Short Research Article

Characterization of *Spirogyra* using Thermogravimetric/ Derivative Thermogravimetric (TG/DTG) analysisand Bomb Calorimeter for EnergyApplication

.

ABSTRACT

Biomassisusuallyconsideredasdifferenttypesoflignocellulosicmaterialshavingvariedcompositionpotentialto utilize in the useful forms of energy as a substitute of conventional fossil fuels. Algal biomass has multi facet applicationin research and development such as source of nutrients, biochemical, cosmetics andbiofuels. However, thisnewly developedenergysourcemetthe requirement of low and medium scale power generation due to low thermal efficiency.Inpresentstudy,freshwateralgae*Spirogyra*takenassourceofbiomassandanalyzedforThermogravimetric (TG)andcalorificvaluesanalysis.WefoundthecalorificvalueIs2129.4Kcal/KgandTGAresultsshowthatalgalbiomassdecreaserapidlyafterreachingthetemperatureover300^{0}C.Theresultobtainedinthispapermaybeusedinfutureasreference material for algae based biomass for energyapplication.

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

1.INTRODUCTION

Postindustrialrevolutionhasnotonlyincreasedthedemandofenergybutalsopollutedtheenvironmentmanifold.There isasignificantincreaseofemissionofCO_2,SO_X,NO_Xandparticulatematterintheenvironmentduetoanthropogenic activities.Inthepresentscenariocleanandemissionlessenergyisnotonlyachoicebutalsoacompulsionunder obligationofKyotoprotocoltocurbtheemissionofvariousGHGs.Todealwithglobalwarmingandavoiddangerous climate change, keeping the temperature below 2^{O}C is also desirable under the Paris agreement. All these concernsmay be addressed by introducing renewable energy resources. (1.) Renewable energy comprisessolar, wind, hydropower, tidalwavesandbiomassenergy.Algalbiomassmainlycomposedofcellulose,hemicelluloseandlignin.Biomassis usuallyconsideredasdifferenttypesofwastematerialshavingvariedcompositionthatmaybeutilizedasasubstituteof conventionalfossilfuels.Compositionwiseitisconstitutedofcarbon,nitrogen,hydrogen,oxygenandsulphur.Biomass energy is not only clean source of energy, but also considered as fuel substitution of fossil fuels having the samebenefits intermsofoperationandimprovingenvironmentalbenefitsofenergygeneration.Asanenergysourcebiomasscanbe used directly or indirectly converted into other energy forms through various routes namely biochemical& thermochemical. Besidesthatbiomassresourceshavemorepotentialthanotherrenewableenergyintermsof sustainability.The1stand2ndgenerationfuels,consistingofmaize,cerealcropsandsoybeans,areenvironmentally friendly but conflict with food supply. Algae come under 3rdgeneration food mainlycomposed of lipids, proteins and small fraction of cellulose and are different from its feedstock of a crop food(2.).

ThealgalapplicationofenergygenerationwasinitiatedbyU.S.governmentin1960andcommonlyknownasASP (AquaticSpeciesProgram),forthedevelopmentofalgaebasedtechnology.ItwasfurtherextendedinHawaii,justafter the period of oil crisis and mid-east war. The Japanese government also started the project in time period of 1990-96with theinnovativeideaofCO_2fixation.Theseprojectsconcludedwithvaluableresultslikenewstrainsdevelopmentforlipid production, principle of aquaculture and photo bioreactor design. In 21stcentury, continuous efforts are mainly focusedon how to grow algae in large aquaculture and make the economic balance.(10)

In India, algae projects started in 2011 incollaborationof nine premier research institutes led by CSMCRI (CentralSalt MarineandChemicalResearchInstitute)withthedevelopmentofalgaebiodieselwithtraditionalbiodiesel.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 anotherphase. Although production of biodiesel has shown that harvesting procedure and lipid production put the environment at riskand costenergywaste.Somestudiesusefermentationprocesses,whichareanaerobicinnatureinwhichsugarsare convertedintocellularenergyandtherebyproduceethanolandcarbondioxideasmetabolicwasteproducts.Anaerobic digestionessentiallyoccursinabsenceofoxygenandmediatedbymicroorganismstoconvertbiomassintobiogas,butit 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 fromJatropha, some strains of Algae are selected and harvested for obtaining the different products like bio oil, syngas throughdifferent processeslikeliquefaction&gasification.Althoughdifferentprocessesareavailableforconversionofbiomassinto energy,thermochemicalconversionisconsideredasaoneofthepromisingroutes.Thermochemicalconversionincludes combustion,gasification,pyrolysisandliquefaction.Combustionisthechemicalreactionoccurringathightemperatureto convertbiomassintousefulenergyproductsinpresenceofoxygen.Recentlyresearchisgoingonfortheproductionof biodieselthroughthepyrolysisprocess.Althoughveryfewstudiesaboutcombustionbehaviorofalgaehavebeen reported, mostly studied about microalgae *Chlorella* species. The combustion behaviors are analyzedthrough thermogravimetric (TG) analysis, of biomass in different oxygen concentrations and N_2/O_2 ratio (12,13).

In 2014, Lopez-Gonalez (14) reported that certain microalgae like *chlorella vulgaris, Scenedesmusalmeiensisand Nannochloropsisgaditana*are potential biomass for combustion application through TGA-MS-DSC analysis. In thisstudy, we analyze the *Spirogyra* in TG/DTG and bomb calorimeter to provide the detail information of algalbiomass mainly for combustion application**.**

2. MATERIAL ANDMETHODS

Toanalyzealgalbiomassforenergyproduction,wehaveselectedSpirogyrabasedontheirchemicalcomposition.& specialties in energy application analyzed through TG/DTG and bombcalorimeter**.**

2.1 Biomass Selection: Algae has explored for decades mainly due to energy application. For that we haveto analyzechemicalcompositionthroughproximateandultimateanalysis.However,thequantity&potentialinbiomassfor energy production is also important for energy production. Therefore, in this study, we selected *Spirogyra sp.* thathas beenusedinmulti-application,productionofenergyisoneofthem.Recently,ithasbeenreportedthat*Spirogyra sp.* having potential for producing biodiesel (15). The algal biomasses are collected from ponds nearby the Meerutdistrict Uttar Pradesh, India. The collected algal biomasses are kept for sun drying and powdered for furtheruse.

Table 1: The lipid percentage of algae andmicroalgae

Microalgae/Macroalgae species.	Lipid (% Dry wt.)
Spirogyra	20-32
Monallanthussalina	>20
Nannochloropsis sp. (fresh water)	20-35
Nannochloropsis sp.(sea water)	31-68
Neochlorisoleoabundans	35-54
Botryococcusbraunii	25-75
Chlorella sp.	28-32
Phaeodactylumtricornutum	20-30
Nitzschia sp.	45-47
Cylindrotheca sp. 16-37	16-37
Crypthecodiniumcohnii	20

Dunaliellaprimolecta	23

References[3-9]

2.2 Calorific Value Detection: The calorific value of algal biomass is determined by evaluation of gross calorificvalue (GCV)ofpreparedsample.Itmeasurestheenergycontentofaunitmasssampleinabombcalorimeter.Inthismethod calorificvalueisdeterminedbyburningaweighedbiomasssampleundercontrolledconditioninanoxygenbomb calorimeter.

2.3TG/DTGAnalysis: Thealgaesampleinpowderformkeptinoven(40^{0}C).overnightbeforetestingthestarting temperatureis90^{0}Cforaround30minutesmainlyfordryingpurposeofthebiomassandkeepthemoisturewithinlimit. Finally temperature increased up to 900^{0}C to analyze the thermal stability and oxidative stability ofsample.

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

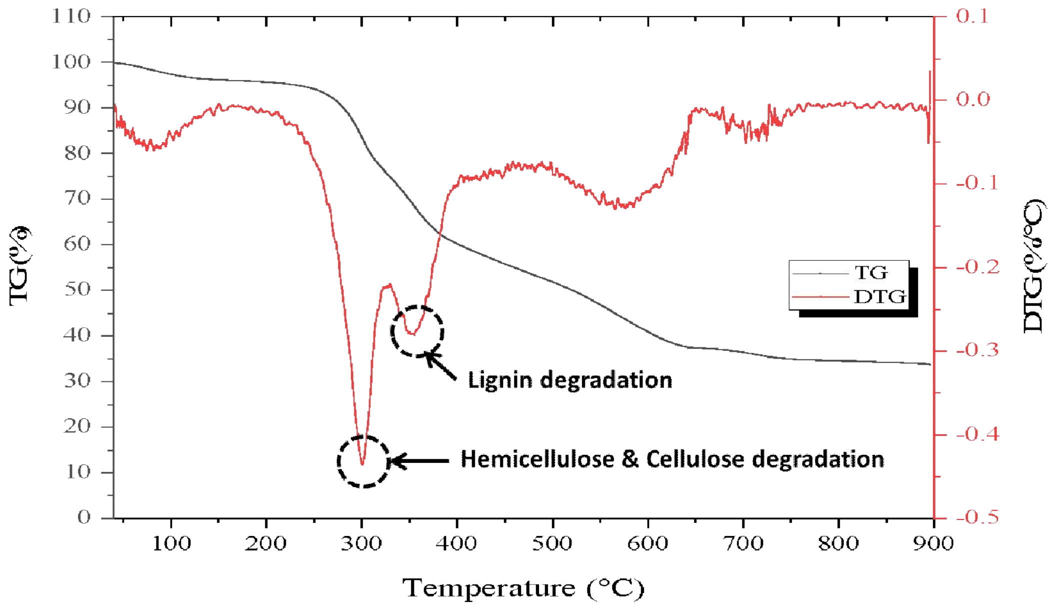
	J/g	**Kcal/KG**	**Types of Biomass**	**Reference**
.Spirogyra	8,900.89	2,129.4	Non-food	In this study
Chlorella	21,174.5	5,057.4	Non-food	[18]
Spirulina	20,866.3	4,983	Non-food	[18]
Coal	28,665.6	6,846.7	Fossil fuel	[18]
Diesel	42,000~49,500	10,047.8~11,842.1	Fossil fuel	[16]
Coconut	35,000~38,100	8,373.2~9,114.8	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 ANDDISCUSSION:

The algal biomass samples were tested for calorific value and TG /DTGanalysis**.**

3.1 **Calorific Value Analysis of *Spirogyra*:** Each sample after drying had been tested for its calorific value. Tomake analysiscomparableandmeaningful,examplesoffossilfuelslikecoal&dieselhadalsobeentakenasreference.The calorificvalueofcoal&vegetableoilishigherthanthatofalgalbiomass(Table 2)Howeveralgalbiomassincombinationwithother biomass can be used to get better results in terms of calorificvalue.

3.2 **TG&DTG of*Spirogyra*:**Themajorcomponentsofalgalbiomassesarewater,lipid,protein,cellulose&lignin. TheTG&DTGcurveisshowninfigure1.Thesampledecreasedafter300^{0}Candabout65%ofthesampleburntafter 900^{O}C.IntheDTGcurve,thefirstpeakat300^{O}Coccursduetocellulosedecayandthesecondpeakat355^{0}Cisdueto lignin decay of the lignocellulosic biomass.



.

Figure: 1 TG & DTG Curves of Spirogyra

3.3Discussion: 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 asSpirogyra[19]ThecalorificvalueofalgalbiomassshowthatpotentialofalgaetobematerialasbiofuelandTG analysisresultsshowthatthermalstabilityofthebiomassbehaviorincombustionsystem.Accordingtoresultcalorific valueof*Spirogyra*isnotonlylessthanfossilfuelbutalsolessthanothermicroalgaeItmayduetohigherpercentageof lignin in sample biomass, which remains unburnt in samples about 35% even at high temperature. In TGtesting combustion take place in two stages. In first stage almost carbohydrate combusted,in second stage nitrogen and sulphur combustedasapartofproteindegradation.TGanalysisresult(Fig:1)showsthesampledecreasedrapidlyat300^0Candbeyond650^0C theratebecomesalmostconstantbecausepresenceoflignin.DTG(Derivativethermogravimetric)istheinterpretation of weight loss or weight gain over temperature and curve shows that hemicellulose & cellulosedegradationoccurs at 300^0C and lignin degradation started at355^0CIt has been also found that apart from energy generation *Spirogyrasp*. demonstrated potential for the treatment of municipal waste water and biochemical component 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 *Spirogyrasp.* 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.Besidesthis,algalbiomassshouldbemixedwithothermaterialstoincreasethecalorificvalueforbetterheatperformance. ThecalorificvalueandTGanalysisshowthatalgalbiomasshaspotentialasabiofuelseitheraloneorincombinationwithotherbiomassforbetterresults.Sometimesthecompositionofmulticomponentsystemsresultsbetter,whenTGcoupledwithMS (TG-MS) with risingtemperature

5.ABBREVIATIONS

TGA-MS-DSC: Thermogravimetric analysis-Mass spectrometry-Differential scanning calorimetry
TG :Thermogravimetry
DTG:Derivativethermogravimetry

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 andSustainable Energy Reviews*, *16*(7),5280-5284.

2.Sims,R.,Taylor,M.,Saddler,J.,&Mabee,W.(2008).From1st-to2nd-generationbiofueltechnologies.*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).IncreaseinChlorellastrainscalorificvalueswhengrownin 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 microbiologyand 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 microalgaNannochloropsis gaditana. *Biomolecular engineering*, *20*(4-6),237-242.

10.Scragg,A.H.,Spiller,L.,&Morrison,J.(2003).Theeffectof2,4-dichlorophenolonthemicroalgaChlorellaVT-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).Thermogravimetricanalysisofthecombustionofmicroalgaeandmicroalgae blended with waste in N2/O2 and CO2/O2 atmospheres. *Bioresource technology*, *102*(2),1879-1885.

13.Pane,L.,Franceschi,E.,DeNuccio,L.,&Carli,A.(2001).Applicationsofthermalanalysisonthemarine phytoplankton, Tetraselmissuecica. *Journal of thermal analysis and calorimetry*, *66*(1),145-154.

14.López-González,D.,Fernandez-Lopez,M.,Valverde,J.L.,&Sanchez-Silva,L.(2014).Kineticanalysisand thermal characterization of the microalgae combustion process by thermal analysis coupled tomass spectrometry. *Applied Energy*, *114*, 227-237.

15. Konga, A. K., Muchandi, A. S., &Ponnaiah, G. P. (2017). Soxhlet extraction of Spirogyra sp. algae: analternative 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 comprehensivereviewofbio-dieselasalternativefuelforcompressionignitionengines.*Renewableand Sustainable Energy Reviews*, *28*,410-424.

17.Chen,A.P.,Basha,R.H.,&Torii,S.(2014).ClassificationofBiomassBasedonItsRoleofCombustionfor SustainableandRenewableSourceofEnergyUsingProximateandUltimateAnalysis.*InternationalJournalof Earth Science & Engineering*,*7*(01).

18. Chen, A. P., & Torii, S. (2015). Characterized the Microalgae (Chlorella and Spirulina) and Macro Algae byUsing TGAandBombCalorificMeterfortheBiomassEnergyApplication.In*ProceedingsoftheInternational Conference on Power Engineering-15 ICOPE* (Vol. 15).

.

19Sohail, 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

: