubes (CNT) along with hydrogen in a two-stage waste tyre catalytic pyro-gasification process. Four different catalysts were employed to investigate the best for CNT production. An operating temperature of 600°C and 800°C were employed in the pyrolysis and gasification stages respectively. The CNT produced from the process was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectrometry. The obtained results from the Raman spectrometry showed that Ni/Al ₂ O ₃ produced the highest hydrogen production along with a multi-walled CNT (MWCNT) formation. In addition, the SEM and TEM analysis conducted

showed that the CNT formed replicates MWCNT in terms of its structure and the presence of filamentous carbon respectively.

546 NE–Not Employed; NR–Not Reported; ^{db}–Dry Basis; ^a–By Difference.

547

548 From the summary of previous works presented in **Table 4**, the production of value-
549 added carbon products still has a long way to go. This process is largely stalled by the
550 gasification process which hindered the quality and quantity of char produced in cases where
551 activated carbon, carbon black and char are the target carbon products. In cases where CNMs
552 are the target product, the process differs. In order to produce CNM such as CNT from waste
553 tyre gasification, catalyst plays a big role. The nature of the catalyst determines the quality and
554 structural properties of the CNT Zhang *et al.* [89]. This process is quite complex and only a
555 few authors have explored CNT production from waste tyre gasification and gasification in
556 general such as Larionov *et al.* [64] who used different gasification techniques to produce CNT
557 from waste tyres. One gasification technique tried in that work was electric arc technology
558 which is a very complex setup to develop on a large scale for continuous production. In
559 addition, the environmental effect as well as the economics of this process have not been
560 evaluated. In conclusion, a detailed techno-economic study on valuable carbon production from
561 waste tyre gasification is required.

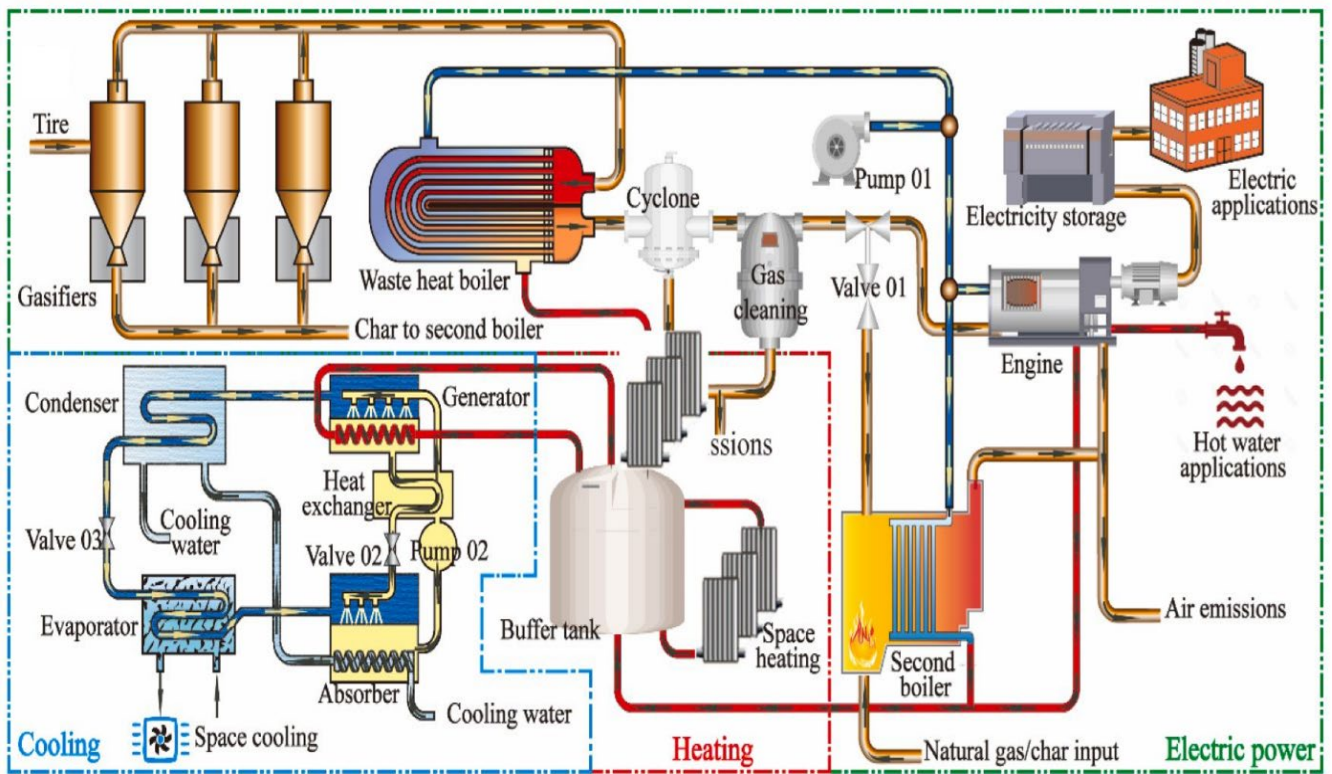
562 **3.5. Waste Tyre Gasification Targeted at Other Products along with Energy Production**

563 Most of the previous works focused on waste tyre-to-syngas or waste-tyre-to-hydrogen
564 and/or carbon products. Only a few authors investigate the end use of these key products.
565 Energy in the form of heat and electricity as well as valuable industrial chemicals (see **Fig. 5**),
566 can be further produced from waste tyre gasification and co-gasification processes. Some of
567 the works that focused on these areas are reviewed in this section

568 Zang *et al.* [57] designed a trigeneration system from waste tyre gasification as shown
569 in **Fig. 7**. The trigeneration system includes cooling during summer, heating during winter and
570 electricity production. Waste tyres and pine wood were combined in different ratios (0:100,
571 50:50 and 100:0) to generate power which was applied to an office building at the University
572 of Iowa. The results from their experiment show that the average combined heat and power

573 (CHP) efficiency from the system is between 32%_{LHV} for waste tyre only to 49%_{LHV} when
 574 waste tyre is combined with pine wood. This result is based on the design options such as the
 575 gasifier type, period of the year, feed ratio, and gasifier operating condition among others. In
 576 addition, the authors also estimated the breakeven levelized cost of electricity (LCOE) from
 577 the process to be between \$0.009/kWh to \$0.12/kWh based on the design option.

578



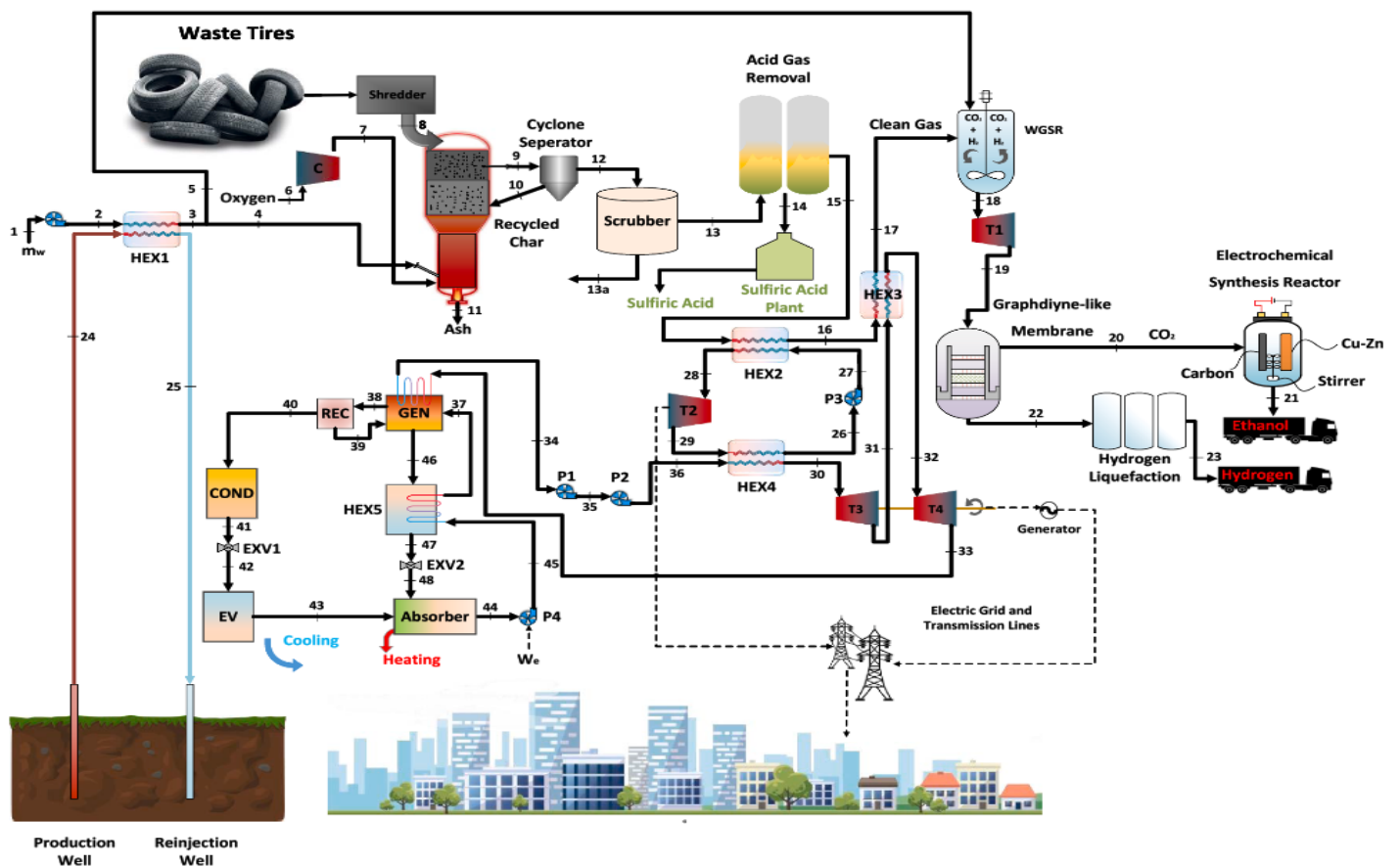
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580 **Fig. 7.** Flow diagram of waste tyre gasification trigeneration system (Reprinted with
 581 permission from the original published in Zang *et al.* [57]).

582 Kahraman and Dincer [120] proposed a geothermal-energy-supported integrated waste
 583 tyre gasification multigeneration system for a community setting as shown in **Fig. 8.** The
 584 system is designed for gasification products (hydrogen, electricity, cooling and heat) and by-
 585 products (ethanol and sulphuric acid). In order to achieve maximum production from the
 586 design, the authors investigated the effect of operational parameters to improve production
 587 rates as well as energy and exergy efficiencies while minimizing both greenhouse gas

588 emissions and environmental wastes. The result obtained from the process simulation shows
 589 that the net electricity generation as well as the heating and cooling capacities were around 18
 590 MW, 5 MW and 49 MW respectively for a 10 kg/s waste tyre feed at 1250°C. In addition, the
 591 production rates of hydrogen and ethanol from the process were found to be 3.02 kg/s and 0.13
 592 kg/s respectively. The energy and exergy efficiencies of the overall system were around
 593 ~71.5%_{LHV} and ~69.9%_{LHV} respectively.

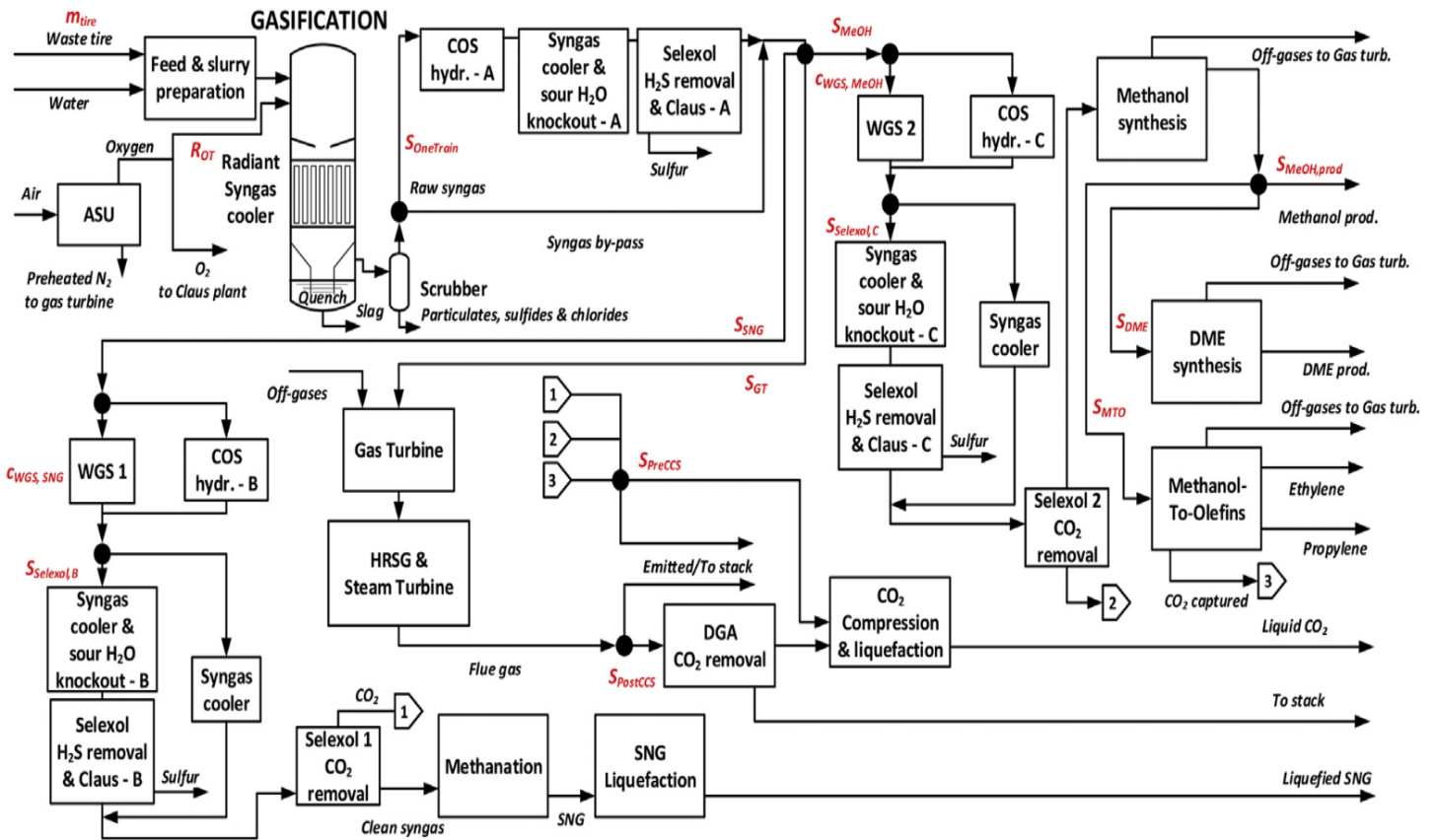
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597 **Fig. 8.** Flow diagram of a geothermal-energy supported integrated waste tyre gasification
 598 multigeneration system for community setting (Reprinted with permission from the original
 599 published in Kahraman and Dincer [120]).

600

616 Subramanian *et al.* [92] developed a model which combined the polygeneration of
617 multiple products from waste tyre gasification process as shown in **Fig. 10**. The model was
618 used to determine the optimal design and operation of a system that employs waste tyre
619 gasification as the key operation to produce varieties of products which include a mixture of
620 electricity, industrial chemicals and fuels. For process optimization, the authors used mixed-
621 integer non-linear programming (MILP). The outcome of the experiment reveals that, while
622 electricity generation is preferred in the base case with historically market pricing, methanol,
623 liquefied synthetic natural gas (SNG), and dimethyl ether (DME) are preferred in more likely
624 scenarios in which the relevant product fetches higher prices. The authors also came to the
625 conclusion that pre-combustion CO₂ capture is favoured at lower CO₂ tax rates and post-
626 combustion CO₂ capture is only optimal in scenarios with higher rates. The fact that the optimal
627 product portfolio fluctuates dramatically with shifting market conditions encourages the
628 construction of flexible polygeneration processes that are able to alter operational conditions
629 in order to improve profitability by taking advantage of price peaks.



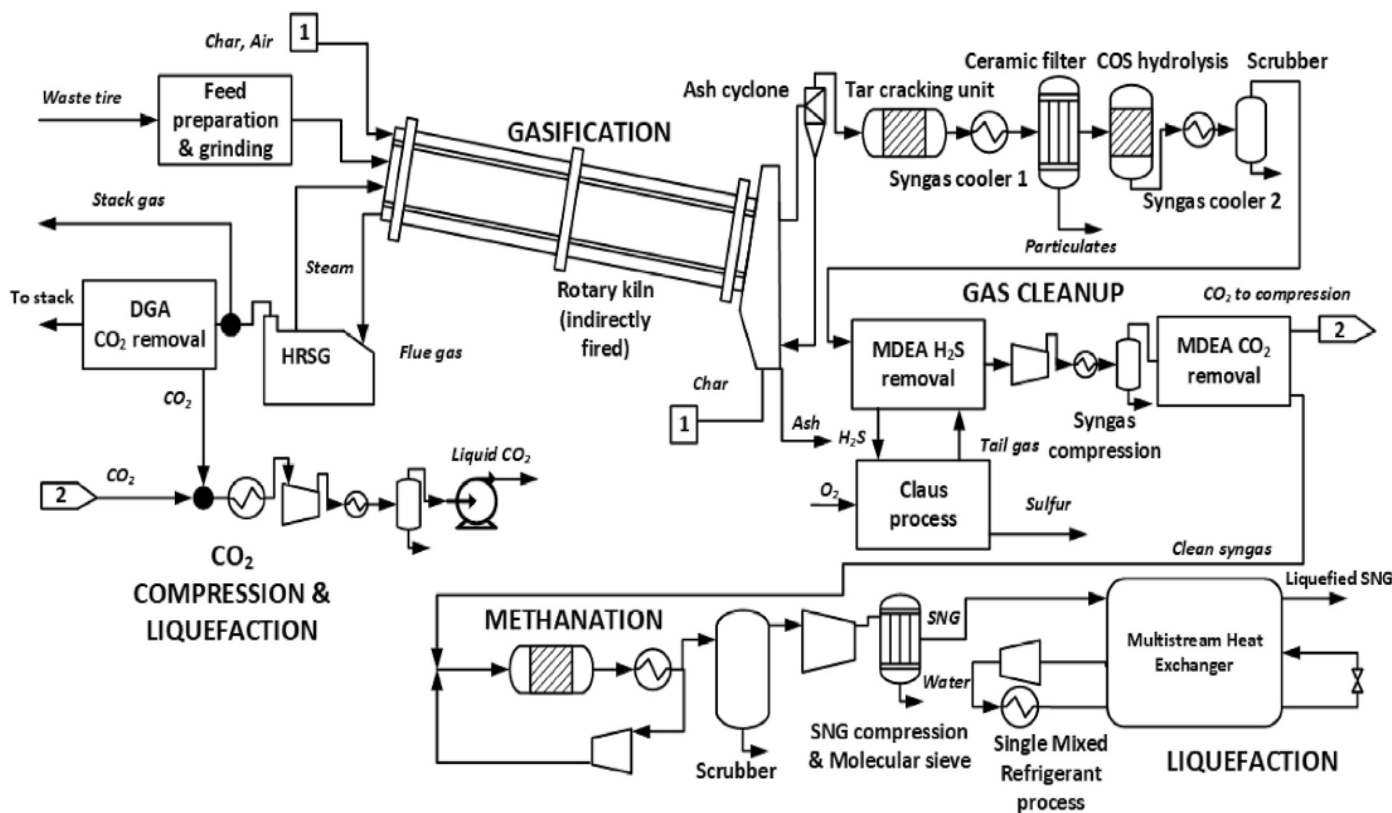
631 **Fig. 10.** Block diagram waste tyre gasification polygeneration system (Reprinted from the original
 632 published in Subramanian *et al.* [92]).

633

634 Subramanian *et al.* [147] proposed a production route for liquified synthetic natural gas (LSNG)
 635 from waste tyre gasification in Norway and the United States (see **Fig 11**). The authors employed a
 636 combination of mathematical and empirical models along with experimental data in the process. Three
 637 design scenarios were investigated which include production without CO₂ capture and sequestration
 638 (CCS), production with precombustion CCS as well as production with both pre-combustion and post-
 639 combustion CCS. From the results obtained from process economics the production, the authors
 640 established a minimum selling price (MSP) for the LSNG produced from the process. For the process
 641 to be economically feasible in the United States, MSPs of \$16.7, \$17.5 and \$19.9 GJ_{LHV,SNG} are required
 642 for the three design cases respectively. Meanwhile, the MSPs for the waste tyre-to-LSNG production

643 process in Norway were estimated at \$20.9, \$21.8 and \$24.9 per $GJ_{LHV,SNG}$ respectively. The authors
 644 concluded that the process with pre-combustion and post-combustion CCS (scenario 3) is
 645 technologically feasible and environmentally feasible, especially in Norway where it was implemented
 646 for energy generation. In addition, the MSP is greatly influenced by plant scale and tipping fees, while
 647 other parameters have minimal effect on the production process.

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650 **Fig. 11.** Process flow diagram showing waste tyre to LSNG (Reprinted from the original published in
 651 Subramanian *et al.* [147]).

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655 **3.6. Modelling Waste Tyre Gasification Process**

656 The modelling of physical, chemical, and biological processes is basically aimed at
657 giving a full mathematical description of the processes. Modelling can be used to predict
658 reactor operating conditions, product yield and composition. The most widely used gasification
659 models are the thermodynamic equilibrium model and the kinetic model [148]. A deep survey
660 on gasification modelling choices found that around 66% of authors who have worked on the
661 simulation of gasification processes utilize some type of equilibrium model while others utilize
662 some type of kinetic model [149]. ~~The optimization of gasification parameters such as the~~
663 ~~feedstock flow rate, GA ratio, ER, GT, and GP must be done in order to achieve a desirable~~
664 ~~syngas composition and yield. A change in any of these parameters can have a substantial~~
665 ~~impact on the product compositions and the gasifier performance [150].~~Very good A great
666 insight and economically efficient routes can be obtained by simply combining mathematical
667 models and process simulation with physical experimentation. A good model can be used to
668 predict the accurate representation of the chemical and physical phenomena occurring inside
669 the gasifiers used in gasification processes [150]. A model that best fits experimental data can
670 reveal to a great extent the major trends in a multivariate system and can also be employed by
671 process engineers in scaling up a reactor to an industrial scale [148]. All possible reactions
672 between the species would ensure the predictability of a model as well as the transport
673 phenomena as realistic as possible. Before modelling waste tyre gasification processes, key
674 gasification reactions such as the ones presented in **Table 5** have been used.

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Table 5. Waste tyre gasification reactions ([86]).

Reaction Equation	Reaction Name	Heat of Reaction (MJ/kmol)	Reaction Number
$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$	WGS/CO Shift	-41	R-1
$C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$	Methane Formation/Methanation	-75	R-2
$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$	Boudouard Reaction	+172	R-3
$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$	Water Gas Reaction	+131	R-4
$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$	Steam Methane Reforming	+208	R-5
$C_{(s)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{(g)}$	Carbon Partial Combustion	-111	R-6
$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$	CO Partial Combustion	-283	R-7
$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons H_2O_g$	Hydrogen Partial Combustion	-242	R-8

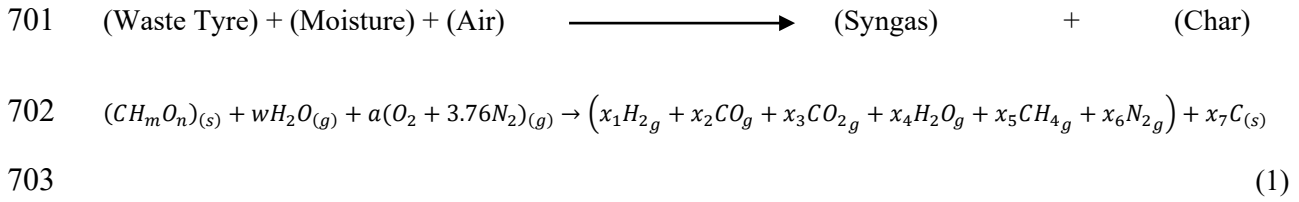
681

682 *3.5.1. Kinetic Model*

683 Rate-based models attempt to predict product gas concentration with suitable kinetic
684 structure for both homogenous and heterogenous processes occurring in the reactors. However,
685 a large amount of unknown dynamic parameters makes product estimation difficult to measure
686 for fluidized bed gasification [15]. Modelling the kinetics of the thermal degradation process
687 of waste tyres can provide a detailed insight into the various mechanisms responsible for waste
688 tyre gasification and predict potential difficulties in a gasification reactor. Previous
689 investigations have created gasification models based on information gathered from
690 thermogravimetric analysis (TGA), which quantify the sample weight loss with time and
691 temperature [151-156]. Zang *et al.* [86] applied a kinetic model to simulate waste tyre
692 gasification problem in a fixed bed reactor that assumes the simplified gasification process
693 shown by Eq. 1. In addition, the authors broke down waste tyre gasification process into zones
694 (Zone-A and Zone-B) to simplify each of the reactions and equations required to model the
695 zone. A sub-stoichiometric environment is present in Zone-A, where the fuel sample is

696 subjected to pyrolysis and oxidation. A full description of the model is given below. The
 697 products formed in Zone-A undergo reduction in Zone-B into the final product gases based on
 698 kinetically controlled chemical reactions.

699 First, the combustible part of waste tyre is represented by CH_mO_n with the assumption
 700 that waste tyre contains only Carbon, Hydrogen, and Oxygen [157].



704 The values of m and n can be estimated from Eqs. 2-3.

705
$$m = \frac{\%H \times MW_C}{\%C \times MW_H} \quad (2)$$

706
$$n = \frac{\%O \times MW_C}{\%C \times MW_O} \quad (3)$$

707 where $\%C$, $\%H$ and $\%O$ are the compositions (wt.%) of C, H, and O in the waste tyre
 708 while MW_C , MW_H , and MW_O are their respective molecular weights. The moisture content
 709 present in the sample was accounted for separately as shown in Eq. 1. The quantity of air
 710 required in the process is determined from the ER. w indicates the number of moles of the
 711 moisture content (MC) in the waste tyre and can be obtained from Eq. 4.

712
$$w = \frac{MC}{(100-MC) \times (100-ASH)} \times \frac{MW_F}{MW_W} \quad (4)$$

713 where ASH represent the ash content in the waste tyre as obtained from the proximate
 714 analysis. MW_W and MW_f represents the molecular weights of H_2O and CH_mO_n respectively.

715 a represents the number of moles of O_2 from the air per mole of CH_mO_n and can be
 716 obtained from Eq. 5.

$$717 \quad a = \frac{1 + \frac{m}{4} - \frac{n}{2}}{ER} \quad (5)$$

718 where ER is the defined by Eq. 6.

$$719 \quad ER = \frac{\frac{\dot{m}_{O_a}}{\dot{m}_{wt}}}{\frac{\dot{m}_{O_{st}}}{\dot{m}_{wt}}} = \frac{\dot{m}_{O_{st}}}{\dot{m}_{O_a}} \quad (6)$$

720 where \dot{m}_{O_a} , $\dot{m}_{O_{st}}$, and \dot{m}_{wt} represents the mass flow of actual O_2 , stoichiometric O_2 and
 721 waste tyre respectively. The seven unknown variables ($x_1 - x_7$) requires seven different
 722 equations to estimate their values. From the atomic balance of the key elements (C, H, O, N),
 723 four equations can be expressed as shown in Eqs. 7-10 [157].

$$724 \quad \text{Carbon (C) Balance: } 1 = x_2 + x_3 + x_5 + x_7 \quad (7)$$

$$725 \quad \text{Hydrogen (H) Balance: } m + 2w = 2x_1 + 2x_4 + 4x_5 \quad (8)$$

$$726 \quad \text{Oxygen (O) Balance: } n + w + 2a = x_2 + 2x_3 + x_4 \quad (9)$$

$$727 \quad \text{Nitrogen (N) Balance: } 3.76a = x_6 \quad (10)$$

728 Zone-A follows that the reaction R-1 (i.e., WGS) (see **Table 5**) $CO_{(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$
 729 and $H_2_{(g)}$ are in chemical equilibrium. The equilibrium constant (k_1) of R-1 is a function of the
 730 temperature of the zone (i.e., $k_1 = f(T_{Zone-A})$) and can be associated to the number of moles
 731 ($x_1 - x_4$) of the reacting species in as:

$$732 \quad k_1 = \frac{x_1 x_3}{x_2 x_4} \quad (11)$$

733 Also, $CH_{4(g)}$ is assumed to be produced from the methanation reaction (R-2) in the zone

734 Hence,

$$735 \quad k_2 = \frac{x_5}{x_1^2} \quad (12)$$

736 where k_2 is the equilibrium constant of R-2. The values of the equilibrium constant
 737 (k_1, k_2) are estimated from the change in Gibbs functions (\bar{g}_i^0) between the gaseous species
 738 ($CO_{(g)}, H_2O_{(g)}, CO_{2(g)}, H_{2(g)}$ and $CH_{4(g)}$) in the products and reactants at T_{Zone-A} as shown in
 739 Eqs, 13-14.

$$740 \quad k_1 = \exp\left(-\frac{\bar{g}_{CO_2}^0}{RT_{Zone-A}} - \frac{\bar{g}_{H_2}^0}{RT_{Zone-A}} + \frac{\bar{g}_{CO}^0}{RT_{Zone-A}} + \frac{\bar{g}_{H_2O}^0}{RT_{Zone-A}}\right) \quad (13)$$

$$741 \quad k_2 = \exp\left(-\frac{\bar{g}_{CH_4}^0}{RT_{Zone-A}} + 2\frac{\bar{g}_{H_2}^0}{RT_{Zone-A}}\right) \quad (14)$$

742 where R represents the universal gas constant which is ~ 8.314 kJ/kmol K, T_{Zone-A}
 743 represent Zone-A temperature and can be estimated from the energy balance across the zone
 744 by factoring the gasification reactor heat loss (Q_{loss}). The yield of the solid char from the
 745 process is evaluated as the fixed carbon (FC) from waste tyre proximate analysis (on dry basis)
 746 which is divided into carbon solid (C) and the CH_4 formed on the char surface from
 747 methanation reaction (R-2). Therefore,

$$748 \quad x_5 + x_7 = \frac{FC}{C} \quad (15)$$

749 where C is the carbon content from the ultimate analysis of the waste tyre sample
 750 (wt.%). The authors also made the assumption that changes in both the kinetic energy and
 751 potential energy were not considered in all the streams, hence, the energy equation applied
 752 across Zone-A in steady-state as:

$$753 \quad H_{in} + Q_{loss} = H_{out} \quad (16)$$

754 where H_{in} and H_{out} are the enthalpies entering and leaving Zone-A. In addition, one
 755 mole of CH_mO_n , in Eq. 16 can be expressed as:

$$\begin{aligned}
& \bar{h}_{f_{wt}}^0 + a \int_{T_0}^{T_a} \bar{c}_{p,O_2} dT + 3.76a \int_{T_0}^{T_a} \bar{c}_{p,N_2} dT + w \bar{h}_{f_{H_2O}} + Q_{loss} = \\
& = \sum_{i=1}^6 x_i \left[\bar{h}_{f_i}^0 + \int_{T_0}^T \bar{c}_{p,i} dT \right] + x_7 \bar{c}_{p,C} (T - T_0) + m_{ash} c_{p,ash} (T - T_0)
\end{aligned}
\tag{17}$$

where $i = 1 - 6$ represents the gaseous species ($H_{2(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $H_2O_{(g)}$, $CH_{4(g)}$, and $N_{2(g)}$) respectively, the ash and char leaving zone energy streams were also accounted for. In Eq. 17 above, $\bar{h}_{f_i}^0$ and $\bar{c}_{p,i}$ represent the formation enthalpies and the specific heat capacities of the gaseous and carbon species respectively, T_a is the temperature of the air that is fed into the gasification reactor, T_0 is the waste tyre feed temperature (25°C). The disparities in the $\bar{c}_{p,i}$ of the gaseous with temperature have been accounted as:

$$\bar{c}_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3
\tag{18}$$

where the values of a_i , b_i , c_i and d_i of each species can be obtained from Perry [158], however, the values of the $c_{p,char}$ and $c_{p,ash}$ are given as 1 $\text{kJkg}^{-1}\text{K}^{-1}$ and 0.84 $\text{kJkg}^{-1}\text{K}^{-1}$ respectively [15, 159].

In Zone-B, reactions R-2 to R-5 from **Table 5** were the reduction reactions considered in modelling the zone. The net reaction rates in this zone are expressed by Arrhenius type kinetic rate equation (Eqs. 19-22):

$$r_{R2} = C_{RF} A_{R2} \exp\left(-\frac{E_{R2}}{RT}\right) \left(y_{CO_2} - \frac{y_{CO}^2}{K_{R2}}\right)
\tag{19}$$

$$r_{R3} = C_{RF} A_{R3} \exp\left(-\frac{E_{R3}}{RT}\right) \left(y_{H_2O} - \frac{y_{CO} y_{H_2}}{K_{R3}}\right)
\tag{20}$$

$$r_{R4} = C_{RF} A_{R4} \exp\left(-\frac{E_{R4}}{RT}\right) \left(y_{H_2}^2 - \frac{y_{CH_4}}{K_{R4}}\right)
\tag{21}$$

$$r_{R5} = C_{RF} A_{R5} \exp\left(-\frac{E_{R5}}{RT}\right) \left(y_{H_2O} y_{CH_4} - \frac{y_{H_2}^3 y_{CO}}{K_{R5}}\right) \quad (22)$$

where C_{RF} is the char reactivity factor, (A_R) and (E_R) are the activation energy and pre-exponential factor for each of the reactions. The A_R and E_R of the forward reactions can be found in Wang and Kinoshita (1993) [160]. The equilibrium constants ($K_{R2} - K_{R5}$) as well as the specific rates of reactions ($r_{R2} - r_{R5}$) and of the backward reactions can be evaluated from the forward reactions as expressed in Eqs. 23-26. The active sites on the char surface are taken into account by C_{RF} .

$$K_{R2} = \exp\left(-2 \frac{\bar{g}_{CO}^0}{RT} + \frac{\bar{g}_{CO_2}^0}{RT}\right) \quad (23)$$

$$K_{R3} = \exp\left(-\frac{\bar{g}_{CO}^0}{RT} - \frac{\bar{g}_{H_2}^0}{RT} + \frac{\bar{g}_{H_2O}^0}{RT}\right) \quad (24)$$

$$K_{R4} = \exp\left(-\frac{\bar{g}_{CH_4}^0}{RT} - 2 \frac{\bar{g}_{H_2}^0}{RT}\right) \quad (25)$$

$$K_{R5} = \exp\left(-\frac{\bar{g}_{CO}^0}{RT} - 3 \frac{\bar{g}_{H_2}^0}{RT} - \frac{\bar{g}_{CH_4}^0}{RT} + \frac{\bar{g}_{H_2O}^0}{RT}\right) \quad (26)$$

Following the exit from the pyro-oxidation zone, the product gases move into Zone-B (also known as the reduction zone). Based on the flow rate of the dry waste tyre sample delivered to the gasifier (m_F), the flowrate of each species at Zone-B entrance was determined as follows:

$$X_i^0 = \frac{m_F(1 - ASH/100)}{MW_F} x_i. \quad i = 1 \text{ to } 7 \quad (27)$$

where x_i represent the number of moles of species formed per mole of CH_mO_n in Zone-A. The mass flow rate of the ash flowing with the product is given by Eq. 28.

$$m_{ash} = \frac{m_F ASH}{100} \quad (28)$$

The geometry of Zone-B is thought to be divergent in nature, with the entire zone divided into a number of elemental control volumes (k) that have constant temperatures and

796 concentrations [86, 161]. The energy and mass balances of each specie were calculated for each
 797 of the control volumes, taking into account the rate of species creation and/or consumption
 798 according to various reaction equations, such as the heat loss equation from the gasification
 799 reactor [86]. Eq. 29 provides the balance across the control volume for any species.

$$800 \quad X_i^k = X_i^{k+1} + R_i^k \Delta V_k \quad (29)$$

801 where R_i^k is the net formation rate of species (i) and ΔV_k is the volume of the respective
 802 k. The R_i^k of each specie is presented in **Table 6**.

803 **Table 6.** Net rate of formation of different species according to Eqs.23-26 ([86])

Species	R_i (mol m ⁻³ s ⁻¹)
H ₂	$r_{R-2} - 2r_{R-4} + 3r_{R-5}$
CO	$2r_{R-2} + r_{R-3} + r_{R-5}$
CO ₂	$-r_{R-2}$
H ₂ O	$-r_{R-2} - r_{R-5}$
CH ₄	$r_{R-4} - r_{R-5}$
N ₂	0
C	$-r_{R-2} - r_{R-3} - r_{R-4}$

804

805 Zone-B temperature was estimated from Eq. 30, the temperature and concentration of
 806 each species exiting the final k determines their values in the product gases leaving the
 807 gasification reactor.

$$808 \quad \sum_{i=1}^6 X_i^{k-1} \left(\bar{h}_{f_i}^0 + \int_{T_0}^{T^{k-1}} \bar{c}_{p,i} dT \right) + X_7^{k-1} \bar{c}_{p,C} (T^{k-1} - T_0) + m_{ash} c_{p,ash} (T^{k-1} - T_0) + Q_{loss}^k$$

$$809 \quad = \sum_{i=1}^6 X_i^k \left(\bar{h}_{f_i}^0 + \int_{T_0}^{T^k} \bar{c}_{p,i} dT \right) + X_7^k \bar{c}_{p,C} (T^k - T_0) + m_{ash} c_{p,ash} (T^k - T_0)$$

810

(30)

811 where Q_{loss}^k indicates the rate at which heat dissipates from the final k. Since hot gases
812 in this zone tend to migrate up toward the area around the exhaust, it was presumed that heat
813 loss from the gasification reactor was not taken into account.

814 In addition, Isaac *et al.* [119] also applied kinetic models in the isothermal gasification
815 of waste tyres. Two kinetic models namely the random pore model (RPM) and grain model
816 were employed; however, this model does not describe the entire gasification process as they
817 were both targeted at the char product. The same applies to Molino *et al.* [83] who also
818 employed RPM to model and predict the surface areas and burn-off of the activated carbon
819 produced from waste tyre gasification.

820 In conclusion, Eqs. 1-30 sums up the kinetic model that has been frequently employed
821 for modelling waste tyre gasification in a downdraft fixed bed reactor. Even though the model
822 combines some thermodynamics principles to estimate some of the variables, the model relies
823 on kinetic parameters determined from gasification experiments. ~~In addition,~~ Another disputed
824 assumption is that kinetic models also assume the gasification process to be one-dimensional
825 (in space). In addition, one of the assumptions made is the waste tyre comprises mainly of C,
826 H, and O, in most cases, sulphur is one of the components of waste tyre and the formation of
827 sulphurous compounds could mean a great problem in real-life application when it is ignored.
828 Even though the main pollutants in the waste tyre gasification process that contain sulphur are
829 SO₂ and H₂S, the primary source of SO_x emissions is the high-temperature oxidation of waste
830 tyres [162]. Janajreh *et al.* [70] investigated the different products from waste tyre gasification
831 and concluded that up to 44 different species (including all sulphur compounds) can be
832 obtained from waste tyre gasification.

833 3.5.2. Thermodynamic Equilibrium Model (TEM)

834 Thermodynamic equilibrium models (TEMs) have proven to be much more convenient
835 because they are independent of the type of gasifier adopted and can also use thermodynamic
836 properties of the variables to guide the design, evaluation and improvement [163]. TEMs also
837 have their limitations. For example, they cannot be used for spatial designs, sub-equilibrium
838 operations or process dynamics and control. ~~Some of the studies that have employed TEMs in~~
839 ~~waste tyre gasification are examined below.~~ Jarungthammachote and Dutta [164] developed a
840 TEM to predict the composition of producer gas in a downdraft solid waste gasifier. The model
841 applies the second law to analyze the gasification system on municipal solid waste. In order to
842 improve the model, WGS reaction and methane reaction were adopted to correct the
843 equilibrium constant. While varying the moisture content of the feedstock, the authors reported
844 a high yield of H₂ and CO₂ while other products have a lower yield when compared with lower
845 moisture content value. This method has been employed by other authors in waste tyre
846 gasification [55, 86]. Janajreh *et al.* [70] applied TEM to simulate waste tyre gasification in
847 two different gasification reactors (plasma and conventional). ~~A comparison between plasma~~
848 ~~gasification process and conventional air gasification model was performed via simulation~~
849 ~~using Aspen Plus software.~~ The approach does not require chemical reactions nor does it
850 require the selection of intermediate reactions using equilibrium constant. In the work, the
851 authors used a non-stoichiometric Gibbs energy minimization approach to model waste tyre
852 gasification process. This approach minimizes the total Gibbs energy ($\bar{g}_{T,P}^t$) of a system by
853 employing the constrained atomic mass balance equation which provides room for the
854 formation of other species produced during waste tyre gasification experiment [70]. The
855 description of the process is given in Eqs. 31-40.

$$856 \bar{g}_{T,P}^t = g(n_1, n_2, n_3, \dots, n_i) \quad (31)$$

857 where $\bar{g}_{T,P}^t$, and n_i represent the total Gibbs free energy, and mole fraction of each of
 858 the species respectively. To compute the n_i , several steps are required, the first includes the
 859 definition of the material balance for each element present within the system.

$$860 \quad \sum_i n_i a_{ij} = A_j \quad (j = 1, 2 \dots w)$$

861 (32)

862 where a_{ij} represents the number of atoms of the j^{th} element in each molecule of the
 863 chemical species (i), A_j represents the total number of atomic masses of the j^{th} element inside
 864 the system while w represents the total number of atoms present inside the system. Lagrange
 865 principles were applied to Eq. 32 to give:

$$866 \quad \sum_j \lambda_j \left(\sum_i n_i a_{ij} - A_j \right) = 0$$

867 (33)

868 A new function, F is formed by adding Eqs. (31) and (33)

$$869 \quad F = \bar{g}_{T,P}^t + \sum_j \lambda_j \left(\sum_i n_i a_{ij} - A_j \right)$$

870 (34)

871 The minimum value of F is obtained when the partial derivative of F with respect to
 872 n_i at specified conditions (temperature and pressure) approaches 0 as shown in Eq. 35.

$$873 \quad \frac{\partial F}{\partial n_i} = \frac{\partial \bar{g}^t}{\partial n_i} + \sum_j \lambda_j a_{ij} = 0 \quad (i = 1, 2, \dots n)$$

874 (35)

875 The equation can be re-written as:

$$876 \quad \mu_i + \sum_j \lambda_j a_{ij} = 0$$

877 (36)

878 where μ_i is known as chemical potential which is defined as:

879
$$\mu_i = \bar{g}_i^0 + RT \ln \left(\frac{f_i}{f_i^0} \right)$$

880 (37)

881 where $\bar{g}_i^0 = \Delta\bar{g}_{fi}^0$ is the standard state Gibbs energy of formation, T is the temperature
 882 of the system, R is the universal gas constant, $\frac{f_i}{f_i^0}$ is the fugacity ratio of the species. For ideal
 883 gases at the standard pressure. The $\frac{f_i}{f_i^0}$ term can be replaced by the mole fraction of the species
 884 as given by Eq. 38.

885
$$\mu_i = \bar{g}_{fi}^0 + RT \ln \left(\frac{n_i}{n_{total}} \right)$$

886 (38)

887 By substituting, Eq. 36 in Eq. 39, we have,

888
$$\bar{g}_{fi}^0 + RT \ln \left(\frac{n_i}{n_{total}} \right) + \sum_j n_j a_{ij} = 0 \quad (i = 1, 2, \dots, n)$$

889 (39)

890 Eq. 39 represents n equilibrium equations which refers to each specie present within the
 891 system. In addition, all the participating specie are a combination of the basic elements present
 892 in the waste tyre sample (CHNOS), therefore, the energy balance is given as:

893
$$h_{f_{CHONS}}^0 + m\Delta h_{o_2} + p\Delta h_{H_2O} = \sum_{i=product} n_i \Delta h_i$$

894 (40)

895 where $h_{f_{CHONS}}^0$ represent the enthalpy of formation of waste tyre and Δh is the relative
 896 enthalpy of each species within the system.

897

898 The proposed TEM model by Janajreh *et al.* [70] took into account several feedstocks
 899 (which also included waste tyres) and two gasification modes (plasma and conventional). ~~The~~
 900 ~~results of both plasma and conventional gasification methods were evaluated on the basis of~~

901 ~~efficiency of the gasification process.~~ The result obtained from the process shows that the
902 ~~waste tyre gasification efficiency (the LHV of the syngas divided by the LHV of the feed)~~ of
903 plasma reactor was estimated to be around 43%_{LHV}, while that of conventional reactor is
904 approximately 74%_{LHV}. Janajreh *et al.* [165] in another study combined the equilibrium
905 constant method (ECM) with the element potential method (EPM) to model waste tyre
906 gasification process. The ECM was used to determine the concentration of the species at
907 equilibrium as well as the temperature and pressure of the products exiting the gasifier. The
908 EPM on the other hand was employed to detect the presence of graphite in the product stream.
909 The basic assumptions made in the implementation of these models include the assumption of
910 infinite residence time, the system is in both chemical and thermodynamic equilibrium, no
911 spatial distribution of species as well and no account for the kinetics of the reactions. Mozarafi
912 *et al.* [166] also applied TEM to model waste tyre gasification, ~~the authors also applied the~~
913 ~~minimization of Gibbs energy~~ similar to Janajreh *et al.* [70]. The authors employed penalty
914 method to account for mass balance constraints in the objective function. The authors
915 validated their model based on the prediction of thermal parameters of adiabatic combustion
916 of propane at stoichiometric air to fuel ratio. ~~The goal of the validation was to assess the~~
917 ~~reliability of their model in predicting adiabatic temperature.~~ The authors concluded that the
918 proposed TEM could be used as a reference simulator to forecast adiabatic temperature and
919 product distribution in the thermolysis and air gasification of waste tyres.

920 In conclusion, TEM only forecasts the performance bounds of a specific gasifier under
921 a specific set of operating parameters. Syngas and other product composition measurements
922 frequently deviate from the equilibrium's ideal [149]. The two most frequently mentioned and
923 notable differences between ideal equilibrium forecasts and experimental findings are first,
924 higher CH₄ concentrations in the final syngas relative to the equilibrium CH₄ concentration,
925 and second, higher levels of unreacted char in some instances [149]. The cons of using this

926 method include non-consideration of tars and heat losses, limited to fluidized bed reactors,
927 assumes zero-dimensionality of the reactor, and it is not ideal for low temperature operations.

928

929 3.5.3. Other Models Employed in Waste Gasification

930 Generally, the modelling of waste tyre gasification process over the years has based
931 their simulation on the kinetic model and TEM [55, 70, 86, 165-168]. However, due to the
932 simplified assumptions and errors involved in TEM and also the uncertainty in kinetic
933 parameters of tyre gasification for predicting the presence of hydrocarbon products, neither
934 method may be best suited for fluidized bed simulation [86, 169]. Hannula and Kurkela [148]
935 proposed a semi-empirical model (SEM) to model fluidized bed gasification reactors. The
936 authors however did not apply this model to waste tyre gasification. Zang *et al.* [86] and Fajimi
937 *et al.* [55] have applied SEM to model waste tyre gasification in a fluidized bed reactor in the
938 Aspen Plus environment. SEM was basically used to account for ammonia, hydrocarbon
939 formation and carbon conversion by using ER as the key parameter.

940 **4.0. Research Gaps Waste Tyre Gasification Challenges and Limitations**

941 Waste tyre gasification has its challenges and limitations that need to be addressed. One
942 of the main issues is the cost of building and operating gasification plants, which can be
943 relatively high compared to traditional waste management methods [93]. For instance, the total
944 plant cost of the fluidized bed gasifier is more than \$10 million for a commercial scale plant
945 [86, 93]. The high capital cost of gasification plants is partly due to the complex and
946 sophisticated nature of the technology, as well as the need for advanced pollution control
947 systems. Most times, these cost do not include the cost of syngas cleaning operation, ash
948 handling, waste tyre pretreatment operations, tar cracking etc [93]. This cost factor also can
949 make it difficult for waste tyre gasification to compete with other waste management options
950 (such as pyrolysis), particularly in regions with limited financial resources. Another issue with

951 waste tyre gasification is the potential for emissions of harmful pollutants, such as dioxins and
952 furans. These pollutants can be produced during the gasification process, particularly if the
953 plant is not equipped with adequate pollution control systems. To address this issue, many
954 waste tyre gasification plants employ advanced scrubbing and filtration technologies to remove
955 these harmful pollutants from the gas stream.

956 Another general problem encountered in waste tyre gasification is the existence of tar
957 in syngas. These tars are made up of heavier aromatic hydrocarbons, and present major
958 difficulties for the usage of syngas downstream. Tar-designated compounds have the ability to
959 damage downstream equipment and applications through a variety of mechanisms, from as
960 simple as blocking flow channels in internal combustion engines and turbines to as serious as
961 contaminating catalytic layers in fuel cells and alcohol synthesis processes [170]. As such, in
962 order to achieve the maximum permitted limits, syngas must be cleaned to the degree required
963 by certain uses [171]. It is critical to have a solid understanding of the chemistry and design of
964 gasifiers, the formation of tar during waste tyre gasification, the composition-based
965 classification of tar, the necessary level of tar removal from syngas, and the science behind tar
966 removal technology. It is abundantly clear that the current secondary tar removal technologies
967 cannot produce the required syngas purity without multistage cleaning in addition to in situ
968 mitigation of tar production. Since most other solutions involve the use of syngas cooling for
969 tar removal, catalytic tar removal techniques have demonstrated tremendous promise for
970 removing tar with high thermal stability without sacrificing cold gas efficiency [170]. For
971 successful application, it is necessary to address catalyst deactivation caused by coke, fouling,
972 and sintering, as well as other syngas contaminants. In modelling waste tyre gasification
973 process, the difficulty in determining the effect of hydrodynamic variables on gasification when
974 using TEMs is a big disadvantage. A kinetic model would be necessary if the aim was to
975 understand or optimize the impact of variables like feed density, reactivity, and particle size

976 distributions on the final syngas composition, carbon conversion, as well as system
977 performance. However, the kinetic and transport parameters typically required in kinetic
978 models are hard to find. Even if these variables are measured, the final model will still be
979 somewhat constrained to the particular gasifier type, design, feedstock, agent, and operating
980 range combination for which the rate expression form and parameter values are appropriate.

981 **5.0. Conclusion and Recommendations for Future Works**

982 ~~In conclusion, waste tyre gasification is a promising technology for managing waste~~
983 ~~tyres by converting them into energy rich gases and other valuable industrial products.~~

984 The possibility of producing valuable products while lowering carbon footprints and
985 producing energy carrier fuels like syngas and hydrogen are the key areas of attention for
986 current waste tyre processing research. Typically, elevated temperatures are necessary to carry
987 out the process of extracting valuable materials from waste tyres. It is therefore practical to
988 employ the gasification process to meet the requirements and obtain hydrogen and/or syngas
989 in addition to valuable carbon products. In addition, Considering the enormous waste generated
990 globally on an annual basis, the high-energy fuel produced from gasification technology could
991 be used to replace fossil fuels. However, there are still challenges and limitations that need to
992 be addressed, particularly with regard to cost and emissions control. Further research and
993 development are needed to improve waste tyre gasification technology and make it more
994 economically viable for widespread adoption in both developed and developing countries. In
995 addition, after taking a big-picture view of the literature, the following areas are recommended
996 for careful investigation.

997 *1. Tar Consideration:* Controlling the composition of the final product and increasing
998 the hydrogen-rich syngas production depend heavily on understanding the processes
999 involved in waste tyre gasification, including tar formation and conversion. Currently,

1000 the majority of research on tar formation and conversion
1001 having only one model compound in use. However, the various components in tar
1002 interact with one another, making it a complex mixture. Therefore, to comprehend
1003 the mechanism of tar reformation under actual conditions, the catalytic reformation
1004 of a combination of several model compounds should be investigated. Furthermore,
1005 the majority of tar research has concentrated on light components; however, more has
1006 to be done to further the study of heavy tar conversion.

1007 2. *Waste tyre Gasification and Carbon Nanomaterials*: Few studies have proven that
1008 carbon nanomaterial such as carbon nanotube (CNT) can be produced from waste tyre
1009 gasification. Zhang *et al.* [89] were the last authors who attempted this and proved
1010 CNT could be produced from waste tyre gasification. In addition, are limited research
1011 on modelling CNT production from waste tyre gasification.

1012 3. *Environmental Impact of Waste Tyre Gasification*: The investigation of the
1013 environmental impact of waste tyre gasification emission through a detailed life cycle
1014 assessment (LCA) is vital as this can ease the adoption of waste tyre gasification
1015 technology. Investigating the LCA of the process is required to ensure that we actually
1016 do have a net environmental benefit. In addition, LCA is required to determine and
1017 understand the best processes and routes for using waste tyres considering both
1018 environmental and economic trade-offs. To the best of our knowledge, only
1019 Santasnachok and Nakyai [61] and Batuecas *et al.* [172] have researched this area,
1020 however, a more detailed approach is required.

1021 4. *Waste tyre Gasification and Artificial Intelligence (AI)*: The application of artificial
1022 intelligence (AI) in waste tyre gasification processes is still in its infancy with limited
1023 work available in this area. With the aid of experimental and literature data, AI
1024 algorithms could be used to predict critical waste tyre gasification parameters such as

1025 the heating value, syngas composition, and thermal efficiency amongst others.
1026 Authors such as Pandey *et al.* [173], Mutlu & Yucel [174], and Han *et al.* [175] have
1027 all applied AI techniques to predict biomass gasification parameters. However,
1028 besides Ozonoh *et al.* [176] who employed AI in predicting waste tyre gasification
1029 emissions, critical works in AI applications in waste tyre gasification are currently
1030 unavailable to the best of our knowledge.

1031 5. *Hydrothermal Gasification of Waste Tyres*: The gasification of waste tyres at
1032 supercritical conditions is an interesting area that is still lacking detailed research. As
1033 discussed earlier in section 3.1.1.2, this is a promising gasification technology and
1034 very limited works are available in this area.

1035 6. *Solar-assisted Waste Tyre Gasification*: Solar-assisted gasification has a number of
1036 advantages over traditional gasification, as was previously mentioned. Sideways solar
1037 concentrator integrated gasifiers offer a workable alternative for lowering emissions
1038 from the gasification process and helping to increase the calorific value of syngas
1039 [80]. Only a few authors [72-75] have research in this area. In the last decade, no
1040 work on solar-assisted gasification has been available.

1041 **Declaration of Conflict of Interest**

1042 The authors declare no conflicts of interest

1043 **Acknowledgements**

1044 The authors acknowledged the University of Johannesburg for its financial support.

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