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Experimental and Modeling Investigation of Partial Oxidation of Gasification Tars

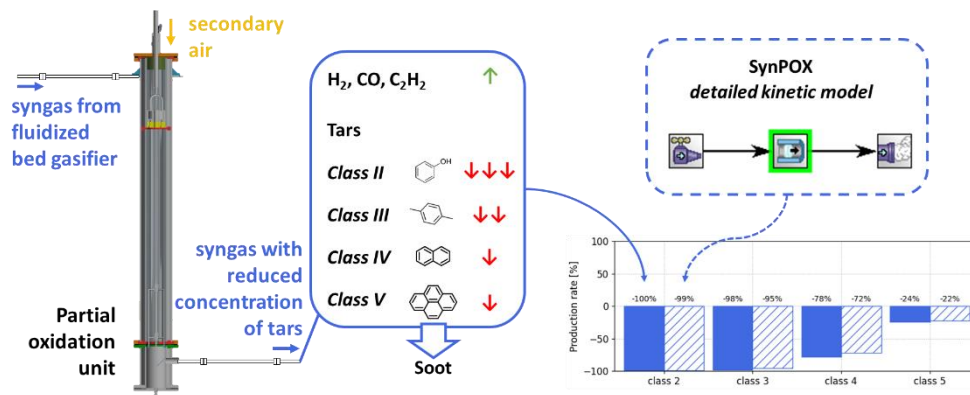
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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Fluidized bed gasifier and partial oxidation unit coupled at pilot-scale.
- Detailed kinetic model developed including heavy tars and soot formation.
- Comparison between experiments and model predictions.
- An equivalence ratio of 0.10 for secondary air recommended to reduced 90% of tars.

15 **ABSTRACT**

16 Among the methods to reduce tar emission, the partial oxidation (POX) of biomass gasification tars has
17 been studied both experimentally at a pilot-scale and numerically. The gasification producer gas was
18 obtained at a temperature of 800°C in an air-blown fluidized bed with an equivalent ratio (ER) of 0.25. For
19 the POX unit, two secondary ER values were selected: 0.05 and 0.10, with the option of pre-heating air or
20 not. Multiple advanced analytical methods were employed to provide a detailed composition of the
21 producer gas, tars and acid gases. The POX unit demonstrated the ability to reduce tar levels by 60 to 90%
22 depending on the secondary ER (from 6.5 to 2.4 and 0.72 $\text{g}_{\text{tars}}/\text{Nm}^3$, excluding benzene). The lighter tars
23 were almost completely eliminated. The permanent gases were barely modified while the light
24 hydrocarbons (except C_2H_2) and benzene were significantly reduced. Consequently, there was a slight
25 decrease in the lower heating value. These results were compared to an isothermal plug flow reactor
26 model, which utilized a detailed radical kinetic scheme constructed from various sources to account for all
27 the species measured during the experiments as well as soot mass yield. The model provided relatively
28 accurate predictions of the hydrocarbon species variations, even though it did not consider the mixing
29 between air and syngas at the inlet of the POX unit.

30

31 **KEYWORDS**

32 Biomass gasification, Tars, Partial oxidation, Detailed kinetic model.

33

34 **1. INTRODUCTION**

35 Biomass has been utilized for centuries as a heat source and material [1]. Currently, there is a growing
36 interest in using biomass as a substitute for fossil fuels in the production of energy and chemicals.

37 Pyrogasification processes offer a way to produce these bio-based products. With a limited amount of
38 oxygen, gasification produces a synthetic gas mainly composed of H₂, CO, CO₂, CH₄ and lights hydrocarbons
39 (C₂+). This technology is commercially viable for energy production (power and heat). However, a portion
40 of the solid fuel remains in the syngas as simple aromatics (BTX) and polycyclic aromatic hydrocarbons
41 (PAHs), which pose challenges to the overall process due to the risk of clogging downstream equipment.
42 Additionally, the handling of tar sludge after capture is complex and costly. Tar removal is also necessary
43 for various applications of syngas, such as gas engines, gas turbines, Fischer-Tropsch processes, and H₂
44 recovery [2,3]. Moreover, the release of these compounds into the atmosphere is environmentally
45 harmful, with sixteen of these PAHs classified as priority pollutants by the United States Environmental
46 Protection Agency [4].

47 Over the past few decades, several physical, chemical and catalytic cleanup strategies have been
48 developed [2]. These methods are classified as primary or secondary based on their application location.
49 Primary methods aim to prevent tar formation inside the reactor through reactor technology, optimization
50 of the gasification parameters, gasifying agent and fluidized bed media. The addition of alkali and alkaline
51 earth metal species during gasification can reduce tar production [5]. Secondary methods focus on
52 eliminating tars after the gasifier, using high, mild or low-temperatures techniques, either in a dry or wet
53 process [2,6]. Generally, a combination of primary and secondary methods is required to meet quality
54 standards.

55 The secondary elimination of gasification tars can occur through three cracking modes at elevated
56 temperatures. Thermal cracking involves the pyrolytic decomposition of tar molecules in the gas phase at
57 high temperature (>900°C) without catalyst and under inert atmosphere. Numerous studies have explored
58 the mechanisms and kinetics of thermal cracking of tars, focusing on pyrolysis vapors (Table 1) and model
59 molecules derived from primary and secondary tars from the pyrolysis reaction, such as benzene, catechol,

60 toluene, naphthalene. However, less information is available regarding the thermal decomposition of
61 tertiary tars typically present in producer gas, specifically refractory PAHs. Furthermore, implementing
62 thermal cracking at an industrial scale is challenging due to heat transfer difficulties and the negative
63 impact of the external energy required to achieve cracking temperatures on overall process efficiency.

64 Catalyst cracking enables tar elimination at lower temperatures by using a catalytic material to decrease
65 the required activation energy. This method is the most effective for removing tars from producer
66 gas/syngas. Heterogeneous catalysts typically employed for tar elimination can be natural minerals which
67 are generally cheaper than synthetic catalysts. However, rapid catalyst deactivation necessitates specific
68 reactor configurations, such as circulating fluidized bed systems or switch reactors, increasing operational
69 complexity. Additionally, catalyst attrition and irreversible deactivation require substantial catalyst
70 replacement, resulting in higher operational expenditure [6–9]. However, catalyst cracking for tar
71 abatement is beyond the scope of this study.

72 Partial oxidation (POX) increases the temperature of the syngas by oxidizing a portion of it with oxygen.
73 This process accelerates tar cracking and polymerization pathways different from those observed in
74 pyrolytic thermal decomposition. According to Hoeven et al. [10], oxygen serves as an excellent initiator
75 of free radicals, such as hydrogen (H), oxygen (O), hydroxyl (OH) and hydroperoxy (HO₂), and plays a crucial
76 role in chain initiation and subsequent reactions. Furthermore, oxygen facilitates the exothermic oxidation
77 of hydrocarbons, generating the heat required for propagation reactions. However, an excess amount of
78 oxygen can lead to the production of too many PAHs and even soot [11,12].

79 Table 1 provides an overview of studies that have examined the potential of thermal cracking and partial
80 oxidation of pyrolysis vapors, model molecules and gasification syngas in reducing tar content. The
81 formation of heavier PAHs from simple aromatics or naphthalene at high temperature has been identified
82 [13,14]. Additionally, soot is produced through a polymerization/sooting mechanism from inlet tars at high

83 temperature [13,15]. H₂ has been found to act as an inhibitor of PAHs and soot formation [13,16] while
 84 steam has a minimal influence on tar reduction [15,16]. High temperature around 1200°C must be reached
 85 to achieve 90% tar reduction through thermal cracking [14]. In the partial oxidation, the addition of oxygen
 86 can hinder the sooting process and contribute to better tar reduction compared to thermal cracking by
 87 promoting the formation of free radicals, thus accelerating tar destruction [12,13,17,18]. The primary tars
 88 are transformed into lower molecular weight tars [18].

89 According to Wu et al., the maximum reduction of tar from pyrolysis vapors at 900°C occurs at an
 90 equivalence ratio (ER) of 0.34. However, a higher ER can result in the combustion of non-condensable
 91 gases like H₂, CO and CH₄ [12,17]. In the case of a biogasification syngas a tar reduction of 90% can be
 92 achieved with an air/fuel ratio of 0.2 [13]. It is worth noting that there are very few studies available that
 93 have specifically investigated the partial oxidation of gasifier producer gas, and those that exist have
 94 mostly used simulated syngas (refer to Table 1) [13,15].

95 **Table 1: Thermal cracking (TC) and partial oxidation (POX) studies.**

Type ^a	Year/author	Experiments <i>Feedstock/model molecules</i>	Model	Ref.
Producer gas/syngas				
TC	2004 Houben	Wood (willow) syngas in a TR ^b (L=700 mm, D=75 mm, 0.015-0.6 Nm ³ /h)	No	[11]
	2009 Valin	Model syngas (CH ₄ , H ₂ , CO, CO ₂ , H ₂ O, N ₂) in a cylindrical reactor (1-2 Nm ³ /h)	PFR, two detailed kinetic model compared (127 species, 1207 reactions vs 159 species, 773 reactions)	[19]
POX	2005 Houben	Naphthalene (2.6 mg/Nm ³) in a simulated syngas (H ₂ , CH ₄ , N ₂) in a combustion burner	No	[13]
	2013 Svensson	Model validation on experimental TC data from [19]	Dynamic model (FDM): 53 species 325 reactions (GRI-Mech 3.0). Static model (series of CSTR): 157 species 872 reactions.	[15]
Model molecules				
TC	1992 Blekkan	CH ₄ in a TR ^b (L=1 m, D=9 mm)	No	[20]

	1996 Jess	Naphthalene, toluene and benzene in a TR ^b (L=50 cm, D=20 mm)	10 reactions	[16]
	1999 Sarobe	Acenaphtho[1,2-a]acenaphthylene, Fluoranthene, Benzo[k]- and Benzo[j]fluoranthene in a QT ^b (L=40 cm, D=25 mm)	No	[21]
	2016 Gai	Naphthalene, anthracene in a FB ^b (D=20 mm, H=42 mm)	No	[22]
POX	2007 DeCoster	Anthracene in a two-stage laminar-flow drop-tube furnace	No	[23]
	2008 Thomas	Catechol in a laminar flow QT ^b (D=2 mm)	No	[24]
	2017 Zhang	2-methoxyphenol, anisole, furfural, toluene in a flow QT ^b D=8 mm L=350 mm	Detailed kinetics (201 species, 1100 reactions)	[17]
	2019 Peng	Phenanthrene in a QT ^b D=30 mm L=500 mm	No	[25]
Pyrolysis vapors (PV)				
	2000 Brandt	Wood chips in a two-stage gasifier (100-hWth)	No	[26]
	2001 McGrath	Cellulose and pectin pyrolysis in a two-zone QT ^b (200 mg, 300-600°C)	No	[27]
	2011 Wu	Rice straw in a SP ^b (4 kg/h, 500°C) + electrically heated POX reactor	No	[12]
	2013 Wongchang	Wood in a free fall pyrolyzer (0.536 g/min, 600°C)	No	[14]
	2021 Tanoh	Green waste in a RK ^b (6 kg/h, 800°C) + electrically heated non-catalytic TR ^b	PFR ^b & detailed kinetics	[28]
POX	2011 Su	Rice straw in a SP ^b (1-10 kg/h, 500°C) + electrically heated POX reactor	2D-CFD isothermal 900°C (CO ₂ , CH ₄ , H ₂ , N ₂ , H ₂ O, phenol toluene). Tars = benzene, toluene, phenol, naphthalene (16 reactions, 11 species)	[29]
	2011 Wu	See above.		[12]
	2013 Ahrenfeldt	Pine wood in a SP ^b (1.16 kg/h, 600°C) + electrically heated POX reactor	No	[18]
	2014 Weston	Wood pellets in a pyrolyzer (500-800°C, 100 g per batch) + Coanda burner	No	[30]
	2015 Mao	Biomass tar in a micro FB ^b reactor for liquids (H=88 mm).	No	[31]
	2015 Thimthong	Cedar sawdust fast pyrolysis in a tubular vertical TSR ^b (0.09-0.20 g/min, 700-800°C)	PFR ^b & detailed kinetics (8159 reactions, 548 species)	[32]
	2021 Tanoh	See above.		[33]

^aThermal cracking (TC) or partial oxidation (POX)

^bScrew pyrolyzer (SP), plug flow reactor (PFR), two-stage reactor (TSR), fluidized bed (FB) rotary kiln (RK), quartz tube (QT), tubular reactor (TR), diameter (D), length (L).

96 Significant efforts have been made to develop kinetic mechanisms that provide a deeper understanding
97 of the phenomena involved (as shown in Table 1). These mechanisms are essential for the proper design
98 and scaling up of a POX unit. However, extrapolating the observed mechanisms observed from model
99 molecules and controlled gas environments to a real gasification environment is not a straightforward task
100 due to the complex chemistry of tertiary tars. Given the number of species and the mechanism pathways
101 in such a system, a limited set of reactions is insufficient to accurately replicate the detailed composition
102 at the reactor outlet. Radical kinetic mechanisms have been formulated for thermal cracking and oxidation
103 of biomass products. For instance, Dhahak et al. (2019) developed a comprehensive model of biomass
104 pyrolysis and oxidation that includes PAHs up to chrysene ($C_{18}H_{12}$) as well as a mechanism for NO_x
105 formation, encompassing 710 species and 5035 reactions [34]. Norinaga et al. (2009, 2013) developed
106 similar models for thermal cracking under pyrolytic conditions [35,36]. The main advantage of these
107 detailed kinetic models is that they avoid lumping processes. Thus, the detailed composition of the gas is
108 predicted. If computational time is reasonable, such models can enhance the accuracy of process model
109 predictions for tar formation by utilizing complete kinetics and not overly simplified kinetics [37].

110 In this study, the focus was on investigating the partial oxidation of a real producer gas stream through
111 both experimental and numerical approach. The experimental setup involved conducting partial oxidation
112 experiments in a dedicated partial oxidation unit (POX) that was electrically heated and well-insulated.
113 These experiments were performed downstream of a 5 kg/h air-blown bubbling bed gasification reactor.
114 By utilizing a real syngas instead of a simulated one, the study aimed to achieve greater accuracy since
115 generating the heaviest PAHs in a simulated syngas can be challenging. The results obtained from the POX
116 experiments were compared to reference tests conducted without the POX unit to evaluate the impact of
117 POX reactions on gasification indicators and pollutant contents. To complement the experimental findings,
118 numerical modeling of the POX unit was carried out using ANSYS Chemkin Pro. The composition of the
119 producer gas, which was experimentally measured at the gasification reactor's exit, served as input for the

120 numerical simulations. The overall objective of this study was to demonstrate the reliability and
121 effectiveness of advanced kinetic modeling techniques when dealing with the complex composition of a
122 real producer gas.

123 The novelty of this research lies in two key aspects:

124 1) A comprehensive analysis of the detailed composition of gasification tars before and after partial
125 oxidation in a pilot plant that is coupled with a fluidized bed gasifier. This detailed characterization
126 offers valuable insights into the behavior and transformation of tars during the partial oxidation
127 process.

128 2) A detailed kinetic model was developed, specifically designed to account for the thermal cracking
129 and oxidation of tars up to C₂₄ including soot formation. The model's accuracy and predictive
130 capabilities were validated using a real biomass gasification producer gas.

131 Overall, this study contributes to advancing the understanding of partial oxidation processes and highlights
132 the importance of employing advanced kinetic modeling approaches when dealing with the complex
133 composition of real producer gases.

134 **2. MATERIAL AND METHODS**

135 **2.1. Feedstock, experimental rig and analytical methods**

136 The feedstock material utilized in this study consisted of pellets made from medium density fiber board
137 (MDF). The chemical composition and other properties of the MDF material were thoroughly described in
138 a separate publication [38]. Notably, the nitrogen content in the MDF material was relatively high at 3.5
139 wt.% (on a dry basis), due to the use of urea-formaldehyde resins for panel fabrication. The water content
140 was approximately 5 wt.%.

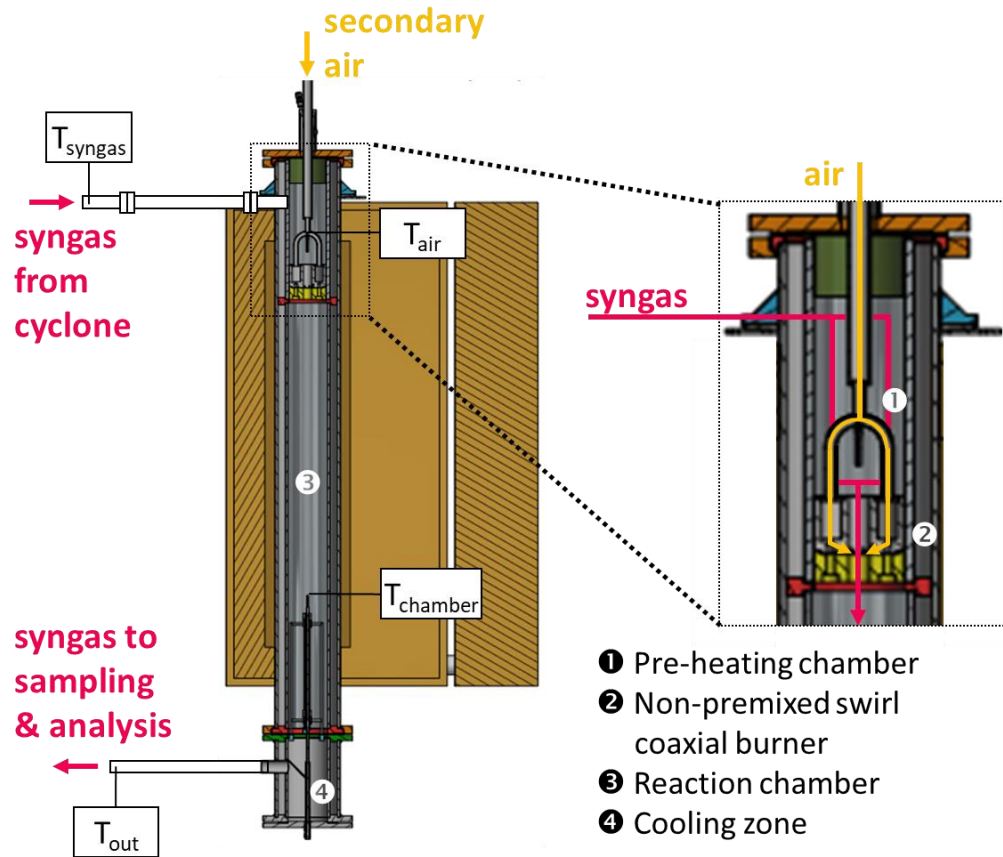
141 The experimental setup for gasification involved the following components: (i) a double-screw feeding
142 system, (ii) an externally heated bubbling bed gasification reactor, where air was used as the gasifying
143 agent, (iii) a cyclone separator and, (iv) a cooling system incorporating a Venturi scrubber.

144 To analyze the gas composition and tar content, several analytical techniques were employed. The
145 concentration of permanent gases, including N₂, CO, CO₂, H₂, CH₄, C₂H₂, C₂H₆, C₃H₄ and C₃H₆, was measured
146 every 3 minutes using a micro-gas chromatography (μ -GC) with N₂ as the tracer gas. Tar molecules were
147 collected in a series of wet impingers filled with 2-propanol and quantified by GC-MS-FID and HPLC-UV.
148 Additionally, a semi-quantitative analysis of light and heavy tar molecules was conducted using
149 Synchronous Fluorescence Spectroscopy (SFS). SFS is a rapid technique that utilizes the correlation
150 between the emission spectral band and the number of aromatic rings, particularly for linear PAHs [39]. A
151 comprehensive description of the experimental setup and all analytical methods can be found in the
152 referenced publication [38].

153 **2.1.1. Partial oxidation unit**

154 A scheme of the oxidation unit (POX) developed at LRGP is depicted in Figure 1. The POX unit was coupled
155 downstream of the cyclone separator and consisted of several components: a pre-heating chamber, a non-
156 premixed swirl coaxial burner, a reaction chamber and a cooling zone.

157 The producer gas stream, coming from the cyclone, entered the preheating chamber of the POX unit at
158 approximately atmospheric pressure. From there, the gas stream passed through the central tube of the
159 burner and was mixed with an airflow injected tangentially by the swirl coaxial burner. The gas-centered
160 swirl coaxial burner comprised a pre-injection chamber where the airflow was equally distributed to five
161 injection holes, each with a diameter of 3.5 mm. These injection holes were inclined at a 45° angle with
162 respect to the two axes, creating a turbulent flow to ensure efficient mixing of the gases. The secondary
163 air flow was injected at constant flow rate, controlled by a mass flow controller (Brooks 5851s). In some
164 tests, the air was preheated before entering the POX unit. During preliminary design simulations, it was
165 observed that local high-temperature spots (~2000 K) developed in the zone adjacent to the injection. To
166 prevent damage to the reactor walls, which were made of SIRIUS steel, the reaction chamber was enclosed
167 by an inner tube of SiC with a thickness of 1 cm. The space between the inner SiC tube and the outer SIRIUS
168 steel was left empty to minimize heat transfer by conduction. The reaction chamber's final volume, located
169 inside the SiC tube, was approximately 11.5 L (inner diameter 10.2 cm, length 140 cm). To maintain a
170 uniform temperature, the POX unit was uniformly heated by an external oven, which helped compensate
171 for heat losses resulting from the small size of the pilot plant. Finally, a cooling chamber was positioned at
172 the bottom of the POX unit.



173

174

Figure 1: Scheme of the POX unit.

175 Temperature measurements were taken at crucial points within the POX unit (see Figure 1) and
 176 corresponds to: the inlet of the producer gas to the swirl burner (T_{syngas}), the inlet of airflow to the pre-
 177 distribution chamber (T_{air}), the temperature of the reaction chamber (T_{chamber}) and the temperature at the
 178 exit of the cooling zone (T_{out}). The thermocouple of the reaction chamber was centered by a radial support
 179 and placed at the end of the reaction chamber. The temperature of this thermocouple was used to monitor
 180 the reaction chamber.

181 2.1.2. Experimental conditions

182 In order to evaluate the impact of POX reactions on gasification, the results obtained for the POX tests
 183 were compared with three repeated reference tests (REF) that were conducted without the POX unit and

184 described elsewhere [38]. The main operating parameters of the gasification reactor, including the reactor
 185 temperature, feedstock flow rate, primary air flowrate and test duration, were maintained constant for all
 186 tests. These parameters were set to 800°C, 4.4 kg/h, 4.5 Nm³/h and 2 h, respectively. The air-to-fuel
 187 equivalence ratio (ER) inside the reactor was also kept constant at 0.25 for all tests. Previous publications
 188 have explored the variations of these parameters and their influence on syngas production [38,40]. A total
 189 of 4 POX tests were conducted, specifically varying the temperature and secondary air flow rate. Table 2
 190 provide a summary of the targeted values for the different parameters in these four POX tests.

191 **Table 2: Operating parameters of the partial oxidation unit.**

Test (ER-T _{chamber})	REF	0.05-1025	0.1-1034	0.1-1059	0.1-1100
Secondary air flow rate (NL/h)	-	1000	2000	2000	2000
Temperature set-point of secondary air preheating, °C	-	20	20	500	500
Temperature set-point of the POX unit external oven, °C	-	1100	1100	1150	1200
ER secondary	-	0.05	0.1	0.1	0.1
ER total	0.25	0.30	0.35	0.35	0.35

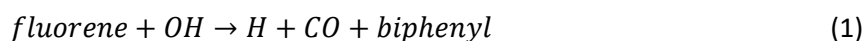
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193 2.2. Modeling and numerical methods

194 2.2.1. Kinetic mechanism

195 A detailed radical kinetic mechanism was developed to describe the oxidation and formation of biomass
 196 tars. The mechanism was constructed by merging two main mechanisms obtained from various literature
 197 sources [34–36,41]. The first component of the mechanism, BioPOX-2 was originally developed by Darido
 198 et al. [42], which was an extension of BioPOX-1 from Dhahak et al. [34] (634 species and 4759 reactions).
 199 BioPOX-2 includes the kinetics of biomass pyrolysis and oxidation, as well as the formation of PAHs up to
 200 chrysene (C₁₈H₁₂). It also incorporates a mechanism for NO_x formation.

201 The second component of the mechanism was derived from the work of Norinaga et al. (2009) [35], which
 202 focused on pyrolysis conditions. This mechanism was used to include the kinetics of heavy PAHs ranging
 203 from C₁₀ to C₂₄ which were measured in the experiments but not accounted for in the BioPOX-2
 204 mechanism. Furthermore, additional oxidation reactions for these heavy PAHs were incorporated from
 205 the work of Norinaga et al. (2013) [36]. To account for the oxidation of fluorene, which is an important
 206 reaction product, an extra lumped reaction (1) was included in the mechanism. The formulation of this
 207 reaction followed the methodology employed by the CRECK modeling group of Politecnico di Milano [43],
 208 and the kinetic parameters recommended by this group [44].



209 Phenanthrene and anthracene, which were originally lumped together in the BioPOX-2 mechanism, were
 210 treated as separate species. These two species were measured separately in experiments and follow
 211 different reactions paths in Norinaga's mechanisms.

212 Regarding the formation of soot, it is generally accepted that soot is a product of partial oxidation
 213 reactions. In line with previous findings by Saggese et al. [45], it was assumed that soot originates from C₂₀
 214 precursors. Therefore, reactions 2 and 3 were included in the mechanism to provide an estimate of soot
 215 formation and growth from acetylene [41]. The kinetic parameters for these reactions can be found in
 216 Table 3.



217 **Table 3: Kinetic parameters.**

Reaction	A	Ea (cal/mol)	Ref
1	$4.0 \cdot 10^{13} \text{ s}^{-1}$	$7.0 \cdot 10^3$	[44]
2	$5.0 \cdot 10^6 \text{ s}^{-1}$	$3.99 \cdot 10^4$	[41]
3	$2.5 \cdot 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$9.99 \cdot 10^3$	[41]

218

219 The SYNPOX model for SYNgas Partial OXidation - contained 742 species and 5093 reactions. This kinetic
220 model can be found in the Supplementary material.

221 To validate the SYNPOX model, experimental data from Tanoh's study [36], were utilized. This comparison
222 includes a wide range of species including light gases such as H₂, CH₄, CO, CO₂, acetylene, ethylene, and
223 water, as well as eight aromatics and PAHs from benzene up to pyrene. It also includes comparisons with
224 tar, gas and soot mass fractions. The overall agreement is quite satisfactory for all species and for thermal
225 cracking and steam cracking conditions (see section 8.2 in Supplementary Material).

226

227 **2.2.2. Plug-flow reactor model**

228 The POX pilot was simulated using an ideal plug-flow reactor model with dimensions matching the reaction
229 chamber of the POX unit (10.2 cm in diameter and 1.1 m in length). The simulation was performed using
230 ANSYS Chemkin Pro 17.0 and a Python software interface was utilized for easier management of the
231 results. The inlet composition of the syngas was obtained from the REF experiments (gasification test
232 without POX unit). The syngas and air were assumed to be premixed and injected at the inlet of the reactor.
233 The inlet temperature was calculated using the RK-ASPEN thermodynamic model in AspenPlus 8.8. The
234 pressure was assumed to be constant and close to atmospheric, while the air composition was considered
235 to be 21%v O₂ and 79%v N₂. The 1D-model assumed that the gas temperature was radially uniform and
236 equal to the temperature measured by the thermocouple (T_{chamber} temperature).

237 In an industrial-scale POX unit, the thermal conditions would typically approach adiabatic conditions.
238 However, due to the scale of the pilot plant, it was necessary to heat the reactor to compensate for heat
239 losses at the reactor's surface. The heat transfer mechanism in this setup is complex, involving convection

240 and conduction heat transfer through the layers of the reactor (including the inox outer layer and the
 241 annular gap between the outer layer and the SiC inner layer). Radiative heat fluxes between the oven and
 242 the reactor's outer layer, as well as between the metal layers and the inner surface, also need to be
 243 determined. Additionally, the presence of soot in the gas phase further complicates the heat transfer
 244 analysis. The heat flux profile from the oven is likely not uniform along the POX chamber in the
 245 experimental setup. Considering these complexities and uncertainties, it is more appropriate at this stage
 246 to use an isothermal condition based on a real measurement, rather than making assumptions about the
 247 heat flux using a specific boundary condition such as $q = U \cdot (T_{gas} - T_{surface})$ or $q = q_0$.

248 **Table 4: Boundary conditions of the CHEMKIN PRO plug flow model**

Reactor model	Test	T inlet (°C)	T chamber measured (°C)	Inlet volumetric flowrate (standard m ³ /min at 298.15K)
Ideal plug flow	0.05-1025	599	1025	0.188
	0.10-1034	555	1034	0.206
	0.10-1059	607	1059	0.206
	0.10-1100	674	1100	0.206

249

250 3. RESULTS AND DISCUSSION

251 3.1. Partial oxidation cracking tests

252 Table 5 details the main temperatures, gas composition and product yields for both reference (REF) and
253 POX tests. The tar yields as shown in Figure 2, were classified according to the ECN tar classification system
254 [46]: class 2 for heterocyclic components, class 3 for light hydrocarbons without condensation and water
255 solubility issues, class 4 for 2-3 rings PAHs and class 5 for heavy polyaromatic hydrocarbons (4-5 rings
256 PAH's). The yields of all gas and tar molecules quantified in this study were detailed in Table S1
257 (supplementary materials).

258 From Table 5, it can be observed that the temperature achieved inside the POX unit were close to the
259 targeted temperatures. In all POX tests, the temperature inside the reaction chamber exhibited a slight
260 increase during the first 30 minutes of the test and then remained steady. The lower temperatures
261 measured at the inlet of the secondary air stream for the tests 0.05-1025 and 0.1-1034 were a result of
262 the absence of air preheating in these cases.

263 Comparing to the average gas concentrations between the reference test (REF) and the four POX tests, a
264 clear decrease in CH₄, C₂-C₃ hydrocarbons and benzene can be observed, while there is a marked increase
265 in CO and acetylene (C₂H₂). This decrease in light hydrocarbons and benzene leads to a decrease in the
266 volumetric LHV of the gas. The introduction of additional air flow in the tests 0.05-1025 and 0.1-1034
267 resulted in an increase in H₂ and CO concentrations, and a decrease in CO₂ and C₂H₂. The increase in the
268 temperature of the reaction chamber in the tests 0.1-1034, 0.1-1059 and 0.1-1100 did not show any
269 notable global trend, within experimental uncertainty. However, the methane concentration decreases
270 with the temperature increase in the tests with an ER of 0.10, which is consistent with thermal cracking of
271 methane above 1000°C, as observed by Valin et al. [47].

272 The residual concentration of O₂ in the syngas analyzed could result from imperfect syngas and air mixing
 273 in the POX or from air linkage during sampling and analysis.

274 The test 0.1-1034 exhibits noticeable higher cold gas efficiency, carbon and hydrogen conversions.
 275 However, this may be attributed to an overestimate of the gas yield in this particular test.

276 **Table 5: Main operation conditions, gasification indicators and products yield in reference and partial**
 277 **oxidation experiments.**

Case	REF	0.05-1025	0.1-1034	0.1-1059	0.1-1100
Gasifier					
Test duration, h		1.43	1.73	1.61	1.38
Consumed feed, kg (as received)		6.6	7.96	8.04	6.3
Fuel feed rate, kg/h	4.5 ± 0.1	4.6	4.6	4.5	4.6
Bed temperature, °C	800 ± 2	794	789	801	796
Freeboard temperature, °C	757 ± 1	761	762	765	762
ER (reactor)	0.25 ± 0.01	0.25	0.25	0.25	0.25
Partial oxidation unit					
Secondary air flow rate, NL/h	-	1020	1980	1980	1980
Air preheating set-point, °C	-	-	-	500	500
Airflow inlet T _{air} , °C	-	406 ^b	304 ^b	466	565
Producer gas inlet T _{syngas} , °C	-	614	587	629	691
POX external oven set-point, °C	-	1100	1100	1150	1200
Reaction chamber T _{chamber} , °C	-	1025	1034	1059	1100
Cooling chamber exit T _{out} , °C	-	647	601	657	668
Gas residence time, s	-	1.0	0.9	0.9	0.9
ER (total)	0.25 ± 0.01	0.30	0.36	0.37	0.36
Syngas indicators					
Gas Yield η_{syngas} , Nm ³ /kg feed (daf)	1.78 ± 0.05	2.03	2.33	2.27	2.24
LHV _{syngas} , MJ/Nm ³	4.54 ± 0.05	3.82	4.16	3.63	3.43
Cold gas efficiency %CGE ^c	44.3 ± 0.02	42.5	53.4	45.2	42.8
Carbon conversion %C ^d	76.8 ± 0.02	64.2	76.1	72.0	67.0
Hydrogen conversion %H ^d	48.0 ± 0.02	42.9	52.6	44.4	42.6
Gas composition, %_{mol} (N₂ free, dry)					
H ₂	17.4 ± 0.6	16.4	18.3	18.0	19.9
CO	29.3 ± 0.2	31.9	36.7	35.5	34.5
CO ₂	39.8 ± 0.4	38.1	32.5	36.7	35.8
CH ₄	9.1 ± 0.1	8.7	8.5	7.0	6.1
C ₂ H ₂	0.33 ± 0.02	1.54	1.33	1.35	1.26
C ₂ H ₄	3.0 ± 0.1	1.0	0.4	0.3	0.2
C ₂ H ₆	0.36 ± 0.01	0.01	0	0	0
C ₃ H ₄	0.04 ± 0.004	0.02	0.02	0.01	0.01
C ₃ H ₆	0.29 ± 0.04	0.01	0.01	0	0

O ₂	0.4 ± 0.2	2.3	2.3	1.1	2.4
Tar yield, g/kg_{feed} (daf)					
Total ^a	11.6 ± 0.2	4.7	1.7	2.0	1.4
Gas dew point, °C	171.7	188.1	184.0	183.7	187.5
Water and acid gas yields, g/kg_{feed} (daf)					
NH ₃	18.5 ± 4.9	19.2	25.9	27.8	18.9
HCN	2.5 ± 0.3	3.2	1.4	6.2	6.0
H ₂ O	342 ± 13	386	361	388	389

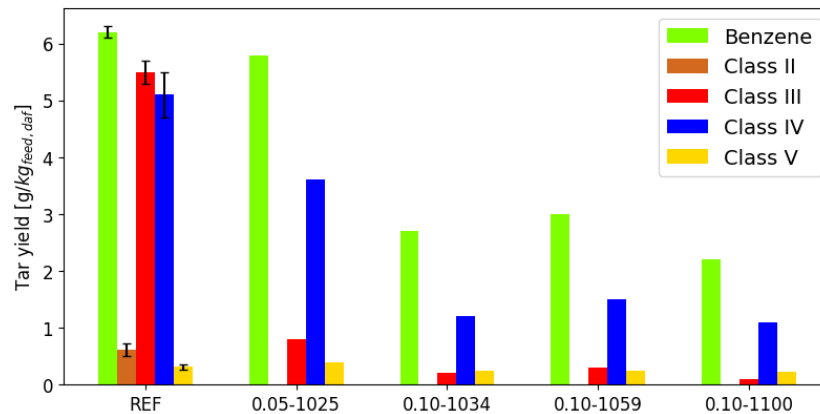
^aTotal tar yield was calculated excluding benzene.

^bNo preheating for secondary air.

$${}^c\%CGE = \frac{LHV_{syn\ gas}}{LHV_{feed}} \cdot \eta_{syn\ gas}$$

^d $\%C = \frac{\dot{m}_{C,gas}}{\dot{m}_{C,biomass}}$; $\%H = \frac{\dot{m}_{H,gas}}{\dot{m}_{H,biomass}}$ where $\dot{m}_{C,gas}$ and $\dot{m}_{H,gas}$ are the carbon and hydrogen mass flowrates in the gas generated (permanent gases: H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₄, C₃H₆), $\dot{m}_{C,biomass}$ and $\dot{m}_{H,biomass}$ the carbon and hydrogen mass flowrates from the biomass.

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279

280

Figure 2: Tar composition in the different tests (tar groups according the ECN tar classification).

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Compared to the REF test, the POX tests conducted with a secondary ER of 0.05 and 0.1 resulted in a

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significant reduction in overall tar yield, by 60% and 90%, respectively. In terms of tar concentration, the

283

POX unit led to a decrease from 6.5 g/Nm³ (dry gas, C₆H₆-free) in the REF tests to 2.3 g/Nm³ (dry gas, C₆H₆-

284

free) in the test 0.05-1025. Furthermore, increasing the secondary air flow in the test 0.1-1034 further

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reduced the tar concentration to 0.72 g/Nm³ (dry gas, C₆H₆-free). On the other hand, the increase in the

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temperature of the reaction chamber did not show any significant variation in the overall tar yield within

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experimental uncertainty. This finding confirms that the main factor in tar reduction is the addition of

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external oxygen. Inside the POX unit, the chemical composition of tars underwent substantially

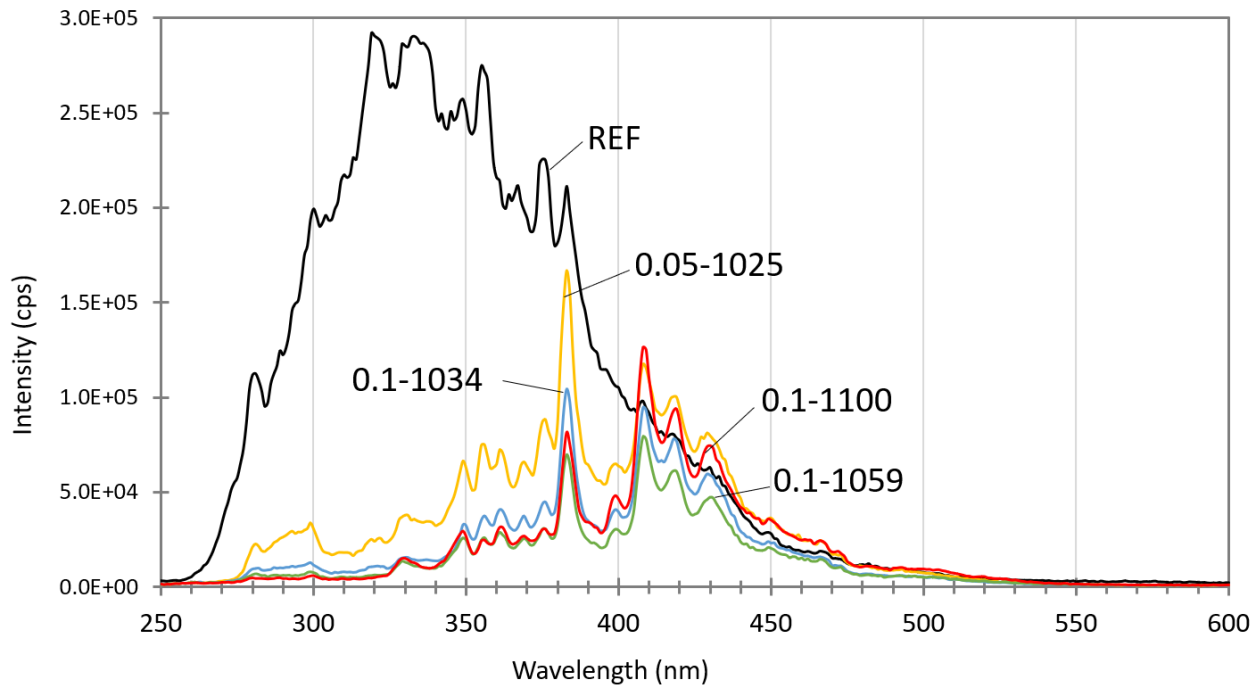
289 modifications. For example, in the test 0.05-1025 compared to the REF values, there was a drastic
290 reduction in the yields of tar groups II, III and IV by 100%, 86% and 30%, respectively. On the other hand,
291 the yield of group V increased by 26%. A closer examination of individual tar yields, detailed in Table S1
292 (supplementary materials), revealed a significant increase in certain molecules of group IV, such as
293 phenanthrene and fluoranthene, as well as other heavier molecules from group V present in trace
294 concentrations, such as benzo[b]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene,
295 benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. Conversely, there was a reduction in the yields of some
296 molecules of group IV, including naphthalene, acenaphthylene, fluorene and anthracene, which explains
297 the 30% overall drop observed for the group. This observation aligns with previous studies as the
298 production of heavier tars from naphthalene observed by Houben et al. [13]. Moreover, increasing the
299 secondary air flow rate in the test 0.1-1034 led to a more severe reduction in the yields of groups IV and
300 V. In this case, all molecules of group IV showed a negative yield. These results suggest a dependence on
301 the amount of oxygen available through secondary air injection, indicating the influence of secondary air
302 on the unit's efficiency, as observed in previous studies [12,18,26,29]. The tar reduction also resulted in
303 the consumption of light hydrocarbons and benzene, which can be beneficial for further upgrading of the
304 syngas to produce H₂ or CH₄.

305 The substantial modifications in the chemical composition of tars caused by the POX reactions were further
306 supported by synchronous fluorescence spectra (SFS). Figure 3 displays the SFS of tar samples
307 corresponding to reference and POX tests. These results clearly indicate a decrease in the tar content in
308 the producer gas and a shift to longer wavelengths, indicating a predominance of heavy tars in the overall
309 composition.

310 Finally, the yield of water increased after the POX tests due to oxidation reactions. The water composition
311 was calculated by difference based on the overall atomic mass balance. The ammonia composition remains

312 approximately constant within the uncertainty range, around $\pm 4.9 \text{ g/kg}_{\text{feed daf}}$, as observed through
313 repeated REF tests. No clear trend was observed when varying temperature or ER. A slight increase in HCN
314 was observed, reaching approximately twice the inlet feed rate at the highest temperatures. The global
315 nitrogen content in the syngas slightly increased with temperature.

316



317

318 **Figure 3: Synchronous Fluorescence spectra (offset = 20 nm).**

319

320 3.2. Modeling results

321 In the subsection, two specific cases are presented for conciseness. The two tests with the most different
322 conditions are chosen. Tests 0.05-1025 and 0.10-1100 present two different ER, with and without air
323 preheating. The detailed analysis of the other two cases can be found in Supplementary Material 3.

324 The detailed composition of the syngas at the inlet and outlet is shown in Figure 4 for ER = 0.5 and Figure
325 5 ER = 0.10. These figures also include a comparison with the model results. The results demonstrate a
326 good agreement between the experimental data and the plug flow model for the permanent gases (H₂,
327 CO, CO₂, CH₄). The fate of lights hydrocarbons was accurately reproduced, showing an increase in
328 acetylene and a decrease in others C₂-C₃ hydrocarbons.

329 The model successfully reproduced the trends observed in the tar composition regrouped by ECN classes.
330 Tar classes II to IV decreased, while class V increased at lower ER (0.05-1025) and showed slight reductions
331 or remained stable at higher ER (0.10-1100). Overall, the model's predictions aligned with experimental
332 observations, particularly at the higher ER (0.10). However, there were discrepancies for certain individual
333 tar species such as phenylethyne, acenaphthene and heavy PAHs (C₂₀₊), where the model did not
334 accurately predict their behavior. This discrepancy could be attributed to the chosen mechanism for soot
335 formation, which considers C₂₀₊ as precursors. Additionally, the prediction of tar class V was reasonably
336 satisfactory in case of ER = 0.10 (experimental reduction of 24% compared to a model reduction of 22%).
337 This can be attributed to the predominance of pyrene in class V tars, while other heavy PAH components
338 were present in trace amounts in the experiments (Figures S3 and S4 in supplementary material). The
339 model is able to give global trends in case 0.05-1025 but is not necessarily optimized for all individual
340 species. It should be noted that the isothermal profile assumed in the plug flow model may differ
341 significantly from the actual thermal profile in the experimental setup. For the acid gases the prediction
342 for NH₃ fell within the uncertainty range, but HCN consumption contradicted the experimental increase
343 observed in case of 0.10-1100.

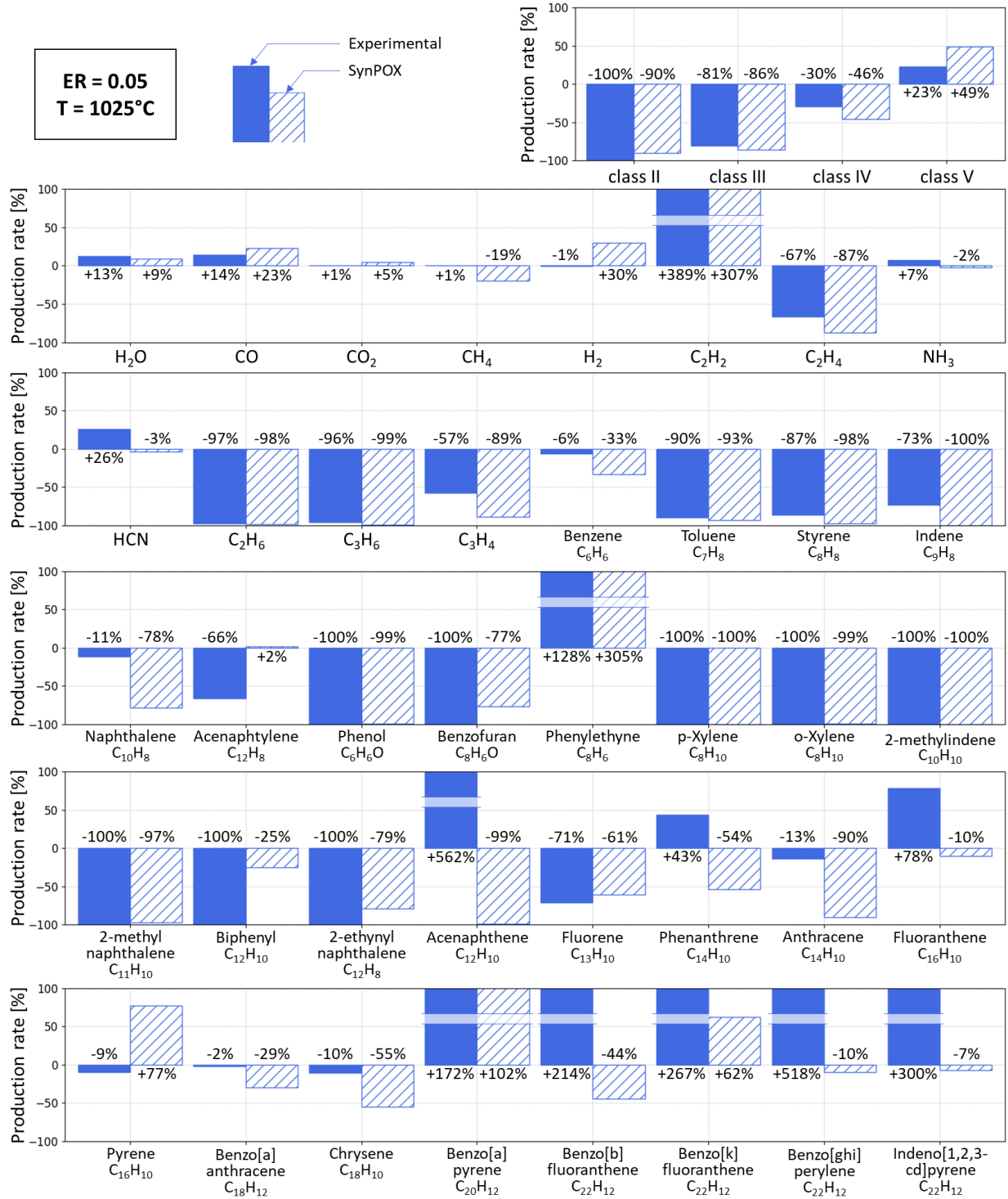
344 Regarding soot formation, the model predicts an increase with temperature (Table 6). Although soot
345 collection was not performed in the present work, the excellent agreement between the computed data
346 using the SYNPOX model and literature experimental data obtained by [33] under similar thermal cracking

347 and oxidative conditions around 1200°C (slightly higher than the present study) suggests that the predicted
 348 trend for soot formation under the present study conditions is likely valid. The validation comparison sets
 349 of the SYNPOX model are presented in Supplementary Material 2. This tend to confirm that heavy PAHs
 350 C₂₀₊ are soot precursors [45].

351 **Table 6: Soot production and tar reduction.**

Case (ER-T _{chamber})	0.05-1025		0.10-1034		0.10-1059		0.10-1100	
	Exp.	Model	Exp.	Model	Exp.	Model	Exp.	Model
Soot production (mg/kg _{biomass dry})		49.1		45.0		62.2		102.3
Tars class II	-100%	-90%	-100%	-97%	-100%	-98%	-100%	-99%
Tars class III	-81%	-86%	-96%	-95%	-95%	-95%	-98%	-95%
Tars class IV	-30%	-46%	-76%	-69%	-71%	-70%	-78%	-72%
Tars class V	+23%	+49%	-27%	-1%	-26%	-7%	-24%	-22%

352

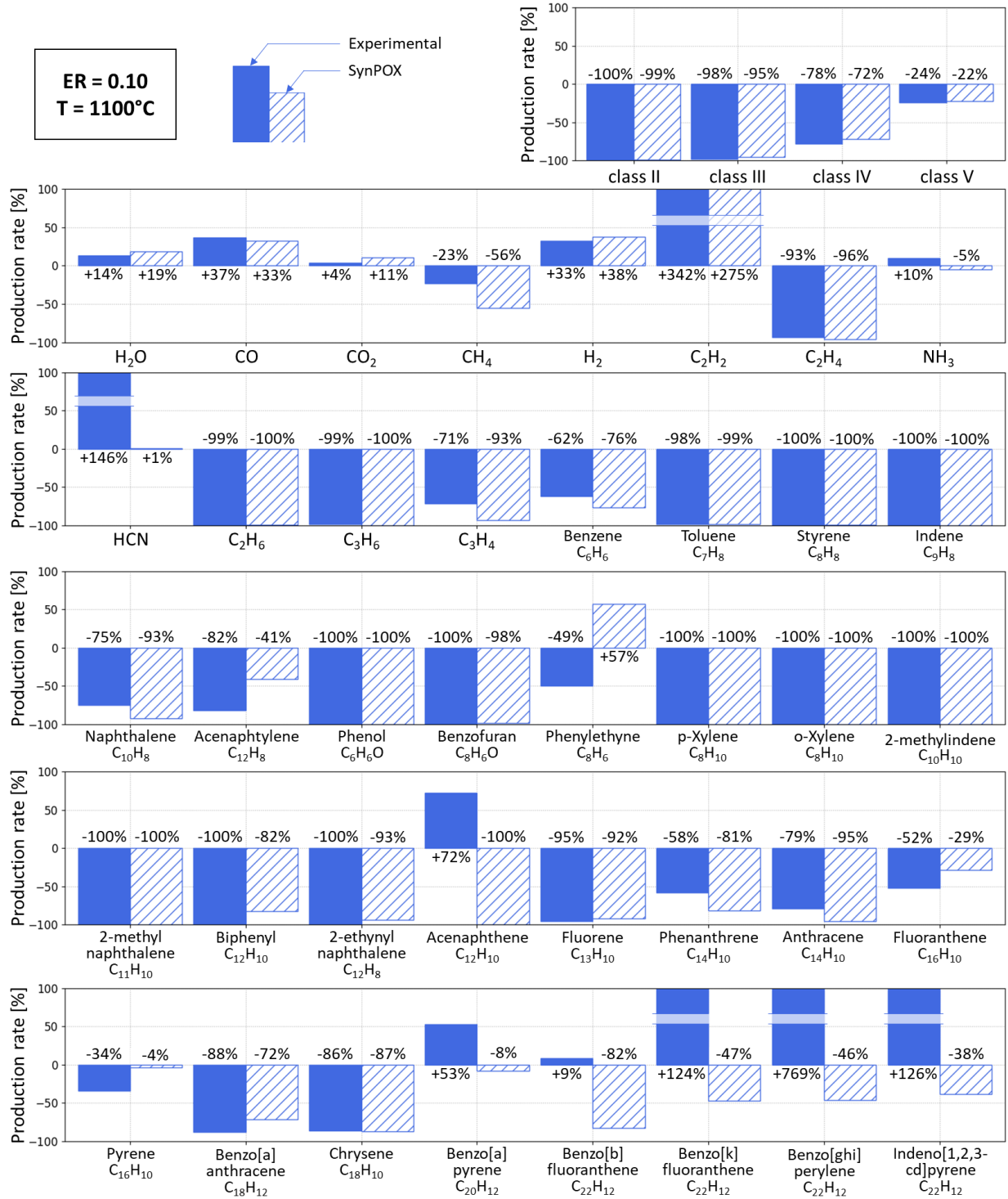


353

354 **Figure 4: Experimental and modelled syngas production rate after POX unit for case 0.05-1025.**

355

Simulated composition from plug flow.



356

357 **Figure 5: Experimental and modelled syngas production rate after POX unit for case 0.10-1100.**

358

Simulated composition from plug flow.

359 Based on the results obtained, the following recommendations can be made:

- 360 - To significantly reduce the tar content, an equivalence ratio around 0.10 must be reached.
- 361 - An attention should be made on the production of heavy PAHs and the formation of soot.
- 362 - The partial oxidation unit could contribute to the enrichment of syngas in CO and H₂.

363 This kinetic mechanism developed in this study provides a valuable tool for estimating the potential
364 reduction of tars through partial oxidation, considering parameters such as residence time and amount of
365 oxygen. Despite the complexity of the kinetic model (hundreds of species including radicals and thousands
366 of reactions), the 1D plug flow model offers a fast and efficient solution. This model can be coupled with
367 process modeling software, such as Aspen Plus, to incorporate realistic complex systems beyond the scope
368 of model molecules [48].

369 It is worth noting that the assumption of perfect mixing at the inlet of the plug flow reactor may be
370 questionable, particularly due to the presence of high oxygen concentration zones near the air nozzles,
371 which can lead to localized hot spots. To gain deeper insights into these hot spots and improve the
372 prediction of heavy PAHs, the kinetic model could be incorporated into computational fluid dynamics (CFD)
373 simulations. This type of simulation would provide more accurate predictions for heavy PAHs and
374 contribute to the design and optimization of partial oxidation units.

375

376 **4. CONCLUSION**

377 This study presented detailed composition of syngas produced from a biomass gasification fluidized bed
378 reactor (5 kg/h pilot-scale) coupled with a partial oxidation unit. The secondary air injected to the POX unit
379 was varied with different equivalence ratio (0.05 and 0.10) and with or without air preheating to examine
380 the impact of temperature on the unit efficiency. The results demonstrated a significant reduction in tar

381 content ranging from 59 to 88% under these conditions. The addition of oxygen was found to be the
382 primary factor contributing to this reduction, rather than temperature increase. To achieve a 90%
383 reduction in tars, an equivalence ratio of 0.10 was recommended.

384 The reduction in tars was accompanied by an increase in the average molecular weight of PAHs, which are
385 known precursors for soot formation. The partial oxidation also led to an enrichment of CO and H₂
386 concentrations in the syngas.

387 Additionally, a detailed radical kinetic model was developed and refined to incorporate the formation of
388 heavier tars and soot. The model results were compared to experimental data and showed a good overall
389 agreement, particularly for the equivalence ratio of 0.10. The major components and most tar molecules
390 were accurately modeled.

391 These data and kinetic model offer the opportunity to simulate and optimize partial oxidation units
392 without compromising the complexity of the involved species and kinetic mechanisms. By integrating the
393 kinetic model into computational fluid dynamics (CFD) models, a more comprehensive understanding of
394 the complex hydrodynamics and critical design aspects of such units can be achieved.

395

396 **5. SUPPORTING INFORMATIONS**

397 The supporting information files 1 and 2 presents the thermodynamic properties of SynPOX model and
398 the kinetic model. The supporting information file 3 presents: 1) the detailed product composition of each
399 experiment, 2) a validation of the SynPOX model for the soot formation, and 3) additional results for the
400 cases not presented in the full-length article (0.1-1034 and 0.1-1059).

401

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406

407 7. REFERENCES

- 408 [1] Smil V. Energy Transitions: Global and National Perspectives. Second edition. Santa Barbara, California
409 Denver, Colorado: Praeger, an imprint of ABC-CLIO, LLC; 2017.
- 410 [2] Woolcock PJ, Brown RC. A review of cleaning technologies for biomass-derived syngas. Biomass and
411 Bioenergy 2013;52:54–84. <https://doi.org/10.1016/j.biombioe.2013.02.036>.
- 412 [3] Jenbacher GE. Technical Instruction No.: 1000-0302. Fuel Gas Quality, Special Gases 2009.
- 413 [4] Bensabath T, Monnier H, Glaude P-A. Detailed kinetic modeling of the formation of toxic polycyclic
414 aromatic hydrocarbons (PAHs) coming from pyrolysis in low-pressure gas carburizing conditions.
415 Journal of Analytical and Applied Pyrolysis 2016;122:342–54.
416 <https://doi.org/10.1016/j.jaap.2016.09.007>.
- 417 [5] Yu J, Guo Q, Gong Y, Ding L, Wang J, Yu G. A review of the effects of alkali and alkaline earth metal
418 species on biomass gasification. Fuel Processing Technology 2021;214:106723.
419 <https://doi.org/10.1016/j.fuproc.2021.106723>.
- 420 [6] Valderrama Rios ML, González AM, Lora EES, Almazán del Olmo OA. Reduction of tar generated during
421 biomass gasification: A review. Biomass and Bioenergy 2018;108:345–70.
422 <https://doi.org/10.1016/j.biombioe.2017.12.002>.
- 423 [7] Ren J, Cao J-P, Zhao X-Y, Yang F-L, Wei X-Y. Recent advances in syngas production from biomass
424 catalytic gasification: A critical review on reactors, catalysts, catalytic mechanisms and mathematical
425 models. Renewable and Sustainable Energy Reviews 2019;116:109426.
426 <https://doi.org/10.1016/j.rser.2019.109426>.
- 427 [8] Anis S, Zainal ZA. Tar reduction in biomass producer gas via mechanical, catalytic and thermal
428 methods: A review. Renewable and Sustainable Energy Reviews 2011;15:2355–77.
429 <https://doi.org/10.1016/j.rser.2011.02.018>.
- 430 [9] Shen Y, Yoshikawa K. Recent progresses in catalytic tar elimination during biomass gasification or
431 pyrolysis—A review. Renewable and Sustainable Energy Reviews 2013;21:371–92.
432 <https://doi.org/10.1016/j.rser.2012.12.062>.
- 433 [10] van der Hoeven TA. Partial product gas combustion for tar reduction. Dissertation Abstracts
434 International 2007;68. <https://doi.org/10.6100/IR616553>.
- 435 [11] Houben MP. Analysis of tar removal in a partial oxidation burner 2004.
436 <https://doi.org/10.6100/IR572600>.
- 437 [12] Wu W, Luo Y, Chen Y, Su Y, Zhang Y, Zhao S, et al. Experimental Investigation of Tar Conversion under
438 Inert and Partial Oxidation Conditions in a Continuous Reactor. Energy Fuels 2011;25:2721–9.
439 <https://doi.org/10.1021/ef200297s>.
- 440 [13] Houben M, Delange H, Vansteenhoven A. Tar reduction through partial combustion of fuel gas. Fuel
441 2005;84:817–24. <https://doi.org/10.1016/j.fuel.2004.12.013>.

- 442 [14] Wongchang T, Patumsawad S, Fungtammasan B. An Analysis of Wood Pyrolysis Tar from High
443 Temperature Thermal Cracking Process. *Energy Sources, Part A: Recovery, Utilization, and*
444 *Environmental Effects* 2013;35:926–35. <https://doi.org/10.1080/15567036.2012.707748>.
- 445 [15] Svensson H, Tunå P, Hulteberg C, Brandin J. Modeling of soot formation during partial oxidation of
446 producer gas. *Fuel* 2013;106:271–8. <https://doi.org/10.1016/j.fuel.2012.10.061>.
- 447 [16] Jess A. Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid
448 fuels. *Fuel* 1996;75:1441–8. [https://doi.org/10.1016/0016-2361\(96\)00136-6](https://doi.org/10.1016/0016-2361(96)00136-6).
- 449 [17] Zhang R, Zhao S, Luo Y. Experimental and Modeling Investigation on the Effect of Intrinsic and Extrinsic
450 Oxygen on Biomass Tar Decomposition. *Energy Fuels* 2017;31:8665–73.
451 <https://doi.org/10.1021/acs.energyfuels.7b00989>.
- 452 [18] Ahrenfeldt J, Egsgaard H, Stelte W, Thomsen T, Henriksen UB. The influence of partial oxidation
453 mechanisms on tar destruction in TwoStage biomass gasification. *Fuel* 2013;112:662–80.
454 <https://doi.org/10.1016/j.fuel.2012.09.048>.
- 455 [19] Valin S, Cances J, Castelli P, Thiery S, Dufour A, Boissonnet G, et al. Upgrading biomass pyrolysis gas
456 by conversion of methane at high temperature: Experiments and modelling. *Fuel* 2009;88:834–42.
457 <https://doi.org/10.1016/j.fuel.2008.11.033>.
- 458 [20] Blekkan EA, Myrstad R, Olsvik O, Rokstad OA. Characterization of tars and coke formed during the
459 pyrolysis of methane in a tubular reactor. *Carbon* 1992;30:665–73. [https://doi.org/10.1016/0008-6223\(92\)90186-Z](https://doi.org/10.1016/0008-6223(92)90186-Z).
- 460 [21] Sarobe M, Kwint HC, Fler T, Havenith RWA, Jenneskens LW, Vlietstra EJ, et al. Flash Vacuum
461 Thermolysis of Acenaphtho[1,2-a]acenaphthylene, Fluoranthene, Benzo[k]- and Benzo[j]fluoranthene
462 – Homolytic Scission of Carbon-Carbon Single Bonds of Internally Fused Cyclopenta Moieties at $T \geq$
463 1100 °C. *Eur J Org Chem* 1999;5:1191–200. [https://doi.org/10.1002/\(SICI\)1099-0690\(199905\)1999:5%3C1191::AID-EJOC1191%3E3.0.CO;2-W](https://doi.org/10.1002/(SICI)1099-0690(199905)1999:5%3C1191::AID-EJOC1191%3E3.0.CO;2-W).
- 464 [22] Gai C, Dong Y, Yang S, Zhang Z, Liang J, Li J. Thermal decomposition kinetics of light polycyclic aromatic
465 hydrocarbons as surrogate biomass tar. *RSC Adv* 2016;6:83154–62.
466 <https://doi.org/10.1039/C6RA15513H>.
- 467 [23] DeCoster J, Ergut A, Levendis YA, Richter H, Howard JB, Carlson JB. PAH emissions from high-
468 temperature oxidation of vaporized anthracene. *Proceedings of the Combustion Institute*
469 2007;31:491–9. <https://doi.org/10.1016/j.proci.2006.07.211>.
- 470 [24] Thomas S, Wornat MJ. The effects of oxygen on the yields of polycyclic aromatic hydrocarbons formed
471 during the pyrolysis and fuel-rich oxidation of catechol. *Fuel* 2008;87:768–81.
472 <https://doi.org/10.1016/j.fuel.2007.07.016>.
- 473 [25] Peng N, Huang C, Su J. An experimental and kinetic study of thermal decomposition of phenanthrene.
474 *Journal of Hazardous Materials* 2019;365:565–71. <https://doi.org/10.1016/j.jhazmat.2018.11.026>.
- 475 [26] Brandt P, Larsen E, Henriksen U. High Tar Reduction in a Two-Stage Gasifier. *Energy Fuels*
476 2000;14:816–9. <https://doi.org/10.1021/ef990182m>.
- 477 [27] McGrath T, Sharma R, Hajaligol M. An experimental investigation into the formation of polycyclic-
478 aromatic hydrocarbons (PAH) from pyrolysis of biomass materials. *Fuel* 2001;80:1787–97.
479 [https://doi.org/10.1016/S0016-2361\(01\)00062-X](https://doi.org/10.1016/S0016-2361(01)00062-X).
- 480 [28] Tanoh TS, Ait Oumeziane A, Lemonon J, Escudero-Sanz FJ, Salvador S. A novel two-stage gasification
481 strategy for nitrogen-free syngas production- pilot-scale experiments. *Fuel Processing Technology*
482 2021;217:106821. <https://doi.org/10.1016/j.fuproc.2021.106821>.
- 483 [29] Su Y, Luo Y, Chen Y, Wu W, Zhang Y. Experimental and numerical investigation of tar destruction under
484 partial oxidation environment. *Fuel Processing Technology* 2011;92:1513–24.
485 <https://doi.org/10.1016/j.fuproc.2011.03.013>.
- 486
487

- 488 [30] Weston PM, Sharifi V, Swithenbank J. Destruction of Tar in a Novel Coandă Tar Cracking System.
489 Energy Fuels 2014;28:1059–65. <https://doi.org/10.1021/ef401705g>.
- 490 [31] Mao Y, Dong Y, Wang B, Chang J, Yu J, Zhang Y, et al. Characteristics and kinetics of biomass tar cracking
491 in a micro fluidized bed. RSC Adv 2015;5:82845–52. <https://doi.org/10.1039/C5RA13323H>.
- 492 [32] Thimthong N, Appari S, Tanaka R, Iwanaga K, Kudo S, Hayashi J, et al. Kinetic modeling of non-catalytic
493 partial oxidation of nascent volatiles derived from fast pyrolysis of woody biomass with detailed
494 chemistry. Fuel Processing Technology 2015;134:159–67.
495 <https://doi.org/10.1016/j.fuproc.2015.01.029>.
- 496 [33] Tanoh TS. Production d'un syngaz par pyrogazéification de biomasse en vuv d'une biométhanation.
497 Université de Toulouse, 2021.
- 498 [34] Dhahak A, Bounaceur R, Le Dreff-Lorimier C, Schmidt G, Trouve G, Battin-Leclerc F. Development of a
499 detailed kinetic model for the combustion of biomass. Fuel 2019;242:756–74.
500 <https://doi.org/10.1016/j.fuel.2019.01.093>.
- 501 [35] Norinaga K, Deutschmann O, Saegusa N, Hayashi J. Analysis of pyrolysis products from light
502 hydrocarbons and kinetic modeling for growth of polycyclic aromatic hydrocarbons with detailed
503 chemistry. Journal of Analytical and Applied Pyrolysis 2009;86:148–60.
504 <https://doi.org/10.1016/j.jaap.2009.05.001>.
- 505 [36] Norinaga K, Shoji T, Kudo S, Hayashi J. Detailed chemical kinetic modelling of vapour-phase cracking
506 of multi-component molecular mixtures derived from the fast pyrolysis of cellulose. Fuel
507 2013;103:141–50. <https://doi.org/10.1016/j.fuel.2011.07.045>.
- 508 [37] Srinivas S, Field RP, Herzog HJ. Modeling Tar Handling Options in Biomass Gasification. Energy Fuels
509 2013;27:2859–73. <https://doi.org/10.1021/ef400388u>.
- 510 [38] Ruiz M, Schnitzer A, Arnoux P, Mauviel G. Gasification of N-rich fibreboard in an air-blown fluidized
511 bed reactor: A study on the fate of tars, NH₃ and HCN during oxidative mild Hot Gas Filtration. Fuel
512 2021;303:121317. <https://doi.org/10.1016/j.fuel.2021.121317>.
- 513 [39] Kister J, Pieri N, Alvarez R, Díez MA, Pis JJ. Effects of Preheating and Oxidation on Two Bituminous
514 Coals Assessed by Synchronous UV Fluorescence and FTIR Spectroscopy. Energy Fuels 1996;10:948–
515 57. <https://doi.org/10.1021/ef950159a>.
- 516 [40] Lardier G, Kaknics J, Dufour A, Michel R, Cluet B, Authier O, et al. Gas and Bed Axial Composition in a
517 Bubbling Fluidized Bed Gasifier: Results with Miscanthus and Olivine. Energy Fuels 2016;30:8316–26.
518 <https://doi.org/10.1021/acs.energyfuels.6b01816>.
- 519 [41] Septien S, Valin S, Peyrot M, Spindler B, Salvador S. Influence of steam on gasification of millimetric
520 wood particles in a drop tube reactor: Experiments and modelling. Fuel 2013;103:1080–9.
521 <https://doi.org/10.1016/j.fuel.2012.09.011>.
- 522 [42] Darido J, Dhahak A, Bounaceur R, Le Dreff - Lorimier C, Leyssens G, Cazier F, et al. Emissions from a
523 Domestic Wood Heating Appliance: Experimental Measurements and Numerical Study Using an
524 Equivalent Reactor Network (ERN) Approach Coupled with a Detailed Chemical Mechanism. Energy
525 Fuels 2021:acs.energyfuels.1c01927. <https://doi.org/10.1021/acs.energyfuels.1c01927>.
- 526 [43] Stagni A, Cuoci A, Frassoldati A, Faravelli T, Ranzi E. Lumping and Reduction of Detailed Kinetic
527 Schemes: an Effective Coupling. Ind Eng Chem Res 2014;53:9004–16.
528 <https://doi.org/10.1021/ie403272f>.
- 529 [44] Pejpichestakul W, Ranzi E, Pelucchi M, Frassoldati A, Cuoci A, Parente A, et al. Examination of a soot
530 model in premixed laminar flames at fuel-rich conditions. Proceedings of the Combustion Institute
531 2019;37:1013–21. <https://doi.org/10.1016/j.proci.2018.06.104>.
- 532 [45] Saggese C, Sánchez NE, Frassoldati A, Cuoci A, Faravelli T, Alzueta MU, et al. Kinetic Modeling Study of
533 Polycyclic Aromatic Hydrocarbons and Soot Formation in Acetylene Pyrolysis. Energy Fuels
534 2014;28:1489–501. <https://doi.org/10.1021/ef402048q>.

- 535 [46] Rabou LPLM, Zwart RWR, Vreugdenhil BJ, Bos L. Tar in Biomass Producer Gas, the Energy research
536 Centre of The Netherlands (ECN) Experience: An Enduring Challenge. *Energy Fuels* 2009;23:6189–98.
537 <https://doi.org/10.1021/ef9007032>.
- 538 [47] Valin S, Cances J, Castelli P, Thiery S, Dufour A, Boissonnet G, et al. Upgrading biomass pyrolysis gas
539 by conversion of methane at high temperature: Experiments and modelling. *Fuel* 2009;88:834–42.
540 <https://doi.org/10.1016/j.fuel.2008.11.033>.
- 541 [48] Demol R, Dufour A, Rogaume Y, Mauviel G. Production of Purified H₂, Heat, and Biochar from Wood:
542 Comparison between Gasification and Autothermal Pyrolysis Based on Advanced Process Modeling.
543 *Energy Fuels* 2022;36:488–501. <https://doi.org/10.1021/acs.energyfuels.1c03528>.
544