

1 **Catalytic pyrolysis of plastic waste using metal-incorporated activated**
2 **carbons for monomer recovery and carbon nanotube synthesis**

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8

9 Abstract

10 As the global plastic waste crisis intensifies, innovative and sustainable solutions are urgently
11 needed. This study evaluated waste-derived metal-incorporated activated carbon (AC)
12 catalysts for the pyrolysis of mixed plastic waste to generate value-added products, focusing
13 on product yield distribution, composition, hydrogen, and carbon nanotube (CNT) formation.
14 Pyrolysis-catalysis experiments were conducted using a two-stage fixed-bed reactor, wherein
15 the temperature was maintained at 500 °C in first stage (pyrolysis) and varied (500, 600, and
16 700 °C) in the second stage (catalysis). The tested ACs were incorporated with nickel (Ni-AC),
17 iron (Fe-AC), and zinc (Zn-AC) to assess the impact of metal particles distributed on the
18 carbonaceous support in the second stage. The results from the ACs were compared to those
19 obtained using zeolite (H-ZSM-5), Raw-AC, and non-catalytic runs. The Ni-AC and Fe-AC
20 demonstrated superior catalytic activity, with Ni-AC being more efficient in producing
21 hydrogen (4.24 wt%) and CNTs (34.5 wt%) with diameters of approximately 30 nm, and Fe-
22 AC leading to higher gas yields (68.8 wt%) and CNTs (12.4 wt%) of around 60 nm. In contrast,
23 Zn-AC and Raw-AC presented limited effectiveness, although Raw-AC moderately
24 outperformed Zn-AC with enhanced gas yields and reduced oil/wax yields. The zeolite H-ZSM-
25 5 exhibited the highest gas yields (78 wt%), converting heavy fractions into lighter molecules,
26 notably the monomers ethylene and propylene. These findings provide valuable insights into
27 catalyst selection and optimization for plastic waste pyrolysis processes, with H-ZSM-5 being
28 the most effective catalyst for monomer recovery, and Ni-AC and Fe-AC demonstrating
29 promising results.

30 Keywords: chemical recycling, biochar, hydrogen, sustainability, circularity

31 1. Introduction

32 Due to their durability and versatility, plastic products have become an integral part of
33 everyday life. However, the same characteristics that make plastics so useful also contribute
34 to a mounting global waste crisis. Mismanaged plastic waste poses substantial threats to
35 terrestrial and aquatic ecosystems, and current waste management practices such as
36 landfilling, and incineration have significant environmental and health repercussions [1, 2].
37 Despite widespread recycling efforts, only a small fraction (approximately 32%) of plastic
38 waste is currently recycled effectively, while the vast majority is destined to landfills or

39 incineration [3]. Therefore, innovative alternative methods to manage plastic waste in a more
40 sustainable way are necessary.

41 The field of plastic waste management is undergoing a transformative change, thanks to the
42 integration of technologies such as cold plasma-assisted pyrolysis (CPAP), microwave-assisted
43 pyrolysis (MAP), hydrothermal processing (HTP), selective solvolysis (SS), and advancements
44 in biological treatments, mechanical recycling, and artificial intelligence. CPAP is regarded for
45 its energy efficiency and enhanced chemical selectivity under a highly reactive environment
46 at low temperatures [4, 5]. MAP stands out for its rapid and selective heating, optimizing
47 energy consumption and offering adaptability for various plastic waste types [6, 7]. HTP and
48 SS allow the recovery of monomers for the subsequent manufacture of new plastics [8-10].
49 In addition, breakthroughs in enzyme engineering, like the creation of more potent PET-
50 degrading enzymes, are speeding up the biological decomposition of plastics [11]. AI and
51 robotics are being enhanced to improve sorting efficiency, ensuring that plastics are
52 effectively separated for recycling [12, 13].

53 Waste-derived materials, such as biochar and activated carbon, have been increasingly
54 recognized as potential catalysts for the pyrolysis of plastic waste [14-16]. Their use not only
55 reduces waste but also provides an economically viable option for sustainable waste
56 management, as these materials can be obtained at lower costs than other widely used
57 catalysts such as commercial zeolites [17].

58 Activated carbons usually present a hierarchical structure due to their wide distribution of
59 pore sizes [18]. The use of catalysts with this structure has several advantages for the pyrolysis
60 of plastic waste, such as the potential to improve the efficiency and selectivity of the process
61 through multiple approaches [19]. One of the most notable benefits of hierarchical catalysts
62 is the enhanced accessibility they provide. Since the bulky nature of the plastic can lead to
63 steric hindrances or diffusion constraints, the presence of micropores, mesopores, and
64 macropores within a hierarchical catalyst ensures that plastic waste can readily access the
65 catalyst's active sites [20]. Micropores contribute to the adsorption and desorption of
66 reactants and products, while mesopores facilitate efficient mass transport and diffusion.
67 Macropores, on the other hand, aid in preventing pore blockage and promoting bulk transport
68 [21]. The multilevel pore structure significantly enhances the accessibility of pyrolytic volatiles
69 to the catalytic sites, thereby improving the overall reaction rate [22]. Moreover, the

70 hierarchical pore structure permits improved mass transport of reactants and products
71 throughout the catalyst. The interconnected network of pores enables the diffusion of large
72 molecules to the internal active sites, and the efficient removal of reaction products [23]. This
73 minimizes diffusional limitations and prevents pore blockage, leading to a more effective
74 pyrolysis process. The role of support materials in determining catalyst properties is essential,
75 since they aid in the dissemination of active metal particles, enabling improved mass
76 transport and providing a suitable environment for chemical reactions to occur, owing to their
77 unique physical and chemical structure [24].

78 Johar et al. [25] designed a biologically nickel-bound biochar catalyst for the depolymerization
79 of polyethylene into high-value chemicals via microwave-assisted pyrolysis. This catalyst
80 effectively enhanced the production of C₆-C₁₂ aliphatics, dehydrocyclization of linear alkanes,
81 and H₂ release as gaseous fraction. Wang et al. [26] employed nanocellulose-derived biochar
82 as a catalyst for pyrolyzing low-density polyethylene (LDPE) into hydrogen and liquid fuels.
83 The study revealed that at 500 °C and a biochar to LDPE ratio of >3, the plastic could be
84 completely degraded into liquid and gas without wax formation. Moreover, the biochar
85 catalyst proved efficient in converting real waste plastics (e.g., grocery bags and packaging
86 trays) into valuable liquid and H₂-enriched gas products. In a separate study [27], biochars
87 derived from agricultural waste (corn stover and Douglas fir) were utilized for the pyrolysis of
88 waste plastics (i.e., PS, PET, PP, LDPE, and HDPE). The corn stover biochar, which resulted in
89 a liquid yield of approximately 40 wt%, without wax formation, generated 60-80 vol% of H₂
90 in the gas yield, and exhibited high activity after 20 cycles of reuse. Similarly, Park et al. [28]
91 examined the application of nickel-incorporated lignin-derived biochar for HDPE gasification.
92 The biochar catalyst demonstrated high H₂ yields (0.093 mmolH₂ g⁻¹_{plastic}) from the gasification
93 process, which was attributed to the high dispersion/distribution of Ni on the biochar. The
94 study concludes that Ni supported on char could be an economically feasible catalyst for
95 producing hydrogen from gasification of plastics.

96 The plastic waste pyrolysis products are diverse and valuable, including light oil (naphtha),
97 hydrogen, CNTs, and monomers. CNTs have a wide range of applications in various fields such
98 as electronics, energy storage, and materials science [29, 30]. Recent studies have shown that
99 CNTs can be produced from plastic waste pyrolysis, and the quality and quantity of CNTs can
100 be controlled by adjusting the pyrolysis conditions and the type of catalyst used [31].

101 Monomers, as the building blocks of polymers, are another valuable product that can be
102 obtained from plastic waste. For example, up to 50 wt.% ethylene monomers can be
103 recovered from polyethylene waste through pyrolysis, albeit at high temperatures (1000 °C)
104 [32].

105 This study is motivated by the need to overcome the limitations present in existing plastic
106 waste recycling approaches and aims to explore effective alternatives. A noticeable gap exists
107 in literature regarding the performance differentiation of various metal-incorporated
108 activated carbons in plastic pyrolysis [26, 27, 33]. Research deficiency in the investigation of
109 activated carbon catalytic pyrolysis of plastics highlights the need for comprehensive studies
110 focused on understanding the catalytic pyrolysis process. Additionally, lack of in-depth
111 exploration into the mechanisms governing the selectivity among various catalysts in the
112 production of hydrogen, carbon nanotubes, and monomers also underscores a knowledge
113 gap that is crucial for enhancing the efficiency and selectivity of catalytic pyrolysis processes,
114 contributing to the production of valuable by-products. Moreover, an underexplored area is
115 the impact of distinct catalyst bed temperatures within two-stage reactors, where initial
116 pyrolysis and catalysis-driven processes are spatially segregated. Our focus is on the catalytic
117 pyrolysis process, a promising strategy for alleviating plastic waste issues while
118 simultaneously enabling the extraction of valuable chemical derivatives. We delve into an in-
119 depth analysis of Ni, Fe, and Zn-loaded activated carbons as catalysts, aiming to evaluate their
120 efficacy in augmenting plastic waste recycling efficiency and their selectivity in producing
121 hydrogen, carbon nanotubes, and monomers. Emphasis is placed on assessing the interplay
122 of temperature variations and distinct catalysts on the yields and compositions of oil, gas,
123 char, and carbon deposition. This inquiry, rooted in the application of waste-derived catalysts
124 in plastic waste pyrolysis, aspires to enhance the eco-friendliness of recycling processes and
125 underscores the viability of these catalysts as substitutes for traditional materials.

126 2. Materials and methods

127 *2.1. Plastic waste*

128 Plastic waste samples, consisting of HDPE, LDPE, PP, PS, and PET, were obtained from Byker
129 Household Waste Recycling Centre in Newcastle upon Tyne. Each type of plastic was isolated,
130 washed, dried, and cut into 1 mm² squared pieces. Proximate analysis, following the British

131 standard BS-1016-3, was conducted to determine the moisture, ash, volatile matter, and fixed
 132 carbon content of the samples. Elemental analysis was conducted using a CHN628 Series
 133 Elemental Determinator at the Advanced Chemical and Materials Analysis (ACMA) unit at
 134 Newcastle University. The results, presented in Table 1, indicate that the samples consisted
 135 primarily of volatile matter (95.4 wt%), with low levels of ash (2.37 wt%) and negligible
 136 moisture (0.15 wt%). The most abundant elements in the plastic samples are C and H, while
 137 the oxygen content is minimal for all plastics, except for PET. For every pyrolysis run,
 138 simulated mixtures were prepared based on the reported composition of global primary
 139 plastic waste generation (i.e., 20% HDPE, 28.5% LDPE, 27.5 PP, 9% PS, and 15% PET) [34].

140 Table 1. Proximate analysis (as received), and elemental analysis (dry ash-free basis) of plastic
 141 waste samples (wt%). Error bars are based on the standard deviation of measurements
 142 conducted in triplicate.

Sample	Moisture	Ash	Fixed Carbon	Volatile matter	C	H	N	O ^a
PP	0.15 ±	2.18 ±	0.21 ± 0.07	97.61 ±	84.89	13.91	0.21	0.99
	0.04	0.12		0.38				
LDPE	0.17 ±	6.12 ±	0.60 ± 0.25	93.28 ±	84.66	14.24	0.43	0.67
	0.08	0.29		2.12				
PET	0.26 ±	0.70 ± 0.1	8.28 ± 1.74	91.03 ±	62.56	4.28	0.12	33.04
	0.13			0.41				
HDPE	0.04 ±	0.14 ±	0.22 ± 0.09	99.64 ±	86.02	13.82	0.02	0.14
	0.03	0.06		0.52				
PS	0.12 ±	2.43 ±	2.36 ± 1.18	95.21 ±	91.79	7.67	0.09	0.45
	0.07	0.08		1.19				

143 ^a by difference.

144 2.2. Catalyst preparation and characterisation

145 The activated carbon (AC) was produced in-house by subjecting walnut shells to heat
 146 treatment at a temperature of 700 °C in the presence of flowing CO₂ for 1 h. The selection of
 147 these conditions was based on their previous demonstration of generating ACs possessing
 148 high porosity and high surface area [35]. After the reaction, the AC was pulverized using a

149 mortar and subsequently sifted to obtain a fine powder with a diameter of approximately 50
150 μm .

151 For metal loading, nickel was chosen due to its outstanding catalytic properties, which
152 enhance the cleavage of plastic waste C-C bonds, promote the decomposition of long-chain
153 hydrocarbons, and provide high selectivity for H_2 and CNTs [36]. Nickel particles act as active
154 sites for catalytic reactions, while the highly porous structure of AC offers a substantial surface
155 area for both the dispersion of nickel and the adsorption and subsequent dissociation of
156 hydrocarbon molecules [37]. Similar to the catalytic effect of nickel, the active sites of iron
157 catalysts promote the cleavage of C-C and C-H bonds in the long-chain plastic molecules,
158 which facilitates their conversion into smaller products [38]. Zinc has been shown to have
159 catalytic properties that are beneficial to plastic waste pyrolysis, such as enhances gas yields
160 compared to non-catalytic pyrolysis, and the improved quality of oils [39].

161 The wet impregnation method was used for metal incorporation. A 100 mL solution
162 containing either nickel nitrate hexahydrate, iron (III) nitrate nonahydrate, or zinc nitrate
163 hexahydrate (Sigma Aldrich) was prepared and combined with raw AC. The proportions of
164 nitrate salts and AC were determined to achieve a 2:1 mass ratio of AC to the resulting metal
165 oxide after calcination. The resulting slurries were vigorously stirred for 12 h at 60 °C, then
166 dried in an oven at 105 °C for 12 h, calcined at 600 °C in a flow of nitrogen (100 ml min^{-1}) for
167 4 h, and finally ground and sieved into fine particles of around 50 μm diameter. The H-ZSM-5
168 zeolite (312 $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, $413 \text{ m}^2 \text{ g}^{-1}$ surface area) was calcinated in static air at 550
169 °C for 4 h at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$.

170 The composition and structure of the catalysts were analysed through Scanning Electron
171 Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).
172 SEM images and EDX elemental mapping were obtained in a JEOL JSM-5610LV SEM operating
173 at low vacuum and coupled with an energy dispersive X-ray spectroscopy (EDX) module. The
174 analyses were conducted on uncoated samples mounted on standard SEM stubs.

175 XRD analysis was performed in a PANalytical X'Pert Pro MPD with Xcelerator detector using
176 $\text{Cu K}\alpha$ radiation.

177 The micropore volume and surface area of the AC samples and zeolite were evaluated by CO_2
178 adsorption at a temperature of 0 °C by means of an Hiden Isochema Intelligent Gravimetric

179 Analyser (IGA). Isotherms were recorded at each pressure point (0-100 kPa) in an ultrahigh
180 vacuum system. Prior to each run, 50 mg of the AC sample was degassed at 120 °C overnight
181 under vacuum ($<10^{-6}$ Pa) for all moisture to be removed until achieving a constant weight
182 before a static gas sorption/desorption isotherm was recorded. The CO₂ adsorption-
183 desorption isotherm was analysed using the Dubinin-Radushkevich (DR) model. The
184 mesopore volume and surface area of the samples were evaluated by N₂ physisorption
185 isotherms at 77 K using a Micromeritics TriStar II Plus and Brunauer-Emmett-Teller (BET)
186 equation with samples dried at 105 °C overnight and outgassed at 350 °C at high vacuum for
187 24 h prior to analysis.

188 *2.3. Pyrolysis setup*

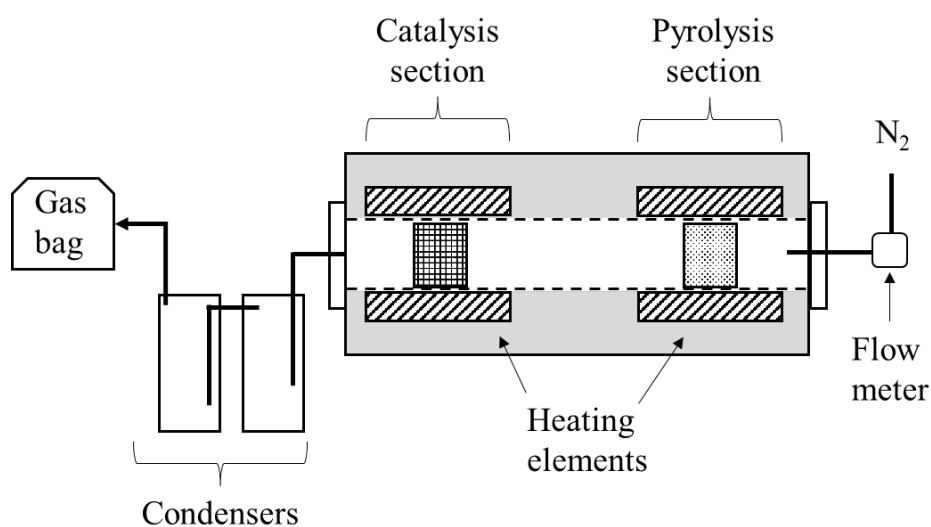
189 The experimental configuration involved a two-stage fixed-bed stainless steel reactor (1.25 in
190 diameter, and 17 in length) fitted with two heating bands (spaced 5.1 in apart) for
191 independently controlled temperatures for the two zones. The outlet of the reactor was
192 connected to the condensers cooled at -13 °C using a saturated frigorific solution of salt and
193 ice water as illustrated in Figure 4. Before initiating the experiments, the reactor was purged
194 with N₂ for 30 min to ensure the system is air-free (verified by GC analysis). Following this, the
195 first reactor stage (pyrolysis section), holding 3 g of plastic mixture was heated at a rate of 20
196 °C min⁻¹ and sustained at 500 °C for 40 min at a fixed N₂ carrier gas flow rate of 40 ml min⁻¹.
197 Quartz wool and a metallic mesh support which held 0.5 g of catalyst (i.e., 1:6 plastic-to-
198 catalyst ratio) were placed in the second stage where the temperature was varied (500 – 700
199 °C). During the non-catalytic pyrolysis experiments, only quartz wool was in place with no
200 catalyst. Non-condensable gases were collected at the outlet of the condenser system using
201 multiple Tedlar gas bags and the entirety of the gas products were collected. The mass
202 differences in the crucible, condensers, and catalyst bed pre- and post-reaction were
203 employed to calculate the masses of the produced char, oil, and catalyst carbon deposition,
204 respectively. In cases where carbon nanotubes were detected, carbon deposition was
205 referred to as CNT, and their masses were calculated by subtracting the mass of carbon
206 deposition on Raw-AC from the masses observed on Ni-AC and Fe-AC at each respective
207 temperature. The total mass of gaseous products was determined using gas chromatography,
208 considering the known N₂ flow rate, collection time, and mol% of the samples. Equation 1
209 describes the mass balance:

210
$$M_{plastic} = M_{products} = M_{oil} + M_{gas} + M_{char} + M_{C\ deposition} \quad (1)$$

211 Where M stands for mass. The product yields were then calculated by equation 2:

212
$$Y_i = 100 \left(\frac{M_i}{M_{plastic}} \right) \quad (2)$$

213 Where Y is the yield (wt%), and the subscript *i* denotes the type of product (oil, gas, char, and
 214 carbon deposition. All yields reported in this study are referred to the initial mass of plastic
 215 waste. Non-catalytic pyrolysis at 600 °C was conducted in triplicate to test reproducibility and
 216 the experimental errors on product yields and compositions were extrapolated to all tested
 217 conditions.



218
 219 Figure 4. Schematic diagram of the pyrolysis-catalysis reactor and condensation system.

220 **2.4. Product analysis**

221 Non-condensable gases were collected for a total of 50 min and analysed offline using a
 222 Varian 450 gas chromatography equipped with both TCD and FID detectors. These detectors
 223 enabled the concurrent analysis of permanent gases (e.g., H₂, N₂, O₂, and CO), CO₂, and
 224 hydrocarbons (C1 – C4). The TCD inlet, detector, and oven temperatures were regulated at
 225 250 °C, 175 °C, and 175 °C, respectively. Three columns were integrated into the GC,
 226 specifically a Hayesep T ultimet, a Hayesep Q ultimet, and a Molecular Sieve 13X. The gas
 227 specimen from the TCD detector was subsequently conducted into an Rt-Alumina
 228 BOND/MAPD column (30 m x 0.32 mm x 5 µm) connected to the FID detector, which was
 229 adjusted to 255 °C. The column was situated in an isolated oven with a programmed
 230 temperature sequence: Initially stabilized at 40 °C for 2 min, incrementally raised to 50 °C at

231 a rate of 4 °C min⁻¹, maintained for 0.5 min, then escalated to 80 °C at 8 °C min⁻¹, and finally
232 increased to 145 °C at 20 °C min⁻¹.

233 Liquid products collected from the condensers after the system cooled down were dissolved
234 in a 1:1 mixture of ethyl acetate and n-hexane and characterised using an Agilent 5977B MSD
235 MS Single Quadrupole Mass Analyzer, linked to an Agilent 8890 Gas Chromatography system
236 and utilizing an HP-5MS column (30 m x 0.25 mm x 0.25 µm). The inlet and detector
237 temperatures were fixed at 280 °C, while the oven's temperature program commenced at 60
238 °C for 0.5 minutes, increased to 280 °C at a rate of 6.5 °C min⁻¹, and finally held at 280 °C for
239 13 min. For quantitative analysis, an Agilent 7820 Gas Chromatograph was employed,
240 featuring an identical column and heating protocol as previously described. An internal
241 standard (methyl stearate) and an external standard (C₇ – C₄₀ saturated alkanes, Sigma
242 Aldrich) were utilized for quantification purposes. The relative response factor (RRF) of each
243 analyte was determined using known external and internal standard concentrations, and their
244 peak area results via equation 3:

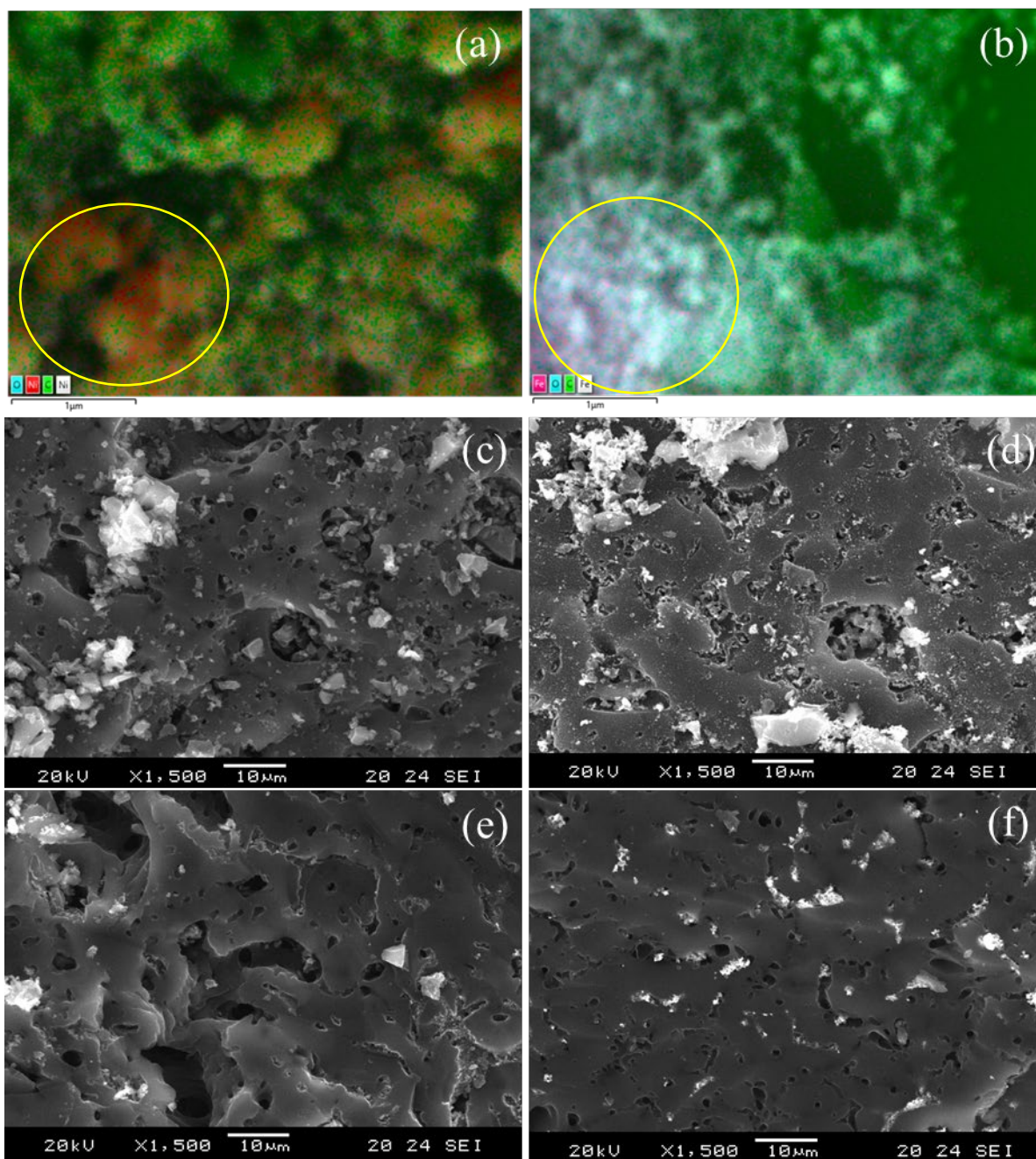
$$245 \quad \frac{A_x}{C_x} = RRF \left(\frac{A_{is}}{C_{is}} \right) \quad (3)$$

246 Where A is the peak area, C is the concentration, and the subscripts “x” and “is” stand for
247 analyte, and internal standard, respectively. The concentrations of the sample compounds
248 were then calculated using their peak areas, the internal standard peak area, and the
249 corresponding RRF according to equation 3. The masses of the sample compounds were then
250 related to the initial plastic mass to determine their yields (wt%). For simplicity, hydrocarbons
251 were categorized into three groups based on their carbon numbers <C₁₀ (light), C₁₀-C₁₈
252 (medium), and >C₁₈ (heavy/wax) hydrocarbon fractions, respectively.

253 3. Results and discussion

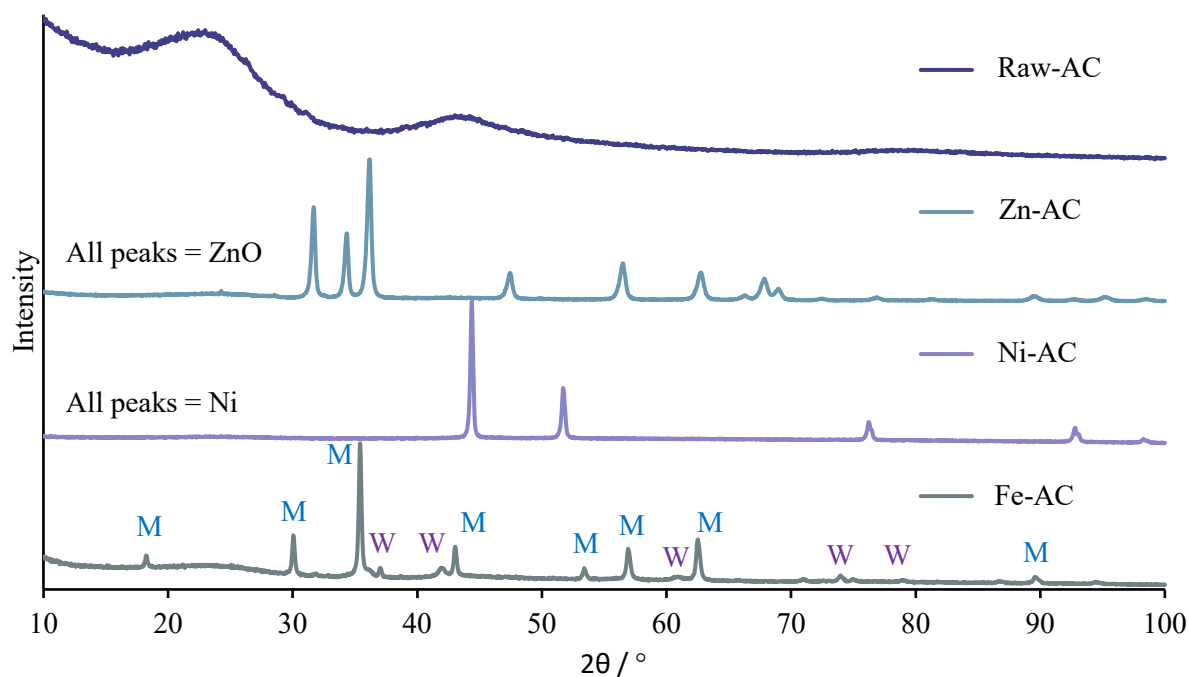
254 3.1. Catalyst characterisation

255 In Figure 1 (a-b), the EDX elemental mapping shows that the metallic particles (highlighted in
256 red/pink) were evenly dispersed across the AC catalyst surface. The macropore structure can
257 be visualised in Figure 1 (c-f), this shape allows the bulky hydrocarbon volatiles to access the
258 internal matrix of the catalyst more easily, where reaction occurs on the surface of the
259 mesopores and micropores [40].



260
 261 Figure 1. EDX mapping of nickel (a) and iron (b) incorporated AC, and SEM images of raw AC
 262 (c), nickel (d), iron (e), and zinc (f) incorporated AC.

263 Figure 2 illustrates the XRD patterns indicating the identified phases of raw and metal-
 264 incorporated AC catalysts.



265

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Figure 2. XRD spectra of AC catalysts (M = magnetite (Fe_3O_4), W = wuestite (FeO)).

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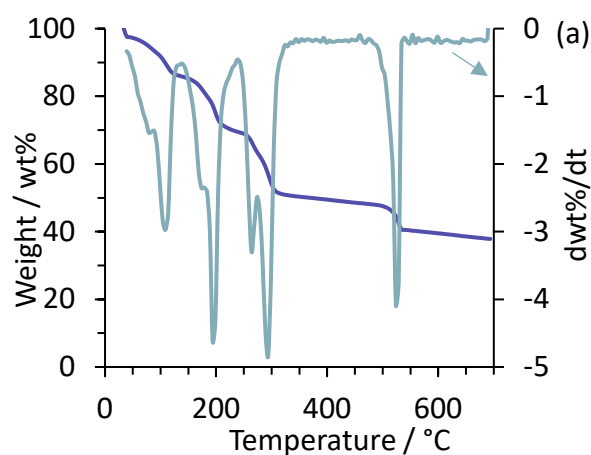
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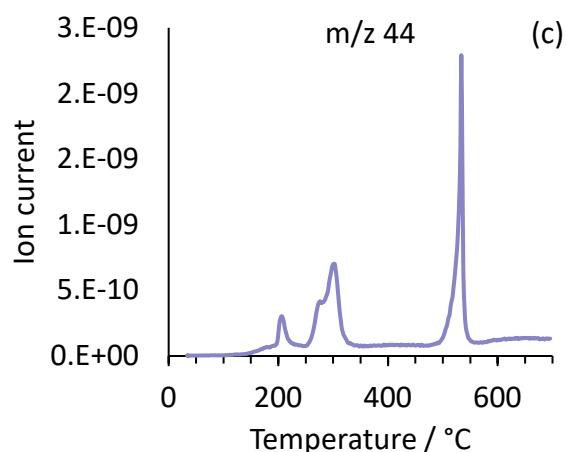
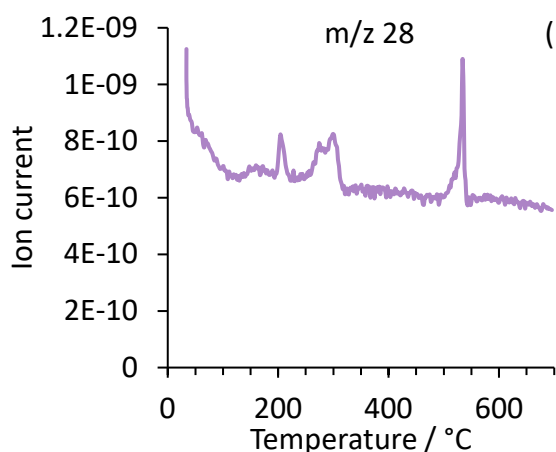
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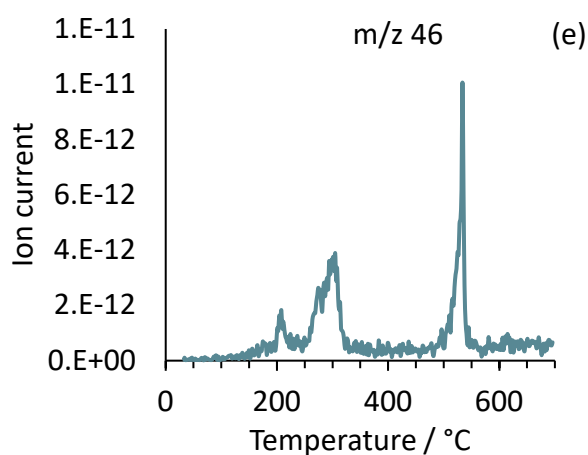
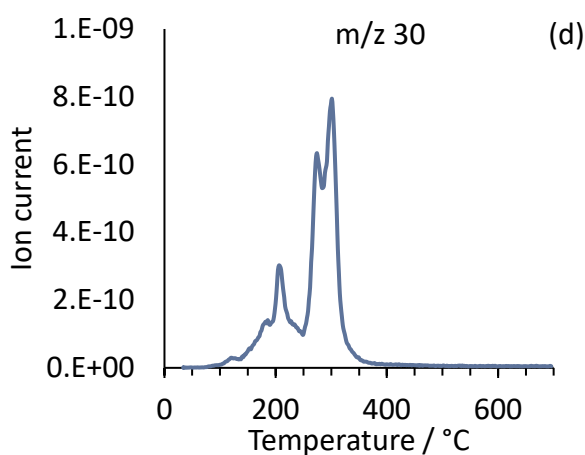
The Raw-AC sample had insufficient peaks to determine its existing phases. Hexagonal ZnO was the only phase detected in Zn-AC, face-centred cubic nickel was the only phase of Ni-AC, and Fe-AC contained two forms of iron oxide: cubic Fe_3O_4 and FeO . Crystalline nickel oxide was absent, and only metallic nickel particles were detected. This characteristic in Ni-AC was examined via TG-MS analysis using a NETZSCH STA 449 F3 Jupiter fitted with QMS 403 Quadro/ Aëolos. The analysis was carried out within a helium environment, with temperatures varying between 35-700 °C at a heating rate of 10 °C min^{-1} . The range for mass measurement spanned from 10-150 m/z. As shown in Figure 3, the analysis indicates a series of mass losses, indicative of an interaction of nickel oxide and carbon in the catalyst support upon heating. This can result from the support reacting with the oxygen in NiO to release gaseous oxides. Between 150-300 °C, NO and/or NO_2 were detected, while CO and CO_2 were observed between 490-540 °C, confirming the reduction of nickel within the Ni-AC catalyst.



279



280



281

282 Figure 3. Ni-AC activation TGA results (a), MS results of m/z 28 (b), m/z 44 (c), m/z 30 (d),
 283 and m/z 46 (e).

284 Surface area and pore volume results are summarised in Table 2. As a result of biomass
 285 undergoing thermal processing with CO₂, the raw AC exhibits a highly porous structure with
 286 a micropore volume of 0.2055 cm³ g⁻¹ and a micropore surface area measuring 551.5 m² g⁻¹.
 287 However, following the wet impregnation method, the overall surface area of the catalysts

288 decreased. The most notable reduction occurred in the Ni-AC, followed by Fe-AC, while the
 289 Fe-AC structure was the least affected by the metal impregnation procedure.

290 The isotherms of all catalysts (Figures S1-4) follow a Type I isotherm, indicating the
 291 domination of micropores in the carbon matrix. The micropore volume measured via N₂
 292 adsorption ($V_{DR\ N_2}$) of Raw-AC was 0.034 cm³ g⁻¹. This value is markedly lower than the volume
 293 determined through CO₂ adsorption (V_{CO_2}), which was 0.2055 cm³ g⁻¹. This indicates the
 294 activated diffusion effect of N₂ at cryogenic temperatures (-196 °C), which can be attributed
 295 to the exceedingly narrow pore structure of Raw-AC. Therefore, these constricted micropores
 296 may not contribute to the gas-solid reactions during pyrolysis. The $V_{DR\ N_2}$ of Ni-AC was 0.123
 297 cm³ g⁻¹, which is similar to the V_{CO_2} 0.1259 cm³ g⁻¹. These are open micropores where gas can
 298 easily diffuse into for any gas-solid reactions. The similarity of V_{CO_2} (0.1471 cm³ g⁻¹) and $V_{DR\ N_2}$
 299 (0.141 cm³ g⁻¹) in Zn-AC indicates the open micropore structure, where gases can easily diffuse
 300 into these micropores for reactions.

301 Table 2. Pore volume and surface area results of AC catalysts.

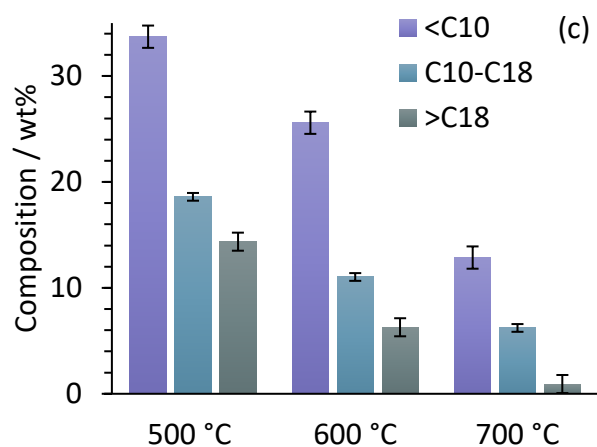
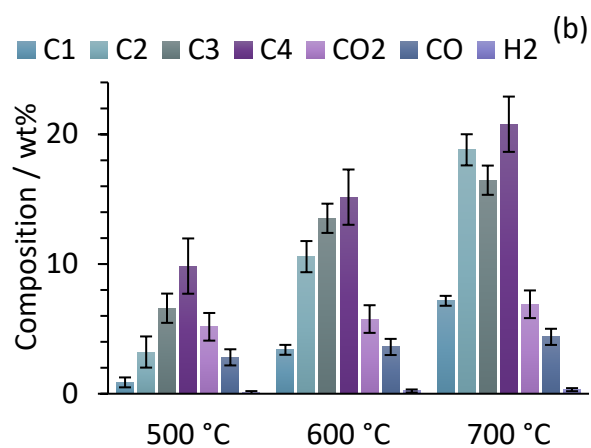
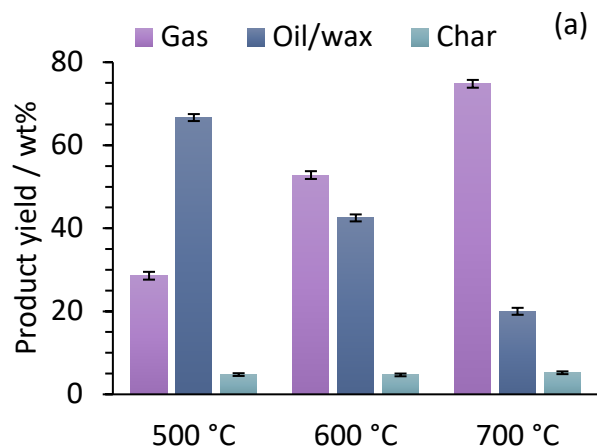
Catalyst	$S_{BET}^a / m^2 g^{-1}$	$V_{total}^b / cm^3 g^{-1}$	$V_{DR\ N_2}^c / cm^3 g^{-1}$	$V_{meso}^d / cm^3 g^{-1}$	$S_{CO_2}^e / m^2 g^{-1}$	$V_{CO_2}^f / cm^3 g^{-1}$
Raw-AC	111.19	0.043	0.034	0.009	551	0.2055
Ni-AC	308.36	0.147	0.123	0.024	338	0.1259
Fe-AC	314.24	0.171	0.127	0.044	473	0.1763
Zn-AC	351.88	0.174	0.141	0.033	395	0.1471

302 ^a S_{BET} = Surface area of carbon measured from N₂ adsorption at -196°C; ^b V_{total} = Total pore
 303 volume measured from N₂ adsorption -196 °C, at $p/p_0 = 0.995$; ^c $V_{DR\ N_2}$ = Micropore volume
 304 measured from N₂ adsorption at -196°C at $p/p_0 = 0.001-0.1$; ^d V_{meso} = Mesopore volume
 305 calculated from $V_{meso} = V_{total} - V_{DR\ N_2}$; ^e V_{CO_2} = Micropore volume measured from CO₂
 306 adsorption at 0°C; ^f S_{CO_2} = micropore surface area from CO₂ adsorption at 0°C.

307 3.2. Non-catalytic pyrolysis

308 Pyrolysis in the absence of catalyst was carried out at temperatures of 500, 600, and 700 °C
 309 in the second stage of the reactor to establish a baseline for examining the impact of catalysts
 310 on product yields and compositions. Product yields and compositions are shown in Figure 5.
 311 A summary of non-catalytic pyrolysis product yields in literature and this study is presented
 312 in Table 3. The variations in product yields and compositions observed in these studies can be

313 attributed to several factors such as the reactor configuration, types of plastic waste and their
314 contaminants, which vary between the samples used by different researchers. Broadly
315 speaking, however, similar trends in product distribution and a shift to lighter hydrocarbon
316 products at higher temperatures were seen in both the current and literature non-catalytic
317 pyrolysis studies.



321 Figure 5. Product yields (a), gas composition (b), and oil composition (c) of non-catalytic
 322 pyrolysis at different catalyst bed temperatures.

323 Table 3. Summary of non-catalytic pyrolysis yields in literature and in this study.

Plastic mixture	Temperature / °C	Gas yield / wt%	Oil yield / wt%	Char / wt%	Reference
PP, PET, PS, LDPE, HDPE	500	31.7	66.6	1.7	[41]
	600	35.0	61.7	3.3	
	700	38.3	60.0	1.7	
	800	51.7	46.6	1.7	
PP, PET, PS, LDPE, HDPE	500	5	86	9	[42]
PP, PET, PS, HDPE, PVC	500	41.5	53	5.5	[43]
PP, PVC, HDPE, ABS, PS	500	15 - 25	70 – 80	10 – 15	[44]
PP, PET, PS, PE, PVC	500	34	65.2	0.8	[45]
PP, PET, PS, LDPE, HDPE, PVC	500	9.8	55.1	2.8	[46]
	550	24.5	57.1	5.9	
	600	43.3	43.2	7.6	
	650	88.8	20.5	--	
	700	68.9	18.4	--	
PP, PET, PS, LDPE, HDPE	500	28.6	66.7	4.8	This study
	600	53.2	42.5	4.3	
	700	74.8	20.0	5.2	

324 The gas composition (Figure 5(b)) primarily consisted of C₁ – C₄ hydrocarbons (71 – 84 wt%
 325 with respect to the total gas yields), along with minor quantities (16 – 29 wt%) of H₂, CO, and
 326 CO₂. The yields of CO and CO₂ increase at higher temperatures (≥600 °C), which can be
 327 attributed to PET decarboxylation reactions within the mixed plastic waste [47]. Furthermore,
 328 at reaction temperatures ≥600 °C, CO₂ interacted with plastic volatiles through hydrocarbon
 329 dry reforming reactions to produce CO and H₂ ($xCO_2 + C_xH_y \rightarrow 2xCO + \frac{y}{2}H_2$) [48]. H₂ was
 330 detected across all experimental conditions, but production remained relatively low
 331 compared to other components, with a maximum yield of only 0.31 wt% at 700 °C. Elevated
 332 temperatures during pyrolysis of plastics facilitated the cleavage of C-C bonds at arbitrary
 333 positions along the polymer or hydrocarbon chain, with an average paraffinic bond energy of
 334 83 kcal mol⁻¹, through a random chain scission mechanism [49]. Consequently, as the reaction
 335 proceeded, each remaining bond exhibited an equal likelihood of rupture, thereby generating
 336 a diverse range of hydrocarbons from C₁ to C₃₀₊ [41]. Concurrently, the cleavage of carbon-
 337 hydrogen (C-H) bonds was restricted, with an average paraffinic bond energy of 97 kcal/mol

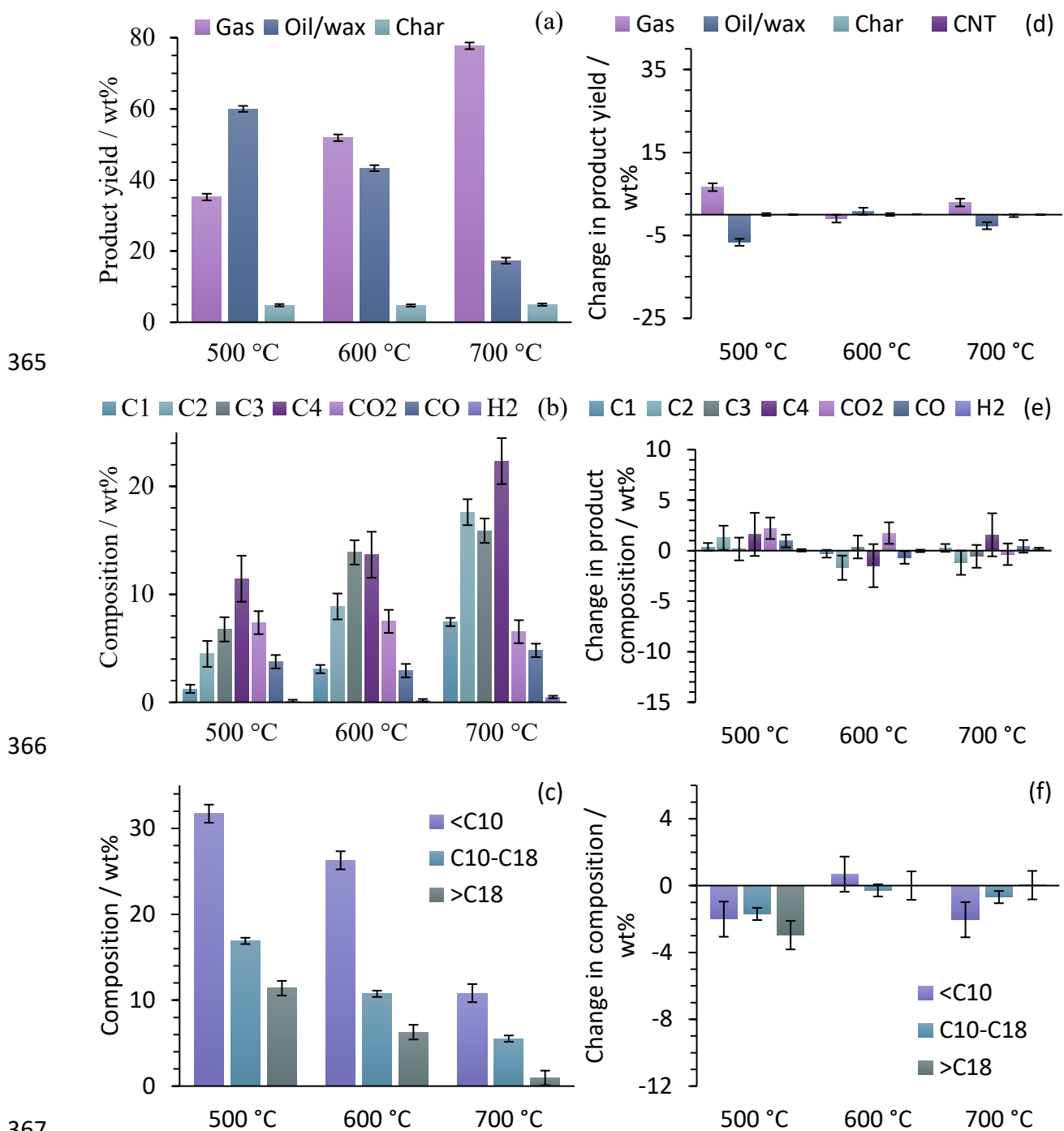
338 [49], resulting in a minimal release of H₂. The yields of light gases (C₁-C₄) increased significantly
339 with temperature. At 500 and 600 °C, the yield of C₃ compounds was higher than those of C₁
340 and C₂. However, as the temperature rises to 700 °C, the rate of increase of propane and
341 propylene was less pronounced compared to those of ethane and ethylene since there was a
342 higher conversion of heavier compounds (\geq C₃) into lighter gaseous molecules (C₁ and C₂) at
343 these conditions, as evidenced in Figure 5(b).

344 The liquid products (Figure 5(c)) consisted of a mixture of oil and wax, with their relative
345 proportions varying based on the processing conditions (i.e., 4.6 – 21.5 wt% with respect to
346 the total liquid products). Approximately 300 distinct compounds were identified, most of
347 which were present in relatively low concentrations. The light hydrocarbon fraction, which
348 corresponds to the carbon number range of naphtha [50], was predominant under all
349 examined conditions during non-catalytic pyrolysis. A reduction in all fractions was observed
350 with increasing temperature, which is attributable to the conversion of these compounds into
351 gaseous hydrocarbons via thermal cracking reactions. The main change in the oil products
352 with operating temperature was the marked decrease in the wax content, significantly
353 decreased as the pyrolysis temperature increased. The mass percentage of wax with respect
354 to the total oil yield was 21.5 wt% at 500 °C, which decreased to 14.5 wt% at 600 °C. With a
355 subsequent increase to 700 °C, the wax fraction was further reduced to a negligible 4.6 wt%.

356 *3.3. Catalytic pyrolysis*

357 *3.3.1. Raw AC*

358 The Raw-AC exhibited moderate catalytic effects, with product yields displayed in Figure 6.
359 Contrasting with non-catalytic pyrolysis, the Raw-AC catalysed process at 500 °C yielded a
360 lower oil/wax output (60 wt% vs. 67 wt%) and a higher gas production (35 wt% vs. 29 wt%).
361 Upon increasing the temperature to 600 °C, the differences between both processes became
362 negligible. At 700 °C, the gas yield from Raw-AC catalysed pyrolysis surpassed that of the non-
363 catalytic run, reaching 78 wt% compared to 75 wt%. These findings revealed that Raw-AC may
364 exert a small catalytic influence on product yields at low and high temperatures.



367
 368 Figure 6. Product yields (a), gas composition (b), and oil composition (c) of pyrolysis-catalysis
 369 using Raw AC at different catalyst bed temperatures. (d) – (f) Analogous plots showing the
 370 wt% change in product yields and compositions versus the non-catalytic pyrolysis stage-only
 371 values presented in Figure 5.

372 The influence of Raw-AC on gas composition at 500 °C, as illustrated in Figure 5.8(a), was
 373 evident in the enhanced CO₂ production, yielding 7.38 wt% compared to 5.15 wt% in the non-
 374 catalysed process. This increase may stem from minor oxidation reactions facilitated by the

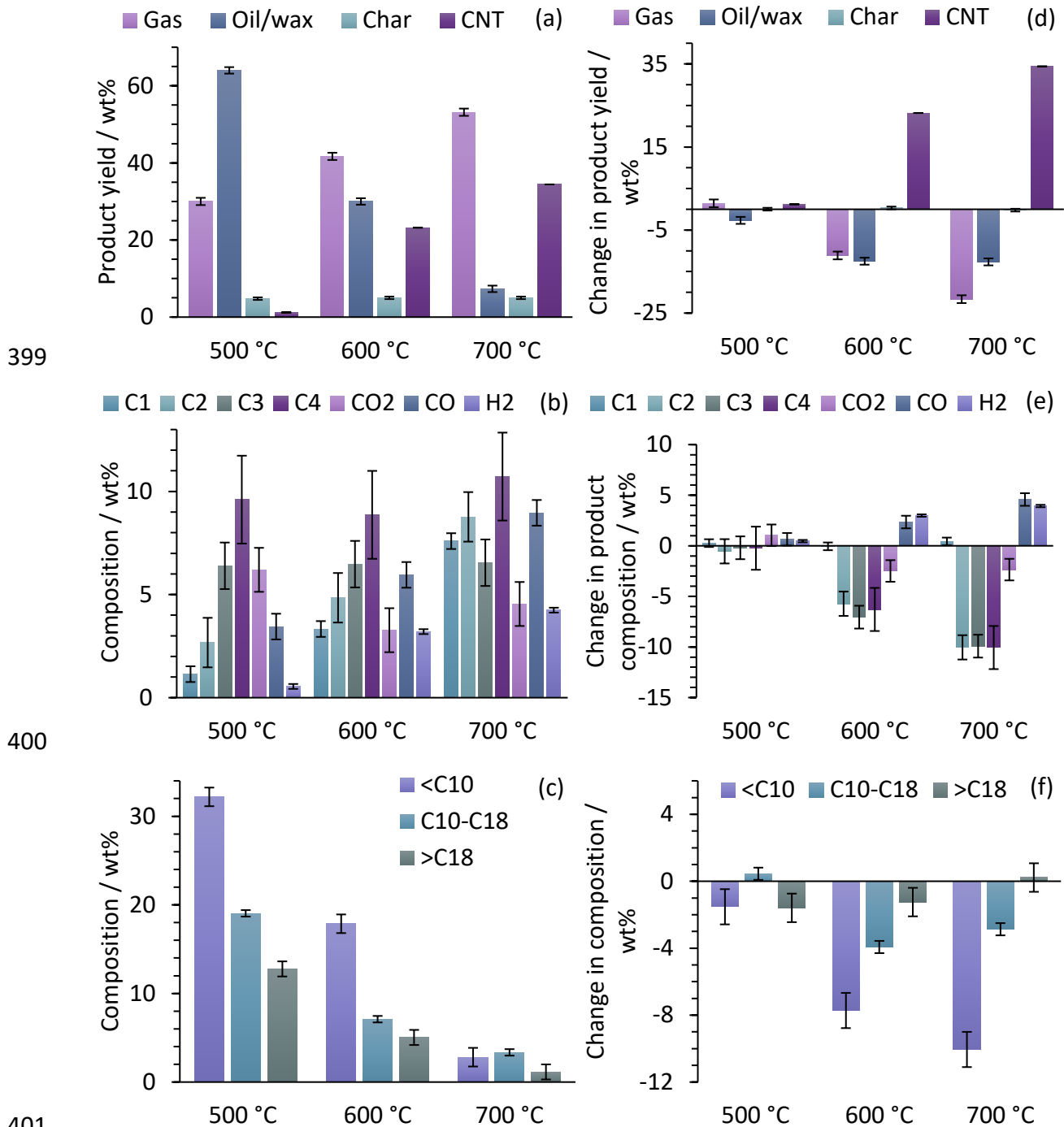
375 AC, as a similar marginal increment was observed across all AC-catalysed runs at low
376 temperature (500 °C). At 600 °C, the gas composition results corresponded with the yield
377 findings, with no substantial differences in product formation, except for CO₂, which rose
378 from 5.76 wt% to 7.50 wt%.

379 Regarding oil/wax composition (Figure 5.8(b)), all results lied within the experimental error
380 margins; thus, no significant differences in liquid product compositions were discernible
381 between Raw-AC catalysed pyrolysis and non-catalytic pyrolysis across the investigated
382 temperature range.

383 *3.3.2. Nickel-incorporated AC*

384 Reports of catalytic cracking of short chain alkanes in the literature suggest a possible
385 sequence for the catalysis process: volatile hydrocarbons undergo dissociative chemisorption
386 on the nickel surface, forming adsorbed reactive hydrocarbon fractions (e.g., methyl and
387 methylene radicals) which can then participate in subsequent reactions [51]. The subsequent
388 transformations involve the rearrangement of carbon atoms on the nickel particle surface and
389 yields gaseous products (e.g., C₁-C₄, and H₂) and solid carbon.

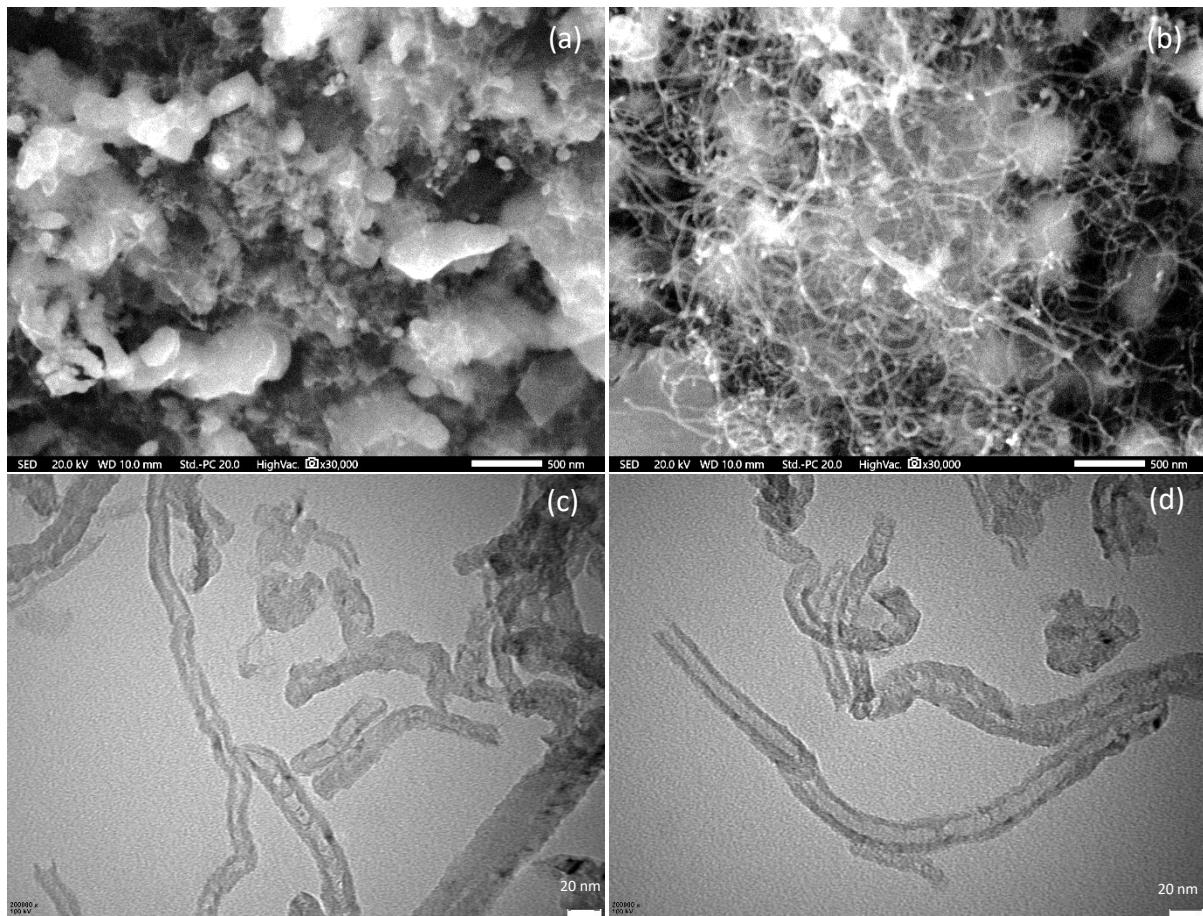
390 The production of gaseous and oil/wax compounds (Figure 7(a)) demonstrated a similar
391 pattern in response to increasing temperatures as the non-catalytic pyrolysis process.
392 However, at 600 °C, the gas yield was lower than that obtained from the non-catalytic
393 experiments (42 wt% compared to 53 wt%). The oil yield also decreased (with 30 wt% in
394 contrast to 43 wt% during non-catalytic pyrolysis). This phenomenon can be attributed to the
395 generation of carbon CNTs on the catalyst surface, as their formation occurs at the expense
396 of gaseous and liquid byproducts. Figure 8 presents a comparison of the Ni-AC catalyst surface
397 before and after pyrolysis at 600 °C, clearly showing the formation of CNTs as an entangled
398 array of narrow “line like” features. The diameters of the CNTs were approximately 30 nm.



402 Figure 7. Product yields (a), gas composition (b), and oil composition (c) of pyrolysis-catalysis
 403 using Ni-AC at different catalyst bed temperatures. (d) – (f) Analogous plots showing the
 404 wt% change in product yields and compositions versus the non-catalytic pyrolysis stage-only
 405 values presented in Figure 5.

406 As illustrated in Figure 7(a), temperatures exceeding 600 °C promoted CNT formation. The
 407 nickel particles in the AC serve as catalysts for CNT growth by promoting the breakdown of
 408 hydrocarbon molecules and enabling the rearrangement of carbon atoms into a filamentous

409 nanotube configuration [52]. Nickel promotes the cleavage of C-H bonds [53] which can result
410 in subsequent reactions such as functionalisation, rearrangement, or coupling reactions. The
411 high formation of carbon nanotubes promoted by Ni-AC could be explained by the enhanced
412 C-H cleavage which leads to coupling reactions in which new C-C bonds are formed and
413 rearranged into CNTs. The CNT yield increased from a negligible 1.2 wt% to 23.2 wt% upon
414 increasing the temperature from 500 to 600 °C and continued to rise to 34.4 wt% at 700 °C.



415
416 Figure 8. SEM comparison of fresh (a) and spent (b) Ni-AC, and TEM images (c-d) showing
417 the morphology and size of the synthesized carbon nanotubes.

418 At 700 °C, CNT synthesis occurred at the expense of the liquid portion of the products as well
419 as the gaseous fraction, as evidenced by the significantly reduced gas and oil production
420 versus the Raw-AC, 53 and 7.3 wt% down from 78 and 20 wt%, respectively. This implies
421 consumption of the thermal products produced in the first stage by the second catalytic stage
422 to form CNTs.

423 The production of C_1 (Figure 7(b)) demonstrated a consistent positive correlation with
424 temperature and showed a significant increase when the temperature is increased from 600

425 to 700 °C, resulting in the yield more than doubling from 3.3 wt% to 7.6 wt%. This also
426 significantly exceeded the yield seen from the output of the non-catalytic pyrolysis or in the
427 Raw-AC case, implying the change results from the Ni-AC catalysing a reaction. The yields of
428 ethane and ethylene followed a comparable increasing trend with temperature, while
429 maintaining consistent proportions relative to one another, but now with lower overall
430 production than the non-catalytic benchmark. Conversely, the production of propane and
431 propylene remained stable across the entire temperature range examined. These
432 observations imply that the primary thermal cracking of long-chain hydrocarbons led to an
433 enhanced generation of lighter molecules such as C₁, and C₂ compared to C₃. The production
434 of C₁ and C₂ compounds may also be favoured due to secondary dehydrogenation reactions
435 facilitated by the Ni-AC catalyst in conjunction with the temperature conditions. As a result,
436 it can be inferred that the Ni-AC catalyst exhibited high selectivity for C₁ and C₂ compounds
437 over C₃. A similar conclusion can be drawn for C₄ compounds, which displayed a similar
438 variability as C₃ compounds. The yield of CO₂ exhibited minor fluctuations within the range of
439 3.3 wt% to 6.2 wt%. Conversely, CO production demonstrated a consistent increase, nearly
440 doubling for each 100 °C temperature increment. Specifically, CO yield increased from 3.5
441 wt% to 6 wt% as temperature rose from 500 to 600 °C, and further augmented to 9 wt% at
442 700 °C. This behaviour can be attributed to the catalytic influence of nickel particles, which
443 promote Boudouard and hydrocarbon reforming reactions at elevated temperatures (>600
444 °C) [48]. The Boudouard reaction generates CO through the combination of carbon and CO₂,
445 while the reforming reaction transforms CO₂ and hydrocarbons into CO and H₂. These
446 mechanisms also adduce the enhanced production of H₂, which markedly increases from 0.5
447 wt% to 3.2 wt% upon increasing the temperature from 500 to 600 °C, and subsequently to
448 4.2 wt% at 700 °C. Although the H₂ yield may appear comparatively low, the volume
449 percentage of H₂ in the gaseous product mixture at 600 and 700 °C constituted 62.1 and 57.7
450 vol%, respectively. It is important to note that these reactions are not prominent at 500 °C,
451 meaning that temperatures of around 600 °C or higher are required to optimise H₂ and CO
452 production. The mixture of these gases, referred to as syngas, is an important commercial
453 product due to its role as a precursor for numerous industrial chemicals (e.g., alcohols, olefins,
454 and ammonia) through advanced chemical manufacturing processes such as the Fischer-
455 Tropsch synthesis [54].

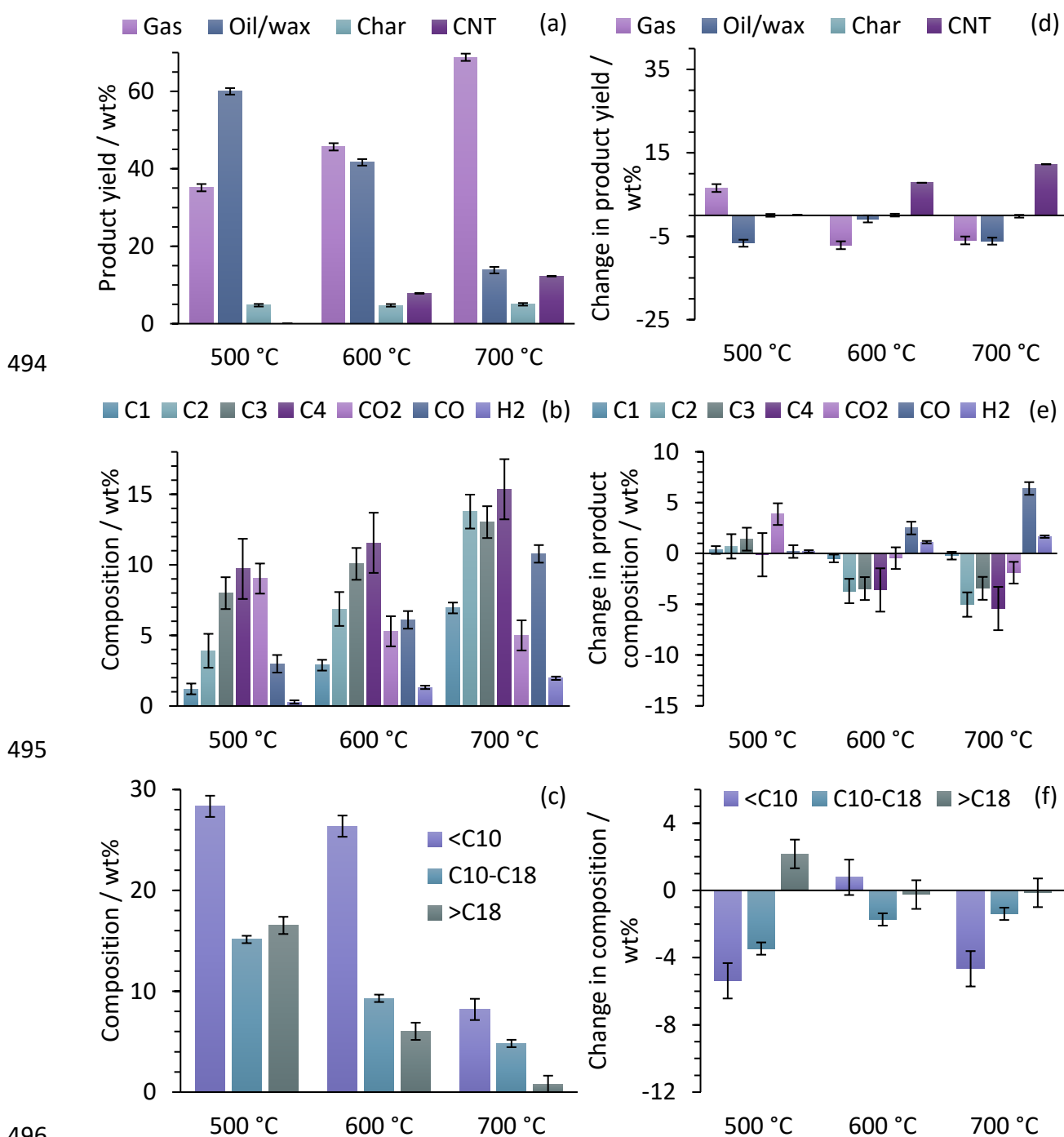
456 As in the case of non-catalytic experiments, a consistent decrease in oil/wax yields was
457 observed, maintaining relatively stable proportions among the three liquid hydrocarbon
458 fractions, as illustrated in Figure 7(c). However, a significant reduction in the light fraction
459 (<C₁₀) occurred at 700 °C. The relative proportion of the light fraction to the total oil yield
460 exhibited a minor increase from 50.3% at 500 °C to 59.5% at 600 °C, followed by a drastic
461 decline to 38.5% at 700 °C. This indicates that at elevated temperatures (≥ 700 °C), the
462 products favoured by the Ni-AC catalyst, such as CO, H₂, and CNTs, were predominantly
463 generated at the expense of the light oil fraction.

464 *3.3.3. Iron-incorporated AC*

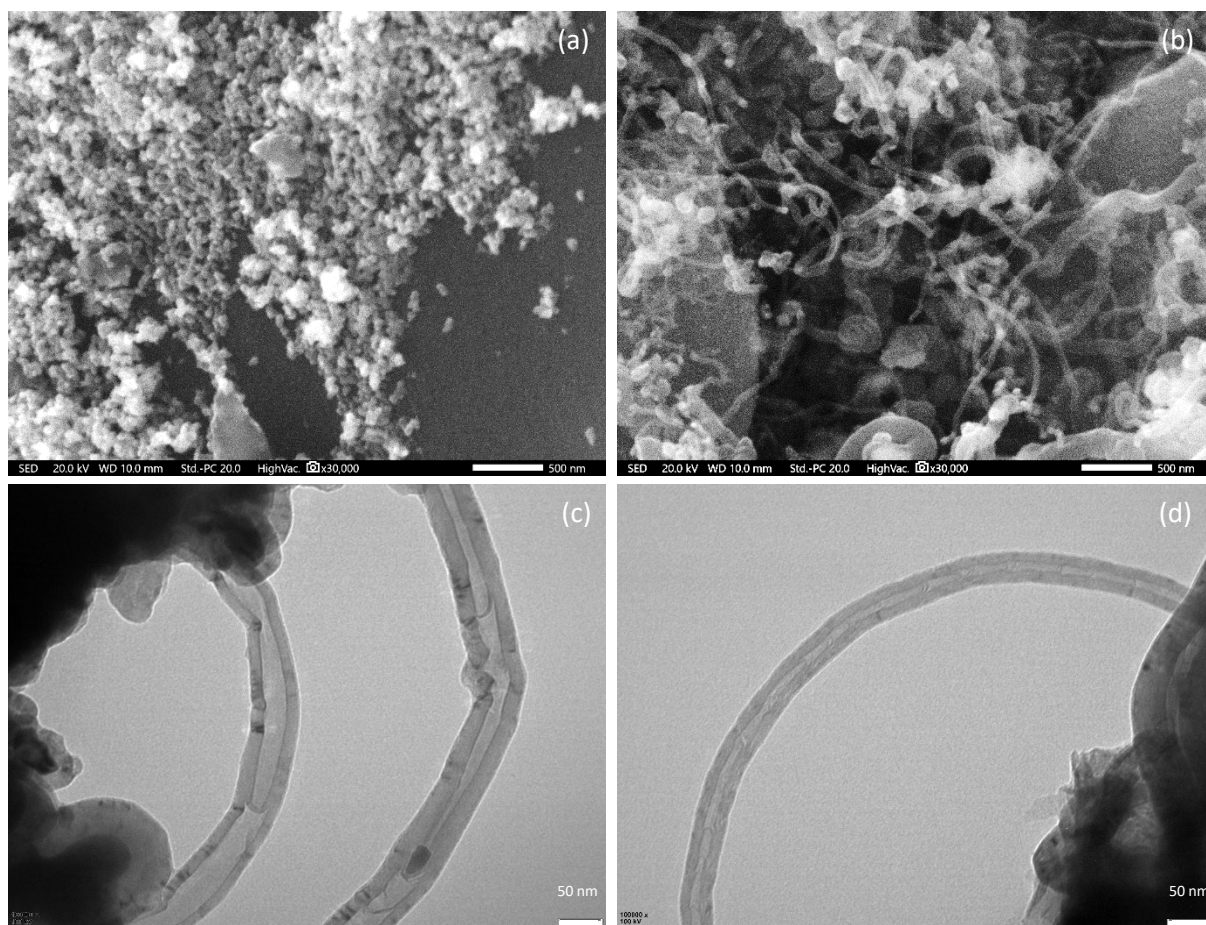
465 The product yields from catalytic pyrolysis using Fe-AC are presented in Figure 9. When
466 comparing the outcomes of the non-catalytic runs to those employing Fe-AC, the oil/wax
467 yields at 500 °C were slightly lower (60 wt% vs. 66.6 wt%), while the gas yield was higher by a
468 similar magnitude (28.6 wt% vs. 35.1 wt%). However, at 600 °C, the oil/wax yields remained
469 practically unchanged, but the gas yield declined to 45.7 wt% in the presence of Fe-AC
470 compared to 52.8 wt% in non-catalytic runs. Under these conditions, the CNT yield
471 experienced a substantial increase (from 0.1 wt% at 500 °C to 7.8 wt% at 600 °C), suggesting
472 that CNT formation at 600 °C primarily occurred at the expense of gaseous compounds. This
473 behaviour became more pronounced at 700 °C, with both liquid and gas yields decreasing by
474 approximately 6 wt% compared to non-catalytic runs. The lower gas yields, particularly at
475 elevated temperatures (600-700 °C), can be explained by the shift in product distribution
476 towards CNTs, as more carbon is consumed from the plastic volatiles for the growth of CNTs
477 instead of forming gaseous hydrocarbons. The yield of CNTs was negligible at 500 °C;
478 however, as the temperature rose to 600 and 700 °C, the CNT formation increased to 7.8 wt%
479 and 12.27 wt%, respectively. Figure 10 shows a comparison of the Fe-AC catalyst surface
480 before and after pyrolysis, illustrating the formation of carbon nanotubes, which had a
481 diameter of approximately 60 nm.

482 The high production of CO₂ at 500 °C (Figure 9(b)) may be ascribed to a minimal extent of
483 carbon oxidation within the AC. This is corroborated by the slightly increased yields of CO₂
484 (1.7 wt% on average) observed in the AC-catalysed experiments compared to their non-
485 catalytic counterparts. However, with rising temperatures and considering the restricted
486 oxygen presence in the plastic sample, the formation of CO₂ gradually shifted toward CO. The

487 CO yield notably increased at higher temperatures, with 3 wt% at 500 °C, 6.1 wt% at 600 °C,
 488 and 10.8 wt% at 700 °C. This occurrence can be explained by the catalytic influence of iron
 489 particles, which facilitate hydrocarbon reforming reactions, yielding CO and H₂. Consequently,
 490 the H₂ production significantly increased at high temperatures (0.28 wt% at 500 °C, 1.32 wt%
 491 at 600 °C, and 1.97 wt% at 700 °C). The substantial H₂ release is directly correlated with the
 492 formation of CNTs, as the cleavage of C-H bonds is intensified, and a substantial supply of
 493 carbon atoms becomes accessible for CNT synthesis.



497 Figure 9. Product yields (a), gas composition (b), and oil composition (c) of pyrolysis-catalysis
498 using Fe-AC at different catalyst bed temperatures. (d) – (f) Analogous plots showing the
499 wt% change in product yields and compositions versus the non-catalytic pyrolysis stage-only
500 values presented in Figure 5.



501
502 Figure 10. SEM comparison of fresh (a) and spent (b) Fe-AC, and TEM images (c-d) showing
503 the morphology and size of the synthesized carbon nanotubes.

504 The yields of C_1 - C_4 gases (Figure 9(b)) exhibited a similar increase with temperature, as
505 observed in prior experiments. As the temperature increased from 500 to 600 °C, their
506 relative rates of increase were analogous, but ethane and ethylene production at 700 °C
507 surpassed that of other hydrocarbon gases. This implies that the catalytic cracking of high
508 molecular weight hydrocarbons in the presence of Fe-AC at 700 °C was intensified, and the
509 catalyst exhibited heightened selectivity toward C_2 compounds, of which the majority (73%
510 of C_2 compounds) was ethylene. The formation of light paraffins and olefins is favoured due
511 to the additional hydrogenation reactions and C-H bond cleavage facilitated by the catalyst.

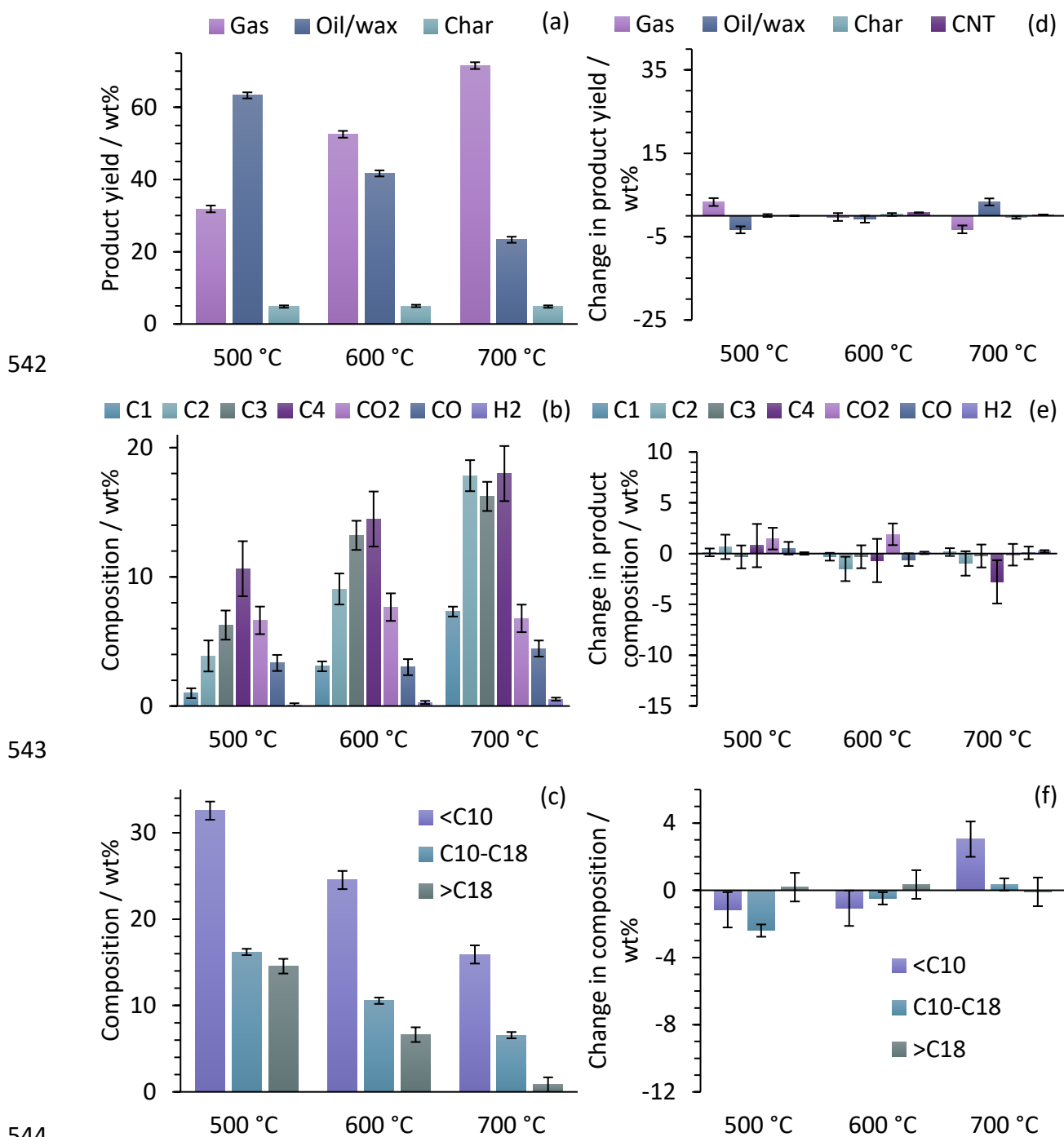
512 The high yield of the light oil fraction at 600 °C (Figure 9(c)) supports previous assertions that
513 CNT formation predominantly arises from the gaseous products. Conversely, at 700 °C, a
514 substantial decline in the light oil fraction was detected, indicating a higher catalytic
515 selectivity for H₂, CO, light hydrocarbon gases, and CNT formation over light oil products.

516 *3.3.4. Zinc-incorporated AC*

517 The product yields from Zn-AC catalysed pyrolysis (Figure 11(a)) were similar to those
518 obtained from non-catalytic pyrolysis. At a temperature of 500 °C, the oil/wax yield reached
519 63 wt%, while the yield for non-catalytic pyrolysis was marginally higher at 67 wt%.
520 Concurrently, the gas yield was 31.9 wt%, compared to a slightly lower yield of 29 wt% for the
521 non-catalytic pyrolysis. At 600 °C, the discrepancies in product yields between both processes
522 became insignificant. At 700 °C, the Zn-AC catalysed pyrolysis produced an oil/wax yield of 23
523 wt%, which is 17 % higher than the non-catalytic counterpart. The corresponding Zn-AC gas
524 yield, however, was 72 wt%, constituting a 4 % decrease compared to the non-catalytic runs.
525 Overall, the Zn-AC catalyst exhibited a subtle inclination towards gas yield at 500 °C, an
526 inconsequential effect at 600 °C, and a slight preference for oil/wax formation over gaseous
527 products at 700 °C. Nonetheless, the distinctions between the catalytic and non-catalytic
528 processes remained relatively mild, and the catalytic activity of Zn particles on AC was
529 significantly lower than that of Ni-AC and Fe-AC. Carbon deposition on the catalyst surface
530 was found to be negligible (0.3 – 0.7 wt%), therefore, these results were omitted from Figure
531 11(a).

532 The compositions of gas and oil/wax products are illustrated in Figure 11(b). The most notable
533 variation in gas compositions lied in the CO₂ yield at lower temperatures (<700 °C), where the
534 presence of the Zn-AC catalyst led to an increase compared to the non-catalytic pyrolysis runs.
535 At 500 °C, the CO₂ production for the catalytic process was 6.6 wt%, whereas the non-catalytic
536 process produced 5.1 wt%. This difference persisted at 600 °C, with the catalysed CO₂ yield at
537 7.6 wt% and the non-catalytic yield at 5.7 wt%. However, the CO₂ yields for both processes
538 converged at 700 °C. The remaining gas components exhibited negligible differences at
539 corresponding temperatures in comparison to the non-catalytic pyrolysis, as they fell within
540 the respective experimental error margins.

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Figure 11. Product yields (a), gas composition (b), and oil composition (c) of pyrolysis-catalysis using Zn-AC at different catalyst bed temperatures. (d) – (f) Analogous plots showing the wt% change in product yields and compositions versus the non-catalytic pyrolysis stage-only values presented in Figure 5.

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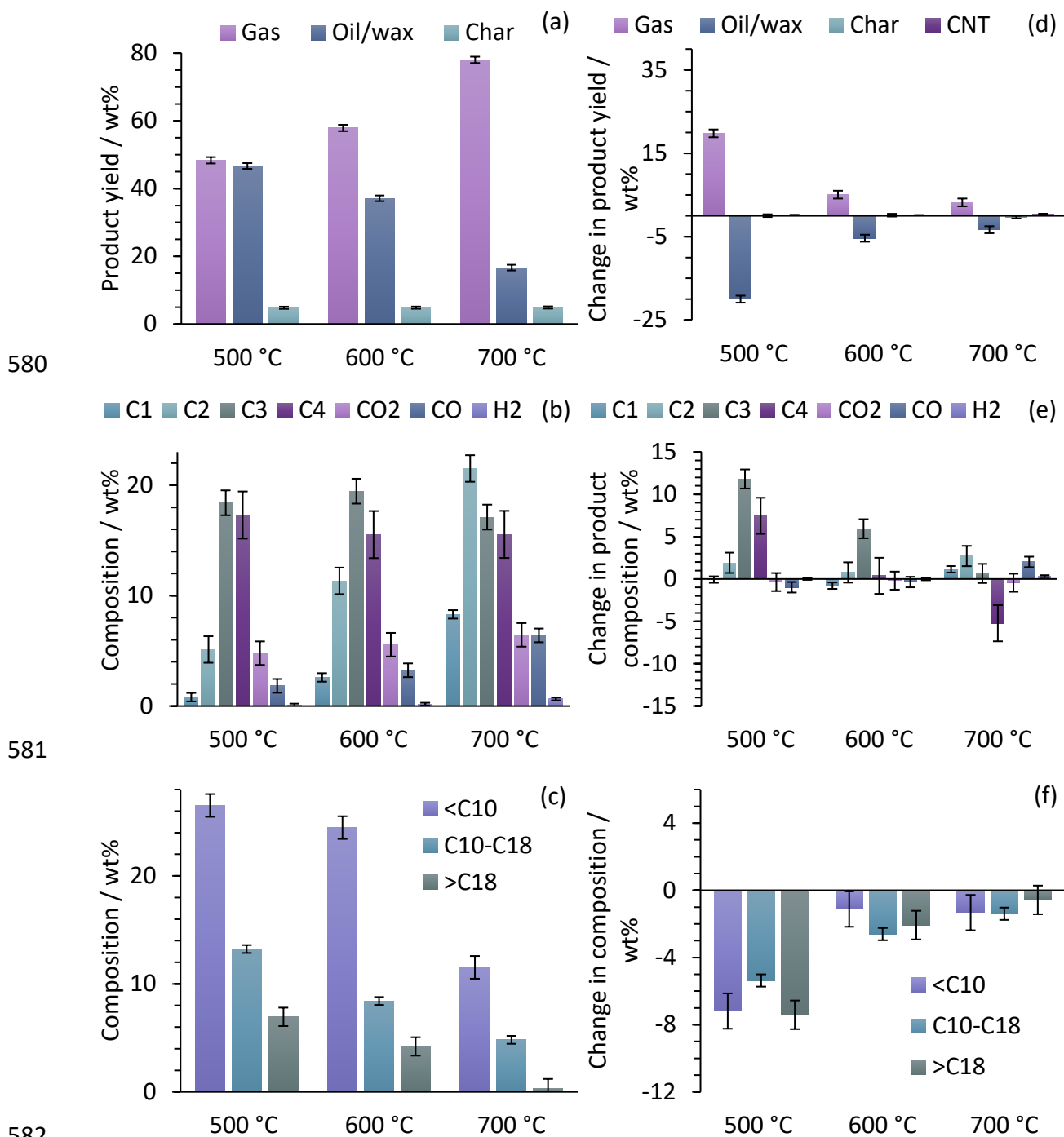
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As shown in Figure 11(c), the most pronounced difference in the oil/wax composition at 500 °C involves the medium oil fraction, which was marginally lower in the Zn-AC catalysed process compared to the non-catalytic process (16.2 wt% vs. 18.6 wt%). This indicated that

552 the reduction in the medium oil fraction primarily contributed to the overall decrease in liquid
553 product yield observed in Figure 11(a), as some of this fraction was converted into gaseous
554 products, consequently resulting in a modest increase of the gas yield. At 600 °C, no
555 statistically significant disparities in oil/wax composition were detected between the
556 catalysed and uncatalyzed experiments, which is consistent with the negligible differences
557 observed in product yields at this temperature. However, upon increasing the temperature
558 to 700 °C, the light oil fraction exhibits a higher value (15.9 wt% vs. 12.86 wt%), accounting
559 for the higher oil/wax yield and lower gas yield at this elevated temperature.

560 *3.3.5. Zeolite H-ZSM-5*

561 Zeolite H-ZSM-5 demonstrated a significant impact on the product yield distribution,
562 favouring the production of lighter gaseous compounds, as shown in Figure 12. When
563 comparing the catalytic process to non-catalytic pyrolysis at 500 °C, the H-ZSM-5 zeolite
564 promoted a notable decrease in the oil/wax yield from 66.6 wt% to 46.7 wt%, alongside a
565 concurrent increase in the gas yield from 29 wt% to 48 wt%. The observed outcomes
566 demonstrate the effectiveness of the H-ZSM-5 zeolite in cleaving long-chain hydrocarbons
567 present in plastic waste volatiles into lighter gaseous compounds at moderately low
568 temperatures. This behaviour can be attributed to the distinct physicochemical characteristics
569 of the H-ZSM-5 zeolite, which exhibits pronounced acidity and high shape selectivity [55]. The
570 acidic sites of the zeolite facilitate the scission of C-C bonds within long-chain hydrocarbon
571 molecules, whereas its well-organized pore structure promotes diffusion and enables the
572 selective conversion of specific hydrocarbons [56, 57]. At 600 °C, the differences between the
573 catalysed and non-catalysed processes became slightly less evident, but the influence of H-
574 ZSM-5 zeolite on product yields remained discernible. The oil/wax yield reduced from 43 wt%
575 to 37 wt%, while the corresponding gas yield exhibited an increase from 53 wt% to 58 wt%.
576 Upon further increasing the temperature to 700 °C, H-ZSM-5 catalysis lead to an additional
577 decrease in oil/wax yield to 16.6 wt%, and an increase in gas yield to 78 wt%. These findings
578 demonstrate that the H-ZSM-5 catalyst exerts a substantial impact on the distribution of
579 product yields.



582 Figure 12. Product yields (a), gas composition (b), and oil composition (c) of pyrolysis-
 583 catalysis using zeolite H-ZSM-5 at different catalyst bed temperatures. (d) – (f) Analogous
 584 plots showing the wt% change in product yields and compositions versus the non-catalytic
 585
 586 pyrolysis stage-only values presented in Figure 5.

587 The carbon accumulation on the catalyst was minimal (<0.5 wt%), demonstrating the efficacy
 588 of the two-stage reactor design in averting catalyst deactivation due to excessive carbon
 589 deposition, which can result in pore obstruction.

590 Although the differences in liquid and gaseous product yields (catalytic vs. non-catalytic
591 pyrolysis) were less pronounced at high temperatures (>600 °C), with differences of
592 approximately ± 5 wt%, the product quality was significantly enhanced, favouring lighter
593 compounds over heavier ones. The gas product composition depicted in Figure 12(b) shows
594 that at 500 °C, H-ZSM-5 zeolite significantly enhanced C₃ compounds yield from 6.6 wt% to
595 18.4 wt% (of which 78.3% is propylene). Furthermore, C₄ gas production notably increased
596 from 9.8 wt% to 18.4 wt%, ethane and ethylene production slightly rose from 3.2 wt% to 5.1
597 wt%, and CO yield moderately decreased from 2.8 wt% to 1.8 wt%. The primary product
598 resulting from the conversion of volatiles into gases at low temperature was predominantly
599 propylene, a valuable monomer in the chemical manufacturing industry. As the temperature
600 increased to 600 °C, the only significant difference was observed in the C₃ compounds, with
601 propane and propylene production increasing from 13.5 wt% to 19.5 wt% (of which 91.2% is
602 propylene), and the remaining products staying within the experimental error. This
603 observation corresponds with the approximately 5.5 wt% gas yield increase at this
604 temperature, indicating that H-ZSM-5 zeolite selectively converted liquid products into
605 propane and propylene. These outcomes are consistent with findings reported in the
606 literature, where high conversion of plastic waste volatiles into propylene has been achieved
607 using zeolite H-ZSM-5 catalyst [58-60]. At 700 °C, H₂ production doubles to 0.64 wt%, CO and
608 C₁ yields moderately rise from 4.4 wt% to 6.4 wt% and from 7.1 wt% to 8.3 wt%, respectively.
609 Owing to enhanced thermal cracking, C₄ compound production declined from 21 wt% to 16
610 wt%, while C₂ compounds yield increased from 19 wt% to 22 wt%.

611 The liquid product composition was significantly influenced by the H-ZSM-5 catalyst, as
612 illustrated in Figure 12(c). All oil/wax fraction yields at 500 °C were lower than those observed
613 in non-catalytic pyrolysis. At 500 °C, the light fraction increased from 50.6 wt% to 56.8 wt%
614 (with respect to the total liquid product yield) in the presence of H-ZSM-5 zeolite, while the
615 medium fraction remained relatively constant (around 28%), and the heavy wax decreased
616 from 21.5% to 14.9%. At 600 °C, no significant differences were observed in light oil yields,
617 which were approximately 25 wt%. At 700 °C, the relative amount of light fraction with
618 respect to the total oil yield increased from 64.3 wt% to 69.1 wt%, while the medium fraction
619 and heavy wax decreased from 31.1% to 28.9%, and 4.6% to 2.1%, respectively. The H-ZSM-5
620 catalysed pyrolysis yielded a higher proportion of light oil and a lower proportion of heavy

621 wax at all three temperatures compared to non-catalytic pyrolysis. The gas and liquid product
622 compositions support the notion that H-ZSM-5 zeolite enhances the production of light
623 molecules at the expense of heavier ones. This is achieved through a series of complex
624 reactions, including cracking, cyclization, and isomerization, occurring at the zeolite's active
625 sites [61]. As a result, the overall yield of heavy wax is substantially reduced, demonstrating
626 the effectiveness of H-ZSM-5 zeolite in cracking long-chain hydrocarbons, particularly at
627 relatively low temperatures during plastic waste pyrolysis.

628 *3.3.6. Catalyst performance comparison*

629 A higher catalytic activity was observed for Ni-AC, Fe-AC, and H-ZSM-5 in comparison to Zn-
630 AC and Raw AC. The influences of Ni-AC and Fe-AC catalysts on the process displayed
631 analogous patterns, with the production of H₂, CO, and CNTs (exclusively identified with Ni-
632 AC and Fe-AC) rising as the temperature increases. Regarding product yields, the process was
633 similar for both catalysts at 500 °C; however, as the temperature increases, the yields of
634 gaseous and liquid products catalysed by Ni-AC progressively decreased, concomitant with an
635 increase in CNT production. An intensified formation of CNTs was attained using the Ni-AC
636 catalyst compared to those obtained with Fe-AC (1.2 wt% vs. 0.1 wt% at 500 °C, 23.2 wt% vs.
637 7.8 wt% at 600 °C, and 34.4 wt% vs. 12.3 wt%). Consequently, it can be inferred that Ni-AC is
638 more effective at producing high yields of CNTs (and the associated increase in H₂ yields). This
639 finding contrasts with other studies in the literature. For instance, Liu et al. [62] compared the
640 effects of iron, nickel, and cobalt on metal oxide supports as catalysts for CNT synthesis from
641 methane at 900 °C, concluding that iron produces higher quality CNTs. This was attributed to
642 iron's high carbon solubility, which impacts CNT nucleation and growth through various
643 mechanisms, such as: (i) enhancing carbon supply for CNT development; (ii) generating a
644 higher concentration force to expedite CNT formation; (iii) influencing CNT cap structure
645 nucleation; and (iv) dictating the specific CNT variety produced [62, 63]. Acomb et al. [31]
646 compared the effects of several metal oxides including iron alumina and nickel alumina on
647 CNT formation from plastic waste at 800 °C, and also found iron to be more effective (i.e.,
648 higher yields) than nickel. The higher carbon solubility of iron compared to that of nickel was
649 determined to be responsible for the higher CNT yields. Moreover, the interactions between
650 the metal and the catalyst support were found to play a crucial role in CNT formation, with
651 excessively strong interactions inhibiting production and weak interactions leading to metal

652 sintering and low yields [31]. Since iron has a higher carbon solubility than nickel, there may
 653 be a stronger interaction between the AC support and iron particles, thus hindering CNT
 654 formation. Nonetheless, this interaction is not excessively strong, as Fe-AC still allowed some
 655 CNT formation, albeit in lower amounts than those obtained using Ni-AC. It can be concluded
 656 that nickel and iron particles exhibit an intermediate interaction with the AC, enabling carbon
 657 nanotube formation. These results demonstrate that AC is a suitable support for nickel and
 658 iron catalysts in facilitating plastic waste pyrolysis.

659 The surface areas and pore volumes of spent Ni-AC and Fe-AC catalysts are shown in Table 4.
 660 The mesopore volume (V_{meso}) of Ni-AC increased significantly from 0.024 to 0.156 $\text{cm}^3 \text{g}^{-1}$,
 661 while the micropore volume ($V_{\text{DR N}_2}$) was reduced from 0.123 to 0.055 $\text{cm}^3 \text{g}^{-1}$. This resulted
 662 in a total pore volume increase of 42.8% (from 0.147 to 0.210 $\text{cm}^3 \text{g}^{-1}$). After reaction, the
 663 isotherm (Fig. S2) changes from Type I into Type II/IV isotherms, suggesting that the gas reacts
 664 with carbon in Ni-AC catalyst and widens the pores, creating more mesopores at an expense
 665 to micropores. Compared to the fresh catalyst, the BET surface area (S_{BET}) of Ni-AC decreased
 666 from 308.36 to 129.23 $\text{m}^2 \text{g}^{-1}$ after pyrolysis. This is explained by the formation of CNTs, which
 667 can block pores and reduce the accessible surface area on the catalysts.

668 The gas-solid reactions with Fe-AC significantly consume the carbon in the catalyst and
 669 decrease the S_{BET} (from 314.24 to 59.22 $\text{m}^2 \text{g}^{-1}$), V_{total} (from 0.171 to 0.083 $\text{cm}^3 \text{g}^{-1}$), and $V_{\text{DR N}_2}$
 670 (from 0.127 to 0.027 $\text{cm}^3 \text{g}^{-1}$). The isotherm (Fig. S3) changes from type I/II into type II
 671 isotherm after pyrolysis, which also indicates the reaction between carbon and gas. The
 672 evident changes in pore volumes for both catalysts are a consequence of the restructuring of
 673 the catalyst carbon matrix during CNT growth. The more pronounced structural changes in
 674 Ni-AC compared to Fe-AC suggest that Ni is a more active catalyst for CNT growth in activated
 675 carbon supports.

676 Table 4. Surface area and pore volume of catalysts after pyrolysis at 700 °C.

Catalyst	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{total}} / \text{cm}^3 \text{g}^{-1}$	$V_{\text{DR N}_2} / \text{cm}^3 \text{g}^{-1}$	$V_{\text{meso}} / \text{cm}^3 \text{g}^{-1}$
Ni-AC spent	129.23	0.210	0.055	0.156
Fe-AC spent	59.22	0.083	0.027	0.056

677 Utilizing Zn-AC and Raw-AC catalysts resulted in a marginal decrease in liquid product yields
 678 and a slight increase in gas yields compared to non-catalytic pyrolysis. However, these

679 catalysts exhibited limited efficacy since the product yields were similar to non-catalytic
680 pyrolysis when considering the experimental error range. Raw-AC displayed a slightly higher
681 catalytic performance compared to Zn-AC, with moderately increased gas yields and reduced
682 oil/wax yields. At 700 °C, the most significant difference was noted, as Raw-AC achieved a gas
683 yield of 77.7 wt% while Zn-AC only reached 71.5 wt%. This discrepancy can be attributed to
684 the substantial reduction in surface area (from 551.4 to 394.7 m² g⁻¹) and porosity (from 0.206
685 to 0.147 cm³ g⁻¹) of Zn-AC after the wet impregnation method, whereas Raw-AC retains its
686 highly porous structure, providing access to internal active sites. Moreover, research has
687 suggested that temperatures exceeding 700 °C are necessary to sufficiently activate biochar
688 for pyrolysis or gasification processes [64-66]. Consequently, it can be inferred that Zn-AC was
689 not entirely activated at the temperatures examined in this study. Although the active sites
690 in Raw-AC exhibit much lower catalytic activity than those in Ni-AC and Fe-AC, the naturally
691 occurring metals present in the raw biochar become increasingly active as the temperature
692 intensifies, particularly at ≥ 800 °C [41].

693 The H-ZSM-5 catalyst displayed the most remarkable reduction in oil/wax yields and increase
694 in gas yields among all the catalysts examined, with these variations being significant across
695 all temperature ranges. Regarding oil/wax composition, H-ZSM-5 outperformed other
696 catalysts in converting heavy fractions to lighter counterparts. Moreover, H-ZSM-5 was the
697 most appropriate catalyst for monomer recovery, with ethylene and propylene yields
698 considerably higher than those observed with other catalysts (18 wt% and 16 wt% at 700 °C,
699 respectively). Ni-AC and Fe-AC also exhibited promising results, but with a markedly different
700 selectivity, with catalytic activities comparable to that of H-ZSM-5 but with selectivities
701 toward H₂, CO, and CNT production. Although all catalysts showed improved cracking at
702 elevated temperatures, H-ZSM-5 proved most effective at low temperature (500 °C).

703 For economic feasibility analysis and comparisons of the different catalysts' application,
704 various factors such as capital investments, maintenance costs, and scalability need to be
705 considered. However, these were all beyond the scope of this work, therefore, simple
706 comparisons on economic benefits can be based on the estimated values of key products.
707 According to 2024 forecasts, naphtha-range hydrocarbons are priced at approximately 0.64
708 USD kg⁻¹ [67, 68], while short multi-walled CNTs (> 92% purity) cost around 487 USD kg⁻¹ [69].
709 On a basis of 1 kg of plastic feed, the pyrolysis process for different catalysts would produce

710 the key product value presented in Table 5. For Raw-AC and Zn-AC, the main product was light
711 oil (produced at 500 °C), whereas for Ni-AC and Fe-AC, the key product were CNTs (produced
712 at 700 °C), assuming 100% generation efficiency.

713 Table 5. Comparison of key product value from different catalysts.

Catalyst	Light oil yield / kg	CNT yield / kg	Total key product value / USD kg ⁻¹ _{plastic}
Raw-AC	0.3171	--	0.203
Zn-AC	0.3255	--	0.208
Ni-AC	--	0.344	167.5
Fe-AC	--	0.123	59.9

714 The significant price disparity between light oil and CNTs likely stems from the high costs of
715 CNT production, extraction, purification, and classification, not accounted for in this study.
716 Moreover, the assumed 100% CNT generation efficiency is not guaranteed due to potential
717 amorphous carbon deposits on the catalysts. The results in Table 5 are intended for
718 comparative purposes only and do not reflect the actual revenue of an industrial-scale plant.
719 Such an assessment requires a dedicated technical and economic analysis, representing a
720 potential area for future research. Additionally, the study's products, particularly CNTs, need
721 further separation and processing before marketing, highlighting the need for additional
722 research into the separation and quality assessment of CNTs derived from plastic waste
723 pyrolysis.

724 4. Conclusions

725 In this study, a comprehensive analysis of the performance of various catalysts, including Ni-
726 AC, Fe-AC, Zn-AC, Raw AC, and H-ZSM-5, for the pyrolysis of plastic waste was conducted. The
727 investigation primarily focused on the product yield distribution, composition, and carbon
728 nanotube formation. The key findings are outlined below:

- 729 • The Ni-AC and Fe-AC catalysts demonstrated superior catalytic activity compared to
730 Zn-AC and Raw AC. Both Ni-AC and Fe-AC displayed similar trends with increasing
731 temperature, resulting in enhanced yields of H₂, CO, and CNTs.
- 732 • The Ni-AC catalyst was more efficient in producing CNTs, yielding significantly higher
733 amounts than those obtained using Fe-AC.

- 734 • The CNTs synthesized using Ni-AC and Fe-AC possessed diameters of approximately
735 30 nm and 60 nm, respectively. The results demonstrated that AC is an appropriate
736 support for nickel and iron catalysts, facilitating plastic waste pyrolysis.
- 737 • The Zn-AC and Raw-AC catalysts presented limited effectiveness compared to the
738 other catalysts. Raw-AC outperformed Zn-AC, with moderately enhanced gas yields
739 and reduced oil/wax yields.
- 740 • The H-ZSM-5 catalyst presented the most significant reduction in oil/wax yields and
741 increase in gas yields across all examined temperature ranges. It surpassed other
742 catalysts in converting heavy fractions into lighter counterparts and proved to be the
743 most suitable catalyst for monomer recovery, with markedly higher ethylene and
744 propylene yields. In contrast to the AC catalysts, syngas and CNTs are not produced.

745 Acknowledgements

746 This research was funded by the Mexican National Council of Humanities, Sciences, and
747 Technologies (CONAHCYT) via PhD studentship 2019–000021–01EXTF-00104. SEM, EDX, GC-
748 MS, and XRD analyses were provided by the Advanced Chemical and Materials Analysis
749 (ACMA) unit at Newcastle University. HHP was supported by the Royal Academy of
750 Engineering (Grant No: FF\1920\1\45), and The Royal Society (under Grant No:
751 ICA\R1\191220) United Kingdom.

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Citation on deposit: Martínez-Narro, G., Phan, H. H., Hassan, S., Beaumont, S. K., & Phan, A. N. (2024). Catalytic pyrolysis of plastic waste using metal-incorporated activated carbons for monomer recovery and carbon nanotube synthesis. *Journal of Environmental Chemical*

Engineering, 12(2), Article 112226. <https://doi.org/10.1016/j.jece.2024.112226>

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