Thermogravimetric analysis of gasification and pyrolysis of algae biomass

Maxim Tsvetkov[1*], *Andrey* Zaichenko[1], *Dmitry* Podlesniy[1], *Elena* Latkovskaya[2], *Yuliya* Tsvetkova[1], and *Vladimir* Kislov[1]

[1]Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, Chernogolovka, Russia
[2]Sakhalin State University, Yuzhno-Sakhalinsk, Russia

Abstract. In the present paper, the case of the brown algae *Saccharina japonica* from Aniva Bay (Sea of Okhotsk, Sakhalin Island) was investigated by a thermogravimetric analysis up to 700°C at different atmospheres. The elemental composition, lower heating value, ash content, and biochar yield of the algae were examined. The analysis showed that carbohydrates like alginate, mannitol, fucoidan, and laminarin were decomposed between 250-350°C, while proteins and lipids were burned out between 500-550°C.

1 Introduction

The global supply of traditional energy has been negatively affected by rapid population growth and unrestricted industrialization activities [1-2]. Many countries still heavily rely on fossil fuels to meet their increasing energy needs [3-4]. However, this prolonged dependence on fossil-based fuels exacerbates the already alarming effects of climate change [5]. Energy-related activities have emitted around 30-40 billion metric tons of carbon dioxide, which contributes to the greenhouse effect [6]. Unless there are significant changes in technology and policies, both energy consumption and emissions will continue to rise in the coming decades [7].

Different approaches have been suggested to address greenhouse gases and their associated problems, ranging from partial to complete solutions [8]. For example, technology of carbon capture, utilization, and storage (CCUS) has the capability to decrease greenhouse gas emissions by capturing atmospheric carbon dioxide or CO_2 emissions from fixed sources [9]. According to the International Energy Agency, CCUS is expected to play a significant role in achieving a 19% reduction in greenhouse gas emissions by 2070, effectively eliminating 6.9 Gt CO_2 annually [10].

There are alternative approaches to reduce carbon dioxide emissions. These include enhancing the efficiency of current technologies [11], creating new environmentally friendly devices [12], and transitioning to renewable energy sources [13]. The adoption of renewable energy sources is particularly promising as it offers a rapid solution to move away from fossil fuels [14].

* Corresponding author: tsvetkovmv@gmail.com

After the energy crisis of the 1970s, various countries have shown significant interest in biomass as a renewable and environmentally friendly fuel source to promote domestic energy production while minimizing harm to the environment. Because biomass is abundantly available worldwide, it holds the top spot as the most dependable among all known renewable energy sources for energy production [15]. Thermochemical conversion processes play a crucial role in the efficient and long-term utilization of biomass. These processes, such as direct combustion, gasification, pyrolysis, torrefaction and liquefaction offer versatility by enabling the production of diverse forms of bioenergy and bioproducts from various types of raw biomass and waste residues [16-19].

Gasification is a versatile technology that plays a crucial role in utilizing biomass [20]. It allows utilizing of various types of biomass and enables the production of a wide range of products [21]. Essentially, gasification can convert any form of biomass into syngas, which predominantly consists of hydrogen, carbon monoxide, carbon dioxide, and methane [22]. This syngas can then be used to generate various forms of energy or energy carriers, such as heat, power, biofuels, hydrogen, biomethane, and even chemicals. Established technical processes exist for synthesizing Fischer-Tropsch diesel, dimethyl ether, methanol, and methane from this syngas. The process of biomass gasification involves partially oxidizing the carbon of biomass at high temperatures with a controlled amount of oxidant, which can be air, pure oxygen, or steam [23]. The properties and composition of the resulting syngas are influenced by factors such as the type of biomass used, the gasifier design, and the operational conditions, including the choice of oxidant and temperature in the gasifier. When air is used for gasification, the resulting syngas has a heating value of 5-7 MJ/m3 [24]. However, when pure oxygen or steam is employed as the oxidant, the heating value of the syngas increases by 2-3 times.

Pyrolysis refers to the decomposition of biomass through heating without oxygen presence, leading to the creation of charcoal, liquids, and gases as byproducts [25]. The result of this process is called biochar or char, which has high carbon content. Some of the volatile materials are turned into a liquid called tar or bio-oil, along with a mix of non-condensable gases. The bio-oil is stored for later use in energy production, while the gases are used to provide heat for the pyrolysis reactor [26]. The pyrolysis products are produced through the decomposition of the solid biomass and the transformation of volatile materials into gases, secondary tar, and char [27]. One great advantage of pyrolysis is that it can be carried put at lower temperatures (typically between 400-700°C) compared to gasification (>700°C) and combustion (>900°C) processes. Pyrolysis can be categorized as either slow or fast depending on the operating conditions. In slow pyrolysis, biochar is produced through long residence times lasting from hours to days under low temperatures (around 400 °C). On the other hand, fast pyrolysis involves a very short residence time (<2 s), an extremely high heating rate (~100 °C/s), and a moderate temperature (around 500 °C), resulting in a high yield of bio-oil [28]. Various reactors and processes have been developed for pyrolysis of biomass from sources such as wood and algae. These include the bubbling fluidized-bed reactor [29], circulating fluidized-bed reactor [30], filtration combustion reactor [31-32], and hybrid filtration combustion reactor [33]. Numerous studies have utilized TGA to analyze gasification and pyrolysis processes Algae, found in aquatic habitats, are part of the plant kingdom and conduct photosynthesis with the help of chlorophyll. Unlike traditional plants, they don't have differentiated roots, stems or leaves. They can be found in various environments such as freshwater, lakes, ponds and oceans. While most algae are small, some marine seaweed can grow to lengths tens of meters. Algae play a crucial role in converting carbon dioxide (CO_2) into valuable substances like lipids, proteins, and carbohydrates [34-35]. Certain types of algae, particularly seaweed, are notably recognized for their ability to produce and store large amounts of carbon materials due to their impressive size and the rate of growth. One example of this is Saccharina

japonica (outdated name Laminaria japonica), a species of brown algae rich in carbohydrates that can be utilized for anaerobic fermentation [36]. Interestingly, pre-treatments for this seaweed may require minimal or no special processing.

Macroalgae biomass, through processes such as anaerobic digestion, pyrolysis, and gasification, can generate methane (CH_4), bio-oil, and syngas by using thermochemical approaches [37]. This opens up possibilities for alternative energy sources and diverse for various applications of algae [38].

Thermogravimetric analysis (TGA) is a dependable technique used to investigate the mechanisms and kinetics of biomass gasification and pyrolysis. It entails measuring changes in the mass of the sample per unit volume over controlled temperature conditions [39]. TGA operates similarly to a laboratory gasifier, allowing the use of oxidizing agents as carrier gases and the attainment of high reactor temperatures. By combining TGA with advanced technologies like Fourier transform infrared spectroscopy (FTIR), researchers can obtain additional valuable insights into the thermal decomposition of samples [40], particularly to develop precise kinetic models that elucidate the underlying mechanisms once specific onset temperatures or residence times.

This study aims to identify the thermal degradation parameters of algae by examining the combustion behavior of *Saccharina japonica* algae in order to predict how it may be decomposed during combustion.

2 Methodology

Algae were collected from marine bay (Aniva Bay) located on Sakhalin Island in the Sea of Okhotsk. The composition of algae biomass can vary between batches and over the course of a harvesting season. Therefore, algae from the same batch were used for all the experiments.

To eliminate sea salts, sand, and other impurities, the original *Saccharina japonica* seaweed samples underwent three rounds of washing with distilled water in an ultrasonic bath. Following the washing process, the samples were dried in a Binder oven at 105°C until a constant weight was achieved, with measures taken to ensure that the samples were not damaged. To model the processes of pyrolysis of the algae *Saccharina japonica*, it was analyzed by TGA/DSC on a synchronous thermal analyzer “STA 449 F3 Jupiter” coupled with a quadrupole mass spectrometer “QMS 403 Aëolos Quadro” (NETZSCH, Germany, 2019). The samples were heated from room temperature to temperatures of 700°C at a rate of 30°C/min, holding at the final temperature for one hour. The heating rate has minimal impact on the characteristics of thermogravimetric curves [41]. Consequently, a heating rate of 30°C/min was selected for this work, since it’s typical rate of many thermochemical processes [42-43].

The detailed method for producing biochar from the algae *Saccharina japonica* is described in [38], and the heating temperature regime aligned with this one which used in our study. To carry out elemental analysis of the algae *Saccharina japonica* and the biochar from the algae *Saccharina japonica* by combustion in an oxygen stream, we used an elemental composition analyzer CHNS Vario El Cube (Elementar Analysensysteme GmbH).

3 Results and Discussion

The results of TG curves of the *Saccharina japonica* samples at final temperature equal 700°C at different atmospheres are shown in Figures 1 and 2.

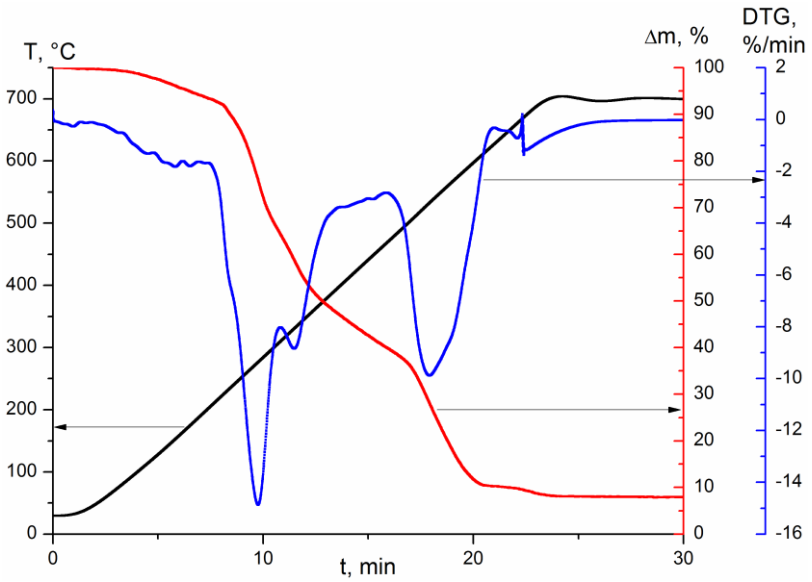

Fig. 1. TG curves of *Saccharina japonica* at air atmosphere (heating rate: 30 °C/min).

The DTG curve at air atmosphere had three extensive peaks between 30 and 700°C: 276°C, 330°C and 532°C. The patterns of DTG showed similar peaks at inert atmosphere: 271 and 324°C. However, the maximum of the peaks is shifted to the left and there is no peak at temperatures above 500°C. As demonstrated previously, the first and second peaks between 250-350°C corresponded to the decomposition of carbohydrates like alginate, mannitol, fucoidan, and laminarin, while the third peak between 500-550°C was associated with the burnout of proteins and lipids, according to [44].

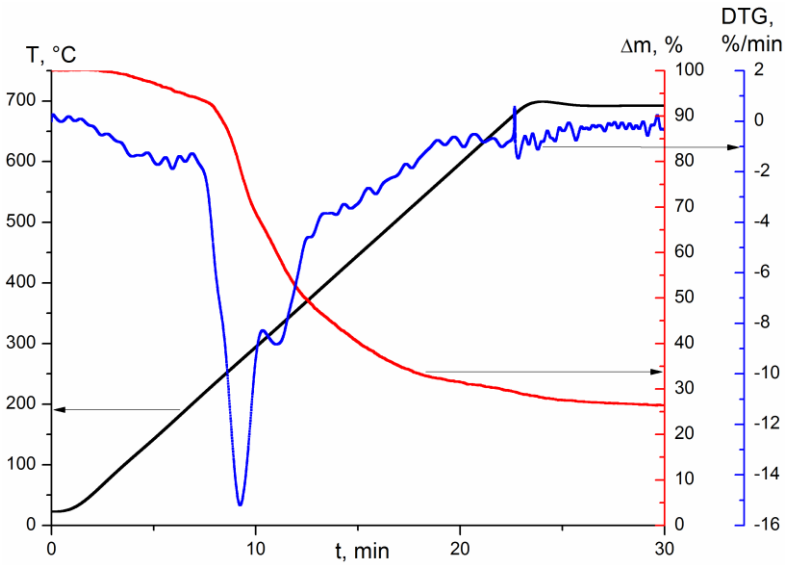

Fig. 2. TG curves of *Saccharina japonica* at helium atmosphere (heating rate: 30 °C/min).

The TG curves allow calculating the ash and char amounts at a final temperature of 700°C. The ash content is 7.86% and semi-coke is 16.45%, determined from the mass fraction differences of residues formed in air vs helium. Given the semi-coke amount and elemental compositions of algae *Saccharina japonica* and its biochar, the lower calorific value and other properties can be estimated. The lower heating value was calculated using the Mendeleev formula.

The elemental composition (excluding ash) and lower heating value of the algae *Saccharina japonica*, as well as one of the biochar derived from *Saccharina japonica* at 700 °C are provided in Table 1. The lower heating values of fuels were determined based on their dry mass.

Table 1. Characteristics of the algae *Saccharina japonica* and the biochar derived from the algae *Saccharina japonica* (wt.%).

Element / Sample	C	H	N	S	O (by difference)	Lower heating value, MJ/kg
Saccharina japonica	39.82	4.99	1.21	1.04	45.08	13.85
Biochar from the *Saccharina japonica* (at 700 °C)	45.06	1.28	1.95	1.74	42.11	12.2

4 Conclusion

This study examined the behavior of the algae *Saccharina japonica* when heated at helium and air atmospheres. The goal was to better understand the thermochemical processes of algae gasification and pyrolysis. A deeper insight into the characteristics of these processes is crucial for the thermal transformation and industrial utilization of algae. Thermogravimetric analysis can help optimize thermal process parameters. This increases the value of algae by assessing their thermal stability. Thermogravimetric analysis is also an important method for determining the dynamics and kinetics of thermal decomposition across various algal species. However, TGA only observes thermal degradation. It can be combined with other analytical techniques like Fourier transform infrared spectroscopy, mass spectrometry, and gas chromatography–mass spectrometry to study evolved gases and other thermochemical properties. Integrating artificial intelligence with TGA techniques offers a promising approach, along with those techniques, for optimizing parameters and developing bioenergy production.

Acknowledgement

This work funded by the Ministry of Science and Higher Education of Russia, theme #FFSG-2024-0016 "Development of physical and chemical foundations of promising technologies and materials for energy-efficient use of traditional and alternative carbon-containing resources" and theme #FEFF-2022-0027 "Carbon balance of biomorpholithosystems of the coast and adjacent marine areas of the marginal seas of the Far East". This work was performed using the equipment of the Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS (http://www.icp.ac.ru/en).

References

1. A. Rehman, M.M. Alam, I. Ozturk, R. Alvarado, M. Murshed, C. Işık, H. Ma, Environ. Sci. Pollut. Res., **30(4)**, 9699-9712 (2023)

2. X. Yuan, C. W. Su, M. Umar, X. Shao, O.R. Lobonţ, J. Environ. Manage., **308**, 114648 (2022)
3. P.F. Borowski, Energies, **15(24)**, 9289 (2022)
4. J.L. Holechek, H.M. Geli, M.N. Sawalhah, R. Valdez, Sustainability, **14(8)**, 4792 (2022)
5. L. Yang, X. C. Wang, M. Dai, B. Chen, Y. Qiao, Energy, **228**, 120533 (2021)
6. E. Yoo, U. Lee, G. Zang, P. Sun, J. CO_2 Util., **65**, 102212 (2022)
7. X. Li, C. J. Raorane, C. Xia, Y. Wu, Fuel, **334**, 126684 (2023)
8. L. Bentoumi, A. Miles, Z. Korei, Solar Energy, **268**, 112311 (2024)
9. A.M. Gambelli, Energies, **16(10)**, 4077 (2023)
10. Y. Guo, L. Luo, T. Liu, L. Hao, J. Environ. Sci., **136**, 682-697 (2023)
11. K. Mishra, S.S. Siwal, A.K. Saini, V.K. Thakur, Fuel, **332**, 126169 (2023)
12. T.M. Gür, Prog. Energy Combust. Sci., **89**, 100965 (2022)
13. M. Tsvetkov, A. Zaichenko, D. Podlesniy, E3S Web of Conferences, **419**, 01010 (2023)
14. M.V. Tsvetkov, V.M. Kislov, E.A. Salganskii, Russ. J. Appl. Chem., **92**, 1465-1479 (2019)
15. J. Lee, S. Kim, S. You, Y.K. Park, Renew. sustain. energy rev., **178**, 113240 (2023)
16. M. Toledo, A. Arriagada, N. Ripoll, E.A. Salgansky, M.A. Mujeebu, Renew. Sustain. Energy Rev., **177**, 113213 (2023)
17. V.V. Dorokhov, G.S. Nyashina, P.A. Strizhak, J. Environ. Sci., **137**, 155-171 (2024)
18. I.A. Makaryan, E.A. Salgansky, V.S. Arutyunov, I.V. Sedov, Energies, **16(6)**, 2916 (2023)
19. V.M. Zaichenko, K.O. Krysanova, Y.D. Pudova, A.Y. Krylova, Solid Fuel Chem., **56(4)**, 259-264 (2022)
20. A. Gani, M. Zaki, R. Mamat, M. Nizar, S. M. Rosdi, S. Yana, R. E. Sarjono, Case Stud. Chem. Environ. Eng., **8**, 100439 (2023)
21. V.M. Kislov, Y.Y. Tsvetkova, E.N. Pilipenko, M.A. Repina, M.V. Salganskaya, Russ. J. Phys. Chem. B, **17(2)**, 374-380 (2023)
22. V.M. Kislov, M.V. Tsvetkov, A.Y. Zaichenko, D.N. Podlesniy, M.V. Salganskaya, Y.Y. Tsvetkova, E.A. Salgansky, Russ. J. Phys. Chem. B, **17(4)**, 947-952 (2023)
23. M. Toledo, A. Arriagada, N. Ripoll, E.A. Salgansky, M.A. Mujeebu, Renew. Sustain. Energy Rev., **177**, 113213 (2023)
24. G. Nyashina, V. Dorokhov, D. Romanov, P. Strizhak, Environ. Sci. Pollut. Res., **30(9)**, 24192-24211 (2023)
25. L.R. Jeeru, F.K. Abdul, J.S. Anireddy, V.P. Ch, K.N. Dhanavath, Chem. Eng. Process., **185**, 109311 (2023)
26. V.M. Kislov S.V. Glazov, M.V. Salganskaya, E.N. Pilipenko, Y.Y. Tsvetkova, Russ. J. Appl. Chem., **94(3)**, 347-353 (2021)
27. V.M. Kislov, A.F. Zholudev, M.B. Kislov, E.A. Salgansky, Russ. J. Appl. Chem., **92**, 57-63 (2019)
28. D. Xu, J. Lin, R. Ma, J. Hou, S. Sun, N. Ma, Fuel, **333**, 126449 (2023)
29. A. Soria-Verdugo, E. Cano-Pleite, A. Passalacqua, R. O. Fox, Fuel, **339**, 127365 (2023)

30. S.J. Kim, J.H. Moon, S.H. Jo, S.J. Park, Fuel, **334**, 126612 (2023)
31. V. M. Kislov, M. V. Tsvetkov, A. Y. Zaichenko, D. N. Podlesniy, E. A. Salgansky, Russ. J. Phys. Chem. B, **15**, 819-826 (2021)
32. A. Arriagada, M. Toledo, R. E. Hayes, P. A. Nikrityuk, J. Energy Inst., 101489 (2023)
33. S. Caro, D. Torres, M. Toledo, Int. J. Hydrog. Energy, **40(6)**, 2568-2577 (2015)
34. M. Farghali, I. M. A. Mohamed, A. I. Osman, Environ. Chem. Lett. **21**, 97-152 (2023)
35. V. V. Afanas' ev, E. M. Latkovskaya, A. V. Uba, A. I. Levitsky, Conference on Physical and Mathematical Modeling of Earth and Environment Processes, 495-501 (Cham: Springer Nature Switzerland, 2022)
36. M. Narayanan, Renew. Sustain. Energy Rev., **190**, 114081 (2024)
37. M.V. Tsvetkov, A.Yu. Zaichenko, D.N. Podlesniy, M.A. Repina, A.A. Glukhov, E3S Web of Conferences **419**, 01010 (2023)
38. A.A. Belmesov, A.A. Glukhov, R.R. Kayumov, Coatings, **13(12)**, 2075 (2023)
39. C.B. Felix, W.H. Chen, A.T. Ubando, Chem. Eng. J., **445**, 136730 (2022)
40. M. Li, Y.S. Zhang, S. Cheng, B. Qu, Chem. Eng. J., **457**, 141368 (2023)
41. J. Escalante, W.H. Chen, M. Tabatabaei, Renew. Sustain. Energy Rev., **169**, 112914 (2022)
42. A.Y. Zaichenko, M.V. Tsvetkov, D.N. Podlesniy, M.V. Salganskaya, E.A. Salgansky, J. Phys. Conf. **1276(1)**, 012083 (IOP Publishing, 2019)
43. A.I. Osman, M. Farghali, I. Ihara, Environ. Chem. Lett., **21(3)**, 1419-1476 (2023)
44. J.H. Choi, S.S. Kim, H.V. Ly, J. Kim, H.C. Woo, Biomass & Bioenergy, **98**, 112-123 (2017)