

Volatile Compounds of Algal Biomass Pyrolysis

Héctor Alfredo López-Aguilar ¹, David Quiroz-Cardoza ² and Antonino Pérez-Hernández ^{2,*} 

¹ Departamento de Ingenierías/Ingeniería en Energías Alternativa, Universidad La Salle de Chihuahua, 31020 Chihuahua, Mexico; hlopez@ulsachihuahua.edu.mx

² Departamento de Metalurgia e Integridad Estructural, Centro de Investigación en Materiales Avanzados, 31136 Chihuahua, Mexico; david.quiroz@cimav.edu.mx

* Correspondence: antonino.perez@cimav.edu.mx; Tel.: +52-4391101

Abstract: The use and transformation of biomass into highly valuable products is a key element in circular economy models. The purpose of this research was to characterise the volatile compounds and the temperature at which they are emitted during the thermal decomposition by pyrolysis of algal biomass while looking at three different types: (A1) endemic microalgae consortium, (A2) photobioreactor microalgae consortium and (A3) Caribbean macroalgae consortium. Furthermore, the ultimate (CHON) and proximate (humidity, volatile solids and ashes) compositions of the algal biomass were determined. Some volatile species were identified as having potential industrial interest for use as precursors and intermediaries, such as commercially used aromatic compounds which if not suitably managed can be harmful to our health and the environment. It is concluded that the pyrolysis of algal biomass shows potential for the generation of valuable products. The information generated is useful, especially the temperature at which volatility occurs, in order to access the valuable compounds offered by the algal biomasses, and under the concept of biorefinery convert the issue of biomass disposal into a sustainable source of raw materials.

Keywords: devolatilisation; biorefinery; TG-GC-MS; thermal decomposition



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1. Introduction

Biomass use and the circular economy are closely linked in terms of the availability of materials and energy production [1]. In general, biomass mainly consists of food processing waste, crop waste and dry biomass from leaves [2]. However, there is worldwide interest in the exploitation of algae based processes and products, essentially due to the diversity of this biomass's chemical composition, as well as its broad spectrum of secondary metabolites. Under the concept of a low-carbon circular bioeconomy, it has been discovered that it is both environmentally and financially desirable to simultaneously combine the algae CO₂ deposits and waste flow phytoremediation, with the synthesis of high value-added products [3,4].

Thermochemical conversion is an attractive option for the treatment and conversion of the biomass [5], as it displays great efficiency, as well as producing a wide range of substances [6]. Thermochemical conversion by pyrolysis, combustion and gasification are the most commonly used technologies in the biomass processing industry [7,8]. Furthermore, pyrolysis in particular, as well as being a precursor to the thermochemical processes of gasification and combustion, is one of the most promising routes for thermochemical conversion in the production of fuel and other chemical compounds [5,9]. Pyrolysis is a process in which superimposed reactions are produced in the absence of oxygen. It is a highly versatile technology that takes advantage of all of the fractions making up the biomass [10,11]. In general, it was identified that higher temperatures and longer residence times promote the production of volatile gases as the main product of pyrolysis, whereas lower temperatures and longer residence times lead to the formation of solids [8].

It was also discovered that the high heating value (HHV) of the biomass pyrolysis gas is directly associated with the pyrolysis temperature i.e., as the pyrolysis temperature increases the HHV also increases [12]. The macroalgae-based syngas generates a higher energy content (4.6–17.2 MJ/kg) in comparison to microalgae-based syngas (1.2–5.1 MJ/kg), although when a suitable feedstock is selected the bio-oil yield generated from algal biomass can exceed 55% (>40 MJ/kg) [13].

Diverse studies were carried out to observe the pyrolytic behaviour of biomasses, mainly using thermogravimetric (TG) analysis [5,14,15]. TG analysis has been used as a proven technique to study the thermochemical phenomena of microalgae. The advantages of using a thermogravimetric analyser are its easy operation, minimal use of raw material, precise control and ability to record temperature and sample weight loss [16]. Sukarni (2020) studied the combustion process and the kinetic parameters of the microalgae *Spirulina*, synthetic waste and mixture of both. He observed that variances in organic and mineral compounds in typical microalgae species lead to differences in thermal degradation [17]. Meanwhile, Jabeen et al. (2020) proposed an alternative thermogravimetric analytical procedure for the proximate analysis of algal biomass, using *Spirulina* and *Chlorella* as model algae [18].

Other authors have studied the volatile compounds (VCs) released during the pyrolysis of the biomasses using gas chromatography techniques, such as analytical pyrolysis-mass spectrometry (PyGC/MS) [19,20] and GC/MS attached to a tube furnace [9]. Furthermore, it was found that applying the technique of thermogravimetric characterisation coupled with gas chromatography/mass spectrometry (TG-GC/MS) enables information on the sample's mass loss and VCs released at certain temperatures to be obtained, simultaneously [8,10,21,22].

Diverse studies show the importance of studying the VCs of pyrolysis in order to promote the use of biomass [23–25]. However, the characterisation of VCs of biomasses is an ongoing challenge due to their diverse origins, forms and complexities [20,26]. The objective of this investigation was to study the thermal decomposition of algal biomass by pyrolysis and determine the main volatile metabolites emitted using TG-GC/MS coupling techniques. According to Vieira et al. (2020) under the framework of a circular economy all of the biomass fractions must be valued in order to make its use competitive [3]. Therefore, studying the VCs will promote the exploitation of the compounds offered by algal biomasses under the concept of biorefinery.

2. Materials and Methods

This research analysed 3 types of algae: (A1) endemic microalgae consortium from a body of water (unidentified), (A2) microalgae consortium cultivated in a photobioreactor (*Spirulina* microalgae) and (A3) Mexican Caribbean macroalgae consortium (*Sargassum natans* & *S. fluitans*).

The endemic microalgae studied were obtained from the peri-urban dam Chuvíscar in Chihuahua city, Mexico (28°35'56" N, 106°6'59" W). The sample of cultivated microalgae was obtained from an experimental photobioreactor prototype from the start up Alis Algae Solutions, which used waste water as a culture medium. The photobioreactor prototype is a closed vertical reactor made of polycarbonate in the shape of a hexagonal prism with a flat bottom and a gas diffuser, which combines the mechanism of a column of bubbles with an air-lift type reactor in order to cultivate *Spirulina* microalgae.

The *Sargassum* macroalgae samples were gathered from Caribbean beaches in the hotel coastal area of Cancun, Mexico (21°4'04.1" N, 86°46'33" W).

The biomasses were washed with drinking water, dried in the sun for three days at normal environmental temperature and stored for characterisation in high-density polyethylene bags. They were then dried in an electric oven at 105 °C. The samples were sieved using a 100 mesh and stored in a dryer for subsequent characterisation. According to Mlonka-Mędrak et al. (2019) the particle size of the biomass is an important parameter that must be considered when planning the thermal conversion process [8].

For the ultimate analysis, the C, H, O and N elements present in the biomass samples were determined via the chromatography of elements in a Thermo Scientific Flash Smart device with a Porapak PQS column and molecular sieve, using helium as the carrier gas.

The determination of volatile solids (VS), percentage humidity, and ashes of the biomass samples were determined using TG. STA Regulus 2500 Netzsch equipment was used with a heating ramp rate of 10 °C/min from 20 to 1000 °C with a sample of mass 10 mg in an alumina crucible using helium (99.999%) as a carrier gas with a flow rate of 50 mL/min. The derivative time thermogravimetric analysis (DTG) was also performed.

The TG, DTG curves combined with the GC/MS results were used to describe the pyrolysis process [10,27]. The volatile metabolites emitted during pyrolysis were determined using the TG-GC/MS coupling technique with the same temperature ramp and experimental conditions as the TG. An STA Regulus 2500 Netzsch attached to an Agilent 7890B Gas Chromatograph device and a mass spectrometer 5977B (GC/MS) via a JAS transfer line were used. Helium (99.999%) was used as a carrier gas at a flow rate of 50 mL/min in a Porapak 19091S-433UI column of 30 m coupled to a quadruple MS simple, using a mass range from 35 to 450 m/z to characterise the emitted volatiles. 48 injections of the STA to the GC/MS system were carried out for each experiment within a total time of 110 min, during the pyrolysis thermal treatment at a constant temperature of 150 °C in the column.

Agilent MassHunter software was used to gather and analyse chromatographic peaks. Only peaks with areas that represent 5% or more of the largest peak area in the chromatogram and with a degree of certainty greater than 60% were included for identification. The compounds were identified using the database of National Institute Standard and Technology (NIST).

3. Results and Discussions

3.1. Ultimate Analysis

Table 1 displays the values obtained in the ultimate analysis of algal biomasses.

Table 1. Ultimate analysis of biomasses by elemental chromatography.

Algal Biomass	% C	% H	% O	% N	C/N	Molar	
						O/C	H/C
Endemic microalgae consortium (A1)	20.551	2.622	36.508	1.359	15.122	1.333	1.52
Photobioreactor microalgae consortium (A2)	14.549	1.908	31.142	2.164	6.723	1.607	1.563
Caribbean macroalgae consortium (A3)	28.8	3.4	39.7	1.2	24	1.035	1.407

The pyrolysis behaviour largely depends on the chemical structure of the biomasses. The C/N ratio is an important parameter in the study of thermochemical processes, which is useful in determining the most suitable energy conversion process. It was discovered that higher ratio values indicate a more suitable biomass for the gasification process [7,15]. However, lower values of this ratio in the biomasses confirm that the development of NO_x would be minimised in the pyrolysis [28]. These observations are consistent with the potential for using the Sargassum macroalgae via gasification and the lower production of NO_x in the pyrolysis of the algae cultivated in a photobioreactor.

Several authors have reported very variable C/N ratios in biomasses ranging from 8.72 to 58 [29]. In our study, the values are found in the range of 6.72 to 24.

Furthermore, Filer et al. (2019) identified that a C/N ratio close to 40 leads to optimal operation for the anaerobic digestion of the biomasses [30]. This is a value found to be within the range recommended by Al Seadi et al. (2013), in the production of biogas which is 16 to 45 for efficient digester performance [31]. If this ratio is high the nitrogen is rapidly consumed and biogas production decreases and if low, inhibitors such as ammonia and volatile fatty acids can accumulate [32]. The C/N ratio for Sargassum was determined to be

within this range for biogas production (Table 1) and this was shown in previous studies [33]. For their part, the endemic macroalgae and the microalgae of the photobioreactor show less potential for biogas production.

The energy content of the samples also depends on their inherent bonds of O-C and H-C. Table 1 shows the molar ratios O/C and H/C found for the biomasses of this study, and indicates the carbonisation degree for the samples. The raw materials for the biochars show O/C ratios in the range of 0.4 to 0.9 and H/C ratios between 1.3 and 1.9, whereas after the pyrolysis process the fuel biochars and carbons show O/C values in the range of 0.05 and 0.5 and H/C ratios between 0 and 1.5 [34]. The biomasses analysed presented O/C values exceeding 1 in all cases, and H/C values exceeding 1.4 which indicate greater oxidation and less condensation of the samples.

3.2. Proximate Analysis

Table 2 shows the proximate analysis obtained by thermogravimetry for each of the biomasses.

Table 2. Proximate analysis of biomasses by TG.

Algal Biomass	% Humidity	% VS	% Ash
Endemic microalgae consortium (A1)	0.27	3.73	94.25
Photobioreactor microalgae consortium (A2)	5.61	68.70	18.86
Caribbean macroalgae consortium (A3)	3.03	33.08	50.02

Variability in the percentage humidity determined was mainly affected by the drying technique, the presence of intermolecular water and the susceptibility of the dry biomasses to reabsorbing humidity from the atmosphere.

Several authors identified a VS range for diverse biomasses of 3.93 to 96.96% [10,20,23,24,28,35–38]. The VS content found in *Laminaria digitate*, *Ascophyllum nodosum* and *Chaetomorpha* macroalgae was 25.5, 63.3 and 84.3%, respectively [39] while *Spirulina platensis* microalgae contained 77.96% [17], and *Chlorella vulgaris* microalgae 84.3%, [18]. The presence of ash in biomasses has appeared in the range between 0.34 and 52.39% [7,9,10,20,24,28,35,36,39,40], for *Laminaria digitate*, *Ascophyllum nodosum* and *Chaetomorpha* macroalgae are 59.9, 31.8 and 67.6%, respectively [39]. Additionally, for *Spirulina platensis* and *Chlorella vulgaris* microalgae it was observed 10.14 and 5.3% [17,18].

This research found VS values between 3.73 and 68.7% and for ashes between 18.86 and 94.5%, respectively (Table 2). The presence of VS is related to the organic matter and the amount of ash with the presence of mineral compounds found in the algal biomass. The ash content and its chemical composition cause significant issues during thermal processing, considering the dirt and slag generated, as well as the corrosion of metal surfaces in the boiler systems [8]. An example of this is the case with the endemic microalgal biomass that displayed 94.25% ash.

Figures 1–3 show the thermograms of the algal biomasses studied and the differential curves of the same. Within the range of 150 and 360 °C, with a greater volatile generation rate at 180 °C, the decomposition of both proteins and soluble polysaccharides occurs. At higher temperatures (maximum rates at 271 and 411 °C) the cellulose present in the cellular walls decomposes, as well as other insoluble polysaccharides, and the lipids present decompose between 330 and 560 °C [22,26].

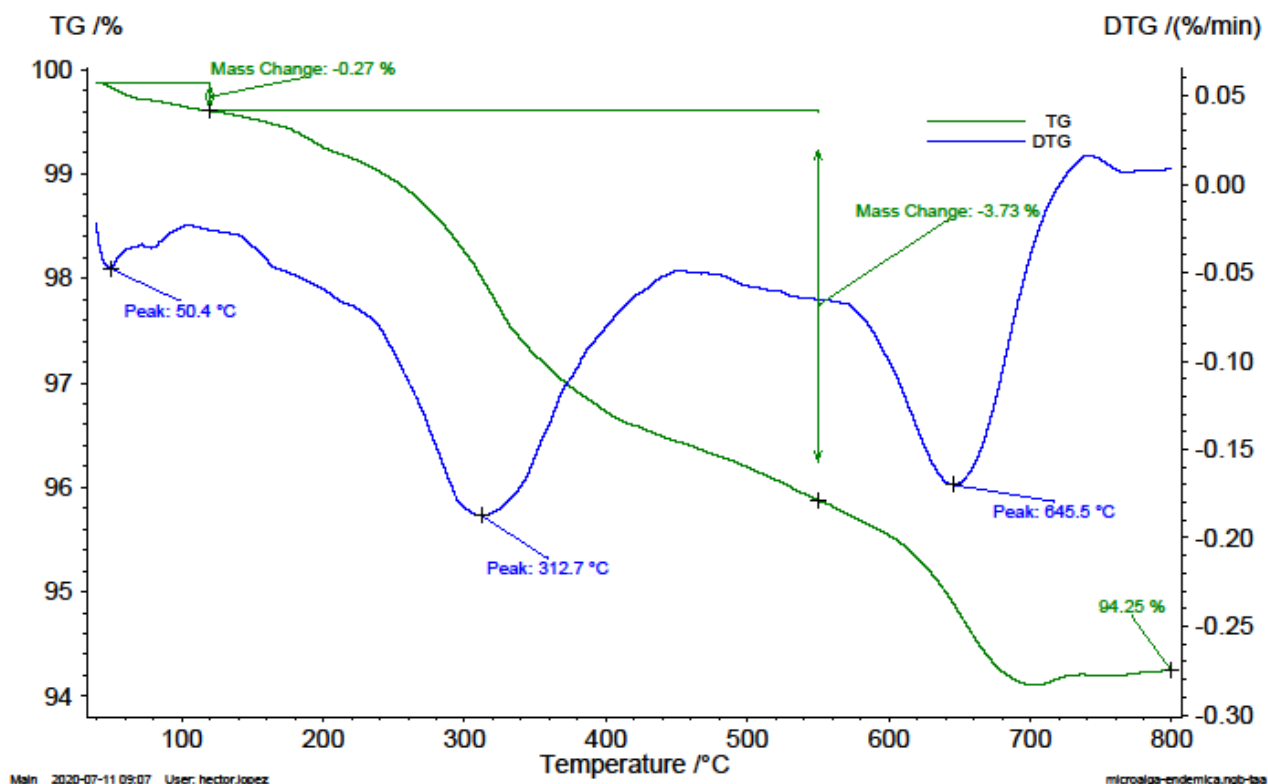


Figure 1. TG an DTG thermograms of endemic microalgae consortium sample (A1).

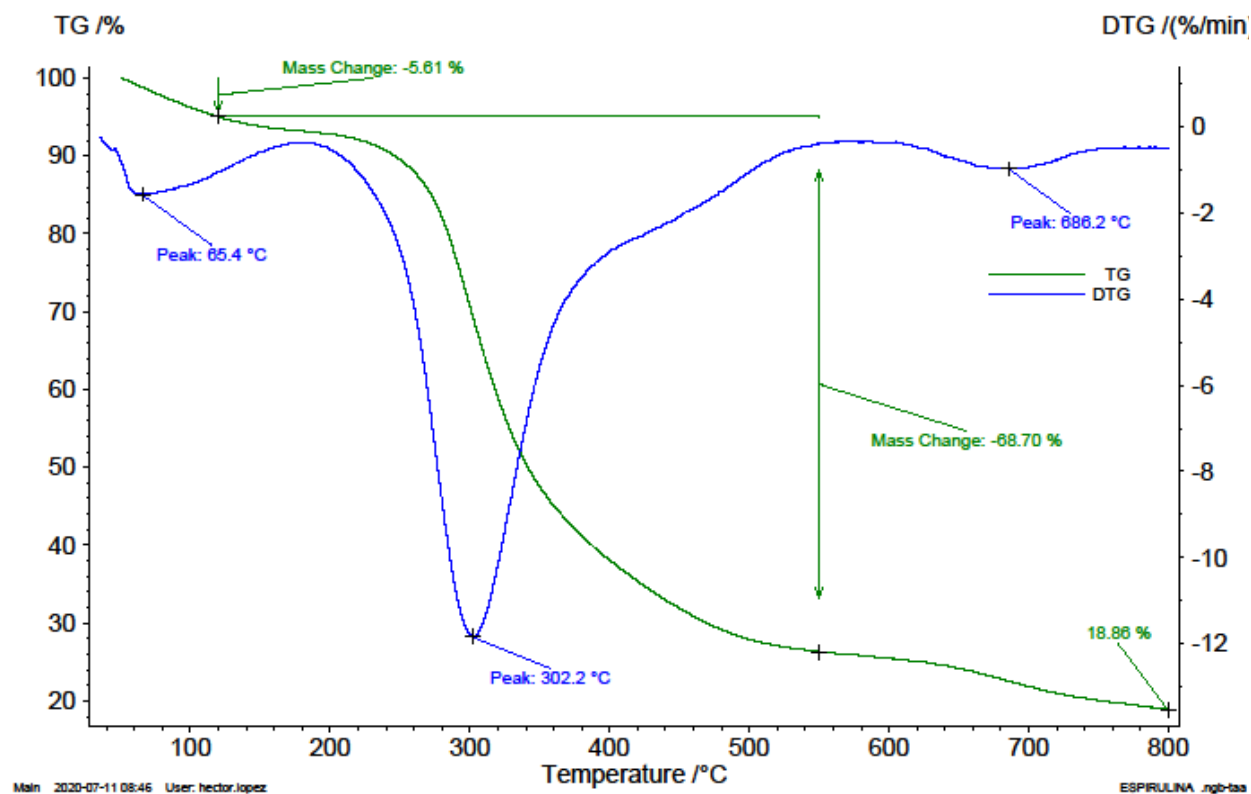


Figure 2. TG an DTG thermograms of photobioreactor microalgae consortium sample (A2).

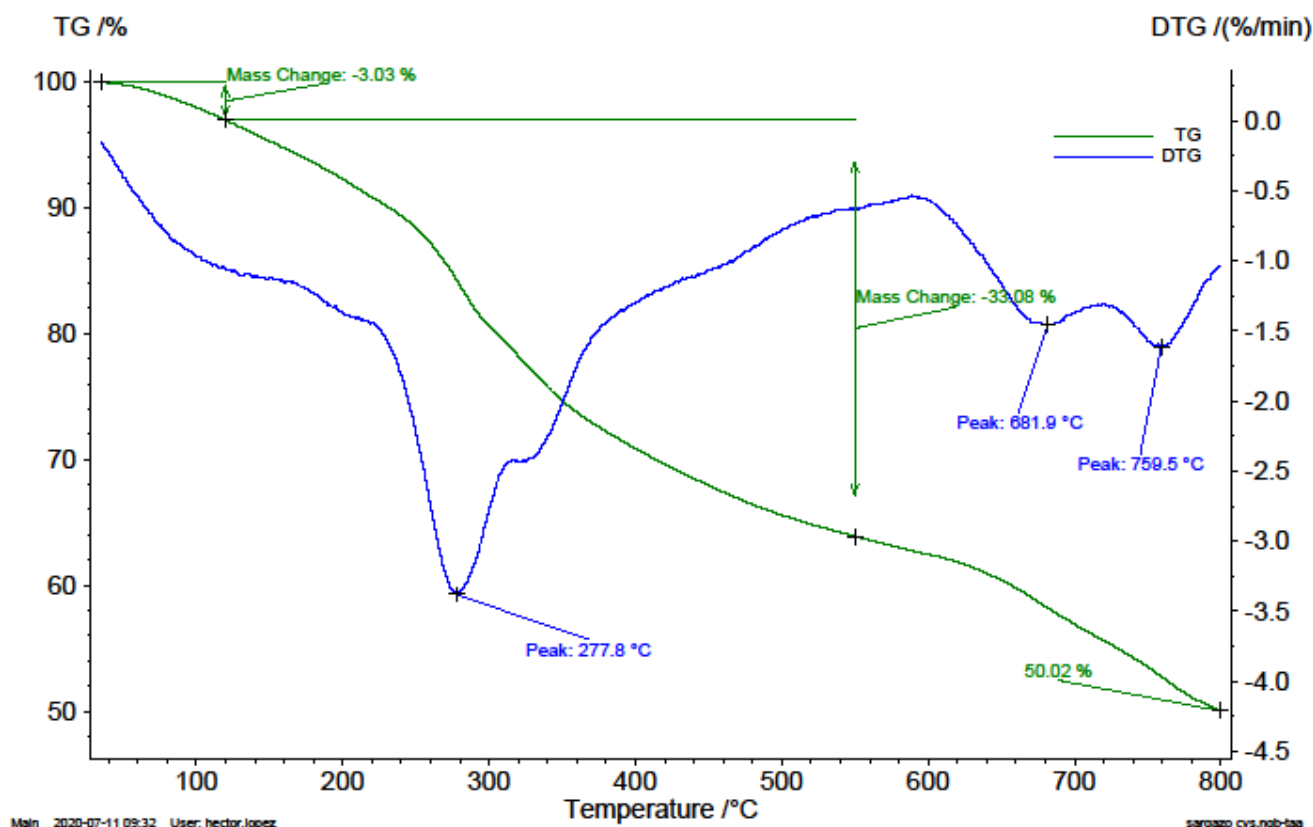


Figure 3. TG and DTG thermograms of Mexican Caribbean macroalgae consortium sample (A3).

In the thermograms, Figure 1, the first drop associated with the humidity present in the sample is identified at a rate of 0.05%/min. The highest peak on the DTG curve shows a maximum rate of 0.19%/min and is related to the decomposition of saccharides (cellulose). The second highest peak was at a rate of 0.17%/min, related to the thermal decomposition of the carbonates and the sulphated salts present. The great amount of ash generated may indicate the presence of recalcitrant compounds in the sample.

Figure 2 shows the TG and DTG thermograms of microalgae consortium sample cultivated in a column photobioreactor. A loss in mass of 5.61%, associated with humidity, is observed even after drying at 150 °C, which is associated with the water chemically bound to the cellulose structure of the algae. The greatest material decomposition and emission of the highest number of volatiles were observed between 300 and 400 °C, ending at 500 °C.

A maximum weight loss rate of 11.84%/min, at 302.2 °C was identified on the DTG curve of the microalgae cultivated in the photobioreactor and associated with the decomposition of the cellulose. The second highest peak on the DTG curve is associated with the humidity loss of the sample, at a maximum rate of 1.56%/min. Above 550 °C, the occurrence of calcite decarbonisation and devolatilisation of CO₂ are observed, respectively. The presence of carbonates and sulphates in the sample of up to 20% is also deduced. A slight drop between 600 and 800 °C associated with the thermal decomposition of the carbonates and probable metallic sulphates present is identified, with a maximum devolatilisation rate of 0.97%/min at 686.2 °C.

In the thermogravimetric analysis obtained for the Sargassum (Figure 3), the maximum decomposition rate of the biomass on the DTG curve was 3.38%/min, and the overlapping of two peaks is observed which could be associated with the decomposition of the hemicellulose, cellulose and salts present in the biomass. Within the interval from 600 to 800 °C of the DTG curve, two main peaks were identified with rates of 1.46%/min and 1.62%/min, the first related to the decomposition of sulphated metal compounds present

and the second with the decarbonation. The ash, determined as 65% of the sample weight from combustion tests that are not presented in this work, will be material rich in CaO and CaCO₃ that could not be decomposed.

In agreement with several authors the greatest mass loss for the biomasses occurs between 150 and 500 °C [21,28].

In this work, It was identified that the main devolatilisation reactions of microalgal pyrolysis occur between 160 and 600 °C. And the maximum devolatilisation rates of the biomasses studied were observed within the temperature range of 207.1 and 312.7 °C. The microalgal biomass cultivated in a photobioreactor displayed the greatest weight loss of 11.84%/min at 302.2 °C (Figure 1). The endemic algae biomass displayed the lowest devolatilisation rate of 0.19%/min at 312.7 °C (Figure 2). The VC generation rates are mainly associated with the cellulosic compounds of the biomasses according to Zong et al. (2020) who states that cellulose in pure form decomposes between 302.9 °C and 387.8 °C with a 96.66% volatile content [20].

3.3. TG-GC/MS Analysis

Lignocellulosic biomass is a complex mixture of carbohydrate polymers such as cellulose, hemicellulose, lignin and trace amounts of other substances. Its thermal decomposition occurs through a series of complex and competitive reactions, that depend on conditions such as reaction temperature, residence time and biomass properties, where units of intermediate polymeric macromolecules are decomposed into more simple units, thereby forming organic products [41,42]. The TG-GC/MS coupling system enables a correlation to be made between the thermal behaviour of the decomposition of materials and the composition of the pyrolytic gas [8].

Table 3 shows the fragments of molecular ions detected during the pyrolysis of the GC/MS analysis of A1 algae.

Table 3. Volatile compounds detected during the pyrolysis of the GC/MS analysis of endemic micro-algae consortium sample (A1).

Label	Bio-Compound	Molecular Formula	Devolatilisation Temperature
1	4-Amino-1-pentanol	C ₅ H ₁₃ NO	189 °C
2	N-methyltaurine	C ₃ H ₉ NO ₃ S	208 °C
3	Carbamic Acid	H ₂ NCOOH	228 °C
4	6-Methylbicyclo [2.2.1] hept-2ene-5-carboxylic acid	C ₉ H ₁₂ O ₂	249 °C
5	Alanine	C ₃ H ₇ NO ₂	268 °C
6	N-vinylimidazole	C ₅ H ₆ N ₂	289 °C
7	Trimethylamine	C ₃ H ₉ N	309 °C
8	3-Acetyl-1H-pyrroline	C ₆ H ₇ NO	329 °C
9	3-Cyclohexene-1-propanol	C ₉ H ₁₆ O	369 °C
10	Cyclobutene, 2-propenylidene	C ₇ H ₈	408 °C
11	Phosphorocyanidous difluoride	CF ₂ NP	429 °C
12	3-Amino-4-pyrazolecarbonitrile	C ₄ H ₄ N ₄	448 °C
13	1H-Imidazole, 4-(2-propenyl)	C ₆ H ₈ N ₂	468 °C
14	2-Octamine	C ₈ H ₁₉ N	488 °C

Table 4 shows the fragments of molecular ions that were detected during the pyrolysis of the GC/MS analysis of A2 algae.

Table 5 shows the fragments of molecular ions detected during the pyrolysis of the GC/MS analysis of A3 algae.

During the pyrolysis of the algal biomass the diversity of volatile compounds was determined, and as well as the compounds shown in Tables 3–5 the main products were CO, CO₂ and H₂O [11,22]. However, these gasses were not shown in the result tables as they were not considered important for this study.

Table 4. Volatile compounds detected during the pyrolysis of the GC/MS analysis of photobioreactor microalgae consortium sample (A2).

Label	Bio-Compound	Molecular Formula	Devolatilisation Temperature
1	Carbamic acid	H ₂ NCOOH	189 °C
2	N-Methyltaurine	C ₃ H ₉ NO ₃ S	228 °C
3	Alanine	C ₃ H ₇ NO ₂	268 °C
4	2-Formylhistamine	C ₆ H ₉ N ₃ O	289 °C
5	1-Butanamine	C ₄ H ₁₁ N	309 °C
6	Benzeneethamine	C ₈ H ₁₁ N	329 °C
7	Ethylamine	C ₂ H ₅ NH ₂	369 °C
8	7-Octen-2-ol-, 2-Methyl-6-Methylene	C ₁₀ H ₁₈ O	389 °C
9	Toluene	C ₆ H ₅ CH ₃	429 °C
10	2-Octamine	C ₈ H ₁₉ N	448 °C
11	SecButylamine	C ₄ H ₁₁ N	468 °C
12	1H-Pyrrole, 2-5-dihydro-1-nitroso	C ₄ H ₆ N ₂ O	488 °C

Table 5. Volatile compounds detected during the pyrolysis of the GC/MS analysis of the Mexican Caribbean macroalgae consortium sample (A3).

Label	Bio-Compound	Molecular Formula	Devolatilisation Temperature
1	Benzenemethanol	C ₆ H ₅ CH ₂ OH	109 °C
2	Benzoic acid	C ₆ H ₅ COOH	109 °C
3	Carbamic acid	H ₂ NCOOH	109 °C
4	Ethane	CH ₃ CH ₃	109 °C
5	Furfural	C ₅ H ₄ O ₂	109 °C
6	Tetrazine	C ₂ H ₂ N ₄	109 °C
7	Propenoic acid	C ₃ H ₄ O ₂	109 °C
8	Hydrazine	N ₂ H ₄	130 °C
9	Methanesulfonic acid	CH ₄ O ₃ S	150 °C
10	Propano-2-ol	(CH ₃) ₂ CHOH	190 °C
11	Fumaric acid	C ₄ H ₄ O ₄	210 °C
12	Pentanoic acid	C ₅ H ₁₀ O ₂	290 °C
13	Diglycolic acid	C ₄ H ₆ O ₅	330 °C

Tables 6–9 shows the compounds of interest detected, Chemical Abstracts Service (CAS) numbers and some of their main characteristics.

Table 6. Volatile compounds (carboxylic acids) detected in the TG-GC/MS coupling analysis of the algal biomass during pyrolysis.

Carbamic acid (463-77-4)

Devolatilises at: 228, 189 and 109 °C in algal samples: endemic microalgae, microalgae cultivated in a photobioreactor and Sargassum respectively.

Carbamic acid is an important carboxylic acid in living systems that is enzymatically produced from urea [43]. It has been detected in phytoplankton blooms [44], as well as by pyrolysis in lignocellulosic waste oils [45].

Unstable chemical species, although stable in salt and ester forms. It is an intermediate product in photodecomposition of the carbofuran pesticide of the carbamate chemical group [46].

Carbamates are a group of pesticides similar to organophosphate pesticides and are N-methylcarbamates derived from carbamic acid [47]. In agreement with de Llasera & Bernal-González (2001) traces of carbamate pesticides were detected in samples of underground and surface water in Mexico, as these kinds of pesticides are commonly used in maize, wheat and fruit fields [48]. Furthermore, carbamate acid can be used for the synthesis of 1-phenyl-3-(4-phenyl-piperazine-1-yl)-propyl ester, a compound that can be used as centrally acting analgesic [49].

Table 6. *Cont.***Diglycolic acid (110-99-6)**

Devolatilises at 330 °C, in Sargassum.

It is a dibasic carboxylic acid that has been used in the manufacture of adhesives, and in the chemical industry as organic synthesisers, a calcium and iron sequestrant and as a neutralising agent [50].

Fumaric acid (110-17-8)

Devolatilises at 210 °C, in Sargassum.

Significant dicarboxylic acid broadly used in the food, chemical, agricultural and pharmaceutical industries [51].

It can be created by the skin after sun exposure and so its esters are used in the treatment of psoriasis. Its esters are also effective in preventing the growth of fungus and show antimicrobial activity [52].

Methanesulfonic acid (75-75-2)

Devolatilises at 150 °C, in Sargassum.

Compound used for organic chemical synthesis [53].

Pentanoic acid (109-52-4)

Devolatilises at 290 °C, in Sargassum.

Carboxylic acid used in the synthesis of esters is a chemical product of industrial importance. It is a compound obtained in the petrochemical industry [54]. The pentanoic acid compounds display metalloproteinases inhibitor properties associated with a variety of cellular and pathological functions, and also related to cytotoxic properties [55].

Propenoic acid (79-10-7)

Devolatilises at 109 °C, in Sargassum.

Carboxylic acid used in the production of acrylates. The growing demand for acrylates is related to their absorbency and use in nappies and sanitary products [56].

Table 7. Volatile compounds (amines) detected in the TG-GC/MS coupling analysis of the algal biomass during pyrolysis.**1-Butanamine (109-73-9)**

Devolatilises at 309 °C, in microalgae cultivated in a photobioreactor.

Displays antifungal activity [57].

2-Formylhistamine (NA)

Devolatilises at 289 °C, in microalgae cultivated in a photobioreactor.

This compound was identified at 342 °C, in pine biomass [58].

It is also found in the extract of the perennial plant *Cissus quadrangularis* L. [59].

2-Octamine (93-16-3)

Devolatilises at 488 °C, in endemic microalgae.

It is a primary amine used for the synthesis of organic compounds.

Octamines are also known as oligoamines, and the synthesis of these kinds of compounds has been studied as they have antiproliferative effects on cell lines associated with prostate cancer [60].

Alanine (56-41-7)

Devolatilises at 268 °C, in endemic microalgae and in microalgae cultivated in a photobioreactor.

Contains an amine group and a carboxylic acid group. Also identified by others, in the algae in pyrolytic processes [11,22,61]. Other authors have determined the presence of free D-alanine in diverse algal species [62–64].

It was found that β -alanine is a non-essential amino acid of great interest for the use in the improvement of sporting performance [65].

Ethylamine (75-04-7)

Devolatilises at 369 °C, in microalgae cultivated in a photobioreactor.

It is a primary amine. It is used in organic synthesis, specifically for the manufacture of drugs, resins and as a rust inhibitor, among others [66,67].

SecButylamine (13952-84-6)

Devolatilises at 468 °C, in microalgae cultivated in a photobioreactor.

It is a primary amine. It is used as an intermediary in processes for the manufacture of chemical products, and is used as a food additive characterised by its fishy aroma [68]. Also displays fungicidal action [69].

Table 7. *Cont.***Trimethylamine (75-50-3)**

Devolatilises at 309 °C, in endemic microalgae.

It was detected in the culture medium of *Ochromonas* as a biogenic amine excrete by the algae [70]. The presence of trimethylamine is very common in marine algae and was detected in 23 of 28 analysed species [71].

It is broadly used in the choline synthesis industry, in herbicides or plant growth inhibitors, strongly basic ionic exchange resins, colourant levelling agents and in basic colourants [72].

Table 8. Volatile compounds (aromatic) detected in the TG-GC/MS coupling analysis of the algal biomass during pyrolysis.**3-Acetyl-1H-pyrroline (1072-82-8)**

Devolatilises at 329 °C, in endemic microalgae.

Its derivatives are commonly used as intermediate products in the synthesis of diverse agrochemicals, pharmaceutical products, dyes and other synthetic organic compounds [73]. It is also obtained from the hydrolysis of Cyanobacteria green algae, of the *Oscillatoria* genus [74].

Benzoic acid (65-85-0)

Devolatilises at 109 °C, in *Sargassum*.

It is an aromatic carboxylic acid present in plants and phytoplankton species [44].

It is used as a flavour enhancer and preservative, analgesic, antiseptic and chemotherapeutic [75].

It is a precursor to the synthesis of organic compounds and used in the food industry to prevent the decaying of food caused by microorganisms [76].

It has been used in the diet for piglets [77,78]. Also, it is an alternative for increasing the nutraceutical and nutritional quality of germinated wheat [79].

Benzenethamine (64-04-0)

Devolatilises at 329 °C, in microalgae cultivated in a photobioreactor.

It has antioxidant, antimicrobial and anti-inflammatory activity, and is the main bioactive compound identified in the biomass of *P. bifurcatum* fern [80].

Benzenemethanol (100-51-6)

Devolatilises at 109 °C, in *Sargassum*.

It is an aromatic alcohol used as a general solvent for ink, wax, varnish, paint, etc.

Benzenemethanol was observed in the volatile oil extracted from the plant species *Ligustrum lucidum* traditionally used for medicinal purposes [81]. It was also found in diverse species of marine algae [61].

Furfural (98-01-1)

Devolatilises at 109 °C, in *Sargassum*.

It is used in the production of resins and lubricants.

It is a base for producing levulinic acid, that can work as a chemical platform with applications in the pharmaceutical and agricultural sectors, and also as a fuel or fuel additive [82,83].

It was found in the volatile compounds of the beef cattle excrement [19] and its main pyrolytic product of the carbohydrates of *A. nodosum*, *C. linum* and *L. digitata* macroalgae [Wahab et al.] and other biomass polysaccharides [20,26,84]. It is a product of the decomposition of xylan hemicellulose [85].

N-methyltaurine (107-68-6)

Devolatilises at 208 °C and 228 °C in Endemic and Cultivated Microalgae respectively.

It is an aminosulphonic acid and a metabolite derived from taurine found in a type of red algae and a key intermediate in the synthesis of surfactants [86].

Lower volatilisation temperatures are obtained than in pine biomass, in the range of 338 and 342 °C [52]. It is potentially effective against muscular atrophy [87].

Table 9. Volatile compounds detected in the TG-GC/MS coupling analysis of the algal biomass during pyrolysis.

1H-Imidazole,4-(2-propenyl) (50995-98-7)
Devolatilises at 468 °C, in endemic microalgae. It is applied as a drug that resists anaerobic bacteria, trichomonas, amoeba [88] and as an anti-tumour agent [89]. The imidazoles have a tubulin inhibition action that detains the cellular cycle in the G2/M phases, inducing apoptosis of cancerous cells [90].
3-Amino-4-pyrazolecarbonitrile (16617-46-2)
Devolatilises at 448 °C, in endemic microalgae. From its Alkylation (or arylation), derivatives of pyrazolo[3,4-d] pyrimidine can be obtained, favourable antagonists of the human A3 human adenosine receiver [91]. In general the derivatives of pyrazole present a range of medical chemistry and pharmacology applications [92].
7-Octen-2-ol,2-Methyl-6- Methylene (543-39-5)
Devolatilises at 389 °C, in microalgae cultivated in a photobioreactor. It is a monoterpene and tertiary alcohol used as an ingredient in fragrances [93,94].
Cyclobutene, 2-propenylidene (52097-85-5)
Devolatilises at 408 °C, in endemic microalgae. Identified as a compound in the urine of the mammal species <i>Tupaia belangeri</i> [95]. It was also detected during the pre-symbiotic stage between the ectomycorrhizal fungus <i>Tuber borchii</i> Vittad. and <i>Tilia americana</i> L during the formation of ectomycorrhizae [96].
Ethane (74-84-0)
Devolatilises at 109 °C, in Sargassum. It is generally obtained from petrol and mainly used to produce polyethylene. It was also found to be a hormone for stress response and development derived from plants displaying effects on plant growth [97]. It shows potential for generating energy.
Hydrazine (302-01-2)
Devolatilises at 130 °C, in Sargassum. Hydrazine is used in the synthesis of pesticides, and also as a base for foaming agents, reducing agent for the recovery of metals and rust inhibitor. It is a volatile nitrogenous compound detected in phytoplankton blooms [44].
N-vinylimidazole (1072-63-5)
Devolatilises at 289 °C, in microalgae cultivated in a photobioreactor. Proposed as a bactericidal barrier by injecting this compound into medical-grade poly-vinyl chloride catheters [98]. This polymer and monomer of N-vinylimidazole prevent the rusting of stainless steel [99].

In agreement with several authors carboxylic acids (Table 6) and amines (Table 7) produced during the pyrolysis of marine algae were identified [11,22,61]. Furthermore, in accordance with many authors aromatic compounds (Table 8) produced by the pyrolysis of microalgae were determined [3,84]. It was proposed that the algae's proteins could be combined with the carbohydrates and react to form aromatic compounds such as phenols, pyrroles and indoles [26]. In the specific case of Sargassum, the production of volatile aromatic compounds could be related to the presence of complex aromatic polyphenols identified in the macroalgae [100]. In the same manner, the presence of some alcohols were also determined in the pyrolysis of the algal biomass. It was found that the linoleic fatty acids are the precursors of aldehydes that can be subsequently reduced to alcohols by dehydrogenases. Furthermore, according to Yang et al. (2019) reactions such as decarboxylation and deoxygenation of carbohydrates in the algae can give alcohols as a result [26].

The pyrolysis of algae has not been commercialised and only tested at bench scale [26]. However, the presence of compounds of commercial interest in the pyrolytic gasses makes the pyrolysis process a promising technology for the disposal of biomasses and the production of high value products.

Further studies are required to evaluate the volatile compounds produced by the pyrolysis of algae with other chromatography techniques such as PyGC/MS, in order to validate the findings of this investigation.

The fragments of molecular ions detected using the TG-GC/MS technique are related to the pyrolytic VCs that can be obtained from the algal pyrolysis. However, it is necessary to validate that the compounds detected are not the product of the interaction of VCs with the plasma in the chromatography technique.

The VCs that can be obtained from the algae are a mixture of compounds, and to select the most advantageous volatile compound recovery technique it is necessary to also investigate the location of the target compound within the biochemical system and the volatility of the target molecule, as well as its distribution across the phases under real production conditions [3]. It is advisable to carry out a quantitative analysis of the volatile compounds of interest in large-scale pyrolytic systems, especially those determined with devolatilisation within the range of 207.1 and 312.7 °C.

It was identified that the algae adapt to abiotic stress (humidity, mineral composition and temperature, quantity and intensity of light) during their life cycle. Therefore, different compositions and properties of the liberated VCs involve different algae species, and growth and reaction conditions [26,61]. Therefore, it is advised to carry out a seasonal analysis of the algae species available each season and the VCs that can be obtained with biomass pyrolysis for its use as part of a circular economy model.

After the VCs are extracted the residual biochar could be used as fuel. Likewise, the biochar could potentially be used as an adsorbent medium for the filtration of fluids or in application to soils in combination with either organic or inorganic fertilizers due to its pore structure and surface area, as well as the presence of N, P and K [101]. Its characterisation is needed to identify the best use for this biochar.

4. Conclusions

This research analysed samples of algal biomasses: consortium of endemic microalgae from a body of water, consortium of microalgae cultivated in a photobioreactor and *Sargassum* macroalgae consortium. It was determined that the most part of the material is decomposed to VCs under the TG conditions. Furthermore, the VCs show potential for application in the generation of valuable chemical substances. The study was limited to the semi-analytical and qualitative analysis of the species. Further quantitative analysis of the substances produced is required in order to evaluate their feasibility as valuable products. As well as the volatile compounds of industrial value detected during the pyrolytic decomposition, aromatic compounds were also identified, such as toluene and benzaldehyde which when burned emit substances that are harmful to the ecosystem. Due to this fact, the studied algal biomasses are not recommended for direct use as fuel due to the potential risk of generating toxic gases. It is advisable to evaluate the release of the VCs found in the pyrolysis for the production of biochar, given that some are potential sources for environmental contamination.

The comprehensive use of biomasses available as part of the circular economy is imperative. The use and implementation of photobioreactors as greenhouse gas capturing systems in urban areas and the use of algal biomass generated in urban bodies of water and the ocean via pyrolysis are promising technologies for converting the issue of biomass disposal into a sustainable source for raw materials.

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References

1. Sherwood, J. The significance of biomass in a circular economy. *Bioresour. Technol.* **2020**, *300*, 122755. [[CrossRef](#)] [[PubMed](#)]
2. Stoumpou, V.; Novakovic, J.; Kontogianni, N.; Barampouti, E.M.; Mai, S.; Moustakas, K.; Malamis, D.; Loizidou, M. Assessing straw digestate as feedstock for bioethanol production. *Renew. Energy* **2020**, *153*, 261–269. [[CrossRef](#)]
3. Vieira, K.R.; Pinheiro, P.N.; Zepka, L.Q. Volatile organic compounds from microalgae. In *Handbook of Microalgae-Based Processes and Products*; Academic Press: Cambridge, MA, USA, 2020; pp. 659–686.
4. Leong, Y.K.; Chew, K.W.; Chen, W.-H.; Chang, J.-S.; Show, P.L. Reuniting the Biogeochemistry of Algae for a Low-Carbon Circular Bioeconomy. *Trends Plant Sci.* **2021**, *26*, 729–740. [[CrossRef](#)] [[PubMed](#)]
5. Rasool, T.; Kumar, S. Kinetic and Thermodynamic Evaluation of Pyrolysis of Plant Biomass using TGA. *Mater. Today: Proc.* **2020**, *21*, 2087–2095. [[CrossRef](#)]
6. Chew, J.J.; Doshi, V. Recent advances in biomass pretreatment—Torrefaction fundamentals and technology. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4212–4222. [[CrossRef](#)]
7. Castellucci, S.; Cocchi, S.; Celma, C.B. Energy characterization of residual biomass in Mediterranean Area for small biomass gasifiers in according to the European Standards. *Appl. Math. Sci.* **2014**, *8*, 6621–6633. [[CrossRef](#)]
8. Mlonka-Mędrała, A.; Magdziarz, A.; Dziok, T.; Sieradzka, M.; Nowak, W. Laboratory studies on the influence of biomass particle size on pyrolysis and combustion using TG GC/MS. *Fuel* **2019**, *252*, 635–645. [[CrossRef](#)]
9. Ningbo, G.; Baoling, L.; Aimin, L.; Juanjuan, L. Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times. *J. Anal. Appl. Pyrolysis* **2015**, *114*, 155–162. [[CrossRef](#)]
10. He, Q.; Ding, L.; Gong, Y.; Li, W.; Wei, J.; Yu, G. Effect of torrefaction on pinewood pyrolysis kinetics and thermal behavior using thermogravimetric analysis. *Bioresour. Technol.* **2019**, *280*, 104–111. [[CrossRef](#)]
11. López-González, D.; Fernandez-Lopez, M.; Valverde, J.; Sanchez-Silva, L. Pyrolysis of three different types of microalgae: Kinetic and evolved gas analysis. *Energy* **2014**, *73*, 33–43. [[CrossRef](#)]
12. Hlavsová, A.; Corsaro, A.; Raclavská, H.; Juchelková, D.; Škrobánková, H.; Frydrych, J. Syngas Production from Pyrolysis of Nine Composts Obtained from Nonhybrid and Hybrid Perennial Grasses. *Sci. World J.* **2014**, *2014*, 723092. [[CrossRef](#)]
13. Lee, X.J.; Ong, H.C.; Gan, Y.Y.; Chen, W.H.; Mahlia, T.M.I. State of art review on conventional and advanced pyrolysis of macroalgae and microalgae for biochar, bio-oil and bio-syngas production. *Energy Convers. Manag.* **2020**, *210*, 112707. [[CrossRef](#)]
14. Martí, B.V.; Gaibor-Chávez, J.; Niño-Ruiz, Z.; Cortés-Rojas, E. Development of biomass fast proximate analysis by thermogravimetric scale. *Renew. Energy* **2018**, *126*, 954–959. [[CrossRef](#)]
15. Czajka, K.; Modliński, N.; Kisiela-Czajka, A.M.; Naidoo, R.; Peta, S.; Nyangwa, B. Volatile matter release from coal at different heating rates—Experimental study and kinetic modelling. *J. Anal. Appl. Pyrolysis* **2019**, *139*, 282–290. [[CrossRef](#)]
16. Bach, Q.-V.; Chen, W.-H. Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review. *Bioresour. Technol.* **2017**, *246*, 88–100. [[CrossRef](#)] [[PubMed](#)]
17. Sukarni, S. Thermogravimetric analysis of the combustion of marine microalgae *Spirulina platensis* and its blend with synthetic waste. *Heliyon* **2020**, *6*, e04902. [[CrossRef](#)] [[PubMed](#)]
18. Jabeen, S.; Gao, X.; Altarawneh, M.; Hayashi, J.-I.; Zhang, M.; Dlugogorski, B.Z. Analytical Procedure for Proximate Analysis of Algal Biomass: Case Study for *Spirulina platensis* and *Chlorella vulgaris*. *Energy Fuels* **2019**, *34*, 474–482. [[CrossRef](#)]
19. Calderón, F.J.; McCarty, G.W.; Reeves, J.B. Pyrolysis-MS and FT-IR analysis of fresh and decomposed dairy manure. *J. Anal. Appl. Pyrolysis* **2006**, *76*, 14–23. [[CrossRef](#)]
20. Zong, P.; Jiang, Y.; Tian, Y.; Li, J.; Yuan, M.; Ji, Y.; Chen, M.; Li, D.; Qiao, Y. Pyrolysis behavior and product distributions of biomass six group components: Starch, cellulose, hemicellulose, lignin, protein and oil. *Energy Convers. Manag.* **2020**, *216*, 112777. [[CrossRef](#)]
21. Ischia, M.; Perazzolli, C.; Maschio, R.D.; Campostrini, R. Pyrolysis study of sewage sludge by TG-MS and TG-GC-MS coupled analyses. *J. Therm. Anal.* **2006**, *87*, 567–574. [[CrossRef](#)]
22. Sanchez-Silva, L.; López-González, D.; García-Minguillán, A.; Valverde, J.L. Pyrolysis, combustion and gasification characteristics of *Nannochloropsis gaditana* microalgae. *Bioresour. Technol.* **2013**, *130*, 321–331. [[CrossRef](#)]
23. Gao, N.; Li, A.; Quan, C.; Du, L.; Duan, Y. TG-FTIR and Py-GC/MS analysis on pyrolysis and combustion of pine sawdust. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 26–32. [[CrossRef](#)]
24. Lin, Y.; Liao, Y.; Yu, Z.; Fang, S.; Ma, X. A study on co-pyrolysis of bagasse and sewage sludge using TG-FTIR and Py-GC/MS. *Energy Convers. Manag.* **2017**, *151*, 190–198. [[CrossRef](#)]
25. Xin, X.; Pang, S.; Mercader, F.D.M.; Torr, K.M. The effect of biomass pretreatment on catalytic pyrolysis products of pine wood by Py-GC/MS and principal component analysis. *J. Anal. Appl. Pyrolysis* **2018**, *138*, 145–153. [[CrossRef](#)]
26. Yang, C.; Li, R.; Zhang, B.; Qiu, Q.; Wang, B.; Yang, H.; Ding, Y.; Wang, C. Pyrolysis of microalgae: A critical review. *Fuel Process. Technol.* **2019**, *186*, 53–72. [[CrossRef](#)]
27. Kmita, A.; Fischer, C.; Hodor, K.; Holtzer, M.; Rocznik, A. Thermal decomposition of foundry resins: A determination of organic products by thermogravimetry–gas chromatography–mass spectrometry (TG–GC–MS). *Arab. J. Chem.* **2016**, *11*, 380–387. [[CrossRef](#)]
28. Mishra, R.K.; Mohanty, K. Kinetic analysis and pyrolysis behaviour of waste biomass towards its bioenergy potential. *Bioresour. Technol.* **2020**, *311*, 123480. [[CrossRef](#)]

29. Marquez, G.P.B.; Santiañez, W.J.E.; Trono, G.C.; Montañó, M.N.E.; Araki, H.; Takeuchi, H.; Hasegawa, T. Seaweed biomass of the Philippines: Sustainable feedstock for biogas production. *Renew. Sustain. Energy Rev.* **2014**, *38*, 1056–1068. [\[CrossRef\]](#)
30. Filer, J.; Ding, H.H.; Chang, S. Biochemical Methane Potential (BMP) Assay Method for Anaerobic Digestion Research. *Water* **2019**, *11*, 921. [\[CrossRef\]](#)
31. Al Seadi, T.; Dros, B.; Fuchs, W.; Rutz, D.; Janssen, R. Biogas digestate quality and utilization. In *The Biogas Hand-Book*; Woodhead Publishing: Sawston, UK, 2013; pp. 267–301.
32. Lee, J.; Hong, J.; Jeong, S.; Chandran, K.; Park, K.Y. Interactions between substrate characteristics and microbial communities on biogas production yield and rate. *Bioresour. Technol.* **2020**, *303*, 122934. [\[CrossRef\]](#)
33. López-Aguilar, H.A.; Kennedy-Puentes, G.; Gómez, J.A.; Huerta-Reynoso, E.A.; Peralta-Pérez, M.D.R.; de la Serna, F.J.Z.-D.; Pérez-Hernández, A. Practical and Theoretical Modeling of Anaerobic Digestion of *Sargassum* spp. in the Mexican Caribbean. *Pol. J. Environ. Stud.* **2021**, *30*, 3151–3161. [\[CrossRef\]](#)
34. Santín, C.; Doerr, S.H.; Merino, A.; Bucheli, T.D.; Bryant, R.; Ascough, P.; Gao, X.; Masiello, C. Carbon sequestration potential and physicochemical properties differ between wildfire charcoals and slow-pyrolysis biochars. *Sci. Rep.* **2017**, *7*, 11233. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Saidur, R.; Abdelaziz, E.; Demirbas, A.; Hossain, M.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289. [\[CrossRef\]](#)
36. Motte, J.-C.; Escudié, R.; Bernet, N.; Delgenes, J.-P.; Steyer, J.-P.; Dumas, C. Dynamic effect of total solid content, low substrate/inoculum ratio and particle size on solid-state anaerobic digestion. *Bioresour. Technol.* **2013**, *144*, 141–148. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Moset, V.; Al-Zohairi, N.; Møller, H. The impact of inoculum source, inoculum to substrate ratio and sample preservation on methane potential from different substrates. *Biomass Bioenergy* **2015**, *83*, 474–482. [\[CrossRef\]](#)
38. Carlini, M.; Castellucci, S.; Moneti, M. Biogas Production from Poultry Manure and Cheese Whey Wastewater under Mesophilic Conditions in Batch Reactor. *Energy Procedia* **2015**, *82*, 811–818. [\[CrossRef\]](#)
39. Wahab, M.A.; Kebelmann, K.; Schartel, B.; Griffiths, G. Valorization of macroalgae digestate into aromatic rich bio-oil and lipid rich microalgal biomass for enhanced algal biorefinery performance. *J. Clean. Prod.* **2022**, *341*, 130925. [\[CrossRef\]](#)
40. Tuentner, E.; Delbaere, C.; De Winne, A.; Bijttebier, S.; Custers, D.; Foubert, K.; Van Durme, J.; Messens, K.; Dewettinck, K.; Pieters, L. Non-volatile and volatile composition of West African bulk and Ecuadorian fine-flavor cocoa liquor and chocolate. *Food Res. Int.* **2020**, *130*, 108943. [\[CrossRef\]](#)
41. Klinger, J.L. *Modeling of Biomass Torrefaction and Pyrolysis and Its Applications*; Michigan Technological University: Houghton, MI, USA; ProQuest LLC: Ann Arbor, MI, USA, 2015.
42. Van der Stelt, M.J.C.; Gerhauser, H.; Kiel, J.H.A.; Ptasinski, K.J. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass Bioenergy* **2011**, *35*, 3748–3762. [\[CrossRef\]](#)
43. Khanna, R.; Moore, M. Carbamic acid: Molecular structure and IR spectra. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1999**, *55*, 961–967. [\[CrossRef\]](#)
44. Ali, G. Identification of volatile organic compounds produced by algae. *Egypt. J. Phycol.* **2004**, *5*, 71–81. [\[CrossRef\]](#)
45. Adesemuyi, M.F. Pyrolysed Products from Lignocellulosic Wastes: Production, Characterisation and Their Effect on Soil Properties, Okra, Insect and Microbial Growth. Ph.D. Thesis, Federal University of Technology, Akure, Nigeria, 2020.
46. Bachman, J.; Patterson, H.H. Photodecomposition of the Carbamate Pesticide Carbofuran: Kinetics and the Influence of Dissolved Organic Matter. *Environ. Sci. Technol.* **1999**, *33*, 874–881. [\[CrossRef\]](#)
47. Silberman, J.; Taylor, A. *Carbamate Toxicity*; StatPearls Publishing: Treasure Island, FL, USA, 2018.
48. De Llasera, M.G.; Bernal-González, M. Presence of carbamate pesticides in environmental waters from the northwest of Mexico: Determination by liquid chromatography. *Water Res.* **2001**, *35*, 1933–1940. [\[CrossRef\]](#)
49. Chae, E.; Yi, H.; Choi, Y.; Cho, H.; Lee, K.; Moon, H. Synthesis and pharmacological evaluation of carbamic acid 1-phenyl-3-(4-phenyl-piperazine-1-yl)-propyl ester derivatives as new analgesic agents. *Bioorganic Med. Chem. Lett.* **2012**, *22*, 2434–2439. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Roscher, A.A.; Jussek, E.; Noguchi, T.; Franklin, S. Fatal accidental diglycolic acid intoxication. *Bull. Soc. Pharmacol. Environ. Pathol.* **1975**, *3*, 3–13. [\[CrossRef\]](#)
51. Guo, F.; Wu, M.; Dai, Z.; Zhang, S.; Zhang, W.; Dong, W.; Zhou, J.; Jiang, M.; Xin, F. Current advances on biological production of fumaric acid. *Biochem. Eng. J.* **2019**, *153*, 107397. [\[CrossRef\]](#)
52. Silvestre, J.; Mercader, P.; Giménez-Arnau, A. Dermatitis de contacto por dimetilfumarato. *Actas Dermo-Sifiliográficas* **2010**, *101*, 217–222. [\[CrossRef\]](#)
53. Corma, A.; Leyva, A.; Rubio Marqués, P. Proceso de Obtención de Aminas Secundarias a Partir de Nitrobenzeno en un Solo Reactor. Patent Number ES2472344 A1, 20 June 2014.
54. Al-Naji, M.; Van Aelst, J.; Liao, Y.; D'Hullian, M.; Tian, Z.; Wang, C.; Gläser, R.; Sels, B.F. Pentanoic acid from γ -valerolactone and formic acid using bifunctional catalysis. *Green Chem.* **2019**, *22*, 1171–1181. [\[CrossRef\]](#)
55. Mukherjee, A.; Adhikari, N.; Jha, T. A pentanoic acid derivative targeting matrix metalloproteinase-2 (MMP-2) induces apoptosis in a chronic myeloid leukemia cell line. *Eur. J. Med. Chem.* **2017**, *141*, 37–50. [\[CrossRef\]](#)
56. Bauer, W., Jr. Acrylic acid and derivatives. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2000.

57. Zou, C.-S.; Mo, M.-H.; Gu, Y.-Q.; Zhou, J.-P.; Zhang, K.-Q. Possible contributions of volatile-producing bacteria to soil fungistasis. *Soil Biol. Biochem.* **2007**, *39*, 2371–2379. [\[CrossRef\]](#)
58. Chen, Y.; Wang, L.; Zhao, M.; Ma, H.; Chen, D.; Zhang, Y.; Zhou, J. Comparative Study on the Pyrolysis Behaviors of Pine Cone and Pretreated Pine Cone by Using TGA–FTIR and Pyrolysis-GC/MS. *ACS Omega* **2021**, *6*, 3490–3498. [\[CrossRef\]](#)
59. Kumar, T.S.; Anandan, A.; Jegadeesan, M.; Appl, A.; Res, S. Identification of chemical compounds in *Cissus quadrangularis* L. Variant-I of different sample using GC-MS analysis. *Arch. Appl. Sci. Res.* **2012**, *4*, 1782–1787.
60. Valasinas, A.; Reddy, V.K.; Blokhin, A.; Basu, H.S.; Bhattacharya, S.; Sarkar, A.; Marton, L.J.; Frydman, B. Long-chain polyamines (oligoamines) exhibit strong cytotoxicities against human prostate cancer cells. *Bioorg. Med. Chem.* **2003**, *11*, 4121–4131. [\[CrossRef\]](#)
61. Vilar, E.G.; O'Sullivan, M.G.; Kerry, J.P.; Kilcawley, K.N. Volatile compounds of six species of edible seaweed: A review. *Algal Res.* **2019**, *45*, 101740. [\[CrossRef\]](#)
62. Nagahisa, E.; Kanno, N.; Sato, M.; Sato, Y. Occurrence of Free D-Alanine in Marine Macroalgae. *Biosci. Biotechnol. Biochem.* **1995**, *59*, 2176–2177. [\[CrossRef\]](#)
63. Yokoyama, T.; Tanaka, Y.; Sato, M.; Kan-No, N.; Nakano, T.; Yamaguchi, T.; Nagahisa, E. Alanine racemase activity in the microalga *Thalassiosira* sp. *Fish. Sci.* **2005**, *71*, 924–930. [\[CrossRef\]](#)
64. Nishimura, K.; Tomoda, Y.; Nakamoto, Y.; Kawada, T.; Ishii, Y.; Nagata, Y. Alanine racemase from the green alga *Chlamydomonas reinhardtii*. *Amino Acids* **2006**, *32*, 59–62. [\[CrossRef\]](#)
65. Hobson, R.M.; Saunders, B.; Ball, G.; Harris, R.C.; Sale, C. Effects of β -alanine supplementation on exercise performance: A meta-analysis. *Amino Acids* **2012**, *43*, 25–37. [\[CrossRef\]](#)
66. Vashi, R.T.; Desai, S.A.; Desai, P.S. Ethylamines as corrosion inhibitors for zinc in nitric acid. *Asian J. Chem.* **2008**, *20*, 4553.
67. Shi, F.; Cui, X. *Catalytic Amination for N-Alkyl Amine Synthesis*; Academic Press: Cambridge, MA, USA, 2018.
68. McKee, J.M. Butylamines. In *Encyclopedia of Toxicology*, 3rd ed.; Academic Press: Cambridge, MA, USA, 2014; p. 589. [\[CrossRef\]](#)
69. Yoshikawa, M.; Eckert, J. The mechanism of fungistatic action of sec-butylamine: I. Effects of sec-butylamine on the metabolism of hyphae of *Penicillium digitatum*. *Pestic. Biochem. Physiol.* **1976**, *6*, 471–481. [\[CrossRef\]](#)
70. Herrmann, V.; Jüttner, F. Excretion products of algae: Identification of biogenic amines by gas-liquid chromatography and mass spectrometry of their trifluoroacetamides. *Anal. Biochem.* **1977**, *78*, 365–373. [\[CrossRef\]](#)
71. Steiner, M.; Hartmann, T. The occurrence and distribution of volatile amines in marine algae. *Planta* **1968**, *79*, 113–121. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Aitani, A.M. Oil refining and products. In *Encyclopedia of Energy*; Elsevier: Amsterdam, The Netherlands, 2004; Volume 4, pp. 715–729. [\[CrossRef\]](#)
73. Nathaniel, C.R.; Neetha, M.; Anilkumar, G. Silver-catalyzed pyrrole synthesis: An overview. *Appl. Organomet. Chem.* **2021**, *35*, e6141. [\[CrossRef\]](#)
74. Kawale, H.; Kishore, N. Production of hydrocarbons from a green algae (*Oscillatoria*) with exploration of its fuel characteristics over different reaction atmospheres. *Energy* **2019**, *178*, 344–355. [\[CrossRef\]](#)
75. Sepúlveda, L.V.; González-Morales, S.; Mendoza, A.B. Ácido benzoico: Biosíntesis, modificación y función en plantas. *Rev. Mex. Cienc. Agrícolas* **2015**, *6*, 1667–1678. [\[CrossRef\]](#)
76. Yerlikaya, O.; Gucer, L.; Akan, E.; Meric, S.; Aydin, E.; Kinik, O. Benzoic acid formation and its relationship with microbial properties in traditional Turkish cheese varieties. *Food Biosci.* **2021**, *41*, 101040. [\[CrossRef\]](#)
77. Gheler, T.R.; Araújo, L.F.; Silva, C.C.D.; Gomes, G.A.; Prata, M.F.; Gomide, C.A. Uso de ácido benzoico na dieta de leitões. *Rev. Bras. Zootec.* **2009**, *38*, 2182–2187. [\[CrossRef\]](#)
78. Pérez Alvarado, M.A.; Cervantes López, J.; Braña Varela, D.; Mariscal Landín, G.; Cuarón Ibargüengoytia, J.A. Ácido benzoico y un producto basado en especies de *Bacillus* para proteger la productividad de los lechones y al ambiente. *Rev. Mex. Cienc. Pecu.* **2013**, *4*, 447–468.
79. Salas-Pérez, L.; Gaucín-Delgado, J.M.; Preciado-Rangel, P.; Fortis-Hernández, M.; Valenzuela-García, J.R.; Ayala-Garay, A.V. Efecto del ácido benzoico en la capacidad antioxidante de germinados de trigo. *Rev. Mex. Cienc. Agrícolas* **2016**, *17*, 3397–3404.
80. Chinaka, I.C.B.; Okwudili, O.S.; Nkiru, D.-A.I. Chemical Composition, Antioxidant and Antibacterial Properties of Chloroform Fraction of *Platyserium Bifurcatum*. *Adv. Res. Life Sci.* **2018**, *2*, 1–6. [\[CrossRef\]](#)
81. Jinshun, L. Study on the chemical composition of the volatile oil in *Ligustrum lucidum*. *Zhongguo Yao Xue Za Zhi* **2005**, *40*, 178–180.
82. Dashtban, M.; Gilbert, A.; Fatehi, P. Production of furfural: Overview and challenges. *J. Sci. Technol. Forest Prod. Process* **2012**, *2*, 44–53.
83. Dutta, S.; De, S.; Saha, B.; Alam, I. Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. *Catal. Sci. Technol.* **2012**, *2*, 2025–2036. [\[CrossRef\]](#)
84. Biller, P.; Ross, A. Pyrolysis GC–MS as a novel analysis technique to determine the biochemical composition of microalgae. *Algal Res.* **2014**, *6*, 91–97. [\[CrossRef\]](#)
85. Dhyani, V.; Bhaskar, T. Pyrolysis of Biomass. Cellulose. In *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*; Academic Press: Cambridge, MA, USA, 2019; pp. 217–244. [\[CrossRef\]](#)
86. Lindberg, B.; Bjerrum, J.; Lundén, R.; Prydz, H. Methylated Taurines and Choline Sulphate in Red Algae. *Acta Chem. Scand.* **1955**, *9*, 1323–1326. [\[CrossRef\]](#)
87. Nguyen, K.H.; Ito, S.; Maeyama, S.; Schaffer, S.W.; Murakami, S.; Ito, T. In Vivo and In Vitro Study of N-Methyltaurine on Pharmacokinetics and Antimicrobial Atrophic Effects in Mice. *ACS Omega* **2020**, *5*, 11241–11246. [\[CrossRef\]](#)

88. Liu, Q.-M.; Luo, Y.-S.; Wang, H.; Peng, W.-X.; Wu, Y.-Q.; Zhang, D.-Q.; Ma, Q.-Z. Determination of chemical components of benzene/ethanol extractive of beech wood by GC/MS. In Proceedings of the 2008 2nd International Conference on Bioinformatics and Biomedical Engineering, Shanghai, China, 16–18 May 2008; pp. 2776–2779. [\[CrossRef\]](#)
89. Chan, C.L.; Lien, E.J.; Tokes, Z.A. Synthesis, biological evaluation, and quantitative structure-activity relationship analysis of 2-hydroxy-1H-isoindole-1-one derivatives as new cytostatic agents. *J. Med. Chem.* **1987**, *30*, 509–514. [\[CrossRef\]](#)
90. Liu, R.; Huang, M.; Zhang, S.; Li, L.; Li, M.; Sun, J.; Wu, L.; Guan, Q.; Zhang, W. Design, synthesis and bioevaluation of 6-aryl-1-(3,4,5-trimethoxyphenyl)-1H-benzo[d]imidazoles as tubulin polymerization inhibitors. *Eur. J. Med. Chem.* **2021**, *226*, 113826. [\[CrossRef\]](#)
91. Venkatesan, G.; Paira, P.; Cheong, S.L.; Vamsikrishna, K.; Federico, S.; Klotz, K.-N.; Spalluto, G.; Pastorin, G. Discovery of simplified N2-substituted pyrazolo[3,4-d]pyrimidine derivatives as novel adenosine receptor antagonists: Efficient synthetic approaches, biological evaluations and molecular docking studies. *Bioorg. Med. Chem.* **2014**, *22*, 1751–1765. [\[CrossRef\]](#)
92. Khandelwal, S.; Tailor, Y.K.; Rushell, E.; Kumar, M. Use of sustainable organic transformations in the construction of heterocyclic scaffolds. In *Green Approaches in Medicinal Chemistry for Sustainable Drug Design*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 245–352. [\[CrossRef\]](#)
93. Vankar, P.S. Essential oils and fragrances from natural sources. *Resonance* **2004**, *9*, 30–41. [\[CrossRef\]](#)
94. McGinty, D.; Lapczynski, A.; Bhatia, S.; Letizia, C.; Api, A. Fragrance material review on 7-octen-2-ol, 2-methyl-6-methylene-, dihydro derivative. *Food Chem. Toxicol.* **2010**, *48*, S46–S51. [\[CrossRef\]](#) [\[PubMed\]](#)
95. Wanlong, Z.; Fangyan, Y.; Zhengkun, W. Study of chemical communication based on urine in tree shrews *Tupaia belangeri* (Mammalia: Scandentia: Tupaiidae). *Eur. Zool. J.* **2017**, *84*, 512–524. [\[CrossRef\]](#)
96. Menotta, M.; Gioacchini, A.M.; Amicucci, A.; Buffalini, M.; Sisti, D.; Stocchi, V. Headspace solid-phase microextraction with gas chromatography and mass spectrometry in the investigation of volatile organic compounds in an ectomycorrhizae synthesis system. *Rapid Commun. Mass Spectrom.* **2003**, *18*, 206–210. [\[CrossRef\]](#)
97. Chang, C.; Bleecker, A.B.; Caldwell, K.S.; Langridge, P.; Powell, W. Ethylene Biology. More Than a Gas. *Plant Physiol.* **2004**, *136*, 2895–2899. [\[CrossRef\]](#)
98. Meléndez-Ortiz, H.I.; Alvarez-Lorenzo, C.; Concheiro, A.; Jiménez-Páez, V.M.; Bucio, E. Modification of medical grade PVC with N-vinylimidazole to obtain bactericidal surface. *Radiat. Phys. Chem.* **2016**, *119*, 37–43. [\[CrossRef\]](#)
99. Öncül, A.; Çoban, K.; Sezer, E.; Şenkal, B.F. Inhibition of the corrosion of stainless steel by poly-N-vinylimidazole and N-vinylimidazole. *Prog. Org. Coat.* **2011**, *71*, 167–172. [\[CrossRef\]](#)
100. Alzate-Gaviria, L.; Domínguez-Maldonado, J.; Chablé-Villacís, R.; Olguin-Maciel, E.; Leal-Bautista, R.M.; Canché-Escamilla, G.; Caballero-Vázquez, A.; Hernández-Zepeda, C.; Barredo-Pool, F.A.; Tapia-Tussell, R. Presence of Polyphenols Complex Aromatic “Lignin” in *Sargassum* spp. from Mexican Caribbean. *J. Mar. Sci. Eng.* **2020**, *9*, 6. [\[CrossRef\]](#)
101. Morali, U.; Şensöz, S. Pyrolysis of hornbeam shell (*Carpinus betulus* L.) in a fixed bed reactor: Characterization of bio-oil and bio-char. *Fuel* **2015**, *150*, 672–678. [\[CrossRef\]](#)