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# THERMAL ANALYSIS OF MICROALGA BIOMASS FOR APPLICATIONS IN ENERGY PRODUCTION THROUGH GASIFICATION PROCESS

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**Abstract.** Energy is essential for improving human living conditions, but, at the same time it is necessary to provide not only energy, but it clean and renewable. One way to ensure the generation of clean and renewable energy is through biomass gasification process. However, there is still a lack of data in the literature for different biomass gasification process. This work performs thermal analysis in the microalga, *Chlorella* sp., in order to verify the behavior and characteristics of this biomass for application in energy production through gasification process. Thermal analysis of TGA/DTG and calorimetry were performed. It was possible to define two stages of thermal degradation (30 °C - 500 °C and > 500 °C) attributed to the volatilization of different compounds. The peak of mass loss rate occurs at approximately 560 °C, which must be related to the thermal degradation of char formed by biomass. It is noticed a great ash presence at the end of the temperature of 800 °C, which can be a harmful factor for its application in the gasification. Finally, the calorific value of the microalga, presenting a value close to the other feedstock.

**Keywords:** Thermal analysis, Biomass, Microalgae.

## 1. INTRODUCTION

In the world, more than 2 billion people do not have access to energy, and its services, which are fundamental prerequisites for poverty reduction and human development, moreover, the use of clean energy provides positive consequences such as minimizing local pollution and reducing health impacts, as well as mitigating global warming (Souza *et al.*, 2015).

So far, the majority of the world energy production is still based on fossil fuels, as shown by the International Energy Agency (IEA, 2018), where oil, coal and natural gas accounted together for 81 % of the global primary energy supplied in 2016, respectively 32 %, 27 % and 22 %. The problems resulted by the utilization of nonrenewable energy sources as main sources for energy generation are well-known and have several issues related, like the rising of raw petroleum cost, environmental changes worldwide, ecological degradation and etc. (Chowdhury *et al.*, 2019). Due to these facts, new alternative sources for energy generation are required to replace the traditional ones, one kind of generating clean and renewable energy is through bioenergy.

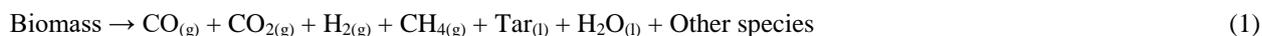
Röder and Welfle (2019) define bioenergy as the form of energy generated from biomass, which is the organic matter provided by plants and animals, such as agricultural and forest residues, energy crops, organic wastes and others. It can also be easily stored and used when needed in form of feedstock or energy carrier, as solid, liquid and gas fuel (Röder and Welfle, 2019), these energy carriers are commonly known as biofuels. However there are several troubles to overcome and only recently the understanding of bioenergy has advanced considerably, with a better knowledge of the challenges and opportunities involved in this production (Souza *et al.*, 2015). In this context, the use of biomass for the generation of energy is essential to achieve objectives related to clean and renewable energy and the sustainable development.

### 1.1 Gasification process

There are different ways of producing biofuels through biomass, it may be by chemical, biochemical and thermochemical routes (Kassim *et al.*, 2014). Still in agreement with Kassim *et al.* (2014), the thermochemical processes stand out among the others, because these kind of processing can produce different types of biofuels using a single step, being more favorable than the biochemical and chemical ones. One of the thermochemical processing is through the gasification.

Gasification is the thermochemical transformation of solid or liquid biomass into a mixture of components such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), tar, water vapor (H<sub>2</sub>O) and others

(Sikawar *et al.*, 2017). The concentrations of the components are determined through operational parameters like biomass characteristics, gasifying media (which can be water steam, air, CO<sub>2</sub> or O<sub>2</sub>), temperature and pressure inside the gasifier and the utilization or not of catalysts (Sikawar *et al.*, 2017). According with Sikawar *et al.* (2017), the Eq. (1) represent a simplified gasification reaction.



After the conversion of carbonaceous feedstock in a mixture of fuel gases, it is still possible to purify the gases, generating the syngas (H<sub>2</sub> + CO), which is versatile, and can be used for the production of chemicals or fuels (Chum *et al.*, 2015).

## 1.2 Microalgae as biofuel feedstock for gasification process

Microalgae are among the oldest forms of life on the planet, being the precursors of plants, which are microscopic photosynthetic organisms found throughout the world, according with Mata, Martins and Caetano (2010) and Scott *et al.* (2010), they are mainly distributed in the waters in marine and freshwater environments, but can also be found on the surface of some types of soils. They have been considered as a non-food alternative for the production of bioenergy and may supply totally or partially the limited oil reserves (Loures, *et al.*, 2018).

According with Kassim *et al.* (2014) microalgae is a source of promising biomass feedstock, since these have great advantages in relation to the lignocellulosic origin ones as: higher rates of growth, do not compete with farmland, can be produced in places with high concentrations of CO<sub>2</sub>, as in exhaust gases from power plants, in addition to producing more biomass and lipids.

The specie of microalga *Chlorella sp.* has been cultivated for a long time (Borzani *et al.*, 2001), it is a microscopic, unicellular and spherical microalga, with a diameter ranging between 5-10 μm (Illman, Scragg and Shales, 2010), besides being one of the most robust, resisting possible contamination in open ponds systems, fast-growing and easy to cultivate (Huntley and Redalje, 2007). Another point to highlight is the possibility of producing biomass for biofuels and, at the same time, treating waste water from microalgae (Amaral, 2014).

As reported by Cai *et al.* (2017) properties data of biomass are essential for the design and implementation of processes aimed at producing biofuels, such as gasification. However, reliable literature data on the area of gasification of microalgae biomass are very scarce and further research is needed (Brennan and Owende, 2010).

Therefore this work focuses on the survey of behavior and properties of the microalgal biomass of *Chlorella sp.* through the thermal analysis, in order to produce energy by gasification.

## 2. MATERIALS AND METHODS

### 2.1 Microalga biomass

The biomass samples used in this work were from the line of the marine microalga *Chlorella sp.*, donated by the Foundation of Fisheries of the State of Rio de Janeiro - FIPERJI, and grown in the Bioenergy and Environment Laboratory of CEFET/RJ campus Angra dos Reis, Angra dos Reis, Rio de Janeiro, Brazil. Where used bubble column photobioreactor for the cultivation and growth of the biomass and artificial lighting, fig. 1.



Figure 1. Biomass growing in bubble column photobioreactor.

## 2.2 Medium for microalgae cultivation

Table 1 shows the composition of the culture medium (f/2), non countabilizing the amount of silica, the concentrations adopted were the same as those of Lourenço (2007) and are widely used in marine microalgae research to maintain the cell bank, preparation of inocula and obtaining biomass. The culture medium was prepared in distilled water. Finally, the reagents were of standard analytical grade for microbiology, which allows less variability and greater precision in the culture medium.

Table 1. Reagents in the composition of f/2 medium, adapted from Lourenço (2007).

Reagents	Concentration
Sea salt	33.3 g/l
NaNO <sub>3</sub>	75 g/l
NaH <sub>2</sub> PO <sub>4</sub> .H <sub>2</sub> O	5 g/l
FeCl <sub>2</sub> .6H <sub>2</sub> O	3.15 g/l
Na <sub>2</sub> EDTA	4.3 g/l
ZnSO <sub>4</sub> .7H <sub>2</sub> O	22.2 mg/l
MnCl <sub>2</sub> .4H <sub>2</sub> O	180 mg/l
Na <sub>2</sub> MoO <sub>4</sub> .2H <sub>2</sub> O	6.3 mg/l
CoCl <sub>2</sub> .6H <sub>2</sub> O	10 mg/l
CuSO <sub>4</sub> .5H <sub>2</sub> O	9.8 mg/l
Thiamine (B1)	100 mg/l
Cyanocobalamin (B12)	0.5 mg/l
Biotin (B7)	0.5 mg/l

## 2.3 Termogravimetric analysis (TGA)

The analysis was performed on a thermal analyzer (SDT Q600, TA Instruments). The microalgae biomass samples, approximately 5 g, were thermally decomposed into an oxidative (synthetic air) atmosphere, with the gas inlet rate (20 mLmin<sup>-1</sup>) and heating ramp (10 °Cmin<sup>-1</sup>), heating from 30 °C to 800 °C. The weight loss was recorded as a function of temperature (TGA curve) and the weight loss rate was recorded as the derivative thermogravimetry (DTG) curve.

## 2.4 Energy content evaluation

To determine the energy content on the biomass, small amounts of the sample were placed in a closed calorimeter, then pure oxygen was introduced into the vessel, with a pressure between 30 bar and 32 bar, resulting in the complete combustion of the material. The procedure was performed in duplicate and the final value taken was the arithmetic mean of the results obtained.

## 3. RESULTS AND DISCUSSIONS

### 3.1 TG/DTG analysis results

Figure 2 shows the results obtained by the thermogravimetric analysis of the biomass sample under air atmosphere at a heating ramp of 10 °C/min exhibiting the weight loss and the rate of weight loss found. Through the TGA curve (in black) and the DTG curve (in red) it is possible to identify the thermal behavior of the microalga *Chlorella sp.*, where with the increase of temperature enables to observe its thermal degradation on air atmosphere.

According to Tang, Ma and Lai (2011), the thermal decomposition of microalgae under air is generally divided into two stages (solid black line). And each stage has subdivisions (dashed black line) according to the processes identified by the DTG curve (López-González *et al.*, 2014).

The first stage, between room temperature up to approximately 500 °C, correspond with the loss of moisture plus the devolatilization process of the biomass, where four sub-steps were observed. In the first sub-step, 30 °C until 150 °C, was a slight loss of mass, around 5 %, which is possible associated to loss of moisture, related to the evaporation of the water contained in the biomass and light volatile compounds, a similar result was observed by Shuping *et al.* (2010).

Then the devolatilization of the material, starting at approximately 150 °C and going up to 500 °C, at this stage the largest loss of mass occurs, about 43 %, such loss of mass is caused by the release of organic compounds which leads to the formation of char (Tang, Ma and Lai, 2011). The sub-steps II, III and IV might be related with the decomposition of carbohydrates and proteins (Laiate, 2018; López-González *et al.*, 2014), also lipids and char oxidation (López-González *et al.*, 2014).

The second stage, temperatures above 500 °C, exhibit the highest weight loss rate, in the approximate temperature of 560 °C. This implies that the previous devolatilization of the biomass led a high formation of char (López-González *et al.*, 2014), occurring the thermal decomposition of it. After this process, the mass loss occurred very slow and at the end temperature (800 °C) the percent of weight left was close to 22.66 %.

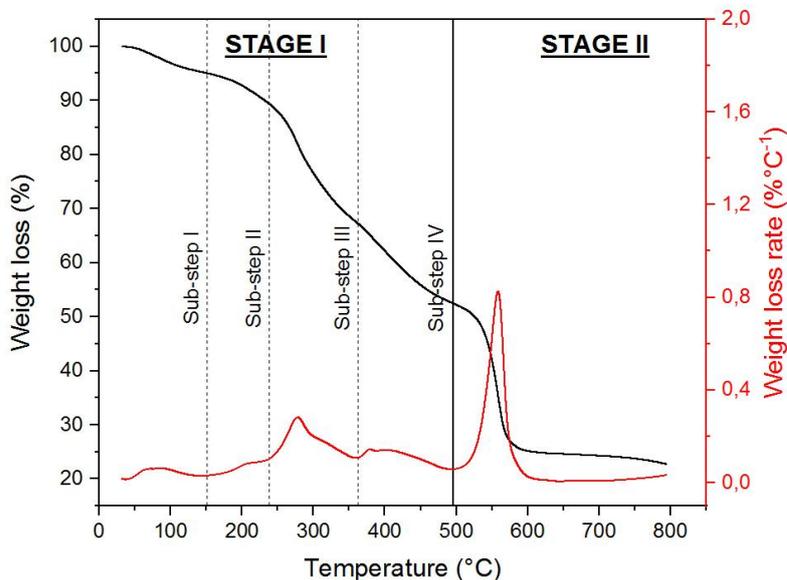


Figure 2. TGA (black) and DTG (red) curves results for microalga biomass under oxidizing (air) atmosphere.

López-González *et al.* (2014) exposes that the lower thermal resistance in the microalgae biomass implies in lower reacting temperatures, what is associated with lower operational costs, on the other hand, the higher ash content verified on the analysis, compared to lignocellulosic biomass (between 2-7 wt. %), causes problems such as slagging and fouling for applications as in the gasification process.

### 3.2 Higher heating value of the biomass

Table 2 shows the values found for the higher heating value of the *Chlorella sp.* samples and the average value. According to Laiate (2018), the proximity of the values obtained indicated that the biomass samples were very homogeneous and similar.

Table 2. Higher Heating Value (HHV) of *Chlorella sp.* microalga biomass.

Sample	HHV (MJ/kg)
1	16.33
2	16.37
Average	16.35

The heating value of the biomass is essential for the determination of the energy released, as heat, during the complete combustion of the material, moreover, at constant pressure the modulus of heat power is equal to the modulus of the combustion enthalpy (Laiate, 2018). The term “higher” is related to the recovery of energy through the condensation of water from the combustion gases (Çengel and Boles, 2013). Table 3 presents the comparison between the HHV of *Chlorella sp.*, obtained in this work, with other biomasses from different types.

Table 3. Comparison between the higher heating value (HHV) of different biomass feedstocks.

Biomass feedstock	HHV (MJ/kg)	Reference
<i>Chlorella sp.</i>	16.35	This work
<i>Chlorella minutissima</i>	16.61	Laiate (2018)
Rice husks	13.24	Wilson <i>et al.</i> (2011)
Palm stem	17.38	Wilson <i>et al.</i> (2011)
<i>Spirulina platensis</i>	19.67	Yang <i>et al.</i> (2013)
Eucalyptus globulus	16.49	Yang <i>et al.</i> (2013)

It is observed that the higher heating value for the microalga *Chlorella sp.* is close to the results from the other biomasses. Thus, in terms of heating value, its application in the gasification process is possible, a similar result was found by Laiate (2018). Another important point is that HHV, besides being the most important parameter for determining the energy content of a fuel, in association with other analysis, becomes a necessary property of biomass for the development of thermochemical fuel conversion simulations (Laiate, 2018).

#### 4. CONCLUSIONS

This paper focuses on the thermal analysis of microalgal biomass of the species *Chlorella sp.* for possible application for power generation in the gasification process. By means of the TG/DTG analysis, it was verified that as the thermal degradation of the biomass under the conditions used, it is possible to identify low reaction temperatures for the biomass, which is related to lower operating costs, besides a great presence of ash at the end of the process, when compared with lignocellulosic biomass, which may be an impediment to its use in the gasification process. In addition, its higher calorific value was similar to that found in other sources of biomasses studied for the application in gasification.

#### 5. REFERENCES

- Amaral, M.S., 2014. *Cultivo da microalga marinha Chlorella sp. como fonte de matéria prima para a produção de biodiesel*. M.Sc. dissertation, Universidade de São Paulo, Escola de Engenharia de Lorena, Lorena, Brasil.
- Borzani, W., Schmidell, W., Lima, U.A. and Aquarone, E., 2001. *Biotecnologia Industrial: Fundamentos*. Edgar Blücher, São Paulo, 1<sup>st</sup> edition.
- Brennan, L. and Owende, P. 2010. "Biofuels from microalgae - A review of technologies for production, processing, and extractions of biofuels and co-products". *Renewable and Sustainable Energy Reviews*, Vol. 14, No. 2, pp. 557-577.
- Cai, J., He, Y., Yu, X., Banks, S.W., Yang, Y., Zhang, X., Yu, Y., Liu, R. and Bridwater, A.V., 2017. "Review of physicochemical properties and analytical characterization of lignocellulosic biomass". *Renewable and Sustainable Energy Reviews*, Vol. 76, pp. 309-322.
- Çengel, Y.A. and Boles, M.A., 2013. *Termodinâmica*. AMGH, Porto Alegre, 7<sup>th</sup> edition.
- Chowdhury, H., Loganathan, B., Mustary, I., Alam, F. and Mobim, S.M.A., 2019. "Algae for biofuels: The third generation of feedstock". In Basile, A. and Dalena, F. (ed) *Second and Third Generation of Feedstocks: The Evolution of Biofuels*. Elsevier, Amsterdam, Netherlands.
- Chum, H.L., Nigro, F.E.B., McCormick, R., Beckham, G.T., Seabra, J.E.A., Saddler, J., Tao, L., Warner, E. and Overend, R.P., 2015. "Conversion Technologies for Biofuels and Their Use". In Souza, G.M., Victoria, R.L., Joly, C.A. and Verdade, L.M. (ed) *Bioenergy & Sustainability: bridging the gaps*. SCOPE, vol. 72, Paris, France.
- Huntley, M.E. and Redalje, D.G., 2007. "CO<sub>2</sub> Mitigation and Renewable Oil from Photosynthetic Microbes: A New Appraisal". *Mitigation and Adaptation Strategies for Global Change*, Vol. 12, pp. 573-608.
- IEA, 2018. "World Energy Balances: Overview (2018 edition)". International Energy Agency. 28 May. 2019. <<https://webstore.iea.org/world-energy-balances-2018-overview>>.
- Illman, A.M., Scragg, A.H. and Shales, S.W., 2000. "Increase in *Chlorella* strains calorific values when grown in low nitrogen medium". *Enzyme and Microbial Technology*, Vol. 27, pp. 631-635.
- Kassim, M.A., Kirtania, K., De La Cruz, D., Cura, N., Srivatsa, S.C. and Bhattacharya, S. 2014. "Thermogravimetric analysis and kinetic characterization of lipid-extracted *Tetraselmis suecica* and *Chlorella sp.*" *Algal Research*, Vol. 6, pp. 39-45.
- Laiate, J., 2018. *Estudo do Processo de Cultivo da Microalga Chlorella minutissima e Caracterização Termoquímica de sua Biomassa para Aplicação em Gaseificação*. Ph.D. thesis, Universidade Estadual Paulista, Faculdade de Engenharia de Guaratinguetá, Guaratinguetá, Brasil.
- López-González, D., Fernandez-Lopez, M., Valverde, J.L. and Sanchez-Silva, L. 2014. "Kinetic analysis and thermal characterization of the microalgae combustion process by thermal analysis coupled to mass spectrometry". *Applied Energy*, Vol. 114, pp. 227-237.
- Lourenço, S.O., 2007. *Cultivo de microalgas marinhas: Princípios e aplicações*. RiMa, São Carlos, 1<sup>st</sup> edition.
- Loures, C.C.A., Amaral, M.S., Da Rós, P.C.M., Zorn, S.M.F.E., Castro, H.F. and Silva, M.B., 2018. "Simultaneous esterification and transesterification of microbial oil from *Chlorella minutissima* by acid catalysis route: A comparison between homogeneous and heterogeneous catalysts". *Fuel*, Vol. 211, pp. 261-268.

- Mata, T.M., Martins, A.A. and Caetano, N.S., 2010. "Microalgae for biodiesel production and other applications: A review". *Renewable and Sustainable Energy Reviews*, Vol. 14, pp. 217-232.
- Röder, M. and Welfle, A., 2019. "Bioenergy". In Letcher, T. M. (ed) *Managing Global Warming: An Interface of Technology and Human Issues*. Academic Press, London, UK.
- Scott, S.A., Davey, M.P., Dennis, J.S., Horst, I., Howe, C.J., Lea-Smith, D.J. and Smith, A. G., 2010. "Biodiesel from algae: challenges and prospects". *Current Opinion in Biotechnology*, Vol. 21, pp. 277–286.
- Shuping, Z., Yulong, W., Mingde, Y., Chun, L. and Junmao, T., 2010. "Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer". *Bioresource Technology*, Vol. 101, No. 1, pp. 359-365.
- Sikawar, V.S., Zhao, M., Fennell, P.S., Shah, N. and Anthony, E.J., 2017. Progress in biofuel production from gasification. *Progress in Energy and Combustion Science*, Vol. 61, pp. 189-248.
- Souza, G.M., Victoria, R.L., Verdade, L.M., Joly, C.A., Netto, P.E.A., Cruz, C.H.B., Cantarella, H., Chum, H.L., Cortez, L.A.B., Diaz-Chavez, R., Fernandes, E., Fincher, G.B., Goldemberg, J., Nogueira, L.A.H., Huntley, B.J., Johnson, F.X., Kaffka, S., Karp, A., Leal, M.R.L.V., Long, S.P., Lynd, L.R., Macedo, I.C., Filho, R.M., Nassar, A.M., Nigro, F.E.B., Osseweijer, P., Richard, T.L., Saddler, J.N., Samseth, J., Seebaluck, V., Somerville, C.R., van der Wielen, L., Sluys, M.A.V., Woods, J. And Youngs, H., 2015. "SCOPE Bioenergy & Sustainability: Technical Summary". In Souza, G.M., Victoria, R.L., Joly, C.A. and Verdade, L.M. (ed) *Bioenergy & Sustainability: bridging the gaps*. SCOPE, vol. 72, Paris, France.
- Tang, Y., Ma, X. and Lai, Z., 2011. "Thermogravimetric analysis of the combustion of microalgae and microalgae blended with waste in N<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/O<sub>2</sub> atmospheres". *Bioresource Technology*, Vol. 102, No. 2, pp. 1879-1885.
- Wilson, L., Yang, W., Blasiak, W., John, G.R. and Mhilu, C.F., 2011. "Thermal characterization of tropical biomass feedstocks". *Energy Conversion and Management*, Vol. 52, No. 1, pp. 191-198.
- Yang, K.C., Wu, K.T., Hsieh, M.H., Hsu, H.T., Chen, C.S. and Chen, H.W., 2013. "Co-gasification of woody biomass and microalgae in a fluidized bed". *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 44, pp. 1027-1033.

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