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Valorization of algal waste via pyrolysis in a fixed-bed reactor: production and characterization of bio-oil and bio-char

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Abstract:

The aim of the present work is to develop processes for the production of bio-oil and bio-char from algae waste using the pyrolysis at controlled conditions. The pyrolysis was carried out at different temperatures 400-600 °C and different heating rates 5-50 °C/min. The algal waste, bio-oil and bio-char were successfully characterized using Elemental analysis, Chemical composition, TGA, FTIR, ¹H-NMR, GC-MS and SEM. At a temperature of 500 °C and a heating rate of 10 °C/min, the maximum yield of bio-oil and bio-char was found to be 24.10 and 44.01wt%, respectively, which was found to be strongly influenced by the temperature variation, and weakly affected by the heating rate variation. Results show that the bio-oil cannot be used as bio-fuel, but can be used

as a source of value-added chemicals. On the other hand, the bio-char is a promising candidate for solid fuel applications and for the production of carbon materials.

Keywords: Pyrolysis; Algal waste; Bio-oil; Bio-char; Characterization

1. Introduction

Biomass has attracted a great attention as a source for renewable and clean energy (Chen et al., 2015; Ertaş and Hakkı Alma, 2010). Biomass can be converted directly into liquid, gaseous and solid fuels, usable for transport, heat and power production (Demiral et al., 2012). Among a large variety of biomass resources, marine biomass has been considered to be a precious material for the third generation bio-fuels feedstock (Demirbas, 2011; Li et al., 2012). The marine areas of Morocco include almost 3500 km of coastline (Ainane, 2011). Red macroalgae (*Gelidium sesquipedale*) are considered economically valuable resources due to their ability to produce high yields of commercially valuable biomass (Hanif et al., 2014). Morocco the third producer in the world (Mouradi-Givernaud et al., 1999). The *Gelidium* represents 90% of the harvest of the marine algae treated locally and that generates an important quantity of waste (production of 870 tons/years) that cannot be treated very well (Ennouali et al., 2006). Biochemical and thermochemical processes are used for converting waste to bio-fuel and/or other products. Among these technologies, pyrolysis is a promising technology, more favorable and economical for converting algal biomass into energy fuels (Ferrera-Lorenzo et al., 2014a, 2014b; Francavilla et al., 2015; Hui Zhao et al., 2013). The thermal decomposition in the absence of oxygen and at temperatures (400-600 °C)

results in liquid products (bio-oil or pyrolytic oil); carbon-rich solid residues (bio-char); and gaseous products (Chaiwong and Kiatsiriroat, n.d.; Choi et al., 2016; Francavilla et al., 2015; Hu et al., 2013; Ross et al., 2008; Yanik et al., 2013). Bio-oil is considered to be a very promising biofuel and may be used as fuel for heat, power or combined heat and power, or as an intermediate feedstock for various chemicals and liquid transport fuels production. The bio-char is also a useful product that can be used for soil amendment and to sequester carbon in the soil, bio-energy (high calorific value) or environmental-contaminant removal. The Characteristics of pyrolysis products depend on the experimental parameters: final temperature, heating rate, residence time, type of pyrolysis reactor, type of biomass used...etc. The effects of each factor are closely interconnected, which requires more knowledge of the operating conditions of the pyrolysis process to produce bio-oil and bio-char with excellent fuel properties.

A number of studies regarding bio-oil and bio-char production from various sources of biomass have shown that liquid and solid fuels can be produced from biomass (Ben Hassen-Trabelsi et al., 2014; Chaiwong and Kiatsiriroat, n.d.; Choi et al., 2016; Demiral et al., 2012; Ertas and Hakkı Alma, 2010; Hu et al., 2013; Kraiem et al., 2015; Onay, 2007; Onay and Koçkar, 2006, 2004; Ross et al., 2008; Yanik et al., 2013). However, very little information is available on the process of pyrolysis of macroalgae into bio-oil and bio-char and analysis of the characteristics of these products (Chaiwong and Kiatsiriroat, n.d.; Choi et al., 2016; Hu et al., 2013; H. Zhao et al., 2013). Hu et al. (2013) have reported the properties of bio-oils produced by pyrolysis of blue-green algae blooms. The experiments were performed in a fixed-bed reactor and the effects of pyrolysis temperature, particle size and nitrogen flow rate on product yields were studied. The results showed that a maximum oil yield of 54.97% was obtained at a final

pyrolysis temperature of 500 °C, a particle size below 0.25 mm and a nitrogen flow rate of 100 mL min⁻¹. The bio-oil was characterized with a high heating value of 31.9 MJ kg⁻¹ and an O/C molar ratio of 0.16 at optimum conditions. The authors have shown that the pyrolysis of algal biomass is a promising process for both renewable fuel production and lake environment improvement. Zhao et al. (2013) also investigated the properties of bio-oil produced by fast pyrolysis of macroalgae in a Free-fall Reactor. The bio-oil obtained was analyzed by elemental, GC-MS, and FT-IR analysis. The results showed that the average heat value was 25.33 MJ kg⁻¹ and the oxygen content was 30.27 wt%. The results suggested that macroalgae presents as a good bio-oil feedstock candidate. Choi et al. (2016) pyrolyzed Brown algae in a fixed bed reactor under pyrolysis temperature (430-530 °C) and holding time (4-10min). The maximum yields of bio-oil and bio-char were approximately 48.4 and 32.3wt%, respectively, when prepared at 450 °C for 8 min. The results showed that the bio-char has properties, including a comparatively high nutrient content (Ca, K, Mg, N, and P), that make it suitable for use as a soil additive, and for long-term soil carbon sequestration. Francavilla et al. (2015) carried out pyrolysis of *G.gracilis* (macroalgae) residue in order to investigate the production of bio-oil and bio-char within a pyrolysis temperature range of 400-600 °C. Results showed that the bio-oil yield is high (65 wt%) at a pyrolysis temperature 500 °C and a bio-char yield ranging between 33 wt% (400 °C) and 26.5 wt% (600 °C). Bae et al. (2011) studied the effect of pyrolysis temperature on production and characterization of bio-oil from three marine macroalgae, and they concluded that the bio-oil yield reached a maximum, within the range of 37.5-47.4 wt.%, at 500 °C. The compounds identified suggest that pyrolysis can be used to produce bio-oils for various uses, such as chemical feedstock, through further treatment. However, these studies only focused

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on bio-oil analyses, a comprehensive characterization including both bio-oil and bio-char is necessary.

In this study, algal waste after extraction of agar-agar was chosen as source of algal biomass because there is no study on the influence of operating conditions on production and characterization of bio-oil and bio-char from algal waste via pyrolysis. The major challenge in the energy field is the search for process to convert biomass wastes into biofuel with excellent fuel properties. Aim of this study was (i) to investigate the influence of experimental parameters on the pyrolysis of algal waste; (ii) to determine the suitable experimental parameters to achieve maximum bio-oil yield; and (iii) to characterize the bio-oil produced under suitable pyrolysis conditions using elemental analysis, TGA, FTIR, $^1\text{H-NMR}$, GC-MS is characterized. The use of chemical and physical Characteristics was also performed in order to investigate the proprieties of the produced bio-char.

2. Materials and methods

Algal waste used in this study as a feedstock was obtained from the industrial processing of red macroalgae to obtain Agar product (SETEXAM company, Kenitra-Morocco). Prior to use, algal waste was air dried, ground and sieved to obtain particles in the ranges of 0.5-1 mm. Thermogravimetric curves were obtained at four different heating rates (5, 10, 20 and 50 $^{\circ}\text{C min}^{-1}$) between 105 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$. Nitrogen gas was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. A flow rate of around 60 ml min^{-1} was fed to the system from a point below the sample and a purge time of 60 min (to be sure the air was eliminated

from the system and the atmosphere is inert). The balance can hold a maximum of 45 mg; therefore, all sample amounts used in this study averaged approximately 20 mg. Proximate analysis was conducted using a thermogravimetric analyser (METTLER TOLEDO-TGA/DSC 3+). The moisture content is determined by the mass loss after the sample is heated to 105 °C under N₂. The volatile matter corresponds to the mass loss between 105 and 900 °C under N₂. Fixed carbon is the solid combustible material that leads to the mass loss at 900 °C when the atmosphere is switched from N₂ to air (Saldarriaga et al., 2015); the residue left is the ash content. Ultimate analysis for C, H, N and S content was performed using an elemental analyzer (vario MICRO cube V4.0.2). The H/C, O/C molar ratios and empirical formula were calculated from elemental composition. Higher heating value (HHV) of samples was experimentally measured using a bomb calorimetric (Model 1261, Parr Instruments) according to ASTM D 5865-04.

2.1. Pyrolysis procedure

The pyrolysis experiments were performed using a stainless steel fixed-bed reactor. The experiments were carried out in two series. The first group of the pyrolysis experiments was performed to determine the effect of the pyrolysis temperature on the pyrolysis product yields and the pyrolysis conversion. A sample of 20 g of algal waste was placed in the reactor and nitrogen gas (flow rate of 0.1 L/min) was introduced for 15 min to remove air in the reactor. The sample was pyrolyzed from an initial temperature (25 °C) to a final temperature (350, 400, 450, 500, 550 or 600 °C) with a heating rate of 10 °C/min and held for 20 min at the final temperature. The liquid products were condensed in a trapping system and recovered by washing with dichloromethane

(DCM). The aqueous phase was separated from bio-oil by decantation. The anhydrous sodium sulphate was added into the bio-oil and the solvent mixture to remove any remaining water. After the solvent was separated from the bio-oil using a rotary evaporator, the bio-oil was weighed and its yield was determined. The bio-char in the reactor was weighed and the gas yield was calculated by determining the weight difference. The second group of experiments was performed with four heating rates, namely, 5, 10, 20 and 50 °C/min at the pyrolysis temperature of 500 °C. This was in order to examine the influence of heating rate on the pyrolysis product yields. In this study, the pyrolysis experiments were repeated three times to confirm the reproducibility. The products yields are mean values of three equivalent experiments.

$$\text{Bio - oil yield (\%)} = \frac{\text{bio - oil collected weight}}{\text{initial feedstock weight}} \times 100$$

$$\text{Bio - char yield (\%)} = \frac{\text{Bio - char weight}}{\text{initial feedstock weight}} \times 100$$

$$\text{Gas yield (\%)} = 100 - (\text{bio - oil yield} + \text{bio - char yield})$$

2.2. Bio-oil and bio-char characterization

The bio-oil selected for the characterization was that which gave the maximum bio-oil yield at the temperature of 500 °C and heating rate of 10 °C/min. The bio-char obtained at the same conditions was also characterized.

2.2.1. Elemental composition and ash content

The elemental composition (CHN-O) and ash content of the bio-oil and bio-char were determined with the same methods used for raw material.

2.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopic analyses were performed to determine the distribution of functional groups present in pyrolysis products (bio-oil and bio-char). The FTIR spectra of the produced bio-oil and bio-char were recorded using a Bruker Tensor 27 infrared spectrometer in the wavelength range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} and accumulation of 16 scans.

2.2.3. $^1\text{H-NMR}$ spectroscopy

$^1\text{H-NMR}$ spectra were recorded on 600 MHz Bruker spectropin instruments. The bio-oil sample was diluted with CDCl_3 .

2.2.4. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (Thermo scientific ISQ single quadrupole) was used to analyze the bio-oil fraction. By comparing the recorded mass spectra of compounds with those given in the NIST2008 c2.0/Xcalibur data system library, provided by the instrument software, compound identification was done.

Bio-oil were separated by silica capillary column, using helium as the carrier gas (1.2 mL/min). The injection volume was 1 μL using a 20:1 split ratio and an injector temperature of 260 $^\circ\text{C}$. The GC temperature sequence was 70 $^\circ\text{C}$ start, hold 2 min, ramp at 10 $^\circ\text{C}/\text{min}$ to 300 $^\circ\text{C}$ and hold at 300 $^\circ\text{C}$ for 5 min.

2.2.5. Scanning Electron Microscopy (SEM)

The morphology of raw waste and its bio-char was investigated by a scanning electron microscope (phenom Pro X). SEM was carried out using an electron acceleration of 15 kV. Images were taken at a magnification of 3000 \times .

3. Results and discussion

3.1. Algal waste characteristics

The main characteristics of algal waste including the results of proximate and ultimate analyses are given in Table 1, where composition analysis gave 35.27 wt% C, 4.71 wt% H, 4.44 wt% N, 0.73 wt% S, 54.85 wt% O. The heating value of the algal waste was 14.98 MJ/kg, which is relatively high compared to other agricultural residues (Nanda et al., 2016). It was observed that the algal waste contains a high ash content (12.09 %) which is consistent with previous observations of the high ash content in aquatic flora from natural ecosystems, including micro- and macro-algae. The presence of high ash content in the algal waste favors the formation of char since inorganic compounds in the ash are known to catalyze the formation of char during pyrolysis (Maddi et al., 2011).

3.2. Thermogravimetric analysis of algal waste

The thermogravimetric analysis was performed to determine the pyrolysis process temperature. The algal waste was heated from 105 °C to 900 °C at four heating rate of 5, 10, 20 and 50 °C/min in a nitrogen atmosphere. Figure 1 shows the behavior of the algal waste under these conditions. The main mass change seen between 250 °C and 600 °C is attributed to de-volatilization stage in which the pyrolysis main process occurred. This mass loss represents the decomposition of carbohydrate and the protein content (Kim et al., 2013). The maximum thermal degradation of the algal waste was at approximately

340-380 °C (depending on heating rate). Moreover, a significant proportion of inorganic materials in kelps decompose at 600 - 800 °C, probably a consequence of metal carbonates (Norouzi et al., 2016). The TGA curve indicates that over 60wt% of the algal waste is thermally degraded when the reaction temperature is beyond 380 °C. It follows that the algal waste pyrolysis should be performed at temperatures higher than 380 °C. For this reason, algal waste pyrolysis at the five reaction temperatures of 400, 450, 500, 550 and 600 °C were considered.

3.2. FTIR characterization of algal waste

The FTIR spectrum of algal waste is shown in Figure 2. The FTIR analysis was conducted to observe the organic functional groups. The wide band between 3500-3100 cm^{-1} assigned to O-H stretching vibrations. This band indicates the presence of polysaccharides and proteins in the algal waste. The absorption band located at 1640 cm^{-1} , originated from conjugated carbonyl groups (located at α -position). The C-H bending vibrations at 1370 cm^{-1} -1422 cm^{-1} , together with the C-O bending vibration at 1235 cm^{-1} were found in the spectra of algal waste, and this suggests the presence of fats and esters (Zou et al., 2009). The absorbance peak at around 1030 cm^{-1} was also observed and that was possibly from C-O stretching vibrations.

3.3. Effect of final temperature and heating rate on yields of pyrolysis products

Pyrolysis temperature is the most important parameter affecting the product yields. The distribution of pyrolysis products from pyrolysis of algal waste at various final pyrolysis temperatures such as 400, 450, 500, 550 and 600 °C is as shown in figure 3a. It can be seen that the conversion yield increased from 47.91 to 59.64 % when the pyrolysis

temperature was increased from 400 to 600 °C. The bio-oil yield was 19.90 % at the lowest temperature of 400 °C, this data reflects incomplete pyrolysis of algal waste. The peak yield of bio-oil was 24.10 % at 500 °C after which it decreased to 22.30 % at 600 °C. The increase in the yield of bio-oil from 400 °C to 500 °C is explained by the increase of the primary decomposition of the algal waste or the secondary decomposition of the bio-char residue, as the pyrolysis temperature increases. The decrease in the yield bio-oil from 500 °C to 600 °C may be due to the secondary cracking of the pyrolysis vapors at higher temperatures. The yield of bio-char markedly always decreased from 52.09 to 40.36 wt.%, while the yield of gaseous product gradually rose from 21.81 to 31.44 wt.% as the pyrolysis temperature rose from 400 to 600 °C. The decrease in the char yield may be attributed to either the greater primary decomposition of algal waste at higher temperature or the secondary thermal decomposition of the char formed before being entrained out of the reactor. The gas increase is speculated to be owing to the secondary cracking of the char and the pyrolysis vapors.

Due to the maximum oil yield obtained in the first set of experiments, the pyrolysis temperature was held constant at 500°C. Figure 3b shows the pyrolysis product yields were obtained at four heating rates of 5, 10, 20 and 50 °C/min with the final pyrolysis temperature being 500 °C. The bio-oil yield was 22.30 %, 24.10 %, 23.50 % and 22.70 % for the heating rates of 5, 10, 20 and 50 °C/min, respectively. The bio-char yield decreased from 45.23 % to 42.31 % and the gas yield increased from 26.67 % to 28.69 % with an increasing heating rate from 5 °C/min to 50 °C/min. The slight decrease in the bio-char yield and the little increase in the gas yield are due to secondary cracking of

the pyrolysis vapors and secondary decomposition of the bio-char at higher heating rates.

All experiments indicate that the pyrolysis temperature at 500 °C and the heating rate of 10 °C/min are the parameters that result in a maximum bio-oil yield of around 24.10%.

It is known that the final temperature has a significant effect on yield and composition of pyrolysis products (Bae et al., 2011; Ben Hassen-Trabelsi et al., 2014; Choi et al., 2016; Hu et al., 2013; Onay, 2007). The increase of the final temperature is always followed by an important decrease of bio-char yield and an increase in the gases amounts. On the other hand, the bio-oil reaches a maximum in the temperature range of 500-550 °C. For example, Choi et al. (2016) studied the pyrolysis of brown alga and evaluated the effect of the final temperature (430-530 °C) on product distribution. They found that the bio-char yield steadily decreased from 34.50 to 25.5wt%, with rising temperature. This was the opposite of the gas yield, which increased from 20.30 to 27.2 wt%. The yield of bio-oil reached a maximum value of 48.40 wt% at 450 °C (48.40wt%), and then decreased as the temperature increased. Bae et al. (2011) investigated the effect of the pyrolysis temperature (300-600 °C) on the pyrolysis characteristics of bio-oil in a quartz U-tube reactor. They found that the maximum production of bio-oil was achieved at 500 °C. Furthermore, They Argued that this was due to the secondary tar reactions in the vapor phase since the liquid yields decreased while corresponding the gas yields increased at 600 °C. The pyrolysis of macroalgae offers a new opportunity for feedstock production; however, the utilization of bio-oil as a fuel product needs further assessment. Hu et al. (2013) studied the pyrolysis of blue-green algae blooms in a fixed-bed reactor for bio-oil production. The effect of process parameters such as pyrolysis temperature, particle size and sweep gas flow rate on the

yields of pyrolysis products and their chemical compositions were investigated. When the temperature was increased from 300 °C to 700 °C in 50 °C increments, the char yield decreased sharply from 57.09% to 20.39%, while the gas yield rose dramatically from 16.25% to 41.33%. In particular, the bio-oil yield did not display monotonic trends with the increasing temperature. The bio-oil yield achieved the maximum of 54.97 % at the final pyrolysis temperature of 500 °C.

The decrease of the bio-oil yield at higher pyrolysis temperatures is due to the secondary reactions that, in parallel cause the increase in of the gas yield. The decrease of the bio-char yield with increasing temperature may be attributed to either a greater primary decomposition of the raw material at higher temperatures or to the secondary decomposition of the solid product, leading to an increase of the pyrolysis conversion. The yield of non-condensable gas products increases due to the secondary decomposition of the bio-char at higher temperatures, which also contribute to the increasing of the gas products yield with increasing temperature (Onay, 2007; Onay and Koçkar, 2006, 2004; Rahman et al., 2014).

The rest of this study, only bio-oil and bio-char that were obtained under the most suitable conditions, a temperature of 500 °C and a heating rate of 10 °C/min were retained for next characterization.

3.4. Bio-oil characterization

3.4.1. Elemental composition and ash content

The ultimate analysis, proximate analysis and calorific value of the bio-oil are shown in Table 1. As can be seen, the bio-oil has a high carbon (51.12%) content and a low oxygen content (37.20%) content, whereas there is a slight increase in the hydrogen

(5.81%) content compared to the raw algal waste (35.27 %, 54.85 % and 4.71 %, respectively). The results show an increase in HHV and a decrease of the H/C molar ratio of the bio-oil compared to the raw material. The average chemical composition of the bio-oil is $\text{CH}_{1,364}\text{O}_{1,546}\text{N}_{0,078}$.

3.4.2. FTIR characterization

The bio-oil was analyzed by FTIR spectroscopy (Figure 2), the functional groups and related classification of compounds were listed in Table 2. The absorption peak at 3200-3600 cm^{-1} indicated the presence of oxygenated compounds (O-H group). The presence of methyl and methylene groups (alkanes, alkenes) is indicated by the intense peak of C-H stretching vibrations between 2800 and 3000 cm^{-1} (three peaks at 2852, 2925 and 2960 cm^{-1}) and by C-H deformation vibrations between 1350 and 1475 cm^{-1} (three peaks at 1376, 1411 and 1452 cm^{-1}) (Francavilla et al., 2015). The C=O deformation vibrations with absorbance at 1700 cm^{-1} indicate the presence of ketones, carboxylic acid or aldehydes groups. The intense peak 1656 cm^{-1} represents C=C stretching vibrations, which is indicative of alkenes. In addition, the absorbance peaks at 1730-1150 cm^{-1} , corresponding to the presence of heteroatoms (i.e. N and O) functionality, were also observed, which was consistent with results of the GC-MS analysis presented in Table 3. The peaks appear in the range of 1475-1525 cm^{-1} and 700 and 900 cm^{-1} , attributable to the aromatic stretching vibrations, indicating the presence of aromatic compounds in bio-oil. Moreover, the acid compounds are represented by the C-O stretching peaks observed between 1210 cm^{-1} and 1320 cm^{-1} . The peaks between 1000 and 1200 cm^{-1} are due to the presence of alcohols, phenols, ethers and esters showing the C-O stretching vibrations.

3.4.3. Chemical composition (GC/MS)

GC-MS analysis was carried out in order to determine the component of organic compounds in the bio-oil produced at the optimum pyrolysis conditions. As can be seen in Figure 4, bio-oil produced from algal waste is a very complex mixture, and more than 200 compounds were detected in the bio-oil. When mass spectra were compared to the NIST library data, 30 compounds with more than 1.5 % of the total area (defined by the percentage of the compound's chromatographic area out of the total area) were identified; the results is presented in Table 3. The bio-oil from algal waste pyrolysis was composed of a very complex mixture of organic compounds of 5-20 carbons. It can be seen that the bio-oil was mainly composed of phenols, acids, alkanes, furans, ketones, and alcohols and nitrogen-containing heterocycles (indoles and pyridines). The components of the bio-oil were similar to the liquid product obtained by other researchers (Ferrera-Lorenzo et al., 2014b; Ross et al., 2008). The most abundant compound Phenols accounted for 24.79 %. These derivatives of phenolic fragments might be derived from the thermal decomposition of protein, which are known as the polyphenolic components in aquatic biomass (Ross et al., 2008). Different types of acids and alkanes were identified, and they mostly converted from carbohydrates degradation. The nitrogen-containing heterocyclic compounds in algal bio-oils, such as indoles and pyridines, were assumed to be derived from protein degradation (Zhou et al., 2010). Among the compositions of bio-oil, Phenol (8.82 area %), Phenol 4-methyl- (13.47 area %), Heptadecane (5.12 area %), n-Hexadecanoic acid (10.96 area %), Hexadecanamide (4.41 area %) showed the highest selectivity. This result is consistent with the FTIR result of bio-oil.

3.44. $^1\text{H-NMR}$ characterization

To have a clearer understanding of the compound distribution of the whole bio-oil, an analysis was carried out using $^1\text{H-NMR}$. NMR spectra provided complementary functional group information to the FTIR spectrum and the ability to quantify integration areas. The $^1\text{H-NMR}$ spectrum of the bio-oil is shown in Figure 5. The percentages of the proton types that were calculated on the basis of the chemical deviation values obtained from the $^1\text{H-NMR}$ spectra are in Table 4. The most up-field region from 0.5 to 1.5 ppm, represented aliphatic protons that were attached to carbon atoms, at least two bonds, removed from a C=C double bond or heteroatom (O or N). This region contains 32.31% of the protons in bio-oil. The next integral region from 1.5 to 3.0 ppm represents protons of aliphatic carbon atoms that may be bonded to a C=C double bond (aromatic or olefinic) or are two bonds away from a heteroatom (O or N). These protons contribute with 29.61 % of the protons in the bio-oil. The typical compounds with these functional groups in the region 0.5-3.0 ppm were confirmed by GC/MS and FTIR. The region in 3.0-4.5 ppm contributes 5.99% of the protons in bio-oil, which represent protons on carbon atoms next to an aliphatic alcohol and nitrogen connected to methylene groups. The region 4.5 and 6.0 ppm represents aromatic ether proton and many of the hydrogen atoms of carbohydrate-like molecules. The value of proton percentage was 6.64 %. The region of the spectrum between 6.0 and 9.5 ppm corresponds to the aromatic protons, aldehyde protons, and also those in hetero-aromatics containing oxygen and nitrogen and the content of this region was 25.45 %. The bio-oil produced by pyrolysis cannot be used as fuel due to its high water and oxygen contents and the presence of unsaturated and phenolic compounds. As a result,

bio-oil need to be upgraded or pre-treated to improve their quality before being used as bio-fuel. The compounds identified in the bio-oil from waste algal suggest that pyrolysis can be used to produce bio-oil for various uses, such as in the petrochemical industry and as high added value chemicals, through further treatment.

3.5. Bio-char characterization

3.5.1. Elemental composition and ash content

The ultimate analysis, proximate analysis and calorific value of bio-char from the pyrolysis of algal waste are listed in Table 1. The bio-char have high carbon content (52.95 %), moderate oxygen content (38.00 %), low hydrogen content (2.83 %) and high nitrogen content (6.22 %). The ash content is high (around 31,52 %). In comparison to the raw algal waste, the O and H contents decrease in the bio-char due to dehydration, decarbonylation and decarboxylation reactions, which is consistent with the FTIR results. The hydrogen content decreases in the bio-char, probably due to the aromatization of the bio-char and evolution of H₂, as light molecular hydrocarbons (CH₄ and C₂) were formed during the pyrolysis process. The carbon content and HHV make the bio-char from pyrolysis of algal waste acceptable for use as a renewable solid fuel.

3.5.2. FTIR characterization

The bio-char from pyrolysis of algal waste was also characterized by FTIR (figure 2). Remarkable changes have been found for the FTIR spectra of Bio-char (Figure 2) compared to that of the raw material, which indicated an effective conversion of the waste algal under pyrolysis conditions (temperature of 500 °C and heating rate of 10 °C/min). The O-H stretching vibration at 3600-3100 cm⁻¹ in the FTIR spectra of the bio-

char sharply decreased after pyrolysis, probably due to the dehydration of the waste algal together with the release of an amount of water. The bands occurring at 2860-2970 cm^{-1} , which can be assigned to the C-H alkyl functional groups, were almost absent in the bio-char. The peaks between 1900 and 2300 cm^{-1} indicate carboxyl and carbonyl groups. Strong peaks which are representative of aromatic C=O and C=C functional groups at 1400 cm^{-1} as well as a peak at 875 cm^{-1} which correlates with aromatic C-H stretching. A wide band from 900 to 1200 cm^{-1} shows aromatic C-O and phenolic O-H functional groups. The peaks between 700 and 900 cm^{-1} was assigned to aromatic C-H stretching vibrations that indicate the presence of adjacent aromatic hydrogens in bio-char. Similar to the results obtained by the Zhou et al. (2010).

The spectrum of bio-char from waste algal suggests the presence of a variety of oxygen functional groups, as well as aromatic carbon groups (bio-char was mainly an aromatic polymer carbon atom). The spectrum correlates well with the elemental analysis, which also revealed a relatively high amount of retained oxygen content.

3.5.3. Scanning electron microscopy

The morphology of raw waste and its bio-char has been studied by scanning electron microscopy (SEM). The obtained photographs for raw waste and its bio-char are shown in Figure 6. From these micrographs, it is clear that the raw waste and its bio-char show different behaviours regarding their morphologies. The morphology of the bio-char shows more void space and higher porosity on its surface, confirming that the produced bio-char has a higher surface area than the raw waste material. This can be attributed to the fact that thermal treatment improves the porous structure of bio-char due to the loss of mass of part of volatiles from the starting algal waste leaving the skeletal structure.

4. Conclusion

In this study, the algal waste had been converted to bio-oil and bio-char by pyrolysis. The maximum yields of bio-oil and bio-char were approximately 24.1 and 44.01wt%, respectively, at the pyrolysis temperature was 500 °C for heating rate of 10 °C/min. The bio-oil was composed of phenols, acids, alkanes, furans, ketones, and alcohols and nitrogen-containing heterocycles. This preliminary study has shown that the bio-oil cannot be used as bio-fuel, but can be potentially used as a source of value-added chemicals. In addition, the bio-char shows good properties as a solid fuel and as a carbon source for producing carbon materials.

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Figure 1

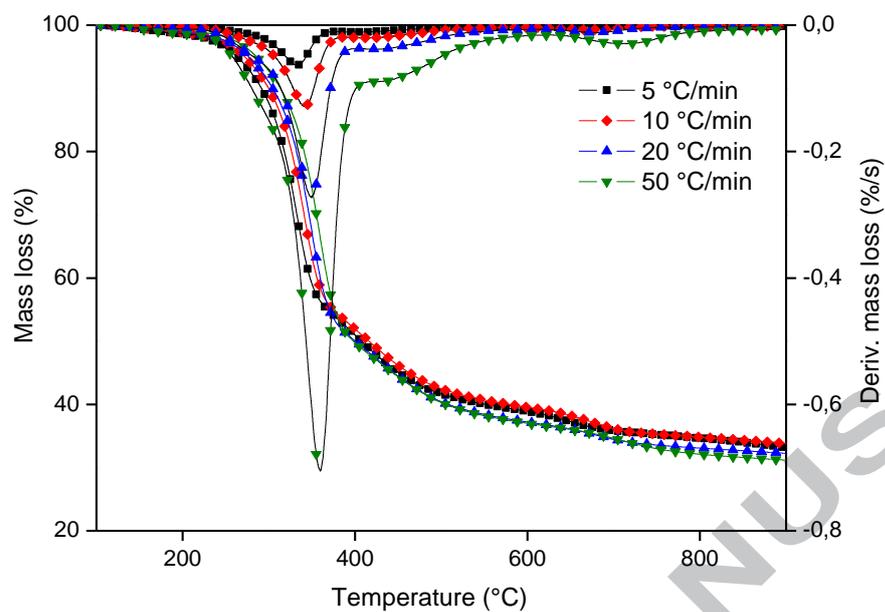
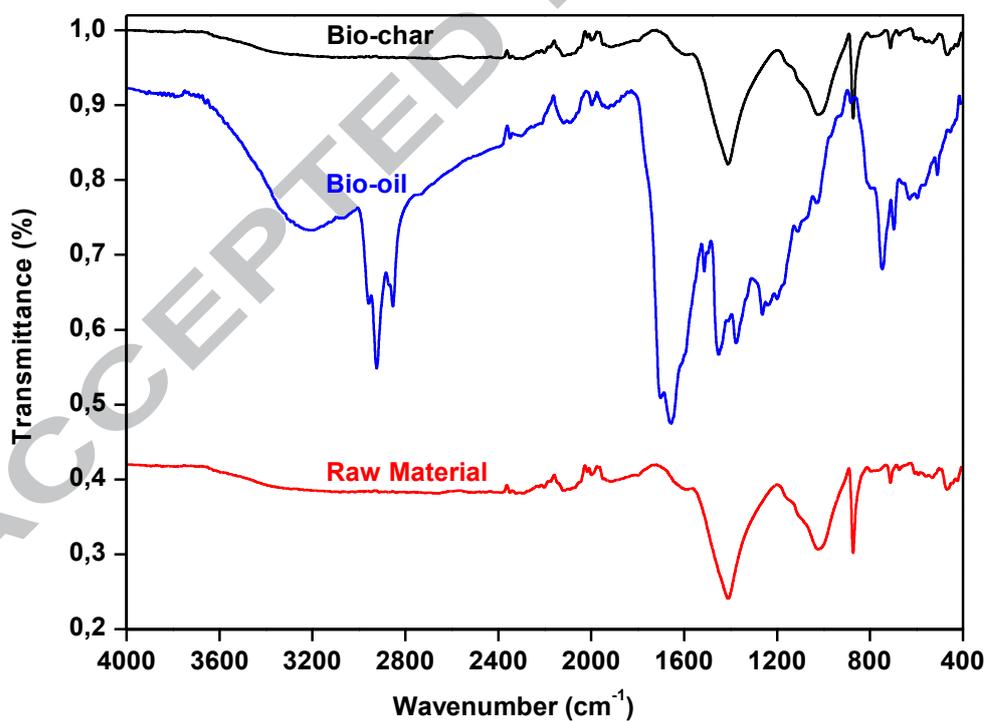


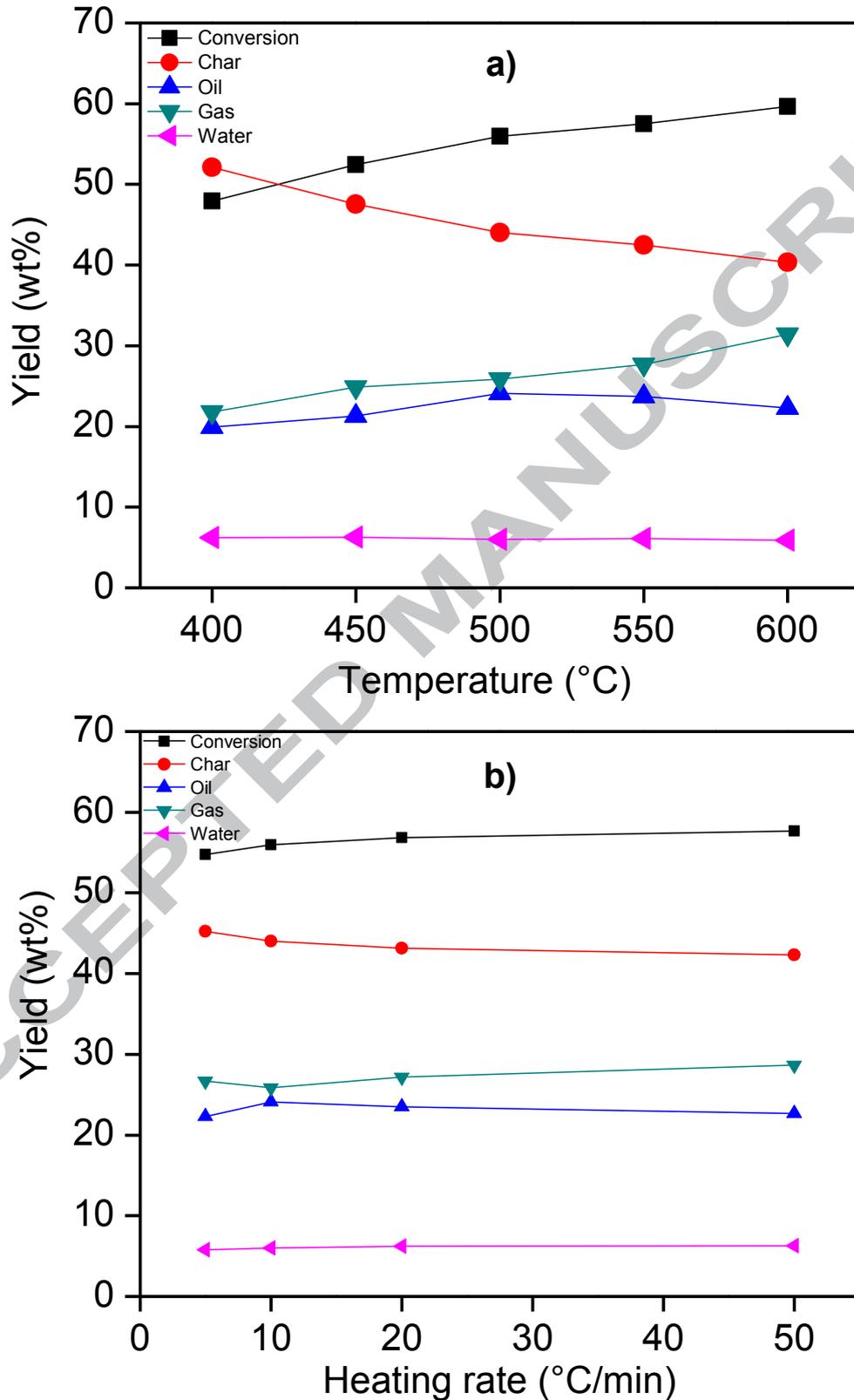
Figure 2



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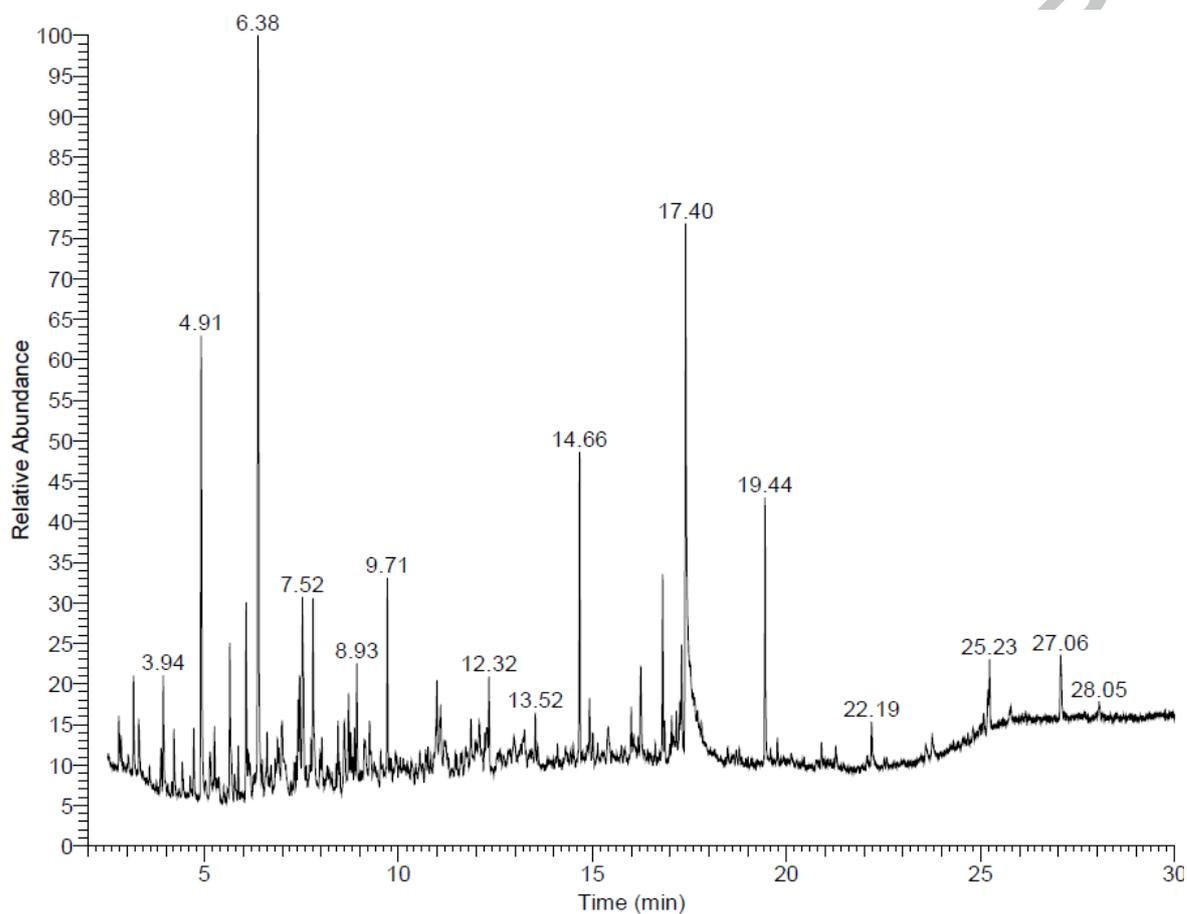
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Figure 3:



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Figure 4



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Figure 5

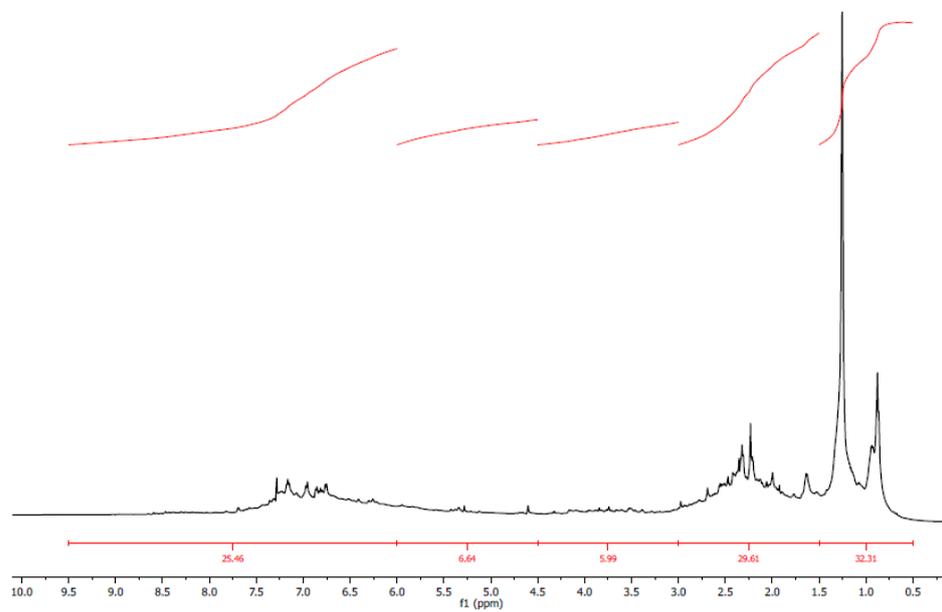
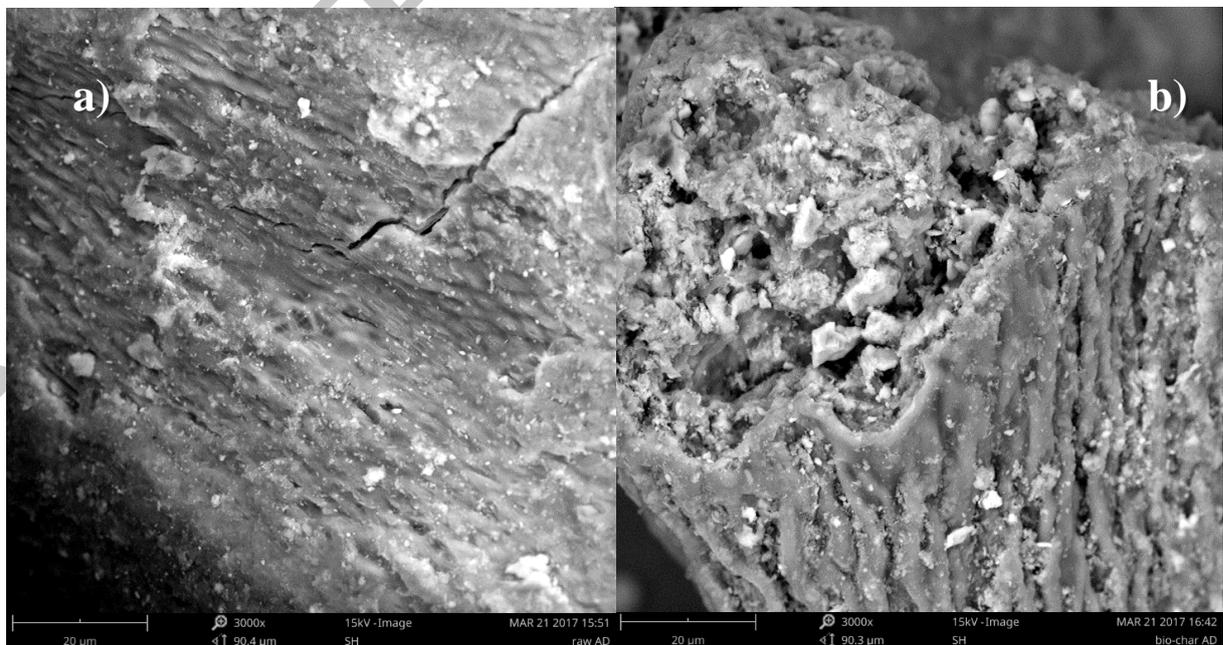


Figure 6



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Table 1:

		algal waste	Bio-oil	Bio-char
Proximate analysis (wt.%)	Moisture	5.04	14.22	4,05
	Volatile matter	68.91	86,75	24,70
	Ash	12.09	1,7	31,52
	Fixed carbon	19.00	11,55	43,78
Ultimate analysis (wt.%)	C	35.27	51,12	52,95
	H	4.71	5,81	2,83
	N	4.44	4,68	6,22
	S	0.73	1,19	--
	O	54,85	37,2	38.00
HHV (MJ/kg)		14.98	19.91	23.09
Atomic	H/C	1,603	1.364	0.639
	O/C	1.166	0.546	0.538
Empirical formula		$\text{CH}_{1,603}\text{O}_{1,166}\text{N}_{0,108}$	$\text{CH}_{1,364}\text{O}_{1,546}\text{N}_{0,078}$	$\text{CH}_{0,639}\text{O}_{0,538}\text{N}_{0,101}$

Table 2:

Frequency range, cm^{-1}	Frequency, cm^{-1}	Group	Class of Compound
3300-3600	3230	O-H stretching	Polymeric O-H
3050-2800	2852, 2925, 2960	C-H stretching	Alkanes
1690-1750	1700	C=O stretching	Ketones, aldehydes, carboxylic acids
1570-1680	1656	C=C stretching	Alkenes
1475-1525	1515	C=Cring stretching	Aromatics
1475-1330	1390, 1411, 1450	C-H deformation	Alkanes
1280-1200	1260, 1240	C-H stretching	Aromatics
1000-1200	1026, 1110, 1195	C-O stretching	Alcohols, esters, ethers
885	885	C-H deformation	Aromatics
750	750	Adjacent C-H deformation	Aromatics
696	696	Out of plan =CH deformation	Alkenes
615	615	Out of plan O-H deformation	Polymeric O-H

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Table 3:

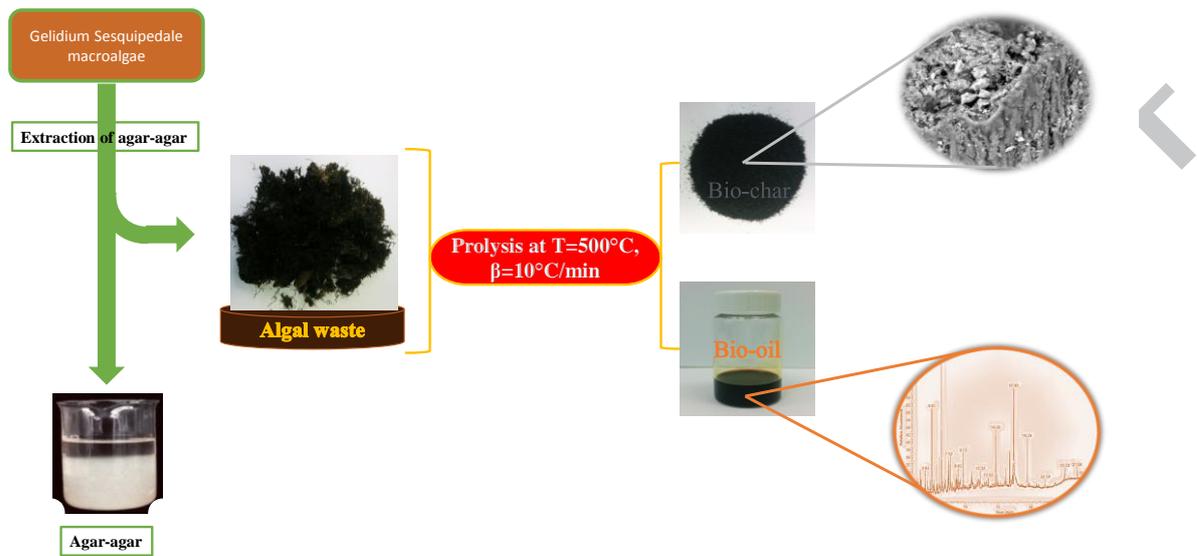
N°	Retention time (min)	Compounds	Molecular formula	Area (%)
1	3,17	2-Furanmethanol	C ₅ H ₆ O ₂	1,73
2	3,94	Ethanone, 1-(2-furanyl)-	C ₆ H ₆ O ₂	2,24
3	4,91	Phenol	C ₆ H ₆ O	8,82
4	5,65	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C ₆ H ₈ O ₂	3,2
5	6,07	Phenol, 2-methyl-	C ₇ H ₈ O	3,67
6	6,13	(3S,4R,5R,6R)-4,5-Bis(hydroxymethyl)-3,6-dimethylcyclohexene	C ₁₀ H ₁₈ O ₂	1,66
7	6,38	Phenol, 4-methyl-	C ₇ H ₈ O	13,47
8	6,61	2,5-Pyrrolidinedione, 1-methyl-	C ₅ H ₇ NO ₂	1,37
9	6,88	2,4-Imidazolidinedione, 3,5,5-trimethyl-	C ₆ H ₁₀ N ₂ O ₂	1,51
10	7	Maltol	C ₆ H ₆ O ₃	2,97
11	7,45	Glutarimide	C ₅ H ₇ NO ₂	2,8
12	7,52	Phenol, 2,4-dimethyl-	C ₈ H ₁₀ O	4,26
13	7,8	Phenol, 4-ethyl-	C ₈ H ₁₀ O	3,39
14	8,44	1,4:3,6-Dianhydro-à-d-glucopyranose	C ₆ H ₈ O ₄	1,66
15	8,61	3-phenyl-2-butenal	C ₁₀ H ₁₀ O	1,7
16	8,71	Oxalic acid, 2-isopropylphenyl pentyl ester	C ₁₆ H ₂₂ O ₄	1,51
17	8,93	Benzenepropanenitrile	C ₉ H ₉ N	2,02
18	9,25	1H-Indol-4-ol, 3-methyl-	C ₉ H ₉ NO	1,4
19	9,71	Indole	C ₈ H ₇ N	3,08
20	10,99	1H-Indole, 7-methyl-	C ₉ H ₉ N	2,27
21	11,08	Benzenecetic acid, 4-(1H-1,2,3,4-tetrazol-1-yl)-	C ₉ H ₈ N ₄ O ₂	1,66
22	11,21	3-Isobutyldihydropyrazin-2-one	C ₈ H ₁₂ N ₂ O	1,8
23	12,28	4-(4-Methylphenyl)pyridine	C ₁₂ H ₁₁ N	1,4
24	12,32	Pentadecane	C ₁₅ H ₃₂	1,54
25	14,66	Heptadecane	C ₁₇ H ₃₆	5,12
26	16,24	2-Pentadecanone, 6,10,14-trimethyl-	C ₁₈ H ₃₆ O	1,84
27	16,81	Hexadecanenitrile	C ₁₆ H ₃₁ N	3,63
28	17,29	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a;1',2'-d]pyrazine	C ₁₄ H ₂₂ N ₂ O ₂	2,9
29	17,4	n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	10,96
30	19,44	Hexadecanamide	C ₁₆ H ₃₃ NO	4,41

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Table 4:

Chemical shift (ppm)	Type of protons	Area (%)
0.5-1.5	-CH ₃ , -CH ₂	32.31
1.5-3.0	CH ₃ -C=O, CH ₃ -N, Ar-CH ₃ , Ar-CH ₂ -	29.61
3.0-4.5	CH ₃ -C=O, -CH ₂ O-, -CH ₂ -N-	5.99
4.5-6.0	ArOCH ₃ , HC=C-(non-conjugated)	6.64
6.0-9.5	ArH, -CHO	25.45



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- Waste algal was pyrolyzed to get value added materials: bio-oil and bio-char

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