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1 Effects of titania based catalysts on in-situ pyrolysis of *Pavlova* microalgae

2
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9 10 **ABSTRACT**

11 *Pavlova* microalga was pyrolysed in presence of titania based catalysts in a fixed bed reactor at
12 various temperatures. The effects of catalysts on *Pavlova* microalga pyrolysis was investigated.
13 A large fraction of the starting energy (~63-74 % daf) was recovered in the bio-oils when the
14 catalysts were used. The bio-oil yield was 20% higher in presence of Ni/TiO₂ (22.55 wt.%) at
15 500 °C. The High Heating Values of the produced bio-oils were in the range of ~35-37 MJ/kg
16 and suffered strong deoxygenation, with O content (% daf) diminished from 51 wt.% to ~9-12
17 wt.%. The ¹H Nuclear Magnetic Resonance and Gas Chromatography Mass Spectrometry
18 suggested that the titania catalysts enlarged the aliphatics and aromatic compounds and
19 decreased oxygenates in the bio-oils. Ni/TiO₂ had the greatest activity in increasing aliphatic
20 protons (60%) and decreasing coke formation. Its enhanced cracking activity was due to its
21 higher availability on the catalyst surface, compared to Co and Ce, and to strong interaction
22 between Ni and TiO₂ support. Despite the fact that the bio-oils were partially de-nitrogenated,
23 the N-content still represent a major limitation for their use as bio-fuels without further
24 upgrading.

25 **Keywords:** Bio-oil, *Pavlova*, Pyrolysis, deoxygenation, Catalyst, Titania

26 1. Introduction

27 Microalgae are promising feedstock for bio-fuels, chemicals, food, cosmetics and
28 healthcare and have been cultivated in open ponds or raceways as human and animal feed
29 supplements on an industrial scale [1-3]. Microalgae have several advantages over terrestrial
30 crops: (i) can grow in open water such as sea water and ponds or in photobioreactors on non-
31 arable lands ii) have higher lipid content (some up to 80 %) iii) do not compete with food crops
32 (iv) have higher CO₂ capture capacity and can remove and recycle nutrients from waste water
33 and flue gases [4-5]. Over the decades, different approaches for the production of bio-fuels from
34 microalgae have emerged, such as biogas from anaerobic digestion, biodiesel (from fatty acids),
35 hydrogen (from gasification) and bio-oils from liquefaction and pyrolysis [6,7]. Microalgae
36 contain three main components in varying amounts: lipids (3–50 wt%), carbohydrates (10–50
37 wt%) and proteins (6– 65 wt%).

38 Compared to more established routes such as algal fatty acids to biodiesel, the
39 thermochemical conversion of algae can advantageously convert completely the algal biomass,
40 which makes the process more attractive [5]. In recent years, pyrolysis of both lignocellulosic
41 and algal biomass has been widely investigated. Pyrolysis refers to thermal depolymerisation
42 or organics at moderate temperatures (400–600 °C) in absence of oxygen.

43 One of the most challenging barriers to the thermo-chemical conversion pathway is the
44 high moisture content of microalgae. A study indicates that mechanical dewatering prior a 2000
45 t/day microalgae catalytic pyrolysis facility, can produce 21.4 million gallons of biofuel per
46 year at a cost of \$1.49 per liter, which is similar to the gasoline cost range in Europe in 2016
47 (~1.2-1.7 \$ per liter, globalpetrolprices) [8] .

48 Pyrolysis of many algal species has been studied including *Nannochloropsis*, *Chlorella*,
49 *Tetraselmis*, *Isochrysis* and *Microcystis*. In a previous study, Miao et al. [9] performed the fast
50 pyrolysis of *Chlorella prothothecoides* and *Microcystis aeruginosa* species grown

51 phototrophically. They obtained bio-oil yields of 18% and 24% with HHVs of 30MJ/kg and
52 29MJ/kg, respectively. Belotti et al. [10] studied the pyrolysis of *Chlorella vulgaris* grown in
53 complete and nitrogen starved medium. They found that the fast pyrolysis of nitrogen starved
54 *Chlorella vulgaris* yielded 42.2% of bio-oil at 400 °C. The bio-oil produced from nitrogen
55 starved algae had higher amount of fatty acids and lower amount of nitrogenous species,
56 resulting in an improved quality.

57 Although pyrolysis is recently attracting rising interest for the producing of liquid fuels,
58 the resulting bio-oils have several drawbacks, such as low heating value, high viscosity, high
59 oxygen content and high acidity, which limit their widespread use and need to be upgraded first.
60 Catalytic fast pyrolysis involves the catalytic conversion of primary pyrolysis vapours to less
61 oxygenated liquid fuels by eliminating oxygen as CO, H₂O and CO₂ [11]. The catalysts can be
62 added directly to biomass in the pyrolysis reactor or added in a downstream reactor to upgrade
63 the hot pyrolysis vapours [12]. Acidic metal oxides (e.g. Al₂O₃), sulfated metal oxides (e.g.
64 SO₄²⁻/TiO₂) and transition metal oxides (e.g. CeO₂, TiO₂) have been investigated as catalysts in
65 lignocellulosic materials pyrolysis [13-16]. Metal oxides such as TiO₂ and CeO₂ catalysts
66 decreased the liquid and organic product yields and increased gas, water, and solid products
67 yields; where carboxylic acids like acetic acid were transformed to gasoline-range organics, by
68 elimination of O₂ as CO₂ and water [15,17]. CeO₂ was found to be highly performing for this
69 scope and also tolerant to water. Employing Al₂O₃ and TiO₂ as supports or doping them with a
70 strong base improved their catalytic activity [12]. Other intensively investigated catalysts for
71 microalgae pyrolysis are Na₂CO₃ and ZSM-5-based zeolites [18-21]. Na₂CO₃ tend to increase
72 the gas yields while decreasing the bio-oil yield, in which an energy recovery of 40% of bio-oil
73 was achieved [19]. HZSM-5 increased the hydrocarbons fraction and in particular the aromatics
74 [20]. For example, *Chlorella* sp. bio-oils (43-50 wt%) was enriched in hydrocarbons in the
75 organic phase (from 21 wt% in absence of catalyst to 43 wt%) [21].

76 *Pavlova* sp. is known to be able to synthesize DHA and EPA (essential n-3 PUFA) in
77 larger amounts. The potential of the *Pavlova* sp. as n-3 PUFA source in marine fish nutrition
78 was investigated by Rehberg-Haas [22]. However, there is no reported study regarding the
79 evaluation of *Pavlova* sp. as a biomass feedstock for bio-oil generation. Since characteristics
80 such as low cost, availability, sustainability, resistance to attrition and catalytic activity are
81 important criteria for the selection of catalysts, there is a great interest in developing catalysts
82 from non-nobel metals and rare materials. Under this scenario, TiO₂ represents a promising
83 candidate as catalyst for biomass conversion technologies. Kaewpengkrow et al. [23] performed
84 the catalytic upgrading of pyrolysis vapors from *Jatropha* wastes using alumina, zirconia and
85 titania. They found that alumina and titania yielded high hydrocarbons and less oxygenates,
86 while hydrocarbon selectivity was the highest with titania based catalysts. Lu et al. [24] studied
87 the catalytic fast pyrolysis of cellulose mixed with sulphated titania to produce
88 levoglucosenone. They found that the SO₄²⁻/TiO₂ (anatase) decreased the early cellulose
89 breakdown temperature and changed the pyrolytic product considerably resulting the best
90 catalyst for levoglucosenone production. Mante et al. [25] used anatase TiO₂ nanorods, CeOx–
91 TiO₂ mixed oxides, pure CeO₂, ZrO₂, and MgO as catalysts for the catalytic conversion of
92 biomass pyrolysis vapors into hydrocarbons. Ceria-based catalysts resulted very effective in
93 producing ketones.

94 The cracking properties of nickel, ceria and titania can be advantageous to the in-situ
95 removal of oxygen from the microalgal bio-oils. To the best of our knowledge, there is no single
96 study available in the literature on the comparison of product yields and compositions of bio-
97 oils attained by catalytic pyrolysis of *Pavlova* microalga with titania based catalysts and their
98 deoxygenation effect. Accordingly, the aim of this study is to screen and compare the effects
99 of ceria and titania based catalysts on *Pavlova* pyrolysis yield and products selectivity.

100

101 2. Experimental

102 2.1 Feedstock preparation

103 *Pavlova sp.* was acquired from Varicon Aqua Solutions. The biochemical composition
104 of *Pavlova* algae in terms of proteins, carbohydrates and lipids was also provided by Varicon
105 Aqua Solutions. The microalgae were dried in an oven at 50 °C, milled to a particle size between
106 80 and 140 meshes (105-174 µm) and stored in a desiccator for further use.

107 2.2. Catalyst preparation and characterization

108 Commercial ceria (CeO₂) and titania (TiO₂) nanopowders were purchased from Sigma-
109 Aldrich. Titania (TiO₂) based catalysts were prepared according to the procedure shown in Fig.
110 S1. As shown in Fig. S1, metal based TiO₂ sols were prepared firstly by refluxing a solution
111 containing titanium (IV) butoxide, propan-2-ol, nitric acid and fixed amount of cerium (III)
112 nitrate (Ce(NO₃)₃·6H₂O), cobalt (II) acetylacetonate (Co(C₅H₇O₂)₂) or nickel (II) nitrate
113 hexahydrate (Ni(NO₃)₂·6H₂O) using an oil bath at around 95°C for 24 hours. After the reflux
114 period, the resulting sol was dried and calcined in a furnace (Carbolite, CWF 1100) under
115 airflow at the rate of 1°C min⁻¹ to 100 °C for 12 h.

116 The physical characteristics of the different catalysts were determined by N₂ adsorption
117 method at -195.8 °C using Micromeritics Gemini VII instrument [5], while Quantachrome
118 Instruments Autosorb IQ Station 2 was used for the titania based catalysts. The catalysts were
119 outgassed overnight at 180 °C. Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–
120 Halenda (BJH) equations were used for determining the materials surface and pore size
121 distribution/volume. The mineral phases and elemental composition of the catalysts were
122 checked by powder X-ray diffraction using a Bruker D8 Advance powder diffractometer (Ge-
123 monochromated Cu Kα1 radiation; wavelength=1.5406 Å, 40 kV, 30 mA) with Sol-X Energy
124 Dispersive detector. The data were obtained over the angular range 5°-85° degrees in two-theta
125 under atmospheric pressure.

126 2.3. Feedstock and products analyses

127 2.3.1. Proximate and ultimate analysis

128 The proximate analyses were conducted according to ASTM standards (D2016, E872-
129 82, D1102-84). C, N and H were determined using LECO CHNS-932 analyzer, while O content
130 was obtained by difference. Higher heating values (HHV) of samples were obtained using the
131 Dulong's Formula [23].

132 2.3.2. Proton nuclear magnetic resonance (^1H NMR) analysis

133 ^1H NMR analyses were performed using a Bruker Avance III operating at 400 MHz. The
134 samples were dissolved in CDCl_3 (1:1 volume ratio) and TMS (tetramethylsilane) was used as a
135 internal standard.

136 2.3.3. TGA analysis

137 Thermogravimetric analysis (TGA) was carried out using a TA Q500 in presence of N_2
138 for determining volatiles and in presence of air to determine the fixed carbon and ash content.
139 The method used is described in details in a previous work [13].

140 2.3.4. Gas chromatography–Mass spectrometry (GC–MS) analysis

141 An Agilent GC-MS 7890A/5975C series (column: HP 235–INNOWAX; transfer line at
142 270 °C, ion source at 250 °C and electron energy of 70 eV) was used for the GC-MS analysis
143 of the bio-oils [26]. The bio-oil components were identified using mass spectral libraries
144 (PMW_Tox3.1, Wiley7n.1 and NIST05a.L).

145 2.3.5. Coke analysis

146 Coke yield on catalysts was determined by the weight change during combustion using
147 an Exstar TG/DTA 7200 in a 70 mL/min air flow. In a typical run, approximately 10 mg of

148 sample was placed in the ceramic crucible and heated from 25 °C to the final temperature of
149 900 °C at a rate of 10 °C/min.

150 2.4. Pyrolysis experiments

151 The pyrolysis experiments of *Pavlova* were performed using a semi-fixed-bed reactor.
152 The set-up was previously described [26]. The catalytic and non-catalytic algae pyrolysis
153 experiments were performed at temperatures of 450, 500 and 550 °C at a constant heating rate
154 100 °C/min under N₂ atmosphere with a flow rate of 545 ml/min. The reactor temperature was
155 kept constant at the final temperature for 60 min.

156 Actual pyrolysis tests were performed feeding 3 g of material per test (1.5g *Pavlova* and
157 1.5g catalyst). The bio-oils were recovered in three Dreshel bottles immersed in a ice-water
158 bath with temperature kept constant at 0°C.

159 The remaining solid was recorded as bio-char yield (subtracting the catalyst weight).
160 The amount of gaseous products was calculated by subtraction of solid and bio-oil yields from
161 the amount of initial raw material.

162 The distribution of the parent algal material energy in the pyrolysis products was based on the
163 pyrolysis material balance and HHV of bio-oils and bio-chars. The energy content of each
164 product (bio-char and bio-oil) was calculated by multiplying the HHVs to the wt% of the
165 products recovered. The energy content of bio-gas was calculated by subtracting the energy
166 content of the bio-char and bio-oil from the starting energy content of the raw material
167 (microalgae) [13].

168 **3. Results and discussion**

170 3.1. Feedstock characterization

171 Ultimate and proximate analyses of *Pavlova* were performed and the results are reported
172 in Table S1. This alga strain has large protein content (43%) and a moderate amount of lipids

173 (20%) and carbohydrates (26%). The *Pavlova* moderate lipid content reduces this microalga
174 suitability for biodiesel production, but enhances its suitability for pyrolysis. The large protein
175 content, which was similar to that of other algal species such as *Scenedesmus obliquus*,
176 *Chlorella vulgaris* and *Spirulina platensis* [27], resulted in high nitrogen content (4.81%). Ash
177 content (24.45%) and fixed carbon (11.60%) were rather great compared to values of other
178 algae species [28]. The decomposition behaviour of *Pavlova* was estimated using TGA/DTG
179 (Fig. S2). According to Fig.S2, the *Pavlova* decomposition occurs between 105 and 800 °C (53.
180 9 % weight loss) that includes three main steps (at 130, 250, 455°C), corresponding to
181 carbohydrates, proteins and lipids volatilisation [5]. The material left behind (40 %) at 800 °C,
182 represents the fixed carbon and ash.

183 3.2. Catalyst characterization

184 Table 1 shows the surface area, pores size and volume of the synthesised catalysts
185 assessed using N₂ adsorption isotherms at 77 K. The addition of metal oxides to TiO₂ influenced
186 its catalyst properties. When we look at the loaded TiO₂ based catalysts, we see that there were
187 clear differences between them. The specific surface areas (SBET) of Ce/TiO₂, Co/TiO₂ and
188 Ni/TiO₂ catalysts were 126.80, 278.50 and 229.60 m²/g, respectively, while starting TiO₂ had
189 only ~9.5 m²/g. All synthesised catalysts had a pore distribution between 17 and 300 Å,
190 indicating the presence of micropores (<20 Å) and mesopores (>20 Å). Ni/TiO₂ had an average
191 pore size of 58.06 Å (similar to the starting TiO₂), while Co/TiO₂ and Ce/TiO₂ had smaller
192 average pore size (~29-31 Å). This may indicate that Co and Ce are deposited in the pores
193 partially reducing their size.

194 The X-ray diffraction patterns of the prepared catalysts with TiO₂ support are shown in
195 the Supplementary data (Fig. S3), which shows the X-ray diffraction patterns of metal loaded
196 nanoparticles of Ni/TiO₂, Co/TiO₂ and Ce/TiO₂. Tetragonal anatase phase was confirmed by
197 Powder Diffraction Standards (JCPDS) Card File no. 21-1272. Additional peaks of brookite at

198 ca. 31.4° were further observed in the metal loaded nanoparticles. Only small diffraction peaks
199 of metal oxides (NiO, CoO and CeO₂) phase were detected for the samples as they are hidden
200 from the large peaks of TiO₂. This could be due to their occurrence being in highly dispersed
201 phase within TiO₂ matrix or due to detectable limit of the diffractometer. EDS analysis
202 confirmed the elemental composition as 1.6wt%, 3.98wt% and 1.36wt% for Co, Ce and Ni
203 loaded TiO₂ catalysts, respectively.

204 3.3. Effect of temperature on products distribution

205 The total volatiles (bio-oil+gas yields) and distribution of products obtained by
206 pyrolysis of Pavlova with titania based catalysts with (1:1 ratio) and without catalyst is given
207 in Table 2. High char yields were probably due to the slow heating rate used (100°C/min) during
208 pyrolysis [29]. For example, when temperature was increased from 450 to 550 °C, the
209 conversion (total volatiles) was increased from 51% to 61% in the non-catalytic runs and from
210 52% to 63.7% in the catalytic runs with CeO₂. Similar trend was observed with TiO₂ catalysts.
211 The higher bio-oil yield was obtained at 500 °C, with Ni/TiO₂ producing the highest (22.5
212 wt%). The bio-oil yields were increased first at 500°C and then decreased at 550 °C. This result
213 is in accordance with previous work [30].

214 3.4. Effect of catalysts on product distribution

215 Catalytic pyrolysis favours deoxygenation by removal of CO, CO₂ and H₂O [26,31].
216 When we look at the effect of titania based catalysts used in this study, we see that all had a
217 positive effect and increased the total volatiles compared to non-catalytic runs, with Ni/TiO₂
218 being the most effective.

219 The use of a neutral catalyst support (TiO₂) that does not promote acid catalyzed
220 polymerization of the various components of *Pavlova* increase the conversion of char, when
221 coupled with cracking metals such as Ni. Iliopoulou et al. found out that the addition of NiO to

222 a zeolite led to a decrease in the total condensed organic hydrocarbon phase during beech
223 pyrolysis vapours, and increased the yields of aromatic hydrocarbons. Also, H₂ production and
224 C₂–C₆ gas-phase hydrocarbons increased with nickel, with an emphasis on C₄–C₆ alkanes
225 [32]. In our work, the highest amounts of total volatiles of 63.7 % and 64.1% were obtained
226 with CeO₂ and Ni/TiO₂ respectively, but the amount of Ce loaded on the TiO₂ support was 3
227 times larger than that of Ni (see Section 3.2). Thereofre, Ni had the largest impact on the
228 microalgae decomposition, which could be linked to the fact that Ni was deposited on the
229 surface of the catalyst, while the Co and Ce were also deposited in the materials pores, as
230 indicated by the pores size distribution.

231 A large fraction of the starting microalgae was found in the gas product, with yield increasing
232 sharply according to temperature increase to 550°C. This is due to the long residence time (60
233 min) and high cracking capacity of ceria. As for the bio-oil yields, ceria and nickel containing
234 catalysts were the most effective and the highest bio-oil yields were obtained in their presence
235 (Ce/TiO₂: 21.7 % and Ni/TiO₂: 22.5 %). This result is in agreement with our previous studies
236 on *Nannochloropsis*, *Tetraselmis* and *Isochrysis* catalytic pyrolysis, where Ni containing
237 catalysts resulted in the highest bio-oil yields and good deoxygenation effect [5,26]. These low
238 bio-oil yields can be linked to the relatively low content in fatty acids of the pyrolysed specimen
239 (20 wt%). Despite this, a notable fraction of the microalgae energy content was recovered in
240 the bio-oils. Ni/TiO₂ was the most effective maintaining 74.59 % (daf) of *Pavlova*'s energy in
241 the bio-oil, (55.72 % without catalyst) (Fig. 1). This indicates that deoxygenation of *Pavlova* in
242 the presence of nickel is very effective and can be attributed to the cracking activity of Ni and
243 synergic effect of Ni-Ti [32]. TiO₂ alone did not show any benefit in terms of increasing the
244 conversion of *Pavlova*, but as soon as Ni was added to the support, the reduction in char yield
245 and the increase in volatile species was clear. This agrees to a previous work, where Ni addition
246 to zeolite led to higher conversion of oxygenates and lower rate of deactivation [33].

247 The nitrogen distribution in the products of catalytic and non-catalytic pyrolysis of
248 *Pavlova* at 500 °C is given in Fig 2. Bio-oil obtained without catalyst contained about 34.27
249 wt% of the nitrogen, while 31.21 wt% remained in the solid bio-char and 34.52 wt% went into
250 the gas products. The use of titania based catalysts lowered the nitrogen content in the bio-oils
251 to about 26% (from 34%). N removal was comparable with that obtained by staged
252 hydrothermal liquefaction (1st stage: 225°C, 15 min; 2nd stage: 350°C, 60 min) [34]. In a
253 previous work, the hydrodenitrogenation performance of a TiO₂-promoted Ni₂P catalyst was
254 studied. It was found out that both the denitrogenation activity and the hydrogenation activity
255 of Ni₂P were enhanced by the addition of TiO₂ [35]. In this work, as supported by the N content
256 of bio-chars and bio-oils (Tables 3 and 4), the N removed from the bio-oils went in the gas
257 phase (possibly in form of NH₃) thanks to the cracking capability of the metals loaded in the
258 TiO₂ support. Among the catalysts, Ni and CO loaded TiO₂ were the best performing ones.

259 The TGA curves of the coked spent titania catalysts are shown in Fig. S4, where the
260 mass lost between 600 and 900 °C was associated to coke combustion. Ni/TiO₂ (5.0%) had the
261 lowest amount of coke, while Co/TiO₂ (15.3%) and CeTiO₂ (15%) had the highest. These
262 results are substantially consistent with the pyrolysis mass balances (Table 2), which show their
263 catalytic activities in terms of high total volatiles. Ni/TiO₂ and Co/TiO₂ have larger surface and
264 pore volume compared to the other materials (see Table 1). The fact that Ni was mostly loaded
265 in the surface of the catalyst, while Co entered the support pores, can explain the higher coke
266 reduction capacity of the Ni/TiO₂ catalyst.

267

268 3.5. EA, TGA, ¹H NMR and GC–MS analyses

269 The HHVs and elemental analyses of the bio-chars produced at 500 °C are shown in
270 Table 3. The produced bio-chars had carbon content between 38 and 42 wt% and HHV between
271 5 and 7 MJ/kg. Van Krevelen diagram showing *Pavlova*, *Chlorella* and *Nannochloropsis* bio-

272 chars obtained at 500°C along with coal is given in Fig. 3. As seen in Table 3 and Fig. 3, *Pavlova*
273 bio-chars had lower HHVs than *Chlorella* and *Nannochloropsis* obtained at the same
274 temperature. This is because most of the starting microalgae energy was recovered in the bio-
275 oils. The *Pavlova* bio-chars have high ash and nitrogen contents, which make them suitable as
276 soil amendment rather than solid bio-fuel. The HHVs and elemental analyses of the bio-oils are
277 given in Table 4 and the corresponding Van Krevelen diagram is shown in Fig. 4. All bio-oils
278 had higher HHV and lower oxygen contents than raw feedstock. Nitrogen content of bio-oils
279 was lower in presence of catalysts decreasing from 8.75 wt% without catalyst to a minimum of
280 6.12 wt% in presence of Co/TiO₂. Nitrogen compounds originated from chlorophyll and
281 proteins present in raw feedstock. Although N was reduced, its content still represents a problem
282 for potential NO_x emission during combustion. The bio-oils produced in the presence of
283 catalyst had higher HHVs than the one without catalyst. The most effective catalysts in
284 improving the bio-oil quality were Ce/TiO₂ and Ni/TiO₂, which increased the HHVs of bio-oils
285 up to about 37 MJ/kg, compared to non-catalytic run (33.32 MJ/kg). As seen in the Van
286 Krevelen diagram (Fig. 4), the *Pavlova* bio-oils had greater HHVs than *Chlorella* (ZSM-5) and
287 *Nannochloropsis* [5]. This indicates that not only the catalyst but also the feedstock composition
288 affects the deoxygenation during pyrolysis. The pyrolysis bio-oils from *Pavlova* were also
289 enriched in carbon and hydrogen content in presence of the catalysts, which makes them more
290 suitable for fuel use compared to lignocellulose-derived bio-oils [36].

291 Most of the bio-oils were virtually ash free and composed of only volatiles. The bio-oil
292 obtained with Ni/TiO₂ had the highest amount of low molecular weight volatiles while Co/TiO₂
293 contained the highest amount of ash (Bio-oils proximates are presented in Table S2).

294 The integration of selected regions of the proton-NMR spectra versus specific chemical
295 shift ranges are presented in Table 5. NMRs, which give an overview of the chemical
296 functionalities present in the bio-oils, show that titania catalysts altered the functionalities

297 distribution. The aliphatic proton region of the titania catalysts oils (0.0 to 1.5 ppm) was the
298 most abundant. Ni/TiO₂ had the highest percentage of aliphatic protons (~60% of all), while
299 the not metal loaded TiO₂ had the lowest (~50 % of all). The next integrated region from 1.5 to
300 3.0 ppm (aliphatic protons bonded to C=C double bond (aromatic or olefinic) or H two bonds
301 away from a heteroatom) did not show clear differences between bio-oils obtained without and
302 with catalyst. The region of the spectra (3.0-4.4 ppm) that characterises the aliphatic
303 alcohol/ether protons, or methylene groups joining two aromatic rings were less in presence of
304 Ni/TiO₂ and Co/TiO₂ (~3 %). This sharp decrease in alcohols is mainly ascribable to the
305 cracking of phytol, with Ni/TiO₂ being the most effective catalyst. The protons in the
306 carbohydrates/aromatic ether (4.4-6.0 ppm) region were found to be in small amounts (~0.5-
307 1.5 %) in all bio-oils, with lower level in presence of titania based catalysts. These results are
308 in accordance with the elemental (Table 4) and GC-MS (Table 6) analyses of bio-oils, which
309 show lower oxygen contents when the catalysts were used. The aromatic region of the spectra
310 (6.0-9.5 ppm) contain ~8-12 % of the protons in the bio-oils. This region represents both
311 hydrogen atoms in benzenoid aromatic compounds and in heteroaromatics containing nitrogen
312 and oxygen such as indole (see Table 6). All catalysts, except Ni/TiO₂, increased the percentage
313 of protons slightly in this region compared to non-catalytic run. Aldehydes and carboxylic acids
314 (9.0-10.1 ppm) were not detected in the bio-oil without catalyst and detected only in very small
315 amounts in other bio-oils. This is a clear difference with lignocellulosic bio-oils that are
316 particularly rich in oxygenated compounds. According to the proton NMR analyses, the bio-
317 oils obtained from pyrolysis of *Pavlova* contain greater percentages of the aliphatic protons.

318 GC-MS analysis of the *Pavlova* bio-oils produced at 500°C was carried out in order to
319 determine the main products and to compare the effects of different catalysts. The list of the
320 identified compounds with main functionalities identified by GC-MS from pyrolysis of *Pavlova*
321 is given in Table 6. Bio-oils from *Pavlova* were composed of a mixture of different

322 functionalities such as aliphatics, monoaromatics, oxygenates, nitrogenates and polycyclic
323 compounds. Aliphatics (alkanes and alkenes) were mainly generated during the
324 depolymerisation of algal saturated and unsaturated fatty acids. Among the aliphatics, tridecane,
325 tetradecane, pentadecane, neophytadiene, pentadecene, tetradecene were identified. Aliphatics
326 are considered as valuable compounds due to their contribution to high heating value products.
327 Represented chemical functionalities are not quite consistent with those detected by ^1H NMR.
328 This can be ascribed to the different classification used for the two techniques, where
329 tetradecanenitrile, dodecanenitrile and hexadecanenitrile, which have long-chain aliphatic
330 parts, were not considered aliphatics in GC-MS. The main monoaromatics were phenol, phenol
331 substitutes and benzenes, which were produced from algal components thermal cracking, metal
332 promoted cracking, dehydration, decarbonylation and decarboxylation reactions.

333 Oxygenated compounds (e.g. alcohols, ethers) were not abundant in the bio-oils, while
334 the bio-oils were rich in nitrogen containing compounds (e.g nitriles, amines and indole).

335 The presence of the titania catalysts affected the distribution and number of the
336 identified chemicals. When we consider the catalysts effect, we see that TiO_2 and Ni/TiO_2 have
337 increased the fractions of monoaromatics considerably than other catalysts. There was a clear
338 increase in aliphatics and decrease in oxygenated compounds in the presence of all titania
339 catalysts, which shows their good cracking properties. Among them, Ni/TiO_2 was found to be
340 the most effective in terms of deoxygenation and denitrogenation of Pavlova bio-oils. Nitrogen
341 compounds were also decreased (except Ce/TiO_2) in the presence of titania catalysts, indicating
342 that TiO_2 has an active role on the O and N elimination capacity. All titania catalysts favoured
343 the formation of polycyclic compounds in varying amounts (Table 6). This can be related to the
344 presence of large mesopores (30-58 Å), which allow large molecules to be adsorbed and re-
345 arranged in polyaromatic structures. The selectivity on mono-aromatics transformation in
346 polyaromatics such as naphthalenes was linked to longer reaction times indicating that first the

347 depolymerised molecules form mono-aromatics and the latter form polycyclic-aromatics by
348 secondary reactions [37].

349 The better activity of Ni/TiO₂ can be partially explained in terms of higher availability
350 of Ni in surface (Co/TiO₂ has higher surface but Co is mostly loaded into the TiO₂ pores) and
351 also can be linked to strong interaction between Ni and TiO₂ support, which lead to superior
352 cracking capacity [38]. This is supported by the increased cracking of long chain alcohols such
353 as phytol (C₂₀H₄₀O) and reduced presence of PAH as reported in Table 6.

354

355 **4. Conclusion**

356 The effects TiO₂ and Ni, Ce, Co loaded TiO₂ and CeO₂ catalysts on the catalytic pyrolysis of
357 *Pavlova* microalgae was studied. The presence of Ni, Ce and CO metals supported on TiO₂
358 affected the product yields distribution and their quality. Presence of Ni/TiO₂ resulted in the
359 highest bio-oil yield (22.55 wt.%) at 500 °C. In addition, the bio-oils obtained in presence of
360 the titania catalysts had high HHV (~35-37 MJ/kg) and were effectively deoxygenated (~9-12
361 wt.%). Deoxygenation power decreased in this order: Ni/TiO₂ > Ce/TiO₂ > Co/TiO₂. Ni/TiO₂
362 was the catalyst that greatly affected the composition of the bio-oil, which resulted enriched in
363 aliphatics and aromatics and depleted in O and N -compounds. The better activity of Ni/TiO₂
364 was related to higher availability of Ni on the catalyst surface, which also led to low coke
365 formation and to strong interaction between Ni and TiO₂ support, which results in enhanced
366 cracking activity.

367

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475 **Figures Captions**

476 **Figure 1.** Energy (daf) distribution in the pyrolysis products.

477 **Figure 2.** Nitrogen (N) distribution in the pyrolysis products.

478 **Figure 3.** Van Krevelen diagram of bio-chars.

479 **Figure 4.** Van Krevelen diagram of bio-oils.

480

481 **Table 1** The physical properties of the synthesized titania supported catalysts.

Catalyst	Surface area (m ² /g)	Pore size (Å)	Pore volume (cm ³ /g)
CeO ₂	18.69	71.04	0.038
TiO ₂	9.48	59.06	0.015
Ce/TiO ₂	126.80	29.68	0.026
Co/TiO ₂	278.50	31.32	0.410
Ni/TiO ₂	229.60	58.06	0.368

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487 **Table 2** The total volatiles^a and distribution of products obtained by pyrolysis of Pavlova with
 488 (1:1 ratio) and without catalyst (Heating rate: 100 °C/min, N₂ flow rate: 545 ml/min)

Temperature (°C)	Total volatiles (%)	Solid (%)	SD	Liquid (%)	SD
450 °C					
No catalyst	51.04	48.96	0.08	14.11	0.30
CeO ₂	52.04	47.96		15.10	
TiO ₂	51.82	48.18		14.44	
Ce/TiO ₂	52.56	47.44	0.64	15.46	1.07
Ni/TiO ₂	52.34	47.66	1.16	15.30	0.46
Co/TiO ₂	51.72	48.28		15.24	
500 °C					
No catalyst	59.10	40.90	0.14	18.68	0.25
CeO ₂	62.14	37.86		21.07	
TiO ₂	60.51	39.49		20.04	
Ce/TiO ₂	62.54	37.46	0.91	21.67	0.05
Ni/TiO ₂	62.84	37.16	0.93	22.55	0.57
Co/TiO ₂	61.15	38.85		20.41	
550 °C					
No catalyst	61.03	38.97		16.57	
CeO ₂	63.74	36.26		17.82	
TiO ₂	62.24	37.76	0.76	17.14	0.18
Ce/TiO ₂	63.64	36.36		17.38	
Ni/TiO ₂	64.10	35.90	1.99	18.71	0.25
Co/TiO ₂	62.02	37.98		17.41	

489 ^aMass fraction percentage of the dry and ash free feedstock.

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496 **Table 3** The results of elemental analysis of Pavlova bio-chars obtained with titania based
 497 catalysts at 500 °C.

Elemental analysis ^a	No catalyst	CeO ₂	TiO ₂	Ce/TiO ₂	Ni/TiO ₂	Co/TiO ₂
Carbon	40.74	40.41	42.10	41.72	38.42	40.03
Hydrogen	1.50	1.46	1.54	1.56	1.47	1.51
Nitrogen	3.64	3.57	3.61	3.37	3.14	3.45
Oxygen ^b	54.12	54.56	52.75	53.35	56.97	55.01
H/C molar ratio	0.44	0.43	0.44	0.45	0.46	0.45
O/C molar ratio	0.99	1.01	0.94	0.96	1.11	1.03
HHV (MJ/kg)	6.18	5.93	6.94	6.74	4.84	5.79

498 ^a Weight percentage on dry and ash free basis. ^bBy difference

499

500 **Table 4** The results of elemental analysis of Pavlova bio-oils obtained with titania based
 501 catalysts at 500 °C.

Elemental analysis ^a	No catalyst	CeO ₂	TiO ₂	Ce/TiO ₂	Ni/TiO ₂	Co/TiO ₂
Carbon	68.31	72.63	72.27	74.32	75.20	73.41
Hydrogen	8.84	9.10	9.02	9.47	9.16	9.36
Nitrogen	8.75	6.43	6.23	6.58	6.17	6.12
Oxygen ^b	14.10	11.84	12.48	9.63	9.47	11.11
H/C molar ratio	1.55	1.50	1.49	1.53	1.46	1.53
O/C molar ratio	0.15	0.12	0.13	0.10	0.09	0.11

HHV (MJ/kg)	33.32	35.56	35.21	37.07	36.95	36.33
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502 ^a Weight percentage on dry and ash free basis. ^bBy difference

503 **Table 5** ¹H NMR Integrations of Pavlova bio-oils formed with titania based catalysts at 500 °C
504 versus specific chemical shift ranges.

Chemical shift region	Proton assignment	Hydrogen content (% of all hydrogen)					
		No catalyst	CeO ₂	TiO ₂	Ce/TiO ₂	Co/TiO ₂	Ni/TiO ₂
0.0 – 1.5	Alkanes	40.476	47.186	49.792	55.074	54.591	60.375
1.5 – 3.0	Aliphatics α-to heteroatom	33.324	33.124	32.655	28.051	30.875	27.185
3.0 – 4.4	Alcohols, methylene-dibenzene	11.672	7.480	4.856	4.329	3.085	3.548
4.4 – 6.0	Methoxy, carbohydrates	4.990	1.631	1.212	0.587	1.574	0.662
6.0 – 9.5	(Hetero-) aromatics	9.552	10.396	11.311	11.920	9.863	8.112
9.5 – 10.1	Aldehydes	-	0.182	0.174	0.039	0.013	0.118

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507 **Table 6** The chemical compounds present in the bio-oils obtained from Pavlova pyrolysis
508 with titania based catalysts at 500 °C.

No	Compounds	Relative abundance (% area)					
		No catalyst	CeO ₂	TiO ₂	Ce/TiO ₂	Co/TiO ₂	Ni/TiO ₂
	<i>Monoaromatics</i>	–			–		
1	(1-Methylbuta-1,3-dienyl)benzene	–			–	4.24	
2	1-Hexyl-4-methylbenzene	–		2.26	–	–	3.81
3	1-Phenyl-1-penten-5-ol	–		2.65	–	–	
4	2-Methyl-3-(methylthio)furan	–		2.58	–	–	

5	Benzyl nitrile	–		–	2.72	1.38
6	Benzeneacetonitrile	–	2.52	–		3.71
7	Phenol	5.77	9.01	6.69	4.32	3.99
8	Maltol	2.33				–
9	Benzene, (methoxymethyl)-	1.26				–
10	Phenol, 2,3-dimethyl-	–		2.71	2.90	–
11	Phenol, 2,4-dimethyl-	–	3.00		–	–
12	Phenol, 2-ethyl-	–		5.04	–	
13	1-Ethyl-1-phenylhydrazine	–		3.52	–	2.41
14	p-Cresol	5.69	7.90	5.05	4.73	4.43
15	Phenol, 2-ethyl-5-methyl-		7.30			
16	Phenol, 2-(1-methylethyl)-		3.61			
17	Phenol, 2,3,5-trimethyl-	–		–		–
18	Phenol, 2,3,6-trimethyl-	–		–	5.23	–
19	Phenol, 2-ethyl-4-methyl-	–		–	–	–
20	2-Ethyl-6-methylphenol	2.94		–	–	–
21	Phenol, 3-ethyl-	5.47	3.86	4.46	–	2.22
22	3-Methyl-4-ethylphenol			–	–	4.45
23	2,4-Diethylphenol			–	–	–
24	2,5-Diethylphenol	1.56		–	–	–
25	Phenol, 3-amino-	2.05		–	–	–
26	N-(1-methyl-2-propynyl)aniline			2.58	3.20	–
27	Furoxan, 4-nitro-3-phenyl-, 2-oxide				5.42	3.61
		27.07	34.68	40.06	25.80	28.07
						47.83
	<i>Aliphatics</i>					
28	Tridecane	–		1.69	–	1.75
29	Tetradecane	–		2.55	–	1.77
30	2-Tetradecene, (E)-	–			–	1.35
31	Pentadecane	1.98		2.39	1.88	2.32
32	2-Methyl-Z-4-tetradecene	–		–	–	0.82
33	1-Pentadecene	–		–	–	3.21
34	2-Pentadecene	–		–	–	
35	2,6,10-Trimethyl,14-ethylene-14-pentadecane	–			8.23	6.33
36	5-t-Butyl-cycloheptene			6.78		–

37	4-Chloro-2-(chloromethyl)-1-butene			1.16			–
38	Neophytadiene		7.90				
		1.98	7.90	14.57	10.11	17.55	14.20
	<i>Oxygenated compounds</i>						
39	Decyl acetate	–	–	–	–	1.58	
40	Pentanoic acid	–	–	–	–	–	0.81
41	Octanoic acid	–	–	–	–	1.92	
42	1-Cyclohexyl-2-methyl-prop-2-	–	–	–	–	3.19	
43	1-Tetradecanol	–	–	2.65	–	–	1.36
44	Butanoic acid	–	–	1.29	–	–	1.07
45	Pentane, 2-methoxy-	–	0.77	–	–	–	1.33
46	3-Acetoxy-5-(acetoxymethyl)cyclohexene	–	–	3.42	–	–	
47	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	–	–	–	–	–	5.19
48	Dimethyl Sulfoxide	2.45	–	–	–	–	–
49	Dodecanoic acid, 4-methyl-, methyl ester	1.06	–	–	–	–	–
50	dl-Erythro-O-methylthreonine	1.26	–	–	–	–	–
51	(-)-(3S,4R,5R)-3-Azido-4-hydroxy-5-methyldihydro-2-(3h)-furanone	1.39	–	–	–	–	–
52	2-Butenoic acid, 3-ethoxy-, ethyl ester	0.57	–	–	–	–	–
53	6-Isopropyl-3-methyl-2-cyclohexen-1-ol	–	–	3.36	–	–	–
54	Cis-chrysanthenol	–	–	–	4.07	–	–
55	Methyl phenyl(2-piperidinyl) acetate	2.45	–	–	–	–	–
56	4-Heptenoic acid, 3,3-dimethyl-6-oxo-, methyl ester	–	–	–	–	2.93	–
	2-Cyclopenten-1-one, 3-(1-methylethyl)-	2.23	–	–	–	–	–
57	(+)-(1S,6R)-6-Phenyl-2-cyclohexene-1-carboxylic acid	0.82	–	–	–	–	–
58	S-Butyl ester of .alpha.-phenylbenzeneethanethioic acid	2.72	–	–	–	–	–
59	Isobutyric acid, tetradecyl ester	–	10.8	–	–	–	–
60	Phytol	20.93	10.8	6.32	5.19	5.93	4.47

	35.88	22.4	17.04	9.26	15.55	14.23
<i>Nitrogen compounds</i>						
61 Benzenepentanamide			–	5.23	–	
62 5-Hepten-2-amine, N,6-dimethyl-		1.28				
63 Propanamide	1.39	0.94	–	–	–	
64 Pyridine, 3-phenyl-			–	–	–	1.72
65 Pyrrolidine, 1-acetyl-	0.57		–	–	–	–
66 Hexahydro-2(1H)-azocinone	1.11		–	–	–	–
67 Butanamide, 3-methyl-	2.03		–	–	–	–
68 N-(1-Methylethylidene)-2-propanamine	0.99		–	–	–	–
69 Butanamide, 3-methyl-	2.08		–	–	–	–
70 Benzenepropanenitrile	7.37	5.67	5.30	3.35	3.61	3.16
71 2-Piperidinone	1,16					
72 Cyclohexanamine, N-cyclopentylidene-					3.48	
73 Tetradecanenitrile	4.31		1.53	13.67	6.90	1.78
74 Pyridine, 4-phenyl-				1.63		
75 1-Buta-1,3-dienyl-pyrrolidine	5.44					
76 N-Ethyl-hexahydro-1H-azepine		2.92				
77 Octanamide		2.06				
78 Hexadecanenitrile	1.66	8.62	2.61	4.88	2.76	2.24
79 Dodecanenitrile		6,1				
80 Indole	4.95	6.25	5.23	7.01	4.68	3.57
81 1H-Indole, 2-methyl-	–	1.04	–	1.58		
82 1H-Indole, 5-methyl-	–		–			0.77
83 1H-Indole, 4-methyl-	–		–		0.80	
84 1H-Indole, 1-ethyl-	–				1.03	–
85 Benzonitrile, 2,4,6-trimethyl-	–			0.66	–	–
86 7-Methyl-1H-indole	–		1.42	–	–	–
87 1H-Indole, 3-methyl-	1.04			–	–	1.03
88 5-(1H-Indol-3-ylmethyl)-2-thioxo-4-imidazolidinone	0.97			–		
	35.07	34.9	16.09	38.01	23.26	14.27
<i>Polycyclic compounds</i>						

89	1H-Indene, 1-methylene-	–			1.14	2.63
90	Naphthalene, 2-methyl-	–	7.46	1.68	3.71	
91	Naphthalene, 1-methyl-	–	–	3.76	4.71	2.63
92	Naphthalene, 1,3-dimethyl-	–	–		6.01	
93	Naphthalene, 1,5-dimethyl-	–	–		–	4.21
94	Naphthalene, 2,7-dimethyl-	–	–	7.42	–	–
95	Naphthalene, 2,6-dimethyl-	–	4.78		–	–
96	Naphthalene, 3-(1-methoxyethyl)-1-methyl-	–		3.96		–
		0	0	12.24	16.82	15.57
	Total	100	100	100	100	100

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