RESEARCH ARTICLE OPEN ACCESS

Fast pyrolysis of microalgae *Nannochloropsis Oculata* for production of green diesel fraction

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ABSTRACT

Nannochloropsis oculata microalgae were grown under controlled conditions. The resulting biomass was extracted with n-hexane and this lipid extract, after solvent vaporization, was pyrolyzed, either alone or in presence of niobium oxide-based catalysts. The catalysts were prepared from niobium hydrated oxide by calcination at 350°C and 700°C, the latter sample being also modified by boron. The pyrolysis, carried out in duplicates at 600°C, occurred in a micro-pyrolyzer connected to a GC-MS analytical system. The yield in oxygenated products decreased significantly, from 46% in the absence of catalyst to 11% for pyrolysis in the presence of NbB700. With the Nb350 catalyst, a small decrease in nitrogen products (nitriles and amides) from 7% in the absence of catalyst to 6% was observed. Aromatic hydrocarbon amount showed a significant increase when comparing non-catalyzed pyrolysis (5%) and pyrolysis in the presence of Nb350 (18%). An increase in saturated hydrocarbons and a high content of light hydrocarbons (C3-C9) was also observed after pyrolysis with Nb350. These results are tentatively linked to acidity and hydrogen transfer properties of this catalyst. Limiting the analysis to the C10-C20 hydrocarbon range, *i.e*. the range of products compatible with green diesel, the total yields varied from 18 to 31, 35 and 27% going from a pyrolysis without catalyst to the catalyzed pyrolysis using Nb350, Nb700 and NbB700, respectively. Within this range, unsaturated compounds appeared always in greater concentration and linear 1-alkenes represented about 50% of the products. Again, the Nb350 catalyst exhibited a remarkable aromatics yield, of about 44% of the total identified hydrocarbons, with simultaneous production of alkenes (41%) and alkanes (14%). Polyaromatics were formed in a very limited amount, and the alkanes are of linear type. Oxygenated products such as alcohols, fatty acids and fatty acid esters were observed, but these products can be further deoxygenated modifying the pyrolysis conditions, or by additional treatments. The general results show that the n-hexane extract of *N. oculata*, pyrolyzed in presence of niobium oxide-based catalysts, can produce deoxygenated molecules precursors of green diesel.

***Keywords* -** Fast pyrolysis, Green diesel, *Nannochloropsis oculata*, Niobium catalysts

Date of Submission: 06-11-2020 Date of Acceptance: 19-11-2020

I. INTRODUCTION

Microalgae biomass is often presented as a promising material for the obtention of several types of specific chemical products, among them carotenes, astaxanthin, omega-3 fatty acids [1], base for pharmaceuticals, nutraceuticals and cosmetics [2]. In a more general way, microalgae are potential raw materials for biofuels such as bioethanol and biodiesel as they may contain both high amounts of polysaccharides and fatty acid-based molecules.

In order to transform microalgae biomass into liquid fuels, many chemical processes could be used, generally based on various consecutive steps such as hydrolysis of polysaccharides, followed by fermentation and separation to obtain bioethanol, or transesterification of oily fraction with light alcohols, separation and purification to obtain biodiesel.

Thermochemical transformations have been used for microalgae biomass conversion, and among them pyrolysis, a reaction performed at high temperature in absence of added oxygen. In fact, pyrolysis and more specifically fast pyrolysis can deoxygenate compounds such as the fatty ones [3,4] to generate hydrocarbons, potential source of “drop in” fuels. The addition of selected catalysts during pyrolysis may further help deoxygenation and introduce some selectivity in the cracked products, when compared to purely thermal cracking. When the weight ratio catalyst/feed is high, fast pyrolysis of fatty compounds performed at temperatures between 450 and 600°C can simulate some reactions occurring during a Fluidized Catalytic Cracking (FCC) process, as the contact time between the reagent and the catalyst is rather short [5]. In fact, co-processing of oxygenated feed with traditional FCC feeds have shown that about 10 % of oxygenated compounds can be added to a heavy oil feedstock, without altering significantly the products yield and quality [6]. So far, the oxygenated compounds tested in FCC coprocessing have been essentially triglyceride-based fractions and crude or upgraded bio-oil from lignocellulosic residues [7, 8], but microalgae biomass or its fatty compounds fraction are potential co-feed alternative [9]. In this case, however, the amino-acid compounds of microalgae [10] and their transformation to volatile nitrogen products during pyrolysis may be detrimental for both biofuel quality and catalysts performance [11, 12].

Many works using microalgae as starting materials for thermal processes to obtain biofuels or “drop in” fractions were reviewed without [13] or in presence of added catalysts [14,15]. These studies often conclude that further research is still required to improve the quality of bio-oil from fast and catalytic pyrolysis of microalgae biomass. When looking on catalysts used for transformation of triglycerides and derived oily molecules, review articles also exist [16-20].

Among the various catalysts used up to now in reactions aimed at transforming microalgae or fatty compounds to deoxygenated products, niobium-based ones were used only in a marginal way. In the case of microalgae pyrolysis, Spirulina maxima was transformed in the presence of hydrated niobium oxide, and the results were compared to those obtained with HZSM-5 catalyst: the former was less efficient in deoxygenation and conversion to aromatic hydrocarbons than the latter [21].

Literature studies on oily compounds transformation in the presence of niobium-based catalysts are also rather limited. Brandão et al. [22] pyrolyzed soybean oil at temperatures between 350 and 400°C, using niobia catalysts, modified or not with mineral acids; the acidity of the organic phase recovered at the end of reaction was always higher than the acidity obtained after simple thermal pyrolysis suggesting that the modified and pure niobium catalysts caused stabilization of fatty acids and therefore were of limited interest for deoxygenation. Reguera et al. [23] used different niobium-based catalysts to crack oleic acid at 400°C. $NbOPO_4$ principally and Nb_2O_5 impregnated with phosphoric acid, to a lower extent, generated satisfactory yields to “diesel fraction”, but also high yields in “lubricant” species, *i.e.* in long carbon chain molecules. These results are probably due to the rather low pyrolysis temperatures used in the preceding studies. In the case of hydrodeoxygenation, Yi et al. [24] used Pd/Nb-SiO_2 catalysts and show that the presence of Nb practically suppressed the C-C bond breaking during the transformation of palmitic acid and other oxygenated compounds. Xia et al. [25] using Pd/$NbOPO_4$ supported catalysts obtained a near quantitative diesel-range alkanes yield, during the transformation of triglycerides under hydrogen pressure and moderate temperature with no or limited catalyst deactivation. A synergistic effect of metallic Pd and strong Lewis acidity of $NbOPO_4$ was advocated to explain the results.

As the number of microalgae able to be used as raw material for biofuel production via pyrolysis is huge, the present study aimed to study specifically *Nannochloropsis oculata*, a microalga object of limited previous studies, although showing a rapid growth rate, a tolerance to various saline media and a satisfactory oily compounds production [26].

The literature presents various pyrolysis and co-pyrolysis works, either through TG or through GC-MS analysis techniques, on different strains of *Nannochloropsis* microalgae, such as *Nannochloropsis gaditana* [27-32], *Nannochloropsis sp*. [4,10,11,33-39], *Nannochloropsis salina* [38, 40], *Nannochloropsis oceanica* [3, 41, 42] and undefined *Nannochloropsis* strains [43-46].

Maguyon and Capareda [47] studied the pressurized thermal pyrolysis of *Nannochloropsis oculata*, between 400 and 600°C, under autogenous pressure. For pyrolysis at 500°C, these authors obtained a bio-oil with a high heating value of about 38 kJ/g, 7% of residual oxygen, and containing some 35% of saturated hydrocarbons, 35% of alkenes and 10% of aromatics, all products having between 8 and 21 carbon atoms in their molecular structure. Du et al. [48] stated that a hydrothermal pre-treatment between 200-220°C was efficient to decrease the amount of nitrogen containing compounds in *Nannochloropsis oculata*, without modifying extensively the amount of the other fractions. Such pre-treatment has been shown useful before pyrolysis, as the final products presented a limited amount of nitrogenated compounds. Valdés et al. [49] studied through TGA and Py-GC-MS techniques *Nannochloropsis oculata* microalgae containing different amounts of proteins, carbohydrates and lipids. Both techniques presented good agreement in the biochemical composition of these microalgae compared to more conventional characterization techniques. Ceylan and Kazan [50] performed non isothermal thermogravimetric analysis of *Nannochloropsis oculata* at different heating rates; a mean activation energy of 152 kJ/mole for the decomposition of the microalga was calculated from the data. Ferreira et al. [51] studied the thermochemical properties of *Nannochloropsis oculata*, before and after extraction with n-hexane-isopropanol mixture, using ultrasound. Raw and extracted biomasses showed some differences during the decomposition steps of lipids and proteins, characterized by TGA. However, the apparent activation energies calculated from the TG curves were similar for both types of samples. Hanif et al. [52] studied the pyrolysis of a mixture of *Nannochloropsis oculata* with cattle manure and cotton gin trash between 400 and 600°C. The bio-oil obtained presented an optimum yield for a pyrolysis temperature of 500°C and a high heating value of 30 kJ/g. The nitrogen products issued from the microalga fraction were diluted by the decomposition products of the other materials feed, allowing the production of potential liquid fuel.

The preceding literature analysis showed that no fast catalytic pyrolysis study of *Nannochloropsis oculata* has been performed, in a 600°C temperature range, and that a very limited number of pyrolysis studies were devoted to the use of niobium oxide catalysts to modify the pyrolysis steps, using microalgae or their extracted fractions. The present study aimed to describe the fast pyrolysis of *Nannochloropsis oculata* lipid extract, either without catalyst, or in the presence of niobium-based catalysts, with a special emphasis towards the formation of hydrocarbons in the diesel range (C10-C20).

The introduction of the paper should explain the nature of the problem, previous work, purpose, and the contribution of the paper. The contents of each section may be provided to understand easily about the paper.

II. MATERIALS AN METHODS

2.1. Catalyst preparation

Three catalysts were used: the first one, Nb350, was obtained from niobic acid HY-340 (supplied by *Companhia Brasileira de Metalurgia e Mineração* (CBMM) - purity greater than 99.8% determined by X-ray fluorescence) through calcination under static air at 350°C for 2h. The second one (Nb700) resulted from a calcination at 700°C under static air, for 2 h, of the same HY-340. The last one, NbB700, was prepared by impregnation of HY-340 with aqueous solution of HBO_3, with theoretical concentration of 10 wt%B, followed by drying at 100°C and a final calcination under air at 700°C for 2 h.

2.2. Preparation of samples used in pyrolysis experiments

The *N. oculata* microalgae was cultivated in 10 L Pyrex Erlenmeyer flasks using a CONWAY medium [78], the sea water being collected at 500 m from the open sea-beach of Salvador-Bahia, Brazil, after two days without rain. The mixture was inoculated with 10 mL of mother strain, permanently illuminated with 15 Watts LEDs (42 µmol photons m^{-2} s^{-1}); a flow of laboratory air was continuously bubbled through the suspension. The microalgae growth was followed by dairy sampling and gravimetric estimation of dried microalgae mass. The cultivation was stopped after a similar sample mass was obtained during two successive days, *i.e.* 30 days in the present case. Microalgae biomass was collected, washed three times with distilled water, each washing being followed by centrifugation. The final solid fraction was dried at 60°C for 24 h, under the form of fine layers deposited in Petri plates. The dried N. oculata was then stored at – 30°C before further use.

The fatty components of the dried biomass were extracted with n-hexane. A volume of 0.3 mL of solvent was added to 0.2 g of the dried hand-ground biomass and the mixture was further hand-ground. New addition of 0.7 mL of solvent to the medium was performed and the suspension, in closed holder, was i/ shacked in Vortex for 2 min, ii/ centrifugated at 4400 rpm for 3 min. 90% of the liquid phase containing extracted species and solvent was collected, and transferred to new holder to allow solvent evaporation. This operation sequence is an adaptation of the method described by Olmstead et al. [64].

2.3. Characterization of Catalysts and N. oculata microalgae

Textural properties of the catalysts were obtained by N_2 adsorption, performed at -196°C, using an adsorption equipment from Quantachrome Instruments, model NOVA 2200. Prior to measurement, the catalyst samples were outgassed in situ under vacuum up to 350°C (10°C /min, 30 min at 350°C, after steps of 15 min at 100°C and 200°C). The thermo-desorption profiles of ammonia (TPD NH_3) were obtained in a Micromeritics Chemsorb 2720 equipment. About 100 mg sample were pre-treated at 300°C, for 1h, under a helium flow (30 $mL.min^{-1}$). After cooling down to room temperature (30°C), a flow of ammonia-helium mixture (10/90 v/v) was deviated through the catalyst sample, for 1h. The elimination of major fraction of weakly adsorbed ammonia was performed at 150°C for 1h under a pure helium flow (30 $mL.min^{-1}$), before cooling down the sample temperature to 30°C. NH3 desorption was followed during the sample heating up to 800°C (heating rate of 10°C min-1) and the amount of desorbed ammonia was quantified using TCD.

Fatty acids of N. oculata microalgae were trans-methylated with boron trifluoride-methanol mixture and the resulting fatty acid methyl esters (FAME) were separated and analyzed by gas chromatography (Clarus 680; Perkin Elmer®) equipped with a flame ionization detector, using a DB-FFAP column (30 m × 0.32 mm × 0.25 µm). The chromatographic conditions were: injector and detector temperatures at 250°C and 280°C, respectively, temperature programming: 150°C for 16 minutes, increase to 180°C (2 °C.min^{-1}) maintained for 25 min., increase to 210°C (5 °C.min^{-1}) maintained for 25 minutes, carrier gas Helium (1.0 mL.min^{-1}), volume injected: 1 µL. Such experiments were run in duplicate. FAME were identified by comparing retention times with a mixture of known esters (C4-C24, 18, 919-AMP; Sigma-Aldrich®). Fatty acids were quantified as percentage (%) of total lipids and compared with internal standard tricosanoic acid methyl ester (C23:0; Sigma Aldrich®). Peak areas were determined using the Clarus Chromatography workstation software to normalize the percentage of total fatty acid areas.

2.4. Pyrolysis

The pyrolysis reactions were carried out in a micro pyrolyzer model EGA/PY-3030D (Frontier Laboratories LTD), connected online with a gas chromatograph coupled to mass spectrometer (Agilent GC-MS 5799A). The flash pyrolysis was carried out under a flow of ultra-pure helium using a single thermal method (Single Shot). In this method the holder containing the sample to be pyrolyzed was first introduced in the equipment and purged from air traces under pure helium flow. During this period, the pyrolysis furnace was preheated to the chosen pyrolysis temperature, 600°C. In a second step, still under pure helium atmosphere, the sample holder was quickly dropped down in the high temperature pyrolysis area where it stayed for 30 s before being removed from the hot zone. The analysis of the pyrolysis products also started after 30 s. In the present experiments, 0.003mL of pure extract or 0.003 mL of extract covered by 3 mg of catalyst were introduced in the sample holder (Frontier inactivated stainless steel cup) and covered by a fine layer of quartz wool. For products analysis, a Frontier UA5-30M-0.25F GC column was used (30m length, 0.25mm diameter, 0.25 Microns stationary phase). The thermal history of the column, for each analysis, was: 40°C (2 min) followed by a heating ramp up to 320°C (20 °C.min^{-1}) maintained for 10 min. MS ion source and interface temperatures were 320°C, m/z values being varied between 40 and 400 in scan mode. Experiments were run in duplicate. For analysis of the products, only peaks with an area equal or larger than 0.5% of the total pyrogram area were considered. Identification was realized using the NIST database and all reported compounds showed an identity probability better than 75%. A pseudo-quantification of the products was obtained dividing the peak area of each product by the area of the whole pyrogram, when considering the global analysis. In the case of analysis of the diesel fraction, the peak area of each selected product was divided by the area of the C10-C20 selected fraction of the pyrogram.

III. RESULTS AND DISCUSSION

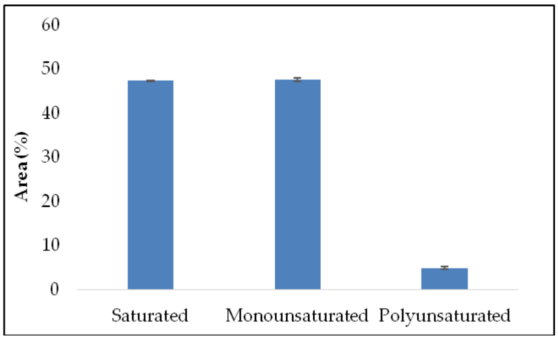
Table 1 gives the BET area of the catalyst samples as well as the amount of ammonia thermo-desorbed.

TABLE 1. Specific surface area and acidity estimation of the niobium-based catalysts

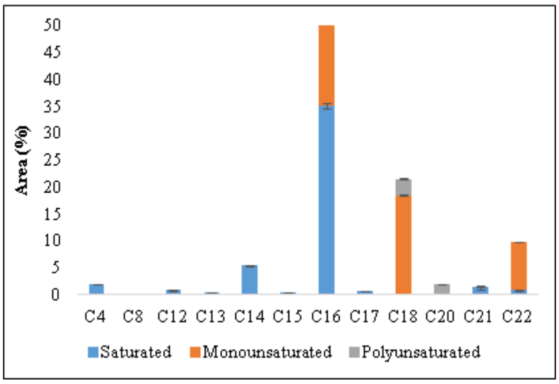
Sample	NH_3 desorbed mmol/g	S_{BET} (m^2/ g)
Nb350	1.1	128
Nb700	<0.1	4
NbB700	0.01	1

Nb_2O_5, heated at 700°C, presented a specific surface area lower than 5 m^2/g and practically no acidity estimated through ammonia adsorbed amount, in agreement with literature data [53, 54]. The addition of B is known to increase the acidity of alumina supported catalysts [55]. When added to Nb700, B did not present any positive effects on both surface area and acidity. By opposition with samples calcined at 700°C, Nb350, presented a specific surface area larger than 120 m^2/g, as well as a rather important acidity, mainly due to middle strength acid sites.

Figure 1a shows the degree of saturation of the fatty acids present in *Nannochloropsis oculata* microalgae, after transmethylation and chromatographic analysis, whereas Figure 1b gives the mean length of C chain of these fatty acids**.**



(a)



(b)

Fig. 1. Composition percentage of fatty acids in *Nannochloropsis oculata* microalgae: (**a**) distribution between saturated, monounsaturated and polyunsaturated fatty acids, (**b**) distribution of the fatty acids as a function of chain length.

Three points may be highlighted: i/ C16:0 and C18:1 are the main fatty acids synthesized under the present conditions, ii/ the amounts of saturated and monounsaturated fatty acids are equivalent, the polyunsaturated species being maintained at a rather moderate level; iii/ the carbon chains of polyunsaturated fatty acids contain 18 and 20 C and that of monounsaturated fatty acids contain 16, 18 and 22 C. On one hand, the fatty acid composition of the present study is not in complete agreement with literature data [56, 57], except the fact that C16 are the main fatty acid generally detected. More specifically, the quantity of C20 is low in the present microalgae, but high in literature data [57, 58]. On the other hand, the fact that both saturated and monounsaturated acids were formed in similar quantities is in acceptable agreement with published data [56, 58]. It must be recalled however, that the exact composition of fatty species present in microalgae is very dependent on the conditions of microalgae growth and harvesting [59, 60]. Although the fatty acids present in *Nannochloropsis oculata* microalgae, may partly differ from other results, the study of their fast pyrolysis can be useful.

Figure 2 presents the pyrograms at 600°C of *N. oculata* extract without (a) and with Nb350 (b), catalysts between retention times of 2 and 24 min. A global examination of these pyrograms shows that the presence of Nb350 caused significant changes in the process, showing a higher number of products and a higher quantity of light species. The main chromatographic peaks in these two pyrograms, and also for Nb700 and NbB700 were associated into unidentified, hydrocarbons, nitrogenated and oxygenated products, and the results are presented in Figure 3a. To estimate the quality of the hydrocarbons produced, the deoxygenated products were divided between alkanes, alkenes, polyunsaturated, naphthenes and aromatic products and their percentage is presented in Figure 3b, for the four different cases of pyrolysis.

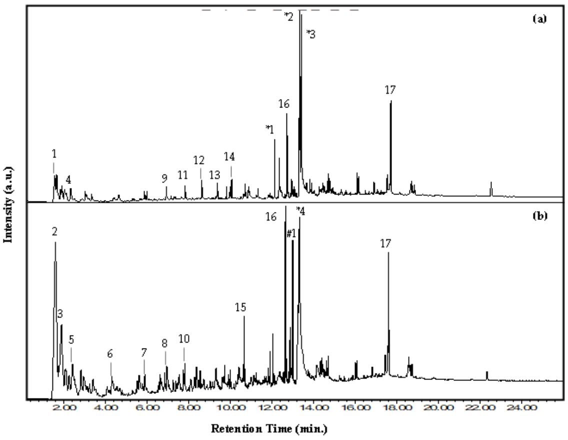
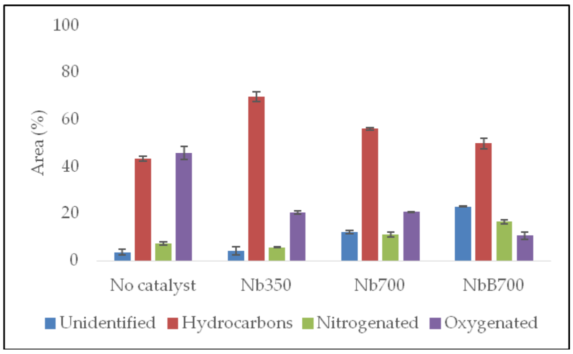
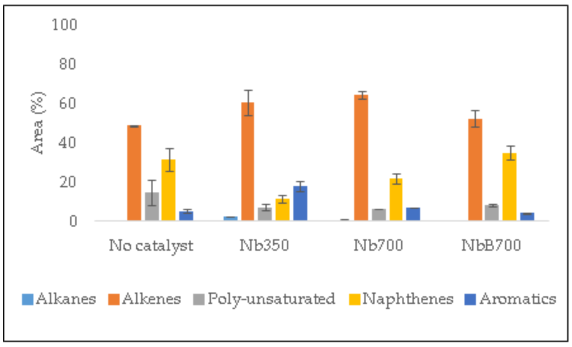


Fig. 2. Pyrograms at 600°C of *N. oculata* extract without (**a**) and with Nb350 (b), catalysts between retention times of 2 and 24 min, and identification of selected product: 1) Propene, 2) 1-Butene, 3) 2-Pentene, (E)-, 4) 1-Hexene, 5) 2-Pentene, 3-methyl-, 6) 1,3,5-Cycloheptatriene, 7) Benzene, 1,3-dimethyl-, 8) Benzene, 1,2,3-trimethyl-, 9) 1-Decene, 10) Benzene, 1-ethyl-2,3-dimethyl-, 11) 3-Undecene, (Z)-, 12) 1-Dodecene, 13) 1-Tridecene, 14) 2-Tetradecene, (E)-, 15) Pentadecane, 16) 3-Octadecyne, 17) Cholesta-3,5-diene, *1) 1-Dodecanol, 3,7,11-trimethyl-, *2) cis-9-Hexadecenoic acid, *3) n-Hexadecanoic acid, *4) 9-Hexadecenoic acid, #1) Pentadecanenitrile.



(**a**)



(**b**)

Fig. 3. Pyrolysis at 600°C of *N. oculata* extract, in absence or presence of niobium-based catalysts: (**a**) percentage of compounds families (unidentified, hydrocarbons, nitrogenated and oxygenated); (**b**) percentage of hydrocarbon families (saturated, monounsaturated, polyunsaturated, aromatics and cyclic).

Figure 3a shows that pyrolysis in presence of catalysts always led to a decrease of oxygenated products, implying that these catalyst favors the deoxygenation pathways of fatty species present in the *N. oculata* microalgae, compared to simple thermal pyrolysis, in agreement what was observed during pyrolysis of fatty acids [17, 19, 61-63]. The yield in oxygenated products decreased significantly, from 46% in the absence of catalyst to 21%, 21% and 11% for pyrolysis in the presence of Nb350, Nb700 and NbB700, respectively. The quantity of unidentified species and of nitrogenated products tend to increase when going from thermal pyrolysis to catalytic pyrolysis in presence of Nb350 < Nb700 < NbB700, suggesting that the extraction with n-hexane, presented as a way to obtain neutral lipids [64], was not fully selective in the conditions employed in the present work, as part of protein fraction was also extracted. With the Nb350 catalyst, a small decrease in nitrogen products (nitriles and amides) from 7% in the absence of catalyst to 6% was observed. Finally, the catalytic pyrolysis allowing the better percentage (around 70%) of deoxygenated products, *i.e.* pure hydrocarbons, was the one performed in presence of Nb350, the catalyst with higher values of specific surface area and acidity. Aromatic hydrocarbon amount showed a significant increase when comparing non-catalyzed pyrolysis (5%) and pyrolysis in the presence of this Nb350 catalyst (18%) (Fig. 3b), fact explained by its initial acidity.

As one objective of the present work was to analyze the efficiency of *N. oculata* to generate by pyrolysis hydrocarbons in the range of C10-C20, compatible with diesel-type fuels, the corresponding fractions of the complete pyrograms were analyzed in greater details.

Figure 4. presents a pyrogram fragment at 600°C of *N. oculata* extract without catalyst between retention times of 6 and 16 min. Alkenes were the main products identified, as well as in all other catalytic pyrolysis cases presented here, a situation also seen when pyrolyzing fatty compounds either without catalyst or in presence of catalysts with limited acidity [62, 65, 66]. The alkenes identified are often alk-1-enes. The second family of products appears to be naphthenes, a class of compounds interesting for fuels, detailed in a limited number of previous studies on fatty acids pyrolysis [67].

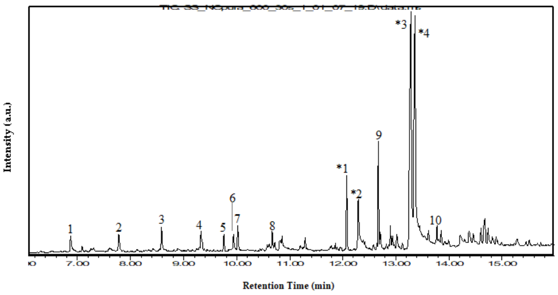
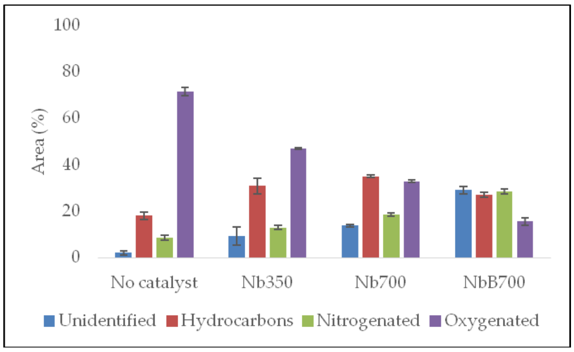
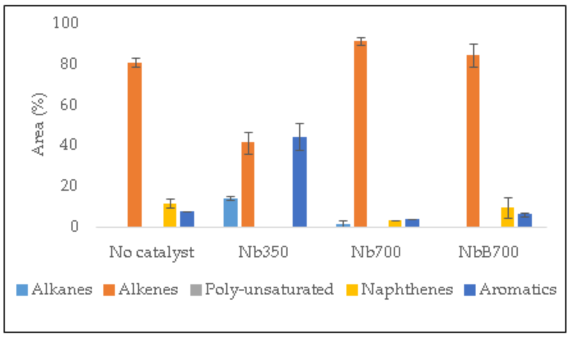


Fig. 4. Pyrogram fragment at 600°C of *N. oculata* extract without catalyst between retention times of 6 and 16 min, and identification of selected product: 1) 1-Decene, 2) 3-Undecene, (Z)-, 3) 1-Dodecene 4) 1-Tridecene, 5) Cyclopropane, 1-heptyl-2-methyl-, 6) Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-, 7) 2-Tetradecene, (E)-, 8) 1-Pentadecene, 9) 3-Octadecyne, 10) Cyclopropane, 1-(1,2-dimethylpropyl)-1-methyl-2-nonyl-, *1) 1-Dodecanol, 3,7,11-trimethyl-, *2) Tetradecanoic acid,*3) cis-9-Hexadecenoic acid, *4) n-Hexadecanoic acid.

A similar analysis realized for Fig. 3 was done for the zoomed fraction of the pyrograms obtained in absence or presence of niobium-based catalysts and is presented in Figure 5, whereas Table 2 summarizes the main hydrocarbons identified in the same range (C10-C20).



(**a**)



(**b**)

Fig. 5. Pyrolysis at 600°C of *N. oculata* extract, in absence or presence of niobium-based catalysts: (**a**) percentage of compounds families (unidentified, hydrocarbons, nitrogenated and oxygenated); in the C10-C20 range and (**b**) percentage of hydrocarbon families (saturated, monounsaturated, polyunsaturated, aromatics and cyclic) in the same range.

The results presented in Figure 5 had some similarities to what was observed for the entire pyrograms (Fig.3) *i.e.* the presence of catalysts in general favored the deoxygenation path, increased the production of hydrocarbons and nitrogenated compounds. Also in this range, alkenes are the major products within the hydrocarbons. The other classes of products are present in limited amount, excepted the aromatics in the case of catalytic pyrolysis in presence of Nb350, as also observed in the whole-range pyrograms. Within this range, this catalyst exhibited a remarkable aromatics yield, of about 44% of the total identified hydrocarbons, with simultaneous production of alkenes (41%) and alkanes (14%). Aromatics formation is associated to the initial acidity of this catalyst. However, due to the middle strength acidity detected for this sample, the quantity of aromatics formed is much lower when compared to H-type zeolites [68-70]. Furthermore, these aromatic products are limited to mono-ring or hydrogenated indane and naphthalene type aromatics, whereas, with highly acidic catalysts such as H-ZSM-5, true polyaromatics and coke precursors are formed [71].

Table 2 showed that the differences in hydrocarbon production obtained by pyrolysis in absence of catalyst and in presence of both Nb700 and NbB700 are very limited suggesting that in the conditions used in the present work no drastic catalytic effect was produced by niobium-based samples treated at 700°C. The main products observed in all cases were 1-alkenes, with distribution between C10 and C15. 1-pentadecene is probably obtained through a dehydration/decarbonylation mechanism of C16:0. Saturated hydrocarbons, resulting from decarboxylation of saturated fatty acids, often observed when pyrolyzing saturated fatty acids [65, 66] are practically not detected in significant amounts using both Nb700 and NbB700, as well as for pyrolysis without catalyst, although the content of saturated fatty species in the original feed is high (see Fig. 1). On the contrary, when using Nb350, besides 1-alkenes, various n-alkanes were identified, together with some mono-ring aromatics, mainly poly-alkyl aromatics. This group of saturated and aromatic products is tentatively associated to the acidity of Nb350, and hydrogen transfer properties, allowing on one hand hydrogenation of 1-alkenes to linear alkanes and, on the other hand, dehydrogenation and cyclisation of linear 1-alkenes molecules to produce aromatic ones. An important point seems linked to the fact that polyaromatics were formed in a very limited amount, and that the alkanes are of linear type, without alkylation, suggesting that the acidity of Nb350 is insufficient to generate fused rings aromatics and iso-alkanes, as seen with more acidic catalysts like protonic zeolites [17, 71] and even moderate acid catalysts such as alumina [66]. Such property needs better care in future studies. Finally, small quantity of cyclopropane-based hydrocarbons was found, although their stability at the pyrolysis temperature employed here is improbable. The same hydrocarbons have been listed in pyrolysis products of triglycerides type feeds [43, 72] but never discussed; it must be recalled that in the NIST Library, the differences in probability of identification between cyclopropanes and alkenes are generally lower than one or two units, and therefore, the possibility that the identified cyclopropanes are in fact alkenes cannot be ruled out, in absence of reference standards.

TABLE 2. Main hydrocarbons identified after pyrolysis at 600°C of *N. oculata*, in the C10-C20 range

Products family	**Main products**			
	No catalyst	**Nb350**	**Nb700**	**NbB700**
Alkenes				
	1-Decene	1-Decene	1-Decene	1-Decene
	3-Undecene, (Z)-	1-Dodecene	1-Undecene	1-Undecene
	1-Dodecene	1-Tridecene	1-Dodecene	1-Dodecene
	1-Tridecene	1-Tetradecene	1-Tridecene	1-Tridecene

Products family	**Main products**			
	No catalyst	**Nb350**	**Nb700**	**NbB700**
	2-Tetradecene, (E)- 1-Pentadecene	1-Pentadecene	1-Tetradecene 1-Pentadecene 5-Octadecene, (E)-	1-Tetradecene 1-Pentadecene
Alkanes				
		n-Tridecane n-Pentadecane n-Hexadecane		
Aromatics				
		Benzene, 1,2-diethyl- Benzene, 1-ethyl-2,3-dimethyl- Benzene, (2-methyl-1-propenyl)- Benzene, (1-methyl-1-propenyl)-, (Z)-		
		Benzene, decyl-		1H-Indene, 5-butyl-6-hexyloctahydro-
	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	Naphthalene, 1,3-dimethyl-	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-
Polyunsaturated				
	3-Octadecyne	3-Octadecyne	3-Octadecyne	3-Octadecyne
Cyclic				
	Cyclopropane, 1-(1,2-dimethylpropyl)-1-methyl-2-nonyl-		Cyclopropane,1-butyl, 2-pentyl	Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)-

Figure 6 presents the distribution of hydrocarbons as a function of the carbon chain length in the C10-C20 range. C18 hydrocarbons are clearly predominant, even without catalysts, for the biomass and conditions used in the present work, despite the important amount of C16 fatty acids detected in the initial biomass (Fig.1). Since unsaturated hydrocarbons are present (Table 2), a moderate hydrogenation will be necessary prior to use this feedstock as green diesel component.

Tables 3 and 4 present some of the oxygenated and nitrogenated products identified in the C10-C20 range.

After pyrolysis without catalyst, the main products observed are carboxylic acids, aldehydes, alcohols, eventually in dehydrogenated form. The same type of products also appears in the case of pyrolysis in presence of catalysts, however in minor content.

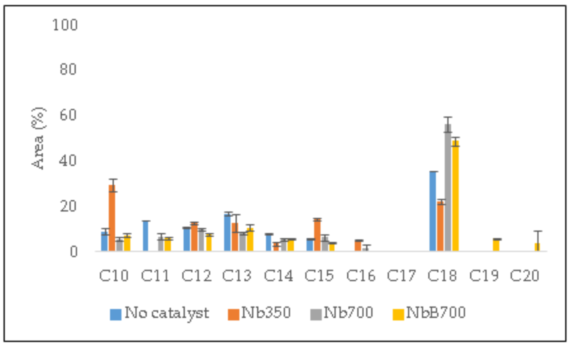


Fig. 6. Distribution percentage of hydrocarbons as a function of chain length in the C10-C20 range issued from pyrolysis at 600°C of *N. oculata* extract, in absence or presence of niobium-based catalysts:

Although often observed in studies on cracking of traditional fatty compounds [73, 74], the presence of alcohols and aldehydes is not quite clear. On one hand, the thermal stability of alcohols in the 500-600°C temperature range is quite limited, due to easy dehydration producing alkenes and ethers [75].

On the other hand, the formation of aldehydes, implying the loss of only one oxygen in fatty acids, is unexpected at a pyrolysis temperature of 600°C, although their formation mechanism was proposed in the literature [74] but for pyrolysis performed in lower temperature range. Aldehydes are known as very stable organic products, but decomposition of such compounds at around 500°C was also described in the literature [76]. Therefore, for both alcohols and aldehydes, further analyses are necessary to understand their presence among the products, and particularly studies on their stability as products or intermediary species at high temperatures are needed. A second type of analysis can also be considered: what is the extent of recombination between water vapor, one of the products of deoxygenation, and alkenes and/or alkynes during transfer of products from the pyrolysis reacting space and the analytical devices, where homogeneous additions could occur.

TABLE 3. Main oxygenated compounds identified after pyrolysis at 600°C of *N. oculata,* in the C10-C20 range

Products family	**Main products**			
	No catalyst	**Nb350**	**Nb700**	**NbB700**
Alcohol				
	1-Dodecanol, 3,7,11-trimethyl-			E-2-Hexadecacen-1-ol
	Z,Z-2,5-Pentadecadien-1-ol			
	Estra-1,3,5(10)-trien-17.beta.-ol			
	Z,E-2,13-Octadecadien-1-ol			
Aldehyde				
	Undecanal, 2-methyl-			
	cis-9-Hexadecenal			
		Octadecanal		
Ether				
				Octadecane, 1-(ethenyloxy)-
Ketone				
	2-Heptadecanone			
			Cyclopentadecanone, 2-hydroxy-	
Fatty Acids				
	Tetradecanoic acid		Tetradecanoic acid	
	cis-9-Hexadecenoic acid	cis-9-Hexadecenoic acid 9-Hexadecenoic acid	cis-9-Hexadecenoic acid	cis-9-Hexadecenoic acid
	n-Hexadecanoic acid		n-Hexadecanoic acid Hexadecenoic acid, Z-11-	n-Hexadecanoic acid
	6-Octadecenoic acid		9-Octadecenoic acid, (E)-	6-Octadecenoic acid, (Z)-
	18-Nonadecenoic acid			
	cis-13-Eicosenoic acid			
Ester				
	Heptadecanoic acid, methyl ester Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester		Methacrylic acid, pentadecyl ester	
			9-Octadecenoic acid (Z)-, methyl ester	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester
Other				
			11-Tetradecen-1-ol, acetate, (Z)-	

TABLE 4. Main nitrogenated products identified after pyrolysis at 600°C of *N. oculata*, in the C10-C20 range

Products family	**Main products**			
	No catalyst	**Nb350**	**Nb700**	**NbB700**
Amine				
	1-Dodecanamine, N,N-dimethyl-		1-Dodecanamine, N,N-dimethyl-	1-Dodecanamine, N,N-dimethyl- Hexadecanamide
Nitrile				
		Tetradecanenitrile Pentadecanenitrile	Tetradecanenitrile Pentadecanenitrile	
Amide				
	9-Octadecenamide, (Z)-	9-Octadecenamide, (Z)-	9-Octadecenamide, (Z)-	9-Octadecenamide, (Z)-
	Octadecanamide	Octadecanamide	Octadecanamide	
				9-Octadecenamide, N,N-dimethyl-
			9-Hexadecenoic acid, pyrrolidide	9-Hexadecenoic acid, pyrrolidide
			13-Methylpentadecanoic acid, pyrrolidide	13-Methylpentadecanoic acid, pyrrolidide
	9-Hexadecenoic acid, pyrrolidide			
	Hexadecanoic acid, pyrrolidide			

The nitrogenated products found and listed in Table 4 are always complex molecules and, with exception of nitriles, are also not expected to survive to the present pyrolysis conditions. However, their presence suggests that together with fatty acid-based molecules, some proteins were extracted by n-hexane solvent: fragments of these molecules, during pyrolysis, can interact with fatty acid species or radicals to create such products, either inside the rapid pyrolysis high temperature space, or during transfer of all species from reacting area to the analytical device.

The final point to be recalled here is that fast pyrolysis, at temperatures between 500-600°C, is theoretically able to completely deoxygenate products like alcohols, esters, ethers and probably aldehydes, either by increasing the ratio catalyst/feed, or by modifying the experimental conditions (temperature, duration of pyrolysis, increase of inert gas flow, introduction of a recirculation device, among others). A strategy that is presently under investigation in the authors group is associated to multiple catalysts bed, to adjust with simple catalysts a sequence of catalytic properties needed to reach the desired quality of products [77]. Therefore, fast pyrolysis, can be considered as an interesting way to deoxygenate to a large extent oily-based feed to obtain precursors of green liquid fuels and chemicals. Although fast micropyrolysis equipment were useful to verify some chemical trends during oily compounds decomposition, specifically when pyrolysis is performed in the presence of catalysts, long term experiments and pilot reactors are also needed to optimize deoxygenation.

IV. CONCLUSIONS

Nb_2O_5, heated at 700°C, presented a specific surface area lower than 5 m^2/g and practically no acidity estimated through ammonia adsorbed amount. When added to Nb700 catalyst, B did not present any positive effect on both surface area and acidity. By opposition with samples calcined at 700°C, Nb350, calcined at 350°C, presented a specific surface area larger than 120 m^2/g, as well as a rather important acidity, mainly due to middle strength acid sites.

Pyrolysis at 600°C of the *Nannochloropsis oculata* microalgae n-hexane extract in the presence of the Niobium based catalysts decreased significantly the yield in oxygenated products, from 46% in the absence of catalyst to 21%, 21% and 11% for pyrolysis in the presence of Nb350, Nb700 and NbB700, respectively. With the Nb350°C catalyst, a small decrease in nitrogen products (nitriles and amides) from 7% in the absence of catalyst to 6% was observed. Aromatic hydrocarbon amount showed a significant increase when comparing non-catalyzed pyrolysis (5%) and pyrolysis in the presence of Nb350 catalyst (18%). This catalyst exhibited an increase in saturated hydrocarbons and a high content of light hydrocarbons (C3-C9) after pyrolysis, behavior tentatively linked to its acidity and hydrogen transfer properties, allowing on one hand hydrogenation of

1-alkenes to linear alkanes and, on the other hand, dehydrogenation and cyclisation of linear 1-alkenes molecules to produce aromatic ones. An important point seems linked to the fact that polyaromatics were formed in a very limited amount, and that the alkanes are of linear type, without alkylation, suggesting that the acidity of Nb350 is insufficient to generate fused rings aromatics and iso-alkanes.

Limiting the analysis to the C10-C20 hydrocarbon range, i.e. the range of products compatible with green diesel, the total yields varied from 18 to 31, 35 and 27% going from a pyrolysis without catalyst to the catalyzed pyrolysis using Nb350, Nb700 and NbB700, respectively. Within this range, unsaturated compounds appeared always in greater concentration and linear 1-alkenes represented about 50% of the products. Again, the Nb350 catalyst exhibited a remarkable aromatics yield, of about 44% of the total identified hydrocarbons, with simultaneous production of alkenes (41%) and alkanes (14%). Oxygenated products such as alcohols, fatty acids and fatty acid esters were observed, but these products can be further deoxygenated modifying the pyrolysis conditions, or by additional treatments. The general results show that the n-hexane extract of *N. oculata*, pyrolyzed in presence of niobium oxide-based catalysts, can produce deoxygenated molecules precursors of green diesel.

ACKNOWLEDGMENTS

This paper was prepared with the support of the Bahia State Research Support Foundation (FAPESB), Higher Education Personnel Improvement Coordination (CAPES) and the National Council for Scientific and Technological Development (CNPq) - Brazil. Furthermore, the authors are grateful to the *Companhia Brasileira de Metalurgia e Mineração* (CBMM) for the Niobium oxide supply, and to the following laboratories of the Federal University of Bahia (UFBA): Laboratory of Fishery and Applied Chromatography (LAPESCA) for the fatty acids profile analysis, Laboratory of Catalysis and Materials (LABCAT) for the TPD-NH_3 analysis, and the Catalysis and Environment Laboratory (CATAM) for the BET analysis.

Conflict of Interest: The authors declare that have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions: conceptualization, M.D, N.F., R.F and E.S.; methodology, M.D, N.F., R.F and E.S.; validation, M.D, N.F., R.F and E.S.; formal analysis M.D, N.F., R.F and E.S.; investigation, M.D, N.F., B.M., B.G., R.F and E.S. ; resources, R.F. and E.S.; data curation, M.D, N.F., B.M., B.G., R.F and E.S.; writing—original draft preparation, M.D, N.F., R.F and E.S; writing—review and editing, M.D, N.F., R.F and E.S; supervision, R.F. and E.S.; project administration, E.S.; funding acquisition, E.S.

Funding: This research was funded by the Bahia State Research Support Foundation (FAPESB), Higher Education Personnel Improvement Coordination (CAPES) and the National Council for Scientific and Technological Development (CNPq) - Brazil.

REFERENCES

[1]. Borowitzka, M. High-value products from microalgae—their development and commercialisation. *Journal of Applied Phycology, 25, 2013, 743–756,*

[2]. Khan, M.; Shin, J.; Kim, J. The promising future of microalgae: current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products. *Microbial Cell Factories, 17, 2018,36.*

[3]. Zhang, Z.; Volkman, J. K. Algaenan structure in the microalga *Nannochloropsis oculata* characterized from stepwise pyrolysis. *Organic Geochemistry, 104, 2017,. 1-7.*

[4]. Chang, G.; Miao, P.; Wang, H.; Wang, L.; Hu, X.; Guo, Q. A synergistic effect during the co-pyrolysis of *Nannochloropsis sp.* and palm kernel shell for aromatic hydrocarbon production. *Energy Conversion and Management, 173, 2018, 545-554.*

[5]. Pinho, A.; Almeida, M.; Mendes, F.; Casavechia, L.; Talmadge, M.; Kinchin, C.; Chum, H. Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production. *Fuel, 188, 2017, 462-473.*

[6]. Pinho, A.; Almeida, M.; Mendes, F.; Ximenes, V.; Casavechia, L. Co-processing raw bio-oil and gasoil in an FCC unit. *Fuel Processing Technology, 131, 2015, 159-166.*

[7]. Bezergianni, S.; Dimitriadis, A.; Kikhtyanin, O.; Kubicka, D. Refinery co-processing of renewable feeds. *Progress in Energy and Combustion Science, 68, 2018, 29-64.*

[8]. Dyk, S.; Su, J.; McMillan, J.; Saddler, J. Potential synergy of drop-in biofuel production with further co-processing at oil refineries. *Biofuels bioproducts Biorefining, 13, 2019, 760-775.*

[9]. Choi, Y.; Elkasabi, Y.; Tarves, P.; Mullen, C.; Boateng, A. Co-cracking of bio-oil distillate bottoms with vacuum gas oil for enhanced production of light compounds. *Journal of*

Analytical and Applied Pyrolysis, 132, 2018, 65-71.

[10]. Wang, X.; Tang, X.; Yang, X. Pyrolysis mechanism of microalgae *Nannochloropsis sp*. based on model compounds and their interaction. *Energy Conversion and Management, 140, 2017, 203-210.*

[11]. Tang, Z.; Chen, W.; Chen, Y.; Yang, H.; Chen, H. Co-pyrolysis of microalgae and plastic: Characteristics and interaction effects. *Bioresource Technology, 274, 2019, 145-152.*

[12]. Bach, Q.; Chen, W. Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review. *Bioresource Technology, 246, 2017, 88–100.*

[13]. Choo, M.; Oi, L.; Show, P.; Chang, J.; Ling, T.; Ng, E.; Phang, S.; Juan, J. Recent progress in catalytic conversion of Microalgae oil to green hydrocarbon: A review. *Journal of the Taiwan Institute of Chemical Engineers, 79, 2017, 116-124.*

[14]. Srikanth, F.; Srivatsa, C.; Bhattacharya, S. A review on catalytic pyrolysis of microalgae to high-quality bio-oil with low oxygeneous and nitrogenous compounds. *Renewable and Sustainable Energy Reviews, 108, 2019, 481-497.*

[15]. Mathimani, T.; Baldinelli, A.; Rajendran, K.; Prabakar, D.; Matheswaran, M.; Leeuwen, V.; Pugazhendhi, A. Review on cultivation and thermochemical conversion of microalgae to fuels and chemicals: Process evaluation and knowledge gaps. *Journal of Cleaner Production, 208, 2019, 1053-1064.*

[16]. Kordulis, C.; Bourikas, K.; Gousi, M.; Kordouli, E.; Lycourghiotis, A. Development of nickel-based catalysts for the transformation of natural triglycerides and related compounds into green diesel: a critical review. *Applied Catalysis B: Environmental, 181, 2016, 156-196.*

[17]. Kubička, D.; Kubičková, I.; Čejka, J. Application of Molecular Sieves in Transformations of Biomass and Biomass-Derived Feedstocks. *Catalysis Reviews, 55, 2013, 1-78.*

[18]. Zhao, C.; Brück, T.; Lercher, J. Catalytic deoxygenation of microalgae oil to green hydrocarbons. *Green Chemistry, 15, 2013, 1720-1739.*

[19]. Yakovlev, V.; Khromova, S.; Bukhtiyarov, V. Heterogeneous catalysts for the transformation of fatty acid triglycerides and their derivatives to fuel hydrocarbons. *Russian Chemical Reviews, 80, 2011, 911-925.*

[20]. Cheng, S.; Wei, L.; Zhao, X.; Julson, J. Application, Deactivation, and Regeneration of Heterogeneous Catalysts in Bio-Oil Upgrading. *Catalysts, 6, 195.*

[21]. Simão, B.; Santana Júnior, J.; Chagas, B.; Cardoso, C.; Ataíde, C. Pyrolysis of *Spirulina maxima*: Kinetic modeling and selectivity for aromatic hydrocarbons. *Algal Research, 32, 2018, 221-232.*

[22]. Brandão, R.; Quirino, R.; Mello, V.; Tavares, A.; Peres, A.; Guinhos, F.; Rubim, J.; Suarez, P. Synthesis, characterization and use of Nb_2O_5 based catalysts in producing biofuels by transesterification, esterification and pyrolysis. *Journal of the Brazilian Chemical Society, 20, 2009, 954-966.*

[23]. Reguera, F.; Araujo, L.; Picardo, M.; Bello, F.; Scofield, C.; Pastura, N.; Gonzalez, W. The use of niobium-based catalysts for liquid fuel production. *Materials Research, 7, 2004, 343-348.*

[24]. Yi, Y.; Xia, Q.; Liu, X.; Lu, G.; Wang, Y. $Pd/Nb_2O_5/SiO_2$ Catalyst for the Direct Hydrodeoxygenation of Biomass- Related Compounds to Liquid Alkanes under Mild. Conditions. *Chem. Sus. Chem., 8, 2015, 1761-1767.*

[25]. Xia, Q.; Zhuang, X.; Li, J.; Peng, Y.; -K.; Liu, G.; Wu, T.; Soo, Y.; Li M.; Gong, X.; Wang, Y.; Tsang, S. Cooperative catalysis for the direct hydrodeoxygenation of vegetable oils into diesel-range alkanes over $Pd/NbOPO_4$. *Chemical Communications, 52, 2016, 5160-5163.*

[26]. Sukarni, S.; Soeparman, S.; Hamidi, N.; Yanuhar, U.; Wardana, I. N. G. Potential and properties of marine microalgae *Nannochloropsis oculata* as biomass fuel feedstock. *International Journal of Energy and Environmental Engineering, 5, 2014, 279-290.*

[27]. Adamczyk, M; Sajdak, M. Pyrolysis Behaviours of microalgae *Nannocholoropsis gaditana*. *Waste and Biomass Valorization, 9, 2018, 2221- 2235.*

[28]. Sanchez-Silva, L.; López-González, D.; Garcia-Minguillan, A. M.; Valverde, J. L. Pyrolysis, combustion and gasification characteristics of *Nannochloropsis gaditana* microalgae. *Bioresource Technology, 130, 2013, 321-331.*

[29]. Sanchez-Silva, L.; López-González, D.; Villaseñor, J.; Sánchez, P.; Valverde, J. L. Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technology, 109, 2012, 163-172.*

[30]. Lopez-Gonzalez, D.; Fernandez-Lopez, M.; Valverde, J. L.; Sanchez-Silva, L. Pyrolysis of three different types of microalgae: Kinetic and evolved gas analysis. *Energy, 73, 2014, 33-43.*

[31]. Lopez-Gonzalez, D.; Puig-Gamero, M.; Acién, F. G.; Gárcia-Cuadra, F.; Valverde, J. L.; Sanchez-Silva, L. Energetic, economic and environmental assessment of the pyrolysis and combustion of microalgae and their oils. *Renewable and Sustainable Energy Reviews, 51, 2015, 1752-1770.*

[32]. Plis, A.; Lasek, J.; Skawińska, A. Kinetic analysis of the combustion process of *Nannochloropsis gaditana* microalgae based on thermogravimetric studies. *Journal of Analytical and Applied Pyrolysis, 127, 2017, 109-119.*

[33]. Pan, P.; Hu, C.; Yang, W.; Li, Y.; Dona, L.; Zhu, L.; Tong, D.; Qing, R.; Fan, Y. The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis sp*. residue for renewable bio-oils. *Bioresource Technology, 101, 2010, 4593-4599.*

[34]. Guo, Q.; Yang, L.; Wang, K.; Xu, X.; Wu, Man.; Zhang, X. Effect of hydration-calcination of CaO on the deoxygenation of bio-oil from pyrolysis of *Nannochloropsis sp*. *International Journal of Green Energy, 16, 2019, 1179-1188.*

[35]. Marcilla, A.; Gómez-Siurana, A.; Gomis, C.; Chápuli, E. ; Catalá, M. C.; Valdés, F, J. Characterization of microalgal species through TGA/FTIR analysis: Application to *Nannochloropsis sp*. *Thermochimica Acta, 484, 2009, 41-47.*

[36]. Chen, W.; Chen, Y.; Yang, H.; Xia, M.; Li, K.; Chen, X.; Chen, H. Co-pyrolysis of lignocellulosic biomass and microalgae: Products characteristics and interaction effect. *Bioresource Technology, 245, 2017, 860-868.*

[37]. Qi, P.; Chang, G.; Wang, H.; Zhang, X.; Guo, Q. Production of aromatic hydrocarbons by catalytic co-pyrolysis of microalgae and polypropylene using HZSM-5. *Journal of Analytical and Applied Pyrolysis, 136, 2018, 178-185.*

[38]. Gelin, F.; Boogers, I.; Noordeloos, A. A. M.; Damsté, J. S. S.; Hatcher, P.G.; Leeuw, J. W.; de. Novel, J. Resistant microalgal polyethers: An important sink of organic carbon in the marine environment? *Geochimica et Cosmochimica Acta, 60, 1996, 1275-1280.*

[39]. Chen, W.; Yang, H.; Chen, Y.; Xia, M.; Yang, Z.; Wang, X.; Chen, H. Algae pyrolytic poly-generation: Influence of component difference and temperature on products characteristics. *Energy, 131, 2017, 1-12.*

[40]. Sudasinghe, N.; Dungan, B.; Lammers, P.; Albrecht, K.; Elliott, D.; Hallen, R.; Schaub, T. High resolution FT-ICR mass spectral analysis of bio-oil and residual water-soluble organics produced by hydrothermal liquefaction of the marine microalga *Nannochloropsis salina*. *Fuel, 119, 2014, 47-56.*

[41]. Zhang, Z.; Volkman, J. K. Corrigendum to Algaenan structure in the microalga *Nannoclhloropsis oculata* characterized from stepwise pyrolysis. *Organic Geochemistry, 104, 2018, 1-7.*

[42]. Chen, W.; Chu, Y.; Liu, J.; Chang, J. Thermal degradation of carbohydrates, proteins and lipids in microalgae analyzed by evolutionary computation. *Energy Conversion and Management, 160, 2018, 209-219.*

[43]. Aysu, T.; Sanna, A. *Nannochloropsis* algae pyrolysis with ceria-based catalysts for production of high-quality bio-oils. *Bioresource Technology, 194, 2015, 108-116.*

[44]. Borges, F.; Xie, Q.; Min, M.; Muniz, L.; Farenzena, M.; Trierweiler.; Chen, P.; Ruan, R. Fast microwave-assisted pyrolysis of microalgae using microwave absorbent and HZSM-5 catalyst. *Bioresource Technology, 166, 2014, 518-526.*

[45]. Bagnato, G.; Boulet, F.; Sanna, A. Effect of Li-LSX zeolite, NiCe/Al_2O_3 and NiCe/ZrO_2 on the production of drop-in bio-fuels by pyrolysis and hydrotreating of *Nannochloropsis* and *Isochrysis* microalgae. *Energy, 179, 2019, 199-213.*

[46]. Rizzo, A.; Prussi, M.; Bettucci, L.; Libelli, I.; Chiaramonti, D. Characterization of microalga *Chlorella* as a fuel and its thermogravimetric behavior. *Applied Energy, 102, 2013, 24-31.*

[47]. Maguyon, M.; Capareda, S. Evaluating the effects of temperature on pressurized pyrolysis of *Nannochloropsis oculata* based on products yields and characteristics. *Energy Conversion and Management, 76, 2013, 764-773.*

[48]. Du, Z.; Mohr, M.; Ma, X.; Cheng, Y.; Lin, X.; Liu, Y.; Zhou, W.; Chen, P.; Ruan, R. Hydrothermal pretreatment of microalgae for production of pyrolytic bio-oil with a low nitrogen content. *Bioresource Technology, 120, 2012, 13-18.*

[49]. Valdés, F.; Catalá, L.; Hernández, M.; García-Quesada, J.; Marcilla, A. Thermogravimetry and Py–GC/MS techniques as fast qualitative methods for comparing the biochemical

composition of *Nannochloropsis oculata* samples obtained under different culture conditions. *Bioresource Technology, 131, 2013, 86-93.*

[50]. Ceylan, S.; Kazan, D. Pyrolysis kinetics and thermal characteristics of microalgae *Nannochloropsis oculata* and *Tetraselmis sp*. *Bioresource technology, 187, 2015, 1-5.*

[51]. Ferreira, A.; Dias, A.; Silva, C.; Costa, M. Evaluation of thermochemical properties of raw and extracted microalgae. *Energy, 92, 2015, 365-372.*

[52]. Hanif, M.; Zwawi, M.; Capareda, S.; Iqbal, H.; Algarni, M.; Felemban, B.; Bahadar, A.; Waqas, A. Product distribution and characteristics of pyrolyzing microalgae (*Nannochloropsis oculata*), cotton gin trash, and cattle manure as a cobiomass. *Energies, 13, 2020, 796.*

[53]. Raba, A.; Bautista-Ruíz, J.; Joya, M. Synthesis and Structural Properties of Niobium Pentoxide Powders: A Comparative Study of the Growth Process. *Materials Research, 19, 2016, 1381–1387.*

[54]. Paulis, M.; Martin, M.; Soria, D.; D'iaz, A.; Odrizola, J.; Montes, B. Preparation and characterization of niobium oxide for the catalytic aldol condensation of acetone. *Applied Catalysis A: General, 180, 1999, 411-420.*

[55]. Chen, W.; Maugé, F.; Gestel, J.; Nie, H.; Li, D.; Long, X. Effect of modification of the alumina acidity on the properties of supported Mo and CoMo sulfide catalysts. *Journal of Catalysis, 304, 2013, 47-62.*

[56]. Hodgson, P.; Henderson, R.; Sargent, J.; Leftley, J. Patterns of variation in the lipid class and fatty acid composition of *Nannochloropsis oculata (Eustigmatophyceae)* during batch culture. *Journal of Applied Phycology, 3, 1991, 169-181.*

[57]. Aussant, J; Guihéneuf, F; Stengel, D. Impact of temperature on fatty acid composition and nutritional value in eight species of microalgae. *Applied Microbiology and Biotechnology, 102, 2018, 5279-5297.*

[58]. Sabzi, S.; Mehrgan, M.; Islami, H.; Shekarabi, S. Changes in biochemical composition and fatty acid accumulation of *Nannochloropsis oculata* in response to different iron concentrations._*Biofuels, 2018, 1-7.*

[59]. Borges, L.; Morón-Villarreyes, J.; D'oca, M.; Abreu, P. Effects of flocculants on lipid extraction and fatty acid composition of the microalgae *Nannochloropsis oculata* and *Thalassiosira weissflogii*. *Biomass and Bioenergy, 35, 2011, 4449-4454.*

[60]. Huang, X.; Huang, Z.; Wen, W.; Yan, J. Effects of nitrogen supplementation of the culture medium on the growth, total lipid content and fatty acid profiles of three microalgae (*Tetraselmis subcordiformis*, *Nannochloropsis oculata* and *Pavlova viridis*). *Journal of Applied Phycology, 25, 2013, 129-137.*

[61]. Maher, K.; Bressler, D. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. *Bioresource Technology, 98, 2007, 2351-2368.*

[62]. Boocock, D.; Konar, S.; Mackay, A.; Cheung, P.; Liu, J. Fuels and chemicals from sewage sludge: 2. The production of alkanes and alkenes by the pyrolysis of triglycerides over activated alumina. *Fuel, 71, 1992, 1291-1297.*

[63]. Fréty, R.; Rocha, M.; Brandão, S.; Pontes, L.; Padilha, J.; Borges, L.; Gonzalez, W.˙ Cracking and hydrocracking of triglycerides for renewable liquid fuels: alternative processes to transesterification. *Journal of the Brazilian Chemical Society, 22, 2011, 1206-1220.*

[64]. Olmstead, I.; Kentish, S.; Scales, P.; Martin, G. Low solvent, low temperature method for extracting biodiesel lipids from concentrated microalgal biomass. *Bioresource Technology, 148, 2013, 615-619.*

[65]. Maher, K.; Kirkwood, K ; Gray, M.; Bressler, D. Pyrolytic decarboxylation and cracking of stearic acid. *Industrial and Engineering Chemistry Research, 47, 2008, 5328-5336.*

[66]. Santos, M.; Arias, S.; Padilha, J.; Carneiro, M.; Sales, E.; Pacheco, J.; Fréty, R. Catalytic cracking of palmitic and oleic acids pre-adsorbed on γ-alumina. *Catalysis Today, 344, 2020,234-239.*

[67]. Kubátová, A.; Šťávová, J.; Seames, W.; Luo, Y.; Sadrameli, S.; Linnen, M.; Baglayeva, G.; Smoliakova, I.; Kozliak, E. Triacylglyceride Thermal Cracking: Pathways to Cyclic Hydrocarbons. *Energy Fuels, 26, 2012, 672−685.*

[68]. Vu, X.; Armbruster, U. Catalytic cracking of triglycerides over micro/mesoporous zeolitic composites prepared from ZSM-5 precursors with varying aluminum contents. *Reaction Kinetics, Mechanisms and Catalysis, 125, 2018, 381-394.*

[69]. Singh, H.; Yusup, S.; Quitain, A.; Kida, T.; Sasaki, M.; Cheah, M.; Ameen, M. Production of gasoline range hydrocarbons from catalytic cracking of linoleic acid over various acidic zeolite catalysts.

Environmental Science and Pollution Research International, 26, 2019, 34039-34046.

[70]. Kadrmas, C.; Khambete, M.; Kubatova, A.; Kozliak, E.; Seames, W. Optimizing the Production of Renewable Aromatics via Crop Oil Catalytic Cracking. *Processes*, 3, 2015, 222-234.

[71]. Benson, T.; Hernandez, F.; Alley, E.; Holmes, W. Elucidation of the catalytic cracking pathway for unsaturated mono-, di-, and triacylglycerides on solid acid catalysts. *Journal of Molecular Catalysis. A, Chemical, 303, 2009, 117-123.*

[72]. Mota, S.; Mancio, A.; Lhamas, D.; De Abreu, D.; Da Silva, M.; Dos Santos, W.; de Castro, D.; Oliveira, R.; Araújo, M.; Borges, L.; Machado, N. Production of green diesel by thermal catalytic cracking of crude palm oil (*Elaeis guineensis Jacq*) in a pilot plant. *Journal of Analytical and Applied Pyrolysis, 110, 2014, 1-11.*

[73]. Leung, A.; Boocock, D.; Konar, S. Pathway for the Catalytic Conversion of Carboxylic Acids to Hydrocarbons over Activated Alumina. *Energy & Fuel, 9, 1995, 913-920.*

[74]. Lapi, H.; Alén, R. Production of vegetable oil-based biofuels—Thermochemical behavior of fatty acid sodium salts during pyrolysis. *Journal of Analytical and Applied Pyrolysis, 86, 2009, 274-280.*

[75]. Palla, V.; Shee, D.; Maity, S. Kinetics of hydrodeoxygenation of octanol over supported nickel catalysts: a mechanistic study. *Royal Society of Chemistry, 4, 2014, 41612-41621.*

[76]. Ho, S. The Thermal Decomposition of Aliphatic Aldehydes. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 276, 1963, 278-292.*

[77]. Fonseca, N.; Pereira, A.; Fréty, R.; Sales, E. Fast Catalytic Pyrolysis of Dilaurin in the Presence of Sodium Carbonate Alone or Combined with Alumina. *Catalysts, 9, 2019, 993-1002.*

[78]. Walne P.R., 1966. Experiments in the Large-Scale Culture of the Larvae of *Ostrea edulis L. Fish. Invest., Ser. 2, 25, 1-53.*

Mailena Dourado, et. al. "Fast pyrolysis of microalgae Nannochloropsis Oculata for production of green diesel fraction." *International Journal of Engineering Research and Applications (IJERA)*, vol.10 (11), 2020, pp 54-68.