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Lithium–Sodium Fly Ash-Derived Catalyst for the In Situ Partial Deoxygenation of *Isochrysis* sp. Microalgae Bio-Oil

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Abstract: The catalytic potential of Na and LiNa fly ash (FA) obtained through a simple solid-state synthesis was investigated for the pyrolysis of *Isochrysis* sp. microalgae using a fixed bed reactor at 500 °C. While both LiNa-FA and Na-FA catalysts reduced the bio-oil yield and increased char and gas production, LiNa-FA was found to enhance the quality of the resulting bio-oil by decreasing its oxygen content (−25 wt.%), increasing paraffins and olefins and decreasing its acidity. The deoxygenation activity of LiNa-FA was attributed to the presence of weak and mild base sites, which enabled dehydration, decarboxylation, ketonisation, and cracking to form olefins. The bio-oil generated with LiNa-FA contained higher amounts of alkanes, alkenes, and carbonated esters, indicating its capacity to chemisorb and partially desorb CO₂ under the studied conditions. These findings suggest that LiNa-FA catalysts could be a cost-effective alternative to acidic zeolites for in situ deoxygenation of microalgae to biofuels.

Keywords: bio-oil; *Isochrysis* sp.; pyrolysis; deoxygenation; catalyst; sodium; lithium



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1. Introduction

It is widely recognised that the development of technologies for converting renewable feedstocks into sustainable fuels is urgently needed, and biomass is a suitable candidate for meeting these requirements [1]. Recently, biofuel production from microalgae has received significant attention due to the potential for thermo-chemical conversion, such as pyrolysis, which can convert the entire algae mass, including proteins and carbohydrates. Previous research has focused on using acid zeolites such as HZSM-5 for algal catalytic pyrolysis, which have been effective in deoxygenating bio-oil to aromatic hydrocarbons [2] but also produce large amounts of coke, requiring constant regeneration. Base catalysts are now becoming more attractive due to their lower cost compared to zeolites and good deoxygenation capacity [3]. Studies on the catalytic pyrolysis of microalgae and duckweed using solid base catalysts have shown that Na₂CO₃ and other alkaline and alkali metal compounds can improve the properties of bio-oil by increasing the volatile matter yield, reducing acid compounds, and promoting alkyl substitution reactions [3]. Babich et al. (2011) studied the catalytic pyrolysis of *Chlorella* sp. in the presence of Na₂CO₃ [4]. A decrease in bio-oil yield was observed (from 55 to 40 wt.%). However, an enhancement of bio-oil properties in terms of calorific value (from 26 MJ/kg to 33 MJ/kg) and energy recovery was also achieved. Moreover, the acid compounds were reduced from 11.5% to 3.6%. The effect of solid base catalyst on the pyrolysis of duckweed was investigated by Yang (2017) by Py-GC/MS and Thermo Gravimetric Analysis (TGA). The solid base catalyst “B” with low BET surface area (6.3 m²/g) and basicity of 1.05 mmol NH₃/g increased the volatile matter yield from 60 to 80 wt.%, reduced acid compounds and promoted alkyl substitution reactions [5]. Xu et al. (2014) also studied the effect of alkaline earth and alkali metals for catalytic pyrolysis of microalgae by TGA [6]. The authors investigated the kinetics

and activation energy from the catalytic pyrolysis using five different catalysts: K_2CO_3 , Na_2CO_3 , CaO , $BaCO_3$, and MgO . The alkaline and alkali metal compounds accelerated the degradation rate of the microalga, with the maximum weight loss rate found in the order $Na_2CO_3 > CaO > K_2CO_3 > BaCO_3 > MgO > \text{no catalyst}$, suggesting Na is the most active.

Isochrysis sp. has been identified among the microalgae species that are suitable candidates for multiple-product algae crops due to its variety of fatty acids that offer a wide scope for several bio-products in a biorefinery approach. Only very few studies are available on *Isochrysis* catalytic pyrolysis. Wang et al. (2015) investigated the pyrolysis of defatted and not-treated *Isochrysis* sp. [7]. The defatted pyrolysis (after lipid removal) at 475 °C produced lower bio-oil yield (36.9 wt.%) compared to the whole microalgae (41.3 wt.%), increased N-heterocyclic compounds (from 25.27% to 36.66%) and phenols (from 19.99% to 31.18%), and decreased hydrocarbons (from 29.87% to 7.41%) [7]. Dong et al. (2014) studied the catalytic pyrolysis of *Isochrysis zhanjiangensis* over ZSM-5, which increased the selectivity and yield of light olefins compared to the non-catalytic run [8]. The study also showed that increasing the neutral lipid content to an optimal level is an effective way to improve the light olefin yield obtainable from the catalytic cracking of microalgae.

Catalytic pyrolysis of *Isochrysis* sp. using a ceria-based catalyst was investigated by Aysu et al. (2016) [9]. The bio-oil yield (26 wt.%) obtained in the presence of Ni-Ce/ Al_2O_3 and Ni-Ce/ ZrO_2 showed an increased energy content (37 MJ/kg) and lower oxygen content (9–15%) compared to the non-catalytic pyrolysis (34.8 MJ/kg and 40%). The bio-oils were also enriched in aliphatics. The same group studied the pyrolysis of *Isochrysis* sp. in the presence of Li-LSX zeolite and micro-silica, demonstrating that acidic Li-LSX-zeolite can be used for reducing nitrogen content in bio-oil and promoting the production of aromatics [10].

Recently, sodium and lithium fly ash-derived sorbents have been developed for high-temperature post-combustion CO_2 capture applications [11,12]. The literature suggests that base catalysts like Na- and Li/Na silicates, derived from coal fly ash, could be cost-effective catalysts for the pyrolysis of microalgae. However, there is a lack of knowledge regarding their potential activity for microalgae pyrolysis. Therefore, this research aims to investigate their potential activity in microalgae pyrolysis.

2. Results and Discussion

2.1. TGA-DTG Pyrolysis

The profiles obtained from the TGA-pyrolysis with the two base catalysts are presented in Figure 1a and compared to Li-LSX zeolite under the same conditions. The volatile matter (VM), including adsorbed moisture obtained in the presence of Li-LSX-zeolite, was the largest (35.3 wt.%), followed by Na-FA (31.9 wt.%), while LiNa-FA resulted in the lowest measurement (25.9 wt.%) [10]. It has to be noted that the decomposition curve for Li-LSX clearly shows 5–6 wt.% more water released than the base catalysts, which decreased the difference in VM reported above. Figure 1b shows the first derivative of the *Isochrysis* weight change, which can be divided into three different decomposition “events”. The first event corresponds to the release of adsorbed water (70–170 °C). The decomposition rate of this event (Phase I) for Na-FA and LiNa-FA was found to be almost half that of Li-LSX-zeolite due to less adsorbed water. The second decomposition event (Phase II) occurred between 250 and 360 °C and was associated with the decomposition of proteins and carbohydrates [13]. Finally, Phase III, with a peak at 475 °C (6.5 min in Figure 1b), represents the decomposition of lipids [9]. Overall, the *Isochrysis* decomposition rates (Table 1) decreased in the order Li-LSX-zeolite > Na-FA > LiNa-FA. The rates associated with the decomposition of carbohydrates and partially fatty acids followed a different trend, being faster in the presence of Li-Na-FA and Na-FA.

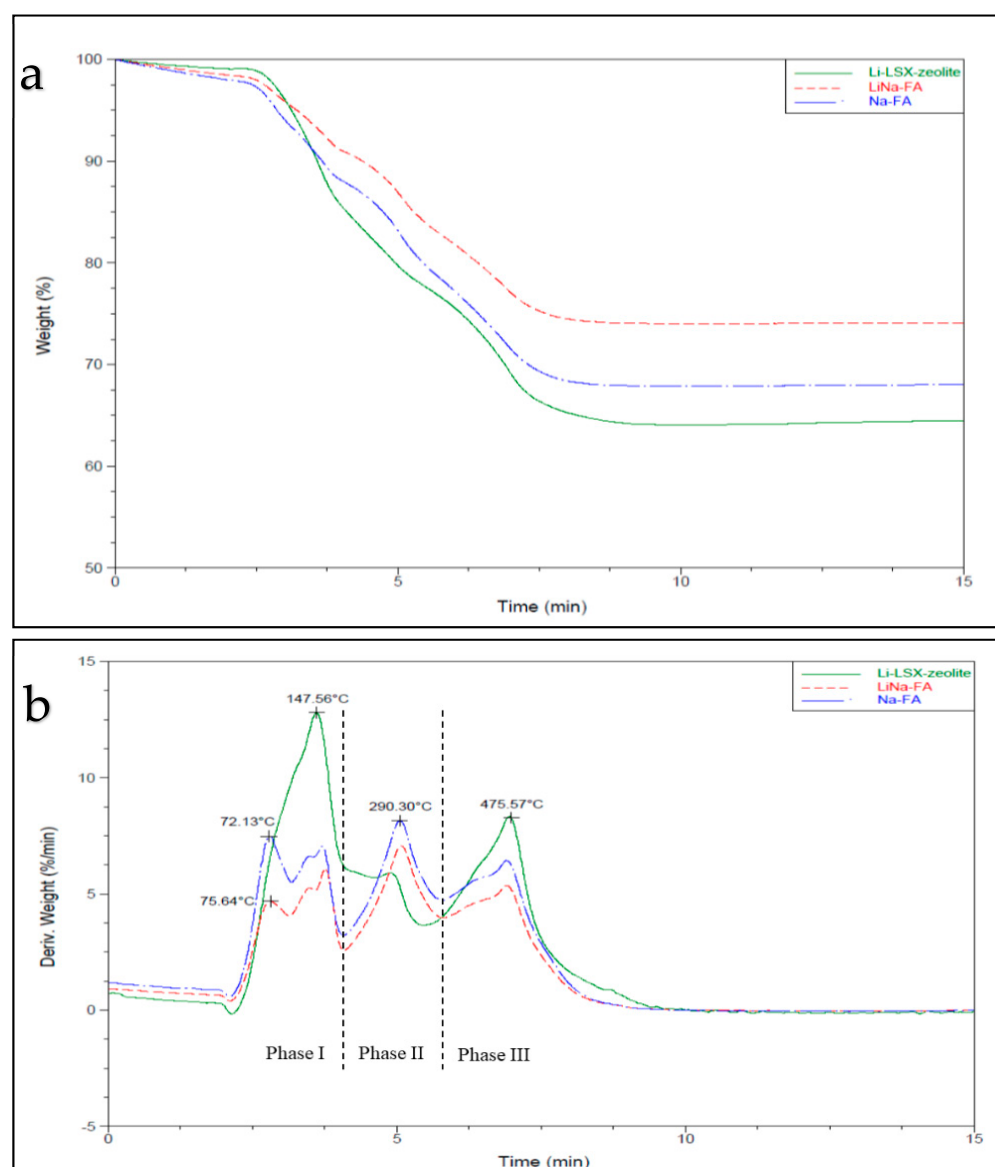


Figure 1. Comparison of (a) TGA and (b) DTG profiles for the microalga pyrolysis in presence of LiNa-FA, Na-FA, and Li-LSX (from [10]). Heating rate of 100 °C/min from 25 °C to 500 °C. Corresponding peak temperatures are also reported.

Table 1. Maximum decomposition of microalgae from DTG of experiments carried out at 500 °C.

Decomposition Rate, wt.%/min	LiNa-FA	Na-FA
Phase I	7.435	4.691
Phase II	8.159	7.014
Phase III	5.329	6.435

2.2. Catalyst Characterisation

Table 2 summarises the textural properties of Na-FA and LiNa-FA. Na-FA and LiNa-FA resulted in a low (BET) surface area ($<1.6 \text{ m}^2 \text{ g}^{-1}$) and micropore volumes ($<0.0002 \text{ cm}^3/\text{g}$) due to the solid-state synthesis method used, suggesting that their catalytic activity is mainly performed on the external surface ($0.78\text{--}1.45 \text{ m}^2 \text{ g}^{-1}$). While the pore size distribution (BJH) of Na-FA and LiNa-FA denoted mostly mesopores and macropores.

Table 2 also reports the basicity of Na-FA and LiNa-FA. Both catalysts have a similar total basicity of around $1.25 \text{ mmol CO}_2/\text{g}$. This basicity can be ascribed to the presence of

alkali metals and corroborate previous assessments [11,12]. To evaluate the strength of the base sites, the dynamic adsorption of CO₂ was evaluated after calcining the materials in N₂ at 700 °C for 30 min. Figures 2, S1 and S2 show the dynamic adsorption of CO₂ from (a) LiNa-FA and (b) Na-FA from 0 to 900 °C in the presence of 20 mL CO₂/min. Despite the two materials having similar total basicity, the strength of the base sites was quite different, with Na-FA having more strong base sites (0.32 mmol CO₂/g), while LiNa-FA resulted in a larger presence of weak (0.52 mmol CO₂/g) and mild (0.72 mmol CO₂/g) base sites. This peculiar difference is reinforced by the fact that CO₂ desorption under the studied conditions started at 600 °C for LiNa-FA but only at 800 for Na-FA (in CO₂ atmosphere). Furthermore, the enthalpy of the reaction indicates that the CO₂ adsorption is endothermic in both cases and requires a larger amount of heat in the presence of Na-FA.

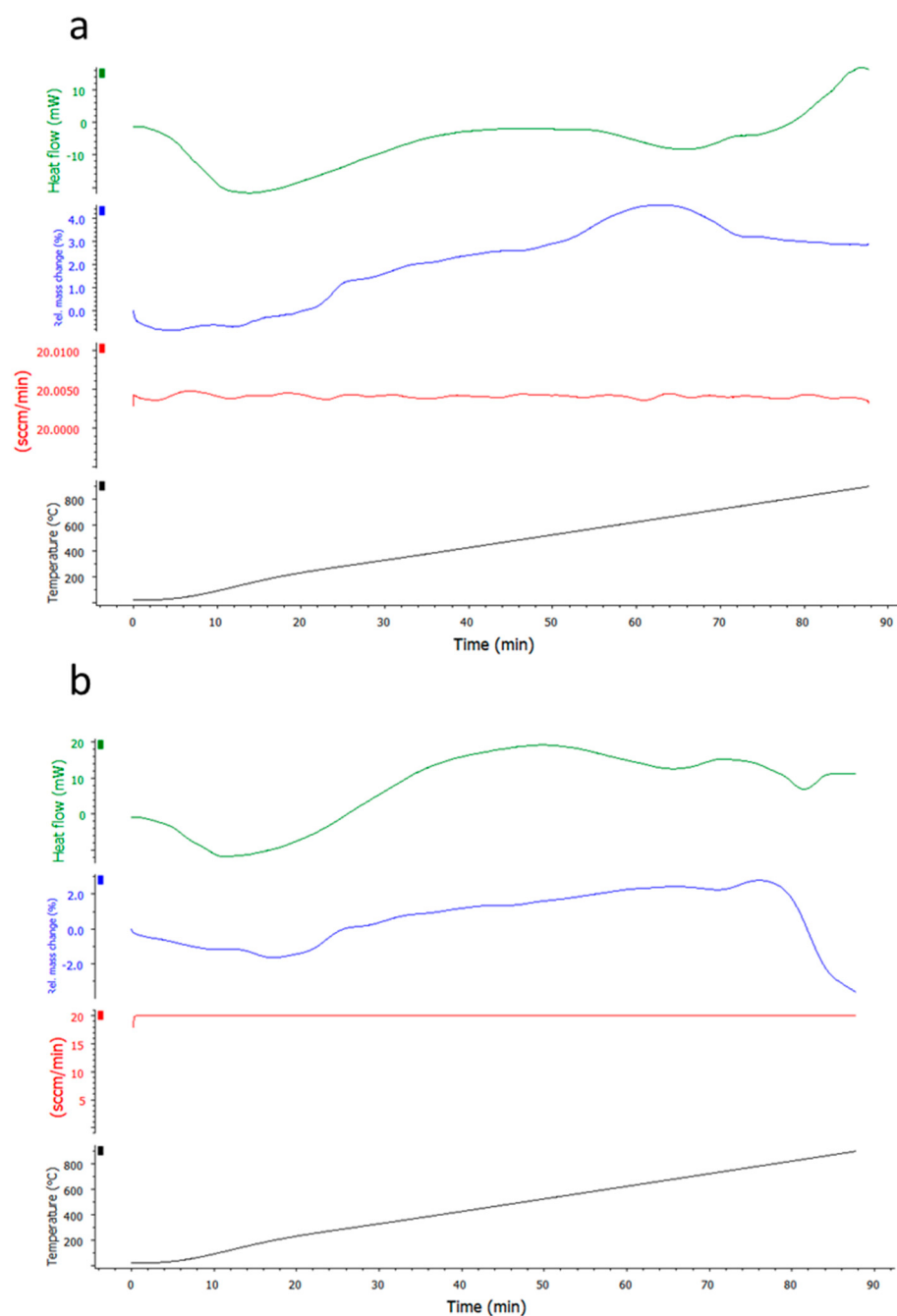


Figure 2. Dynamic CO₂ adsorption (in 20 mL CO₂/min) for base site assessment. (a) LiNa-FA and (b) Na-FA. Temperature change at rate of 20 °C/min.

Table 2. Physical data for catalysts used in this research.

Sample	LiNa-FA	Na-FA
BET surface area (m^2/g)	1.57	0.87
Internal surface [§] (m^2/g)	0.1086	0.0806
External surface [§] (m^2/g)	1.4654	0.7834
Volume _{micro} [£] (cm^3/g)	0.00002	0.00001
Volume _{meso} [£] (cm^3/g)	0.00427	0.00185
Weak base sites (0–300 °C), mmol CO ₂ /g	0.52	0.41
Mild base sites (300–650 °C), mmol CO ₂ /g	0.72	0.50
Strong base sites (650–800 °C), mmol CO ₂ /g	0.00	0.32
Total base sites, mmol CO ₂ /g	1.24	1.23
Enthalpy of CO ₂ adsorption, mJ/mg	1328	2148

[§] T-plot method; [£] HK-method.

Based on the properties described above, the two catalysts are expected to perform in a different way during *Isochrysis* pyrolysis.

Figure 3 shows the FTIR spectra in the 4000–500 cm^{-1} wavelength for Na-FA and LiNa-FA. The region from 4000 to 2300 cm^{-1} does not present any transmission for both samples, indicating the absence of adsorbed water. Small transmission bands are instead visible at 1550–1630 cm^{-1} and 1400–1300 cm^{-1} , assignable to the CO_3^{2-} anion, indicating a minor presence of carbonates. Note that the transmittance intensity for LiNa-FA is lower than that for Na-FA, indicating less carbonate presence, which corroborates the base site analysis (Figure 2) that shows the ability of LiNa-FA to desorb CO₂ at a lower temperature well. Vibrations in the transmission bands between 1250 and 700 cm^{-1} can be assigned to Si–O stretching vibration involving the Si–O–Si entities in silicates, and they appear to be broadened and less intense for the lithium-doped catalyst [12]. The transmission band corresponding to Li–O bond vibrations is typically observed at 416 cm^{-1} , so that cannot be assessed here. However, the different transmission band intensities of the Si–O–Si entities (585, 739, and 765 cm^{-1} for LiNa-FA and 570, 600, and 870 cm^{-1}) suggest the presence of different mineral phases in the two catalysts. Previous work shows that Na was incorporated in Li_4SiO_4 lattice generating a $\text{Li}_x\text{Na}_x\text{SiO}_x$ material [11].

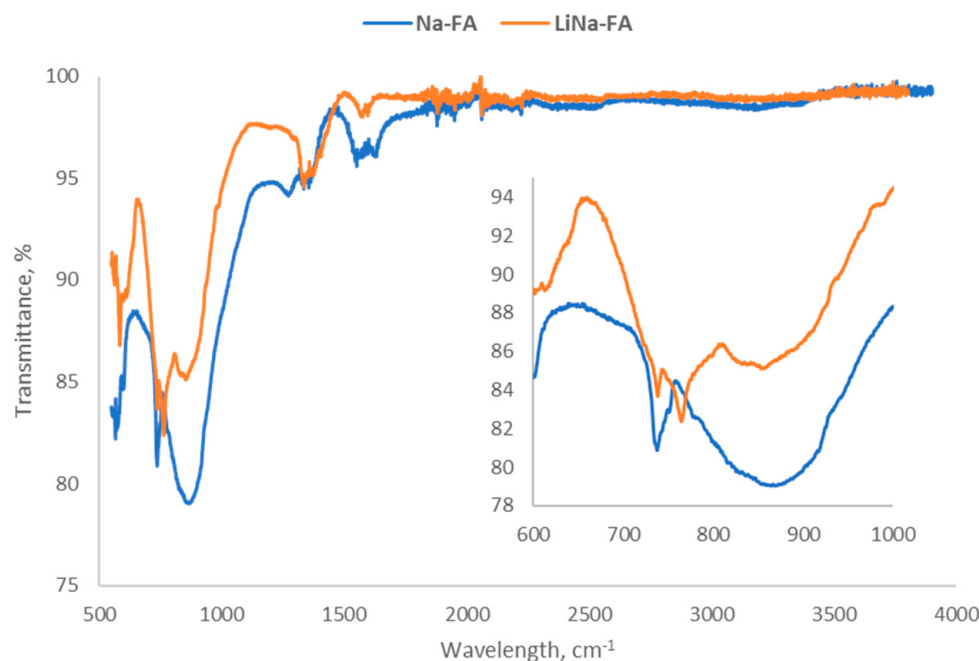
**Figure 3.** FTIR of Na-FA and LiNa-FA.

Figure 4 shows the morphology of Na-FA and LiNa-FA catalysts. Most of the Na-FA particles were 10 to 100 μm in size; however, larger particles/agglomerates of different sizes with an apparent higher tendency to aggregation are also visible in the Na-FA catalyst.

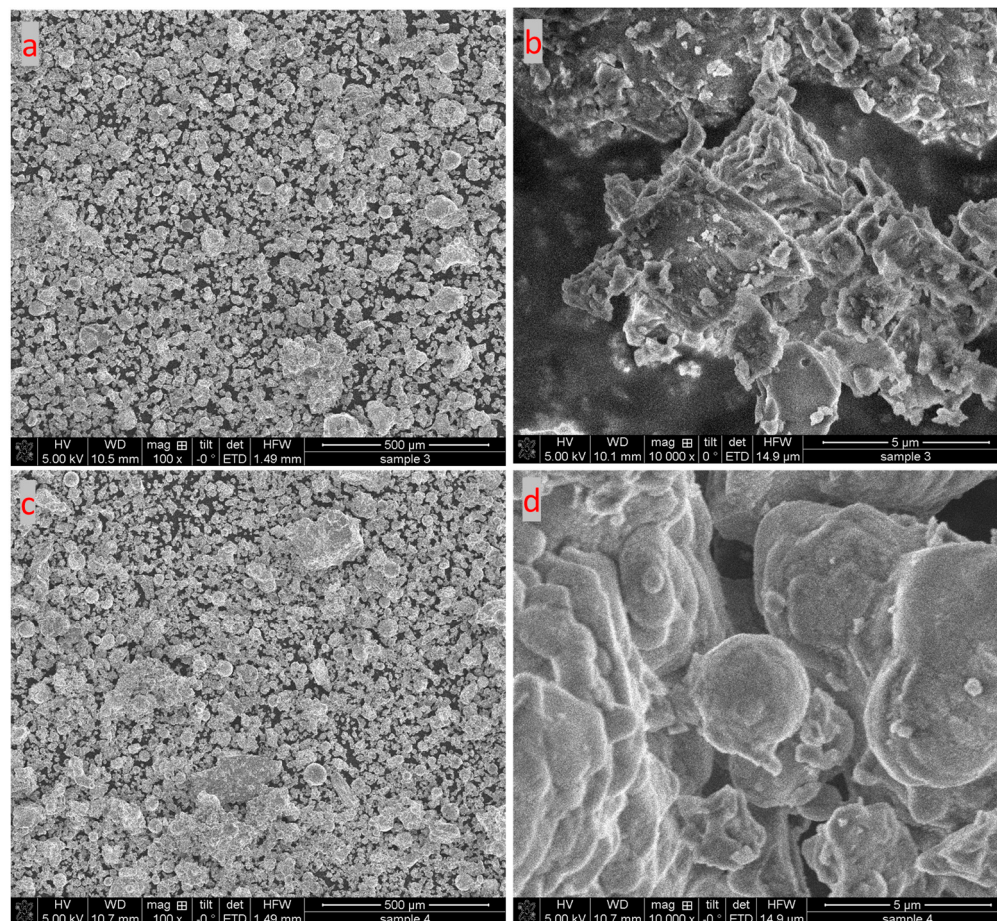


Figure 4. SEM images of (a,b) LiNa-FA and (c,d) Na-FA.

2.3. Catalytic Pyrolysis of Isochrysis

Figure 5 shows the product distribution from the catalytic and non-catalytic pyrolysis of *Isochrysis* sp. A reduction in the oil yield from 37 wt.% (without catalyst) to ~31 wt.% in the presence of catalysts was observed. A similar trend was shown for the acid catalysts [10]. Previous work performed by Chen (2008) showed that both alkaline Na_2SiO_3 and acidic HZSM-5 increased yields of solid products greatly and decreased yields of gaseous products when used for pyrolysing pine wood. However, the yields of liquid products (bio-oil) were not subjected to a dramatic change [14]. Both metal silicate catalysts produced a slightly higher bio-oil yield than acidic catalysts and did not promote gas formation during pyrolysis. Demirbaş et al. (2001) used Na_2CO_3 and K_2CO_3 for gasification of biomass. The presence of alkali metals weakened the intermolecular chain of polymer compounds and promoted dehydration and condensation reactions [15]. Carbohydrates, lipids, and proteins were partly converted into bio-char due to condensation and dehydrogenation reactions [16]. The strong basicity of LiNa-FA and Na-FA decreased the bio-oil yield, which resulted in an increase in the gas yields from 28 wt.% (without catalyst) to 33 wt.% and char via dehydration, condensation, and cracking reactions.

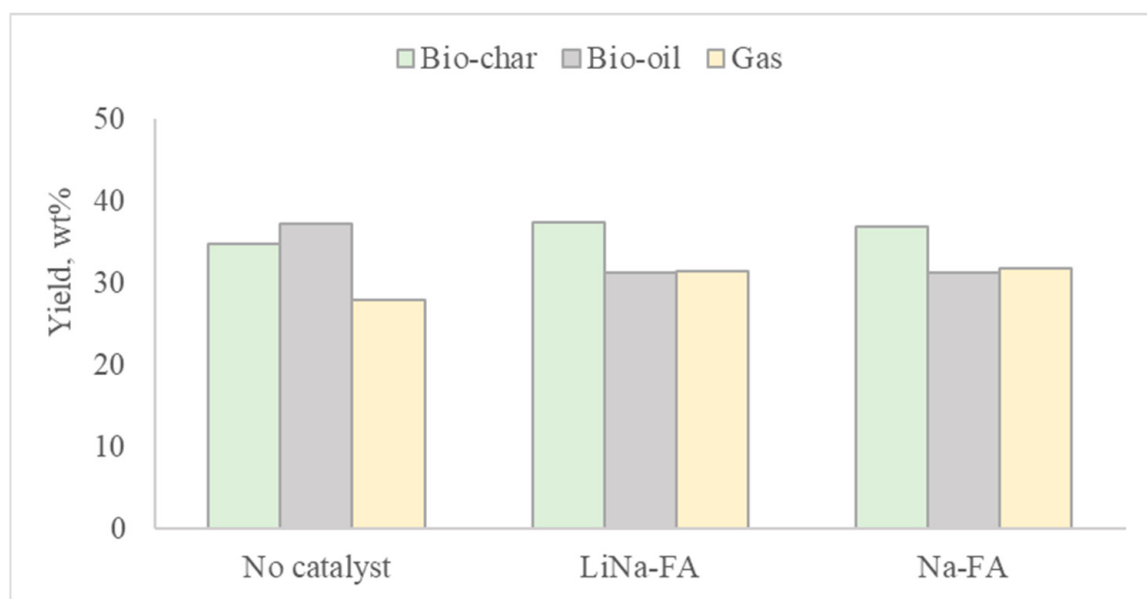


Figure 5. Product distribution from catalytic and non-catalytic pyrolysis at 500 °C.

2.4. Characterisation of Pyrolysis Products

2.4.1. Elemental Analyses of Bio-Chars and Bio-Oils

A further indication of the catalytic activity can be extrapolated from EA and HHV data. Table 3 reports the elemental analyses and high heating value (HHV) of the bio-chars and bio-oils obtained using the catalysts. As expected, the usage of catalysts caused the EA and HHV to improve. While Li-LSX-zeolite reduced O in the bio-char [10], LiNa-FA produced a char with high oxygen content (39.1 to 53.6 wt.%), suggesting that carbohydrates suffered ketonisation and C-C coupling reactions, which also led to condensation reactions and coke/char as observed in previous work [3]. Compared to the non-catalytic test, the LiNa-FA was effective in increasing the C content in the bio-oil by 2.2% and in decreasing the O content by 25%. Oxygen was removed through decarboxylation, decarbonylation, and dehydration reactions, resulting in a high gas yield and low bio-oil yield compared to non-catalytic pyrolysis [4,17]. Pan et al. (2010) studied the catalytic pyrolysis of *Nannochloropsis* sp. in the presence of HZSM-5 using a fixed bed reactor with a catalyst ratio of 1:1 [18]. The study showed a bio-oil decrease in oxygen content from 30.1 wt.% (no catalyst pyrolysis) to 19.5 wt.% (35% reduction), as well as the high heating value (HHV) increasing from 24.4 MJ/kg to 32.2 MJ/kg. A similar HHV increase was obtained in this study (35.5 to 36.7 MJ/kg), although only LiNa-FA enhanced the energy content vs. the uncatalysed run. LiNa-FA was also the only catalyst to reduce O content in the bio-oil, retaining it in the bio-char. This is also confirmed by the lowest O/C molar ratio of 0.11.

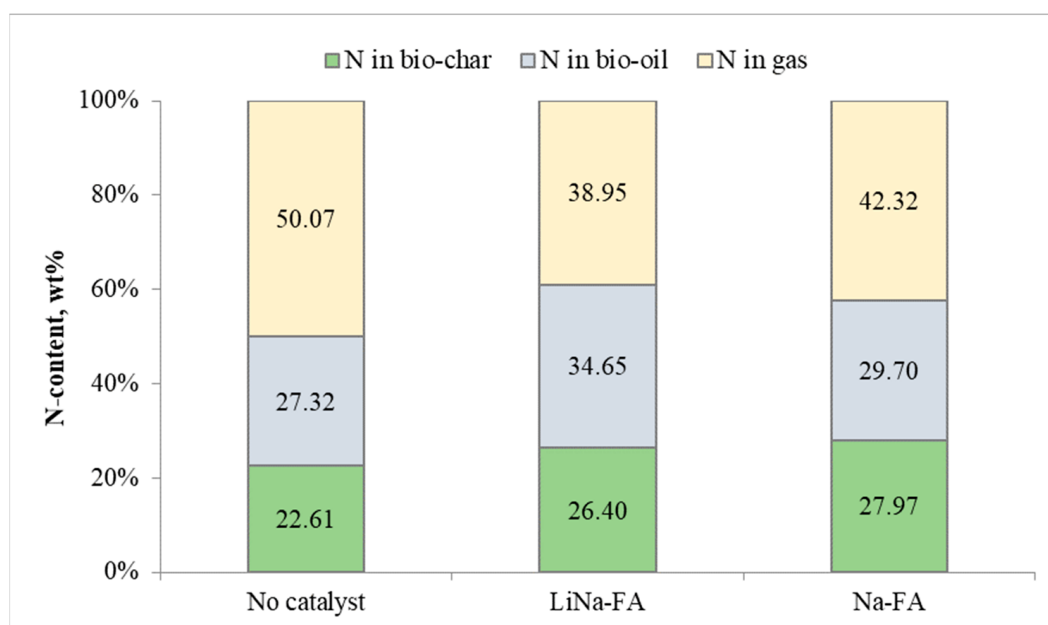
This can be related to the presence of a eutectic mix of Li and Na cations that enhances their diffusion to the surface of the catalyst under pyrolysis conditions facilitating the interaction with the biomass's thermally cracked volatiles. Na-FA catalyst was instead not effective in oxygen removal. Previous work had evaluated the effect of Na₂SiO₃ on the pyrolysis of lignocellulosic biomass, showing the increase in char yield compared to non-catalytic runs [19]. However, the deoxygenation power was not discussed. Regarding the H/C molar ratios, both LiNa-FA and Na-FA decreased the hydrogen content compared to the control, resulting in the highest H/C molar ratio, denoting hydrogen retention. A similar trend was shown by Pavlova bio-oils obtained with a titania-based catalyst, where the H/C molar ratio dropped from 1.55 (without catalyst) to 1.46/1.53 (in the presence of a metal-doped TiO₂ catalyst) [20].

Table 3. Elemental analysis, H/C and O/C molar ratios, and HHV of bio-chars and bio-oils obtained with and without catalysts.

Elemental Analysis	No Catalyst	LiNa-FA	Na-FA
Bio-chars			
Carbon	45.41	42.45	55.87
Hydrogen	2.91	0.20	1.00
Nitrogen	3.41	3.74	4.01
Oxygen	48.24	53.61	39.11
H/C molar ratio	0.77	0.06	0.22
O/C molar ratio	0.80	0.95	0.52
HHV (MJ/kg)	14.25	7.90	15.25
Bio-oils			
Carbon	71.69	73.31	70.70
Hydrogen	10.01	10.04	9.42
Nitrogen	3.89	5.88	5.02
Oxygen	14.41	10.77	14.86
H/C molar ratio	1.68	1.64	1.60
O/C molar ratio	0.15	0.11	0.16
HHV (MJ/kg)	35.27	36.33	34.23

2.4.2. Nitrogen Distribution

The microalgae *Isochrysis* sp. has a high nitrogen content of 5.3 wt.%, which is not ideal for the bio-oil fuel application; denitrogenation via hydrotreating would be required for that purpose. Figure 6 shows the distribution of nitrogen in the products obtained from catalytic and non-catalytic pyrolysis of *Isochrysis* sp. at 500 °C. Without a catalyst, the bio-oil contained approximately 27 wt.% of the nitrogen present in the starting microalgae. However, the use of metal silicate catalysts (in particular LiNa-FA) increased the relative nitrogen content in the bio-oils, which would require denitrogenation before energy applications, but could be advantageous for chemical production and beneficial to reduce the N-related emissions in the gas phase. In contrast, Li-LSX-zeolite was more effective in reducing the nitrogen content in the bio-oils by removing it in the gas phase [10], indicating better performance if the bio-oil is to be used as fuel.

**Figure 6.** Nitrogen distribution in the products.

2.4.3. ^1H NMR

The bio-oils were analysed using ^1H -NMR to determine their chemical functionalities and the effects of different catalysts. Table 4 (and Figure S3) presents the integration of the ^1H -NMR spectra of the *Isochrysis* bio-oils obtained with and without catalysts, while Figure S4 shows the raw proton NMR results. The results showed differences in the distribution of protons in the bio-oils when Na-FA and LiNa-FA catalysts were used. The integrated region (0–1.6 ppm), which represents aliphatic protons, was the most abundant in the bio-oils. Both Na-FA and LiNa-FA increased the aliphatics compared to the control, but Li-LSX zeolite showed even higher aliphatic content [10]. The aliphatic compounds were primarily derived from microalgae fatty acids and carbohydrate degradation.

Table 4. ^1H NMR integrations of *Isochrysis* bio-oils for med at 500 °C versus specific chemical shift ranges.

Chemical Shift Region (ppm)	Type of Protons	No Catalyst	LiNa-FA	Na-FA
0.0–1.6	CH_3 , $-\text{CH}_2-$	60.17	63.06	63.57
1.6–2.2	$-\text{CH}_2-$, aliphatic OH	14.19	15.56	17.01
2.2–3.0	$-\text{CH}_3\text{OC}$, $-\text{CH}_3-\text{Ar}$, $-\text{CH}_2\text{Ar}$	8.73	8.51	7.16
3.0–4.2	$\text{CH}_3\text{O}-$, $-\text{CH}_2\text{O}-$, $=\text{CHO}$	4.38	1.60	1.60
4.2–6.8	$=\text{CHO}$, ArOH , $\text{HC}=\text{C}$ (non-conjugated)	4.55	3.33	3.05
6.8–8.0	ArH , $\text{HC}=\text{C}$ (conjugated)	7.65	7.65	7.01
8.0–10.0	$-\text{CHO}$, $-\text{COOH}$, downfield ArH	0.33	0.29	0.62

The next integrated region (1.6–2.2 ppm), which is associated with alcohols and N-H in amines/amides, confirmed the elemental analysis findings, where LiNa-Fa and Na-FA slightly enhanced their abundance. The resonance between 2.2 and 3.0 ppm (aliphatic protons bonded to $\text{C}=\text{C}$ double bond (aromatic or olefinic) or H two bonds away from a heteroatom) did not show relevant differences. The region of the spectra (3.0–4.2 ppm) that characterises aliphatic alcohol/ether protons, or methylene groups joining two aromatic rings, was less abundant in the presence of the catalysts than without catalyst (4.4%). The protons in the carbohydrate/aromatic ether (4.2–6.4 ppm) region were slightly lower in the presence of the catalysts.

The overall decrease in protons linked to oxygenated species (3.0–6.4 ppm) compared to the non-catalytic test could be due to partial oxygen removal in the presence of the catalysts. These results are consistent with the elemental (Table 3) and GC-MS (Table 5) analyses of bio-oils, which showed lower oxygen contents when LiNa-FA was used. The protons linked to aromatics (6.8–8.0 ppm) did not show a change in abundance, indicating that Na-FA and LiNa-FA are not active in the formation of aromatics. Negligible amounts of aldehydes and carboxylic acids (9.0–10.1 ppm) were detected in bio-oils with and without catalysts (about 0.7%).

Table 5. Gas product distributions with different catalysts.

Gas Compounds, wt.%	No Catalyst	LiNa-FA	Na-FA
H_2	0.11	1.61	1.73
CH_4	1.25	2.93	3.91
NH_3	1.63	0.56	0.49
H_2O	12.93	14.29	18.80
CO_2	1.81	1.13	1.58
Alkenes (C_3H_6 , C_4H_8)	0.37	3.44	0.82
Alkanes (C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12})	3.49	10.15	14.38
CO and/or C_2H_4	7.47	24.69	23.04
Vinylic radical (C_2H_3) and HCN	15.25	39.24	33.54

2.4.4. GC-MS Analysis

The compounds in the bio-oil identified by GC-MS analysis were classified by chemical functionalities into alcohols, aldehydes, aliphatic hydrocarbons (including alkanes, alkenes, alkynes, and cyclic alkanes), aromatics, esters, ethers, ketones, and others, as reported in Figure 7. In contrast, Figure 8 shows the proposed reaction pathways for the degradation of proteins, lipids, and carbohydrates from *Isochrysis* sp. microalgae in the presence of LiNa-FA and Na-FA.

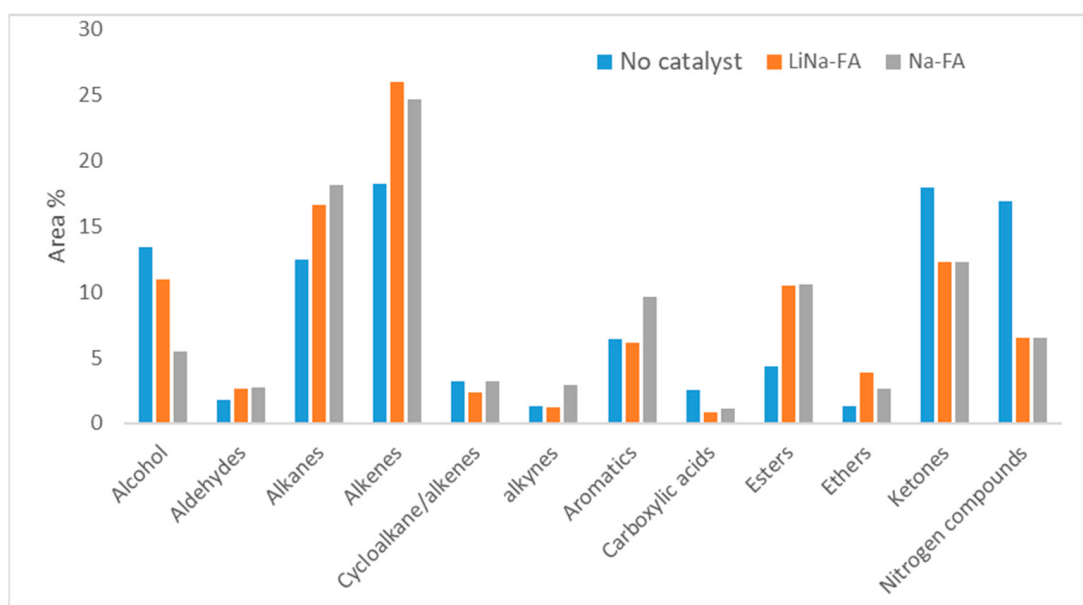


Figure 7. Chemical functionalities in bio-oils from GC-MS.

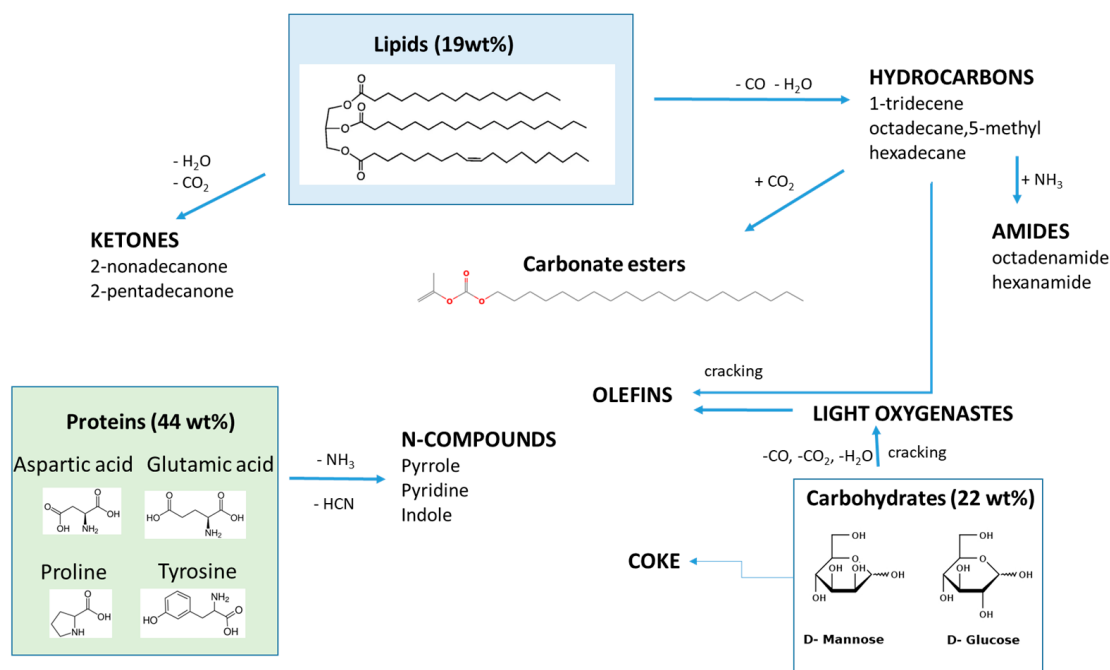


Figure 8. Scheme of catalytic conversion of *Isochrysis* sp. microalgae in presence of LiNa-FA and Na-FA.

When LiNa-FA and Na-FA were used, alkanes, alkenes, ketones, and esters were the most abundant functionalities, whereas alcohols, alkenes, ketones, and nitrogenates

were more abundant in their absence. Alcohols likely formed from the decarboxylation and dehydration of fatty acids, leading to compounds such as 1-tetradecanol, phytol, and 10-undecen-1-ol. LiNa-FA and, in particular, Na-FA favoured the dehydration of alcohols to alkenes, as shown in Figure 7. The microalgae triacylglycerols and fatty acids (mostly myristic, linoleic, oleic, and stearidonic acids) [21] underwent decarboxylation or decarbonylation to form alkanes and alkenes.

A previous work studied the catalytic deoxygenation of fatty acids to produce long-chain olefins, with and without the addition of sacrificial anhydride [22]. Without the anhydride, carboxylic acids are adsorbed on the metal oxide surface and dissociated into acyl and OH[−] over oxygen vacancies, and the C–C is then broken by the metal to generate CO and alkyl cations, followed by deprotonation of the alkyl cations and binding with OH[−] to generate alkenes and water [22]. The resulting compounds include straight-chain alkanes and alkenes that can be used as fuel additives in diesel and aviation fuel to increase octane number in petrol.

The addition of catalysts increases both long-chain paraffins and olefins compared to non-catalytic pyrolysis, with LiNa-FA being more effective in producing olefins. LiNa-FA and Na-FA catalysts also promote esterification reactions, with the formation of more than double the content of esters obtained in the absence of a catalyst. Carbonated esters, such as carbonic acid-eicosyl prop-1-en-2-yl ester, are formed in good quantities, which can be attributed to the catalysts' capacity to chemisorb CO₂ at 500 °C [11]. Long-chain oleochemical carbonates can be used in biodiesel, and their properties resemble those of fatty alkyl esters [23]. Ketones produced by decarboxylation and dehydration reactions, which are typically shown by MgO, instead decrease [3]. The GC-MS data also support the proton NMR data in showing that both LiNa-FA and Na-FA were not effective in aromatisation, which requires Bronsted acid sites [24].

The bio-oil generated from the pyrolysis of microalgae contains a high abundance of nitrogenated compounds, which came from chlorophyll, proteins, and the ammoniation of carboxylic acids from the microalgae lipids. LiNa-FA and Na-FA resulted in less nitrogenated compounds compared to the non-catalytic run, but this contrasts with the elemental analysis. Protein degradation proceeds through an aldol condensation reaction forming free radicals resulting in pyridine, pyrroles, etc. Other amino acids, such as tyrosine-produced phenols and phenylalanine/proline, are rearranged into aromatic hydrocarbons such as toluene and styrene by de-ammoniation or into benzyl-nitrile by dehydrogenation [25,26]. These cyclic compounds can then undergo cracking to form olefins. Amides can be further dehydrated to nitriles (oleannitrile and benzyl nitrile) in the presence of acidic catalysts [27]. Carbohydrates and proteins can undergo Maillard's chemistry, where the carbonyl group (C=O) of the carbohydrate reacts with the amino group (–NH₂) of the amino acid to yield a Schiff base adduct, which further undergoes Amadori rearrangement and forms keto–enol tautomers, which, on cyclisation, yield liquid Amadori compounds, such as indole and phenol [28]. Aldol condensation reactions, which are typically enhanced by base catalysis, are also potential pathways for the condensation of small oxygenates into larger molecules that are further converted to coke [29].

Overall, the study found that the composition of bio-oil obtained from pyrolysis of *Isochrysis* sp. microalgae can be modified with the base Na-FA and LiNa-FA, resulting in a mixture of hydrocarbons and esters that can be used as valuable fuel additives. LiNa-FA was also able to deoxygenate the oil. The activity of the most performing LiNa-FA can be associated with the presence of base sites of both weak and mild strength, with small lithium and sodium cations that can penetrate biomass textures, break intermolecular hydrogen bridges, and thus favour the degradation of biomass through ring scission, depolymerisation, dehydration, and rearrangement to form small decomposition products [30]. Lithium and sodium deoxygenation reactions were driven by the depolymerisation of cellulose through glycosidic bond cleavage, increasing the formation of char by dehydration and recombination and favouring the cleavage of anhydrosugar to produce more light oxygenated compounds and incondensable species [31].

2.4.5. Gas Analysis

Table 5 presents the composition of the gas product obtained from the catalytic and non-catalytic pyrolysis of *Isochrysis* at 500 °C. The presence of catalysts consistently increased the yield of olefins and alkanes, as confirmed by GC-MS results. All catalysts showed cracking activity on the microalgae, resulting in the production of methane (3–4 wt.%), C₂H₄, and other compounds. Moreover, the catalysts promoted the formation of hydrogen (1.5–2 wt.%). Previous studies have shown that alkaline sodium compounds, such as NaOH, Na₂CO₃, and Na₂SiO₃, also promote H₂ formation in microwave pyrolysis of pine wood [14]. The dehydration reaction is an important pathway for removing O in the presence of Na-FA and LiNa-FA, leading to the formation of alkenes and char/coke. This is also supported by the increase in hydrogen content in the gas with LiNa- and Na-FA, which is a sign of condensation reactions with the formation of coke. The amount of NH₃ is lower in the catalytic test than in the non-catalytic test, which supports the GC-MS data on the reaction of NH₃ with paraffins in amide formation and, therefore, retention of N in oil. The gas in the presence of the catalysts seems to contain an abundance of vinylic radicals, which are recognised as an intermediate in the pyrolysis of many hydrocarbons and HCN identified by $m/z = 27$. Although difficult to quantify separately, the % of $m/z = 28$ suggests that the base catalysts promote CO and C₂H₄ formation compared to the non-catalytic run. The low CO₂ content can be explained by the formation of carbonate esters in oil, as discussed in the GC-MS section.

3. Materials and Methods

3.1. Materials

The catalysts (Na-FA and LiNa-FA) were prepared using a solid-state synthesis method by mixing Li₂CO₃ and/or Na₂CO₃ (both from Acros Organics, Geel, Belgium) with coal fly ash collected from a cyclone filter that was rich in SiO₂ (50wt.%), Al₂O₃ (23 wt.%), and Fe₂O₃ (7 wt.%) and had a D(0.5) of 42 µm in an agate mortar and pestle. A molar ratio of Na₂CO₃:FA and Li₂CO₃:Na₂CO₃:FA of 1:1 and 0.5:0.5:1 was used. Then, the mixtures were calcined in ceramic crucible at 800 °C for 8 h [11]. After calcination, the catalysts were ground using a mortar grinder (Pulverisette 2, Fritsch, Idar-Oberstein, Germany) for 1 min to eliminate any potential agglomeration. *Isochrysis* microalgae were obtained from Varicon Aqua Solutions Ltd (Hallow, United Kingdom). in aqueous solution with 8.2% dry weight containing 44% protein, 19% lipids, 25% carbohydrates, and 11% ash. We dried the algae in oven at 60 °C until completely dried, then pulverised them into particle size of <180 µm before storing them in desiccator.

3.2. Methods

3.2.1. TGA Pyrolysis

A TA Q500 (TA Instruments, Eschborn, Germany) was used for the TGA-DTG experiments. About 0.5 g of sample (of each microalgae) was mixed together with the catalyst with ratio of 1:1 using a pestle and mortar for consistency in the pyrolysis tests when catalysts were used. Then, about 10 mg of each sample was placed in a platinum pan and loaded into the TGA furnace. The analysis was performed under a nitrogen gas atmosphere (60 mL/min). The sample was heated at a heating rate of 100 °C/min from 25 °C to 500 °C. The temperature was held for 10 min at 500 °C to permit the complete conversion of the sample. Finally, the system was cooled down from 500 °C to 25 °C at 50 °C/min.

3.2.2. Fixed Bed Pyrolysis

The fixed bed reactor was formed by a (1) gas injection system, (2) pyrolysis reactor (1-inch SS316 tube) and furnace, and (3) stage condenser consisting of two different systems: (a) ice + sodium chloride condenser (−20 °C) and (b) liquid nitrogen condenser (−65 °C). The vertical reactor (1.27 cm diameter, height of 15 cm) was made of 316 stainless steel, with an operating temperature limit of 1000 °C. About 3 g of samples (or samples mixed with

catalyst) were loaded into the reactor for each test. The tests were repeated in triplicates, and the average was reported. Errors in mass balance were found to be <5%.

3.3. Characterisation Techniques

The bio-oils and bio-chars content of C, N, and H were analysed using an CE-440 Elemental analyser (Exeter, Coventry, United Kingdom). The oxygen (O) content was determined by difference using the following formula:

$$\text{Owt.\%}_{\text{DAF}} = 100 - (\text{Cwt.\%}_{\text{DAF}} + \text{Hwt.\%}_{\text{DAF}} + \text{Nwt.\%}_{\text{DAF}} + \text{Swt.\%}_{\text{DAF}}) \quad (1)$$

where C is carbon, H is hydrogen, N is nitrogen, S is sulphur, and DAF is dry ash free. Duplicates were run, and averages were considered.

The higher heating values (HHV) of the feedstocks and liquid/solid products were calculated based on Equation (2) [9].

$$\text{HHV (MJ/kg)} = (0.3491 \times \text{C}) + (1.1783 \times \text{H}) + (0.1005 \times \text{S}) - (0.1034 \times \text{O}) - (0.015\text{N}) - (0.0211\text{A}) \quad (2)$$

GC-MS analysis was performed using a Shimadzu GCMS QP2010 SE equipped with a RXI-5HT column (Restek, Bellefonte, PA, USA). The column (length: 30m, inner diameter: 0.250; film: 0.25 µm) had temperature limits between 40 °C and 300 °C. The oven was programmed to hold at 40 °C for 10 min, ramp at 5 °C/min to 200 °C and hold for 10 min, ramp at 10 °C/min to 250 °C and hold for 10 min, and ramp at 10 °C/min to 295 °C and hold for 10 min. The end of the column was directly introduced into the ion source detector of VG Trio 1000 series. The ¹H NMR of the bio-oils was analysed using a Bruker Avance III (Bruker, Mannheim, Germany) operating at 400 MHz. For samples preparation, bio-oils were diluted in 99.9% of Dichloromethane (CDCl₃) (Merck, Darmstadt, Germany) with ratio of 1:1 by volume and poured into 5 mm NMR tubes. All the acquired NMR spectra were processed through Topspin version 2.1 software (Bruker, Billerica, MA, USA). FT-IR analysis was performed using a Frontier (PerkinElmer, Waltham, MA, USA) assisted with Spectrum™ 10 software (PerkinElmer, Waltham, MA, USA) to acquire and process data. The non-condensable gases were analysed using a Cirrus Mass Spectrometer controlled by Process Eye view software version 1.6 (both from MKS Instruments, Andover, MA, USA). BET surface area measurements, pore size, and pore volume distributions were carried out with a Gemini VII analyser (Micromeritics, Norcross, GA, USA) equipped with multi-tasking software control and single and dual controls. The pore size was calculated using the BJH equation. The catalysts were degassed for 12 h at 200 °C under N₂ gas using a Flowprep 060 (Micromeritics, Norcross, GA, USA). Then, the catalysts underwent analysis using nitrogen as an adsorption gas. Base sites were characterised using a TGA STA PT 1600 (Linseis, Selb, Germany) by CO₂ temperature-programmed adsorption. The temperature programme used was the following: In 20 mL/min CO₂, the temperature was raised from ambient to 900 °C at 20 °C/min. Blank tests (in absence of catalysts) were run prior to the actual tests to remove the buoyancy effect. Potential adsorbed species in the catalysts were removed by heating in Helium at 50 °C/min to 550 °C (50 min). Then, the temperature was decreased to 60 °C for the CO₂ adsorption (30 min), and the degassing was studied up to 600 °C in He (10 °C/min) after a step at 60 °C to allow physisorbed CO₂ to be released.

4. Conclusions

In this work, the chemical transformation of *Isochrysis* sp. microalgae by pyrolysis in the presence of LiNa and Na fly ash catalysts was investigated at 500 °C. Compared to the uncatalysed sample, the yield of bio-oils was lowered using the catalysts due to their enhanced cracking and charring activity. LiNa-FA was particularly effective in decreasing the O content of 25 wt.% by dehydration, decarbonylation, and cracking reactions promoted by its mild and strong base sites. The ¹H NMR and GC-MS analyses indicated that the

addition of LiNa-FA catalyst increased the aliphatic hydrocarbons, esters, and oleochemical carbonates and reduced the content of acids, alcohols, and ketones in the bio-oil.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal13071122/s1>. Figure S1: LiNa-FA base site assessment with quantification using TGA; Figure S2: Na-FA base site assessment with quantification using TGA; Figure S3: Proton NMR integration performed based on the chemical shift region (ppm), which represents different groups attached to the H bonding; 0.0 to 1.6, 1.6 to 2.2, 2.2 to 3.0, 3.0 to 4.2, 4.2 to 6.4, 6.4 to 6.8, 6.8 to 8.0, and 8.0 to 10.0; Figure S4: Proton NMR as received (a) without catalyst; (b) with LiNa-FA; and (c) with Na-FA.

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