

1

2

3

Characterization of *Spirogyra* using Thermogravimetric/ Derivative Thermogravimetric (TG/DTG) analysis and Bomb Calorimeter for Energy Application

5

7

8

9

11

13

14

ABSTRACT

Biomass is usually considered as different types of lignocellulosic materials having varied composition potential to utilize in the useful forms of energy as a substitute of conventional fossil fuels. Algal biomass has multi facet application in research and development such as source of nutrients, biochemical, cosmetics and biofuels. However, this newly developed energy source met the requirement of low and medium scale power generation due to low thermal efficiency. In present study, freshwater algae *Spirogyra* taken as source of biomass and analyzed for Thermogravimetric (TG) and calorific values analysis. We found the calorific value is 2129.4 Kcal/Kg and TGA results show that algal biomass decrease rapidly after reaching the temperature over 300°C. The result obtained in this paper may be used in future as reference material for algae based biomass for energy application.

Key words: *Spirogyra*, Algal Biomass, Calorific Value, Thermogravimetric.

1. INTRODUCTION

Post industrial revolution has not only increased the demand of energy but also polluted the environment manifold. There is a significant increase of emission of CO₂, SO_x, NO_x and particulate matter in the environment due to anthropogenic activities. In the present scenario clean and emission less energy is not only a choice but also a compulsion under obligation of Kyoto protocol to curb the emission of various GHGs. To deal with global warming and avoid dangerous climate change, keeping the temperature below 2°C is also desirable under the Paris agreement. All these concerns may be addressed by introducing renewable energy resources. (1.) Renewable energy comprises solar, wind, hydropower, tidal waves and biomass energy. Algal biomass mainly composed of cellulose, hemicellulose and lignin. Biomass is usually considered as different types of waste materials having varied composition that may be utilized as a substitute of conventional fossil fuels. Composition wise it is constituted of carbon, nitrogen, hydrogen, oxygen and sulphur. Biomass energy is not only clean source of energy, but also considered as fuel substitution of fossil fuels having the same benefits in terms of operation and improving environmental benefits of energy generation. As an energy source biomass can be used directly or indirectly converted into other energy forms through various routes namely biochemical & thermochemical. Besides that biomass resources have more potential than other renewable energy in terms of sustainability. The 1st and 2nd generation fuels, consisting of maize, cereal crops and soybeans, are environmentally friendly but conflict with food supply. Algae come under 3rd generation food mainly composed of lipids, proteins and small fraction of cellulose and are different from its feedstock of a crop food (2.).

The algal application of energy generation was initiated by U.S. government in 1960 and commonly known as ASP (Aquatic Species Program), for the development of algae based technology. It was further extended in Hawaii, just after the period of oil crisis and mid-east war. The Japanese government also started the project in time period of 1990-96 with the innovative idea of CO₂ fixation. These projects concluded with valuable results like new strains development for lipid

production, principle of aquaculture and photo bioreactor design. In 21st century, continuous efforts are mainly focused on how to grow algae in large aquaculture and make the economic balance. (10)

In India, algae projects started in 2011 in collaboration of nine premier research institutes led by CSMCRI (Central Salt Marine and Chemical Research Institute) with the development of algae biodiesel with traditional biodiesel. Recently, Algae has gained attention other than biomass to overcome the problem of low performance and efficiency. For increasing efficiency algae must be pretreated before used in the energy system or transformed into another phase. Although production of biodiesel has shown that harvesting procedure and lipid production put the environment at risk and cost energy waste. Some studies use fermentation processes, which are anaerobic in nature in which sugars are converted into cellular energy and thereby produce ethanol and carbon dioxide as metabolic waste products. Anaerobic digestion essentially occurs in absence of oxygen and mediated by microorganisms to convert biomass into biogas, but it still needs lots of development in terms of yield and efficiency. (11)

In developing countries like India, it's started to gain popularity with the development of technology. Apart from *Jatropha*, some strains of Algae are selected and harvested for obtaining the different products like bio oil, syngas through different processes like liquefaction & gasification. Although different processes are available for conversion of biomass into energy, thermochemical conversion is considered as a one of the promising routes. Thermochemical conversion includes combustion, gasification, pyrolysis and liquefaction. Combustion is the chemical reaction occurring at high temperature to convert biomass into useful energy products in presence of oxygen. Recently research is going on for the production of biodiesel through the pyrolysis process. Although very few studies about combustion behavior of algae have been reported, mostly studied about microalgae *Chlorella* species. The combustion behaviors are analyzed through thermogravimetric (TG) analysis, of biomass in different oxygen concentrations and N₂/O₂ ratio (12, 13).

In 2014, Lopez-Gonzalez (14) reported that certain microalgae like *chlorella vulgaris*, *Scenedesmus almeienseis* and *Nannochloropsis gaditana* are potential biomass for combustion application through TGA-MS-DSC analysis. In this study, we analyze the *Spirogyra* in TG/DTG and bomb calorimeter to provide the detail information of algal biomass mainly for combustion application.

2. MATERIAL AND METHODS

To analyze algal biomass for energy production, we have selected *Spirogyra* based on their chemical composition. & specialties in energy application analyzed through TG/DTG and bomb calorimeter.

2.1 Biomass Selection: Algae has explored for decades mainly due to energy application. For that we have to analyze chemical composition through proximate and ultimate analysis. However, the quantity & potential in biomass for energy production is also important for energy production. Therefore, in this study, we selected *Spirogyra sp.* that has been used in multi-application, production of energy is one of them. Recently, it has been reported that *Spirogyra sp.* having potential for producing biodiesel (15). The algal biomasses are collected from ponds nearby the Meerut district Uttar Pradesh, India. The collected algal biomasses are kept for sun drying and powdered for further use.

Table 1: The lipid percentage of algae and microalgae

Microalgae/Macroalgae species.	Lipid (% Dry wt.)
<i>Spirogyra</i>	20-32
<i>Monallanthus salina</i>	>20
<i>Nannochloropsis sp. (fresh water)</i>	20-35
<i>Nannochloropsis sp.(sea water)</i>	31-68
<i>Neochloris oleoabundans</i>	35-54
<i>Botryococcus braunii</i>	25-75
<i>Chlorella sp.</i>	28-32
<i>Phaeodactylum tricornutum</i>	20-30
<i>Nitzschia sp.</i>	45-47
<i>Cylindrotheca sp.</i>	16-37
<i>Cryptocodinium cohnii</i>	20

<i>Dunaliella primolecta</i>	23
------------------------------	----

References [3-9]

2.2 Calorific Value Detection: The calorific value of algal biomass is determined by evaluation of gross calorific value (GCV) of prepared sample. It measures the energy content of a unit mass sample in a bomb calorimeter. In this method calorific value is determined by burning a weighed biomass sample under controlled condition in an oxygen bomb calorimeter.

2.3 TG/DTG Analysis: The algae sample in powder form kept in oven (40°C), overnight before testing the starting temperature is 90°C for around 30 minutes mainly for drying purpose of the biomass and keep the moisture within limit. Finally temperature increased up to 900°C to analyze the thermal stability and oxidative stability of sample.

Table 2: The Calorific values of *Spirogyra*, microalgae, fossil fuel & other biomass materials

	J/g	Kcal/KG	Types of Biomass	Reference
<i>Spirogyra</i>	8,900.89	2,129.4	Non-food	In this study
<i>Chlorella</i>	21,174.5	5,057.4	Non-food	[18]
<i>Spirulina</i>	20,866.3	4,983	Non-food	[18]
Coal	28,665.6	6,846.7	Fossil fuel	[18]
Diesel	42,000~49,500	10,047.8~11,842.1	Fossil fuel	[16]
Coconut	35,000~38,100	8,373.2~9,114.8	Food	[16]
Soybean	38,310~39,760	9,114.8~9511.9	Food	[16]
Wood Waste	19,450	4,645.6	Food	[17]
Vege-Oil	33,700	8,049.1	Food	[17]

3. RESULTS AND DISCUSSION:

The algal biomass samples were tested for calorific value and TG /DTG analysis.

3.1 Calorific Value Analysis of *Spirogyra*: Each sample after drying had been tested for its calorific value. To make analysis comparable and meaningful, examples of fossil fuels like coal & diesel had also been taken as reference. The calorific value of coal & vegetable oil is higher than that of algal biomass (Table 2) However algal biomass in combination with other biomass can be used to get better results in terms of calorific value.

3.2 TG & DTG of *Spirogyra*: The major components of algal biomasses are water, lipid, protein, cellulose & lignin. The TG & DTG curve is shown in figure 1. The sample decreased after 300°C and about 65 % of the sample burnt after 900°C . In the DTG curve, the first peak at 300°C occurs due to cellulose decay and the second peak at 355°C is due to lignin decay of the lignocellulosic biomass.

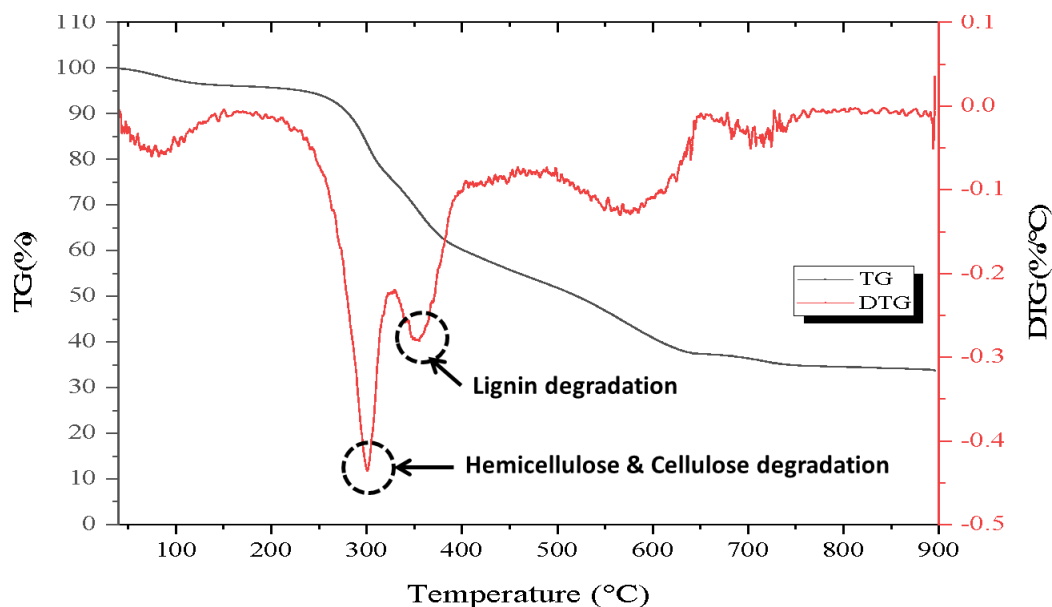


Figure: 1 TG & DTG Curves of Spirogyra

3.3 Discussion: Algae based technologies are reliable energy source that could meet energy requirement of the world. Since algal cell store oil, so their oil content was analyzed by extracting oil using soxhlet extraction method and the best oil producing alga was identified as *Spirogyra* [19]. The calorific value of algal biomass shows that potential of algae to be material as biofuel and TG

analysis results show that thermal stability of the biomass behavior in combustion system. According to result calorific value of *Spirogyra* is not only less than fossil fuel but also less than other microalgae. It may be due to higher percentage of lignin in sample biomass, which remains unburnt in samples about 35% even at high temperature. In TG testing combustion takes place in two stages. In the first stage almost carbohydrate combusts, in the second stage nitrogen and sulphur combust as a part of protein degradation. TG analysis result (Fig:1) shows the sample decreased rapidly at 300°C and beyond 650°C the rate becomes almost constant because of the presence of lignin. DTG (Derivative thermogravimetric) is the interpretation of weight loss or weight gain over temperature and the curve shows that hemicellulose & cellulose degradation occurs at 300°C and lignin degradation started at 355°C. It has been also found that apart from energy generation *Spirogyra sp.* demonstrated potential for the treatment of municipal waste water and biochemical components obtained were suitable for many applications [20].

4. CONCLUSION

In this study, we have analyzed algal biomass of *Spirogyra* and concluded that on the basis of results and discussion that *Spirogyra sp.* is suitable for low and medium scale power generation due to low calorific value and thermal efficiency but having significant lipid percentage 20-32% (Table 1). Therefore, having potential for biodiesel production. Besides this, algal biomass should be mixed with other materials to increase the calorific value for better heat performance. The calorific value and TG analysis show that algal biomass has potential as a biofuel either alone or in combination with other biomass for better results. Sometimes the composition of multi-component systems results better, when TG coupled with MS (TG-MS) with rising temperature.

5. ABBREVIATIONS

TGA-MS-DSC: Thermogravimetric analysis-Mass spectrometry-Differential scanning calorimetry

TG :Thermogravimetry

DTG:Derivative thermogravimetry

132

146

147
 148
 149
 150
 151
 152
 153
 154
 155
 156
 157
 158
 159
 160
 161
 162
 163
 164
 165
 166
 167
 168
 169
 170
 171
 172
 173
 174
 175
 176
 177
 178
 179
 180
 181
 182
 183
 184
 185
 186
 187
 188
 189
 190
 191
 192
 193
 194
 195
 196
 197
 198
 199
 200

REFERENCES

1. Lau, L. C., Lee, K. T., & Mohamed, A. R. (2012). Global warming mitigation and renewable energy policy development from the Kyoto Protocol to the Copenhagen Accord—A comment. *Renewable and Sustainable Energy Reviews*, *16*(7), 5280-5284.
2. Sims, R., Taylor, M., Saddler, J., & Mabee, W. (2008). From 1st-to 2nd-generation biofuel technologies. *Paris: International Energy Agency (IEA) and Organisation for Economic Co-Operation and Development*, 16-20.
3. Chisti, Y. (2008). Biodiesel from microalgae beats bioethanol. *Trends in biotechnology*, *26*(3), 126-131.
4. Illman, A. M., Scragg, A. H., & Shales, S. W. (2000). Increase in *Chlorella* strains calorific values when grown in low nitrogen medium. *Enzyme and microbial technology*, *27*(8), 631-635.
5. Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in energy and combustion science*, *37*(1), 52-68.
6. Pulz, O. (2001). Photobioreactors: production systems for phototrophic microorganisms. *Applied microbiology and biotechnology*, *57*(3), 287-293.
7. Ras, M., Lardon, L., Bruno, S., Bernet, N., & Steyer, J. P. (2011). Experimental study on a coupled process of production and anaerobic digestion of *Chlorella vulgaris*. *Bioresource technology*, *102*(1), 200-206.
8. Ratledge, C. (2004). Fatty acid biosynthesis in microorganisms being used for single cell oil production. *Biochimie*, *86*(11), 807-815.
9. Rocha, J. M., Garcia, J. E., & Henriques, M. H. (2003). Growth aspects of the marine microalga *Nannochloropsis gaditana*. *Biomolecular engineering*, *20*(4-6), 237-242.
10. Scragg, A. H., Spiller, L., & Morrison, J. (2003). The effect of 2, 4-dichlorophenol on the microalga *Chlorella* VT-1. *Enzyme and microbial technology*, *32*(5), 616-622.
11. Wijffels, R. H., & Barbosa, M. J. (2010). An outlook on microalgal biofuels. *Science*, *329*(5993), 796-799.
12. Tang, Y., Ma, X., & Lai, Z. (2011). Thermogravimetric analysis of the combustion of microalgae and microalgae blended with waste in N₂/O₂ and CO₂/O₂ atmospheres. *Bioresource technology*, *102*(2), 1879-1885.
13. Pane, L., Franceschi, E., De Nuccio, L., & Carli, A. (2001). Applications of thermal analysis on the marine phytoplankton, *Tetraselmis suecica*. *Journal of thermal analysis and calorimetry*, *66*(1), 145-154.
14. López-González, D., Fernandez-Lopez, M., Valverde, J. L., & Sanchez-Silva, L. (2014). Kinetic analysis and thermal characterization of the microalgae combustion process by thermal analysis coupled to mass spectrometry. *Applied Energy*, *114*, 227-237.
15. Konga, A. K., Muchandi, A. S., & Ponnaiah, G. P. (2017). Soxhlet extraction of *Spirogyra* sp. algae: an alternative fuel. *Biofuels*, *8*(1), 29-35.
16. Sadeghinezhad, E., Kazi, S. N., Badarudin, A., Oon, C. S., Zubir, M. N. M., & Mehrali, M. (2013). A comprehensive review of bio-diesel as alternative fuel for compression ignition engines. *Renewable and Sustainable Energy Reviews*, *28*, 410-424.
17. Chen, A. P., Basha, R. H., & Torii, S. (2014). Classification of Biomass Based on Its Role of Combustion for Sustainable and Renewable Source of Energy Using Proximate and Ultimate Analysis. *International Journal of Earth Science & Engineering*, *7*(01).
18. Chen, A. P., & Torii, S. (2015). Characterized the Microalgae (*Chlorella* and *Spirulina*) and Macro Algae by Using TGA and Bomb Calorific Meter for the Biomass Energy Application. In *Proceedings of the International Conference on Power Engineering-15 ICOPE* (Vol. 15).
19. Sohail, S., Mumtaz, M. W., Mukhtar, H., Touqeer, T., Anjum, M. K., Rashid, U., ... & Choong, T. S. Y. (2020). *Spirogyra* oil-based biodiesel: Response surface optimization of chemical and enzymatic transesterification and exhaust emission behavior. *Catalysts*, *10*(10), 1214.
20. Ge, S., Madill, M., & Champagne, P. (2018). Use of freshwater macroalgae *Spirogyra* sp. for the treatment of municipal wastewaters and biomass production for biofuel applications. *Biomass and bioenergy*, *111*, 213-223

197

198