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

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Abstract

In this work, we report for the first time the use of Li-LSX-zeolite as catalyst for the catalytic pyrolysis of biomass (*Isochrysis* sp. Microalgae). Li-LSX-zeolite showed a good catalytic performance, principally for bio-oil denitrogenation (mainly in form of NH_3), and good activity for olefins and aromatics production. At 500 °C, 11.8 % aromatics and 23.1% aliphatics were produced. The increase of temperature led to transfer of C to the gas phase, coke formation on the catalyst surface and decrease in N-compounds in the bio-oil. The increase of the catalyst to biomass ratio from 0 to 3:1 resulted in the aromatics being five-fold those non-catalytically obtained and in a higher cracking power that reduced the bio-oil to 23% at expenses of olefins rich gas. However, a linear correlation between coke formation and aromatic yield was observed as the catalyst to microalgae ratio was increased. Therefore, the experimental results indicate that Li-LSX-zeolite could be used as catalyst for in-situ denitrogenation of microalgae bio-oil and for enhancing aliphatics and aromatics formation to be blend in gasoline and diesel and olefins in gas phase.

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

1. Introduction

Microalgae have great potential as feedstock for bioenergy production because of their high productivity, fast growth rate, capability to fix CO_2 and for being not in competition with food crops. The raw microalgae can be pyrolysed to get a liquid bio-oil, which still contains a large fraction of the microalgae initial energy [1]. Oxygen and nitrogen compounds represent the main limitation for the bio-oil implementation as biofuel, and methods/catalysts able to reduce O and N content in the bio-oil during or after its production must be developed. Catalytic pyrolysis is a process in which a catalyst is used to promote deoxygenation of the bio-oils through simultaneous dehydration, decarboxylation and decarbonylation reactions [2–5]. Among these catalysts, zeolitic materials such as ZSM-5 zeolite, have been found to be very active to deoxygenate pyrolysis vapours and to produce aromatic hydrocarbons [6–9].

The simultaneous in-situ deoxygenation and denitrogenation of microalgae pyrolysis bio-oils is somehow a new research topic, with few works available in literature, since nitrogen is typically removed via hydro-processing [10,11]. Despite this, bio-oils hydro-processing consumes large amount of H_2 and the development of in-situ oxygen and nitrogen removal techniques (during pyrolysis) would be a more cost-effective alternative. But also, catalytic pyrolysis has attracted interest for the conversion of biomass into light olefins [12,13].

Isochrysis sp. has been identified among the microalgae species that are suitable candidates for multiple-product algae-crop, due to their variety of fatty acids that offer a wide scope for several bio-products in a biorefinery approach [14]. However, only few studies are available on *Isochrysis* catalytic pyrolysis [15–17]. Dong et al.[15] studied the direct production of light olefins (C_2–C_4) of up to 11 wt.% from *Isochrysis* catalytic cracking at 550-650 °C in presence of modified ZSM-5, being neutral lipids the principal

contributor to olefin production. On the other hand, Wang et al.[17] investigated the direct and indirect (after removal of lipids) pyrolysis of *Isochrysis* at 475 °C. Defatted *Isochrysis* yielded higher total pyrolysis oil (41.3 wt.%) than direct microalgae pyrolysis (36.9 wt.%). However, there was also an increase for N-heterocyclic compounds and phenols and a decrease for hydrocarbons in defatted microalgae pyrolysis oil [17]. In a previous work, we investigated the effect of Ni-Ce derived catalysts on the *Isochrysis* microalgae pyrolysis, being Ni-Ce/ZrO_2 the most effective in terms of mass and energy bio-oil yield with 25.5 wt.% and 77%, respectively.

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

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

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

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

2. Experimental

2.1 Raw material

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

2.2 Catalysts preparation and characterization

Li-LSX-zeolite was acquired from Shanghai Hengye Chemical Industry Co. Ltd. The catalyst was crushed and sieved into a particle size of <180 µm. Then, it was calcined at 550 °C for 5 hours in a muffle furnace. Physical properties of the catalyst were analysed using a Micromeritics Gemini VII instrument. The sample (0.5 g) was outgassed at 200 °C for 12 hours before running the N_2 physisorption isotherms at -195 °C. The surface area was determined by using the standard Brunauer–Emmett–Teller (BET) equation.

Temperature programmed desorption of ammonia (NH_3-TPD) was carried out to determine the acidity distribution and acid strength of the catalysts. For that purpose, a ChemBET TPR/TPD equipment from Quantachrome Instruments fitted with a thermal conductivity detector (TCD). Firstly, 50 mg of sample was degassed under helium flow in quartz U-tube at 200 °C for 2 hours and then cooled down to room temperature in the same flowing helium atmosphere. After that, the sample underwent NH_3 adsorption by flowing 25 ml min^{-1} of a gas mixture of ammonia (10%) in helium at 50 °C until saturation was reached. Then, the sample was exposed to helium gas (25 ml min^{-1}) at the same

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

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

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

2.3 Microalgae and products analysis

2.3.1 Proximate and elemental analysis

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

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

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

2.3.2 Thermogravimetric analysis

A thermogravimetric analyser (TA Q500) was used to determine the moisture and volatile matter contents of the microalgae using N_2 as carrier gas. The temperature programme consisted in heating the sample in nitrogen gas from 20 to 105 °C with a ramp of 15 °C min^{-1} and maintaining the sample at 105 °C for 15 minutes to evaluate the moisture content (MC). Then, the temperature was risen to 800 °C with ramp of 20 °C min^{-1} and hold for 30 minutes to evaluate the volatile matter. Next, the temperature was cooled to 550 °C under nitrogen atmosphere and held at this temperature for about 30 minutes under air flow to establish the ash content. Finally, the fixed carbon content (FC) was calculated by difference (FC = 100 – MC – VM – Ash). Finally, the system was cooled down to 30 °C at 50 °C min^{-1}. The ash content of the sample was determined from the amount of solids that remains at the end of the combustion step, meanwhile the fixed carbon was calculated by subtracting the ash content remaining at the end of the run.

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

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

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

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

Gasoline and diesel fractions were distributed according to their distillation temperatures ranges as follows: gasoline (< 190°C), diesel cut 1 (190-290°C), diesel cut 2 (290-340°C) and vacuum gas oil (340-538°C). Regarding their carbon-length, they are distributed as gasoline (C_5-C_{12}), diesel cut 1 (C_{12}-C_{16}), diesel cut 2 (C_{13}-C_{19}) and vacuum gas oil (C_{20}-C_{28}).

Meanwhile, the non-condensable gases (CO, CO_2, HCs etc.) were collected using gas bags and analysed using a MKS Cirrus II Mass Spectrometer (MS). The instrument was equipped with a quadrupole analyser incorporating a closed ion source, a triple mass filter and a dual (Faraday and Secondary Electron Multiplier) detector system.

2.4 Catalytic pyrolysis experiments

The schematic diagram of the lab-scale experimental setup used for the catalytic pyrolysis experiments is shown in Figure 1. This setup consists of a vertical fixed bed stainless steel reactor (0.75 cm inner diameter and 24 cm length) heated by an electrical furnace. The reaction temperature was measure by K type thermocouple in contact to the catalyst bed inside the reactor. The catalytic pyrolysis tests were carried out by mixing the microalgae 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 N_2 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

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

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

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

3.2 Catalysts characterization

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

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

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

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

3.3 Effect of microsilica and Li-LSX-zeolite catalysts

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

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

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

show remarkable differences between the use of Li-LSX-zeolite and microsilica, the elemental analysis clearly indicate that Li-LSX-zeolite enhanced the bio-oil quality.

The bio-char obtained from the catalytic pyrolysis with Li-LSX-zeolite presented a higher calorific value than that obtained from the non-catalytic pyrolysis, 23.0 vs. 14.2 MJ kg^{-1}, respectively. So, the presence of catalysts produced bio-chars with higher C and N content (Li-LSX-zeolite: 52.0 and 4.7 wt.%, respectively; SiO_2: 48.6 and 4.1 wt.%, respectively) compared to the non-catalytic pyrolysis (45.4 and 3.4 wt.%, respectively). Therefore, catalytic bio-chars could be used as soil amendment due to their high C and N content if the catalysts are separated and recovered (e.g. ex-situ catalytic pyrolysis configuration).

Then, the oxygen remaining in the catalytically obtained bio-chars was lower than in that non-catalytically obtained, with values of 36 and 43 wt.% for Li-LSX-zeolite and SiO_2, respectively, in comparison with 48 wt.%; which could be explained by the strong acidity of Li-LSX-zeolite and its propensity for cracking and aromatisation reactions.

The higher HHV of microalgae chars derived from catalytic experiments was due to the higher carbon and hydrogen contents and therefore lower oxygen (determined by difference) in comparison to the char non-catalytically obtained. This can be explained by the acidity of the employed catalyst, which promoted gas formation (see Figure 3), deoxygenation and cooking reactions. The larger carbon content in Li-LSX zeolite derived char compared to the SiO_2 one can be further explained by the former being more acid than the latter. Moreover, the lower rates of mass transfer in the in-situ configuration, with direct mixing of coke precursors with the catalyst and enhanced coke formation contributed to the high C content [32].

This trend is also shown in the elemental analysis of bio-oils due to the use of Li-LSX-zeolite resulted in a bio-oil with a C content 4 w% higher, while contents of O and N were 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 NH_3. 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 ^{1}H-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 ^{1}H-NMR shows that the protons bonded to oxygenated species (3-

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

3.4 Effect of temperature on catalytic pyrolysis

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

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

Table 5 shows the gas composition obtained from the pyrolysis at different temperatures in terms of C content (rel.%). Increasing temperature cracked aliphatic and nitrogenated compounds in bio-oil into low molecular weight gaseous products such as CO, CO_2, CH_4, H_2 and C_2-C_4 olefins. Thus, the increase of reaction temperature from 400 to 700 °C led to a rise in the olefins carbon content from 29 to 38 wt.%.

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

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

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

Table 6 shows the GC-MS bio-oil composition in terms of C content (rel.%) as a function of the pyrolysis temperature. Increasing the temperature from 400 to 500 °C already resulted in an increased aromatics content from 5.1 to 11.8 rel.% C, respectively. This can be partially attributed to thermal degradation of proteins to phenols and NH_3, Aromatics are mainly produced due to the presence of Brønsted and Lewis acid sites in the Li-LSX-zeolite, which enhance dehydration, decarbonylation and aromatization reactions. Also, low Si/Al ratio has been linked to maximum aromatic yield, due to enhanced concentration of acid sites in close proximity to one another [9]. The pyrolysis of the fatty acids led to the formation of a large fraction of aliphatic, mostly alkanes, which had the maximum rel.% C at 500 °C, with 23.1 % and then decreased to 19.4 % at 700 °C, suggesting transfer of C to gas and coke. A similar trend is shown by the other chemical functionalities.

Temperature had a great effect on removing nitrogen from the bio-oil in favour of gaseous species. Amides, pyridines, nitriles, amines and indoles were among the identified N-compounds. Amides and nitriles can be formed from the reaction of proteins and fatty acids pyrolysis products, while cyclic amides can be formed from protein intramolecular cyclization [25]. Indoles may derive from tryptophan amino acids [41]. Indoles were the 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 CO_2, CO and H_2O, 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 NH_3 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 CO_2 [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 ≈ 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.

Figure 5B shows the bio-oil compounds distribution based on gasoline, diesel and vacuum gasoil fractions, according to ASTM D2887. Only compounds with boiling points within the range were calculated and their weight percentage presented. As can be seen, Li-LSX-zeolite increased the fractions of gasoline and diesel compared to the non-catalytic pyrolysis run. Li-LSX-zeolite exhibits both Brønsted and Lewis acidity and a pores size distribution that promoted the production of both aromatic and aliphatic compounds in the gasoline and diesel range. Most of the compounds produced in the bio-oil are in diesel range (cut 1 and cut 2) with hydrocarbon chains between C_{11}-C_{20} such as n-undecane, n-tetradecane, n-hexadecane and n-octadecane. These long chain aliphatic compounds originates from the decomposition of lipids or fatty acids after cracking, decarbonylation and decarboxylation reactions [15]. Increasing catalyst ratio reduced the diesel cut and vacuum gas oil fraction, and tended to form more aromatic compounds instead.

N-cyclic aliphatic amino acids in the microalgae proteins are converted in heterocyclic compounds, such as indoles and pyrroles, which tend to form coke being unsaturated. Therefore, the decreased in N-compound with the catalyst to microalgae ratio of 3:1can be linked to formation of gaseous CO and NH_3, but also to coking reactions on the catalyst surface.

4. Conclusions

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

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

The increase of the catalyst to biomass ratio from 0.5:1 to 3:1 resulted in 23% bio-oil and 43% gas. Long chain alkanes and protein derived intermediates were cracked in the Bronsted and Lewis acid sites to olefins and aromatics through decarbonylation and NH_3 formation. Regarding to bio-oil denitrogenation, the catalyst amount resulted vital, as N content in bio-oil was reduced from 3.9 wt.% (non-catalytic) to barely 0.8 wt.% (3:1). Also, the aromatics produced with a catalyst to microalgae ratio of 3:1 were five-fold those non-catalytically obtained.

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

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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})
Different catalysts														
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
Different Temperatures, °C														
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
Different Cat.:algae ratios														
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**	**SiO_2**	**Li-LSX-zeolite**
0.0 - 1.6	CH3. -CH2-	63.17	61.07	67.43
1.6 - 2.2	-CH2-, aliphatic OH	13.19	17.67	10.01
2.2 - 3.0	-CH3OC, -CH3-Ar, -CH2Ar	8.73	7.55	6.01
3.0 - 4.2	CH3O-, -CH2O-, =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, downfiled 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_2H_4, C_2H_3, C_3H_6, C_4H_8)	Alkanes (C_3H_8, C_2H_6, C_4H_{10}, C_5H_{12})
Different temperatures, °C					
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
Different Cat.:algae ratios					
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