***Chlorella sorokiniana* thermogravimetric analysis and combustion characteristic indexes estimation.**

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Abstract.

This work aimed to investigate thermal decomposition of microalgae throughout the different culture stages. For this purpose, C*hlorella sorokiniana* was cultured in photobioreactors (PBRs), and microalgae biomass was sampled at different days throughout the development of the culture. The aim was to analyse the energetic value of this biomass by thermogravimetric analysis (TGA) as well as to calculate combustion characteristic indexes during the different culture stages. In all cases, thermal decomposition of microalgae biomass during combustion denoted two stages. The first one encompassed the carbohydrates and proteins decomposition and the breakdown of hydrocarbon chains of fatty acids, whereas the second step was closely related with the combustion of the formed char. Fuel composition analysis denoted a microalgae HHV value quite similar to that of *Poplar* (considered as an energy crop) biomass and slightly higher than published values for herbaceous biomass. In relation with the culture stages, it was found that a better combustion performance (higher thermal indexes as well as

higher DTG_{max} values) for microalgae biomass sampled at days 19 and 21. These results point to the importance of the culture stage for the thermal valorization of microalgae biomass.

1.- Introduction.

The depletion of fossil fuel reserves and the environmental pollution associated to their burning have prompted scientist and engineers to develop new technologies and find alternative energy sources [1]. According to the 2013 Survey of the World Energy Resources (WER), 223 million tonnes of crude oil and 209 million cubic meters of natural gas remain in our planet. These global reserves of crude oil and gas are estimated to last for 56 and 55 years, respectively. This report also estimates that there are 869 million tonnes of coal reserves, which based on current production rates should last for around 115 years [2].

Consequently, biomass fuels are gaining particular attention as an alternative, clean and renewable energy. Among these biofuels, photosynthetic organisms have the advantage to fix CO_2 in the atmosphere and for this reason are considered as CO_2-neutral fuels when being combusted [3]. In this sense, microalgae have been proposed as a third-generation biofuel source due to their rapid growth rate and high oil contents, high yield per area, no competition with crops for arable land or freshwater and their capacity to use of CO_2 as feedstock. In addition, microalgae are able to use nutrients from most wastewaters, providing an alternative method for wastewater treatment [4].

Thermochemical conversion of biomass is considered as one of the most promising routes for biomass utilization [5]. Nowadays, combustion is the most simple and direct technology available for biomass utilization, which is responsible for over 97% of the world´s bio-energy production [6]. For the prediction of combustion performance in

boilers and obtaining relative combustion characteristics of fuels, thermogravimetric analysis (TGA) is known to be most useful [7]. Nevertheless, only very recently were published studies on the TGA of microalgae combustion. Chen et al. [8] reported the combustion behaviour of *Chlorella vulgaris* under different oxygen concentrations. Gai et al. [9] carried out a kinetic analysis of thermal decomposition characteristics of *Chlorella pyrenoidosa* and *Spirulina platensis* under non-isothermal conditions. López et al. [5] investigated thermal behavior of *Nannochloropsis gaditana, Scenedesmus almeriensis* and *Chlorella vulgaris* under oxidizing atmosphere by TGA coupled to mass spectrometry. Liu et al. [10] used TGA for the determination of the ash content and the qualitative or semi-quantitative analysis of the carbohydrates, proteins and lipids in four microalgae species based on TG analysis ash content. These authors [10] pointed to the possible utilization of TGA for microalgae screening and cultivation monitoring. However, to our best knowledge, such an assessment has not been published yet.

During cultivation of microalgae, their growth affects the nutrients removal rates, and a nutrients limitation improves lipids accumulation in microalgal cells [11]. Consequently, cell composition of microalgae varies along the different stages of culture. This feature may affect the behaviour of thermal decomposition [9]. For this reason, it is important to study thermal properties evolution of the microalgae throughout the different culture stages.

In this work, C*hlorella sorokiniana* was cultured and microalgae biomass withdrawn throughout the development of the culture and analyzed by TGA. The aim of this research was to assess the evolution of thermal characteristics of the combustion of microalgae *Chlorella sorokiniana* throughout the different stages of the culture.

2.- Material and methods.

2.1. - Microalgae culture.

The microalgae strain used in this study was *Chlorella sorokiniana* CCAP 211/8 K (UTEX Culture Collection). Inoculum for the experiments was cultivated in 250 ml Erlenmeyer flasks in the standard culture medium Mann and Myers [12], which was autoclaved for 20 min at 1 atm pressure to ensure aseptic ambient. Firstly, the inoculum was cultivated in 250 mL Erlenmeyer flasks and, in a second stage, microalgae were cultured in tubular bubbling photobioreactors (PBRs) at pilot scale (0.0875 m diameter and 0.3 m height with 1.2 l capacity).

PBRs were inoculated with the same volume of pre-cultured microalgae to ensure the same initial concentration (0.1 g l^{-1}.) Growth conditions were maintained constant, under controlled temperature (25±1 ºC), irradiance (µE $m^{-2}s^{-1}$) and photoperiod (12:12), inside a vegetal culture chamber. In the same way, pH was controlled (7.2-7.5) by the injection of 7% CO_2 enriched air, filtered through 0.2 µm sterile air-venting filter (Millex-FG50, Millipore). The PBRs surface was illuminated with 8 fluorescents lamps (33W, 2150 lumen, Philips, France) providing 650 µE $m^{-2}s^{-1}$ light intensity under 12:12 light/dark cycle.

PBRs were operated under two conditions, batch (or discontinuous) or semi-continuous. In the period of time in which the PBRs are in discontinuous mode, point dilutions were made every 24 hours of 0.5 g l^{-1}. These dilutions were not performed when culture was under discontinuous mode. Daily dilution of the culture volume was carried out to guarantee a biomass concentration of 0.5 g l^{-1}. PBRs were then operated in semicontinuous mode until the volume of culture medium exchanged was equal to 2.5 times the volume. Then, the culture was kept in batch mode for three days, after which

the culture was ended. Fig. 1 represents the growth of microalgae biomass in PBRs throughout the culture times. Biomass samples of the culture were taken four times, as indicated in Fig. 1. The first sample was taken after 14 days (t14). The above sample was related with the last day of the cultivation in batch and the first day at which a dilution was effected. The second sample point was done after 17 days (t17) of the start of the trial; this point denoted a middle point during the semi-continuous stage. The third point, at 19 day (t19), was associated with at time at which the semi-continuous stage ended as well as the last dilution was done. The last sampled point, at 21 days (t21) after the start of the experiment was associated with the end of the culture. The above point was at a Batch stage.

Culture growth was monitored by the determination of microalgae biomass concentration. For this purpose, optical density at 680 nm (OD680) was daily measured by spectrophotometric (UV/Vis spectrophotometer BECKMAN DU640). The dry mass biomass concentration was measured by filtering 25 ml of culture thought 0.45 µm filter and drying it in an oven at 105 ºC during 24 h.

Biomass harvested after 14, 17, 19 and 21 under cultivation was centrifuged at 6461 g during 5 min (SIGMA 2-16P). The pellet was washed twice with distilled water, dried in an oven at 105ºC during 24 h and homogenized for subsequent analysis.

2.2.- *Chlorella sorokiniana* elemental, proximate and calorific value analysis.

The fuel properties of this microalgae strain were assessed by the determination of the elemental and proximate analysis as well as by the determination of the calorific value. Moisture content was determined gravimetrically by the oven drying method. Higher heating value (HHV) at a constant volume was measured by means of an adiabatic oxygen bomb calorimeter. A set of standardized rules were used to calculate the

Chlorella sorokiniana values shown in Table 1. Moisture (ASTM 3320), volatiles (UNE 32019), ash content (UNE 32004), carbon, hydrogen and nitrogen (ASTM 5373), sulphur (ASTM 4239). Also, heating value (HHV) was determined according to UNE 32006 rule. For comparison purposes, this Table 1 also shows both the elemental and proximate analysis as well as the heating value for certain biomass crops (poplar and rice) and a fossil fuel (carbon). With this data, authors want to give the readers a preliminary idea about the possible thermal valorization of *Chlorella sorokiniana* biomass.

2.3.- Thermogravimetric analysis (TGA).

Dried and homogenized microalgae biomass samples were preheated according methodology followed by [5] to further reduce the moisture content. Then, samples were milled on a Fritsch mill Model P-19 to a 1 mm particle size. Afterwards, by using a Retch ball mill model MM200, particle sizes around 125 μm were obtained. After such conditioning of microalgae biomass samples, TGA was carried out using a TA Instruments SDT2960, which is able to supply a continuous measurement of sample mass as a function of time or temperature. Milled samples weighing 4–6 mg were placed in a pottery crucible and heated at three heating rates (10, 20 and 40 K min^{-1}) from ambient to 1150 K. This heating was carried out under an air flow of 100 ml min^{-1} (at a gauge pressure of 1 atmosphere) to carry out the combustion process. Then, derivative thermogravimetric curves (burning profiles) were obtained for the combustion of microalgae biomass samples collected throughout the culture.

2.4. – Combustion characteristic indexes.

In agreement with the opinion of several authors, thermal indexes can give fast and truthful information on the kinetics of the combustion of the biomass extracted from the microalgae [5, 13]. The following indexes were calculated in this work:

2.4.1. - Determination of ignition temperature (T_e) and ignition index (D_i).

Considering a typical DTG curve for the combustion of microalgae biomass (Fig. 2), the ignition temperature (T_e) as defined as follows [14, 15]: firstly, through the DTG peak point a, a vertical line was made upward to meet the TG oblique line at point b; secondly, a tangent line to TG curve was made at point b, which met the extended TG initial level line at point c; thirdly, another vertical line was made downwards through point c, which met the cross axle at point d. The corresponding temperature of point d was defined as T_e [16].

The ignition index (Di) represents the ignition capacity of a fuel so that, the higher Di, the easier the fuel ignition occurs. This index was determined by the following equation [17]:

$$D_i = \frac{(\frac{dw}{dt})_{max}}{t_p \cdot t_e} \qquad \text{Eq. (1)}$$

where $(dw/dt)_{max}$ is the maximum combusiton rate (% min^{-1}) , t_p is the time (min) at which the largest peak (at a temperature above 293 K) occurs and t_e is the ignition time (min).

2.4.2. - Determination of burnout index (D_f).

The burnout index D_f denotes the combustion capacity of a fuel and was here determined to evaluate the burnout performance of microalgae biomass. This index values were estimated according to Eq.2 [17]:

$$D_f = \frac{(\frac{dw}{dt})_{max}}{\Delta t_{1/2} \cdot t_p \cdot t_f} \quad \text{Eq. (2)}$$

$\Delta t_{1/2}$ is the time (min), in the first half of the DTG for the particular stage, since the half of the maximum DTG value is reached until achieve this DTGmax value (min), t_f is the time at which the end of the peak takes place (starting counting time zero to 293 Kelvin degrees and considering the final moment as that in which it reaches the 2% of DTG_{max}).

This index is very similar to the D_i but gives greater importance to the end of the peak and does not consider the ignition temperature.

2.4.3. - Devolatilization index (D).

This parameter, which is related to the release of volatiles during combustion, was estimated as depicted in Eq. 3:

$$D = \frac{(\frac{dw}{dt})_{max}}{T_{max} \cdot \Delta T} \quad \text{Eq. (3)}$$

T_{max} is the temperature at which DTG_{max} is achieved (K), ΔT is the difference between T_{max} and T_e (K).

2.4.4. - Combustion characteristic index (S).

This index can be used for a preliminary assessment of the microalgae combustion performance [18] and represents the energy requiered to burn a fuel. The S was calculated according Eq. 4:

$$S = \frac{(\frac{dw}{dt})_{max} \cdot (\frac{dw}{dt})_{mean}}{{T_e}^2 \cdot T_f} \quad \text{Eq. (4)}$$

where $(dw/dt)_{mean}$ is the average combustion rate considering the 1% of the DTG_{max} as the start and the end of the process (% min^{-1}), T_e is the igntion temperature (K) and T_f is the temperature value at which the end of the peak is achieved (1% of the DTG_{max}).

3.- Results and discussion.

3.1.- Fuel properties of *Chlorella sorokiniana*.

Carried out the characterization of *Chlorella sorokiniana*, results obtained are shown in Table 1. Percentages obtained for the C, H, N and S elements are in concordance with the literature related to this microalgae genus (50% for C, 6 –8% in the case of H, 7–10% for N and <1 % talking about S content (w/w)) [19, 20, 5, 21]. In the case of the calorific value, results here obtained are also similar to those obtained by other authors for this particular genus (values about 18-20 MJ kg^{-1} of HHV) [22, 19].

For comparison purposes regarding the fuel quality, besides the data for *Chlorella sorokiniana,* the elemental and proximate analysis as well as the calorific value of an herbaceous crop (rice straw), a lignocellulosic energy crop (poplar) and a bituminous coal [23] exploited in thermal stations) have been depicted in Table 1. Compared with rice straw [24], microalgae showed higher values for all the parameters included in the elemental analysis with a major difference in the case of nitrogen. Regarding the proximate analysis, it is to highlight the relative lower ash content of microalgae, which is an important feature for fuel. Moreover, the HHV of microalgae is higher than that of rice straw. Compared with a lignocellulosic crop (poplar) [25], microalgae have similar H and C contents, but lower N and higher S contents. Meanwhile, the ash content of microalgae is slightly higher and the volatiles content lower than for poplars. In any case, microalgae and poplars have quite similar HHV (around 20 MJ kg^{-1}). In the last term, if we make a comparison between the microalgae and a conventional coal, data showed for the *Chlorella* elemental analysis, H, N and S values are higher for the microalgae (not so in the case of carbon). Following with the comparison between coal and algae, HHV of the coal was higher than the same parameter for the microalgae,

although it was true that the difference was not as large as expected. On the whole, it may be said that *Chlorella sorokiniana* fuel properties are within the range of conventional biomass raw materials.

3.1.- Thermogravimetric analysis (TGA).

Thermal decomposition of *Chlorella sorokiniana* under air atmosphere denoted two stages, which is coincident with published results [8, 26]. These stages may be seen in the DTG profile represented in Fig. 2, which also shows three evident peaks. For each of these peaks, the characteristic temperatures and maximum DTG signal corresponding to the biomass sampled at different culture times (14, 17, 19 and 21 days) and subjected to temperature programmed combustion at different heating rates (10, 20 and 40 K) are depicted in Fig.3. In the same way, most relevant data associated to this figure is shown in Table 2.

The first stage encompasses the devolatilization of the samples and extended until temperatures between 720 and 775 K. As the heating rate increases, this phase ends at a higher temperature (note the 40 K min^{-1} heating rate at all times in Fig 3). Mass loss associated with this stage is due to the release of organic compounds leading to the formation of char [26].

The first stage of microalgae combustion has been subdivided into three sub-steps. The first sub-step (sub-step I in Fig. 2) has been related to intrinsic lipid decomposition, such as aldehydes and ketones [27] as well as it would involve the decomposition of carbohydrates. In this work, this sub-step I was not clearly identifiable for *Chlorella sorokiniana* but overlapped with the second sub-step (sub-step II), which points to the relative low lipid and carbohydrates content of this microalgae biomass. A second sub-step) was at above 580 K has been associated to carbohydrates and proteins

decomposition [28]. In this work, the second sub-step (sub-step II) is the main responsible of peak 1 in Fig. 2, which meant the maximum mass loss (DTG_{max} in Table 2) for the considered culture times under the heating rates here used. Also, as may be seen in Table 2, the larger the heating rate, the higher the T_0, the T_{DTGmax} and the DTG_{max} of the peak 1. On the other hand, under the here used heating rates, the largest DTGmax for peak 1 were determined for microalgae sampled after 21 days under culture, which may be associated to an increase of the protein and carbohydrate content. The major decomposition of these proteins and carbohydrates at time 21 days will next cause a greater amount of char available for the subsequent peaks. The case of a raised ramp (40 K min) for t21 is remarkable. In this case, a large release of carbohydrates and proteins occurs in a short temperature range, which can be seen in Fig. 3D as a narrow and high peak.

A third sub-step (peak 2 in Fig. 2) occurred at a temperature range of 593 – 613 K (Table 2) depending on the heating rate (the lower the heating rate, the lower the temperature at which this second peak starts). Literature indicates that the final decomposition of lipids takes place in this sub-step III. Break-down of hydrocarbon chains of fatty acids plays an important role in this peak [26, 27, 29]. According to results in Table 2, this break-down is maximal after 19 days under cultivation. Furthermore , at 21 days, a lower DTG_{max} points to a less content of hydrocarbon chains of fatty acids to be broke-down. For this particular stage, the delay in the maximum values of the peaks that was experienced in the previous stage, in this case does not occur. In fact, for t19, when using a raised ramp (40 K min^{-1}) the maximum peak for this stage is advanced with respect to the intermediate ramp of 20 K min^{-1} (Fig, 3C).

It is well-known that microalgae lipid accumulation increases under cultivation conditions stressed [30]. This microalgae stress increases with dilutions in the PBRs

where they are hosted. This may explain that peak II, which is closely related to lipid content, has shown the highest DTG_{max} at the time 19 days under culture. As previously indicated, this is the time after the whole semicontinuous stage (repeated dilutions). Thermal indices confirm the above statement for the case of the culture at t19.

The second stage of microalgae temperature programmed combustion has been related with the decomposition of the formed char. This second stage is known to end at variable temperature values depending on the reactivity and the amount of char formed. Results in Table 2 show that this decomposition stage (peak 3 in Fig. 2) took place in a large range of temperatures (between 639 K and 950 K) for the combustion of *Chlorella sorokiniana*. Also, for biomass sampled at the same culture day, the larger the heating rate, the larger the DTG_{max}. For t14 time (Fig. 3A), this peak is clearly differentiated from the rest of peaks, something that does not happen for the rest of times (Fig.3 B,C,D), where this peak 3 is not so visibly recognizable. Talking about peak 3, it is a fact that depending on the heating rate employed, the DTG_{max} value is obtained at different culture days. Thereby, DTG_{max} for 10 K min^{-1} heating rate is showed during t14, for 20 K min^{-1} is the 17 day of the culture the one with a higher value for this parameter and 19 day for the particular case of a 40 K min^{-1} heating rate.

3.2. - Combustion characteristic indexes.

These tables are shown in Table 3.

3.2.1.- Ignition temperature (T_e) and ignition index (D_i).

T_e values in Table 3 ranged between 520 and 550 K for peak 1; between 582 and 610 K for peak 2; and between 725 and 780 K for peak 3. Also, for the combustion of microalgae biomass sampled at each time, the T_e corresponding to each peak were very close under the the heating rates here used. .

Regarding D_i, an increase trend with increasing heating rate may be observed in Table 3. Likewise, it may be seen that, under the heating rates here considered, relative high D_i values were determined at time 14 days (first biomass sampling) for peak 1. Then D_i values decreased at t17 and t19 to next achieve maximum return values at time 21 days (similar or higher than that for the first data values). This trend points to the decrease of microalgae carbohydrates and proteins content during the semi-continuous culture. Compared with the temperature programmed combustion (heating rate of 20 K min^{-1}) of high ash coal [16], *Chlorella sorokiniana* biomass samples in this worked showed to have lower D_i values. When comparing the results of this parameter (for peak 3) with other types of biomass (for example sunflower and rape), *Chlorella* results were lower than these ones. Only at t14 D_i values were similar to the mention biomass fuels. In contrarst, D_i Chlorella values were higher than the obtained for the biomass derived from corn [13, 31].

3.2.2.- Burnout index (D_f) results.

The same trend observed for D_i regarding peak 1 was also observed for D_f (Table 3), which maximum values were reached at the first and last days of biomass sampling. This confirms the lower carbohydrates and proteins content of microalgae sampled during semi-continuous culture.

3.2.3.-Devolatilization index (D) results.

As may be seen in Table 3, for each sampling day, peak 3 showed the lowest D values at any of the heating rates here considered. This is related to the comparatively lower volatiles release that occurs during the second stage of microalgae combustion, which is mostly due to the oxidation of char. In fact, volatiles release occurs during the first stage of combustion, which comprises peaks 1 and 2. Within this parameter, peak 1 results

showed quite similar D values for the first three sampling days (t14, 17 and 19) and an increase for day 21 under the three heating rates here used. For the peak 2, the heating rate plays an important role. While for a slow heating ramp (10 K min^{-1}) high values of this parameter are denoted at the initial times, then, these values are substantially reduced. However, for more pronounced ramps (20 and 40 K min^{-1}) the tendency is the opposite; the highest values are denoted at the end times for this study. These events may be due to the thermal degradability of the hydrocarbon chain fatty acids is only achieved with high heating ramps and end times. Only the remaining lipid decomposing occurs at low ramps.

3.2.4.- Combustion characteristic index (S) results.

As may be seen in Table 3, for biomass sampled at the same day, the faster the heating rate, the higher the S values. This trend is related to the combustion occurring at lower temperatures under relatively slow heating rates. Likewise, it may be observed that, for peak 1, the highest S values corresponded to the combustion of biomass sampled at day 21, which , indicates an improve of the burning performance with culture time [32].

When comparing S values in Table 3 with those determined for other biomass sources under the same or similar heating rate, lower S were here calculated for the combustion of *Chlorella sorokiniana* than for straw dust and wheat straw biomass sources [32]. Moreover, comparing the results here obtained for *Chlorella sorokiniana* to those obtained by other authors for the same microalgae genus [33], higher S values were here found under the same heating rate. Establishing a comparison with the combustion of other microalgae genus, such as *Scenedesmus almeriensis* and *Nannochloropsis gaditana*, under the same heating rate [33], higher S indexes were here determined.

Therefore, under the experimental conditions followed in this study, less energy is required to perform the combustion of *Chlorella sorokiniana*.

3.3- Heating rate influence.

The different heating rates employed throughout this study have an effect on the combustion characteristic indexes as well as the thermogravimetric results.

As the heating rate is increased, the greater are the DTG_{max} values for all the cases. Furthermore, the temperature at which this DTGmax value are obtained (parameter that has been grouped under the acronym $TDTG_{max}$ for this study) also increased as we used higher heating rates, although this increase was not as pronounced as in the case of DTGmax. This fact (the temperatures are not too high) it is suitable for the thermal process, since in this way we will need less energy expenditure to reach the DTGmax.

Taking into account peak 2 (for being the most representative in the thermal microalgae decomposition), it is a fact that if we use a low heating rate (10 K min^{-1}), the maximum indexes values are denoted at the start of the experiment (t14), something that does not happen with the another heating rates, for which the higher values are achieved at the end of the experiment (t19 and, for the most cases, at t21). It would also be good to highlight to the peak three, for many cases and all the heating rates, the maximum values of the indexes are related to the beginning and end of the trial (t14 and t21). In the middle of the experiment (t17 and t19) the values are usually lower.

3.4.- Biomass microalgae concentration.

The concentration of microalgae biomass throughout culture is shown in Fig.1. During the discontinuous phase (also called Batch), biomass concentration increased to a higher rate than during the semicontinuous culture. This fact is attributable to the main

parameter defining the semicontinuous, which is the dilution with a frequency of 24 hours. Therefore, no biomass growth occurred during the semi-continuous culture. Differently, exponential growth was observed under batch culture.

4.- Conclusions.

Chlorella sorokiniana thermal decomposition denoted two stages. The first one encompassed the carbohydrates and proteins decomposition (peak 1) and the break-down of hydrocarbon chains of fatty acids (peak 2), whereas the second step is closely related with the combustion of the formed char (peak 3). Fuel composition analysis denoted a microalgae HHV value quite similar to the same value for *Poplar* biomass and slightly higher values than the published for herbaceous biomass. In relation with the period of time which reflected a better performance (higher thermal indexes as well as higher DTG_{max} values), for virtually all cases, days 19 and 21 were the ones in which both thermal index as TGA values were better.

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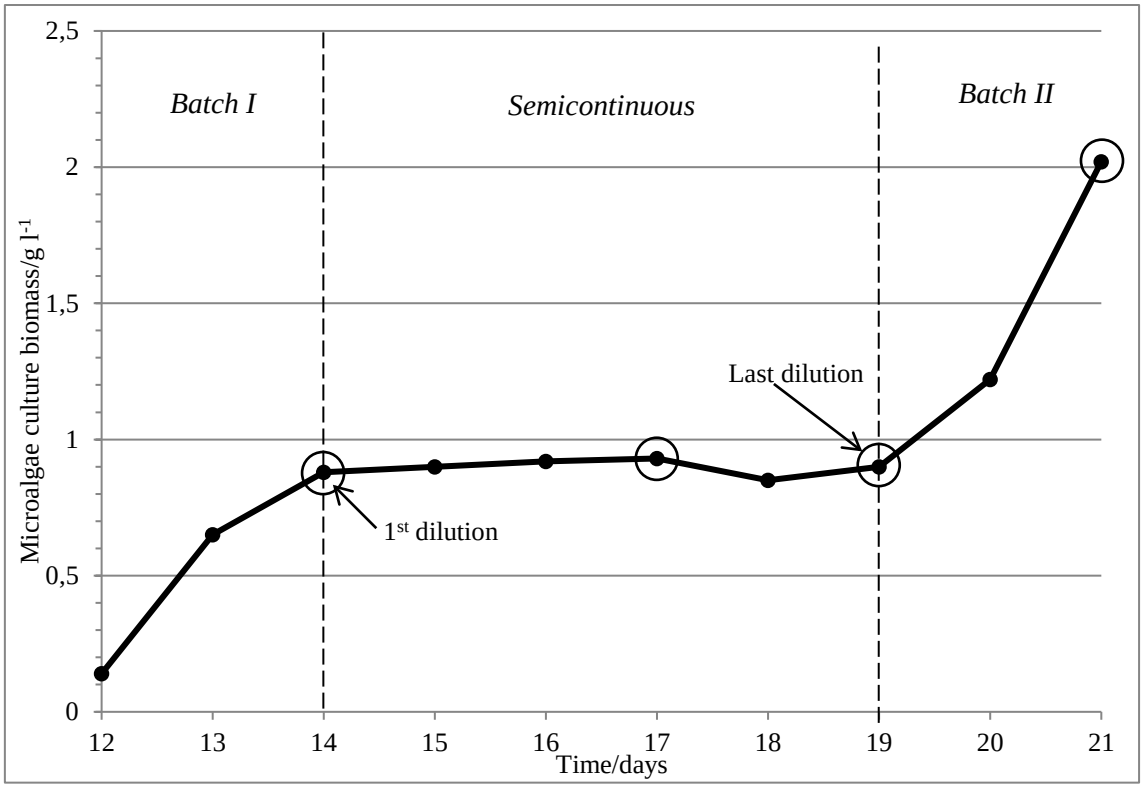


Fig. 1 Concentration of microalgae biomass throughout the culture of *Chlorella sorokiniana* . In circles, days to which samples were taken (14,17,19 and 21).

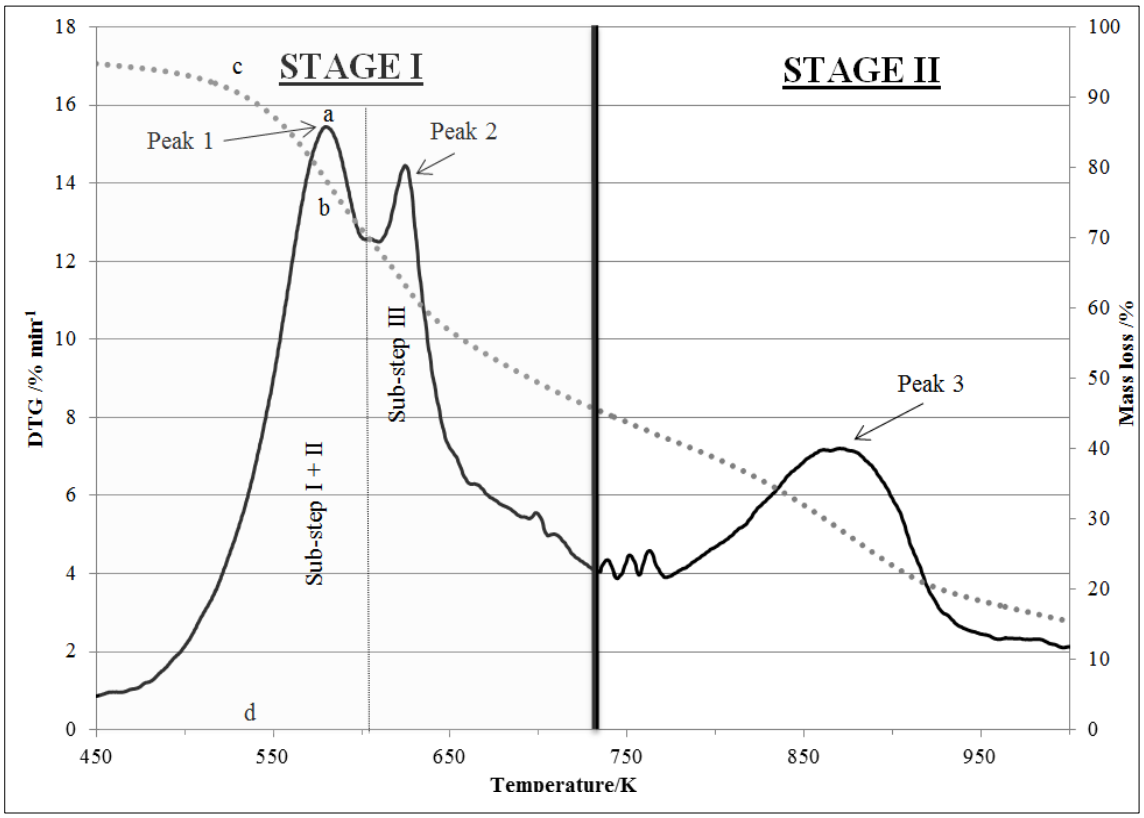
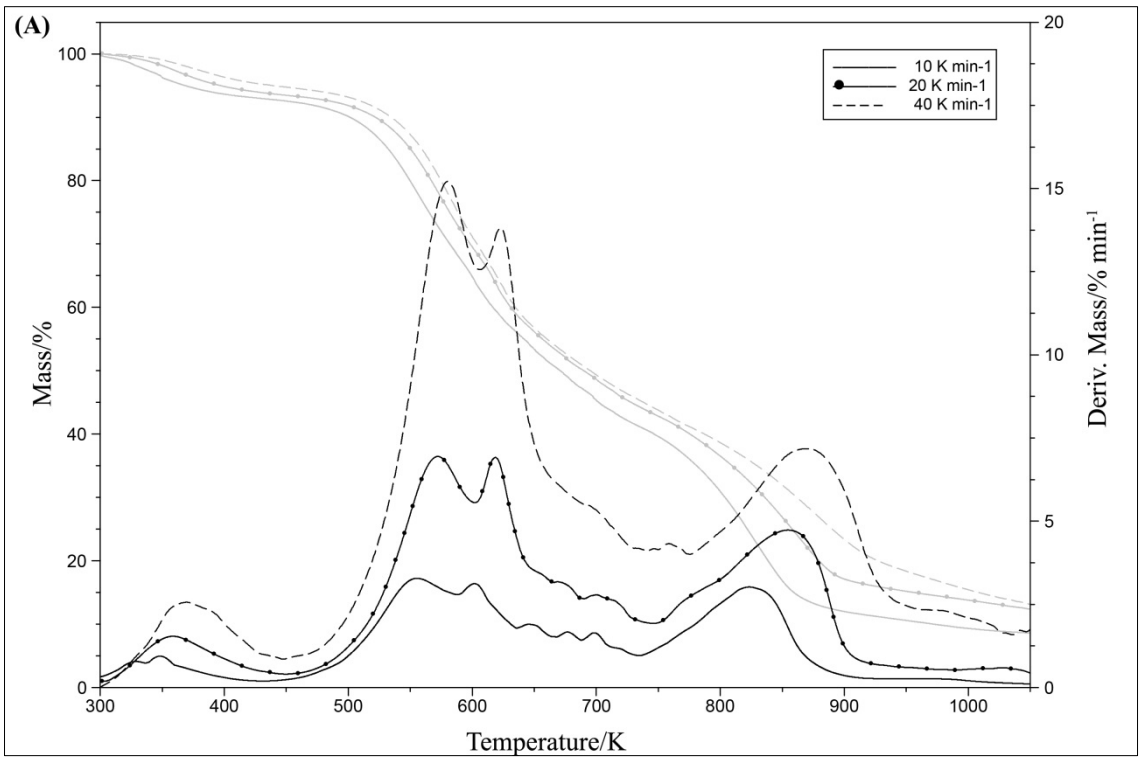
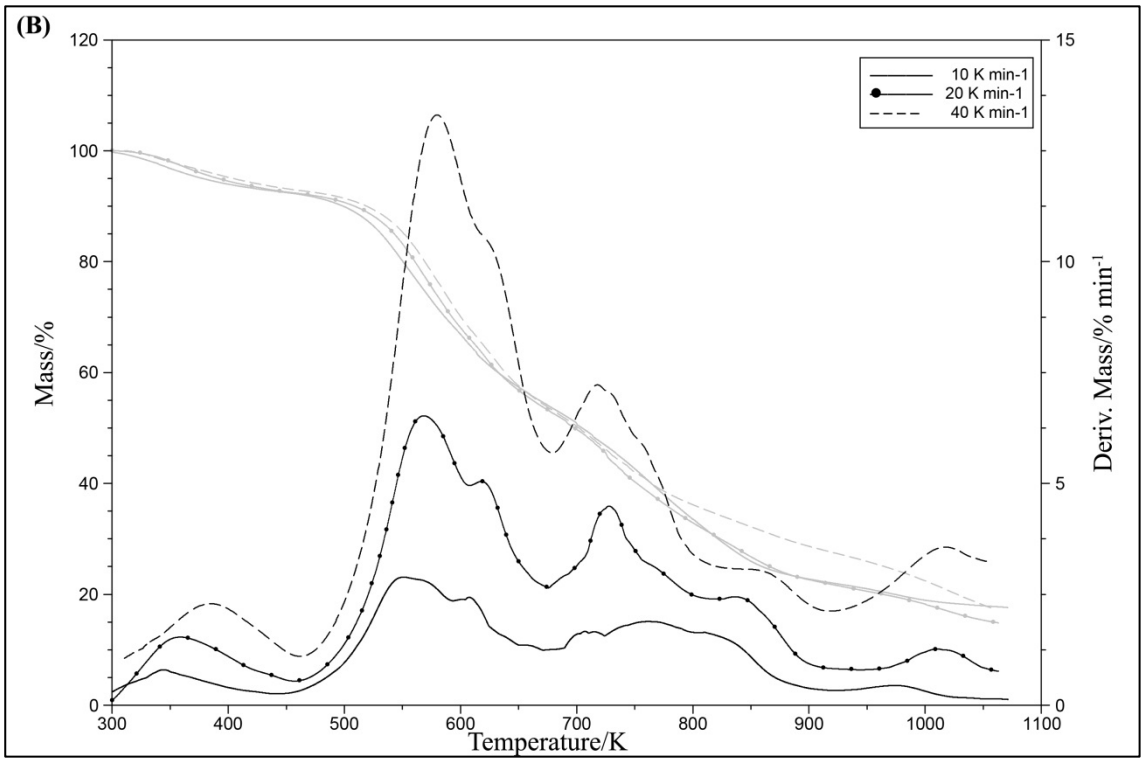
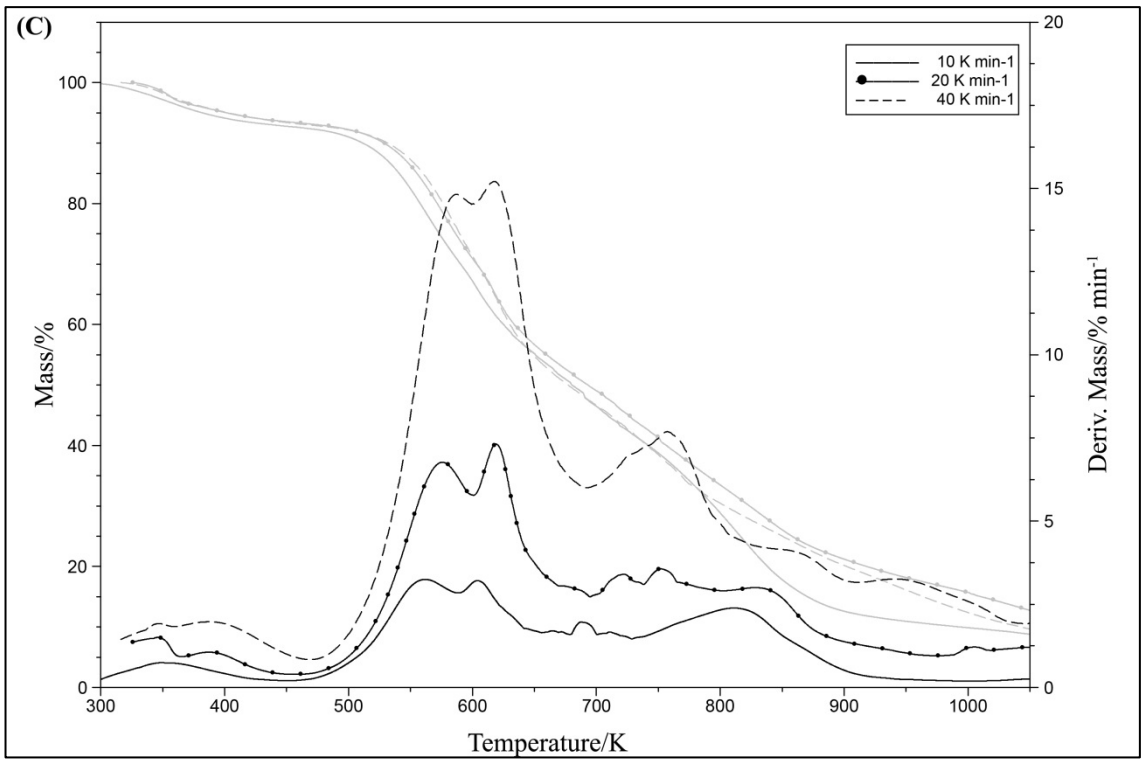


Fig. 2 Thermogravimetric curves for the combustion process of *Chlorella sorokiniana* microalgae. Points a, b, c, and d are employed to calculate ignition temperature (Te) index.


(A)
10 K min-1
20 K min-1
40 K min-1
Mass/%
Deriv. Mass/% min-1
Temperature/K
100
80
60
40
20
0
20
15
10
5
0
300
400
500
600
700
800
900
1000


(B)
10 K min-1
20 K min-1
40 K min-1
Mass/%
Deriv. Mass/% min-1
Temperature/K
120
100
80
60
40
20
0
15
10
5
0
300
400
500
600
700
800
900
1000
1100



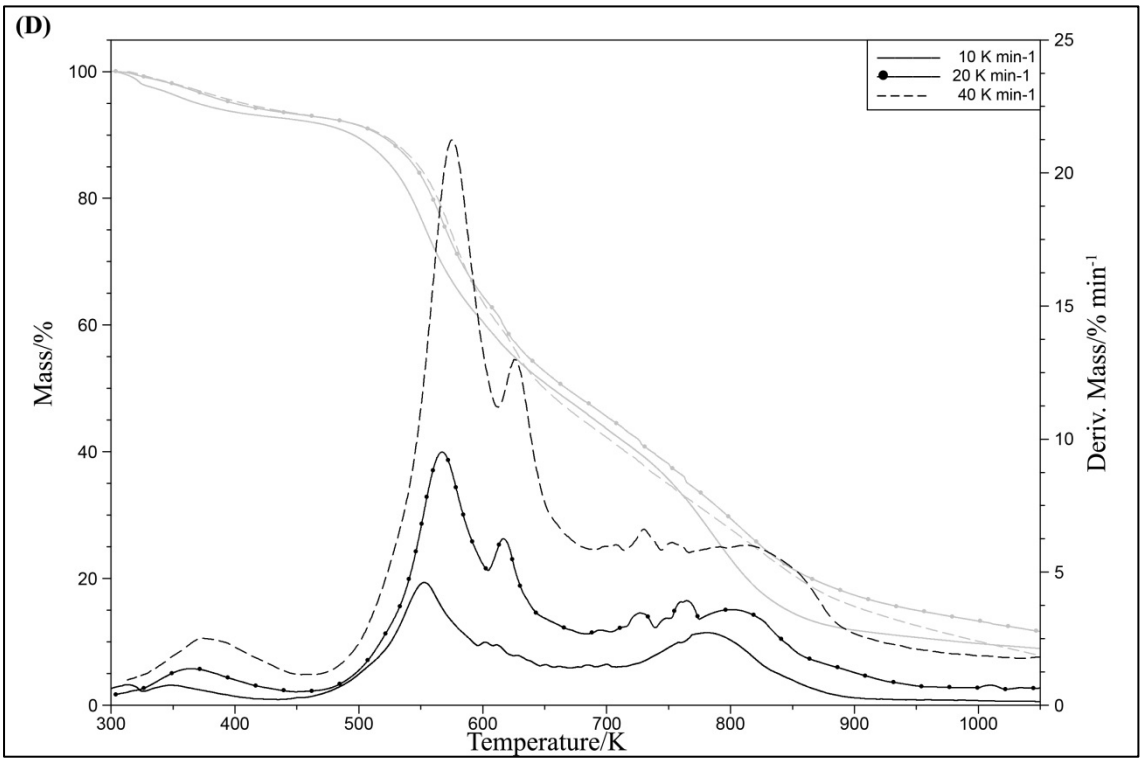


Fig. 3 Thermogravimetric combustion curves at the different heating rates for the times at which *Chlorella sorokiniana* biomass was sampled: (A) 14 days, (B) 17 days, (C) 19 days and (D) 21 days.

Table 1 – Analysis (elemental and proximate) and calorific value of *Chlorella sorokiniana* and three other biomasses for comparison purposes.

	Elemental analysis				**Proximate analysis**			**Calorific value**
	C[a]	H[a]	N[a]	S[a]	Moisture[a]	Ash[a]	Volatiles[a]	HHV[b]/MJ kg^{-1}
***Chlorella sorokiniana* (this work)**	47.9	6.40	8.74	0.78	9.6	7.83	76.1	18.72
Rice Straw [23]	37.87	4.61	0.63	0.14	7.43	19.07	67.95	14.71
***Poplar** [24]**	49.50	5.80	0.56	0.11	7.90	3.28	79.90	19.78
Coal [22]	62.07	2.3	1.16	2.21	11.2	30.33	8.01	24.38

[a] In percentage. All values are in dry basis except moisture.

[b] HHV: high heating value

Table 2 – DTG peaks and characteristic temperatures and maximum values for the temperature programmed combustion under different heating rates of *Chlorella sorokiniana* biomass sampled at different culture times.

Heating rate/K min^{-1})		**10**				**20**				**40**			
Time	**Peak**	**T_o[a]/K**	**T_f[b]/K**	**$TDTG_{max}$[c]/K**	**DTG_{max}[d]/% min^{-1}**	**T_o/K**	**T_f/K**	**$TDTG_{max}$/K**	**DTG_{max}[d]/% min^{-1}**	**T_o/K**	**T_f/K**	**$TDTG_{max}$/K**	**DTG_{max}/% min^{-1}**
14	*1*	443.25	588.52	556.24	3.324	447.28	605.67	573.39	7.024	470.49	600.63	580.45	15.430
	2	594.57	614.75	603.65	2.965	608.77	645.02	616.77	7.636	611.73	661.16	625.85	14.380
	3	737.83	907.32	827.62	3.033	748.93	918.42	854.86	4.767	774.15	949.69	867.97	7.184
17	*1*	453.34	589.53	551.19	2.926	462.42	607.69	563.3	6.648	462.42	617.78	578.43	13.570
	2	593.57	652.08	604.66	2.469	609.71	659.14	621.81	5.421	619.8	670.24	631.90	10.750
	3	669.23	858.59	759.02	1.888	673.27	798.36	726.73	6.933	674.27	808.45	727.74	7.919
19	*1*	467.46	589.53	563.31	3.309	470.49	602.65	575.41	6.885	474.52	603.65	584.49	15.600
	2	594.57	620.81	605.67	3.356	608.72	636.95	616.77	8.082	606.68	677.30	624.81	16.910
	3	735.81	912.36	813.53	2.404	638.96	773.14	749.94	4.453	703.53	812.49	765.07	8.733
21	*1*	456.36	596.59	554.22	4.658	470.49	604.66	568.34	9.831	462.42	610.72	574.40	21.960
	2	598.61	619.87	602.65	2.436	608.74	624.84	616.77	7.184	616.77	679.32	626.86	13.780
	3	715.64	896.22	779.19	2.761	768.13	921.44	804.42	3.592	739.85	903.28	817.53	6.012

[a] T_o: temperature at which a certain peak starts

[b] T_f: temperature at which a certain peak ends

[c] T DTG_{max}: temperature associated to DTG_{max}

[d] DTG_{max}: largest value of DTG in the considered process

Table 3 - Combustion characteristic indexes for the temperature programmed combustion under different heating rates of *Chlorella sorokiniana* biomass sampled at different culture times –

Heating Rate/K min^{-1}	**10**			**20**			**40**		
	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
[a] **T_e/K**									
Time 14	525	595	775	525	600	775	530	600	770
Time 17	520	610	775	520	600	740	530	600	770
Time 19	525	595	730	550	610	820	535	610	780
Time 21	525	582	725	545	610	770	550	605	765
[b] **D_i /% $min^{-3} \cdot 10^{-4}$**									
Time 14	54	41	12	420	280	70	3400	2100	410
Time 17	49	33	5	420	200	37	3000	1600	180
Time 19	52	35	10	360	310	39	3300	2500	230
Time 21	75	25	13	550	300	59	4500	2000	380
[c] **D_f /% $min^{-4} \cdot 10^{-4}$**									
Time 14	11	402	3.30	173	1000	32	3060	5430	277
Time 17	11	43	0.80	187	253	19	2750	3360	256
Time 19	13	55	1.45	159	511	23	3620	5020	395
Time 21	21	264	1.94	352	1450	39	5340	4400	185
[d] **D/% $min^{-1} K^{-2} \cdot 10^{-4}$**									
Time 14	1.98	8.52	0.68	2.59	5.33	0.69	5.39	9.30	0.83
Time 17	1.75	7.15	0.59	2.71	3.86	0.26	5.32	5.51	0.38
Time 19	1.58	6.45	1.32	4.36	19.35	0.16	5.39	25.24	0.18
Time 21	2.97	2.18	1.80	7.78	22.39	0.23	14.35	10.05	0.35
[e] **S/% $min^{-2} K^{-3} \cdot 10^{-7}$**									
Time 14	0.54	0.58	0.14	2.37	2.03	0.35	5.47	5.88	0.58
Time 17	0.43	0.50	0.04	2.10	1.10	0.14	8.50	4.27	0.27
Time 19	0.57	0.51	0.14	2.13	2.53	0.25	11.44	10.52	0.47
Time 21	1.02	0.31	0.21	4.20	2.40	0.39	19.80	6.51	0.91

[a] T_e: ignition temperature

[b] D_i: ignition index

[c] D_f: burnout index

[d] D: devolatilization index

[e] D: combustion characteristic index