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PRODUCTION OF BIOFUEL BASED ON THE TRANSFORMATIONS OF GREENHOUSE GASES

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Abstract. The paper presents ways to reduce the carbon footprint through the reuse of microalgae biomass as biofuels (related to bio -CCU). The processing of microalgae biomass into biochar has applications in c arbon sequestration, as a feedstock for thermal energy production, as well as activated carbon and adsorption of toxic compounds from polluted air, water and soil. That's why presents the results of complex thermogravimetric and differential thermal analyzes of the heat-generating capacity of the biofuel from chlorophyll-synthesizing microalgae *Chlorella vulgaris*, obtained as a result of the sorption of greenhouse gases formed during the burning of solid, liquid, or gaseous fuels. Combustion of samples of biofuel obtained from microalgae, which absorbed, in addition to c arbon dioxide, sulfur dioxide and nitrogen oxides, which is present in ga s emissions, is accompanied by more significant exothermic effects. According to the results of thermal studies, it was established that the heat-generating capacity of such biofuel exceeds the heat-generating capacity of aspen (*Populus tremula),* which is an alternative source of energy in the territory of Ukraine, and is close to the heat-generating capacity of the selectively bred energetic willow (*Salix Viminalis)*.

Keywords: thermogravimetric analyses, differential thermal analyses, microalgae Chlorella vulgaris, greenhouse gases, alternative fuel.

1. Introduction

The escalating emission of carbon dioxide (CO_2) represents a global hazard that demands collaborative efforts between policymakers and scientists. Key international agreements, such as the Paris Agreement and the United Nations Climate Change Conference (COP26), underscore the urgency of addressing anthropogenic climate change as a worldwide public concern. This review examines prominent CO_2 reduction strategies, including carbon capture and storage (CCS), carbon capture, utilization, and storage (CCUS), and carbon capture and utilization (CCU). Among these methods, CCU stands out for its potential to recycle captured CO_2, transforming it into a resource for generating emissions neutral or negative value-added products (VAPs). Within CCU approaches, biologically-mediated CCU (bio-CCU) employing microalgae emerges as a promising biotechnology for signifycantly curbing CO_2 emissions (Dyachok et al., 2021; Dyachok et al., 2020; Dyachok et al., 2017). This review elaborates on the mechanisms of photosynthesis utilized by microalgae to sequester CO_2 and incorporate it into valuable biomolecules. Microalgae efficiently utilize CO_2 as precursors for macromolecules such as lipids, proteins, carbohydrates, and pigments, all discussed in the context of industrial relevance and market value. The review underscores the biofixation potential of microalgae, evident in the diverse VAPs they produce (Camargo & Lombardi, 2018). The rapid reproduction rate and ability to thrive in extreme environmental conditions make single-celled algae, such as microalgae, highly advantageous. Algae demonstrate high proliferation rates, fix CO_2 into carbohydrates and lipids, and can grow in wastewater, contributing to pollution treatment (Lara-Gil et al., 2016; Aslam et al., 2017). CO_2 plays a vital

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role in algal growth, with biomass formed in algal cells being convertible into valuable fuels, chemicals, bioactive compounds, nutraceuticals, pharmaceuticals, and cosmeceuticals (Cheng et al., 2014; Nagappan et al., 2020; Song et al., 2019; Hu et al., 2016). The biological conversion of CO_2 using microalgae serves as a route for carbon capture and fixation (Vuppaladadiyam et al., 2018). Microalgae cultivation in open ponds and photobioreactors has the potential to produce biofuels, nutraceuticals, facilitate carbon sequestration, and treat wastewater (Guo et al., 2017; Cheng et al., 2018). The significant lipid content in microalgae can be transformed into biodiesel through the transesterification process. Biofuels are deemed carbon-neutral, as the CO_2 emitted during combustion is utilized by plants and algae for photosynthesis, leading to CO_2 fixation. Studies have shown the tolerance of microalgae, such as Scenedesmus obliquus, to high concentrations of CO_2 and toxic metals, making them effective in capturing CO_2 from both the atmosphere and industrial flue gas. Additionally, microalgae can fix CO_2 in the form of soluble carbonates. Notably, algae-based biochar finds applications in carbon sequestration, serving as feedstock for activated carbon production and adsorbing toxic compounds from polluted air, water, and soil (Kazamia et al., 2012; Kazamia et al., 2014; Peter et al., 2021).

Unicellular chlorophyll-synthesizing microalgae, including *Chlorella vulgaris*, are also classified as plants, and their biomass, like wood, can be used as an alternative source of energy. As shown by the results of our own research and literature analysis, the thermal effect of microalgae biomass burning is close to, and in some cases, greater than, the thermal effect of wood burning.

Today, it is obvious that the accumulated waste of biotechnological industries, in particular the purification of industrial gas emissions from greenhouse gases, pose a serious threat to the environment, and thus require disposal. Technologies for their disposal should be close to those that occur in natural conditions – the biosphere. It is known that the natural environment is characterized by cyclical processes. Borrowing this ability of the biosphere should become the basis of processes related to recycling and disposal of waste. This is precisely what determines the need to create and agree global measures in the direction of implementing the principles of sustainable development.

This state of affairs encourages the development of methods and methods of using the biomass of chlorophyll-synthesizing microalgae as a potential source of alternative fuel. Therefore, this issue needs to be studied more carefully for the possible use of microalgae biomass, obtained during the purification of industrial gas emissions, as a potential alternative source of energy. In order to attain net-zero emissions by 2050, substantial research and development efforts are essential for advancing efficient technologies that can capture, store, and utilize CO_2 from the atmosphere. These technologies must be sustainable, industrially viable, and cost-effective to meet the ambitious goal of mitigating carbon emissions effectively.

The aim of the work. The aim of the work was to investigate the heat-generating capacity of samples of fuel obtained from the biomass of microalgae *Chlorella vulgaris*, obtained as a r esult of the purification of industrial gas emissions from carbon dioxide with impurities of sulfur dioxide and nitrogen oxides, by the method of complex thermal analysis, as well as to evaluate the influence of sulfur dioxide and nitrogen oxides on the heat-generating capacity of potential fuel and efficiency of its burning processes.

2. Experimental part

The objects of research were samples of the biomass of microalgae *Chlorella vulgaris* obtained as a result of the purification of industrial gas emissions from carbon dioxide e in one case and in the other biomass obtained as a result of the purification of industrial gas emissions from carbon dioxide with impurities of sulfur dioxide and nitrogen oxides in the range of $4{\cdot}10^{-4}$ % vol., $3.4{\cdot}10^{-4}$ % vol. in the culture medium.

Comprehensive thermal analysis of microalgae biomass samples was performed on a Q-1500D derivatograph of the “F. Paulik – J. Paulik – L. Erdey”, connected to an IBM compatible personal computer. Biomass samples were analyzed in dynamic mode with a heating rate of 10 °C/min in an air atmosphere. The weight of the samples was 100 mg. The reference substance was aluminum oxide.

Comprehensive thermal analysis included thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA).

3. Results and discussion

The results of complex thermal analysis of the samples biofuel are presented in the form of thermograms (Figs. 1–2), combined DTG curves (Fig. 3) and Table.

The results of complex thermal analysis of the samples are presented in the form of thermograms (Figs. 1–2).

Results of thermal analysis of samples biofuel

Sample	stage	Temperature interval, °C	Mass loss, %	Effect (t_{max})
Sample 1 Obtained in the presence of CO_2	I	20–175	11.20	endothermic (100 °C)
	II	175–220	1.78	endothermic
	III	220–480	50.41	exothermic (354 °C)
	IV	480–740	33.61	exothermic (564 °C)
Sample 2 Obtained in the presence of CO_2 and SO_2	I	20–166	10.35	endothermic (101 °C)
	II	166–204	0.71	Endothermic
	III	204–445	51.64	exothermic (354 °C)
	IV	445–660	35.30	exothermic (525 °C)

At the first stage of thermolysis in the temperature range of 20–175 °C, the samples lose physically bound moisture. This process is accompanied by the appearance of a clear endothermic effect on the DTA curves, with a maximum at a temperature of 101 °C. It should be noted that sample 1 has a higher content of adsorbed moisture (11.20 %) compared to sample 2 (10.35 %).

In the second stage of thermolysis, the samples lose chemically bound water. This process is accompanied by a slight loss of sample mass and deviation of the DTA channel into the region of endothermic effects. In sample 1, the loss of chemically bound water (1.78 %) is observed in the temperature range of 175–220 °C. This process is accompanied by a characteristic bend in the DTG curve. Sample 2 loses chemically bound water (0.71 %) in the temperature range of 166–204 °C. It should be noted that sample 1 is characterized by a higher content of bound water.

At the third stage of thermolysis, which for sample 1 takes place in the temperature range of 220–480 °C, and for sample 2 in the temperature range of 204–445 °C, active thermo-oxidative and destructive processes take place, which culminate in the flame burning of volatile decomposition products. This is evidenced by the intense loss of mass of the samples and the appearance of a rapid exothermic effect on the DTA curves, with a maximum at a temperature of 354 °C. In the same temperature range, oxidation of sulfur compounds contained in sample 2 to higher oxide forms is possible.

It should be noted that sample 2 has a lower thermal stability compared to sample 1. Thermo-oxidative and destructive processes in this sample occur at lower temperatures, they are accompanied by a deeper extremum on the DTG curve (Fig. 3) and a more rapid exothermic effect on the curve DTA

At the fourth stage of thermolysis, which for sample 1 occurs in the temperature range of 480–750 °C, and for sample 2 in the temperature range of 445–750 °C, the pyrolytic residue of microalgae biomass is burned. This process corresponds to a significant loss of sample mass (33.61 % – sample 1, 35.30 % – sample 2) and the appearance of rapid exothermic effects on the DTA curves. In the same temperature range, it is possible to complete the combustion of sulfur compounds present in sample 2.

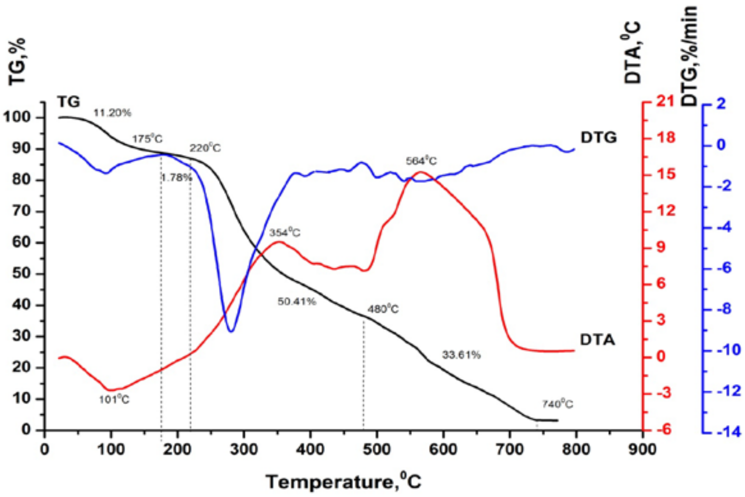

Fig. 1. Thermogram of sample 1

It should be noted that the combustion of the carbonized residue of sample 2 proceeds more intensively than that of sample 1. This is evidenced by the appearance of more rapid exothermic effects on the DTA curves of sample 2 and the shift of the extremes of the differential DTA and DTG curves to the region of higher temperatures. The maximum of the exothermic effect of sample 2 appears on the DTA curve at a temperature of 525 °C, and of sample 1 at a temperature of 564 °C. The extremum of the DTG curve of sample 2 corresponds to a temperature of 505 °C, and of sample 1 to a temperature of 564 °C (Fig. 3).

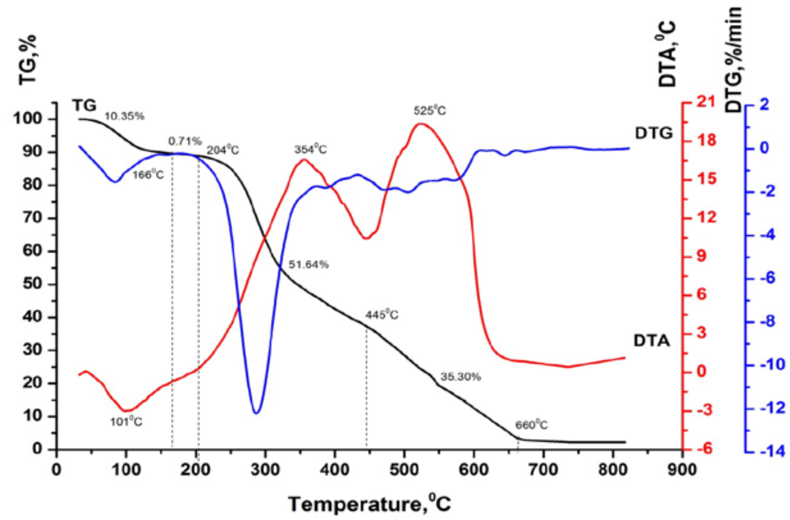

Fig. 2. Thermogram of sample 2

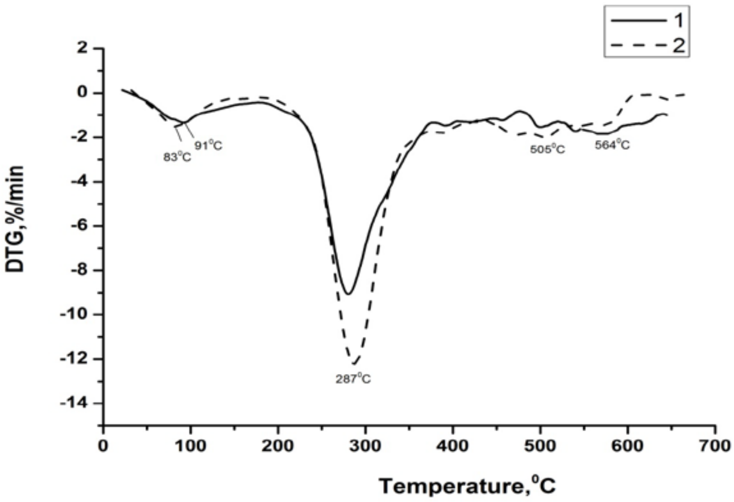

Fig. 3. Thermogravimetric curves: curve 1 – sample 1; curve 2 – sample 2

In Fig. 4 shows a comparison of the DTA curves of samples of three-year-old energy willow *Salix Viminalis* with a particle size of approximately 0.5 mm and single-celled microalgae *Chlorella vulgaris* cultivated in the presence of sulfur oxide. Thermal analysis of willow (*Salix Viminalis*) and microalgae samples was performed under the same conditions.

The exothermic effect observed on the DTA curve of the willow sample in the temperature range of 170–430 °C corresponds to the thermo-oxidative destruction of cellulose, which ends with the flame burning of volatile decomposition products. The next exothermic effect, which appears on the DTA curve in the temperature range 430–552 °C, corresponds to the combustion of the carbonized residue of the sample.

It should be noted that the heat-generating capacity of samples of fast-growing three-year-old willow and unicellular microalgae are close, however, the nature of combustion is somewhat different. The flame combustion of the destruction products of the willow sample proceeds more intensively than that of the sample of microalgae *Chlorella vulgaris*. This is evidenced by the appearance of a faster exothermic effect, compared to the exoeffect of the *Chlorella vulgaris* algae sample. However, the combustion of the pyrolytic residue of the willow (*Salix Viminalis*) sample is accompanied by a less significant release of heat. This process corresponds to a smaller exothermic effect on the DTA curve, which ends at lower temperatures, compared to the microalgae sample (Fig. 4).

Aspen (*Populus tremula L.)* is currently also a classic source of energy of plant origin. This fast-growing tree is widely distributed on the European territory. It is often used in the fuel industry as an energy raw material.

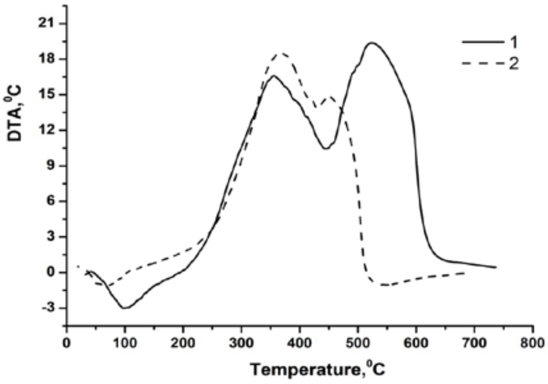

Fig. 4. Comparison of DTA curves of samples:
1– biomass of microalgae (*Chlorella vulgaris)*; 2– energy willow (*Salix Viminalis*) (V. Yalechko et ol., 2015)

In Fig. 5 shows a comparison of the DTA curves of single-celled chlorophyll-synthesizing microalgae *Chlorella vulgaris* and a s ample of aspen trunk wood mixed in equal proportions with aspen bark. Thermal analysis of the samples was carried out under the same conditions.

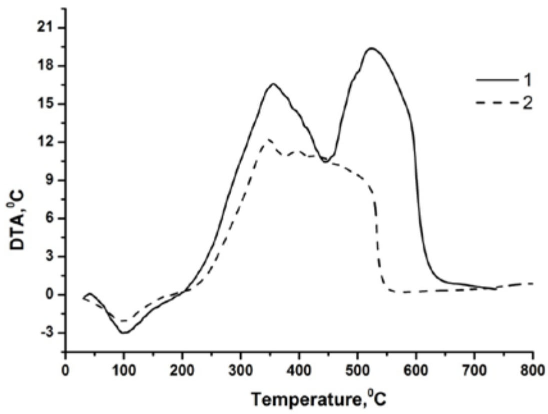

Fig.5. Comparison of DTA samples:
curve 1 – biomass of microalgae (*Chlorella vulgaris*) sample 2; curve 2 –fast-growing aspen (*Populus tremula L.*)

Pyrolysis, which is accompanied by a sharp decrease in the degree of cellulose polymerization, thermo-oxidative destruction and combustion of the destruction products of the aspen sample, occurs in the temperature range of 187–373 °C. This process corresponds to a significant exothermic effect on the DTA curve, with a maximum at a temperature of 347 °C.

Combustion of the pyrolytic residue of the aspen sample, which is accompanied by a wide exoeffect on the DTA curve, occurs in the temperature range of 373–564 °C. It should be noted that the flaming combustion of the destruction products of the aspen sample (*Populus tremula L.*) and the combustion of its carbonized residue is accompanied by less heat release. This is evidenced by the appearance of less rapid exothermic effects on the DTA curve of a sample of fast-growing aspen compared to a sample of chlorophyll-synthesizing microalgae.

According to the results of thermal studies, it can be stated that the biomass sample of microalgae *Chlorella vulgaris* has a higher heat-generating capacity, compared to the sample of aspen (*Populus tremula L.*).

4. Conclusions

According to the comprehensive thermal analysis, the microalgae biomass sample obtained during cultivation with carbon dioxide containing sulfur dioxide and nitrogen oxides, sample 2, has a higher heat-generating capacity compared to sample 1, obtained during the cultivation of microalgae with pure carbon dioxide. Flame combustion of volatile decomposition products of sample 2 and combustion of its carbonized residue is accompanied by a more significant thermal effect compared to sample 1, obtained during cultivation with pure carbon dioxide. The presence of sulfur and nitrogen in sample 2 increases the intensity of destructive, thermo-oxidative and heterogeneous-oxidative processes in them during heating.

The calorific value of microalgae biomass sample 2 exceeds the calorific value of aspen (*Populus tremula L.*), which is considered an alternative source of energy in Ukraine, and is close to the calorific value of the selectively bred energy willow (*Salix Viminalis)*.

Biomass of microalgae *Chlorella vulgaris*, both samples can be recommended as raw material for fuel production.

References

Aslam, A., Thomas-Hall, S. R., Mughal, T. A., & Schenk, P. M. (2017). Selection and adaptation of microalgae to growth in 100 % unfiltered coal-fired flue gas. *Bioresource Technology*, *233*, 271–283. DOI: https://doi.org/10.1016/j.biortech.2017.02.111

Camargo, E. C., & Lombardi, A. T. (2018). Effect of cement industry flue gas simulation on the physiology and photosynthetic performance of Chlorella sorokiniana. *Journal of Applied Phycology*, *30*(2), 861–871. DOI: https://doi.org/10.1007/s10811-017-1291-3

Cheng, D., Li, X., Yuan, Y., Yang, C., Tang, T., Zhao, Q., & Sun, Y. (2019). Adaptive evolution and carbon dioxide fixation of Chlorella sp. in simulated flue gas. *Science of the Total Environment*, *650*, 2931–2938. DOI: https://doi.org/10.1016/j.scitotenv.2018.10.070

Cheng, J., Huang, Y., Lu, H., Huang, R., Zhou, J., & Cen, K. (2014). The oxidation product (NO_2) of NO pollutant in flue gas used as a nitrogen source to improve microalgal biomass production and CO_2 fixation. *RSC Advances*, *4*(79), 42147–42154. DOI: https://doi.org/10.1039/C4RA05491A

Dyachok, V., Huhlych, S., Katysheva, V., & Mandryk, S. (2017). Absorption of carbon dioxide from a mixture of air with sulfur dioxide. *Scientific Works*, *81*(1), 59–65. DOI: https://doi.org/10.15673/swonaft.v81i1.676

Dyachok, V. V., Mandryk, S. T., Huhlych, S. I., & Slyvka, M. M. (2020). Study on the impact of activators in the presence of an inhibitor on the dynamics of carbon dioxide absorption by chlorophyll-synthesizing microalgae. *Journal of Ecological Engineering*, *21*(5), 189–196. DOI: https://doi.org/10.12911/22998993/122674

Dyachok, V., Huhlych, S., Katysheva, V. V., & Mandryk, S. (2021). About the Optimal Ratio Inhibitor and Activators of Carbon Dioxide Sorption Process by Using Chlorophyll-synthesizing Chlorella microalgae. *Journal of Ecological Engineering*, *22*(5), 26–31. DOI: https://doi.org/10.12911/22998993/135900

Guo, Y., Yuan, Z., Xu, J., Wang, Z., Yuan, T., Zhou, W., Xu, J., Liang, C., Xu, H., & Liu, S. (2017). Metabolic acclimation mechanism in microalgae developed for CO_2 capture from industrial flue gas. *Algal Research*, *26*, 225–233. DOI: https://doi.org/10.1016/j.algal.2017.07.029

Hu, X., Zhou, J., Liu, G., & Gui, B. (2016). Selection of microalgae for high CO_2 fixation efficiency and lipid accumulation from ten Chlorella strains using municipal wastewater. *Journal of Environmental Sciences*, *46*, 83–91. DOI: https://doi.org/10.1016/j.jes.2015.08.030

Lara-Gil, J. A., Senés-Guerrero, C., & Pacheco, A. (2016). Cement flue gas as a potential source of nutrients during CO_2 mitigation by microalgae. *Algal Research*, *17*, 285–292. DOI: https://doi.org/10.1016/j.algal.2016.05.017

Kazamia E., Aldridge D. C., & Smith, A. G. (2012). Synthetic ecology – A way forward for sustainable algal biofuel production? *Journal of Biotechnology*, *162*(1), 163–169. DOI: https://doi.org/10.1016/j.jbiotec.2012.03.022

Kazamia, E., Riseley, A. S., Howe, C. J., & Smith, A. G. (2014). An engineered community approach for industrial cultivation of microalgae, *Industrial Biotechnology*, *10*(3), 184–190. DOI: https://doi.org/10.1089/ind.2013.0041

Nagappan, S., Tsai, P. C., Devendran, S., Alagarsamy, V., & Ponnusamy, V. K. (2020). Enhancement of biofuel production by microalgae using cement flue gas as substrate, *Environmental Science and P ollution Research, 27*(15), 17571–17586. DOI: https://doi.org/10.1007/s11356-019-06425-y

Peter, A. P., Khoo, K. S., Chew, K. W. , Ling, T. C. , Ho, S.-H., Chang, J.-S., & Show, P. L. (2021). Microalgae for biofuels, wastewater treatment and environmental monitoring. *Environmental Chemistry Letters*, *19*, 2891–2904. DOI: https://doi.org/10.1007/s10311-021-01219-6

Song, C., Qiu, Y., Li, S., Liu, Z., Chen, G., Sun, L., Wang, K., & Kitamura, Y. (2019). A novel concept of bicarbonate-carbon utilization via an absorption-microalgae hybrid process assisted with nutrient recycling from soybean wastewater. *Journal of Cleaner Production*, *237*, 117864. DOI: https://doi.org/10.1016/j.jclepro.2019.117864

Vuppaladadiyam, A. K., Yao, J. G., Florin, N., George, A., Wang, X., Labeeuw, L., Jiang, Y., Davis, R. W, Abbas, A., Ralph, P., Fennell, P. S., & Zhao, M. (2018). Impact of flue gas compounds on mic roalgae and mechanisms for carbon assimilation and utilization. *ChemSusChem*, *11*(2), 334–355. DOI: https://doi.org/10.1002/cssc.201701611

Yalechko,V., Kochubey, V., Hnatyshyn, Y., Dzyadevych, B., & Zaikov, G. (2015). Investigation of Thermal Power Characteristics of Wood Pulp. *The Chemistry and Physics of Engineering Materials*, *1*, 171–178. Retrieved from https://www.taylorfrancis.com/chapters/edit/10.1201/9780429453601-20/investigation-thermal-power-characteristics-wood-pulp-yalechko-kochubey-hnatyshyn-dzyadevych-zaikov