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1 **Effect of Li-LSX-zeolite on the in-situ catalytic deoxygenation and denitrogenation**
2 **of *Isochrysis* sp. microalgae pyrolysis vapours**

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7 **Abstract**

8 In this work, we report for the first time the use of Li-LSX-zeolite as catalyst for the
9 catalytic pyrolysis of biomass (*Isochrysis* sp. Microalgae). Li-LSX-zeolite showed a
10 good catalytic performance, principally for bio-oil denitrogenation (mainly in form of
11 NH₃), and good activity for olefins and aromatics production. At 500 °C, 11.8 %
12 aromatics and 23.1% aliphatics were produced. The increase of temperature led to transfer
13 of C to the gas phase, coke formation on the catalyst surface and decrease in N-
14 compounds in the bio-oil. The increase of the catalyst to biomass ratio from 0 to 3:1
15 resulted in the aromatics being five-fold those non-catalytically obtained and in a higher
16 cracking power that reduced the bio-oil to 23% at expenses of olefins rich gas. However,
17 a linear correlation between coke formation and aromatic yield was observed as the
18 catalyst to microalgae ratio was increased. Therefore, the experimental results indicate
19 that Li-LSX-zeolite could be used as catalyst for in-situ denitrogenation of microalgae
20 bio-oil and for enhancing aliphatics and aromatics formation to be blend in gasoline and
21 diesel and olefins in gas phase.

22 **Keywords:** catalytic pyrolysis, microalgae, zeolite, bio-oil, denitrogenation, aromatics,
23 Li-LSX-zeolite

24 **1. Introduction**

25 Microalgae have great potential as feedstock for bioenergy production because of their
26 high productivity, fast growth rate, capability to fix CO₂ and for being not in competition
27 with food crops. The raw microalgae can be pyrolysed to get a liquid bio-oil, which still
28 contains a large fraction of the microalgae initial energy [1]. Oxygen and nitrogen
29 compounds represent the main limitation for the bio-oil implementation as biofuel, and
30 methods/catalysts able to reduce O and N content in the bio-oil during or after its
31 production must be developed. Catalytic pyrolysis is a process in which a catalyst is used
32 to promote deoxygenation of the bio-oils through simultaneous dehydration,
33 decarboxylation and decarbonylation reactions [2–5]. Among these catalysts, zeolitic
34 materials such as ZSM-5 zeolite, have been found to be very active to deoxygenate
35 pyrolysis vapours and to produce aromatic hydrocarbons [6–9].

36 The simultaneous in-situ deoxygenation and denitrogenation of microalgae pyrolysis bio-
37 oils is somehow a new research topic, with few works available in literature, since
38 nitrogen is typically removed via hydro-processing [10,11]. Despite this, bio-oils hydro-
39 processing consumes large amount of H₂ and the development of in-situ oxygen and
40 nitrogen removal techniques (during pyrolysis) would be a more cost-effective
41 alternative. But also, catalytic pyrolysis has attracted interest for the conversion of
42 biomass into light olefins [12,13].

43 *Isochrysis* sp. has been identified among the microalgae species that are suitable
44 candidates for multiple-product algae-crop, due to their variety of fatty acids that offer a
45 wide scope for several bio-products in a biorefinery approach [14]. However, only few
46 studies are available on *Isochrysis* catalytic pyrolysis [15–17]. Dong et al.[15] studied the
47 direct production of light olefins (C₂–C₄) of up to 11 wt.% from *Isochrysis* catalytic
48 cracking at 550-650 °C in presence of modified ZSM-5, being neutral lipids the principal

49 contributor to olefin production. On the other hand, Wang et al.[17] investigated the direct
50 and indirect (after removal of lipids) pyrolysis of *Isochrysis* at 475 °C. Defatted *Isochrysis*
51 yielded higher total pyrolysis oil (41.3 wt.%) than direct microalgae pyrolysis (36.9
52 wt.%). However, there was also an increase for N-heterocyclic compounds and phenols
53 and a decrease for hydrocarbons in defatted microalgae pyrolysis oil [17]. In a previous
54 work, we investigated the effect of Ni-Ce derived catalysts on the *Isochrysis* microalgae
55 pyrolysis, being Ni-Ce/ZrO₂ the most effective in terms of mass and energy bio-oil yield
56 with 25.5 wt.% and 77%, respectively.

57 In this work, a low silica X type (LSX) zeolite (Li-LSX-zeolite) was evaluated for the
58 first time as catalyst for the in-situ catalytic pyrolysis of *Isochrysis* sp. This zeolite is
59 generally used for the air separation process at industrial scale for oxygen production.
60 However, its catalytic activity on the biomass depolymerisation and its deoxygenation
61 and denitrogenation potential has never been studied so far. Recently, bifunctional
62 catalysts with both acid and base sites have been shown to be effective in the conversion
63 of biomass to hydrocarbons and on the removal of oxygen. The low Si/Al and the
64 presence of Li suggest that Li-LSX-zeolite could promote oxygen removal and produce
65 olefins and aromatics as other acidic zeolites [7]. Since Li cations preferentially adsorb
66 nitrogen over oxygen [18], its affinity to nitrogen could be beneficial for the
67 denitrogenation of microalgae bio-oils.

68 High surface microsilica has also shown to be active on catalytic pyrolysis of biomass,
69 where the use of microsilica resulted in increased yield (from 6 to 15 wt.%) of dehydration
70 acid-promoted products such as anhydrosugars, compared to standard silica [19].

71 The aim of this work was therefore to study the activity of Li-LSX-zeolite as potential
72 catalyst for the catalytic pyrolysis of microalgae, evaluating their predisposition to in-situ
73 bio-oil denitrogenation, deoxygenation and to evaluate the potential production of

74 aromatics and olefins under different process conditions. Microsilica was also evaluated
75 for comparison.

76 **2. Experimental**

77 ***2.1 Raw material***

78 *Isochrysis* sp. was obtained from Varicon Aqua solutions in liquid form as biomass
79 feedstock. The biochemical compositions (carbohydrates, lipids and proteins) of
80 microalgae provided by the company can be found in the producer website [20]. The algae
81 were pre-dried in an oven at 50 °C for 2 weeks to remove all moisture content and then
82 pulverised and sieved into a particle size of <180 µm.

83 ***2.2 Catalysts preparation and characterization***

84 Li-LSX-zeolite was acquired from Shanghai Hengye Chemical Industry Co. Ltd. The
85 catalyst was crushed and sieved into a particle size of <180 µm. Then, it was calcined at
86 550 °C for 5 hours in a muffle furnace. Physical properties of the catalyst were analysed
87 using a Micromeritics Gemini VII instrument. The sample (0.5 g) was outgassed at 200
88 °C for 12 hours before running the N₂ physisorption isotherms at -195 °C. The surface
89 area was determined by using the standard Brunauer–Emmett–Teller (BET) equation.
90 Temperature programmed desorption of ammonia (NH₃-TPD) was carried out to
91 determine the acidity distribution and acid strength of the catalysts. For that purpose, a
92 ChemBET TPR/TPD equipment from Quantachrome Instruments fitted with a thermal
93 conductivity detector (TCD). Firstly, 50 mg of sample was degassed under helium flow
94 in quartz U-tube at 200 °C for 2 hours and then cooled down to room temperature in the
95 same flowing helium atmosphere. After that, the sample underwent NH₃ adsorption by
96 flowing 25 ml min⁻¹ of a gas mixture of ammonia (10%) in helium at 50 °C until saturation
97 was reached. Then, the sample was exposed to helium gas (25 ml min⁻¹) at the same

98 temperature for 2 hours to remove any physically bound ammonia from the surface. Then,
99 the desorption study was carried out under helium flow by heating the sample from 50 to
100 900 °C at a heating rate of 10 °C min⁻¹.

101 The determination of the weak and strong acid sites by pyridine desorption was carried
102 out at the Quantachrome Materials Characterisation Laboratory in Florida (USA) using a
103 Chemstar Chemisorption Instrument. The Li-LSX-zeolite was degassed at 100 °C for one
104 hour in flowing helium. The sample was then temperature programmed up to 500 °C at a
105 heating ramp of 10 °C min⁻¹ and held at that temperature (2h) to remove bound species
106 and activate the sample. Finally, the sample was cooled down to 120 °C in an atmosphere
107 of flowing helium. Next, the sample was saturated with pyridine at 120°C to minimize
108 the physisorption of the pyridine. The temperature-programmed desorption (TPD) was
109 performed by heating the sample at 10 °C min⁻¹ up to 500 °C.

110 Presence of Lewis and Brønsted acid sites was evaluated by Pyridine-FTIR. Pyridine
111 adsorption was carried out at 150 °C using a Harrick made Praying Mantis cell attached
112 to a PerkinElmer Spectrum GX instrument. The pyridine adsorbed on Lewis and Brønsted
113 acid sites gives characteristic FTIR bands at 1450 and 1540 cm⁻¹, respectively.

114 **2.3 Microalgae and products analysis**

115 *2.3.1 Proximate and elemental analysis*

116 The moisture, volatile matter and ash content of the pre-dried microalgae were determined
117 according to ASTM standards (D2016-74, E872-82, and D1102-84). The elemental
118 analysis (C, H, N) of the dried microalgae and reaction products (bio-char and bio-oil)
119 was carried out using Exeter CE-440 Elemental. The oxygen content was calculated by
120 difference (O=100-C+H+N). The high heating value (HHV) of the microalgae and of the
121 different fractions was calculated according to equation (1), which is a correlation
122 reported to be valid for solid and liquid fuels [21].

123 $HHV \left(\frac{MJ}{kg_i} \right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$ (1)

124 where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulphur and ash
125 contents of *i*.

126 2.3.2 Thermogravimetric analysis

127 A thermogravimetric analyser (TA Q500) was used to determine the moisture and volatile
128 matter contents of the microalgae using N₂ as carrier gas. The temperature programme
129 consisted in heating the sample in nitrogen gas from 20 to 105 °C with a ramp of 15 °C
130 min⁻¹ and maintaining the sample at 105 °C for 15 minutes to evaluate the moisture
131 content (MC). Then, the temperature was risen to 800 °C with ramp of 20 °C min⁻¹ and
132 hold for 30 minutes to evaluate the volatile matter. Next, the temperature was cooled to
133 550 °C under nitrogen atmosphere and held at this temperature for about 30 minutes under
134 air flow to establish the ash content. Finally, the fixed carbon content (FC) was calculated
135 by difference (FC = 100 – MC – VM – Ash). Finally, the system was cooled down to 30
136 °C at 50 °C min⁻¹. The ash content of the sample was determined from the amount of
137 solids that remains at the end of the combustion step, meanwhile the fixed carbon was
138 calculated by subtracting the ash content remaining at the end of the run.

139 2.3.3 Bio-oil and gas analysis (GC-MS and MS)

140 The chemical composition of the bio-oil samples was analysed using Gas
141 Chromatography – Mass Spectrometry (GC-MS), GC 8000 series equipped with VG Trio
142 1000. The column (length: 30 m, inner diameter: 0.25 cm; film: 0.25 µm) is temperature
143 limited from 40 to 300 °C. So, the oven was programmed at 40 °C for 10 min, then ramp
144 at 5 °C min⁻¹ to 200 °C and hold for 15 min, ramp at 10 °C min⁻¹ to 240 °C and hold for
145 15 min, ramp at 10 °C min⁻¹ to 260 °C and hold for 10 min. Helium was used as carrier
146 gas with constant flow rate of 1.7 ml min⁻¹ and an injector split ratio at 1:20 ratio. The
147 end of the column was directly introduced into the ion source detector of VG Trio 1000

148 series. Typical mass spectrometer operating conditions were as follows: transfer line 270
149 °C, ion source 250°C, electron energy of 70 eV. The chromatographic peaks were
150 identified according to the NIST library to identify bio-oil components.

151 The term rel.% C that appears in Tables 3, 6 and 7 refers to the relative % of the
152 compounds from the GC-MS analysis, which has been reported in terms of relative carbon
153 % by considering the average molecular weight (MW) and C number of the main
154 compounds in each functional group. The formula used is the following: $\text{rel.\% C} = (\text{rel\%}_n$
155 $\times \text{average C number}_n) / \text{average MW}_n$; where n represents the average of the main
156 compounds for each functional group.

157 Gasoline and diesel fractions were distributed according to their distillation temperatures
158 ranges as follows: gasoline (< 190°C), diesel cut 1 (190-290°C), diesel cut 2 (290-340°C)
159 and vacuum gas oil (340-538°C). Regarding their carbon-length, they are distributed as
160 gasoline (C₅-C₁₂), diesel cut 1 (C₁₂-C₁₆), diesel cut 2 (C₁₃-C₁₉) and vacuum gas oil (C₂₀-
161 C₂₈).

162 Meanwhile, the non-condensable gases (CO, CO₂, HCs etc.) were collected using gas
163 bags and analysed using a MKS Cirrus II Mass Spectrometer (MS). The instrument was
164 equipped with a quadrupole analyser incorporating a closed ion source, a triple mass filter
165 and a dual (Faraday and Secondary Electron Multiplier) detector system.

166 **2.4 Catalytic pyrolysis experiments**

167 The schematic diagram of the lab-scale experimental setup used for the catalytic pyrolysis
168 experiments is shown in Figure 1. This setup consists of a vertical fixed bed stainless steel
169 reactor (0.75 cm inner diameter and 24 cm length) heated by an electrical furnace. The
170 reaction temperature was measure by K type thermocouple in contact to the catalyst bed
171 inside the reactor. The catalytic pyrolysis tests were carried out by mixing the microalgae
172 with the catalyst according to the selected catalyst to microalgae ratio, with a fixed

173 microalgae amount of 1.5 g, which were properly mixed before placed in the reactor. The
174 pyrolysis tests were carried out at atmospheric pressure and temperatures ranging from
175 400 to 700 °C, with a nitrogen flow of 300 ml min⁻¹, which corresponded to a gas
176 residence time of around 8 seconds.

177 Prior to the pyrolysis experiments, the whole system was purged with N₂ for 10 min to
178 ensure inert atmosphere. Once the furnace temperature reached the desired set point, the
179 reactor was suddenly inserted in the tubular furnace for the pyrolysis reaction to take
180 place. The bio-oil vapours and condensable gases were collected in a cold trap system,
181 while the bio-char was recovered from the reactor after cooling. The condensation system
182 consisted of two Dreschel flasks connected in series in a water-ice bath and one Dreschel
183 flask more placed in a liquid nitrogen bath. The condensable product (bio-oil) was
184 recovered by washing the flasks with acetone. Then, the solvent was evaporated at room
185 temperature for 20 h. Then, the remaining solid was recovered, weighed and recorded as
186 bio-char yield by considering the amount of catalyst. Finally, the non-condensable gases
187 were collected in a 1 litre sampling bag and then analysed by MS. The gas yield (wt.%)
188 was calculated by the difference from overall mass balance ($GAS = 100 - (BIO-OIL +$
189 $CHAR)$). Pyrolysis experiments and products analyses (proximate and EA) were carried
190 out by triplicates to measure the experimental error, which was assessed to be lower than
191 5%.

192 **3. Results and Discussion**

193 ***3.1 Microalgae characterization***

194 Table 1 shows the main characteristics and chemical compositions of *Isochrysis* sp.
195 microalgae. The proximate analysis (wet basis) shows that *Isochrysis* sp. volatile matter
196 content (76.9 wt.%) is higher than other species such as *Chlorella vulgaris* (68.2 wt.%),
197 which is widely been used in the pyrolysis experiments [6,7]. The high amount of volatile

198 matter in biomass strongly influences its thermal decomposition, and provides
199 information on the potential bio-oil yield [22]. Ash content in *Isochrysis* sp. (16.3 wt.%)
200 is similar to that of *Chlorella* (15.1 wt.%).

201 The biochemical composition of *Isochrysis* sp. (Table 1) indicates that the protein content
202 is similar to that of other microalgae species reported in literature, such as *Chlorella*
203 *vulgaris* (42.5 wt.%) and *Thalassiosira weissfologi* (43 wt.%) [23,24]. While microalgae
204 containing higher lipid contents, such as *Chlorella*, are suitable to produce bio-diesel;
205 microalgae less-rich in lipids and richer in carbohydrates, like *Isochrysis* sp., are more
206 suitable to “whole-conversion” technologies, such as pyrolysis and liquefaction.

207 Table 1 also reports the elemental analysis (dry basis) of *Isochrysis* sp., where it can be
208 seen that the microalgae possesses high N content (4.0 wt.%) compared to that of
209 lignocellulose (< 0.5 wt.%), due to their high content in proteins and chlorophyll [8,25].
210 However, *Isochrysis* sp. also present a high O content (35.7 wt.%) as occurs with
211 terrestrial plants. Therefore, methods to reduce both O and N contents would be beneficial
212 to improve the quality of bio-oil obtained from *Isochrysis* sp. microalgae pyrolysis.

213 **3.2 Catalysts characterization**

214 The specific surface area (BET), and total pore volume of Li-LSX-zeolite were 662.02
215 $\text{m}^2 \text{g}^{-1}$ and $0.27 \text{ cm}^3 \text{ g}^{-1}$, respectively. The catalyst is a low silica X type (LSX) zeolite
216 with of Si/Al ratio of 1.0. Instead, the specific surface area (BET) and total pore volume
217 of microsilica were $640 \text{ m}^2 \text{ g}^{-1}$ and $0.40 \text{ cm}^3 \text{ g}^{-1}$, respectively. For comparison, HZSM-5,
218 which has widely been used in catalytic pyrolysis of biomass, had a BET surface of 425
219 $\text{m}^2 \text{ g}^{-1}$.

220 The NH_3 -TPD profile of the Li-LSX-zeolite catalyst resulted in a total acidity of 1.68
221 $\text{mmol of NH}_3 \text{ g}^{-1}$, which is higher than the acidity reported for HZSM-5 (0.61 mmol of
222 $\text{NH}_3 \text{ g}^{-1}$) with Si/Al = 30 [26]. The total acid sites quantified by NH_3 -TPD resulted similar

223 to β -zeolites ((Si/Al = 21): 1.70 mmol of $\text{NH}_3 \text{ g}^{-1}$ (Si/Al = 25): 1 mmol of $\text{NH}_3 \text{ g}^{-1}$), where
224 the number of total acid sites was found to increase with decreasing Si/Al [27]. Nieva et
225 al. [19] studied high surface area (HSA) SiO_2 , where the total acidity of the catalyst was
226 found to be 0.17 mmol of $\text{NH}_3 \text{ g}^{-1}$ (3.3 ml $\text{NH}_3 \text{ g}^{-1}$), which represent weak acid strength.
227 Since NH_3 -TPD can only be used to calculate the total acidity of a solid catalyst, pyridine-
228 TPD was used to quantify the presence of weak, moderate and strong acid sites. Figure
229 2A shows the desorption profile of pyridine from the Li-LSX-zeolite, which clearly
230 indicate the presence of weak acid sites (peak at 237 °C) and strong acid sites (peak at
231 498 °C). Also, the presence of moderate strength acid sites is suggested by the shoulder
232 between the two main peaks. From the quantification of these acid sites can be observed
233 that the abundance of weak and strong acid sites was quite similar. Thus, the weak acid
234 sites concentration (180 – 280 °C) was 2.39 mmol pyridine g^{-1} , while that of strong acid
235 sites (290 – 500°C) was 2.21 mmol pyridine g^{-1} . Therefore, Li-LSX-zeolite possesses
236 acidic properties. Since the catalytic activity of the Li-LSX-zeolite may be explained
237 by the acid sites type, the catalysts were investigated via pyridine adsorption on the
238 catalyst surface using FT-IR spectroscopy. Since pyridine is larger than NH_3 , it can
239 adsorb only on the main zeolite channels (>0.7 nm), which are also the pores range
240 required for catalytic cracking reactions and titrate only to medium and strong acid
241 sites [28]. Figure 2B shows the infrared spectra of Li-LSX-zeolite (dotted line) and
242 pyridine adsorbed on the Li-LSX-zeolite at 150 °C (solid line). After pyridine
243 adsorption, the bands corresponding to the Lewis acid sites (L): 1450 cm^{-1} , and
244 Brønsted acid sites (B): 1540 cm^{-1} were detected together with another strong band at
245 1595 cm^{-1} (denoted as H), which can be assigned to weak hydrogen-bonds between
246 pyridine and the surface silanol groups of zeolite [29]. The band at 1492 cm^{-1} can be
247 attributed to both Lewis and Brønsted acid sites. The ration between bands associated

248 to Lewis acid and Brønsted acid sites suggest that the latter are less abundant. The
249 generation of Lewis acidity could be linked to the Li incorporation in the tetrahedral
250 coordination within the silica framework as observed for other zeolites [29]. In
251 summary, the acid sites characterisation indicates that the Li-LSX-zeolite can be
252 considered as an acid catalyst and its catalytic activity linked to those properties.

253 ***3.3 Effect of microsilica and Li-LSX-zeolite catalysts***

254 To evaluate the effect of the microsilica and Li-LSX-zeolite catalysts on the catalytic
255 pyrolysis of *Isochrysis* sp. at 500 °C with a catalyst to microalgae ratio (1:1), the non-
256 catalytic pyrolysis of same microalgae was carried out without any catalyst. Figure 3A
257 shows the products distribution from the non-catalytic and catalytic pyrolysis of
258 *Isochrysis* sp. A remarkable reduction in the bio-oil yield from 37 wt.% for the non-
259 catalytic test to 28 – 29 wt.% with catalyst was observed. Acid sites on the catalyst surface
260 promoted a series of reactions such as dehydration, decarboxylation, decarbonylation and
261 aromatization; thus, increasing cracking to gaseous and vapours products [13,30]. The
262 cracking activity of the strong acidity of Li-LSX-zeolite and the mild acidic microsilica
263 resulted in an increased gas yield from 28 wt.% (non-catalytic) to \approx 36 wt.% with Li-
264 LSX-zeolite and microsilica.

265 The bio-char yield (\approx 35 wt.%) was not affected by the presence of the catalysts,
266 suggesting that the alkali presence in the microalgae are mostly responsible for the char
267 formation. Bio-char formation is also related to the high microalgae content in proteins,
268 which are partly converted into bio-char during pyrolysis [31].

269 Table 2 reports the elemental analysis and high heating value (HHV) of the obtained bio-
270 chars and bio-oils. As expected, catalytic pyrolysis led to significant improvements
271 compared to the non-catalytic experiment. Also, despite the products distribution did not

272 show remarkable differences between the use of Li-LSX-zeolite and microsilica, the
273 elemental analysis clearly indicate that Li-LSX-zeolite enhanced the bio-oil quality.
274 The bio-char obtained from the catalytic pyrolysis with Li-LSX-zeolite presented a higher
275 calorific value than that obtained from the non-catalytic pyrolysis, 23.0 vs. 14.2 MJ kg⁻¹,
276 respectively. So, the presence of catalysts produced bio-chars with higher C and N content
277 (Li-LSX-zeolite: 52.0 and 4.7 wt.%, respectively; SiO₂: 48.6 and 4.1 wt.%, respectively)
278 compared to the non-catalytic pyrolysis (45.4 and 3.4 wt.%, respectively). Therefore,
279 catalytic bio-chars could be used as soil amendment due to their high C and N content if
280 the catalysts are separated and recovered (e.g. ex-situ catalytic pyrolysis configuration).
281 Then, the oxygen remaining in the catalytically obtained bio-chars was lower than in that
282 non-catalytically obtained, with values of 36 and 43 wt.% for Li-LSX-zeolite and SiO₂,
283 respectively, in comparison with 48 wt.%; which could be explained by the strong acidity
284 of Li-LSX-zeolite and its propensity for cracking and aromatisation reactions.
285 The higher HHV of microalgae chars derived from catalytic experiments was due to the
286 higher carbon and hydrogen contents and therefore lower oxygen (determined by
287 difference) in comparison to the char non-catalytically obtained. This can be explained
288 by the acidity of the employed catalyst, which promoted gas formation (see Figure 3),
289 deoxygenation and cooking reactions. The larger carbon content in Li-LSX zeolite
290 derived char compared to the SiO₂ one can be further explained by the former being more
291 acid than the latter. Moreover, the lower rates of mass transfer in the in-situ configuration,
292 with direct mixing of coke precursors with the catalyst and enhanced coke formation
293 contributed to the high C content [32].
294 This trend is also shown in the elemental analysis of bio-oils due to the use of Li-LSX-
295 zeolite resulted in a bio-oil with a C content 4 w% higher, while contents of O and N were
296 reduced in 8 and 46 %, respectively, with respect to the one non-catalytically produced,

297 denoting a strong propensity of this catalyst toward bio-oil denitrogenation. Even though,
298 HZSM-5 have also shown a significant nitrogen removal when a large amount of catalyst
299 was employed (catalyst to microalgae ratio 20:1), it did not show reduction of nitrogen
300 content at the catalyst to microalgae ratio (1:1) herein used [7,8,33].

301 In presence of catalyst, the oxygen is removed through several reactions such as
302 decarboxylation, decarbonylation and dehydration, resulting in a high gas yield and low
303 bio-oil yield compared to the non-catalytic pyrolysis [4,34,35]. Pan et al. [8] studied the
304 catalytic pyrolysis of *Nannochloropsis* sp. in presence of HZSM-5 using a fixed bed
305 reactor, in which the bio-oil oxygen content decreased with respect to that non-
306 catalytically obtained from 30 to 19.5 wt.%, as well as the high heating value (HHV) was
307 significantly improved from 24.4 to 32.2 MJ kg⁻¹. The HHV of the bio-oil obtained in this
308 study using Li-LSX-zeolite was even higher (36.3 MJ kg⁻¹) than that catalytically
309 obtained by Pan et al. [8] due to a lower bio-oil oxygen content (13 wt.%). However, the
310 deoxygenation activity of the Li-LSX-zeolite (expressed as % of O with respect of that
311 initially contained in the microalgae) using a 1:1 catalyst to microalgae ratio was lower
312 than that observed with the HZSM-5 [8]. The elemental analysis of the bio-oils obtained
313 using microsilica where somehow similar to those obtained in absence of catalysts,
314 suggesting a limited catalytic activity.

315 Overall, the results in Table 2 clearly show that presence of Li-LSX-zeolite catalyst
316 improves the elemental composition and physical properties of the bio-oil with respect to
317 those obtained by using microsilica or without any catalyst.

318 Figure 4A shows the distribution of the nitrogen initially contained in the *Isochrysis* sp.
319 among the products obtained during the catalytic and non-catalytic pyrolysis at 500 °C.
320 Bio-oil obtained without catalyst retained about 27.3 % of the total nitrogen, while 50.1
321 % went into the gas fraction. The use of Li-LSX-zeolite lowered the nitrogen present in

322 the bio-oil to about 11.5 %, which was mostly removed in the gaseous phase (57.4 %),
323 while still 31 % of the nitrogen remained in the bio-char. N in the gaseous phase was
324 mostly in form of NH₃. This denitrogenation activity might be linked to the Li-LSX-
325 zeolite affinity to nitrogen.

326 The GC-MS analysis of the *Isochrysis* sp. bio-oils produced at 500 °C (catalyst to
327 microalgae ratio 1:1) were carried out to determine their composition (in terms of rel.%
328 C content) and to compare the effect of the two catalysts. The identified compounds were
329 grouped in nine different chemical groups as shown in Table 3. Aliphatics were the most
330 abundant for all the bio-oils, while the non-catalytic and the microsilica bio-oils were also
331 rich in nitrogenated compounds, ketones and alcohols (mostly in the non-catalytic bio-
332 oil). Aliphatics (alkanes and alkenes) mainly came from the depolymerisation of algal
333 fatty acids [24]. Among the aliphatics found in the bio-oils were: tridecane, tetradecane,
334 dodecene, 2-hexadecene, docosane and heptadecane. Microsilica did not have the ability
335 to remove nitrogen as Li-LSX-zeolite. The bio-oil obtained using Li-LSX-zeolite
336 contained the largest share of aromatics and the lowest of nitrogen compounds. The main
337 aromatics compounds were phenols, phenol substitutes, benzenes, indoles and
338 naphthalenes. Weak acid sites in microsilica resulted in an increased formation of
339 aliphatics, while Li-LSX-zeolite tended to partially convert long chain alkanes into
340 aromatics and olefins. According to Song et al. [36], strong acid sites are essential for the
341 transformation of olefins into aromatics. The aromatic fractions were also increased due
342 to Diels-Alder and condensation reactions. Du et al. [9] obtained 17 % aromatics from
343 the pyrolysis of *Chlorella* in presence of HZSM-5 with a catalyst to algae ratio of 5:1.
344 The ¹H-NMR of the bio-oils (shown in Table 4) confirm that all the bio-oils are rich in
345 aliphatic protons (0-2.2 ppm) and that the Li-LSX-zeolite promoted aromatics formation
346 (6.8-8 ppm). Also, the ¹H-NMR shows that the protons bonded to oxygenated species (3-

347 6.4 ppm) decrease in the following order: No catalyst (6.5%) > microsilica (4.5%) > Li-
348 LSX-zeolite (3.1%) indicating a higher deoxygenation activity for the lithium zeolite.

349 ***3.4 Effect of temperature on catalytic pyrolysis***

350 The catalytic screening showed that Li-LSX-zeolite is able to denitrogenate and partially
351 deoxygenate the *Isochrysis* sp. bio-oil and promoted the production of aromatics.
352 Therefore, Li-LSX-zeolite was further investigated to establish the effect of temperature
353 and catalyst to microalgae ratio on the products distribution and composition.

354 Figure 3B depicts the products yield obtained from the catalytic pyrolysis of *Isochrysis*
355 sp. at temperatures of between 400 to 700 °C. The gas fraction yield increased steadily
356 from 34 to 48 wt.% at expenses of the bio-char, which decreased from 46 to 28 wt.%,
357 with increasing the reaction temperature from 400 to 700 °C. But also, the bio-char yield
358 decreased at high temperatures due to the increasing cracking activity at 600 and 700 °C.
359 The maximum bio-oil yield was obtained at 500 °C (29 wt.%), decreasing as temperature
360 increased because the pyrolysis vapours underwent secondary cracking reactions at high
361 temperature leading to a higher gas yield, similarly to that obtained in previous works
362 using ceria-based catalysts from *Pavlova* sp. and *Nannochloropsis* microalgae,
363 respectively [37,38].

364 Table 5 shows the gas composition obtained from the pyrolysis at different temperatures
365 in terms of C content (rel.%). Increasing temperature cracked aliphatic and nitrogenated
366 compounds in bio-oil into low molecular weight gaseous products such as CO, CO₂, CH₄,
367 H₂ and C₂-C₄ olefins. Thus, the increase of reaction temperature from 400 to 700 °C led
368 to a rise in the olefins carbon content from 29 to 38 wt.%.

369 The elemental analysis of the bio-chars and bio-oils (Table 2) from the catalytic pyrolysis
370 at different temperature. As expected, the C content in the bio-chars increased according
371 to the increase of temperature to a maximum of 71 wt.% at 700 °C. The increase in the

372 pyrolysis temperature conducted to a further bio-char carbonization due to a larger
373 microalgae devolatilization, giving rise to bio-chars with much higher carbon content and
374 lower oxygen, phenomenon that is well described in literature [39,40].

375 The bio-oil produced between 500 and 700 °C contained the lowest N content of 2.1 –
376 2.3 wt.%. The highest HHV value (36.3 MJ kg⁻¹) was obtained at 500 °C and was
377 somehow comparable to that of petroleum derived fuels (42 MJ kg⁻¹) and diesel (43 MJ
378 kg⁻¹). The decrease of HHV at 700 °C is due to high retention of C in the solid phase.

379 Table 6 shows the GC-MS bio-oil composition in terms of C content (rel.%) as a function
380 of the pyrolysis temperature. Increasing the temperature from 400 to 500 °C already
381 resulted in an increased aromatics content from 5.1 to 11.8 rel.% C, respectively. This
382 can be partially attributed to thermal degradation of proteins to phenols and NH₃,
383 Aromatics are mainly produced due to the presence of Brønsted and Lewis acid sites in
384 the Li-LSX-zeolite, which enhance dehydration, decarbonylation and aromatization
385 reactions. Also, low Si/Al ratio has been linked to maximum aromatic yield, due to
386 enhanced concentration of acid sites in close proximity to one another [9]. The pyrolysis
387 of the fatty acids led to the formation of a large fraction of aliphatic, mostly alkanes,
388 which had the maximum rel.% C at 500 °C, with 23.1 % and then decreased to 19.4 % at
389 700 °C, suggesting transfer of C to gas and coke. A similar trend is shown by the other
390 chemical functionalities.

391 Temperature had a great effect on removing nitrogen from the bio-oil in favour of gaseous
392 species. Amides, pyridines, nitriles, amines and indoles were among the identified N-
393 compounds. Amides and nitriles can be formed from the reaction of proteins and fatty
394 acids pyrolysis products, while cyclic amides can be formed from protein intramolecular
395 cyclization [25]. Indoles may derive from tryptophan amino acids [41]. Indoles were the
396 most abundant nitrogenates in the N-compound group and their content decreased with

397 the increase of temperature: 13.2 rel.% (400 °C) > 2.8 rel.% (500 °C) > 2.2 rel.% (600
398 °C) > 1.8 rel.% (700 °C).

399 Figure 5A shows the results of bio-oils composition based on the products boiling point
400 grouped in 4 fractions. Gasoline fraction was improved with increasing temperature from
401 3.8 to 27 rel.% from 400 °C to 700 °C. The vacuum gas oil decreased from 3.9 to 1.4
402 rel.% decreasing temperatures of 400 to 700 °C, respectively; suggesting that these high
403 molecular weight compounds were cracked into smaller compounds as the temperature
404 increased. The most favourable result, in terms of diesel fraction, was achieved at 500 °C
405 with 24.4 and 22.1 rel.% of diesel cut 1 and diesel cut 2, respectively.

406 ***3.5 Effect of catalyst to microalgae ratio***

407 The effect of catalyst to microalgae ratio (0.5:1, 1:1 and 3:1 g/g) was investigated by
408 varying the amounts of Li-LSX-zeolite (0.75, 1.5 and 4.5 g, respectively) and keeping
409 constant the microalgae amount of 1.5 g during the catalytic pyrolysis of *Isochrysis* sp. at
410 500 °C, whose products distribution is depicted in Figure 3C. There was a substantial
411 reduction in the bio-oil production compared to the non-catalytic tests, since the bio-oil
412 yield decrease from 37 wt.% (non-catalytic) to 30, 29 and 23 wt.% for catalytic tests with
413 catalyst to microalgae ratios of 0.5:1, 1:1 and 3:1, respectively. In parallel, a linear
414 improvement in the gas yield can be observed with increasing catalyst ratio, with a
415 maximum of 43 wt.% obtained using a ratio of 3:1. This effect might be due to the larger
416 the catalyst ratio the longer the contact time between the pyrolysis vapours and the
417 catalyst, which necessarily increases the cracking of these vapours, giving rise to an
418 increment in the production of smaller molecules that remains in the gas phase as non-
419 condensable species [42]. Therefore, high catalyst amount increases the cracking activity
420 of most of the long-chain aliphatic compounds (mainly from fatty acids) generating larger
421 quantities of light olefins and alkanes in the gas phase (see Table 5). Light olefins may

422 be formed by decarbonylation of intermediate oxygenates or from alkyl aromatics [43].
423 During catalytic deoxygenation of bio-oil vapours, the oxygen was released through
424 different reactions: decarboxylation, decarbonylation and dehydration leading to the
425 formation of CO₂, CO and H₂O, respectively. Increasing the catalyst share resulted in
426 higher deoxygenation degree by decarbonylation. The presence of olefins in the gas
427 produced by the non-catalytic pyrolysis of *Isochrysis* sp. can be linked to presence of
428 aliphatic amino acids, such as valine and isoleucine [44]. Proteins also lead to formation
429 of CO and NH₃ in the gas phase in presence of Li-LSX-zeolite. A similar effect was
430 shown by ZSM-5 in the pyrolysis of dried distillers grains (DDGS) [44]. Moreover, the
431 study of model compounds such as leucine and proline clearly indicated that proteins lead
432 to the preferential formation of CO over CO₂ [45]. The large amount of CO produced
433 when using Li-LSX-zeolite suggests that its strong acid sites are very active for
434 decarbonylation of oxygenates.

435 A detailed elemental analysis of the bio-chars and bio-oils obtained from the pyrolysis
436 experiments at different catalyst to microalgae ratio is presented in Table 2. The amount
437 of the Li-LSX-zeolite has a clear effect on the distribution of C, N, H and O in the solid
438 and liquid products. Bio-chars were enriched in C and H, while O content decreased
439 denoting an increasing cracking, cooking and aromatization degree. Regarding bio-oils,
440 in this study the N content was reduced drastically from 3.9 to 0.8 wt.%, when the catalyst
441 to microalgae ratio was increased from 0.5:1 to 3:1. This is in agreement with Gopakumar
442 et al. [7], who got a bio-oil nitrogen content reduction when the catalyst load increased
443 four times that of biomass, remarking that increasing the catalyst ratio enhanced
444 denitrogenation reactions.

445 A detailed nitrogen distribution among the pyrolysis products is illustrated in Figure 4B,
446 in which can be appreciated that nitrogen share of bio-oil drastically decreased from 27

447 % (non-catalytic pyrolysis) to 11.5 and 3.4 % for those catalytic tests with catalyst to
448 microalgae ratios of 1:1 and 3:1, respectively.

449 The chemical composition of the bio-oils obtained with the different catalyst to
450 microalgae ratios is shown in Table 7. As expected, the increase of the catalyst loading
451 resulted in almost doubling the aromatics from ~8 rel.% C (0.5:1) to 14.5 rel.% C (3:1) at
452 the expenses of aliphatics that were cracked down to aromatics and olefins (see Table 5).
453 Moreover, the alcohol and ester functionalities were reduced when the ratio was raised
454 up to 3:1. Aromatic compounds such as benzene, toluene, naphthalene and indene were
455 formed from the thermal and catalytic cracked microalgae fatty acids, proteins and
456 carbohydrates. Mono-aromatics were formed by diffusion of the cracked hydrocarbon
457 pool into the catalyst pores, where they underwent a series of dehydration,
458 decarbonylation, decarboxylation, isomerization and oligomerization reactions. Larger
459 aromatic compounds such as naphthalene, trimethyl naphthalene or dimethyl benzene
460 were formed through secondary alkylation of smaller aromatics or likely formed on the
461 catalyst surface [30]. Increasing the catalyst ratio resulted in a large fraction of
462 polyaromatic compounds (PAH) such as phenanthrene, chamazulene, azulene, etc.

463 Wang and Brown [44] found that that the pyrolysis of protein rich materials, such as dried
464 distillers grains (DDGS), in presence of ZSM-5 (catalyst to biomass ratio of 20:1) resulted
465 in \approx 39 and 12 % of olefins and aromatics, respectively at 600 °C. Similarly, the yield of
466 olefins and aromatics were larger using Li-LSX-zeolite with a 3:1 catalyst to microalgae
467 ratio at 500 °C. This is also supported by the correlation between the aromatic yield and
468 the catalytic coke yield shown in Figure 6, where the coke is defined as the difference
469 between the catalytic coke minus the thermal coke (without catalyst). As can be seen in
470 this figure, there is a linear correlation ($R^2=0.956$) of increasing coke formation with the
471 growth in aromatic yield as the catalyst to microalgae ratio was increased.

472 Figure 5B shows the bio-oil compounds distribution based on gasoline, diesel and
473 vacuum gasoil fractions, according to ASTM D2887. Only compounds with boiling
474 points within the range were calculated and their weight percentage presented. As can be
475 seen, Li-LSX-zeolite increased the fractions of gasoline and diesel compared to the non-
476 catalytic pyrolysis run. Li-LSX-zeolite exhibits both Brønsted and Lewis acidity and a
477 pores size distribution that promoted the production of both aromatic and aliphatic
478 compounds in the gasoline and diesel range. Most of the compounds produced in the bio-
479 oil are in diesel range (cut 1 and cut 2) with hydrocarbon chains between C₁₁-C₂₀ such as
480 n-undecane, n-tetradecane, n-hexadecane and n-octadecane. These long chain aliphatic
481 compounds originates from the decomposition of lipids or fatty acids after cracking,
482 decarbonylation and decarboxylation reactions [15]. Increasing catalyst ratio reduced the
483 diesel cut and vacuum gas oil fraction, and tended to form more aromatic compounds
484 instead.

485 N-cyclic aliphatic amino acids in the microalgae proteins are converted in heterocyclic
486 compounds, such as indoles and pyrroles, which tend to form coke being unsaturated.
487 Therefore, the decreased in N-compound with the catalyst to microalgae ratio of 3:1 can
488 be linked to formation of gaseous CO and NH₃, but also to coking reactions on the catalyst
489 surface.

490 **4. Conclusions**

491 Li-LSX-zeolite showed a good catalytic performance for bio-oil denitrogenation and
492 olefins and aromatics production. The optimum temperature for the *Isochrysis* sp.
493 catalytic pyrolysis in terms of quantity resulted at 500 °C, with a catalyst to microalgae
494 ratio of 1:1 g/g, which yielded 29 wt.% of bio-oil and maximum aromatics (11.8 %) and
495 aliphatics (23.1 %) production, resulting in the larger diesel cut fractions (45%). The

496 increase of temperature led to transfer of C to the gas phase, coke formation on the catalyst
497 surface and decrease in N-compounds in the bio-oil.

498 The increase of the catalyst to biomass ratio from 0.5:1 to 3:1 resulted in 23% bio-oil and
499 43% gas. Long chain alkanes and protein derived intermediates were cracked in the
500 Bronsted and Lewis acid sites to olefins and aromatics through decarbonylation and NH₃
501 formation. Regarding to bio-oil denitrogenation, the catalyst amount resulted vital, as N
502 content in bio-oil was reduced from 3.9 wt.% (non-catalytic) to barely 0.8 wt.% (3:1).
503 Also, the aromatics produced with a catalyst to microalgae ratio of 3:1 were five-fold
504 those non-catalytically obtained.

505 In conclusion, Li-LSX-zeolite showed a very good denitrogenation activity, but a mild
506 deoxygenation capacity compared to ZSM-5, which can be useful for the production of
507 olefins and an alkanes and aromatics rich bio-oil from protein rich materials such as
508 microalgae.

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641 acid, Energy Convers. Manag. 112 (2016) 220–225.
- 642

643 **Tables**644 Table 1. Main characteristics of *Isochrysis* sp. microalgae

Proximate analysis (wet basis, wt.%)	
Moisture content	5.8
Volatile matter	76.9
Fixed carbon	1.0
Ash	16.3
Elemental analysis (dry basis, wt.%)	
Carbon	38.1
Hydrogen	4.9
Nitrogen	4.0
Oxygen	35.7
Higher Heating Value (MJ kg ⁻¹)	15.0
Chemical composition (wt.%)	
Protein	44.0
Lipids	19.0
Carbohydrates	25.0

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Table 2. Elemental analysis, H/C and O/C molar ratios and HHV of bio-chars and bio-oils obtained from the catalytic and non-catalytic pyrolysis of *Isochrysis* sp. at 500°C under different conditions.

	Bio-char (daf, wt.%) [*]							Bio-oil (wt.%)						
	Carbon	Hydrogen	Nitrogen	Oxygen	H/C molar ratio	O/C molar ratio	HHV (MJ kg ⁻¹)	Carbon	Hydrogen	Nitrogen	Oxygen	H/C molar ratio	O/C molar ratio	HHV (MJ kg ⁻¹)
<i>Different catalysts</i>														
Non-catalytic	45.41	2.91	3.41	48.24	0.77	0.8	14.25	71.69	10.01	3.89	14.41	1.68	0.15	35.27
SiO ₂	48.56	4.34	4.12	42.98	1.07	0.66	17.56	71.8	9.71	3.47	15.02	1.62	0.16	34.90
Li-LSX-zeolite	52.00	7.36	4.72	35.91	1.7	0.52	23.04	74.77	9.86	2.11	13.26	1.58	0.13	36.32
<i>Different Temperatures, °C</i>														
400	41.88	7.65	4.45	46.01	2.19	0.82	18.82	70.43	9.05	3.07	17.46	1.54	0.19	33.39
500	52.00	7.36	4.72	35.91	1.7	0.52	23.04	74.77	9.86	2.11	13.26	1.58	0.13	36.32
600	63.22	7.51	2.99	26.28	1.43	0.31	28.16	74.27	8.85	2.12	13.76	1.43	0.14	34.90
700	71.23	7.07	0.11	21.59	1.19	0.23	30.96	71.45	9.25	2.28	17.02	1.55	0.18	34.05
<i>Different Cat.:algae ratios</i>														
0.5:1	47.41	3.61	4.36	44.62	0.91	0.71	16.13	75.57	9.84	3.87	10.72	1.56	0.11	36.81
1:1	52.00	7.36	4.72	35.91	1.7	0.52	23.04	74.77	9.86	2.11	13.26	1.58	0.13	36.32
3:1	64.6	8.99	4.56	21.86	1.67	0.25	30.81	73.99	10.23	0.79	14.99	1.66	0.15	36.32

Table 3. GC-MS analysis of the bio-oils obtained from the non-catalytic and catalytic pyrolysis of *Isochrysis* sp. at 500°C (catalyst to microalgae ratio 1:1)

Group families	C (rel.%)		
	Non-catalytic	SiO ₂	Li-LSX-zeolite
Alcohols	12.35	4.51	2.93
Aldehydes	1.67	0.90	0.73
Aliphatics	26.49	29.94	23.13
Aromatics	2.89	2.02	11.84
Carboxylic acid	2.27	0.93	2.07
Esters	3.67	1.97	3.25
Ethers	0.84	0.78	1.31
Ketones	9.33	3.73	3.43
Nitrogen compounds	12.42	8.35	5.52

Table 4. Proton NMR of the bio-oil obtained from the non-catalytic and catalytic pyrolysis of *Isochrysis* sp. at 500°C (catalyst to microalgae ratio 1:1)

Chemical shift region (ppm)	Type of protons	Non-catalytic	SiO₂	Li-LSX-zeolite
0.0 - 1.6	CH ₃ . -CH ₂ -	63.17	61.07	67.43
1.6 - 2.2	-CH ₂ -, aliphatic OH	13.19	17.67	10.01
2.2 - 3.0	-CH ₃ OC, -CH ₃ -Ar, -CH ₂ Ar	8.73	7.55	6.01
3.0 - 4.2	CH ₃ O-, -CH ₂ O-, =CHO	3.38	1.54	1.74
4.2 - 6.4	=CHO, ArOH, HC=C (nonconjugated)	3.12	3.01	1.35
6.4 - 6.8	HC=C (nonconjugated)	0.43	0.21	0.61
6.8 - 8.0	ArH, HC=C (conjugated)	7.65	8.70	13.66
8.0 - 10.0	-CHO, -COOH, downfield ArH	0.33	0.24	0.13

Table 5. Gas product distributions obtained from the catalytic pyrolysis of *Isochrysis* sp. at different temperatures (at catalyst:algae ratio 1:1) and at different catalyst: algae ratios.

Gas, C wt. %	CO	CO ₂	CH ₄	Olefins (C ₂ H ₄ , C ₂ H ₃ , C ₃ H ₆ , C ₄ H ₈)	Alkanes (C ₃ H ₈ , C ₂ H ₆ , C ₄ H ₁₀ , C ₅ H ₁₂)
<i>Different temperatures, °C</i>					
400	7.03	0.41	0.48	29.17	14.38
500	8.12	0.87	1.17	26.98	8.63
600	8.78	0.49	1.2	33.44	11.88
700	8.87	0.7	1.54	38.23	10.23
<i>Different Cat.:algae ratios</i>					
Non-catalytic	5.22	1.26	0.87	17.14	3.56
0.5:1	8.49	0.93	1.5	26.08	8.14
1:1	8.12	0.87	1.17	26.98	8.63
3:1	9.33	0.97	1.02	33.6	10.99

Table 6. GC-MS analysis of the bio-oils obtained from catalytic pyrolysis of *Isochrysis* sp. at different temperatures (catalyst to microalgae ratio 1:1)

Group families	C (rel.%)			
	Temperature (°C)			
	400	500	600	700
Alcohols	2.12	2.93	2.54	2.20
Aldehydes	4.25	0.73	0.00	0.00
Aliphatics	21.77	23.13	20.90	19.44
Aromatics	5.15	11.84	11.46	10.47
Carboxylic acid	2.18	2.07	1.91	1.93
Esters	2.73	3.25	2.78	1.29
Ethers	0.39	1.31	0.93	0.64
Ketones	3.29	3.43	3.25	2.72
Nitrogen compounds	6.65	5.52	4.61	1.73

Table 7. GC-MS analysis of the bio-oils obtained from catalytic pyrolysis of *Isochrysis* sp. at 500 °C and different catalyst to microalgae ratio

Group families	C (rel.%)			
	Catalyst:biomass (g/g)			
	Non-catalytic	0.5:1	1:1	3:1
Alcohols	12.35	5.36	2.94	1.10
Aldehydes	1.67	0.71	0.73	0.53
Aliphatics	26.49	22.34	23.14	15.18
Aromatics	2.89	7.85	11.85	14.51
Carboxylic acid	2.27	0.99	2.07	1.84
Esters	3.67	7.42	3.25	1.63
Ethers	0.84	2.56	1.31	2.20
Ketones	9.33	3.26	3.43	3.28
Nitrogen compounds	12.42	4.37	5.52	3.82