RIGA TECHNICAL UNIVERSITY

Kaspars Ivanovs

AQUATIC BIOLOGICAL RESOURCE PROCESSING

Doctoral Thesis

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RIGA TECHNICAL UNIVERSITY
Faculty of Electrical and Environmental Engineering
Institute of Energy Systems and Environment

Kaspars Ivanovs
Doctoral Student of the Study Programme “Environmental Engineering”

AQUATIC BIOLOGICAL RESOURCE PROCESSING

Doctoral Thesis

Scientific supervisors
Professor Dr. habil. sc. ing.
DAGNIJA BLUMBERGA

Associate Professor Ph. D.
KRIŠS SPALVIŅŠ

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To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on 30 August 2023 at 14:00 at the Faculty of Electrical and Environmental Engineering of Riga Technical University, Āzenes iela 12 k-1, Room 115.

OFFICIAL REVIEWERS

PhD Timo Laukkanen
Alto University, Finland

PhD Ilze Dzene,
University Kassel, Germany

PhD Ainis Lagzdiņš
Latvia University of Life Sciences and Technologies, Latvia

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Kaspars Ivanovs ……. (signature)
Date: ……

The Doctoral Thesis has been written in English. It consists of Introduction, 4 Chapters, Conclusion, 20 figures, 22 tables, the total number of pages is 215, including appendices. The Bibliography contains 340 titles.

ANOTĀCIJA

Ūdens biomasai salīdzinot ar sauszemes resursiem ir sava specifika un apstrādes problēmātika. Šie resursi ir daļa no ES Zilās izaugsmes stratēģijas un ir daļa no zināšanu ietilpīgas bioekonomikas ekosistēmas. Resursu pārstrādes nodrošināšana un labāko pieejamo tehnoloģisko metožu atrašana veicinās videi draudzīgu resursu izmantošanu un palielinās pievienoto vērtību. Promocijas darbā apskatīta ūdens resursu pārstrāde, analizējot resursu sastāvu, apstrādes tehnoloģijas un iegūstamos produktus, ar konkrētiem piemēriem izvērtēti arī iespējamie apstrādes veidi, veikti atsevišķi eksperimenti. Darba mērķis bija izpētīt ūdens bioresursus, biomasas resursu pārstrādi produktos ar pievienoto vērtību, lai atrastu vislabāko ūdens izcelsmes izejvielu izmantojumu un atbalstītu pāreju uz ilgtspējīgāku aprites ekonomiku izmantojot atjaunojamos ūdens resursus. Promocijas darbs ir balstīts uz septiņām tematiski vienotām zinātniskām publikācijām, kas publicētas zinātniskos žurnālos un ir pieejamas starptautiskās datubāzēs. Darba ievadā ir izklāstīts mērķis un uzdevumi, aprakstīta darba organizācija un sniegts pārskats par praktisko un zinātnisko ieguldījumu. Pirmajā nodaļā ir apkopota zinātniskā literatūra, iepriekšējie pētījumi, kā arī pievērsta uzmanība ūdens bioresursu iezīmēm. Trešajā nodaļā ir rezultāti un diskusija. Darba beigās tiek izdarīti secinājumi.

ANNOTATION

Aquatic biomass has its own specificity and processing challenges compared to terrestrial resources. These resources are part of the EU's Blue Growth Strategy and are part of a knowledge-intensive bioeconomy ecosystem. Ensuring the processing of resources and finding the best available technological methods will promote environmentally friendly use of resources and increase the added value. The thesis examines the processing of aquatic resources by analysing the composition of resources, processing technologies and the products to be obtained, also evaluates the possible ways of processing with specific examples, carried out separate experiments. The aim of the work was to research aquatic bioresources, green processing of biomass resources into value-added products to find best use of aquatic origin feedstocks, and to support the transition to a more sustainable circular economy by leveraging renewable water resources. The Doctoral Thesis is based on seven thematically unified scientific publications published in various scientific journals and are available in international databases. The Thesis introduction outlines the goal and tasks, describes the organization of the work, and provides an overview of practical and scientific contributions. The first chapter summarizes the scientific literature, prior research, and concentrates on the features of aquatic bioresources. The third chapter contains the results and discussion. At the end of the thesis, conclusions are drawn.

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INTRODUCTION

We are being compelled by the climatic backdrop to reconsider our production and consuming practises to reduce global environmental harms – rise of global temperature, dwindling biodiversity, scarcity of resources. As consumerism and human needs are growing it is necessary to increase the variety of resources, enhance and modify resource processing methods, and guarantee product availability. Bioeconomy research comes into play not only promoting improvement measures at all stages and reviews what has been done, but it also serves as a knowledge diffuser making information easier to absorb in society level mainly through inter-sectoral cooperation, and more accessible to all parties involved through information dissemination. Bioeconomy is important to Europe worth about 2.3 trillion euros annually, employs over 18 million people, critical for the environment, food production, and development of rural areas. When the bioeconomy sector and data are sufficiently integrated, it will have a significant impact on the sustainability performance and competitiveness of the bioproducts industry through the processing and analysis of production and other data, enabling accurate and specialised manufacture [1]. Since water make up the majority of the earth's surface, developing and harvesting water resources has enormous potential. Aquaculture, processing, and the natural catch of fish from the sea and ocean support millions and sustain a sizable portion of the world's population. According to the Organisation for Economic Co-operation and Development, oceans contribute $1.5 trillion annually in value-added to global economy and this number could reach $3 trillion by 2030 [2]. Due to the development of society, there is a need to solve problems related to the more efficient use of fishing and aquaculture resources.

Traditionally, catch and aquaculture have been used for food and residues for soil improvement and animal feed. Research in this direction has significantly increased in the past decades. Trying to solve problems of resource depletion, product availability, infrastructure, recycling, and the development of innovative production technologies including previously unused resources and technologies. There are regional differences in the use of water resources for food, employment and technology. To ensure the amount and diversity of resources in the long term, water ecology research is of great importance – monitoring of water quality, biomass amount and diversity, ecology of trophic structure. For some time now, a concept bioeconomy (blue bioeconomy in the context of aquatic resources) has played a very important role. The concept is widely used in scientific research and is used as a policy framework to include the bioresources part of the circular economy. The bioeconomy of aquatic resources is the use of water bioresources to manufacture bioproducts with higher added value. Material processing and product extraction processes are economically efficient and sustainable production is ensured. Sustainable utilization of residues play an important role and could also be feedstock for renewable energy production. The different sectors of the bioeconomy of water bioresources are in different stages of development. Economic considerations play a central role in today's democratic society so in areas with a good economic status where there is availability and low price of energy, good techno-economic approaches to the processing of aquatic bioresources have been created and products with high added value have been developed. That is story of Nordic bioeconomy [3]. Fish, molluscs, aquatic plants, and algae are processed, and various bioproducts are obtained, which, depending on the technological method, may have properties

such as bioactivity. This practical experience of European countries in research and development, creating a successful business is an example for those who have started such expansion of the spectrum of resources only recently. Differences in the specifics of resources, investment strategy, energy prices, support policy, consumer culture, slows down research and development in other regions. Scientific capacity and resource provision determine the pace of academic research development. Research areas cover various contexts e.g., market analysis, economic rationale, production technology, energy consumption, product quality, modelling of resource-technology-product-processing systems, integration of innovative technologies, industry policy development and monitoring. The processing of organic materials derived from aquatic environments is referred to as aquatic biomass processing. The goal of this type of refining is to extract valuable resources from organic material, such as energy, food, and chemicals. Research topic is clearly related to the broader field of renewable energy and sustainable development, as aquatic biomass processing provides a potential source of sustainable energy and materials that could reduce reliance on finite fossil fuel resources.

Topicality

Aquatic biomass processing research contributes to the development of efficient harvesting methods and processing of organic materials. Additionally, research in this field improves our understanding about ecology of aquatic biomass and the potential for sustainable development of resources. Marine environment management, technology, and product development are important in the Baltic Sea region in the blue bioeconomy and effective emission reduction in the European Green Deal policy. A multidisciplinary approach and interdisciplinary research at all levels will facilitate progress in the unattainable direction and will ensure science-based decision-making in research and policy, meeting emission targets, and socio-economic well-being. In context of republic of Latvia, bioeconomy strategy, framework documents, and activity monitoring are important for development, monitoring of the bioeconomy sector is carried out by the smart specialization strategy "Knowledge-intensive bioeconomy". The "National Industrial Policy Guidelines" developed by the Ministry of Economy is a general document that can provide an informative stimulus for both research and business in the context of the bioeconomy. Over the last two decades, the fisheries and aquaculture sectors have been increasingly recognized for their essential contribution to global food security and nutrition. Expanding this role requires scaling up transformative changes in policy, management, innovation, and investment to achieve sustainable, inclusive, and equitable global fisheries and aquaculture. It is necessary to stimulate the application of biorefinery principles in the processing industry. This is done by applying incentives in different places and directions to support best activities possible. These incentives and points of application of force must have a scientifically justified research and factual basis, based on approved system models, market and society trends, and it should be considered that multidisciplinary activity and international cooperation are essential for such logical progress in achieving goals. The monitoring results of smart specialization show that it is necessary to develop innovative processing technologies and create products, since the application of innovative solutions in the processing industry has a low added value. Also, Latvia's bioeconomy strategy needs a multifaceted approach to promote the meaning and significance.

Innovative and thoughtful processing technologies with suitable feedstock create added value, diversify the local economy, and contribute to the development of climate-neutral technologies, employment, education, and social welfare. Therefore, it is a very important task for researchers to create good preconditions by analysing the most important components and modelling processing systems, developing the processing industry as a whole and improving its efficiency and potential added value. Important prerequisites for actions to be fulfilled are the rise of institutional capacity, long-term planning of research work, constructive cooperation with state and local government institutions and the involved industry sectors, and foreign investment, also raising the quality of general and higher education, development and direction motivated by society and the global market. Furthermore, it is essential to understand and define the boundaries of any system as that would facilitate the logical distribution of resources and the use of funding.

Objective of the research

The aim of the Thesis was to research aquatic bioresources and green processing of biomass resources into value-added products to find the best use of aquatic origin feedstocks, and to support the transition to a more sustainable circular economy by leveraging renewable water resources. Based on scientific literature research and experiments, the Thesis outlines aquatic bioresources and generally used processing methods, as well as technique for getting products to better the long-term use of Latvia's aquatic bioresources in a technological sense and in the context of decision-making. Research object is knowledge-based bioeconomy and research subject is processing of aquatic bioresources.

The following tasks have been set to achieve the goal:

1. Evaluate local aquatic bioresources as feedstock for value-added bioproducts – economically low-value fishery by-products and other biomass such as macroalgae, and reed, and describe the main bioproducts from aquatic residue.
2. Research literature for sustainable aquatic biomass processing technologies pre-treatment, green extraction methods, and remaining waste treatment method.
3. Describe aquatic biorefinery stages and essential components to manage aquatic biomass residue issue using it as feedstock. Recommend processing of three blue feedstocks – fish residue, macroalgae, and common reed.
4. Based on conducted research and literature analysis recommend further research direction in aquatic bioresource management in Latvia.

Theoretical and methodological basis

Literature analysis, experiments in the laboratory, data analysis, and technology description analysis were used in the development of the Thesis. Analysis of broad scope of scientific literature was performed and was the main source of information. In-depth review of literature was preformed to assess methodologies for blue-biomass transformation routes. In RTU Biosystems Laboratory, research was conducted where selected resources – round goby, macroalgae, and reed, were studied for processing into bioproducts. Substrates were experimentally converted into oil, protein, biogas, green extracts, and building materials by

using a variety of methods, such as chemical and green extraction, anaerobic digestion, and solar energy. Research experiments and technology analysis are the two main parts of Thesis and tackle the issue of managing aquatic biomass residue.

Main scientific novelties

There are three main novelties of this thesis, and they are mostly related to use of local aquatic biomass. The use of invasive fish species in the extraction of value-added products was studied. The processing of several aquatic bioresources in one functional unit from pre-processing of the material to disposal of the residues in an environmentally friendly way were researched and analysed. A feasibility study and feasibility analysis of a low-temperature biogas and solar hybrid system on a small scale was performed, the need for the system, socially integrative aspects, scale, opportunities for technology diffusion and integration in the overall renewable energy resource system were examined.

Practical contribution

The research on fish waste has evaluated the round goby biomethane potential for use as a feedstock in the production of biomethane, waste protein utilization has also been proposed. The Thesis research studies have contribution to the EU Blue Growth strategy concept, and smart specialization of bioeconomy. The solutions suggested in the Thesis may be used to design policies and strategies, as well as for designing an aquatic pilot biorefinery. Residual secondary biowaste treatment approach using small-scale low-temperature anaerobic digester has also been reviewed.

Structure of the Thesis

The Thesis is based on a set of 7 publications and focuses on the more complete use of water bioresources, finding applications for different feedstocks based on the analysis of individual bioresources. The research is based on the analysis of international and local scientific literature on aquatic bioresources, innovative processing methods, obtainable products, as well as related concepts of knowledge-intensive bioeconomy in the context of blue bioeconomy. In the practical part, the biomass composition analysis and biomethane potential tests were carried out, a feasibility study was carried out for small-scale processing with a plug-flow digester with solar heating. At the end of the Thesis, the suitability of the biorefinery concept for blue-feedstock is discussed and the author's recommendations for research directions that could be developed are given. Aquatic bioeconomy research was divided into several phases. The classic bioeconomy approach – resource-technology-product analysis, was used in overall research to provide results and rationalize discourse. The Fig. 1. acts as “blueprint” for the research. It provides a structure to define how to approach the thesis analytically, methodologically, and philosophically. Literature analysis, laboratory analysis, technology and data analysis were used in the development of the PhD thesis. Research experiments and technology analysis are two main parts of thesis and tackles the issue of managing aquatic biomass residue.

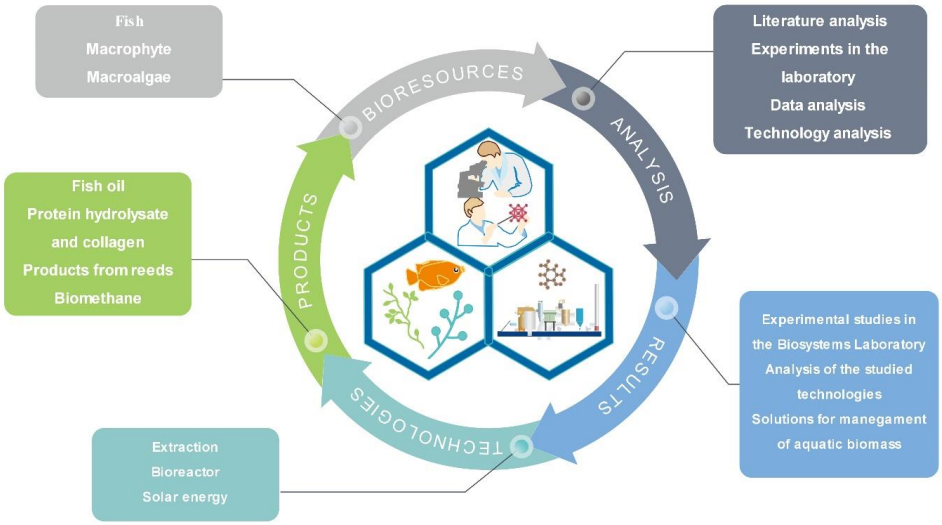

Fig. 1. External layout of Thesis.

Approbation of the research

The Doctoral Thesis was developed as a thematically unified set of publications and is based on the following studies.

Publications included in the Thesis:

1. **Ivanovs, K**., Spalviņš, K., Blumberga, D. Approach for Modelling Anaerobic Digestion Processes of Fish Waste. Energy Procedia, 2018, Vol. 147, pp. 390–396. ISSN 1876-6102.
2. Gruduls, A., Bāliņa, K., **Ivanovs, K**., Romagnoli, F. Low Temperature BMP Tests Using Fish Waste from Invasive Round Goby of the Baltic Sea. Agronomy Research, 2018, 16 (2), pp. 398–409.
3. **Ivanovs, K**., Blumberga, D. Extraction of Fish Oil Using Green Extraction Methods: a Short Review. Energy Procedia, 2017, Vol. 128, pp. 477–483. Available:
4. Melvere, M., **Ivanovs, K**., Pubule, J., Blumberga, D. Use of Round Goby (Neogobius Melanostomus) Processing Waste in Bioeconomy. Energy Procedia, 2017, Vol. 128, pp. 484–490. ISSN 1876-6102.
5. Bāliņa, K., **Ivanovs, K.,** Romagnoli, F., Blumberga, D. Comprehensive Literature Review on Valuable Compounds and Extraction Technologies: The Eastern Baltic Sea Seaweeds. Environmental and Climate Technologies, 2020, Vol. 24, No. 2, pp. 178–195. ISSN 1691-5208. e-ISSN 2255-8837.
6. Muižniece, I., Kazulis, V., Žihare, L., Lupkina, L., **Ivanovs, K**., Blumberga, D. Evaluation of Reed Biomass Use for Manufacturing Products, Taking into Account Environmental Protection Requirements. Agronomy Research, 2018, Vol. 6, Special Iss. 1, pp. 1124–1132. ISSN 1406-894X.

7. **Ivanovs, K.**, Blumberga, D. 2023. Plug flow digester with assisted solar heat: feasibility of small-scale system. Agronomy Research, 21(X), xxx–ccc.

Other publications of the author:

8. **Ivanovs, K.** Pike Esox Lucius Distribution and Feeding Comparisons in Natural and Historically Channelized River Sections. Environmental and Climate Technologies, 2016, 18, pp. 33–41. ISSN 1691-5208. e-ISSN 2255-8837.
9. Priedniece, V., Spalviņš, K., **Ivanovs, K**., Pubule, J., Blumberga, D. Bioproducts from Potatoes. A Review. Environmental and Climate Technologies, 2017, 21, pp. 18–27. e-ISSN 2255-8837.
10. Spalviņš, K., **Ivanovs, K.,** Blumberga, D. Single Cell Protein Production from Waste Biomass: Review of Various Agricultural By-products. Agronomy Research, 2018, Vol. 16, Special Iss. 2, pp. 1493–1508. ISSN 1406-894X.
11. Petrauskaite, E., Vaiskunaite, R., Blumberga, D., **Ivanovs, K.** Experimental Study of Droplet Biofilter Packed with Green Sphagnum to Clean Air from Volatile Organic Compounds. 2017. Pp. 373–378. ISSN 1876-6102.

Participation in scientific conferences:

1. **Ivanovs, K**., Blumberga, D. Extraction of Fish Oil Using Green Extraction Methods: a Short Review. The Conference of Environmental and Climate Technologies CONECT, 2017, October 12–14, 2017, Riga, Latvia.
2. **Ivanovs, K**., Spalviņš, K., Blumberga, D. Approach for Modelling Anaerobic Digestion Processes of Fish Waste. The Conference of Environmental and Climate Technologies CONECT 2018, Vol.147, 390.-396.lpp. ISSN 1876-6102.
3. Bāliņa, K., **Ivanovs, K.,** Romagnoli, F., Blumberga, D. Comprehensive Literature Review on Valuable Compounds and Extraction Technologies: The Eastern Baltic Sea Seaweeds. The Conference of Environmental and Climate Technologies CONECT 2020, May 13–15, 2020, online.
4. **Ivanovs, K.**, Blumberga, D. Plug flow digester with assisted solar heat: feasibility of small-scale system. 13th International Conference "Biosystems Engineering 2023", May 10–12, 2023, Tartu, Estonia.

Supervised Bachelor and Master's Thesis

1. Maira Melvere. Use of Round goby processing residues in the bioeconomy. Master Thesis. RTU, 2017 (in Latvian).
2. Erika Petrauskaite. Analysis and assessment of droplet biofilter packed with sphagnum load. RTU, 2017 (in English).
3. Laura Graudumniece. Utilization of fish processing residues containing connective tissue protein for collagen extraction. RTU, 2019 (in Latvian).

1. LITERATURE REVIEW

1.1. Aquatic bioresources

Aquatic biological resources are a set of organisms (hydrobionts) living in water whose life is not possible, permanently or at certain stages of development, without remaining in water. Aquatic resource management refers to the management and conservation of the aquatic resource base in the context of aquaculture, the concentration and capture of wild fish, and the search and harvest of other aquatic resources such as crabs, shrimps, snails, insects, aquatic plants, and seaweed [3]. Aquatic biological resources have diverse environments (Table 1.1.). Classification of environment is mainly based on geographical, physical, chemical and biological characteristics, which more or less clearly demarcate individual zones. Within each of these vast areas there are many observable and varied sets of ecological conditions resulting from differences in bedrock, proximity to shore, depth, and the chemical-physical state of the water. The primary "topographical" unit used in the ecological classification of environments is the habitat or niche, which is defined as "an area containing a common set of key habitat conditions and life forms adapted to them" [4].

Table. 1.1.

Aquatic resource environment diversity [5]

Inland	**Coastal**	**Open sea**
Riverine	Estuaries	Benthic or pelagic
Rivers	Bays	
Floodplains	Lagoons	
Irrigation Channels	Coral Reefs	
Lacustrine	Mangroves	
Lakes	Mudflats	
Reservoirs	Ponds	
Ponds		

Aquatic ecosystems (both marine and freshwater) have long served as model systems to study the role of environmental stressors on organismal performance and survival, the biogeographic distribution of populations and species, and ultimately ecosystem diversity, functioning, and stability. Climate change, alien species invasions, changes in land use, urbanization and other anthropogenic impacts have been shown to degrade aquatic ecosystems at several levels of biological organization of aquatic ecosystems. Consequently, approaches that incorporate biological traits (e.g., physiological, behavioural, phenological, functional) at multiple spatial and temporal scales are essential to predict the response of aquatic ecosystems to future environmental changes from individual organisms to whole ecosystems. Combining different biological scales has great potential to develop approaches to quantify and predict current and future responses to climate change and human activity [6].

Growth, the size increment with time, is a simple but a vital biological process that integrates several processes and shape the life history of organism. It can be directly related to other life history traits such as natural mortality and fecundity. The ability to accurately model growth has wide applications in population dynamics [7]. Fish and other organism growth,

varies greatly with food quality, availability, temperature, and other environmental factors (levels of irradiation, CO_2 and O_2 concentrations, temperature, pH, nutrients), thus species have different growth rates and maximum achievable population size under different conditions. The ability to adapt to changing environmental conditions varies. Growth rate in artificial conditions is faster, for example farmed cod and salmon grow faster and mature at an earlier age than wild. Growth rate in nature is mainly determined by the region of catch or production, water temperature, water salinity, waves, solar radiation, geology, the dynamics of natural regeneration of the population of the given species [8]. Growth models estimate life history parameters that are used in the management of fisheries stocks. Flinn & Midway, 2021, reviewed age and growth studies and regional stock assessments to examine trends in the use of growth models and model selection in fisheries over time, results showed that there are increase in the use of multi-model frameworks, and covariates such as system (e.g., marine or fresh), location of study, diet, family, maximum age, and range of age data used in model fitting did not contribute to which model was ultimately the best fitting, suggesting that there are no large-scale patterns of specific growth models being applied to species with common life histories or other attributes. Also, there are different models for molluscs [9], crustacean [10], seaweed [11], microalgae [12] for growth modelling in different conditions. In order to ensure long-term availability of resources, researchers try to analyse and quantify population dynamics, and with data sets obtained from research, demonstrate changes in the resources over time. Data therefore plays a vital role in improving the situation and promoting improvement where it is needed. Link *et al*. 2022 using theoretical model tried to estimate and evaluate effects of different classes of perturbation on trophodynamics of marine ecosystems, and concludes that relatively simple equation can depict, capture and predict such a wide range of marine ecosystem dynamics across a broad array of situations is not trivial, and further suggests the robustness of the cumulative trophic theory. Subsequent transfers of production and biomass are efficiency-limited across trophic level and up through a food chain, as in the simple trophic transfer equation (Eq. 1.1.):

$$cumP_{max} = \sum_{1=1}^{TL} PP \cdot TE_i^{TL-1} \qquad (1.1.)$$

where $cumP_{max}$ is the cumulative production of the system;
PP is net primary production (often expressed as net primary production, *PP*);
TL is trophic level;
TE is the average *TL* transfer efficiency.

Thus, production at different trophic levels always results in pyramids because the transfer efficiency is always much lower than 1 and usually close to 0.1, and hence cumulative curves of production are monotonically asymptotic tending to plateau (near the sum of all system productivity, i.e., $cumP_{max}$) [13].

By integrating data from across existing literature, Bar-On & Milo 2019 provided a comprehensive view of the distribution of marine biomass between taxonomic groups, modes of life, and habitats. Results show approximate global situation of the marine ecosystem and highlights the essential differences between marine and terrestrial ecosystems. In contrast to their dominance on land, plants (green algae and seaweed) account for less than 10% of the total biomass in the ocean. Viruses dominate the ocean in numbers but make up only ~1% of the total biomass. Together, animals, protists and bacteria make up ~ 80% of marine biomass, whereas on land only ~2%. The marine fauna is dominated by small mesopelagic fish and

crustaceans, mainly copepods, shrimps and krill. The oceans contain much more consumer biomass (~5 Gt C) than producer biomass (~1 Gt C). Unicellular organisms make up about two-thirds of the total biomass of marine organisms. (Fig. 1.1.). Top part of the image – absolute biomasses of different taxa, and algae are counted as either protists or plants following their taxonomy. Bottom of the image – dissection of the global marine biomass by trophic mode and taxonomy. These estimates are a rough global view [14].

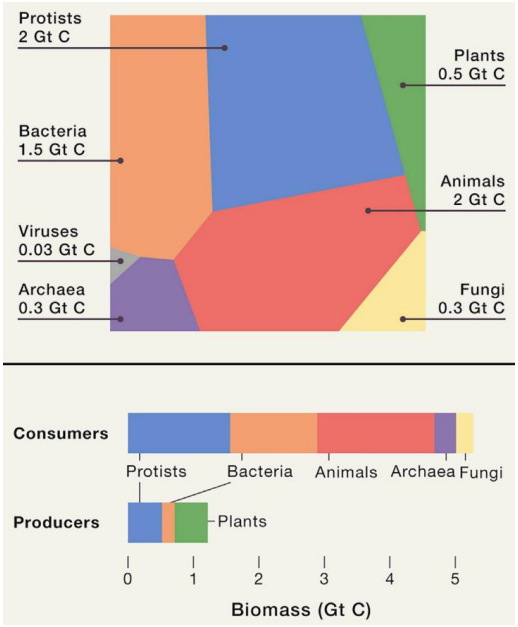

Fig. 1.1. Composition of marine biomass in gigatons of carbon (Gt C) [14]

There are two ways where aquatic biological resources are produced/harvested for commercial gain – from native environment, inside the continent in rivers and lakes, and open seas, oceans (natural catch and harvesting), or in human-adapted natural or artificial environment, with nutrient supply and recovery mechanisms (aquaculture). Food and agriculture organization of the United Nations, in report "The State of World Fisheries and Aquaculture 2022" paints a global picture of the industry. Production from fisheries and aquaculture worldwide is at a record high, and it is predicted that sector will continue to play a significant role in supplying food and nutrition. A record 214 million tonnes of fisheries and aquaculture products were produced in 2020, including 178 million tonnes of aquatic animals and 36 million tonnes of algae, mostly because of the expansion of aquaculture, especially in Asia. There were 20.2 kg meant for food per person (algae excluded). In terms of the fishing fleet, the predicted total number of fishing vessels in 2020 was 4.1 million, a 10 percent decline from 2015, indicating efforts by several nations, particularly China and European nations, to lower the size of the worldwide fleet. Two-thirds of the world's fishing fleet is still based in Asia. Asia accounts for about 75% of the 2.5 million motorised ships that are currently in operation worldwide [15]. A fishery's price, productivity, and bycatch are significantly influenced by the choice of fishing gear. The most common fishing techniques include bottom trawl and seine, dredging, gillnets, longline pelagic trawl and seine, trapnets and fykenets, and

traps and pots. [16]. Resources continue to decline due to overfishing, pollution, poor management and other factors.

In 2020, 78.8 million tonnes from marine waters and 11.5 million tonnes from inland waters made up the 90.3 million tonnes of total catch fisheries production (excluding algae) with an expected value of $141 billion. Of all inland fisheries, Asia produced about two thirds of it. Marine capture production data shows main species of interest. There are 14 main species of finfish, four most frequently caught are Anchoveta, *Engraulis ringens*, Alaska pollock, *Gadus chalcogrammus*, Skipjack tuna, *Katsuwonus pelamis*, Atlantic herring, *Clupea harengus*. Eight main species of Crustaceans most frequently caught are Natantian decapods nei, *Natantia*, Akiami paste shrimp, *Acetes japonicus*, Gazami crab, *Portunus trituberculatus*. Seven species of molluscs most frequently caught are Jumbo flying squid, *Dosidicus gigas*, Various squids nei, *Loliginidae, Ommastrephidae*. Six species of other aquatic animals of which the most frequently caught are Jellyfishes nei, *Rhopilema spp.*, Aquatic invertebrates nei, *Invertebrata*, Sea cucumbers nei, *Holothuroidea*, Chilean sea urchin, *Loxechinus albus*. Aquaculture has great potential to feed the world's growing population. Global aquaculture production reached a record high of 122.6 million tonnes in 2020, including 87.5 million tonnes of aquatic animals worth $264.8 billion and 35.1 million tonnes of algae worth $16.5 billion. Asia dominates aquaculture producing 91.6% of total production. The growth of aquaculture has often come at the expense of the environment. Sustainable aquaculture development remains essential to meet the growing demand for aquatic food products. Major aquaculture species of interest are split in six categories:

1. 15 species finfish in marine and coastal aquaculture 77% of total in category,
    - Atlantic salmon *Salmo salar*, Milkfish *Chanos chanos*, Mullets nei, *Mugilidae*, Gilthead seabream *Sparus aurata*, Large yellow croaker *Larimichthys croceus*, European seabass *Dicentrarchus labrax*, Groupers nei, *Epinephelus spp.*, Coho salmon *Oncorhynchus kisutch*, Rainbow trout *Oncorhynchus mykiss*, Japanese seabass *Lateolabrax japonicus*, Pompano *Trachinotus ovatus*, Japanese amberjack *Seriola quinqueradiata*, Nile tilapia *Oreochromis niloticus*, Barramundi (=Giant seaperch) *Lates calcarifer*, Red drum *Sciaenops ocellatus*.
2. 15 species finfish in inland aquaculture 79.3 % of total in category,
    - Grass carp *Ctenopharyngodon idellus*, Silver carp *Hypophthalmichthys molitrix*, Nile tilapia *Oreochromis niloticus*, Common carp *Cyprinus carpio*, Catla *Catla catla*, Bighead carp *Hypophthalmichthys nobilis*, *Carassius spp*., Striped catfish *Pangasianodon hypophthalmus*, Roho labeo *Labeo rohita*, Clarias catfishes, *Clarias spp.*, Tilapias nei *Oreochromis spp.*, Wuchang bream *Megalobrama amblycephala*, Rainbow trout *Oncorhynchus mykiss*, Black carp *Mylopharyngodon piceus*, Largemouth black bass *Micropterus salmoides*.
3. 8 species of crustacean 95.3 % of total in category,
    - Whiteleg shrimp *Penaeus vannamei*, Red swamp crawfish *Procambarus clarkia*, Chinese mitten crab *Eriocheir sinensis*, Giant tiger prawn *Penaeus monodon*, Giant river prawn *Macrobrachium rosenbergii*, Indo-Pacific swamp crab *Scylla serrata*, Oriental river prawn *Macrobrachium nipponense*, Green mud crab *Scylla paramamosain*.
4. 8 species of molluscs 84 % of total in category,

- Cupped oysters *Crassostrea spp.*, Japanese carpet shell *Ruditapes philippinarum*, Scallops nei *Pectinidae*, Sea mussels *Mytilidae*, Constricted tagelus *Sinonovacula constricta*, Pacific cupped oyster *Magallana gigas*, Blood cockle *Anadara granosa*, Chilean mussel *Mytilus chilensis*.

5. 5 species of other aquatic animals 77.5 % of total in category,
    - Chinese softshell turtle *Trionyx sinensis*, Japanese sea cucumber *Apostichopus japonicus*, Frogs *Rana spp.*, Edible red jellyfish *Rhopilema esculentum*, River and lake turtles *Testudinata*.
6. 8 species of macroalgae 93.7 % of total in category,
    - Japanese kelp *Laminaria japonica*, Eucheuma seaweeds *Eucheuma spp*, Gracilaria seaweeds *Gracilaria spp.*, Wakame *Undaria pinnatifida*, Nori *Porphyra spp*., Elkhorn sea moss *Kappaphycus alvarezi*, Fusiform sargassum *Sargassum fusiforme*, Spiny eucheuma *Eucheuma denticulatum* [15].

In 2020, aquaculture's contribution to global aquatic production reached a new high of 49.2%. Aquaculture of fed aquatic animals continues to outpace non-fed aquatic animal aquaculture. Despite the wide variety of farmed aquatic species, aquaculture production is dominated by a few “keystone” species, most notably grass carp for inland aquaculture and Atlantic salmon for marine aquaculture [15]. Aquaculture farming methods for fish include pond systems, open or submersible net pens, and sticks, ropes, racks, cages are used for the cultivation of shellfish and seaweed. Suitability of sites for nearshore or offshore farming is dependent on several criteria, these include proximity to infrastructure such as ports, processing and distribution centres, as well as physical and biological criteria such as bathymetry, seabed characteristics and contour, current velocities, temperature profiles, dissolved oxygen, turbidity and the frequency of occurrence of harmful algal blooms. For shellfish culture, the quantity of quality of phytoplankton is also an important consideration. Most important feature of offshore sites is wave climate – wave heights, wave periods, frequency and duration of high energy storm conditions, and currents must be known to determine whether a site is suitable, and if so, what type of technology is required for farming [17,18].

Although considered a food industry, aquaculture activities align with a much broader spectrum of ecological concepts, ecosystem dynamics, and research and management-based topics such as conservation, global change, habitat restoration, and sustainability (Table 1.2.). Aquaculture practises, for instance, can aid in the improvement of seaweed farms and the restoration of bivalve ecosystems for species recovery or replenishment. A broader and more interdisciplinary analysis of the ways in which aquaculture might produce benefits for people and ecosystems could teach a lot. A more comprehensive and nuanced understanding of the potential across the spectrum of aquaculture activities could result from understanding the role of bivalves and seaweeds used in aquaculture using key principles in ecology, conservation, or fisheries science, as well as aquaculture research. This could help to develop aquaculture for the conscious provision of ecological, economic, and social values [19].

Table 1.2.

Aquaculture activity, environmental or economic drivers, goals or beneficiaries [19]

	Environmental drivers	←→	Economic drivers
Activity		Restorative aquaculture' (commercial aquaculture with positive ecological value)	Commercial aquaculture
Perceived ecological value	Positive	←→	Low to negative
Target or beneficiary	Conservation, community, indirect commerce (co-benefits, e.g. water quality, fish and invertebrate habitat)	Food production, indirect commerce (co-benefits, e.g. water quality, fish and invertebrate habitat)	Global trade/market
Key research disciplines	Ecology, restoration ecology	Food and sustainability, aquaculture, ecology	Aquaculture, food sciences, husbandry, animal health
Central habitat principles	Habitat provision, bottom-up and top-down processes	Farming and ecosystem productivity	Farming

Macrophytes are a part of any freshwater ecosystem, and the abundance of these resources depends on light, water temperature, water quality, flow, sediment composition, water quality changes, fluctuations in water levels, and also biotic factors – competitive interactions between species [20]. Aquatic plants include all those members of the kingdom *Plantae* that grow in water medium or close to water, except for microalgae, considered as microphytes. Group of macrophytes includes free floating, floating but rooted, submerged, and amphibian plants. Macrophytes have fundamental role regulating biogeochemical cycles, hydrology, and sediment dynamic in their ecosystems. These resources have been extensively studied in context of ecology, remediation and as resource in agriculture for soil improvement [21].

The research papers included in the thesis are linked to aquatic bioresources, which have been obtained in the territory of the Republic of Latvia. The coast of Latvia, the Gulf of Riga and the Baltic Sea are the main places where the fleet of the Republic of Latvia catches most of the fish resources and where marine aquaculture might develop, also inland water resources are utilized. The following paragraphs briefly describe the fisheries situation in the Baltic Sea and Latvia's fisheries contribution. The vertical stratification of the water column distinguishes the shallow, partially confined Baltic Sea from other brackish seas. Through the Belt Seas, periodically salty, oxygenated water from the North Sea spreads into the deeper parts of the Baltic Sea while freshwater flows depart at the surface. The oxygen content of the bottom water is dependent on surface oxygen consumption and North Sea water inflows because stratification prevents oxygen from reaching the deeper seas. These hydrological features result in a restricted

variety of fish species in the basin, with marine species predominating in the southwest and a mix of marine and freshwater species in the northeast (subdivisions 28.1, 29-32). Commonly referred to areas in Baltic Sea are defined as follows – Baltic Proper (Subdivisions 24-29, excluding 28.1), and Central Baltic (Subdivisions 25-29) [16]. ICES (International Council for the Exploration of the Sea) statistical areas are showed in Figure 1.2.

Only a few stocks are the focus of the Baltic Sea's commercial fisheries. The mid-water trawl fisheries for sprat and herring are the pelagic fisheries that provide the highest catches (by weight) in the area. The bottom-trawl fisheries for cod and flatfish are the most significant demersal fisheries. While the pelagic fisheries are more dispersed, the demersal fisheries are concentrated in the south and west of the Baltic Sea. Commercial fishing effort has decreased recently throughout the whole basin. Cod and salmon make up the majority of the species caught in recreational fishing in the Baltic, which also includes a variety of other species. Fishing vessels from nine nations operate in the Baltic Sea, with the highest number of large vessels (> 12 m) coming from Sweden, Denmark, and Poland. Total fishing effort has declined since 2003 [16].

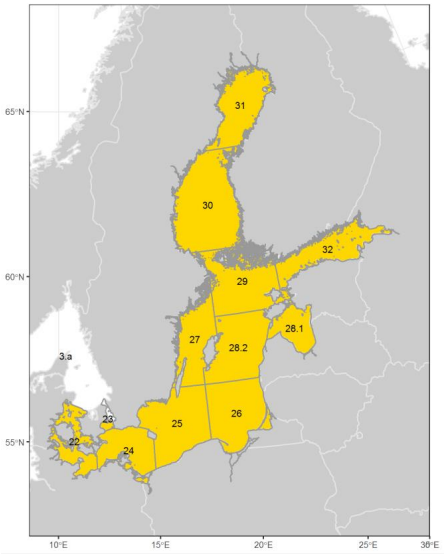

Fig. 1.2. Baltic Sea ecoregion and ICES statistical areas [16]

Species caught in fisheries are either landed or thrown away. Data on landings has been collected consistently for many years, whereas data on discards has only recently been collected consistently. As previously stated, the primary species targeted in commercial fisheries are cod, herring, and sprat, which account for approximately 95% of total catch. Cod fisheries in the Baltic Sea primarily employ demersal trawls and gillnets, whereas herring and sprat are primarily caught using pelagic trawls. Other economically important target fish species include salmon, plaice, flounder, dab, brill, turbot, pikeperch, pike, perch, vendace, whitefish, turbot, eel, and sea trout [16].

Herring and sprat from pelagic fisheries have dominated the overall fish landings from the Baltic Sea since the early 1950s, which peaked at more than 1.2 million tonnes in the mid-1970s. In the late 1980s, a loss in cod abundance was followed by a decline in sprat abundance,

which resulted in a significant drop in overall landings. Early and mid-1990s pelagic landings rose, suggesting a rise in sprat abundance during this time. Total landings in the Baltic Sea have been somewhat steady since 2003. (Figure 1.3.). While anticipated annual recreational catches of salmon have been increasingly inconsistent and sea trout catches have been rising recently, estimated annual recreational catches of western cod have been reasonably stable at around 2500 tonnes. As sprat and herring are target species and other bycatch (such sticklebacks) is also landed, discards for pelagic species in the Baltic Sea are extremely low. For static coastal gears the discard rates are minimal, and for pelagic trawls they are considerably smaller. The benthic species have the highest discard rate but it has been declining since 2016 [16].

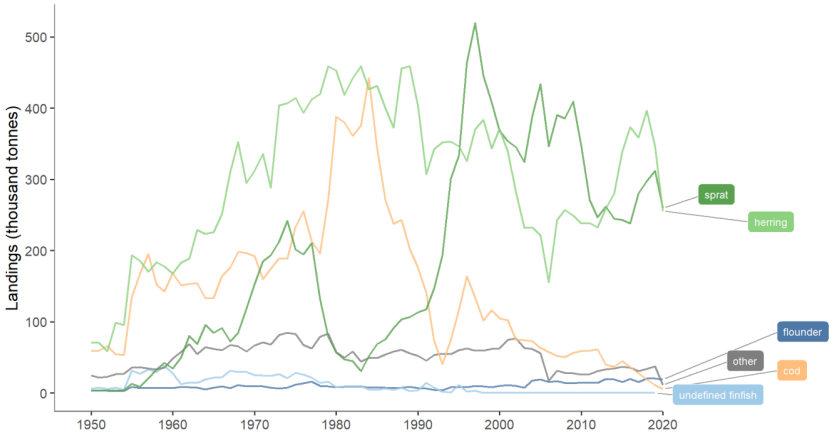

Fig. 1.3. Landings (thousand tonnes) from the Baltic Sea in 1950 – 2020, by species [16]
Historical nominal cathes 1950 – 2010; Official nominal catches 2006 – 2019; Preliminary catches 2020

A total of 610 coastal vessels (under 12 metres) and 55 offshore vessels (12 to 40 metres) are registered in Latvia. The pelagic trawls used by the offshore vessels target sprat in the Baltic main basin and herring in the Gulf of Riga, demersal trawls are used to target cod and flounder in subdivisions 25, 26, and 28. Sprat and herring have made up 92% of all annual landings since 2000. Most of the coastal fleet's boats are under 5 metres in length and use fykenets, trapnets, and gillnets to catch herring, round goby, flounder, smelt, salmon, sea trout, vimba bream, turbot, eelpout, and cod. All coasts have recreational fisheries that mostly catch flounder, cod, perch, and round goby. Fish resources and their utilisation have historically played a significant role in Latvia's national economy. Latvia's fishing activity is mainly concentrated in the Baltic Sea and the Gulf of Riga. In 2020, the fish catch was 104.3 thousand tons, which is 6.5% less than in 2019. Cod catches decreased by 51.9% during the five years from 2016 to 2020. In 2021, the catch of sprat, herring, and cod was 29.1, 27, and 0.7 thousand tons, respectively (Table 1.3.) [16].

Table 1.3.

Key fishery indicators in Latvia 2010–2020, thousand tonnes [16] [22,23]

	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021
Total catches	165.4	155.9	90.4	116.7	120.3	82.3	114.2	119.0	136.4	111.5	104.3	100.8
Fish catches	164.4	155.5	89.8	116.3	120.0	78.5	109.9	119.0	136.4	110.2	102.1	99.1
Catches of crustaceans and mollusc	1.0	0.4	0.5	0.5	0.2	3.8	4.3	0.0	0.0	1.3	2.2	1.7
Catches in inland waters	0.9	0.9	0.9	1.0	1.0	1.1	1.0	1.1	1.2	0.9	1.0	1.1
Catches in the Atlantic[1]	164.5	155.0	89.5	115.8	119.4	81.2	113.2	117.9	135.2	110.6	103.3	98
Catches in the Baltic Sea and the Gulf of Riga	74.0	63.2	57.6	61.0	59.9	62.5	60.4	67.4	70.4	69.7	60.8	58.8
Catches per capita (kg per capita)	78.0	75.1	44.2	57.7	60.1	41.4	58.0	61.0	70.5	58.1	54.7	–

Official statistics portal (table number: ZIS010, ZIS020). [1] – including the Baltic Sea and the Gulf of Riga

Although aquaculture contributes significantly to the fisheries sector, there are currently no farms in the seacoast zones, and it is solely connected to freshwater sources. However, there are indications of interest in marine aquaculture, particularly for native species of shellfish. In 2020, there were 78 registered aquaculture farms with the Food and Veterinary Service of the Republic of Latvia that were actively engaged in their respective industries and employed full-time equivalent of 219 people. To make up for the harm to fish resources caused by the construction of hydropower plants on rivers, water pollution, and the loss of natural habitats, about 5% of all farms are state farms. The remaining 95% are private farms, some of which have ponds for angling. Aquaculture facilities are frequently located in regions that reflect the customs and socioeconomic interests of landowners rather than necessarily being directly tied to the quantity and availability of freshwater. Ponds have been getting fewer while getting bigger in recent years. Recirculation aquaculture systems are being used more and more, which is another trend. The aquaculture industry generated 727 tonnes of fish and crustaceans in 2020, valued at €2.25 million on the market. The main species by far is carp (*Cyprinus carpio*), followed by trout (*Oncorhynchus mykis*), catfish (*Silurus glanis*) and sturgeon (*Acipenser spp*.). Carp contributed to 74.3% of the total aquaculture production volumes, and trout was the second largest species with an 8.2% share [24]. According to the European Maritime and Fisheries Fund operational program from 2014 to 2020 [25], the main challenges for the Latvian fishing sector are developing the port infrastructure and improving the quality, value added, traceability of products landed. Other aims include activities related to new markets, product development and higher pay for those working in the fisheries sector. In the aquaculture sector, the main aim is increasing the output and the level of value addition of farmed fish products.

In the previous decade, the intensification of natural resource management has created interest in biomass substrates that have not been widely used in the national economy so far, and promoted research about macroalgae [26] and macrophytes [27], identification of resources and their possible application in the bioeconomy, for example to produce high added value products, or for use in the energy sector as fuel. Ecological research and remote sensing of the bioresources of Latvian waters and the improvement of these methods in the future can help to quantify available resources, promoting both the protection of habitats and their sustainable management.

1.2. Aquatic biomass processing

The processing of fish and shellfish into food and other value-added products involves many sequential operations, and the main processing stages are primary processing, food processing, and preparation, pre-treatment of by-products, and extraction of value-added products. In the food industry fish, shellfish, and edible algae are referred to as seafood and in non-food food industries as by-products, discards, residue, waste, surplus, biomass, excess, etc. The priority is always to use freshwater or marine biomass in food production first then – for non-food production of feed, materials, and energy. The preparation of seafood for food consists of several stages and it depends on the product, but in any case, the main task of the industry is to meet the demand for seafood products, ensuring their safety and quality. Fish processing involves preparing fish and seafood for delivery to consumers. In food industry, first step after harvesting or catch is to assure quality of raw material. Seafood goes through primary processing – washing, gutting, fileting, shucking, before main process happens. All available methods of food industry are used in seafood processing. Most widely used method to preserve fish is application of low temperatures (chilling, freezing). Processing inactivates bacteria and enzymes resulting in extension of shell life and safe food. Seafood deteriorates very rapidly, and spoilage can be caused by metabolic activity of microorganisms, endogenous enzymatic activity (autolysis) and by chemical oxidation of lipids. Main changes that take place are initially the enzymatic degradation of adenosine triphosphate and related products. Fatty fish are more prone to chemical oxidation of lipids. Enzymes are also responsible for change of colour. Seafood can be classified in to seven groups according to processing method and risk of microbial contamination:

1. Highest risk – molluscs and other seafood eaten without cooking,
2. Fish and shellfish that will be consumed after cooking,
3. Lightly preserved (NaCl < 6% w/v in aqueous phase, pH > 5),
4. Semi-preserved (NaCl > 6% w/v in aqueous phase, pH < 5),
5. Mild-heated products, such as pasteurized and hot-smoked seafood,
6. Heat processed seafood,
7. Lowest risk – dried, dry-salted and smoke-dried products [28].

Pathogens of seafood can be natural, pathogenic *Vibrio*, *Clostridium botulinum, Aeromonas hydrophilla*, occurring during processing – *Listeria monocytogenes*, *Staphylococcus aureus*, or as contaminants *Salmonella spp.*, pathogenic *Escherichia coli*. Other contamination form of seafood are marine biotoxins and chemical contaminants, viruses. Molluscs are filter-feeders and can accumulate more toxic substances and microorganisms through filtering the water in

which they grow for nutrients. Shellfish primary post-harvest methods are shucking by heat or high-pressure, packing, low-temperature pasteurization, or flash-freezing (depending on species and region also low-dose irradiation) followed by frozen storage. Traceability is ensured by labels, barcodes containing information about species, date, time, region of harvest, container number. Later handlers add labels including name of receiver, weight and size of shellfish and new box number [29]. Shellfish are further prepared like fish, it more depends on the consumer market.

Fish are perishable commodity and same means (chilling, freezing) of processing must be done before consumption. In case of fresh fish supply chain fast and safe handling of live or iced fish must be followed. Preservation or freezing percentage are very high in processing chain to guarantee quality, safety, product availability. Degradation of proteins is one of the most important processes influencing the textural quality of fish muscle, post-mortem protein degradation in fish muscle is not fully understood, but it is generally accepted that different proteinases from the protease families of cathepsins and calpains are involved. Lipid hydrolysis and oxidation that produces a range of substances are caused by autolytic processes. Some contribute to protein denaturation by binding to the proteins. These processes can include the increase pro-oxidants and inactivation of antioxidants, activation of enzymes and the disintegration of membranes making them more susceptible to oxidation. To reduce the intensity of the processes, it is necessary to ensure the storage temperature throughout the fish supply chain. After unloading from the ships, the fish are weighed and again iced, sorted, until sale or further transportation. Transportation may take three to four days and are done regularly. If the fish is frozen, it takes place immediately on the fishing vessel or immediately after landing in the port. Storage temperature of – 30 °C or lower are recommended for retaining the quality of the fish. Heat preservation of fish is major method for extending the shelf life of packaged fish because of high safety level, convenience, and a healthy product, and sterilization is the classical method. The products undergo a process aiming to inactivate all pathogenic bacteria and their spores, temperature regime during processing may vary from 110 to 135 °C. When applying high pressure-assisted thermal processing in canning energy consumption can be reduced from 83 to 75 kWh/t, process could be further enhanced by energy recovery reducing the energy input to 67 kWh/t. Seafood can be preserved in several ways by curing – drying, salting, smoking, pickling and marinating, or combinations of these methods (Fig. 1.4.). Renewable energy such as solar heat, and heat from combustion of renewables can be used for drying the fish. The curing process is very diverse and often depends on region and tradition. Fish used for non-food purposes is also chilled or frozen before further processing, providing best possible feedstock. Feedstock composition depends on species, processing method, type of product (fillet or carcass), bycatch is also used as feedstock [29].

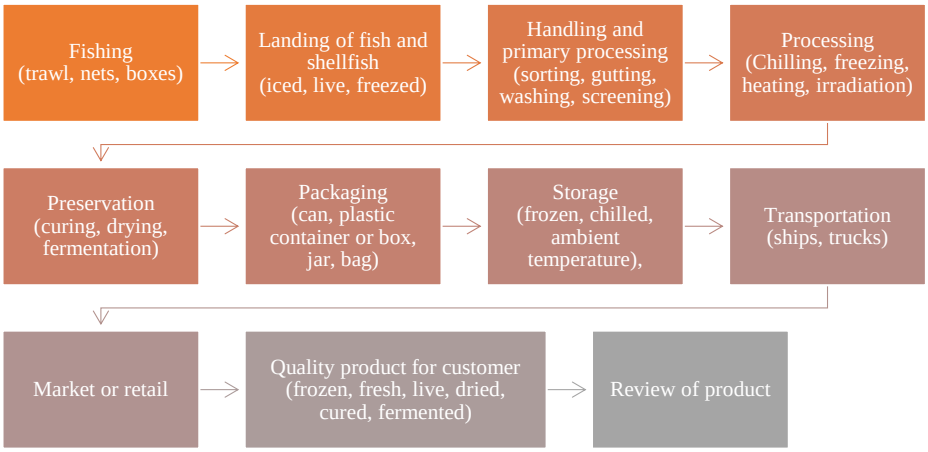

Fig. 1.4. Seafood processing chain from harvesting to consumer (author)

Quality and a healthy product are the main concern throughout the seafood processing cycle. Quality, value and safety of shellfish can be compromised by pollution of marine environments. Bacteriological standards for water quality are crucial for shellfish growing waters. Faecal coliform in water is frequently monitored to ensure that the environments meet established sanitary standards. Shellfish can also spoil during the supply chain due to the higher possibility of bacteriological and chemical contamination due to the mentioned water quality factors [29]. Most temperate shellfish have chilled shelf-life from 6 to 10 days, while warm water counterparts from 8 to 12 days [30]. Monitoring the quality, processing of such species is essential for the products to reach the consumers. High traceability of fish and shellfish also helps to ensure quality. However, if the product is damaged or discards have nowhere to be used, it is possible to use it to create other products by applying different processing technologies make added-value product.

Seafood products have a high nutritional value regarding protein, lipids, and essential micronutrients. Fish are major source of long chain polyunsaturated fatty acids, seafood have a well-balanced amino acid composition, contain high proportions of taurine and choline, vitamins D_3 and B_{12} and the minerals calcium, phosphorus, iodine, and selenium. Also, might provide significant proportions of vitamin A, iron, and zinc. Fish foods have a higher protein content than most terrestrial meats. Aquatic protein is highly digestible and rich in several peptides and essential amino acids that are limited in terrestrial proteins. Composition is subject to number of factors – content of unsaturated fatty acids decreases with increasing temperature and vice versa, salinity impact on fatty acids composition – increased salinity means higher lipid content in fish. In aquaculture under intensive culture conditions – feed composition and feeding regimen [31].

Shellfish broadly consists of two types of invertebrates – crustaceans and molluscs. It is estimated that the ocean is inhabited by more than 50000 species of molluscs, 1000 species of crustaceans. Crustaceans have segmented bodies, protected by hard shells made of chitin – shrimp, lobster, crayfish, crab, krill. Molluscs have soft bodies split into foot and visceral section, divided in cephalopods, and gastropods. Commercially important bivalves are mussels, oysters, clams, and scallops, cephalopods – squid, cuttlefish, and octopus. Gastropod group

contains abalone, sea snail, cockle, whelks, and others. Shellfish, in general, contains – digestible proteins (essential amino acids, bioactive peptides), long-chain polyunsaturated fatty acids, carotenoids (astaxanthin and other), vitamin B12, other vitamins, minerals – sodium, potassium, copper, zinc, phosphate, selenium, iodine [32]. Reported average protein contents (g/100 g raw meat) of various shellfish vary: shrimp, 17.0 to 22.1, scallop, 14.8 to 17.7, squid, 13.2 to 19.6, crab, 15.0 to 18.4; lobster, 18.2 to 19.2; krill, 12.0 to 13.0, clam, 9.0 to 13.0, mussel, 12.6 to 13.0, cuttlefish, 16.6 to 17.3, and oyster, 8.9 to 14.3. Shellfish have low crude lipid contents, average about ~ 2% (0.2 – 7%). Carbohydrate including dietary fibre in shellfish flesh are low, it varies from 1.3% in cooked lobster meat to 2% to 3% in oyster, green mussel. Shellfish are good sources of Na, K, P, Fe, Zn, Se, Cu, and cholesterol, carotenoids, vitamin A, D3. Habitats, season, feed, species, gametogenesis and spawning cycle can influence composition of shellfish [30]. Proximate composition of shellfish and finfish are provided in databases:

- European Food Safety Authority food composition data [33],
- FAO/INFOODS Food Composition Database [34],
- U.S. Dept. of Agriculture database [35].

Seaweed in a global sense is a new branch in seafood sector. In many parts of the world seaweed is used as food source because it is distributed in diverse and extreme environments. Since ancient times until the beginning of the 19th century, people in the East regarded seaweed as a food of great delicacy. It is now recognized that edible macroalgae, which are categorised in more than 600 species, have a great nutritional value which can be influenced by geographical location, growth stage, season, [36]. Cultivation of macroalgae can be done in land-based tanks, ponds or using open sea systems designed with nets, ropes or rafts. Most of the European aquaculture facilities are at sea (offshore or coastal), and 24% are land-based systems [37]. In sea-based systems, the cultivation can be combined with mollusc and/or fish farming in Integrated Multitrophic Aquaculture (IMTA), where macroalgae cultivation can offset the excess of nutrients released by fish farming [38]. Although the consumption of macroalgae is not as widespread in Europe as in Asia, they have attracted attention because their bioactive compounds have earned a reputation as “superfoods”. Quality evaluation is essential before using as supplements. Seaweeds are known as low caloric food, rich in vitamins and minerals. Brown algae are the most consumed 66.5 %, then red 33 % and green 5 %. Brown macroalgal species considered safe for food consumption are *Fucus vesiculosus*, *Fucus serratus*, *Himanthalia elongata*, *Undaria pinnatifida*, *Ascophyllum nodosum*, *Laminaria digitata*, *Laminaria saccharina*, *Laminaria japonica*, *Alaria esculenta*. Macroalgae can be used as alternatives to vegetable sources (legumes) of proteins (red algae: *Pyropia tenera*, *Grateloupia filicina*), as well as for the formation of protein balanced diets with low-costs due to high content present in macroalgae [39].

Most people are not aware that they consume macroalgae but many products, such as meat and dairy products, we consume on daily basis contain macroalgae derived compounds or their extracts [36]. They are valuable due to their high content in compounds with different biological activities, including both complex organic compounds and primary and secondary metabolites – phytopigments (xanthophylls and carotenoids), polyunsaturated fatty acids, phenolic compounds, tannins, peptides, lipids, enzymes, vitamins, carbohydrates, terpenoids, and others. Thus, algae are a viable and economical biomass source of valuable compounds with potential

applications in the nutraceutical, pharmaceutical, chemical, food, and cosmetic industries due to their biologically active and regenerative properties. [38]. Edible seaweeds are a rich and sustainable source of macronutrients (particularly dietary fibre) and micronutrients, but if seaweeds are to contribute to future global food security, legislative measures to ensure monitoring and labelling of food products are needed to safeguard against excessive intakes of salt, iodine, and heavy metals. A number of edible seaweeds are recognized as novel foods in Europe, although the nutritional composition of brown, red, and green seaweeds vary between species, season, and ecology of the harvesting location. Therefore, there is a need to characterize the composition of seaweeds in relation to the influence of location and seasonality on seaweed content. Current efforts to catalogue information on the variability of nutritional composition will facilitate the identification of optimal harvesting periods and/or locations for a given species. Protein content of seaweed has gained considerable attention, given the emerging challenges to improve food security by identifying alternative and sustainable sources. Protein content ranges from 5% to 20 % in brown seaweeds, from 0.7% to 45% in red seaweeds, from 3.4% to 30% in green seaweeds. On dried gram-for-gram basis, seaweeds have protein and amino acid contents comparable to those of beef. The amino acid composition of proteins is critical to determining the value of proteins to the human diet, particularly in achieving an adequate intake of essential amino acids. However, the digestibility of seaweed protein within the gastrointestinal tract will significantly affect the nutritional value of the protein, with protein–polysaccharide interactions reducing digestion efficiency considerably. Fat content of seaweed tends to be low relative to total dry weight. Fatty acid composition varies by season percent fat content is highest in winter and lowest in summer. Total lipid content ranges from 0.29% in *Sargassum polycystum* to 8.88% in *Porphyra spp* [40].

Seaweed with its high fibre content is a promising source in food industry. However, the contribution of whole seaweed to the currently recommended intake of dietary fibre, i.e., 25 g/d, is limited, with a 5-g serving of brown, red, or green seaweed contributing up to 14.28%, 10.64 %, or 12.10 % of dietary fibre intake, respectively. This has led to increasing interest in the industrially applicable extraction and isolation of individual fibre components from seaweed. Seaweeds contain a diverse range of fibre components. Brown seaweeds contain alginate, laminarin, and fucoidan polysaccharides, red seaweeds – agar, carrageenan, porphyran, and xylan, and green seaweeds – ulvan, xylan, and cellulose. The majority of research on the health benefits of seaweed-derived dietary fibre components in humans has focused on potential anti-obesogenic effects, including improved satiation, delayed nutrient absorption, and delayed gastric emptying [40].

Polyphenols are highly complex, structural components of the cell wall. They are often bound to cell wall polysaccharides, protecting against oxidative damage. Brown seaweeds contain diverse flavonoid and phlorotannin polyphenols that vary in structure, molecular weight, and level of isomerization. Carotenoids are a group of tetrapenoid compounds in seaweeds that contribute to photosynthesis. Their antioxidant properties facilitate protection from UV damage. In seaweeds, the main carotenoid with potential application in the food industry is fucoxanthin, extracted from brown seaweeds. Research suggests that fucoxanthin, through its antioxidant activity, have potential as a food preservative to prevent lipid peroxidation in meat. Seaweed also contain micronutrients – iron, magnesium, sodium, iodine

and are a source of both fat and water-soluble vitamins – vitamin A, vitamin C, vitamin B_9, vitamin D_3, vitamin B_{12} [40].

Reed and other macrophytes are not recognized as food items in Europe, they have use in eco-buildings, production of extracts and feedstock in fermentation. Chemical examination of reed bunches taken primarily during the winter seasons in 12 different countries in Europe and Asia shows the average culm diameter of a bunch ranges between 2.4 and 7.7 mm. Crude cellulose accounts for the majority of the dry matter (51.5 ± 2.3 %), followed by crude hemicellulose (26.9 ±2.3 %) and crude lignin (11.9 ±1.3%). Crude ash ranges from 0.69 to 8.07 %. The C/N ratio ranges from 76 to 963, with a mean of 290 [41].

Inverted triangle shows hierarchy for aquatic food recovery the priority is to maximize edible yield, and the least preferred lowest value is given to incineration or landfilling (Fig. 1.5.).

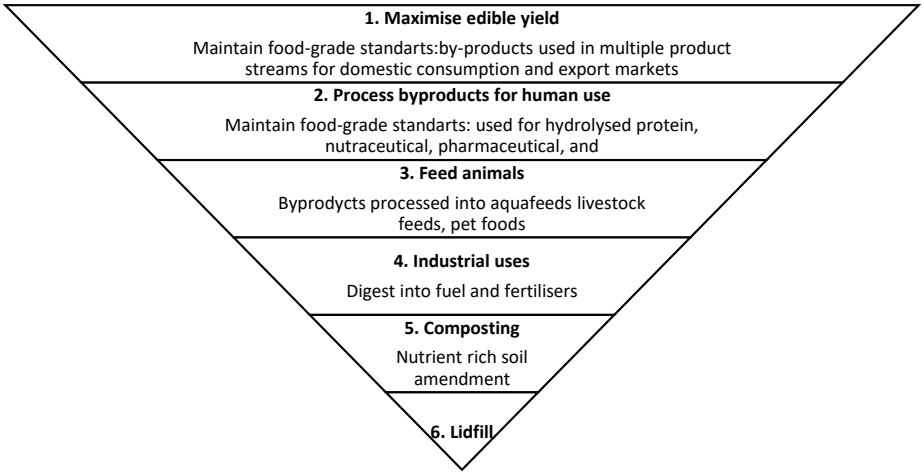

Fig. 1.5. Aquatic by-product food recovery hierarchy, based on Stevens *et al.* 2018 [42]

Waste, discards, and residue from aquatic resources are typically produced throughout the fishing and processing phases. The sustainable utilisation of waste has improved recently. The waste is further increased by the accidental capture of several animals that are not prepared for human consumption. The non-edible components of finfish processing account for 10–50% of the overall weight and comprise the head, gut (viscera), skin, bone, and flesh that is still attached to the bone. The non-edible components of shellfish, particularly those of crustaceans, such as the head, shell (carapace), viscera, and appendages, can make up to 85% of the raw material. Discards are generally dumped on land or hauled into the ocean, depending on the region. A significant portion of these by-products are underutilised, wasted, or discarded. Dumping of these by-products not only results in the loss of a large amount of bioactive rich materials, but also in pollution issues. Recycling by-products into marketable goods can be an effective solid waste management strategy. Fish waste by-products can be used for human consumption (e.g., mince, roe, fish heads, nutraceuticals), agricultural or allied purposes (e.g., fish hydrolysate, fertiliser, compost), and non-nutritional purposes (biodiesel and fuel, chitin and chitosan, caroteniods pigments, leather and gelatine). European Commission regulation on animal by-products (EC No.1774/2002) defines animal by-products as whole or parts of animals or

products that is not fit for and intended for human consumption. Though co-products, co-streams, discards, or waste are synonymously used, the term waste seems to mean the material has no value. There are different terms such as “by-product,” “co-product,” “fish waste,” “fish offal,” “fish visceral mass,” “fish discards,” and so on that are applied to describe the non-edible parts of seafood processing [43]. For finfishes, typical by-products include trimmings, skins, heads, frames (bones with attached flesh), viscera guts and blood. Stevens, *et al*. 2018 reported the fractions of by-product as percentage of total wet weight of Atlantic salmon is viscera (12.5%), heads (10%), frames (10%), skins (3.5%), blood (2%), trimming (2%), belly flap (1.5%) (Fig. 1.6.) [42].

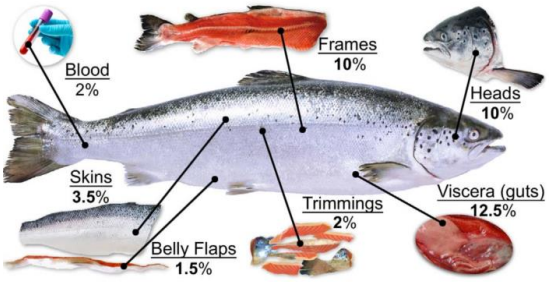

Fig. 1.6. Atlantic Salmon by-product fractions as a percentage of the total wet weight [42]

The composition of the fish depends on the species, sex, diet, season, and state of health. Most fish contain 15 – 30% protein, 0 – 25% fat and 50 – 80% water. Solid fish waste consists of head, fins, scales skin, viscera, and bones. After processing a whole fish, usually about 30 – 50% meat remains, the remaining is 4 – 5% skin, 21 – 25% head and 24 – 34% bones make up more than 45% of the whole fish body. Literature analysis shows that the waste produced by the fishing industry can be classified in several ways:

- by type of waste:
  - solids – liver, skin, roe, milk, digestive organs, head, muscles, bones,
  - liquid – processing wastewater (stickwater, blood, bile), secretions of digestive organs.
- according to the type of further use (disposal):
  - recyclable – do not contain impurities that would significantly complicate their use,
  - non-recyclable (disposable in a landfill) – contain impurities that make their use difficult,
- By the dominant, theoretically obtainable product/substance:
  - waste with increased fish oil content – waste from fatty fish processing,
  - waste with increased protein content (whitefish carcasses),
  - waste with increased collagen content – fish skins and bones,
  - waste with increased content of enzymes – internal organs and digestive tract,
  - waste with an increased content of cryoprotective peptides.
- According to the dominant part of the fish in the waste:
  - whole fish, heads
  - skins,

- bones,
- internal organs,
- mixed.

Liquid waste is called stickwater, is water with solid or liquid impurities, it makes up about 60% of recycled residues by weight. Solids, mainly proteins and fats, each make up 6 – 10 % of stick-water. One of the major problems limiting the use of this type of waste is its variable nature. Solid fish waste consists of the head, fins, skin, internal organs, and skeleton [44] [45]. Generally, shellfish processing are characterized with higher amount of by-products (Table 1.4.).

Table 1.4.

Shellfish processing by-products [43]

Sources		By-products	Percentage of by-products
Crustacean	Shrimp/prawn	Head, shell	65 – 85
	Crab	Back shell, viscera, gills, claws	60 – 70
	Lobster	shell	Up to 60
	Krill	Head, shell	71 – 74
	Crayfish	Head, shell	up to 85
		Head, shell	
Molluscs including cephalopods	Scallop, calm, oyster, mussel etc.	Shell, nonedible body part	60 – 80
	Squid	Ink bag, gladius or pen, liver, other organs	25 – 32
	Octopus	Intestine, mouth apparatus, eyes	10 – 20
Coelenterate and echinoderm	Sea urchin, sea cucumber, jelly fish	–	–

Technology suitability for processing of by-products

Biomass is matter derived from recently living or living organism. Most frequently used to refer to plant material but all biological organisms are source of biomass. Biomass capture carbon dioxide and accumulates in the food chain from lower producer organisms (autotroph) to higher (omnivores). Like any feedstock, biomass has its own challenges – location, seasonality, species (diversity and adaptations of biological organisms to different environmental conditions determine heterogeneous and complex composition), microhabitat conditions, harvest and storage conditions, relatively low energy density, and ambiguity of the market (demand, price, suppliers, distributors). Therefore, ability to measure biomass properties consistently and accurately is critical when planning the processing operations.

Substantial differences in biomass diversity and quantity and compositional characteristics stipulates that there is no univocal way of classification, so biomass can be grouped differently, depending on purpose and scope. According to origin, function, and final products, generally

biomass is categorized in two ways – based on types of biomasses existing in nature or based on the use and application of biomass as feedstock. Biomass studied in this Thesis falls into two classification groups – aquatic biomass (fish, seaweed) and herbaceous biomass (reed) (Table 1.5.), where each in the context of recycling have own technological challenges. Reed habitat is wetlands, literature suggests that reeds are not classified as aquatic biomass and therefore separated as herbaceous biomass. Biomass could be a source of renewable energy and through treatment and conversion processes are converted into different types of energy carriers. The most important parameters determining choice of the production process is renewable end-product required, quality and quantity of biomass, and the cost of the process [46]. Fish, shellfish, and macrophyte in wet weight all show similar moisture content from 60 to 80% and seaweed – 80 to 90%. This means that reduction of moisture content is an indispensable part of aquatic bioresource processing. Only applications where it can be used wet is as unprocessed fertilizer, but in this case, there are cross-contamination and microbiological hazards, so pre-treatment is required. Most often in publications, moisture content is expressed in dry weight, not live weight.

Biomass can be converted into two main types of energy carriers – electrical/heat energy and transportation fuels. Physicochemical characteristics that play a crucial role in directing the available feedstock into both or either of these domains are moisture content (intrinsic/extrinsic), caloric value, proportions of fixed carbon and volatile substances, ash content, and alkali metal content, cellulose/lignin ratio. Common processes involved in biomass conversion into energy are thermochemical conversions, biochemical conversions, and physicochemical conversions [46] (Table 1.6.). The main pre-treatment methods of lignocellulosic biomass:

- Mechanical – milling, ultrasonic [47] [48],
- Chemical – liquid hot water, weak acid, strong acid hydrolysis, alkaline hydrolysis, organosolv, oxidative, ionic liquids [49,50],
- Chemical/Mechanical – steam explosion, ammonia fibre expansion, CO_2, mechanical alkaline pre-treatment [48,51]
- Biological – biological hydrolysis [46].

Table 1.5.

Typical chemical composition of aquatic biomass and herbaceous biomass [46]

Biomass	C* (%)	O (%)	H (%)	S (%)	N (%)	VM (%)	FC (%)	M (%)	A (%)
Aquatic	27 – 43	34 – 46	4 – 6	1 – 3	1 – 3	42 – 53	22 – 33	8 – 14	11 – 38
Herbaceous	42 – 58	34 – 49	3 – 9	< 1 – 1	< 1 – 3	41 – 77	9 – 35	4 – 48	1 – 19
Abbrv.: Carbon (C), Oxygen (O), Hydrogen (H), Sulfur (S), Nitrogen (N), Volatile matter (VM), Fixed carbon (FC), moisture (M), ash (A) content of wt.									

Table 1.6.

Conversion technologies and corresponding products [46]

Process/Technology		Feedstock	Usable product

Thermochemical conversion	Combustion	Agricultural residues, Woody residues, Animal wastes	Heat, Electricity
	Pyrolysis	Agricultural residues, Woody residues	Pyrolysis oil, Producer gas, Char
	Gasification	Agricultural residues, Woody residues	Producer gas, Liquid fuels, Char
	Liquefaction	Agricultural residues, Algal biomass	Fertilizer/biofuel, Syngas, Liquid fuels
Biochemical conversion	Anaerobic digestion	Animal wastes, Sewage sludge	Liquid fuels, Biogas, Electricity
	Fermentation	Agricultural residues, Sugars, Starch	Liquid fuels (bioethanol)
Physicochemical conversion	Esterification /Transesterification	Vegetable oils, Animal fats, Waste oils	Liquid fuels, Glycerol

Additionally, animal biomass has other methods – solid-liquid separation, solar drying, freeze concentration and compaction. However, this does not mean that animal biomass is not pre-treated with the methods listed above. Solid-liquid separation by gravity, mechanical, chemical processes allow a redistribution of nutrients, facilitating their final management. The solid fraction is characterized by a higher concentration in organic matter, organic nitrogen, and phosphorus. In contrast, the liquid fraction is characterized by being less rich in some nutrients than the solid fraction, despite having still dissolved and suspended substances in important quantities, such as ammoniacal nitrogen, potassium, and other soluble salts. The liquid fraction can be used for irrigation on near fields without elevating the soil test phosphorous levels. Solar drying aim to reduce volume of water by drying with solar energy under controlled conditions (e.g. greenhouse system) and is used for wet waste biomass, slurries. Before introducing waste into the greenhouse, pH is modified and, if necessary, biofiltration is applied to generated gases with the aim of minimizing gaseous emissions and odours. Freeze concentration is a technique to remove water from solutions by freezing until the formation and separation of ice crystals occurs. Process involves controlled reduction of the temperature of the solution of interest below its freezing point, in order to avoid reaching the eutectic temperature. The efficiency of the process is determined by the purity of the ice formed (minimum retention of solutes). Method allows a 50% reduction in the high humidity of solid residues. Biomass wet waste mass can be compacted at relatively high temperatures and pressures, then compressed in a die to form pellets. Pelletizing converts to a dry pathogen-free easy to handle, finished product that can be used as a fertilizer, soil amendment, feed additive, or energy fuel. Biological treatment uses naturally occurring microorganisms to change the properties of waste. Nitrification-Denitrification from animal manure is a biological process whose objective is the elimination of nitrogen from the liquid fraction of the slurry. Nitrification is the aerobic oxidation of ammonia to nitrite and nitrate by autotrophic nitrifying bacteria. Denitrification is the anoxic reduction of nitrate to nitrite and nitrogen gas by heterotrophic bacteria. Maximum nitrogen removal efficiencies attainable are up to 70% (rest of N will be separated in the solid fraction, assimilated by the biological sludge, or will remain in the liquid effluent). Composting is a process of aerobic decomposition and stabilization of organic materials in an operating regime that allows reaching temperatures for thermophilic bacteria. With this process a stable and

sanitized solid product is obtained withing several weeks. Moisture content about 60 %, C/N ratio 25 – 30 and sufficient porosity to favour circulation of air inside the stacked material. Compost, the resulting product of this treatment, is an odourless, low-moisture, fine-textured material that can be used in bulk as an organic fertilizer or bagged and sold for use in nurseries and gardens and for potting media. Bio-drying makes use of bioenergy from organic waste with high water content to remove moisture improving utilization value, treatability of the waste. Essential feature of bio-drying is the utilization of thermal energy generated by aeration degradation of organic matter in waste thus achieving self-drying [52].

After biomass pre-treatment and reduction of water content the main process is recovery of substances from the pre-treated matrix called extraction. Seafood waste biomass matrix is characterized by the substance content, if it is nitrogen, lipid, polysaccharide, mineral, lignin based. Quintessential inputs and outputs of extraction process related to the six principles of green extraction are [53]:

1. selection of renewable raw resource;
2. use of water or agrosolvents;
3. reduction and recovery of energy using innovative technology;
4. production of co-products;
5. development of controlled process and reduction of operations;
6. aim for clean green bioactive extract (Fig. 1.7.).

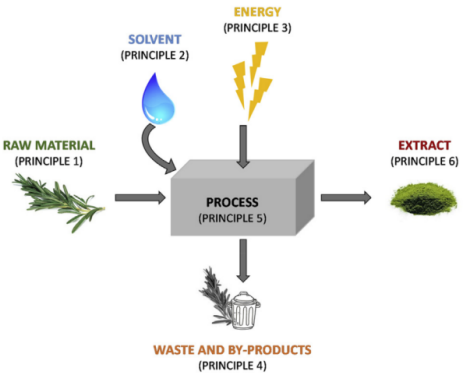

Fig 1.7. Essential inputs and outputs of extraction process related to the six principles of green extraction [53]

Common innovative approaches for the extraction of bioactive compounds are:

- Instant controlled pressure drop (DIC) technology is a thermo-mechanical process based on the theory of instantaneous thermodynamics, applied to heat-sensitive products via treatments of high temperature/high pressure for a short time. DIC process consists of subjecting biological matrices to saturated steam pressure treatments of 100 to 900 kPa for a few seconds, followed by an abrupt and controlled pressure-drop at a rate higher than 500 kPa per second. This leads to a final vacuum of absolute pressure of 10 to 5 kPa, significantly lower than atmospheric pressure at sea level (101.325 kPa). DIC triggers instantaneous autovaporization of water, quick cooling of biological products, and expansion and creation of cells in the matrix [54]. Atlantic salmon *Salmo salar* and white tuna *Thunnus albacore* was used to study the effect of several successive pressure-drops on fish cubes (multi-flash

autovaporization) at 260–540 kPa for 4–46 s, reduction in dehydration time was observed. Shrimp *Penaeus notialis* was used to obtain shrimp snacks and characterize them 400–700 kPa, 70–130 s and 500 kPa; 70 s. More expanded with higher porosity dried material thanks to the mechanical stress caused by vapor generated within the pores. DIC uses high saturated steam pressure and short duration to provide a new way to expand biological matrices, improve drying, decontaminate, and extract biologically active compounds, among other attributes. The application of DIC has shown the possibility of a significant leap in quality improvement and cost reduction in the food industry [55].

- Pulsed electric fields (PEF) treatment involves the exposure of biological cells to high intensity electric field pulses that can alter the structure of the cell membrane. The external electrical field promotes cell electroporation, causing the cell membrane barrier to be compromised and become permeable. Although PEF is commonly used in industry to inactivate microorganisms and extend the shelf life of food products, research has also demonstrated the capability of PEF treatment to enhance the extraction of valuable compounds from plant and animal tissue [56]. PEF is technology that can be applied in treatment of all aquatic biomass [57] [58] [59]. PEF treatment had the ability to improve several processes such as preservation, tenderization, and aging. PEF treatment could be used as a useful strategy to increase water holding properties of products, for by-products valorisation due to its potential to enhance the extraction of high added-value compounds [59]. Hoki fish male gonads were subjected to pulsed electric fields (PEF) treatment at varying field strengths (0.625, 1.25, and 1.875 kV/cm) and frequencies (25, 50, and 100 Hz), at a fixed pulse width of 20 µs. The total lipid yield was increased from 4.1 % to 6.7 % by a relatively mild PEF pre-treatment at a field strength of 1.25 kV/cm and frequency of 50 Hz [56]. In other studies PEF has been used to extract protein hydrolysate, with treatment time 100–800 µs, intensity strength 5–20 kV/cm, and the ratio of material to solvent (3:1–10:1) [59], and antioxidants from fish residues [58].
- Under accelerated solvent extraction (ASE) solvents at high temperature (up to 200 °C) and pressure (up to 20 MPa) are used for the extraction of bioactive compounds. The high temperature and pressure decrease the solvent's surface tension, which facilitates penetration into the pores of matrix, thereby improving the mass transfer of the active compounds to the solvent. The solvent under pressure remains in a liquid state, even at its boiling point, and facilitates extraction at a higher temperature. Under these conditions, solvents that are not efficient in extracting analytes such as phenolic compounds or anthocyanins under normal conditions may be used for the same extraction. Pressurized solvents have improved, featuring desirable physicochemical properties, such as increased diffusivity, solubility, viscosity and dielectric constant, and can be modified by changing temperature and pressure. This is a rapid and efficient process with reduced solvent consumption, but higher temperature-induced damage to heat-labile active compounds. The requirement of large and sophisticated equipment and extraction at higher temperatures are drawbacks to this method [60]. With ASE, extractions can be programmed and automatically run, which is convenient for quality control. A temperature of 183 ◦C, a pressure of 130 bar, and an extraction duration of 3 min enabled recovering rosemary antioxidants [61]. ASE was used to extract sulfated polysaccharides from *Fucus virsoides* and *Cystoseira barbata*, the optimal ASE parameters were 0.1 M H_2SO_4 , for two cycles of 15 min at 140 ◦C [62]. Using agrosolvents non-polar compounds like lipids, carotenoids can be extracted from waste matrix in green manner [63].

- Negative pressure cavitation (NPC) is described as the generation, growth and the subsequent collapse of millions tiny vapor bubbles (voids) in a liquid or at liquid-solid interfaces. High energy will be released by collapse of created bubbles and caused high local temperatures and pressures at a large number of reaction sites that are normally related to the enhanced reaction rates in cavitation systems. Method enhances solvent penetration into the cells, increases surface area of matrix and is used for extraction of phenolic compounds, lipids, proteins, dyes and pigments, aromas and flavours, mostly from plant matrices. Modification of extraction process adding another green extraction method shows increased yields, NPC: negative pressure (MPa): −0.080, extraction duration (min): 30; L/S: 25:1. Enzyme: Incubation T (ºC): 35; time (min): 60; pH: 4 [64].
- Sub-critical water (SBW) is pressurized water in its liquid state in the temperature range from 100 ºC to 374 ºC (T_c = 374 ºC, p_c = 22 MPa). Under these conditions, water presents unique properties such as hydrogen bond weakening, allowing dissociation of water into hydronium ions (H_3O^+) and basic hydroxide ions (OH^-), thus leading to higher ionization constant K_w, that confers hydrolysis properties of water as solvent. At these conditions, the dielectric constant of water decreases with increasing temperature due to hydrogen bond dissociation, allowing water to act as an effective solvent for moderately polar to non-polar substances. The valorisation of Atlantic cod frames from a filleting industry was investigated using SBW extraction and hydrolysis at different temperatures (90, 140, 190 and 250 °C) and 100 bar to obtain extracts rich in proteins, peptides and amino acids. Up to 57.7 g of extract per 100 g of codfish frames were obtained, with nearly total recovery of the protein fraction. According to size exclusion chromatography results at each temperature protein extracts of decreasing molecular weight were obtained. Most of the protein present in the raw material and extracts was collagen and collagen fragments, as suggested by the amino acid profile. The mineralized residue left after SBW treatment of cod frames was identified as practically pure, crystalline, hydroxyapatite, that may find applications in biomedical field and hard tissue engineering [65]. Extraction of the protein and polysaccharide fraction of the industrial solid residue from red macroalgae show high hydrolysis yields for both compounds. Co-solvents including ethanol, methanol, salts, and ionic liquids are used to assist SBW [66].
- Ionic-Liquid-Mediated Extraction (ILE). Ionic Liquids (ILs) are liquid molten salts at temperatures below 100 °C and typically consist of large and unsymmetrical organic cations and organic or inorganic anions. ILs have excellent chemical, thermal, and electrochemical stability, nonflammability, and negligible volatility exhibited by most aprotic ILs, and they are also recognized for their excellent solubilization capabilities for a wide range of compounds and materials, from to naturally extracted to synthetically produced. As well as a good stabilizing medium for proteins, enzymes, nucleic acids, among others [67]. An important feature of ILs is their immeasurably low vapor pressure. Therefore, they have been widely studied as solvents or cocatalysts in various reactions, including organic catalysis, inorganic synthesis, biocatalysts, and polymerization [68]. Ionic liquids have been studied as pre-treatment solvents for the extraction of collagen biopolymer from waste fish scales [69] and for pulping crustacean waste biomass [70].

Other green extraction methods, ultrasound-assisted extraction (UAE), Microwave extraction (MAE), Enzyme-assisted extraction (EAE), Supercritical fluids (SCF) supercritical CO_2 [60] are described in the results. Combination of modern techniques e.g. MAE and PEF,

MAE and SFE, EAE and MAE, NPC and MAE can help effective extraction, and wider range of intermediates[53] [71] [72]. Regardless of which method is chosen it is necessary to carry out a process to ensure the recycling of biomass. Capability to control bioprocesses automatically and accurately in their optimal state is extremely important and allows to reduce or limit production costs and increase yields while maintaining product quality. Due to increased competitiveness, strategies based only on empirical knowledge and incorrect attempts are no longer sufficient or effective. The availability of improved sampling methods together with automated measurement tools (e.g. traditional analytical methods, new sensor technologies, probes and analysers) can significantly reduce the time required for strain selection, process development and process control, reducing the number of steps in the production/cultivation process because especially manual operations, and reducing the spread of errors. Regardless of which biomass is processed, it is essential to choose a suitable analytical method for the specific biomass, reaction, and extracts. The most popular are sensor methods based on mathematical models, as real-time data is obtained based on sensor readings (Fig. 1.8.). Mathematical modelling, monitoring, and the real-time control of bioprocesses is a major challenge. Biotechnologists and control engineers have a task of creating communication platforms between themselves and industry so that the innovations developed can be applied at industrial level. Stochastic and dynamic nature of these systems make bioprocesses modelling, monitoring and control is challenging task because there is significant uncertainty of the models structure and parameters. Implementation of the most suitable type of automated analysis is a main difficulty [73].

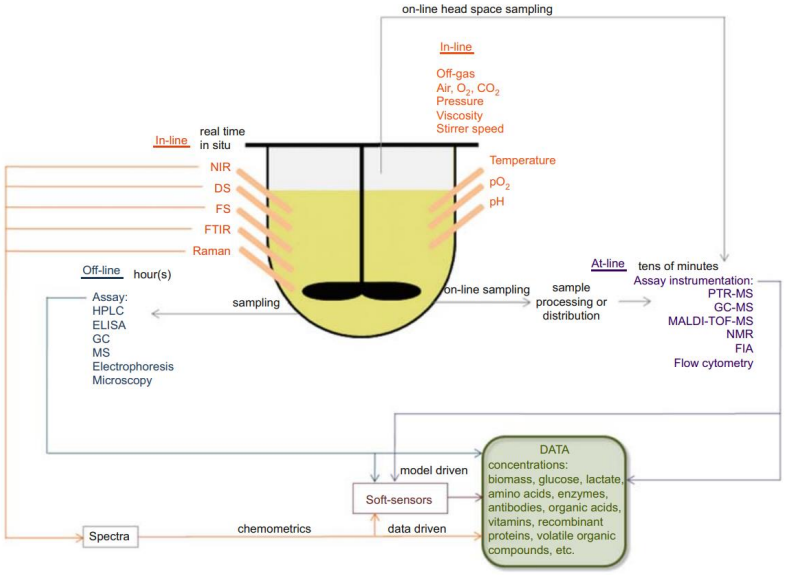

Fig 1.8. Schematic of bioprocess monitoring: variables and different analytical techniques [73] NIR, near-infrared spectroscopy; DS, dielectric spectroscopy; FTIR, Fourier-transform infrared spectroscopy; FS, fluorescence spectroscopy; HPLC, high-performance liquid chromatography; ELISA, enzyme-linked immunosorbent assay; GC, gas chromatography; MS, mass spectrometry; PTR-MS, proton transfer reaction mass spectrometry; MALDI-TOF-MS, matrix-assisted laser desorption ionization time-of-flight mass spectrometry; NMR, nuclear magnetic resonance; FIA, flow-injection analysis.

1.3. Intermediate products from aquatic biomass

After primary processing, further processing technologies follow. As mentioned in preceding paragraphs, specific methodology is determined by the desired final product. In recent years, there has been a significant increase in the interest in marine compounds, studied source organisms, their chemical composition, and biological activities. Carroll *et al. in* 2022 presented review on natural marine products – 1470 new compounds have been described in 2020, and overall, about 39 000 compounds are described in the *MarinLit* database. *MarinLit* has been published by the Royal Society of Chemistry since 2014. Bulk of these compounds are secondary metabolites and intermediates of biochemical reactions that quickly undergo degradation under changing conditions. In any case, it is necessary to study the applicability of these compounds, for example, in pharmacology and animal recuperation in aquaculture [74].

One of the driving forces in marine industry and water resources management in general is scientific research in blue bioeconomy marking outline of development directions and creates an overhead framework for the development of policies, regulations in aforementioned fields of interest. Attractiveness of technology and longevity is provided by approved solutions, transdisciplinary approaches and development in electronics, mechanics, information technology, etc. Biological activity and suitability of marine biopolymers is the direction of research that should be followed to create, for example, solutions for food applications, a niche product. Materials, matter, and energy from aquatic biomass can be obtained by conventional or innovative methods. Conventional methods are already established in processing industry and innovative methods are green, optimized – resource or energy-efficient extraction, RES, greener sourcing. Literature shows that both types of methods under optimal conditions show similar yields. Such a classification into traditional and green processes is usually used in the context of environmental science or for marketing purposes. Therefore, based on the research tasks and the reviewed selected topics of literature, well received innovative laboratory-to-production scale methods or preceding modifications in the extraction of marine biopolymers and lipids are superficially discussed. To ensure the processing of aquatic resources in the most effective way it should be done in one institution because it ensures less transportation, concentration of workers, equipment, raw materials, energy in one place which in turn makes it more profitable. This refers to biorefinery cascade which along with green extraction is briefly discussed in chapter 3.2.

Marine by-products from the fish processing industry and fishery by-catch are an important source of bioactive compounds – proteins, amino acids, peptides, enzymes, collagen, gelatine, lipids, ash, chitin, vitamins and others are of great interest for their high market value [45]. Content and mean market value of high value components obtained from fishery by-products is reported in Table 1.7.

Table 1.7.

Content of high value components in fishery by-products [45]

Fishery By-Products	High Value Components	Content (% w/w)	Market Value (Euro/kg)
Fish skin, scales and bones	Collagen and gelatine	Up to 80% in skin, up to 50% in scales	9–14

Fish skin, scales and bones	Hydroxyapatite	60–70% in bones, up to 50% in scales	n/a
Fish viscera	Enzymes		14.400 (cod proteases)
White fish flesh residues	Free aminoacids	0.8–2% of taurine, 2.7% of creatine (on dry matter)	n/a
Cod liver, mackerel oil	Polyunsaturated fatty acids-PUFA (ω3 and ω6)	50–80% in cod liver, 23% are ω3 PUFA	24 (as cod liver oil)

The added value of fish proteins lies in the properties of their hydrolysates. Marine-derived proteins contain various bioactive peptide sequences which become active after hydrolysation. Biopeptides are released from parent proteins during normal gastrointestinal digestion or during food processing with the use of heat, chemicals, proteolytic enzymes, or microorganisms. Due to having beneficial modulatory functions for some metabolic pathways, these biopeptides may play a vital role in disease prevention and health promotion. Biological activities are largely determined by their structural properties such as molecular weight and the physicochemical characteristics of the amino acids within the sequence. To produce bio-peptides via hydrolysis, variable factors such as pH, time, temperature, the enzymes used, and the enzyme-to-substrate ratio strongly affect the bioactivities of the generated protein hydrolysates and biopeptides, to produce bioactive peptides with high bioactivities these factors should be carefully controlled. Amino acid sequences determine protein structure and function. Therefore, different proteins have diverse molecular properties. i.e., fibrillar collagen, sarcoplasmic, stroma, gelatine, plasma from different sources (microalgae, finfish, crustaceans, molluscs, and coelenteratae) would generate numerous types of peptides with a variety of bioactivities. The biological activities of the released peptides differed for each source due to the initial protein source and the processing conditions used. All types of marine hydrolysates and their peptides have benefited human health with antihypertensive, antioxidant, antidiabetic, anticancer, antimicrobial activities. In vitro, the inhibitory potency of peptides is expressed as the IC_{50} concentration, the peptide concentration which inhibits 50% of activity. Marine peptides show mostly good to potent activity inhibiting (angiotensin-I-converting enzyme (ACE), free radicals, dipeptidyl peptidase (DPP-IV), cancer cells, gram-positive and gram-negative bacteria) [75]. Fish protein composition varies depending on the fish species and season. Fish protein is generally utilized as fishmeal, fish sauce and silage. Fishmeal from pelagic fish is the most widely used product obtained from fishery by-catch, and has an average market value of ~46 euro/ton [45]. Fish protein hydrolysates market size was about USD 420 million globally in 2019 and it is supposed to increase of compound annual growth rate by 4.5% between 2020 and 2026 [76].

Fish skin, tendons, cartilage, bone and connective tissue contain both collagen and gelatine which can be extracted and used in food and pharmaceutical products. Collagen and gelatine are two different forms of same macromolecule, gelatine is a partially hydrolysed form of collagen in a denaturised state. Fishery discards contain collagen at a high extent (around 30%) in skin, fins and bone. The limiting factor for collagen industrial demand, round 320,000 tons/year, is the high cost. The structural and thermal stability of marine derived collagens was found to be weaker than those of mammal, due to their lower proline and hydroxyproline contents, however, they are more easily hydrolysed by proteases and are suitable to be further

processed to produce bioactive peptides. Therefore, bioactive peptides prepared using marine derived collagens have attracted broad attention due to their various promising applications [45] [77]. Marine collagen market has been estimated to reach USD 983.84 million by 2025, growing at a compound annual growth rate of 7.4 %. The growth of the marine collagen market is due to the use of collagen in the cosmetic, food and beverage industry. Fish waste represents a huge and cheap source of collagen for the industry [76].

By-products of fish processing is a great potential source for good quality fish oil, which can be used for human consumption, feed, production of biodiesel. Fishery by-products contain lipids (2 – 30%) in the form of fish oil. Concentration varies depending on the fish species. The fish oil contains two main polyunsaturated fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), that are classified as omega-3 fatty acids. They are mainly found in the marine animals which have high polyunsaturated fatty acid content. Omega-3 fatty acid concentrates are of great interest for the pharmaceutical and food industries, to produce drugs with enhanced performance and nutritional supplements. The global fish oil market size was valued at $1,905.77 million in 2019 and is estimated to reach $2844.12 million by 2027 with a compound annual growth rate of 5.79% from 2021 to 2027. The EU produces approximately 120,000 tons of fish oil each year and Denmark is the largest producing nation [76].

Fish viscera containing enzymes are among the most important fishery by-products, due to their content of digestive enzymes, many of which exhibit high catalytic activities at relatively low concentrations, and high stability in a wide range of pH. They have a wide range of potential industrial applications, including seafood processing for collagen removal. The most important proteases in fish viscera are pepsin and serine proteases – trypsin, chymotrypsin, collagenase, elastase. Enzymes can be endogenous or produced by the fish microbiota, they represent a large percentage of bioactive compounds present in fishery by-catch or by-products and are commercially extracted on a large scale but to date their potential application has been only partially disclosed. Proteases are the most used enzymes, probably in relation to the wide range of applications in food, detergents, pharmaceuticals industries. The enzyme market size was around $6.3 billion in 2017 and will see growth of around 6.8% in the compound annual growth rate through 2024. The expansion of the food and beverage industry due to the growing needs of the population, including the need to improve the flavour, quality and texture of food is leading to continued growth of enzymes market [76].

Chitin is a structural component in shrimp and crab shells and squid pens. Marine chitins have been utilized to produce vast array of bioactive products including chitooligomers, chitinase, chitosanase, antioxidants, antidiabetic compounds and prodigiosin, a potential candidate for cancer. Chitosan is commercially obtained mainly from chitin by the deacetylation process performed by the addition of alkali solutions. Chitin and chitosan are ubiquitous marine polysaccharides and over the years they have attracted a great deal of attention in food, pharmaceutical and health applications due to their distinctive biological and physicochemical characteristics. The adhesive nature of chitin and chitosan, together with their antioxidant and antimicrobial properties, is a very important property for biomedical and pharmacological applications and in food industry in food additives and packaging materials [45]. From the economical viewpoint, chitin is available in the market with a price of 500 €/kg (10 – 1000 euro/kg), whereas chitosan's price strongly depends on the purity and the molecular weight, although it is 1100 –1200 €/kg [78]. It was estimated at 106.9 thousand metric tons in

2020, and it is expected now to reach a revised size of 281.7 thousand metric tons by 2027 with an increase at a compound annual growth rate of 14.8% in the period 2020–2027 [76].

Fish waste is also a source of natural pigments, such as carotenoids, and minerals, including calcium, phosphorous and hydroxyapatite. The fish bones from fish processing operations can be used to produce calcium. For bones to be a fortified food they should be converted into edible form by softening their structure with thermal treatment with water and acetic acid solutions or by superheated steam. Fish bones are a very good source of hydroxyapatite which can be used as a bone graft material in medical and dental applications. The important properties of hydroxyapatite are related to its stability thermodynamic stability at physiological pH [45], [79]. Fishery discards provide an interesting source of high added value compounds, such as hydroxyapatite, collagen, gelatine, lipids, enzymes, hydrolysates and bioactive peptides, with great potential for different applications. Fishery discards have been considered as important sources of high value nutraceuticals and other ingredients such as natural food additives, bioactive compounds. Since fish feeding require supplementation of vitamins, minerals, and antioxidants, this could be provided by fishery by-products. Marine bioactives appear to fit the criteria established for functional food ingredients, since they are naturally occurring compounds widely available, and their isolation/extraction for feed is relatively cost-effective. Fields of application of fishery by-catch or processing by-products depending on their unique structural and functional characteristics, marine-derived bio-active compounds can be exploited in different pharmaceutical (biomedical, nutraceutical), cosmetical, and biotechnological (chemical or industrial) application fields [45].

Main field of application of seaweed are food industry, biofuel production, bioactive antioxidant and antimicrobial compounds, healthcare and cosmetic industry, biofertilizer and wastewater treatment [38]. Foremost use of seaweed polysaccharides is in food industry. Alginate, carrageenan, agar as food additives with emulsifying, stabilizing, foaming, filler, gelling, binder properties are used in ice-ream, meat, soft drinks, dairy, low fat products, beer, and wine products, and other. These compounds have the ability to control starch retrogradation, replace fat, enhance flavour and improve fibre content, and sensorial, nutritional value [36], [39]. Increasing research in food products and increase in the market for algae products is expected to make space for new products and brands in Europe. Algae-based products can benefit compared to existing products if companies advertise positive properties – essential nutrients and products green fingerprint [80]. Several studies have revealed that seaweed is an excellent source of various proteins (amino acids, peptides, phycobiliproteins, lectins) with functional biological properties (antihypertensive, antioxidant, antidiabetic, anti-inflammatory, anticancer, antimicrobial). Currently, the use of seaweed proteins in human nutrition is rare. Although several publications are available on quality of seaweed protein and its potential functional properties, only few clinical studies have reached logical conclusions about actual functional foods [81]. Recent studies have proposed the use of whole algae or algae extract for the development of new foods, with investigations on the digestibility and bioaccessibility of algal biomass in different food matrixes [82]. Nutritional, physical and sensory evaluations of *Arthrospira platensis* biomass for snack enrichment was investigated [83]. Effect of Spirulina biomass on the technological and nutritional quality of bread wheat pasta was also investigated [84]. Physical and antioxidant properties of gluten-free bread enriched with brown algae *Ascophyllum nodosum* was explored [85]. Biosorption of protein,

minerals (Na, P, Ca, Mg) and phenolic compounds of extruded maize enriched with *Porphyra columbina* was investigated [86]. All these studies have shown the promising impact of consuming algae-based foods under in vitro experimental studies linked with the bioaccessibility of nutrients [82].

Aquatic invertebrates are a major source of natural products that can find applications as pharmaceutics, cosmetics, antibiotics, antifouling products, and biomaterials. Symbiotic microorganisms are often the real producers of many secondary metabolites initially isolated from marine invertebrates, however, a certain number of them are synthesized by the macro-organisms [87]. Groups of marine invertebrates and products derived from them are:

- Sponges – hydroxyapatite, calcium carbonate, bio-silica, chitin, collagen,
- Cnidarians – hydroxyapatite, collagen,
- Mollusks – proteins for marine glues, calcium carbonate,
- Echinoderms – collagen, proteins, magnesium calcite,
- Tunicates – tunicin – a highly crystalline cellulose nanofiber, proteins.

Given the unique and particular characteristics of these organisms most developed applications aim at bone tissue engineering, and other innovative biomedical applications – scaffolds for regenerative medicine, dentistry, bioadhesives [87].

Reed biomasses are used both fresh and dry, fresh shredded and mulched or balled are used in agriculture for soil improvement. Dry reed with moisture content below 20% in construction [88]. Reed biomass is used in variety of added value products – in construction as sound and thermal insulation [89], roofing, combustion [90], ethanol [91], fertilizer [21], biogas, paper and pulp, and feedstock for other products – organic acids, pharmaceuticals, commodity chemicals [88]. Some mineral concentrations can be above the desirable threshold for production, such as nitrogen, sulphur, iron. To examine local needs and application possibilities for reed biomass improved knowledge is needed [92]. Value of reed biomass depends on demand. Highest value of biomass is when high-quality and dense stands are used in construction for roofs and panels, in addition, in this case, long-term use of the resource is ensured. Other uses compete and most advantageous option with the highest added value depends on the supply of reed and technology availability.

1.4. Blue bioeconomy concepts contributing to sustainability

There are several concepts that promote sustainable view on examining past events and tackling future challenges in freshwater and marine bioeconomy sectors. Internationally used general term “bioeconomy” refers to the share of the economy based on processes, products, and services derived from biological resources, and it is crosscutting, encompassing multiple sectors, in whole or in part. Bioeconomy is one of key components of the sustainable future economies – development of and transition to predominantly a bioeconomy as a means to address climate change, food security, energy independence, and sustainability of environment. Advancements in bioeconomy have also opportunity to diversify the industries and jobs, improve human health through the development of new drugs, and boost rural development [93]. Basically, “the bioeconomy encompasses the production of renewable biological resources and conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products and bioenergy”, concept covers agriculture, forestry, fisheries,

food, and parts of chemical, biotechnological sectors, and energy industries, and has powerful innovation potential [94]. Blue bioeconomy is the part of bioeconomy based on the use of organisms in oceans, seas, lakes, rivers, and aquaculture facilities. In comparison, the term "blue economy" covers all maritime sectors, including, for example, offshore energy, shipping, mining, etc., in addition to the blue bioeconomy sectors. There is a consensus that these terms should have broader scope considering future systems and social benefits [95]. Small-scale fisheries and poor coastal communities that feed people in need for protein are the most important for bioeconomy strategies and concepts. One third of the daily protein intake of the world's population is provided by small-scale fisheries. Their work is crucial for alleviation of poverty, especially in countries where the poorest populations have few alternative sources of employment and protein-rich foods. Blue Justice concept emerged as response to concerns about injustices against small-scale fisheries in Blue Economy/Growth agendas. Justice includes a temporal dimension and can include demands for recognition and remediation of past harms. Blue Justice for small-scale fisheries requires information and strategies and, to this end, transdisciplinary research to develop new vocabularies that disrupt dominant discourses on what ocean sustainability is and what it entails. Blue Growth is underpinned by a discourse that frames a trajectory of development that can realize greater revenues from marine resources while at the same time preventing degradation, overuse, and pollution [96].

Blue economy and blue growth concepts are at the heart of most maritime policy initiatives. Blue growth is not a one-size-fits all concept, it is an adaptable framework that can be customized and applied differently across regions and to provide the most benefit to the stakeholders in each case. The economic potential of Blue Growth rests on the notion that there is untapped potential in oceans, seas, and coasts. There are two types of blue economies – mature blue industries, such as maritime transport, shipbuilding, port infrastructure, fishing, and offshore platforms for hydrocarbon extraction, and there are emerging blue industries, such as renewable marine energy production, marine biotechnology, subsea mapping and mining, and numerous forms of aquaculture. Recently European Commission's Blue Economy Strategy has adopted the language of "sustainable blue economy," which "encompasses policies guiding the specific blue economic activities as well as the horizontal support instruments such as blue skills and careers, ocean knowledge and research & innovation, investment, ocean literacy and planning". Nowadays diplomacy is mainly oriented to identifying common points of interest among sovereign states. Whether in academic or military circles, there is general agreement that the complexity of international relationships demands more investment in diplomacy. The global challenges that threaten humanity cannot be solved by addressing climate change alone. Other global challenges relate to the impact of climate change, but their combined effects, however, and mutual synergistic impacts reach much further than that described within the climatic effects. The clear political and scientifically backed messages from government leaders and civil society committed to confront the challenges of climate change at the different climate action summits do need to be supported and help pave the way towards more profound changes in other areas. This is the correct way to proceed, but on its own, will be insufficient to tackle other key challenges facing mankind [96].

Biodiplomacy must be comprehensive and global. In order to fully address the issues affecting the biosphere, it must be global in its geographic scope, integrative in that it must juggle and fully involve various societal, political, and economic interests, expertise, scientific,

and technological disciplines, and industrial sectors, ensuring that it promotes more inclusive societies. Additionally, it must work toward achieving international collaboration, while also supporting sustainability and a circular bioeconomy capable of fostering a planet teeming with life for coming generations. It must also be conscious of the limits and potentials of living resources. To deal with unique biological characteristics including renewability, a degree of closeness to climatic neutrality, and significant circularity, biodiplomacy must consider the "bio" specificities. Additionally, biological resources have a great deal of potential for new uses, including prolonged life. These are all vital elements that can help fulfil the objectives of sustainable development and the requirement for resource efficiency. By establishing the common ideals that serve as the cornerstones of biodiplomacy, Europe is taking the lead in the movement toward an integrated and inclusive response to global challenges. This process can be led by the EU in a special way. It won't be established through a solemn founding ceremony, but rather through instances of trustworthy behavior and the attainment of modest successes. This process will continue to spread throughout the world when additional nations, potentially under duress from their citizens, join in. As catalysts to launch and start the process and to put in place the instruments for its execution, unifying political efforts, such as the EU Green Deal, are crucial. But society as a whole must be the primary source of encouragement and support. Everyone should be urged to participate in this new "catharsis" on how to preserve the earth for future generations while balancing the sustainable quality of life seen in developed countries with the wise use of natural and renewable resources [96].

In the context of sustainable bioeconomy principles, appropriate monitoring indicators have been found from FAO programs. These indicators will aid in monitoring and assessing the sustainability of policymakers' bioeconomy initiatives and interventions as well as those of producers and manufacturers. The concept proposes a constrained number of basic indicators to keep the monitoring technically and financially possible while considering all three dimensions of sustainability. It is possible to distinguish between two sets of indicators: 1. At the territorial level (which includes indicators for the Sustainable Development Goals that are pertinent to the bioeconomy); and 2. At the product/value chain level, which includes indicators for standards, certifications, and labels. The use of participative methodology, which allows for flexibility to consider the circumstances and particular needs of the stakeholders, is required to discover meaningful criteria and indicators. Additionally, it makes it easier to add new indicators, which helps to improve the monitoring strategy over time and adapt indicators to changing sector and policy demands. The body of existing literature demonstrates that the relationship between the bioeconomy and SDGs can vary greatly depending on the strategic goals that a nation chooses for its bioeconomy. The country context will therefore be particularly important for developing bioeconomy plans to promote progress in linked SDGs, as it may modify the nation's primary sustainability goals (and in turn, SDG implementation strategies) [97]. The EU Bioeconomy Monitoring System [98] is publicly available on the web platform of the EC Knowledge Centre for Bioeconomy.

Aquatic food systems are a potent option that can address the dual problems of environmental sustainability and food security. FAO is committed to the Blue Transformation initiative, a forward-thinking approach that aims to strengthen the contribution of aquatic food systems to feeding the world's expanding population by establishing the requisite legal, policy, and technical frameworks. To ensure that fisheries and aquaculture grow responsibly and

without displacing anyone, especially those communities that depend on the sector, Blue Transformation suggests several initiatives. Technology advancements and environmentally friendly laws and practises are essential building elements [15]. If we are to achieve the United Nations 2030 Agenda, blue transformation demands commitment from both the public and business sectors, particularly considering the COVID-19 pandemic's reversal of previously positive trends. To fully utilise the benefits that fisheries and aquaculture have to offer, Blue Transformation demands a commitment from governments, the commercial sector, and civil society. Blue Transformation works to advance improved aquatic value chains, sustainable aquaculture expansion and intensification, and efficient management of all fisheries. To boost equal access to profitable markets and increase output, proactive public and commercial collaborations are required. In order to expand availability and improve access, aquatic foods must also be included in national food security and nutrition programmes along with campaigns to raise consumer awareness of the benefits [15].

The new landing obligation's ultimate objectives share a lot in common with two other EU policies, Blue Growth and the 2020 EU Strategy, which are both concerned with fostering sustainable socioeconomic and environmental growth in the marine and maritime EU zone. Using the oceans and seas, which have enormous potential for growth and innovation, the EU may find new methods to generate economic growth and help it get out of its current crisis by pursuing a long-term strategy known as "Blue Growth". The EU blue economy indicates 5.4 million jobs and a gross added value of over €500 billion annually when all activities dependent on the sea are considered. By 2030, several ocean-based industries might provide more value added and jobs than the whole global economy, and the ocean economy's output could more than double, according to the Organization for Economic Co-operation and Development. The blue biotechnology, which involves transforming raw marine materials into products with high economic value useful for various biotechnological applications, is a key component of the blue growth strategy. These products could be used to create innovative markets and further the objectives of the EU strategies. In this situation, fish by-products and discards could be valued to spur economic expansion. New applications for fish waste could also lower costs related to the requirement to land the fish as well as the severe environmental issues brought on by the vast amount of waste [76].

It is also clear that much too much of the aquatic biomass we get from the water, whether farmed or captured, is squandered. Traditional fisheries have reached their maximum capacity, unless we wish to harvest lower down the food chain, which is debatable. However, by introducing new technologies and enhancing our knowledge of life in the seas, from the microbiome to the interactions of creatures in ecosystems, we can eliminate waste and utilise marine biomass in a sustainable manner. Finally, people's perceptions of how aquatic resources should be utilised must be altered. The continued development of multi-stream biorefineries will boost aquatic food production while increasing the economic value of aquatic biomass, so contributing to the improvement of the blue bioeconomy [99] , [100]. The bioeconomy will necessarily raise demands on arable land to produce feed, food, fibre, and fuel since mankind lives in a resource garden in which everyone has his/her part tied to lifestyle and economic behaviours. As a result, the shift to renewable raw resources will exacerbate current and create new land use problems. These interconnected conflicts must be addressed. Spatial planning may help the government regulate the spatial demands of the bioeconomy on the one hand, and

secure land for the production of biological raw materials on the other [101]. The bioeconomy's next phase is to scale up such that more commodities and processes reach market maturity in shorter time intervals. Traditional sectors, such as the construction and steel industries, must embrace bioeconomy ideals. In this regard, the use of carbon from CO_2 as a bio-based building block is intriguing, as it opens prospects for carbon-intensive processes that can be connected to CO_2-utilizing biological processes that are already established with phototrophic microorganisms and bacteria. The chemical and textile industries are good examples of industries that have already embraced the notion and concept of bio-based production and technology, however more widespread usage of bio-based principles and materials is still required. The global bioeconomy is structured into a number of high-level fora and organisations. With the maturing of the bioeconomy and its growing influence on the industry's transition to a sustainable and climate-neutral economy, it is critical to discuss strategy alignment, consolidate roadmaps, and link activities [102].

2. METHODOLOGY

2.1. Review of literature

Reviewing previous relevant literature is an essential part of research in all disciplines, research projects and theses. Depending on the field, the author begins with a description of previous research to map and evaluate the research area, to define the research objective, justify the research question, hypotheses [103]. Literature review is essentially a collection of available thematic documents containing facts, concepts, data, and evidence published from a particular point of view to obtain or express those points of view about the nature of the subject and how it should be examined [104]. For a literature review to be a sound research methodology, as with any other study, appropriate steps must be taken to ensure that the review is accurate and reliable. The value of the work depends on the clarity of what is done, what is found and how it is reported [103]. A detailed review of a specific region of scientific literature is important to define and identify study problems to inform future research in this area. Although literature review research has been shown to serve multiple uses. These include a theoretical framework for further study, mastering the research area of a subject of interest, or solving practical questions through experience in the current literature on the subject. Research reviews are most often written as the introductory section of an essay focusing on a particular study, or as one of the opening sections of dissertation or an analytical paper [105]. One of the key issues and goals of real public research policy is open access to scientific knowledge. The results demonstrate a beginning long tail distribution and a strong increase in the variety of articles in the subject of bioeconomy. A steady increase in the percentage of open access publications, from 31% in 2015 to 52% in 2019, has led to the availability of 45.6% of the papers. Open access is less prevalent in the fields of applied research in chemical, agricultural, and environmental engineering, but more prevalent in the fields of energy and fuels, forestry, and green and sustainable science and technology [106].

This PhD thesis and set of publications are based on review of selected topics of aquatic bioresource bioeconomy and case laboratory research. The preparation of the literature review included five stages:

1. Study question formulation and purpose.
2. Searching for the existing literature.
3. Inclusion examination.
4. Evaluation of primary research quality.
5. Data processing, summarization interpretation (Fig. 2.1.).

Some of the questions author asked during the literature analysis and research process were:

- What is the composition of aquatic biomass waste and how can it be used?
- What bioproducts could be produced from fish and their remains?
- Can coastal round goby be used for fish oil and fish meal production?
- What are the innovative fish oil extraction methods?
- What to do with residual fish biomass or fish biomass that cannot be used in the creation of innovative products?
- What biogas system solution can be used in the local processing of producing household waste?

- Are there any other aquatic bioresources that can be used in the bioeconomy, used in the development and production of products with added value?
- How can aquatic biomass residue management issue be solved?

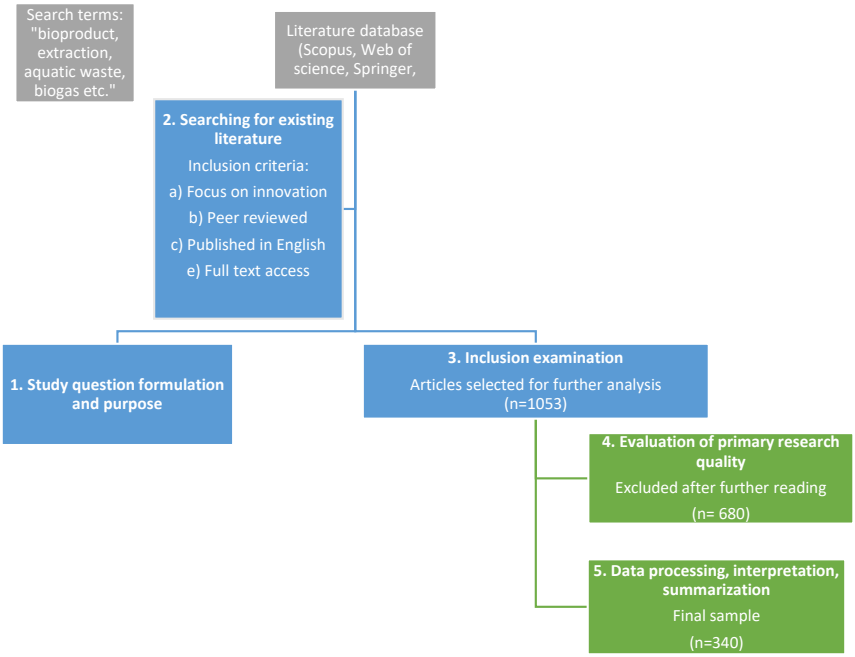

Fig. 2.1. An overview of scientific paper selection

2.2. Empirical studies and data analysis

2.2.1. Extraction of lipids from fish waste

Lipid extractions from fish and fish residues were carried out in the following steps: first, preparation of biomass, then analytical lipid content determination, extraction of lipid from round goby with heat and microwaves, indication of lipid quality, and analysis of round goby nutritional value.

Preparation of fish biomass

The round goby used in laboratory research was caught with fishing nets on April 5, 2017, at 12:00 on the coast of the Baltic Sea (coordinates: 56.516325; 20.946526). This was one of the first fishing days when the round goby appeared on the coast of the Baltic Sea. The fish were stored on ice after capture and transported to the RTU Institute of Energy Systems and Environment (IESE) Biosystem laboratory for experiments within 40 hours. Visual evaluation showed that the fish is of good quality and freshness.

For further studies, the fish carcass and head were used separately. In this experiment, the internal organs were removed and placed in the freezer at –18 °C for storage for future experiments. Homogenization was performed prior to lipid extraction. Before homogenization, the fish are rinsed under running tap water then cut into smaller pieces about 1-2 cm in size. To obtain a homogeneous mass, blender with a maximum power of 750 W was used. Fish heads

achieved size to an average of 1-2.5 mm. The fish carcass is mixed with distilled water (in a ratio of 1:5) and homogenized to a size of 0.2-0.7 mm (Fig. 2.2.).

Fig. 2.2. Preparation of biomass and lipid extraction in laboratory

Determination of total lipid content

Total lipid content was determined using the Bligh/Dyer method, which was compared to the alternatives in [112]. The previously prepared fish sample is cleaned several times to remove any solid particles such as skin, fins, and scales. The material was weighed at 100 g, then extraction solvents (chloroform 100 mL and methanol 200 mL) were added. To ensure homogeneous homogenization of the material, the fish mass and solvents were mixed and added to a blender, then 100 ml of chloroform was added to the homogenized material and the mass was blended again for 30 seconds. Following that, 100 mL of distilled water. At room temperature, the mixture is stirred for 30 seconds. The resultant liquid was placed into 50 ml test tubes, which were then centrifuged at 7500 rpm for 15 minutes. The liquid part was separated from the supernatant. The supernatant is treated with 10 mL of chloroform and 10 mL of methanol. The sample was then centrifuged for 10 minutes at 7500 rpm. The supernatant is separated again.

Following centrifugation, the methanol and chloroform mixture was put to a separatory funnel and allowed to settle for 15 minutes. Chloroform settles in the lower section, while methanol settles in the upper part. Filter paper with anhydrous sodium sulfate is used to properly remove and purify the lower layer (Na_2SO_4). Two times of filtering were performed, with the second employing filter paper without anhydrous sodium sulfate. Transfer the filtrate to a flask with a flat bottom, then evaporate the chloroform at 60 °C to produce an oil which is solvent-free. Before further investigation, the oil was stored in a sealed container at –18 °C in the freezer. Three times, the experiment was conducted individually utilizing the fish head and body of the fish. [113,114].

Lipid quality determination methodology

Lipid quality was compared using the amount of lipids obtained, color and viscosity, saponification value, and oxidative quality of the oils (acid value and content of free fatty acids).

The saponification value is an important lipid analysis to consider when evaluating the subsequent manufacturing process. The saponification value of fish oil was determined according to the official methodology of the American Oil Chemists' Society (AOCS) [113]. The content of free fatty acids (%) and the amount of acids were determined according to the official method of AOCS Ca 5a-40. Protein content was determined using the Kjeldahl method. The method was developed in 1883 by the scientist Johan Kjeldahl, and it consists of heating the substance with sulfuric acid, which oxidizes and decomposes the organic matter, releasing the reduced nitrogen in the form of ammonium sulfate. By determining the content of protein, fat, water, and ash in fish, it is also possible to calculate the amount of carbohydrates. This calculation was performed according to the official methodology of AOAC, 2002. The moisture and ash content of the body and head of the goby were also determined. Data obtained according to standards mentioned in the next chapter. Moisture content in fish is determined by calculating changes in body weight before and after heating. In total, the test was carried out for 20 hours, a temperature of 105 °C was maintained for drying. The ash content was obtained according to the AMC (Royal Society of Chemistry Committee for Analytical Methods) modified method without the addition of magnesium acetate [113]. A drying oven Ecocell 55 was used to determine the moisture composition. The drying process took an average of 5 h. The analysed sample was weighed every 1 h, after 4 min of cooling in a desiccator until mass stabilization was achieved. After obtaining the data, the amount of moisture is calculated by 2.2.1.1. formula.

$$M\% = \frac{m_1 - m_2}{m_1 - m_0} \times 100\% \qquad (2.2.1.1.)$$

where $M\%$ – moisture content (%)

m_2 – container and dried sample mass, g,

m_1 – container and fresh sample mass, g,

m_0 – container mass, g.

Ash content was determined according to the method from AMC 1979, modified without the addition of magnesium acetate. Initially, sample dishes are heated at 500 °C for 80 minutes and cooled to room temperature (30 minutes). The containers are weighed. On average, 5 g +/- 0.1 g of the sample (separately for the body and head of the fish) is consecrated in each dish. Then the sample is dried and ashed by carefully heating to a temperature of 550 °C. A heating rate of 50 °C/h is maintained. The total heating is carried out for 11 h. Constant heating at 550 °C is maintained for 3 h. The sample is then cooled in a desiccator (30 min) and weighed. After weighing, the sample is reheated at 100 °C for 30 min and weighed again. This process is repeated until a constant sample mass is obtained, with an accuracy of 0.1 mg. The ash content is calculated according to 2.2.1.2. formula. The smallest mass obtained after heating is used for the calculation.

$$A^d = \frac{m_{ash}}{m_{sample-2}} * 100\% \qquad (2.2.1.2.)$$

where A^d - ash content (%);

M_{ash} – ash mass (g);

$m_{sample-2}$ – sample mass (g).

Organoleptic properties of lipid

The basic indicators of oil quality are taste, smell and colour, which are the organoleptic properties of oil. In this case, the colour of the oil is determined by visually comparing the obtained samples with each other, also based on the literature. A comparison is also made between fish head and fish carcass oils. The smell and taste should be neutral. An intense specific and uncharacteristic taste or smell indicates that the secondary oxidation of the oil has begun, and quality has been lost. It should be noted that the assessment of these quality characteristics is more subjective. Significant deviations are immediately noticeable and indicate a low-quality extract, the further evaluation of which may be worthless.

Saponification value

Saponification value is an important factor that should be taken into account when evaluating the further production process. The saponification value of fish oil is determined according to the AOCS methodology. Initially, 1 g of oil is prepared and dissolved in 12.5 ml of 0.5 N ethanolic potassium hydroxide. The resulting solution is boiled for 30 minutes until the oil drops disappear. It is then cooled to room temperature. Phenolphthalein indicator is added to the solution and titrated with 0.5 N HCl until the pink/pink color disappears completely. The resulting solution is placed separately for further calculation [115]. To obtain the base sample, the methodology described above is repeated, but without the addition of oil. After preparing the base sample, the calculation is performed according to the Eq. 2.2.1.3.

$$SV = \frac{56{,}1(a-b)\ x\ N}{W}, \qquad (2.2.1.3.)$$

where *SV* – saponification value;

a – 0,5 mol/l volume of hydrochloric acid consumed in the base test (ml)

b – 0,5 mol / l volume of hydrochloric acid consumed in the test (ml);

N – hydrochloric acid normality.

W – weight of oil sample (g).

Free fatty acids and acid value

Free fatty acid content (%) is determined according to the AOC Official Method Ca 5a-40.

A 7 g sample is weighed into a 250 ml Erlenmeyer flask, to which are added 75 ml hot neutralized 95% ethanol and 2 ml 1% phenolphthalein indicator mixture. Hot neutralized 95% ethanol is prepared by adding 2 ml of 1% phenolphthalein indicator to the ethanol. The solution is heated until it begins to boil. Ethanol is neutralized by adding 0.25 N sodium hydroxide solution until a faint permanent pink color appears. The oil sample is titrated with 0.25 N sodium hydroxide until the first permanent pink color appears with the same intensity as that of neutralized ethanol before the sample was added [115]. A permanent pink color should last at least 30 seconds. The obtained results are used to calculate the free fatty acid content according to 2.2.1.4. for the formula.

$$FFA = \frac{ml\ alkali\ \text{x}\ \text{N} \times 28{,}2}{\text{W}} \qquad (2.2.1.4.)$$

where *FFA* – free fatty acid content (%),

ml alkali – 0,25N NaOH change between base and sample titration,

N – NaOH normality,

W – weight of oil sample (g).

Oil oxidation can be indirectly determined by the acid value. The acid content is calculated according 2.2.1.5. formula.

$$AV = 1{,}99 \times FFA \quad (2.2.1.5.)$$

where *AV* – acid value (mg KOH/g),

FFA – free fatty acid content (%).

Determination of protein content

The protein content was determined according to the original Kjedal method at scientific institute *IFSAHE "BIOR"*, Lejupes iela 3. Initially, 5 g of homogenized fish sample is mixed with potassium sulfate (K_2SO_4) and copper sulfate ($CuSO_4$). The sample is placed in a Kjedal flask and concentrated sulfuric acid was added to them and heated for an average of 2 hours (360 – 410 °C) (or until the concentration remains constant). Distilled water was added and the prepared sample was placed in a machine that distils the resulting ammonia. Ammonia was mixed with boric acid, which is simultaneously titrated with 0.1 M sulfuric acid [116]. The nitrogen content was calculated according to formula 2.2.1.6.

$$N = \frac{0.7(V1-V0)}{M} \quad (2.2.1.6.)$$

where *N* – nitrogen (%);

V1 – 0.1 M sulfuric acid consumed in sample test (ml)

V0 – 0.1 M sulfuric acid consumed for the base test (ml);

M – sample mass (g).

The amount of protein was calculated according to 2.2.1.7. formula. The percentage is determined from the total sample, incl. amount of moisture [117].

$$P\ \% = 6.25 \text{ x } N \quad (2.2.1.7.)$$

where *N* – nitrogen (%).

According to the methodology described, several separate attempts were made for the oil obtained from the head and body of the fish. The results are compared with each other to evaluate the feasibility and profitability of production.

Extraction of lipid from round goby

Evaluation of oil extraction from round goby was performed in laboratory scale using the traditional fish oil extraction method – centrifugation after heating, and an innovative method – centrifugation after microwave pre-treatment. Mechanical and microwave method is used and compared to determine the most effective oil extraction method. Methods are similar, because the biomass is heated until the cell degradation process takes place. Extraction schemes are portrayed in the Fig. 2.3. Three different variables are chosen which can affect the result when using the mechanical extraction method – temperature, time, solvent ratio. Using three different variable parameters as minimum it was necessary to make nine experiments in a certain order to determine the most effective combination. To avoid the boiling point maximum temperature of extraction is set to 90 °C, however the lowest temperature is – 70 °C.

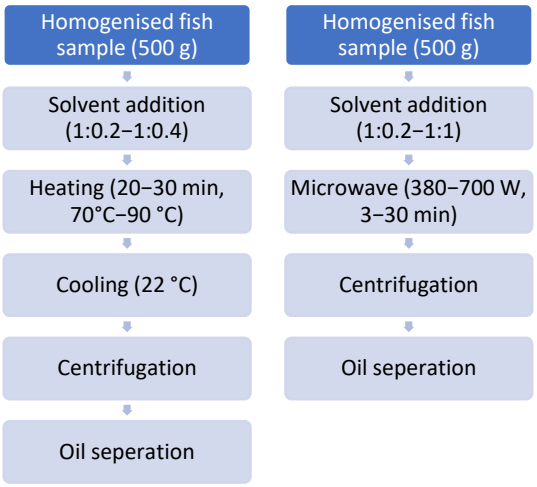

Fig. 2.3. Lipid extraction with heat (left) and microwave extraction (right) [118]

The optimal heating period is on average 3 – 30 min, which is used while obtaining oil from various fishes, these values are also a minimal and maximum time of extraction. Distilled water was used a solvent for microwave extraction and heat extraction. It is possible to vary it to increase the amount or the quality of the oil. Microwave oven power output is varied within 380 W to 700 W, time is varied from 3 min to 30 min, solvent: fish ratio is varied within 1:0.4 to 1:1 [118].

2.2.2. Biochemical methane potential from fish waste

Substrate (collection, pre-treatment, and storage)

Round goby used within the batch tests for the evaluation were freshly caught on Baltic Sea costal area in August 2015 (biomass 2) and April 2017 (biomass 1), near the city of Liepaja, Latvia. Fish samples were transported with plastic bags to the Biosystem Laboratory at the Riga Technical University, separated in smaller portions and then frozen at –18 °C. Prior experiments biomass was thawed at room temperature. Then fish were skinned, gutted, deboned, and beheaded. Processing waste – heads, intestines, and skin/bone mixture was used for further biochemical methane potential (BMP) testing. Each fish waste fraction was separately homogenized using 1500 W kitchen blender and given to total solids (TS) and volatile solids (VS) content analyses. Homogenized samples were frozen again at –18 °C. Thawed a day before the start of BMP tests. Values of total solids (TS) and VS volatile solids (VS) values were determined prior to the experiments based on ISO Standards (ISO 14780:2017, ISO 18134 2:2017, ISO 18134 3:2015). TS was obtained by placing a sample into an oven for 18 hours at 105 °C, and then the dry sample was finely ground and placed into an oven for 5 hours at 105 °C. VS were obtained by placing 5 g of totally dry sample into an oven for 11 hours with a heating step 50 °C and then kept at 550 °C for 3 hours to be able to obtain the VS content as a fraction of TS (% of TS). The results are presented in Table 2.1.

Table 2.1.

TS and VS content of inoculum and fish waste fractions

Substrate	TS, %	VS, % of TS
Inoculum 1	2.0	60.5
Inoculum 2	1.9	60.5
Inoculum 3	1.9	60.5
Heads[1]	20.5	76.5
Skin/bone mix[1]	22.2	75.3
Intestines[1]	36.7	82.6
Heads[2]	19.8	76.5
Skin/bone mix[2]	19.4	75.3
Intestines[2]	30.1	82.6
Inoculums 1, 2, 3 – inoculums for experiment 1, 2 and 3; [1] – biomass 1; [2] – biomass 2.		

Inoculum

Sewage sludge was collected from local wastewater treatment plant "Daugavgriva" (Riga district, Latvia) directly from biogas bioreactors. Prior to the BMP experiments, the inoculum was incubated for 6 days at 37 °C, with regular degassing. Inoculum was always evaluated for TS and VS content using ISO standards:

ISO 14780:2017 – Solid biofuels — Sample preparation, defines methods for reducing combined samples (or increments) to laboratory samples and laboratory samples to sub-samples and general analysis samples and is applicable to solid biofuels [119].

ISO 18134 2:2017 – Solid biofuels — Determination of moisture content — Oven dry method — Part 2: Total moisture — Simplified method, describes the method of determining the total moisture content of a test sample of solid biofuels by drying in an oven and is used when the highest precision is not needed, e.g. for routine production control on site [120].

ISO 18134-3:2015 – Solid biofuels — Determination of moisture content — Oven dry method — Part 3: Moisture in general analysis sample ISO 18122:2015, describes the method of determining the moisture in the analysis test sample by drying in an oven [121].

BMP test method

Biochemical methane potential (BMP) tests are a popular method to determine the methane potential and biodegradability of residual biomass. In the BMP test, the substrate is mixed with a culture of anaerobic bacteria obtained from an active bioreactor. The bottles are then stored at a stable temperature and constantly stirred for 30 – 60 days. During the test, anaerobic decomposition of the organic content of the substrate produces methane and carbon dioxide. Substrate-derived methane and substrate methane potential, expressed as mass of volatile solids added, are then measured. This can be calculated by subtracting the volume of methane from the blank [122].

BMP tests were used to define the amount of methane produced per kilogram of VS, for an inoculum to substrate ratio (ISR) equal to 3 based on a TS basis. Generally, BMP measuring methods are based on liquid displacement or the displacement of a syringe piston. An alkaline solution for cleaning the biogas (by absorbing the CO_2 fraction) is added in both methods. The method is a well-known approach, but still lacking true standardization [123]. A pH range from

6.5 to 8.2 is optimal for most anaerobic bacteria, including methanogens. Therefore, an alkaline compound is normally added within the solution as a buffer capacity (i.e., sodium hydroxide, sodium bicarbonate or sodium sulphide) [124], in this case 0.7M $NaHCO_3$ solution was used.

BMP is a sensitive method, influenced by the conditions for the anaerobic bacteria to grow. In this light, the analysis of the results can be difficult due to the amount of potentially influential factors, resulting in likely possible errors and/or inaccuracies. Also, the specificity of the laboratory in the BMP test method can contribute to inaccuracies, therefore it is desirable to stick to a uniform test methodology, ensuring as much as possible the same conditions [122]. Suitability of BMP is showed in Table 2.2.

Table 2.2.

Power and limitations of BMP test [125]

Strength	**Weakness**
☑ Biochemical methane potential (BMP) of a substrate or mixture	☒ Synergistic or antagonistic effects in co-digestion of substrate mixtures, by the addition of trace elements, etc.
☑ Anaerobic biodegradability (by dividing the obtained BMP by a theoretical value)	☒ Long-term effects of nutrients or trace elements due to monotonic feeding
☑ Acute toxicity of an inhibitor present in the substrate or mutually added	☒ Chronic toxicity of an inhibitor present in the substrate or mutually added
☑ Qualitatively describing the kinetic of the AD process	☒ Methane yield, process stability and achievable organic loading rate in a continuously operated system

Experimental set-up

BMP tests were conducted in a batch mode using 100 mL crimp neck ND20 vials with a working volume of 50 mL. Each bottle was filled with 30 mL of distilled water, 20 mL of inoculum and 1mL of 0.7M $NaHCO_3$ buffer basal solution to maintain a neutral pH. Different amount (fresh weight) of different fish waste fraction was added to specific samples based on TS content to maintain ISR around 3. Additionally, reference samples (blanks) containing only inoculum were prepared both for high and low temperature conditions to account for the methane production solely from the fish waste biodegradation. Sample headspace was flushed with N_2 for 30 seconds at flow rate around 2 L/min before sealing them with butyl rubber stoppers and aluminium crimps. The tests were carried out in dark conditions at a mesophilic temperature of 37 °C in *EcoCell LSIS-B2V / EC 111* incubator and at 23 °C for 31 days. The batches were manually shaken one time per day on average. All batch tests were prepared in triplicates.

In total, three experiments were performed. In first experiment fish waste from year 2017 (biomass 1) was used. Tested samples contained heads, skin/bone mixture and intestines. For second and third experiment fish waste from year 2015 (biomass 2) was used. These samples also contained heads, skin/bone mixture, intestines, and additional biomass mixes (consisting of all waste fractions in different shares). First mix (M1) contained all waste fractions in equal share based on TS. Second mix (M2) contained all waste fractions in equal share based on wet weight. Third mix (M3) contained all waste fractions in wet weight ratios: 2-parts heads, 2-

parts skin/bone mixture, 1-part intestines (based on practical fish processing approach when intestines make up only one fifth of total waste amount). Experiments were performed with one-month time shift between them, thus also having slightly different inoculum for each test setup. In total 90 samples were analysed for 6 different feedstock's and two AD temperature conditions.

A volumetric measuring method was used by measuring the biomethane amount through the displacement of a 20 mL syringe piston connected to a batch bottle. For triplicates three best syringes were selected (with lowest friction) and slightly modified (cutting off excess piston rubber to minimize friction). Each syringe was dedicated to specific triplicate in consistent order, thus giving opportunity to see if piston friction changes and affects measurements. To determine the methane concentration without the CO_2 fraction, 5 mL of 3M NaOH alkaline solution was filled into the measuring syringes before each measurement. For extra confidence some of measured samples periodically were left overnight in closed syringes to see if all CO_2 has been absorbed during measurement.

Nevertheless, the syringe method is prone to human error due to its manual operation. In most cases, the incubated bottles are removed from the temperature-controlled environment during gas measurement. These changes in temperature can easily affect the balance between the gas and liquid phases, resulting in changes in headspace gas concentrations and the microbiology of anaerobic digestion [122]. The test execution process is shown in Fig. 2.4.

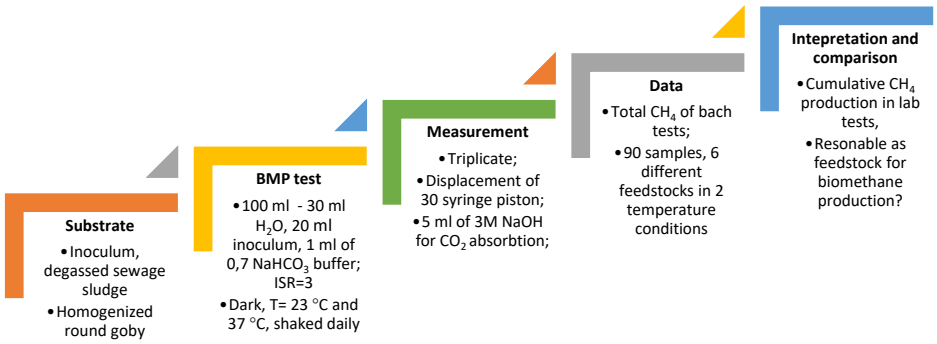

Fig. 2.4. Workflow of biochemical methane potential test.

Theoretical BMP according to Buswell's formula

Depending on the type of biomass, the assessment of BMP can eventually require time of up to 90 days [126]. For a more rapid estimation, a theoretical biomethane potential (BMP_{theo}) can be used from the Buswell equation, formula 2.2.2.1. Once the biomass' chemical compositions of C, H, O are known, it is possible to calculate the BMP_{theo} [127] and the correspondent CH_4 fraction as BMP_{theo}. Experimental yields are usually lower but knowing the theoretical yield value allows to calculate the efficiency of digestion (Eq. 2.2.2.1.).

$$CnHaOb + \left(n - \frac{a}{4} - \frac{b}{2}\right) \quad H2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4}\right) CH4 + \left(\frac{n}{2} - \frac{a}{8} - \frac{b}{4}\right) CO2 \qquad (2.2.2.1.)$$

where, *n* carbon atoms in biomass;
a hydrogen atoms in biomass;
b oxygen atoms in biomass.

The methane yield (BMP_{theo}) from the Buswell's equation can be recalculated with a reference to the unit of gram (i.e. g-VS) in standard condition (i.e. STP) [128], see formula 2.2.2.2.

$$BMPtheo.yield = \frac{\left(\frac{n}{2}-\frac{a}{8}-\frac{b}{4}\right)\cdot 22.4}{12n+a+16b} \cdot \left(STP\,\frac{lCH4}{g-VS}\right) \qquad (2.2.2.2)$$

where *n* carbon atoms in biomass;

a hydrogen atoms in biomass;

b oxygen atoms in biomass.

Chemical composition of fish waste fractions was analysed by the Latvian State Institute of Wood Chemistry.

2.2.3. Multicriteria analysis of common reed use in bioeconomy

Multiple-criteria decision making method was used to evaluate products from reed [109]. It is one of the most commonly used methods in studies that uses both quantitative data (e.g. consumed electricity, emissions, etc.) and qualitative data (interviews, audience opinions, expert testimony) or a mix of both. Multiple-criteria analysis methods, including various modifications, are widely used in different branches of science – product design [129], applications in social, behavioural sciences, and in environmental sciences, especially in sustainable energy planning [130] and regional energy policy and cleaner production [131]. These methods are associated with problem and decision-making structuring and solving involving multiple criteria. Objective is to support the decision-makers who are facing problems. For the best possibilities to be chosen from the offered options, multi criteria decision making technique for order of preference by similarity to ideal solution (TOPSIS).

Multicriteria analysis TOPSIS method was used as reed product analysis method. It is a type of analysis that considers the influence of several weighted factors. It provides an assessment of the situation as close as possible to the real situation. With this method it is possible to compare several alternatives and identify the best of the considered options. In this study, compared alternatives are various products from reed biomass, which are not mutually compatible without an analytical approach. The alternative which is closest to the ideal variant is considered as the best. The TOPSIS method is based on five calculation steps. The first step is to gather information about alternatives and selected criteria. In the second step of the calculation, these data are normalized. The next step is to normalize the data with the weight values and calculate the distance from the maximum and minimum values (distance from the ideal variant). To use this method, information and data from scientific literature and other reliable sources of information (project reports, information which is provided by related industries, project data, etc.) were used to compare products from reed biomass. In the case of lack of data, an environmental engineering assessment, which is based on information on similar products, was considered.

To determine the most promising products from reeds in the TOPSIS method in accordance with the requirements of environmental protection, the main factors, which are affecting the research issue, were defined as 11 indicators (Table 2.3.). Significance or weight of each of the raised factors was determined by assessment of nature conservation experts. Subjectivity of the evaluators was reduced because reasonable data or expert judgment are used to evaluate the product.

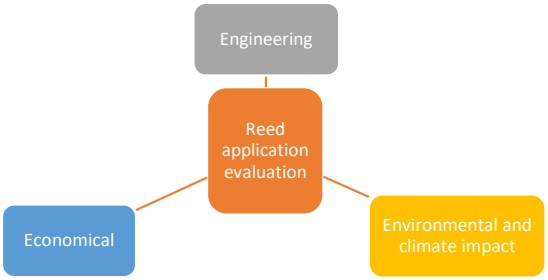

Fig. 2.5. Grouping of evaluation aspects of reed application

TOPSIS is based on the concept that the chosen alternative is the "shortest geometric distance from the positive ideal solution and the longest geometric distance from the negative ideal solution. TOPSIS is a method of compensatory aggregation that compares a set of alternatives by identifying weights for each criterion, normalizing scores for each criterion and calculating the geometric distance between each alternative and the ideal alternative, which is the best score in each criterion". Assumption in this method is that the criteria monotonically decrease or increase. Normalization of values is necessary because the parameters or criteria are incongruous dimensions for multi-criteria analysis. Method allows for compromises between criteria, where a bad result in one criterion could be repudiated with a good result in another criterion and that provides a more realistic modelling shape when compared to non-compensatory methods [132]. The processing of reed biomass for added value involves a set of different activities. Types of reed processing were analysed and compared in the literature review section, using information from scientific articles. Multicriteria analysis includes a set of sequential actions, stages of analysis for performing multicriteria analysis (Fig. 2.6.).

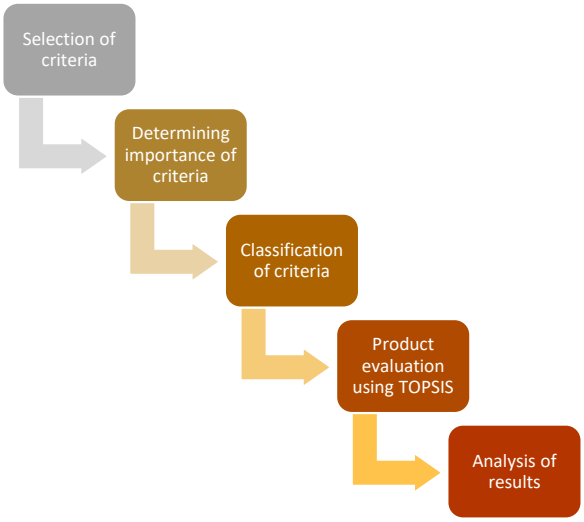

Fig. 2.6. Sequence of steps for performing multicriteria analysis

Limiting factor is the availability of information that influenced the selection of criteria and the selected reed materials that are compared with each other. Criteria are divided into three main criteria groups. Selected evaluation criteria are described in Table 2.3. The criteria were chosen in such a way that all groups of criteria were equally represented. The indicators used in all groups of criteria are often used in multi-criteria analysis and are not very specific, because the products have a relatively low level of complexity and advanced technologies are not widely used in manufacturing. Considering the limited availability of information, indicators are selected based on the analysed sources of information and literature, however, there is a subjective factor. The value of the qualitative indicators was expressed in a descriptive form and quantified on a decimal scale from 1 to 10.

Table 2.3.

Criteria used for multicriteria analysis.

Type of sustainability indicator	**Sustainability indicator**	**Description, quantitative (Q_N) or qualitative (Q_L) examples of indicators**
Climate and environmental	Consumption of resources	Consumption of resources in production process of the product – energy, water, chemicals – m^3H_2O, kWh electricity and heat, kg metal, kg fossil or chemicals, kg bioresources, kWh RES, in kilograms of final product
	CO_2 emissions	Amount of CO_2 emissions arisen in the production process of product: heat or energy – tCO_2e
	Impact on the environment	Impact of raw material extraction and production processes on the environment (air, water, soil, living organisms). Disturbance of hydrobionts – sound, vibration (Hz), pollution (g/hour) emissions of VOC (g/hour), land use (ha).
	Impact on human health	Impact of the product on human health Effect on respiratory and immune-system as substances evaporate from the product.
Technological	Interchangeability	Possibility to replace another biomass with reed biomass which so far has been used to produce the product
	Consumption of reed	Used amount of reed resources (%) in final product
	Stage of manufacture	Stage of manufacture of the product – technological readiness level (TRL1 – TRL9)
	Complexity	Complexity of the technological process – structural complexity of material, spatial scale, technology size, computational intensity)

Economical	Market and investments for launching	Product outlet market (internal or external market; necessary investments for launching the product (R&D, facility, licencing, launching investments EUR)
	Product value	Product added value (EUR/kg), green value

Analytical hierarchy process method is used to determine the importance of selected criteria. An analytic hierarchy process decision matrix is created, shown in the equation 1.:

$$A = [aij] = \begin{bmatrix} 1 & a12 & a13 & \dots & a1n \\ 1/a12 & \ddots & a23 & & a2n \\ 1/a13 & 1/a23 & 1 & & \\ 1/a1n & 1/a2n & 1/a3n & & 1 \end{bmatrix} \quad (2.2.4.1.)$$

where:
$a_1..a_n$ is the value of each specific criterion on a scale of 1-11.
The matrix shown in Equation 2 is created:

$$Bij = \begin{bmatrix} b11 \\ b21 \\ \vdots \\ bn \end{bmatrix} \quad (2.2.4.2)$$

where:
$b_1..b_n$ are values obtained using Equation 3.

$$bij = \frac{aij}{\sum_{i=1}^{n} aij} \quad (2.2.4.3)$$

n digits from column B are used to form the matrix shown in Equation 4.:

$$Cij = \begin{bmatrix} C11 & C12 & \dots & C1n \\ C21 & C22 & \dots & C2n \\ \vdots & & & \vdots \\ Cn1 & Cn2 & \dots & Cnn \end{bmatrix} \quad (2.2.4.4)$$

Importance of percentage criteria is calculated using equation 5.:

$$W = \frac{\sum_{j=1}^{n} Cij}{n} \quad (2.2.4.5)$$

Calculations are made using the above formulas. Criteria are compared in pairs, determining the importance of each criterion, on a scale of 1 to 11, relative to the importance of the compared criterion. The value of the row element is divided by the value of the column element. The sum of the values of each row is divided by the total number of criteria, obtaining the weight of each criterion, as it will be when using TOPSIS calculations. The weight of the indicators of the analytical hierarchy process method can be seen in Thesis results chapter.

TOPSIS requires information on the relative importance of indicators. It was previously obtained using the Analytical Hierarchy method. The method uses the Euclidean distance, which does not take into account the mutual correlation of indicators. TOPSIS consists of the following steps:

1. The construction of the evaluation matrix is based on the available data and information about the criteria. The matrix is composed of 9 alternatives and 11 criteria. Each row of the matrix represents one alternative – one reed product. In the matrix, each unit x_{ij} is the real value of some indicator j belonging to some alternative process i.

2. Normalized matrix using the equation 6.:

$$2. \quad R_{ij} = x_{ij} \div \left(\sum_{j=1}^{n} x_{ij^2}\right)^{\wedge 0,5} \quad (2.2.4.6.)$$

where:

R_{ij} – normalized matrix

x_{ij} – indicator value

1. Obtaining the weighted normalized matrix V_{ij} by multiplying each unit of the matrix R_{ij} by the weight vector wj assigned to it
2. Obtaining the positive ideal and negative ideal solutions using Equations 7. and 8.

$$V^+ = \left(\left(V_{ij}^{max}/j\right), \left(V_{ij}^{max}/j'\right)\right)/(i = 1,2,\dots,n), = (V_1^+, V_2^+, V_3^+, \dots, V_m^+) \quad (2.2.4.7.)$$

$$V^- = \left(\left(V_{ij}^{min}/j\right), \left(V_{ij}^{min}/j'\right)\right)/(i = 1,2,\dots,n), = (V_1^-, V_2^-, V_3^-, \dots, V_m^-) \quad (2.2.4.8.)$$

where:

V^+ - positive ideal solution,

V^- - negative ideal solution,

j=(j=1,2,…,m) is associated with beneficial indicators and

j'=(j=1,2,…,m) is associated with non-beneficial indicators.

3. Determination of the distance from the positive ideal and from the negative ideal solution using equation 9. and 10.

$$S_i^+ = S\left(\sum_{j=1}^{m}(V_{ij} - V_j^+)^2\right)^{0,5}, i = 1,2,\dots n \quad (2.2.4.9.)$$

$$S_i^- = S\left(\sum_{j=1}^{m}(V_{ij} - V_j^-)^2\right)^{0,5}, i = 1,2,\dots n \quad (2.2.4.10.)$$

where:

S_i^+ - distance from the positive ideal solution,

S_i^- - distance from the negative ideal solution,

4. Finding the relative proximity of each alternative process to the ideal solution using Equation 11:

$$P_i = \frac{S_i^-}{(S_i^+ + S_i^-)} \quad (2.2.4.11.)$$

where:

P_i – the ideal solution

5. Ranking of results depending on the relative proximity to the ideal solution.

2.2.4. Analysis of small psychrophilic plug flow digester with assisted solar heat

Processing of food production residues using anaerobic digestion was analysed. As a result of the literature analysis, the most suitable solution for the specific example was found. A preparatory technology and design analysis was performed for the plug flow biogas reactor with solar support. Viability analysis is an essential analysis to be performed prior to pilot scale pilot construction. Based on methodology, main technological requirements, size, output of structure suggested, are clarified. Several assumptions about the state of the system were made. System components and their functions were based on previous scientific work in this field [133,134]. Biogas yield is assumed to be determined only by digester temperature and feedstock. Heat produced by solar collectors is sufficient to heat digester to get the desired temperature; heat exchangers are adiabatic – heat loss with the environment can be avoided.

Reactor volume

Individual parameters for reactor size and solar support system were calculated for quantification of technology. Volume of the reactor was chosen to be adapted with the daily

amount and the degradation rate of the feedstock. Amount of biodegradable waste is equivalent to 130 kg of food waste per day. To achieve the right balance for reactor volume, two parameters were used to calculate the volume of the digester – organic loading rate (OLR) and hydraulic retention time (HRT). OLR describes as the amount of feed processed per unit of the reactor volume per day, expressed in kilograms of total volatile solids (TVS) per day and per cubic meter of the digester (kg TVS/m^3day). The ORL was calculated by Eq. (1). To calculate the organic loading rate, TS and TVS values were adapted from [135]. The higher the OLR, the more sensitive the system becomes, and monitoring system is required to ensure the process efficiency. Plug-flow digesters function with a higher OLR than traditional digesters, up to 10 kg VS/m^3day [136]. Therefore, OLR was increased three times.

$$OLR = \frac{SI \cdot TS \cdot TVS}{DV} \qquad (2.2.4.1.)$$

where *SI* – substrate input, kg/day,
TS – total solids %,
TVS – total volatile solids %,
DV – digester volume, m^3.

HRT is the theoretical time period that the substrate stays in the digester [136]. The HRT was calculated by Eq. (2.2.5.2):

$$HRT = \frac{NDV}{SI} \qquad (2.2.4.2)$$

where *NDV* – net digester volume, m^3;
SI – substrate input, m^3.

It describes the mean retention time. HRT deviates from this value. The HRT must be chosen to allow adequate degradation of substrates without increasing the digester volume.

To evaluate the potential energy produced from the biogas system the energy production in this study was observed. Biogas is directly used for heating as a substitute for natural gas; according to [137] one cubic meter of biogas with 60% methane is equivalent to 4713 kcal or 4.698 kWh electricity. The amount of energy from those aggregates was calculated by Eq. (3) The calorific value of 1 m^3 of the biogas (KJ) is:

$$T_{\mathrm{E}} = E_{\mathrm{b}} \times \mathrm{T}_b \times E_{\mathrm{V}}, \qquad (2.2.4.3)$$

Where, T_{E} – total heat energy per year, kJ;
E_{b} – calorific value of 1 m^3 of biogas with 60 % CH_4;
T_{b} – total biogas volume in m^3 annually;
E_{v} – energetic value of 1 kcal, kJ.

Required solar collector area

Solar collector yield or the useful thermal output of the collectors, depends on the total irradiation onto collector area and the collector efficiency. For estimating the required solar collector area, Zijdemans [138] provides a simple calculation method:

$$A_{\mathrm{abs}} = \frac{Q_{\mathrm{demand}} \cdot SF}{Q_{\mathrm{sol}}} \qquad (2.2.4.3)$$

where A_{abs} – collector absorber area; Q_{demand} – total heat demand; *SF* – desired solar fraction; Q_{sol} – collector yield [139].

3. RESULTS AND DISCUSSION

3.1. Empirical studies carried out in RTU Biosystems Laboratory

3.1.1. Extraction of fish oil from round goby

In order to assess the value of invasive round goby, analysis of the composition of the fish and extraction of different fractions was performed. A quality analysis was also carried out for the fish oil obtained in the extraction. Analysis of round goby composition showed that the average length of specimen is 19.53 cm ± 0.5 cm, and 25% of that is fish head. Carcass weighs 77.46 g ± 2.00 g and head 20.83 g ± 2.00 g.

Initial laboratory centrifugation of thermally pre-treated samples at 7 500 g to 18 000 g showed no visually observable oil recovery. The main component of the supernatant was hydrolysed collagen. The microwave pre-treatment method and similar results and yielded no visible oil fraction. The total lipid content determination with Bligh/Dyer method showed that the highest oil content is in round goby's head 1.00% ± 0.13%, oil content in carcass is lower − 0.67% ± 0.07%. Nutritional composition analysis showed that round goby protein content is 16 g/100 g fish (Table 3.1.).

Table 3.1.

Nutritional composition of round goby

Part of fish	Water	Protein	Fat	Ash	Carbohydrates
Body	83.68% ± 12.86%	16.60% ± 0.40 %	0.67% ± 0.07%	3.75% ± 0.01%	0% ± 1.00%
Head	81.18% ± 1.10%	16.60% ± 0.40%	1.00% ± 0.13%	4.24% ± 0.10%	0% ± 1.00%

Oil quality test values give a general notion about goby fish oil which is good in this case. Further fatty acid analysis was not performed due to low lipid concentrations. Free fatty acid content (%) and acid value indicate that properly stored fish is edible. Acid value from the head (2 mg KOH/g ± 0.47 mg KOH/g) and the body (1.90 mg KOH/g ± 0.06 mg KOH/g) in extracted fish oil is in accordance with the fish oil quality standards (< 3 mg KOH/g). Free fatty acid content (FFA %) in the oil the of round goby head is 1.03% ± 0.24% and in the body 0.96% ± 0.03%. Examination of results show that the oil contains large molecular weight fatty acids, saponification value of oil is 233.4 ± 15.84 mg KOH/g (head) and 244.65 ± 54.94 mg KOH/g (body) (Table 3.2.).

Environment, seasonality, and feeding conditions show the effect on total lipid content of round goby. In other seasons, a slightly higher lipid concentration is possible, but not a significant increase in lipid content. This fact does not make this species suitable for fish oil extraction. For the same species in the Black sea, the lipid content was from 1.60% – 2.65% [140]. The production of fish feed only from this species is also not possible, as a higher lipid content is required for the product to meet the quality criteria in the industry. In that case, mixing of fish with higher lipid content with round goby processing waste is needed. To specify the

nutritional value of the protein fraction, it is necessary to analyse the composition of amino acids. The next chapter deals with the application of this species in the bioeconomy.

Table 3.2.

Qualitative indicators of different fish oils.

Fish	Moisture, %	Ash, %	Lipids, %	Protein, %	Free fatty acids, %	Acid value, mgKOH/g	Saponification, mg KOH/g
Round goby (head)	81.18 ± 1.10	4.24 ± 0.10	1.00 ± 0.13	16.60 ± 0.40	1.03 ± 0.24	2.00 ± 0.47	233.4 ± 15.84
Round goby (corpus)	83.68 ± 12.86	3.75 ± 0.01	0.67 ± 0.07	16.60 ± 0.40	0.96 ± 0.03	1.90 ± 0.06	244.65 ± 54.94
Salmon (head) [141]	63.36	3.52	21.86	11.31	0.17	0.59	
Salmon (courpus) [141]	57.19	3.65	22.65	10.39	0.33	1.17	
Hering (edible part) [142]	64.60		16.40	16.70	0.38		
Herring (waste) [142]	68.60		16.20	11.70	0.71		

3.1.2. Biomethane potential of round goby fish waste

Biomass feedstock processing using anaerobic digestion helps to solve the waste recycling and energy problems. Over the decades, the topic and complexity of research in this field has increased, improving the technological process, and creating various hybrid solutions for more efficient use of wide range of feedstocks. One of the options as a tackle fish waste problem is to process it into biogas, water and digestate. Inoculum and substrate characterization shows that total solids (TS) and volatile solids (VS) content for all three inoculums were similar.

Table 3.3.

TS and VS content of inoculum and fish waste fractions

Substrate	TS, %	VS, % of TS
Inoculum 1	2.0	60.5
Inoculum 2	1.9	60.5
Inoculum 3	1.9	60.5
Heads[1]	20.5	76.5
Skin/bone mix[1]	22.2	75.3
Intestines[1]	36.7	82.6
Heads[2]	19.8	76.5
Skin/bone mix[2]	19.4	75.3

Intestines[2]	30.1	82.6
Inoculums 1, 2, 3 – inoculums for experiment 1, 2 and 3; [1] – biomass 1; [2] – biomass 2.		

TS and VS content for fish heads and skin/bone mixture (furthermore also referred as "skins") was similar both for biomass 1 and biomass 2. (Table 3.3.). TS were around 20% and VS were 75 – 76% of TS. Although homogenized intestine samples seemed more liquid, they showed the highest TS content varying between 36% for biomass 1 and 30% for biomass 2. This could be explained with high lipid content that is not lost during TS drying operation (Table 3.3.).

The fractions of fish waste show slight differences in their chemical composition. Based on the chemical composition, fish intestines show promising theoretical BMP potential, due to higher carbon and hydrogen percentage of TS, and lower ash content than other substrates (Table 3.4.).

Table 3.4.

Chemical composition of different fish waste fractions (for biomass 2)

Substrate	% of TS					
	Carbon (C)	Hydrogen (H)	Oxygen (O)	Nitrogen (N)	Sulphur (S)	Ash
Heads	37.82	4.72	22.51	11.14	0.29	23.51
Skin/bone mix	40.30	5.06	17.37	12.16	0.35	24.75
Intestines	57.17	6.78	12.12	6.17	0.34	17.43
M1	43.55	5.44	19.32	9.53	0.32	21.85
M2	46.89	5.83	16.09	9.64	0.33	21.22
M3	41.51	5.51	20.62	9.77	0.32	22.27

Furthermore, this high lipid concentration [143] is affecting BMP test results, showing the highest methane yield for the samples with intestines both for high and low temperature conditions. Similar effect was observed by Nges *et al*. in 2012 [144]. The VS content for round goby's intestines was similar for both biomass sources reaching 82.6 of TS.

Methane potential of fish waste

Testing was done with slightly modified 20 mL rubber piston syringes containing 5 mL of 3M NaOH solution for CO_2 constantly monitored and no significant change was detected during all three experiments. Periodically, accumulated gas samples were left overnight in closed syringes to check NaOH solution's CO_2 absorption efficiency during slow biogas collection. Fortunately, no visible change in gas volume was ever detected. Consequently, the measured biogas values pertain to the methane content produced. Regarding total accumulated biomethane volume per test vial, significant difference can be seen between the low temperature and high temperature batch samples. Overall, for the samples that were incubated at 23 °C, an average 23% reduction can be observed in total accumulated biomethane volumes (Fig. 3.1., A). This matches with the trends reported in literature stating that by lowering temperature by 10 °C, biogas productions decrease approximately two times [145].

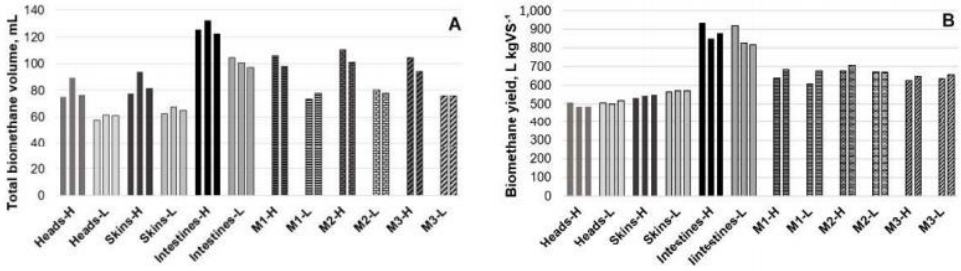

Fig. 3.1. Total accumulated biomethane amount (A) and BMP per 1 kg VS (B) during the Experiments 1, 2, 3. H – 37 °C, L – 23 °C.

After calculating the net biomethane volumes (by subtracting blank sample volumes from the total accumulated biomethane volumes), the difference between low and high temperature samples occurs to be very low. Furthermore, after calculating the final BMP values (always based on the net biomethane volumes) per kg of VS, the overall average BMP results for low temperature samples are only 2% lower than for 37 °C (Fig. 3.1. B). In total, the BMP difference per 1 kg of VS among the two sets of temperature conditions was only 2%. Nevertheless, it must be clarified that the overall difference in total accumulated biomethane amount is 23% (see Fig. 3.1., A). This result may be due to an extra 23 % of total biomethane volume that was contributed by the sewage sludge inoculum at higher temperature.

Methanogenic bacteria activity and growth is much lower at low incubation temperature conditions, thus resulting in a slower augmentation and decay (dead biomass methanation) of the microorganism consortium, thereby lowering the amounts of total produced biomethane. This should be taken into account when designing bioreactor for fish waste and sewage sludge co-digestion at low study suggest that lowered temperature does not have a strong impact on fish waste digestion efficiency and final BMP, however, it affects digestion kinetics. There are a range of possible outcomes that could arise from using sewage sludge as an inoculum for the biomethane generation process. Ability to supply a varied population of microorganisms capable of decomposing a wide range of organic compounds and assisting in the anaerobic digestion process is one possible advantage of using sewage sludge inoculum. Higher biomethane yields and more effective biogas generation may result from this. To ensure that the anaerobic digestion process proceeds effectively, the feedstock must be properly mixed and agitated. Employment of mechanical mixers can accomplish this. Also, ideal temperature range for anaerobic digestion is often maintained by some kind of temperature control in low-temperature biogas reactors. Insulation, HVAC systems, and other temperature control technologies can be used.

During all three experiments the highest BMP values were obtained from batch samples containing fish intestines both in high and low temperature conditions (Fig. 3.1., B). Average biomethane yield from all three experiments at 37 °C 887 L CH_4 $kgVS^{-1}$ and 853 L CH_4 $kgVS^{-1}$ at 23 °C. These high values were reached because of high lipid and protein content, especially in gonads – milt and roe that were present in round goby's abdomens. The theoretical BMP yield of lipids is about 1000 L CH_4 $kgVS^{-1}$, while the theoretical yield of protein is about 490 L CH_4 $kgVS^{-1}$ [144].

BMP values of first experiment are higher than those of second and third, reaching 933 L CH_4 $kgVS^{-1}$ at 37 °C and 917 L CH_4 $kgVS^{-1}$ at 23 °C. In comparison, results from second and third experiment were only 850 – 878 L CH_4 $kgVS^{-1}$ for high and 816 – 826 L CH_4 $kgVS^{-1}$ for low temperature.

Despite similar VS content (82.6%) of round goby's both biomasses this difference in results could be explained due to the fact that for first experiment used fish biomass was caught in spring season (April). In spring time fish are ready for new spawning season and have larger gonads and contain more mature fish eggs, thus increasing overall lipid and protein relative share in viscera. These results are slightly higher than reported 500 L CH_4 $kgVS^{-1}$ for perch (*Perca fluviatilis*) intestines [146] however, this could be attributed to the fact that relative share of gonads in perch abdomen is much smaller (if present at all in different seasons).

The overall average BMPs acquired from three experiments for fish heads at high temperature and low temperature was 494 L CH_4 $kgVS^{-1}$ and 508 L CH_4 $kgVS^{-1}$, respectively. Skin and bone mix showed slightly higher results, therefore average BMP at 37 °C was 542 L CH_4 $kgVS^{-1}$ but at 23 °C 570 L CH_4 $kgVS^{-1}$. At lower temperatures average BMP values are slightly higher than at 37 °C both for heads and skin/bone mixture. It is explained by the fact that for several high temperature samples, after 20 days, biomethane production was delayed, and a slight inhibition of methane production was observable, as blank reference samples on daily basis produced more gas than the samples containing fish waste.

This in fact resulted in negative daily net biomethane values, indicating the start of inhibition which is consequential after digestion of high organic content substrates and rapid VFA accumulation, as can be observed also during dairy product anaerobic digestion [147]. This also is in line with literature where it is suggested that anaerobic digestion under lower temperature conditions is more stable and less volatile fatty acids are accumulated [148]. However, no great change in pH was observed at the end of all experiments, only for few samples lowering from pH 8 to pH 7.7. Summary of BMP values acquired during this research for different fish waste samples can be seen in Table 3.5.

Table 3.5.

Summary of estimated yields from Buswells equation and experimental CH_4 yields

Substrate	BMPtheo (L CH_4 $kgVS^{-1}$)	BMP at 37 °C (L CH_4 $kgVS^{-1}$)	BMP at 23 °C (L CH_4 $kgVS^{-1}$)
Heads[1]	-	509.2 ± 29.5	506.3 ± 1.0
Skin/bone mix[1]	-	533.0 ± 17.8	565.4 ± 110.8
Intestines[1]	-	933.1 ± 60.9	916.9 ± 39.7
Heads[2]	625.0	485.4 ± 20.2	500.8 ± 14.9
Skin/bone mix[2]	728.9	544.9 ± 25.5	572 ± 26.3
Intestines[2]	895.7	849.8 ± 15.4	826.1 ± 26.0
M1[2]	719.4	639.1 ± 4.8	609.2 ± 11.6
M2[2]	791.8	877.6 ± 18.0	672.4 ± 11.0
M3[2]	769.0	626.3 ± 24.5	636.7 ± 2.5
Heads[3]	625.0	488.8 ± 18.6	519.6 ± 19.1
Skin/bone mix[3]	728.9	548.8 ± 24.4	572.2 ± 22.9
Intestines[3]	895.7	877.7 ± 41.8	816.3 ± 51.9
M1[3]	719.4	684.7 ± 17.4	676.5 ± 27.0
M2[3]	791.8	709.2 ± 37.5	668.6 ± 30.7
M3[3]	769.0	649.5 ± 10.3	657.6 + 18.4
[1] – experiment 1 (biomass 1); [2] – experiment 2 (biomass 2); [3] – experiment 3 (biomass 2).			

Three different fish waste fraction mixes were also prepared. First mix (M1) contained all waste fractions in equal share based on TS. Second mix (M2) contained all waste fractions in equal share based on wet weight. Third mix (M3) contained all waste fractions in wet weight ratios: 2 parts heads, 2 parts skin/bone mixture, 1part intestines (based on practical fish processing approach).

M1 average BMP at 37 °C 662 L CH_4 $kgVS^{-1}$ and 642 L CH_4 $kgVS^{-1}$, respectively. M2 average BMP at high temperature was 693 L CH_4 $kgVS^{-1}$ and 670 L CH_4 $kgVS^{-1}$ at low temperature. M3 average BMP at high temperature was 638 L CH_4 $kgVS^{-1}$ and 647 L CH_4 $kgVS^{-1}$ at 23 °C. No significant difference can be seen regarding to anaerobic digestion of these three mixes, thus any of these three compositions can be successfully used for biomethane production. As expected, average BMP was around 660 L CH_4 $kgVS^{-1}$, that is similar to mathematical average from heads, skins and intestines BMPs'. Other authors report similar results for Pacific saury, Nile perch, mackerel and cuttlefish wastes, ranging between 562 –777 L CH_4 kgVS [149,150]. BMP for cod meat and intestine mix was reported to be 503 –533 L CH_4 kgVS, after 14 days long incubation period [151]. Regarding to 14-day period BMP from round goby waste mix is slightly higher reaching approximately 640 L CH_4kgVS^{-1}. In this light, it would be advisable to measure BMP for more extended time period, as far as it is reasonable, to obtain fully total BMP of biomass.

The aquaculture sector faces new issues with the treatment and disposal of saltwater fish wastewater due to the growth in marine land-based recirculating aquaculture systems (RAS) and stricter environmental restrictions. The effects of salt on the biomethanation process are not well understood at this time, however the fish wastewater may be added to biogas reactors in the future. Results on the effects of different salinities of fish wastewater on the biomethanation process and the best co-digestion scenarios for maximum methane potential and secure use in biogas plants revealed that, depending on salinity and organic content, it is possible to efficiently co-digest fish wastewater from 3.22 to 61.85% (v/v, wastewater/manure) and increase the maximum methane production rate from 2.72 to 61.85%, respectively, compared to cow manure mono-digest [152].

Dynamics of biomethane production

Cumulative curves and dynamics of biomethane production are shown in Fig. 2. For high temperature samples the main production was observed during the first 7 – 9 days, accounting for 95% of the total BMP. In turn for low temperature conditions main biomethane production was observed during first 14 –16 days, accounting for 94% of the total BMP (Fig. 3.2.)

Similar pattern regarding to fish waste highest production rate time shift was reported by [153], where highest biogas production rate under thermophilic conditions (50 °C) was achieved on day 10, in comparison to 17 days at mesophilic (35 °C) conditions.

Moreover, this great difference could be also attributed to type of inoculum that was used in this research, because sewage sludge was gathered from bioreactors that normally operate at 37 °C. Shift to low temperature conditions put extra stress on microorganism consortium. It is also suggested that more appropriate microbial consortium can be developed and adapted for fish waste AD by sequential addition of fish based feedstock, thus making optimized inoculum for substrates with low C:N ratios [154].

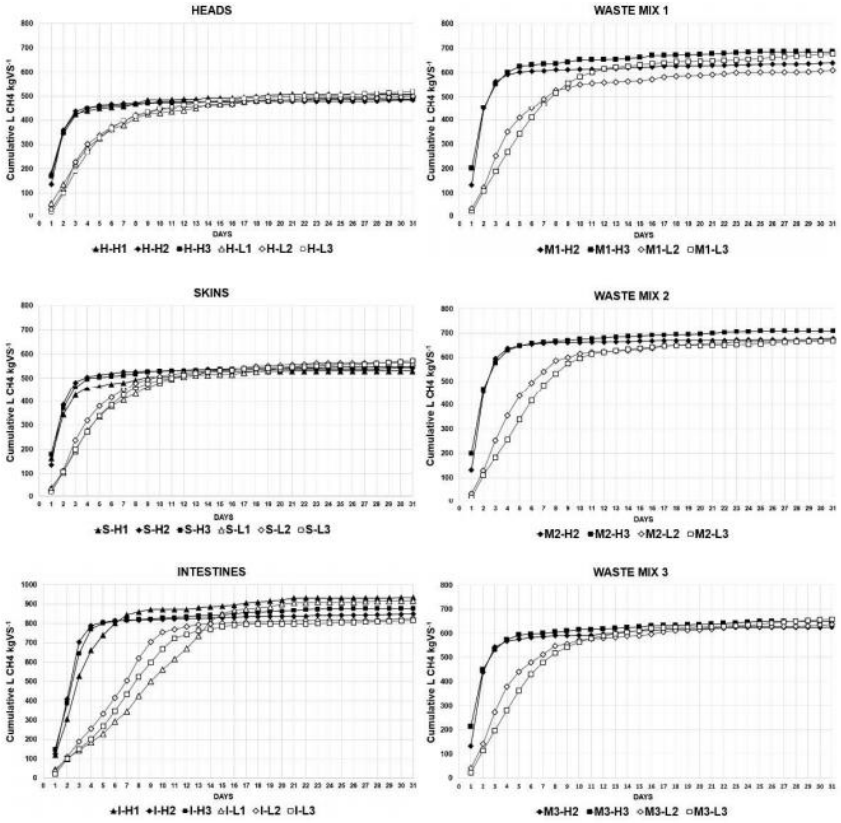

Fig. 3.2. Averaged triplicate methane production dynamics trough experiments 1, 2, and 3. Indexes H stands for 37 C L stands for 23 C stands for experiments 1, 2, 3.

Nevertheless, slower biomethane production rate had no significant impact on final BMP results. In addition, slower digestion time means that substrate needs longer hydraulic retention time (HRT) in digester [145], thus slowing down biogas production or forcing to increase digesters size. On average, lowering fermentation temperature by 10 °C required anaerobic digester's size increases 2 – 2.5 times. However, digester's size can be reduced if shorter HRT is selected. In respect to this research results, it would be more reasonable to use a HRT of 15 days instead of 30 days for low temperature fish waste anaerobic digestion, as more than 94% of BMP is achieved during this short time.

3.1.3. Evaluation of common reed use for manufacturing products

Reed is a widespread invasive plant. From biodiversity point of view reed areas should be reduced. Management and control of reed are resource intensive. Taking this into consideration, reed is an undervalued bioresource that could be used to manufacture bioproducts and get added economic value. There are several inconsistencies between the two sides in terms of availability and quality of resources. Therefore, it is best to use reed as a substitute to other bioresources to produce products.

A multi-criteria analysis was conducted to determine which products can be promising from reed biomass with considering environmental protection requirements. To identify the most promising products from reed, 11 products were studied using the TOPSIS multi-criteria analysis:

1) thermal insulation panel of reed,
2) sound insulation panel of reed,
3) reed roofing,
4) fuel from reed for direct combustion,
5) reed-clay composite,
6) reed-fossil composite material,
7) biogas,
8) extract,
9) bioethanol,
10) activated carbon,
11) paper and cardboard.

Selected products were evaluated in terms of sectors: construction, energy and other products that are not relevant to the two sectors which are mentioned above. Sum of all indicators should be 100. According to experts, the most significant indicator is the impact of the raw material extraction and production process on the environment (air, water, soil, living organisms) and the consumption of resources (energy, water, chemicals) in the production process of the product. The weight which is given by experts in the field of nature protection to the included indicators in the multi-criteria analysis is summarized in Table 3.6.

Table 3.6.

Results of determining the weight of multi-criteria analysis indicators

Criterion	Weight
Stage of manufacture of the product	11
Used amount of reed resources (%) in the final product	6
Outlet market of product	11
Complexity of the technological process	8
Amount of CO_2 emissions which is arisen in the production process of product	5
Consumption of resources (energy, water, chemicals) in the production process of the product	12
Impact of raw material extraction and production processes on the environment (air, water, soil, living organisms)	17
Impact of the product on human health	9
Possibility to replace other biomass with reed biomass which so far is used to produce the particular product	7
Necessary investments for launching the product	8
Product added value	6

The results of the multi-criteria analysis are summarized in Fig 3.3. For the construction industry, five products were analysed from which sound or thermal insulation panels of reed were equally well and promising and the most ancient and most used type of reed – the roofing product. The production of reed composite material with binder of fossil origin is definitely not supported because the production of this product does not match the requirements of environmental protection.

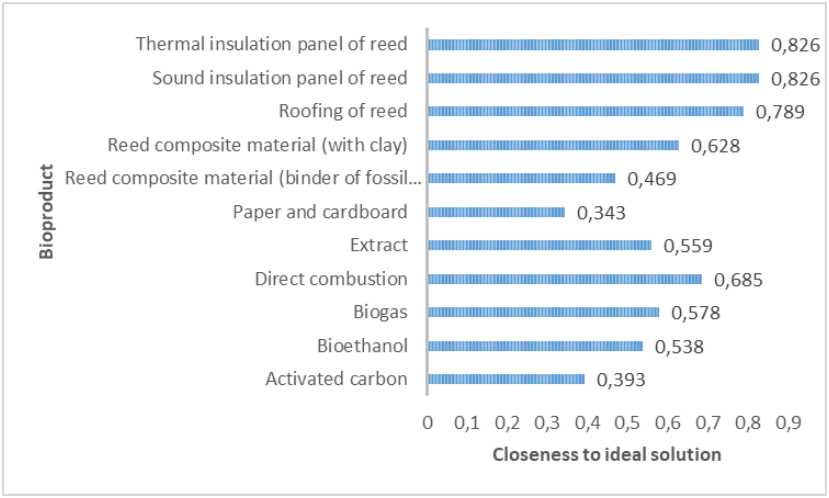

Fig. 3.3. Results of evaluation of products from reed using multi-criteria analysis

For the energy sector, 3 products were analysed of which direct combustion had the best results. This is mainly because this product requires relatively low investment as its production process is simpler.

In the "other products" category were included only 3 products, and extract from reed showed the greatest potential. In this case, for reed extract production, extraction in water technology without any chemical adding is used. So it is environment friendly production process. It should be noted that this product has the highest added value of all analysed, since it can be used in pharmaceutical and cosmetic production, and its production corresponds to the principles of bioeconomy.

By comparing all of the eleven analysed products from reed, the most promising products, in compliance with environmental protection requirements, are reed panels for thermal insulation and sound insulation and roofs from reed (Table 3.3.). The first three products with the highest ratings in the multi-criteria analysis are products from the construction industry.

These are not products with the highest added value, but in any case, from the environmental and climate point of view, are better than products for energy sector, as they can replace the products which are made from fossil fuels and temporarily store carbon so that it does not enter the environment and does not contribute to climate change.

To assess the compliance of the most promising products more fully with the requirements of environmental protection, it would be necessary to make and compare their life cycle analysis to determine their long-term impact on climate and environment. From a business perspective, for the most promising products detailed economic and market analysis is also required.

The results show that, in view of environmental protection requirements, the most promising products are those whose production requires dry, winter-mown reed. Which, in turn, does not coincide with the interests of managers of reed areas who want to reduce these areas and therefore mowing is done in summer during the growing season. Planned and well considered management of reed area is needed to find a solution. It would include those areas where it is necessary to eliminate reed stands, mow in summer, and the rest in winter, to ensure

availability of the resource in the long term. The use of multiple criterion analysis is a time-saving strategy for selecting the optimal bioproduct for analysis. Better data yields more accurate results, however when evaluating the calibre of this data, an expert's opinion is crucial.

3.2. Analysis of researched technologies

3.2.1. Extraction of lipids from fish using green extraction methods

In fish oil extraction from whole fish or fisheries waste both traditional − hydraulic pressing, heat extraction, solvent extraction, and relatively new, innovative and environmentally friendly methods – supercritical fluid extraction, enzyme extraction, microwave-assisted extraction, and ultrasound assisted extraction can be used [155,156]. The main disadvantage of traditional methods from the quality of the product is that the high temperatures degrade heat-sensitive and labile natural compounds, and toxic solvents are used, which remains are present in the final product. Also, traditional methods often have a greater impact on the environment because the extraction process requires a significant amount of heat, there is a risk of organic solvents leaking into the environment [156].

In the last 25 years, the green extraction methods are recognized as a promising alternative to the organic solvents. Mostly it is the supercritical fluid extraction using CO_2, but also other green methods keep up with the SCF-CO_2 regarding extraction yield, product quality, the content of Omega-3 Fatty acids EPA and DHA [157]. Although the green extraction methods can ensure the same quality or product, the green methods like traditional ones also have drawbacks (Table 1). As mentioned above the most famous green extraction method is supercritical fluid extraction (SFE) mostly using CO_2 as a solvent. Supercritical fluid extraction is used to produce high added-value products from plants, microalgae and animal tissue, e.g. fish and fish by-products [158,159].

This method has several advantages, it uses no toxic solvents, the extraction and separation are faster, and thermal process at lower temperatures is much safer as well as its benefits regarding the flexibility of the process thanks to the ability to change the solvent power or supercritical solution selectivity [158]. Except for CO_2 also other compounds are researched for use in the SCF, such as fluorinated hydrocarbons, sulphur, nitrogen oxides, hexafluorides, butane, pentane, hexane [156]. Carbon dioxide is the most traditional SCF solvent because it is easily available at a low price, it is not burning and has low toxicity, high diffusivity with tunable solvent power. The fact that CO_2 at a room temperature is a gas ensures that the solvent is easily detachable from the extraction chamber. Relative to other solvents CO_2 has mild critical conditions (Tc = 303.9 K; Pc = 7.38 MPa) [160]. The four major factors that affect the SCF-CO_2 extraction is pressure, temperature, time, and CO_2 extraction flow rate [161–163] as well as the extraction type: continuous, co-solvent, soaking, and pressure swing [164]. The main limitation of the SCF-CO_2 extraction is its low polarity. CO_2 is a good solvent for non-polar (lipophilic) compounds. Moisture in the sample reduces the contact time between the solvent and solute. The water acts as a barrier against CO_2 diffusion in the sample and the release of lipids from cells. Therefore, before the extraction, it is necessary to dry the sample [163]. Analysis of the literature suggests that SCF-CO_2 method is used in the fish oil extraction in industrial scale for already about 25 years. Extraction yields are similar or even higher than those of traditional extraction methods, and yield of extraction is logically dependent on fish

species and part used for extraction. For example, processing scraps of a hake (*Merluccius Merluccius − Merluccius paradoxus*) can provide around 10 g of oil/100 g of dry raw materials, but the fatty fish species, e.g. salmon *Salmo Salar* and orange roughly *Hoplostethus atlanticus* offcut provide greater quantities of 40 g and 50 g of oil respectively and 100 g dry raw material [160], African Catfish *Clarias gariepinus* − 67 g dry raw material [157], Tuna *Thunnus tonggol* 36.2 g [159]), Indian mackerel 52.3 g oil/100 g dry raw material [165], Longtail Tuna *Thunnus tonggol* head 35.6% [166,167], and about 10 g oil /100 g dry raw material in different parts of sardine [161,163]. As mentioned above, the biomass of fish requires pre-treatment – moisture content reduction below 20%. A freeze-drying method in temperature below – 40 ℃ is used to reduce the moisture, although the particle size reduction does not make a marked difference in the extraction yield [162]. Based on reviewed literature, optimum extraction parameters: pressure 25−40 MPa, T = 40−80 ℃, > 2 mL CO_2/min, soaking time 45 min − 6 h.

Microwave-assisted extraction (MAE) uses the microwaves to warm the solvents in contact with the solid matrix to extract the contents from the sample solution. This extraction process is still in development and it should be improved, and tested on a broad spectrum of sample matrices [168]. Microwave extraction is based on the principle that microwave heating system is very selective and it loses very little heat into the surrounding environment. Direct heating affects polar solvents and/or materials. If it is used for biomass samples, the moisture is reduced, and it results in a considerable pressure generation, which breaks the cell membranes of the animal or plant cell walls freeing up in cells existing materials. Microwave extraction is considered better than traditional solvent extraction methods because it has several advantages − higher extraction rates, lower temperatures, automatization, and a resource to simultaneously produce different samples [169]. However, microwave extraction has two major drawbacks: the heat generation, which can lead to unsaturated fatty acid oxidation and its low efficiency when using volatile solvents. Many factors influence the extraction efficiency: sample particle size, the used solvent, time, capacity, and frequency of microwaves. Microwave extraction method is not widely used. Also, the number of publications about this method in fish oil extraction is relatively small. However, there are some articles that have discussed the oil extraction from fish using MAE. A study that analysed the fat content of frozen fish found that fish oil extraction using MAE gives a similar or even greater yield than traditional extraction methods. For example, Ramalhosa *et al*. in 2012 [168] used the CEM MARS-X 1500 W extraction unit to extract oil from chub mackerel, sardine, and horse mackerel using petroleum ether : acetone (2:1, v/v) as a solvent, extraction yield (raw material) ranged from 4.5% for sardine to 9% for chub mackerel. Prior the extraction fish were homogenized in a blender. In other work, Chimsook and Wannalangka, 2015 [170] used MAE (110 W Microwave power, 60 s) prior to extraction of oil from waste of hybrid strain *Pangasianodon gigas x Pangasianodon hypothalamus*, this yielded at 9.25% of raw material. Shativel *et al.* 2003, used Sharp Carousel 1000 – 2450 W microwave oven to extract catfish liver oil, in this study it was concluded that in comparison to conventional methods the microwave treatment reduces the amount of certain fatty acids in the extract [171].

More recent studies have shown that ultrasonic assisted extraction using acoustic cavitation and mechanical impact can improve the efficiency of extraction. Acoustic cavitation can disrupt the cell wall facilitating the solvent penetration into plant material and allowing the cell to release the product. Ultrasonic mechanical impact offers greater penetration of solvents in the

sample matrix because it increases the surface area of contact between the solvent and the extractable compounds. The ultrasonic-assisted extraction (UAE) requires less extraction time and reduced solvent consumption and can be performed at low temperatures, which can reduce the temperature caused damage and minimize the loss of bioactive substances [172]. Ultrasound is in frequencies above the human's hearing levels ranging from 20 kHz to 10 MHz. Ultrasound is classified by several criteria: the amount of energy generated characterized by the sound power (W), sound intensity (W/m^2), or sound power density (W/m^3). The use of ultrasound can be divided into two types: high intensity and low intensity. Low-intensity ultrasound has a high frequency (100 kHz to 1 MHz), and low-power < 1 W/cm^2, it is used in non-destructive analyses and as an analytical method for assessing the quality to provide information on physical and chemical properties of food products (such as firmness, readiness, sugar content, acidity). While high-intensity ultrasound has a low frequency (100 kHz –16 kHz) and high power (10−1000 W/cm^2) [173]. High-intensity ultrasound is used to speed up and improve the efficiency of sample preparation, as it can change food physical or chemical properties. Ultrasonic extraction is generally recognized as an effective method of extraction, which significantly reduces the time required to increase the productivity and often the quality of the product. Several studies have critically assessed a variety of ultrasonic applications in the industrial extraction of bioactive materials [173,174].

Although MAE and UAE are quite widely used in bioactive material extraction, in fish oil extraction it is almost not used, and there are very few scientific articles on this topic. Abdullah et *al*. 2010 [175] used UAE in ethanol medium for extracting oil from Asian swamp eel *Monopterus albus* fillets. Before the extraction, the material had to be dried (60 °C) and homogenised in a blender. Optimal extraction parameters are 25 kHz, 200 W, 25 kHz, 200 W, 60 min sonication time, and 500 ml of ethanol. The final production − 7.2% of dried fillet material. In another work, Xiao *et al.* [176], extracted 94.82% of total lipids using cyclohexane medium, optimal extraction parameters 4:1 liquid-to-solid ratio at 50 °C within 57 min and 400 W extraction power.

Table. 3.7.

Overview of Green Extraction Methods for Fish Oil Extraction

Extraction method	Brief introduction	Advantages (A) and drawbacks (D)	Main influencing parameters (P) and conditions (C) for extraction
Supercritical fluid extraction (SCF-CO_2) [155,156]	Uses supercritical fluids to separate extractant from matrix using SC-CO_2 as solvent.	(A) Fast. No need for organic solvent and hence extract is very pure. Free of heavy metals and inorganic salts. No chance of polar substances forming polymers. High yield. Lipids can be used for further analysis immediately. Low operating temperatures (40 – 80 C°).	(P) Water content, temperature, pressure. Flow of CO_2. Extraction type: continuous, co-solvent, soaking, pressure swing. (C) Pressure 25 - 40 MPa, T = 40–80 °C, > 2 mL CO_2/min, soaking time 45 min - 6 h.

		(D) Very pricey and complex equipment operating at elevated pressures. CO2 is highly selective – no polar substances are extracted. Supply of clean CO_2 needed. High power consumption.	
Microwave assisted extraction (MAE) [162–164]	Uses microwaves to warm the solvents in contact with the solid matrix to extract the contents from the sample solution.	(A) Decreased extraction time and solvent consumption; higher penetration of chosen solvent into cellular material and enhanced release of cell content in medium. Loses insufficient heat into the surrounding environment. Higher extraction rates, lower temperatures. (D) High power consumption. Heating affects only polar solvents and/or materials. Difficult to scale up. Heat generation, which can lead to unsaturated fatty acid oxidation; low efficiency when using volatile solvents.	(P) Particle size, the used solvent, time, capacity, and frequency of microwaves (C) 110–2450 W, medium – water or organic solvent.
Ultrasound assisted extraction (UAE) [175,176]	Uses ultrasound to penetrate the solvents in contact with the solid matrix to extract the content from the sample solution.	(A) Decreased extraction time and solvent consumption, higher penetration of chosen solvent into cellular material and enhanced release of cell content in medium. (D) High power consumption. Difficult to scale up.	(P) Ultrasonic frequency, power, time and medium. (C) 25 kHz, 200 W – 2450 W, 30 – 60 min sonication time. Medium – ethanol, cyclohexane other organic solvents.
Enzymatic hydrolysis [177,178]	Uses exogenous proteolytic enzymes to digest material to extract oil.	(A) No need for organic solvent. Using commercial low-cost protease provides an attractive alternative. (D) Expensive/difficult to scale up.	(P) Type, activity and amount of protease. pH. Endogenous enzymes absence. (C) Time 1 – 4 h at, temperature 40-60 °C The ratio of enzyme to substrate (E/S) ~ 0.5 – 5%

Another method that the authors find debatable as a green extraction method is an enzymatic hydrolysis. In comparison with the other methods discussed here, it is much more widely studied. Enzymatic hydrolysis is a term that is used if the enzymes are derived from other sources. Adding exogenous enzymes makes digestion process better controllable and reproducible. Thus, enzymatic hydrolysis is an ideal way to recover oil and protein from fish and fishery processing waste. The enzymes and the fish that are used in the process have one thing in common − they must be of food quality, and if the enzymes are of microbial origin, they must not be pathogens. In most cases, alkaline/neutral proteases are used for the hydrolysis because they produce better results than the acidic proteases. Before the extraction, it is necessary to deactivate the exogenous enzymes by heating in about 80−90 ℃ temperature and adjusting the pH. Oil regain yield depends on the used protease, its activity, concentration, pH, temperature, and particle size. It is reported that compared with the traditional thermal extraction enzymatic hydrolysis is better in oil regaining and it competes with the solvent extraction (Table 3.8.)

Table. 3.8.

Pre-treatment method, optimum extraction parameters and yield of enzymatic extraction methods

Fish species and parts	Green extraction technique	Material pre-treatment	Yield	Optimum extraction parameters
Different parts of Mackerel [177]	Enzymatic extraction	Homogenized, heated to deactivate endogenous enzymes, pH was adjusted	Whole fish 7.96 g, Head – 9.80 g, frame 5.96 g, Fin, tail, skin and gut – 11.98 g oil/100g raw material	2% Alcalase enzyme 1 h
Cultured salmon *Salmo salar* [172]	Enzymatic extraction	Homogenization , heating at 90°C for 5 min to inactivate the enzymes	Gut – 13.1 g Head – 59.9 g Frame 78.58 g oil/100g raw material	240 min, 30 °C, 0.5% Sea-B Zyme L200 enzyme
Catla *Catla catla* and rohu *Labeo rohita* visceral waste	Enzymatic extraction	Homogenization 85 °C for 20 min to deactivate endogenous enzymes	From 42% to 74% depending of protease used, highest yield P-amano 74.9 % of extractable oil	0.5%, w/w, 2 h at 40 °C with shaking after every 10 min.

Salmon *Salmo Salar* heads [174]	Enzymatic extraction	Homogenization with grinder, heated to deactivate endogenous enzymes	Neutrase 17.2 %, Flavourzyme 17 %, Alcalase 17.4 % of raw material	The ratio of enzyme to substrate (E/S) was set at 0.05, 2 h at 55 °C
Salmon *Salmo Salar* heads [178]	Enzymatic extraction	Homogenization with grinder, heated to deactivate endogenous enzymes	Neutrase 14.4 % Protamex 14.6 Alcalase 19.6 % Oil of wet weight basis	2 h at 50-55 °C The ratio of enzyme to substrate (E/S) was set at 5%

According to empirical research, green extraction techniques are a great replacement for conventional ones. The quantity and quality of fish oil produced are comparable or perhaps superior. However, in order to adapt to a particular resource scenario, these strategies need to be studied more. Both the pre-processing technology and the actual extraction procedure must be improved. According to evaluated scientific articles, supercritical CO_2 oil extraction is the most promising green extraction technique; other methods are still being developed.

3.2.2. Extraction technologies of valuable compounds from macroalgae

To determine extraction parameters for an application of seaweed extracts it is necessary to define its field of application before using the macroalgae. The degree of purity of the product and impurities are the co-factors that determine the national economy sector in which the extract is to be used. In context of biorefinery the field of application also determines the number of extraction steps, theoretical structure of the plant and technological steps [179,180]. Seaweed composition varies significantly between species depending on nutrient availability. seasonality and other environmental factors [180,181]. The choice of species of algae for desired production is an important factor as it affects not only the ability to produce large-scale biomass but also the composition of valuable compounds under relevant environmental conditions. Although each species of algae offers a unique proportion of proteins. carbohydrates and lipids, some are high in lipids while others are high in protein or carbohydrates. Selection criteria should be based on their nutrient content as well as their specific use requirements [182].

The following criteria should be considered when selecting the appropriate algae for food, feed and fuel production:

- Constantly and steadily growing (open pond/sea);
- Produce large amount of biomass,
- Produce high quality and relatively constant ingredients of desirable nutritional value,
- Survive and grow seasonally and with daily climate change,
- Exhibit high photosynthesis efficiency and energy conversion rate,
- Provide minimal dirt from attachment to environment,
- It is easy to collect and extract substances [183].

Selection of criteria also includes seaweed harvest. pre-treatment and storage methods [184]. According to HELCOM, the following seaweed species are available for biomass extraction in the Baltic Sea: *Furcellaria lumbricalis, Fucus vesiculosus, Cladophora aegagrophila, Laminaria digitata, Chorda filum, Fucus serratus, Chorda tomentosa, Fucus spiralis, Laminaria sacchari* [185]. This list include two of the Eastern Baltic seaweed species used in this research: F*urcellaria lumbricalis* and *Fucus vesiculosus*. There are several steps to increase the efficiency of seaweed extraction to get the highest quality product (Fig. 3.4.).

Extraction process of seaweed can be done in different ways depending on product quality parameters and specific biomolecules needed. Based on previous work [179] it is clear that the use of biorefinery principles is needed to ensure the economical and sustainable extraction of algae products. The conceptual model proposed in the previous work states that a high added value product is obtained and biomass is used with maximum efficiency meaning that physical, chemical and biological transformation processes must operate in a sequential system and in a symbiotic operation to ensure efficient and hence more profitable product production [179].

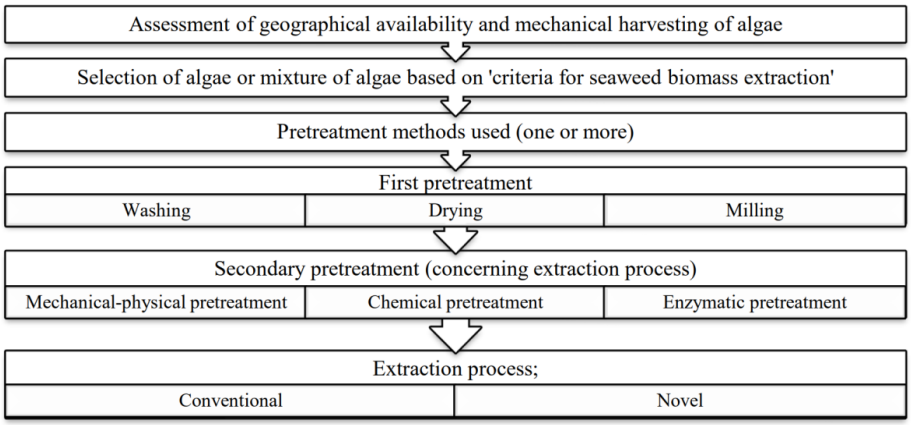

Fig. 3.4. Scheme of seaweed handling before extraction [110]

Existing scientific literature offers two perspectives on extraction. In principle, these are two approaches to the biomass extraction process. First approach is (a) based on the treatment of substrates under defined conditions with conventional extraction methods, in this case, seaweed extraction to obtain biomolecules, (b) Second approach is based on novel extraction techniques and methods that reduce the cost of extraction, reduces the number of extraction steps and increase the yield of biomolecules.

Traditional and innovative methods can be combined to get the best extraction yield at the lowest cost and least impact on the environment. Traditional extraction methods are based on thermomechanical effects and chemical hydrolysis processes, while novel techniques are a significant improvement on existing technologies and are based on the use of physical phenomena (pressure, electric field, ultrasound, microwaves) and biological (enzymes) effects on the matrix [186,187]. This review article does not address groups of substances or compounds that are relatively unexplored and commercially insignificant.

Just before the extraction of the bioactive substances it is necessary to process the biomass in order to obtain maximum yield. Secondary pretreatment methods are divided into three

groups of methods, that can be used to extract different bioactive substances – lipids. pigments. sugars [188]:

- Mechanical-physical pretreatment methods e.g. autoclaving / bead-beating / microwaves/ sonication, freeze-drying, mechanical crushing, lyophilization and pulsed electric field technology.
- Chemical pretreatment methods e.g. liquid nitrogen, nitric acid, acetic acid, hydrolysis by NaOH, HCl, H_2SO_4, NaCl solution, nitrous acid.
- Enzymatic pretreatment methods e.g. cellulase, protease K, driselase, alginate lyase S.

Conventional extraction techniques

Conventional extraction methods use organic solvents (i.e. petroleum ether, hexane, cyclohexane, isooctane, toluene, benzene, diethyl ether, dichloromethane, isopropanol, chloroform, acetone, methanol, ethanol etc.) and acids or alkalis, and water. The main purpose of these aggressive substances is to disrupt cell membranes and allow substances contained in the algae to enter the extraction matrix. According to current trends, the solvent used in the extraction process should be cheap and non-toxic [188].

Several types of extraction methods have been used based on the literature on extraction of bioactive compounds from various matrices. Existing conventional extraction methods include: (1) hydrodistillation; (2) Soxhlet extraction; (3) maceration; (4) percolation; (5) infusion; (6) decoction, and (7) hot continuous extraction [189]. Effectiveness of these methods depends on various influencing parameters, such as solvent properties (polarity, toxicity, volatility, viscosity, purity), sample size and concentration, particle size, time, and polarity of extractant [190,191]. Drawbacks of conventional techniques are the long extraction time, need for very high purity solvents, energy consumption associated with evaporation of a large amount of solvent, relatively low extraction yield, and selective and thermolabile degradation of the components used [192]. Traditional extraction methods are relatively well described in the scientific literature (lab scale). Environmental policy and resource consumption, scientific research viewpoint has advanced green extraction methods (innovative - modern - non-conventional) [186,187,192,193].

Seaweed carbohydrate extraction methods 1) Food grade – agar, alginate, carrageenan, mannitol; 2) Nonfood grade polysaccharides – fucose-containing sulfated polysaccharides/fucoidan, laminaran, ulvan; their sources, structures and physical properties and uses are well described in Rioux and Turgeon, 2015 [194], in context of hydrocolloids [195] and dietary fibers [193]. Generally, seaweed carbohydrate compounds are extracted using following methods i) heating in water ii) by heating in water with an alkali compound (e.g., sodium bicarbonate) followed by cooling, separation and purification. One of the major drawbacks of the current industrial extraction of seaweed hydrocolloids is the huge time and energy and water consumption. Extraction of seaweed hydrocolloids usually takes 3 hours to achieve optimum yield, depending on the types of hydrocolloids involved. Basically, agar, alginate, and carrageenan extraction should take 2 to 4 hours, but with green methods, it may take up to a few minutes [180,194,195]. Seaweed cellulose also belongs to this product group but is not mentioned because existing land-based biomass is a much more accessible and easily obtainable source of cellulose.

Extraction of seaweed proteins, peptides, and amino acids is mainly done on a laboratory scale. Main methods for extracting seaweed protein fractions in the context of traditional methods are solvent extraction, proteolytic hydrolysis (enzymes from microorganisms, plants), hydrolysis by proteolytic microorganisms during fermentation. The overall view of protein in seaweed and extraction methods, is well looked at in Pangestuti and Kim, 2015; Bleakley and Hayes, 2017; Kazir et al., 2019. [196–198]. Algae proteins are extracted by water, acid and alkali methods followed by several centrifugations, dialysis and recovery steps using methods such as ultrafiltration, precipitation or chromatography. Successful extraction of algae proteins can be greatly influenced by the availability of protein molecules, which are significantly inhibited by high viscosity and anion cell wall polysaccharides such as alginates and carrageenans [197].

Marine macroalgae contain relatively small amounts of lipids. Many algae in nature are not intended for oil extraction with existing technological solutions. Macroalgae are generally considered unsuitable for the production of oil-based products since most species have a low total lipid content <5% by weight [181,199]. Content of lipids in dry weight can reach 10 – 20% in some seaweed in order *Dictyotales* [200]. Oils from algae, plant biomass are extracted by a variety of methods including organic solvents and water [201]. However, the green extraction process is better suited for low oil oxidation and high yield [202]. The most common traditional lipid extraction methods are water vapor extraction or solvent extraction, such as soxhlet [189,203].

Seaweed contains a large amount of minerals, up to 30% of dry weight. Minerals include Na, Ca, Mg, K, Cl, S and P and trace elements (Fe, Zn, Mn, Cu). Mineral content of seaweed is generally high (8 – 40%). Minerals and trace elements essential for human consumption are predominantly in brown and red algae [181,199]. Part of the minerals from the algae biomass can be extracted by incineration and acid treatment of the resulting material [204]. Seaweed also contains other groups of substances – pigments, tannins, vitamins, steroids, cellulose, etc. [181,199] which are minor constituents of seaweeds.

Novel extraction techniques

Extraction of biologically active compounds from macroalgae can be accomplished by novel methods. These methods are often qualified as green methods. Green methods have several advantages over conventional, including reduced amount of solvent used (including its recovery), shorter time of extraction, technological performance at lower temperatures. These methods also include improved selectivity for isolation of the desired compounds while avoiding the formation of by-products during extraction and adverse reactions [205]. Most of the extraction methods listed below are considered "green" because they meet the standards that have crystallized in green extraction [206,207]. Compared to conventional extraction methods, main advantages of innovative extraction methods are higher efficiency, use of water, renewable raw materials, more environmentally friendly treatment conditions, significantly reduced use of hazardous chemicals, safer co-solvents, energy efficiency, and reduced derivatives. [189]. Based on reviewed papers [184,188,189,191,192,205,208–210] there are six novel techniques for biomolecule extraction from seaweed:

a) supercritical fluid extraction (SFE) – SC-CO_2;
b) microwave-assisted extraction (MAE);
c) ultrasound-assisted extraction (UAE);

d) high-pressure methods (HPM);
e) ionic liquids extraction (ILE);
f) enzymes-assisted extraction (EAE);
g) pulsed electric field extraction (PEF).

Supercritical fluid extraction (SCF-CO_2) applies supercritical fluids to separate compound from matrix using SC-CO_2 as solvent. The most important factors affecting the extraction are pressure, temperature, time and SC-CO2 flow rate. The prerequisite for the method is extraction in a dry environment where humidity is below 20% in the extraction matrix. As a result, SCF-CO_2 extracts non-polar materials. The co-solvents used, such as methanol or ethanol, make the spectrum and method of extraction more efficient (for polar materials).

Microwave assisted extraction uses microwaves to warm the solvents in contact with solid matrix to extract contents from solution. The solvents used, the temperature range, the time of extraction and the power used affect the MAE. This method makes it easier to obtain a spectrum of different polar compounds. The selectivity is affected by the solvent used. Ultrasound-assisted extraction utilizes ultrasound to penetrate solvents in contact with the solid matrix to extract content from solution. The advantages of the UAE method are the low operating temperatures, efficient cell disruption and various extraction media. Disadvantages are high energy consumption and low extraction volumes, which significantly complicates the technology scale-up. Enzymatic hydrolysis uses exogenous enzymes to digest material. The efficiency of the method is influenced by the enzyme used, its activity and concentration, temperature, pH. Method is ineffective at elevated temperatures due to enzyme denaturation. Hydrolysis is stopped by heating the material. High-pressure methods use solvents under critical conditions (increased temperature and/or pressure) to speed up extraction rate of solvents used. There are different variations of high-pressure methods. For example, “Subcritical Water Extraction (SWE)” and “Accelerated Solvent Extraction (ASE)”. The influencing parameters are pressure, extraction temperature, solvent concentration and time. In the case of water as a solvent and other solvents, these parameters differ significantly.

3.2.3. Approach for modelling anaerobic digestion processes of fish processing waste

Fish waste as substrate in anaerobic digestion

The composition of the solid and liquid fish processing waste depends on the composition of the fish species used, which in turn depends on the sex, feeding habits, season, and health of fish. Fish waste is a mixture of solid and liquid wastes. The solid matter consists of the fish tissues and the bones, and the liquid phase consists of blood-water and stick-water, which are high in proteins and oils. One of the major problems that limit the use of this kind of biological waste is its variable nature. These wastes contain protein (up to 60%), fat (up to 20%) and minerals (calcium and hydroxyapatite from bones and scales), also palmitic acid, oleic acid, monosaturated acids are abundant in fish waste streams (22%) [44]. By the beginning of 2018, literature on the anaerobic digestion of fish and fish waste is rather small – about 20 research papers on this issue. Existing studies show that digestion and co-digestion of fish waste has a very good potential for producing biomethane. Anaerobic digestion studies of fish waste shows potential from 0.2 to 0.9 CH_4 m_3/kg VS added. Fish waste is used in anaerobic digestion experiments as a substrate in pure form and as silage, as well as in co-digestion with cow

manure, sisal pulp, Jerusalem artichoke, strawberry processing waste, water hyacinth (Table 3.9.).

The production of biogas using anaerobic digestion involves the use of different substrates with different properties, however fish processing waste poses a distinct technological problem. Fish waste releases high levels of ammonia when digested, which then inhibits the digestion of substrates [211]. High concentrations of ammonia can result in the accumulation of VFAs (acetic acid as the main type in the batch tests). And depending on reactor type and organic loading rate can inhibit process especially if the substrate is very high in oils [212]. Co-digestion of two different substrates is a technological solution or at least has a mitigating effect for this problem. In current practice, co-digestion is used, where two different substrates (co-substrates) are combined in the reactor to increase the organic matter content and thus achieve higher biogas production. The composition and yield of biogas depend on the raw materials and co-substrate type, pretreatment methods used etc. Substrates with high levels of lipid and easily degradable carbohydrates show a higher methane potential, while lignocellulosic materials shows lower methane concentrations in biogas. Co-digestion also diffuses the content of heavy metals in digestate and generally improve the composition of the digestate to ensure that it can be used as a biofertilizer without treatment. In best practice to avoid process failures, pre-treatment of raw materials is required, e.g. concentration of stick-water to increase solid content, hydrolysis of fish material of high protein content. The application of pre-treatment methods improves the intensity of substrate degradation and thus increases the efficiency of the process. Chemical, thermal, mechanical or enzymatic processes can be used to accelerate the decomposition process, although this does not always result in an increase in the amount of biogas [213]. In our previous work we tested anaerobic digestion of round goby *Neogobius melanostomus* residues in both in mesophilic and thermophilic conditions. The results obtained show great biomethane potential [108]. Extensive and comprehensive further research is needed on various factors of anaerobic digestion of fish waste to further justify the use of fish as a potential substrate in biomethane production. One of best ways to co-digest fish waste is with agricultural waste. Also, this aspect has been studied very little and the experimental data are very limited. Agricultural waste streams have immense potential for energy production both by using dry residues in direct incineration and using dry or wet residues in anaerobic digestion for biomethane production. The global production of agricultural residues from barley, bread, rice, soybean, sugar cane, and wheat are estimated to a total of $3.7^{+1.3}_{-1.0}$ Pg dry matter yr^{-1} [214].

Table 3.9.

Anaerobic Digestion of Fish Waste

Type of waste (Substrate)	Incubation time (days)	BMP	Reference
Salmon heads	33	0.828 ±0.15 CH_4 m^3/kg VS added	[144]
FW	36	F/M ratio 0.2 with a total maximum methane yield 0.165 CH4 m_3/kg VS added COD_{Mn}	[215]
FW	25	0.39 CH_4 m^3/kg VS added	[135]

Nile perch waste	42	0.50 – 61 CH_4 m^3/kg VS added	[150]
FW	15	180 mL/kg of waste	[216]
Jellyfish *Aurelia aurita*	-	121.35 mL/g and 870.12 mL/g	[217]
Tuna, sardine, mackerel waste	67	0.47 – 0.59 g COD-CH_4/g COD added	[218]
FW	67	0.453 – 0.554 CH_4 m^3/kg VS added	[219]
FW	-	0.380 – 0.920 CH_4 m^3/kg VS added	[151]
Round goby waste	-	0.520 – 0.922 CH_4 m^3/kg VS added	[108]
Co-digestion of fish waste			
Type of substrate	BMP		Reference
FWS : JA 1 : 1	0.531 CH_4 m^3/kg VS added		[144]
SE : FCIW 94 : 6	0.205 CH_4 m^3/kg VS added		[220]
FW : SP 33 : 67	0.62 CH_4 m^3/kg VS added		[135]
FW : CM 1 : 1.2	1950 ml CH_4/kg of waste (biogas)		[216]
FW : WH 1 : 2	0.408 CH_4 m^3/kg VS added		[221]
FW : BWS 20 : 80 (%, TS)	0.482 CH_4 m^3/kg VS added		[149]
CM : CI : FS 45 : 22 : 33	0.533 CH_4 m^3/kg VS added		[151]
FWS : CM2 16 : 86	0.400 CH_4 m^3/kg VS added		[222]
FW – fish waste, FWS – fish waste silage, CM- cod meat, CI – cod intestine WH - water hyacinth, SP – sisal pulp, CD – cow dung, SE – strawberry extrudate, JA – Jerusalem artichoke, FCIW – fish canning industry waste, CM2 – cow manure, BWS – bread waste silage.			

Initial state of modelling anaerobic digestion processes of fish waste

The need for model development was determined by the fact that anaerobic digestion is an intricate group of processes and there is no universal model for predicting/analyzing anaerobic digestion of different substrates. The closest to a universal model is anaerobic digestion model no 1 (ADM1) developed by the International Water Association (IWA). It was developed from 1997 to 2002. This model has been widely applied, modified and validated in simulating the digestion of various organic waste. The model includes several phases describing physiochemical and biochemical processes. ADM1 consists of a complex reaction kinetics and many concurrent and sequential reactions, which are primarily classed as physicochemical or biochemical. The complexity of such a model necessitates many input parameters, which ultimately results in a large number of stoichiometric and kinetic equations, identification and manipulation of which may prove challenging. Due to the fact that the models set out in ADM1 and other kinetic models described in [223] require a large amount of specialized data, they are not available to farmers and other interested parties with limited scientific knowledge of anaerobic digestion. In view of the growing interest in anaerobic digestion it is necessary to

increase the range of substrates and the number of biogas plants to use in waste recycling, renewable energy generation and mitigation of greenhouse gas emissions [223].

Approach to the development of anaerobic digestion model of fish waste has arisen from the fact that the fisheries sector in Latvia has a high energy consumption to produce one unit of product. This is because of the use of outdated equipment base and infrastructure. Integrating biogas production into a fishing company technology would increase production efficiency, for example by using biogas combustion heat to dry wood chips or to heat production premises, or by using combined heat and power to generate heat and electricity. Integration of biogas production by anaerobic digestion in the fisheries sector would ensure greater buffering capacity of the regional energy sector. And this is one of the ways to diversify renewable energy – increasing the share of biomethane in the final consumption of renewable energy. In Latvia the existing biomethane production is limited to about 60 biogas plants, of which 83% are agricultural biogas plants, 12% municipal waste landfills and 5% biogas plants for municipal wastewater and food waste. However, there are no biogas plants that produce biomethane as one of the main substrates using fish waste [224]. Our goal is to develop anaerobic digestion model for fish waste to increase the efficiency of biomethane producing and in that way integrating fish waste anaerobic digestion in national economy. The development of the model involves modelling of biochemical and physical processes, incorporation of experimental data, comparison of the deterministic model and the empirical data, the development of a prototype, validation of developed model based on empirical data.

Modelling of biochemical and physicochemical processes includes creation of deterministic mathematical model for the anaerobic digestion processes, defining the components of the system including microorganism groups, fisheries waste and traditional agricultural substrates of high C/N ratio. After that validation and simulation of each model component it is needed to analyze pretreatment as factor and system operating factors (mixing, temperature, pH, etc.). Next task is testing and evaluation of anaerobic digestion processes in a single anaerobic digestion bioreactor system. Later defining of benchmarks for assessing the performance of a system is needed. A very important part of developing a mathematical model is the collection of accurate data in different configurations, meaning planning of experiments and designing experiment plan by analyzing the importance of factors and parameters in order to reduce the number of further experiments to obtain reliable result. For obtaining an empirical model there is need for construction of experimental laboratory stand to test various factors influencing the process in bioreactor system. Experimental stand will produce data that will be used to compare the deterministic model (theoretical model based on literature and assumptions) and for development empirical mode (based on experiments). Last step is building of the prototype and validation of model performing simulations under different conditions. The simulation of model will be validated against data containing different measurement of CH_4 yield and production, VS (volatile solids), TS (total solids), ammonium concentration. Simulation of anaerobic digestion is not only worthwhile when predicting the process, it can also aid to avoid production failures. This, along with optimization, makes it possible to gain improved profitability.

Our vision of what we would like to see in the model is described in this paragraph. Acquired model will allow the biomethane potential of substrate to be predicted – production of CH_4 in the generated models will be simulated with a low percentage of deviation. The model will handle the TS and VS concentration accurately and it will make improvement of the

prediction of NH_4-N compared to other models. The model will allow to predict whether ammonium induced inhibition could be possible. The model will be capable of simulating conditions where the system crashes, therefore it will offer a better overview. In some cases, the model will be based on estimates, meaning output will be affected. The first developed semi-validated models will be later rearranged, and new co-substrates and equipment will be tested to improve quality of the model. Model combined with right measured data, could function as powerful tool for estimation of different process extent in larger scales then laboratory prototype, prediction of biomethane potential (BMP), immobilization, and optimization of the overall anaerobic fermentation process in bioreactor. Knowledge how to utilize fish waste combined with carbon rich substrates to reach the best CH_4 yield will favor the national economy notably fish processors in the long term. Experimental data of anaerobic digestion of fish waste is limited, meaning that additional data collection is required. Laboratory experiments will result in data on:

- main composition of commercial fish species of the Baltic Sea; composition of the processing residues (TS, VS, proteins, lipids), the impact of various pretreatment methods of fish waste on biomethane potential,
- biomethane potential in thermophilic and mesophilic conditions,
- effect of ensiling (as storage method) on biomethane potential of fish waste,
- main composition of the digestate (including heavy metals).

All of this later on can be used to further acquire knowledge of process control, monitoring and development and testing of individual real-time process control solutions.

The first step in designing an anaerobic digestion model of fish waste is to analyze and evaluate the existing literature on theoretical models. The first stage is the mathematical description of relatively simple degradation reactions. The potential biogas yield of anaerobic digestion of a particular type of substrate and the produced gas composition can be determined theoretically by the chemical composition of the used substrates. The production of methane depends on the nutrient content of mainly organic substrates (crude fiber, crude protein, crude protein, N-free extracts) which can be degraded to CH_4 and CO_2. Nutrient content determines the degradability and hence the methane yield that can be obtained by anaerobic digestion. There is a difference between these nutrients in specific methane yield – crude fat (850 l kg VS), crude protein (490 l kg VS), and carbohydrates (crude fiber and N-free extracts, 395 l kg VS) [225]. According to Buswell and Mueller [226], methane and carbon dioxide yield can be calculated with uncertainty of about 5% using Relation (1), contemplating that the chemical composition of used organic matter is known. Relation (1) does not take into account bacterial metabolism – the synthesis of cell biomass and energy for growth and alimentation. According (1), the methane fraction of fully degraded glucose is 50% $C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$.

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} + \frac{c}{4}\right)CH4 + \left(\frac{a}{2} + \frac{b}{8} + \frac{c}{4}\right)CO_2 \quad (3.2.3.1)$$

Organic matter does not consist only from carbon, hydrogen and oxygen. So 25 years later Boyle [227] presented relation modified from relation (1), which included nitrogen and sulphur in the composition of organic matter. This allowed the calculation of the ammonia and hydrogen sulfide fraction in the produced biogas, which should be evaluated by ratio (2).

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3\cdot d}{4} + \frac{e}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} + \frac{c}{4} + \frac{3\cdot d}{8} + \frac{e}{4}\right)CH4 + \left(\frac{a}{2} + \frac{b}{8} + \frac{c}{4} + + \frac{3\cdot d}{8} + \frac{e}{4}\right)CO_2 + d\ NH3 + e\ H_2S \quad (3.2.3.2)$$

Amon *et al*., [228] offers a model that was developed by carrying out a multifunctional analysis of full regression models, which assessed methane yield from the substrate composition of energy crops in mono-fermentation via regression models. Basically, it considers the impact of the content of crude fibre, crude protein, crude fat, and N-free extracts on the methane formation by the following equation:

MEV (l_N CH_4 kg^{-1} VS)
=$x1$ × crude protein (XP) (content in % DM)
+$x2$ × crude fat (XL) (content in % DM) (3.2.3.3)
+$x3$ × crude crude fibre (XF) (content in % DM)
+$x4$ × crude N-free extracts (XX) (content in % DM) [30].

The next stage in the development of the model would be to analyze the anaerobic digestion kinetics considering the growth of microorganisms, substrate degradation, and product formation. The process set can be divided into continuous and discontinuous, depending on the supply of substrate. In continuous processes, the substrate continuously flows and exits from the system, resulting in a process with constant substrate flow and gas production (equilibrium). Therefore, the growth requirements of microorganisms over time are unchanged. The process of molecular degradation is controlled by bacterial growth kinetics and to a large extent depends on the growth medium. Discontinuous processes are fed only once. Consequently, therefore gas production and substrate degradation changes over retention time, by which growth requirements for microorganisms change permanently. The substrate balance of a continuous or a discontinuous process can be expressed as

$$dS/dt = D \times S_0 - D \times S + (dS/dt)_r \quad (3.2.3.4)$$

accumulation input output reaction

where *dS/dt* is the accumulation rate (change of substrate concentration over change in time), *D* is the dilution rate (flow per reactor volume, in 1/h), *S* is the substrate concentration, S_0 is the initial substrate concentration, and (*dS/dt*)r is the reaction rate [223].

3.2.4. Small psychrophilic plug flow digester with assisted solar heat

Layout and concept of technology

In northern Europe production of biogas developed in the middle of the last century as an instrument for wastewater treatment, reducing the bulk of sludge and biogas is used for wastewater station heating. But at the end of the last century, because of the change in the political system in Eastern Europe, biogas production declined to almost zero. In Sweden this was the period when biogas shifted from by-product to the desired energy carrier – it became possible to create a profitable company and entrepreneurs and municipalities worked together to produce vehicle gas and to increase energy efficiency. Since the end of the last century, with the advent of technology and the diversification of different technological styles increased the efficiency of the process technology. Main objective of the technology being studied is to increase the amount of renewable energy at the national level to ensure regional investment potential of the energy sector by increasing the share of biomethane and solar energy in the final energy consumption of renewable energy sector of Latvia. The main importance of a technological solution is to maximize digestion of organic residues by getting higher concentrations of methane in biogas and digestate with less

organic material. Psychrophilic anaerobic digestion with assisted solar heat is a way how to maximize methane content and decrease organics in digestate. Technology is intended for non-profit and autarky, later for economic benefit of biogas plant owners. In this work, we combine biogas production in the mini to small-scale as the main renewable energy resource with solar collector as assisted heat. This is offered as a more efficient and faster alternative for composting of waste and better management of biodegradable residues.

Potential target audience of technology are households, households with farms, small-scale producers of bioproducts with residual biomass. Combining the state of art biogas production technology with the solar collectors (considering the price-performance ratio) can reduce probable costs of heating reactor. Later optimization performance and operation of a hybrid system can result in even greater energy savings when the solar heating system is used and at the given type of reactor to ensure a stable production of biogas throughout the year despite changing seasons [230, 231]. System comprises of five major components: biomass – pre-treatment and feedstock, digestate, psychrophilic plug flow digester, solar collector unit, use of gas. (Fig. 3.5.). Solar collector heat will heat the reactor, if unnecessary, for the heating of accumulator. If it is necessary firewood boiler can be used for heating the bioreactor.

There are few reasons why such hybrid-system must be supported. Solar heat-assisted biogas production is essential because a) almost everywhere in the world there are biomass and sun; b) solar heat energy [232,233], and anaerobic digestion of biomass [234-237] are sufficiently long studied technologies; c) technology can produce both heat and power, and fuel – this enables sector coupling [238]. Additional consideration for the development of technology is that hybrid solar assisted biogas in the micro to small scale serves as a socio-economic integrator of renewable energy sources. It is also a driver of innovative renewable technologies (IRT) and helps the diffusion of knowledge about technologies by bottom-up integration, meaning community initiated and supported.

Solar heat will be used in several ways to assist the anaerobic digestion process, for pre-treatment of the feedstock, heating digester and reducing moisture in biogas produced. Several studies have been conducted on solar assisted biogas e.g. [239–246]. Regional disparities in the availability and form of feedstock, solar intensity, serve as a barrier to technology transfer. Research is compulsory to facilitate the diversification of renewable energy and the development of hybrid systems for energy efficiency [247–251]. Development is needed in this topic to increase knowledge and later instinctively integrate technology in the regional renewable energy sector.

Multi-Locality of Biogas

Anaerobic digestion is complex and optimization is still ongoing, literature review shows that in the production and use of biogas there is no universal solution suitable for all interested parties. Temperature conditions, types and quantities of feedstock, economic situation, the level of education, vary regionally. Researchers agree that the biogas development and innovation process require an active network of heterogeneous peers [252-253]. In addition, biogas policy is often national. Thus, there is a tendency to consider biogas as one homogeneous and a nationwide system, but it is not. Over the years several technological styles have evolved and continue to operate. Production of biogas is because of various motivations. Technology transfer takes place, for example, between the farms,

thus creating new opportunities for cooperation. With biorefineries, there is also an extension of the scope to include more participants and feedstocks. This means that biogas is not just one system as it is usually perceived but several local ones. Problem is that the politics of resilience are developed in such a way it has only one system – one type of production and one kind of use. Therefore, the benefits of diversity of technologies in the medium and long term are lost and hinder the development of the renewable energy industry. To increase biogas production, the diversity of biogas production needs to be recognized and promoted in the research and policy-making process. Diversification of production are essential factor for further development of the renewable energy industry. In the long term, in the European region, diversification of production would promote the flexibility of energy resources, moving towards regional energy autonomy [254-255].

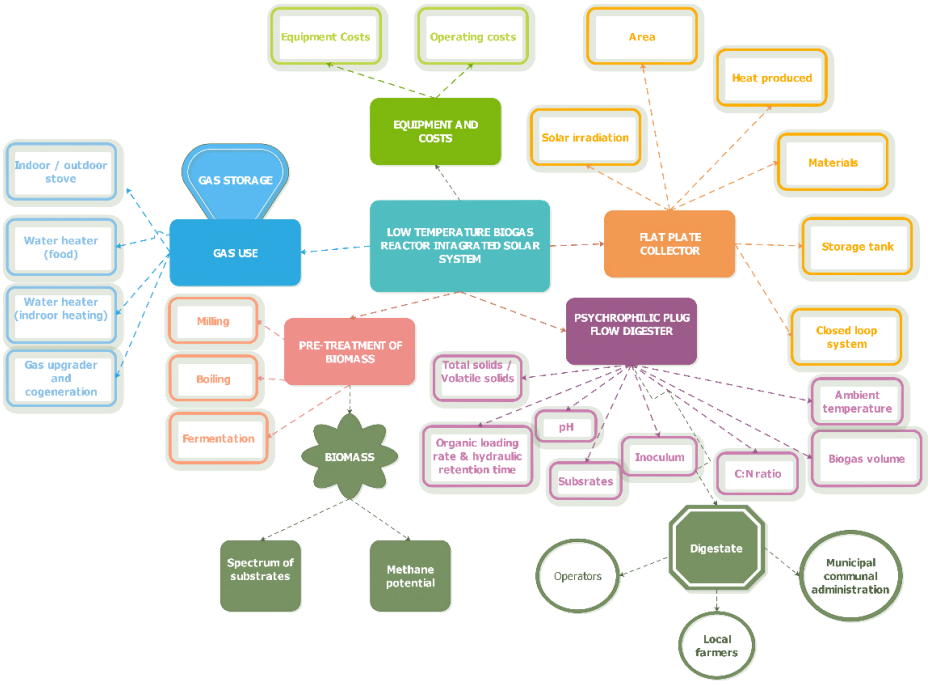

Fig. 3.5. The framework of low-temperature biogas production system with integrated solar heat

Biogas producers and users are in a multi-local system. The authors use term multi-local (multilocality) to denote a variety of technologies, solutions, applications and scales of technology in a certain area or region. Development of biorefinery concepts will contribute to integration of biogas – the expansion of the scope, increase in a number of actors and feedstocks. Research that determines potential of gas production, technological and economic conditions are considered but are vaguely related to the social conditions. Thus, these studies can be very subjective in scientific sense and cannot be used as a basis for political decision making. Researchers should reckon with many technological styles to develop industry policies, research into biogas systems [256].

Development of renewable energy sector policies and support mechanisms require implementation of diversified biogas production, interdisciplinary and applicable scientific research including comprehensive (social) and sectoral (economic) preconditions. The potential for production and uses of biogas globally is very high. At the moment a tiny part of the available resources is used and it needs to be changed. Diversifying the production of biogas with the solar collector support system is a way to promote and improve biogas production and, overall, renewable energies in the region (Fig. 3.6.) [257].

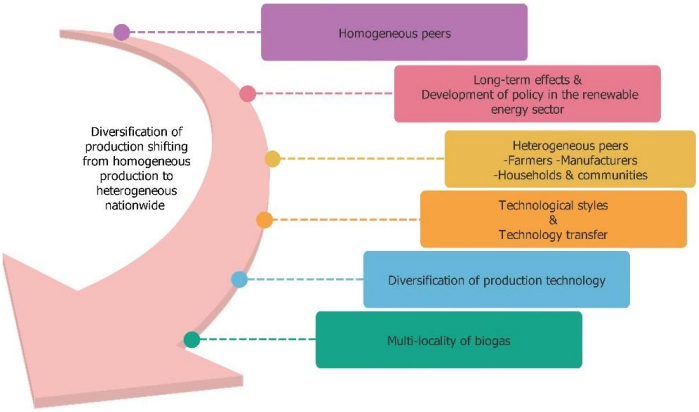

Fig. 3.6. Diffusion of innovation for diversification and increase of biogas production

Small-scale anaerobic digestion system with solar heat support – influencing factors and design investigation

Optimal performance of anaerobic digestion depends on several parameters. Various groups of bacteria are engaged in the production of methane and appropriate conditions must be created to ensure that all microorganisms are in balance. As the complexity of the process is high for anaerobic digestion factors affecting the yield of produced methane is quite large. Absolutely, the temperature matters in biogas production it substantially determines the activity of microorganisms, other key factors are C/N ratio, pH, blending, feedstock, HRT. Anaerobic digestion is a protracted process and the adaptation of microorganisms to a new state when the feedstock or temperature changes is about three weeks. Thus, it is essential to provide a more constant temperature and homogeneous easy to degrade feedstock. Vast majority of the hydrogen-consuming methanogens grow in of 6.7 to 7.5 pH, meaning the neutral pH is beneficial for biogas production. Acid-forming microorganisms grow under mesophilic conditions, but methanogens at higher temperatures. Mixing is also an important for biogas production, too much stresses bacteria and without mixing foam appears. Methane-producing microorganisms grow gradually, with a doubling time of about 5 to 16 days. Accordingly, the hydraulic retention time in the psychrophilic range should be at least 30–60 days. Also important is the feedstock used, its carbon balance with other nutrients, primarily nitrogen, and phosphorus and sulfur. Digestion needs to be done slowly in different circumstances easily disintegrated substrates can cause escalation in acid and inhibition of the process. The carbon to nitrogen proportion needed to be approximately 16:1 to 25:1. Too much carbon or nitrogen increase or decrease biogas production. The concentration of solids in the bioreactor should be between 7% and

14%. The size of the particle of the substrate is less important than temperature and pH. However, the size of the particles affects the rate of deterioration and ultimately generation rate of the biogas [258–259, 269].

Production of the most efficient biogas takes place in the co-fermentation mode with the addition of high carbon substrate to high nitrogen substrate. Depending on the location of the technology, the processing plant can choose a feedstock, for example, sewage treatment activated sludge, manure, plant biomass, silage, damaged fish feed, cereal products, and other food/feed residues can be used [234,237]**.** The psychrophilic reactor is more stable than mesophilic or thermophilic [260], and then the main control parameter is the pH value. When increasing the pH of the reactor, more raw materials with high carbon content should be added. The total dry matter content of the bioreactor should not be greater than 14 % for plug flow digester. This reduces the energy consumption of the mixing system. Required dry matter content of the bioreactor is ensured by diluting feedstock with water. The main advantages of psychrophilic temperatures for anaerobic digestion would be the lower energy input required for heating the reactor, consequently reducing the overall operating cost. Most recent results on microbiological activity in psychrophilic conditions show that lower temperatures require a longer digestion time and lead to higher methane content and lower accumulation of volatile fatty acids compared to mesophilic conditions, although still keeping a similar cumulative biomethane yield in both conditions [261].

Main factors that influence heat produced by solar collector is intensity of sun, type of solar collector generation used, solar collector area, angle, position, height, the height of the surroundings, rotating and rotating rate, capacity, flow rate, material's thermal conductivity, color, insulating and consuming rate. Heat loss from the collector plate depends on several factors. Such as (1) absorption plate temperature, (2) spectral properties of the collector plate, including absorption and emission capacity, (3) air temperature; ambient air and sky conditions; (4) number and characteristics of glass panes and their spacing; (5) the physical properties of the heat for the insulation material used at the edges and at the back; (6) the horizontal inclination of the collector; and (7) the wind speed above the absorber [262].

When solar heat is produced there is a need for heat accumulation. There are few materials used as heat energy storage media, for example, sand-rock minerals, reinforced concrete, cast iron, salt (NaCl), cast steel, silica fire bricks. But the cheapest and most commonly used is water [263]. Water has a high heat capacity (about 4180 $kJ \cdot m^{-3} \cdot K^{-1}$) but is limited to 100 °C unless there is increased pressure. Most materials used for intelligent heat storage range from 900 to 3000 $kJ \cdot m^{-3} \cdot K^{-1}$. Heat conductivity of the following materials ranges from 0.5 to 4 $W \cdot m^{-1} \cdot K^{-1}$ [264]. Main factors that ensure the technical feasibility of a solar thermal storage system are superb technical features. First, high sensible heat storage capacity is essential to reduce the volume and increase the efficiency of the system. Second, a good heat transfer rate should be maintained between the heat storage material and the heat transfer fluid to ensure that the heat energy can be released/absorbed at the desired rate. Third, the storage material should have good stability to avoid degradation (chemical or mechanical) by a specific number of thermal cycles. The cost of a solar thermal storage system consists mainly of three parts: storage material, heat exchanger and land costs. Cost efficiency is usually associated with technical

characteristics. High heat storage power and exceptional heat transfer performance can substantially decrease the size of the system [232].

To build a solar heating system for Latvia, weather data for specific location must be collected. First necessary to acquire data on the sun radiation (global, diffuse, and direct), other environmental factors, such as the outside temperature, the relative humidity of the atmosphere, and the wind speed. Due to temperate meteorological conditions, reactor outages are possible during winter when external heating is required, most likely, the break could be from the beginning of January to March. It should be mentioned that low temperature operation is mainly to avoid the need for electric heating of the reactor during the spring and autumn months, it also ensures a more stable process. Previous studies on solar energy and temperature in Latvia show that from 2015 to 2020 in Riga, Latvia yearly total solar radiance was 1017 kWh/m^2. Planning for energy production rates and heat demand is quite challenging in due to the local climate. Trend indicates that weather in Latvia is erratic, for instance, the maximum ambient air temperature in 2020 was 30.8°C, but by 2021, it had already risen to 37°C in several parts of the country, the lowest ambient air temperature in 2020 was – 10.3°C, but by 2021, – 31°C [335]. Meteorological conditions, region, topography, season, daytime or night, changes vary considerably in different climatic conditions. When developing a solar system, to magnify the use of solar energy, it must be ensured that the system has high heat exchange efficiency and energy recovery. This requires a temperature control system to keep the temperature constant. Heat is stored to match temperature between day and night, sunny or cloudy [265].

It is necessary to achieve the most suitable solution for the solar heating component for the system [266]. The system contains a collector, a heat transfer control pool and a temperature control system. Solar energy is collected by collectors to heat media material for heat transfer. The heated transfer control pool is connected to the heating manifold through the pipelines. Pipelines in a heated transfer basin should be constructed as uniformly as possible to assist in heat transfer (if there is a larger pool, blenders are required). To reduce heat loss, the basin and pipe casing must be insulated. The temperature control system includes a temperature probe. The probe can keep track of the pool temperature and provide a timely response to the controller connected to the pump to control the amount of heat to reach the reaction temperature. Characteristics of the solar component are shown in Table 3.10.

Practice shows that a successful reactor must be capable of taking a sufficient amount of biomass. The reactor as microbiological growth and replication ecosystem of different micro-organisms must be stable, the flow of materials and energy smooth and efficient. It is problematic for a household to choose one appropriate type of digester. Design depends on geographic location, feedstock availability and climatic conditions and other circumstances. From all the distinct digesters, the dome developed by China and the floating drum developed by India continues to operate until today. Plug flow digesters gain attention because of ease of operation and portability [259]. What materials will be used for the construction of the biogas digester depends on the local conditions – geological, hydrological, and locally available materials [267]. In recent years, as a result of technological advances, there has been a proliferation of materials with improved properties and lower costs [259]. For the construction of this type of digester stones and bricks are

used as a building material. With the advancement of technology, PVC and polyethylene are used because they are comparatively inexpensive [268]. From different materials used for the construction of mini-digesters most promising in the case of East Europe are bricks and concrete and plastic – polyvinyl chloride, polyethylene, with or without modifications. Main advantages of plastic are less weight, easily portable, relatively cheap, bricks and concrete have an advantage over maintenance cost and the material is everlasting. Disadvantages of plastic – relatively short life span, disadvantages of bricks and concrete – difficulty to clean, built underground, the possibility of gas escaping through concrete when pressure increases. As research in household biogas digesters shows the psychrophilic biogas reactor in its simplest form may be a plastic or concrete tank, in which anaerobic environments undergo degradation of organics and the formation of biomethane. The decision of the reactor elements is determined by the availability of materials and price. Smaller households or household communities are more suitable small-sized reactors that can be installed in the territory of household and run at ambient temperatures or with solar heating support. Larger farms are better suited for production capacities with concreted large-volume reactors that are insulated or partly below ground level to provide reactor operation in winter [259].

Biogas system comprises the following components:

Pre-treatment tank consists of electrical miller – homogenizer and is used for the feedstock particle size reduction and mixing with water. Feedstock inlet comprises of a container for organic waste and a tube with a diameter of at least 10 cm,

Psychrophilic anaerobic digester – organic waste reservoir in which the feedstock is degraded by anaerobic microorganisms to produce biogas,

Gas storage/reservoir depending on the design can be just a room above the digester or a durable rubber balloon,

Exhaust pipe is a tube of similar size with an inlet pipe connected to the surface at a slightly lower level than the intake pipe to facilitate digester discharge;

Digestate storage is tank made from the impermeable layer for dehydration of digestate or storage,

Gas burner – modified burner for cooking or water heating.

Digester design is adapted to the situational aspects outlined in this paper. Literature review shows it is possible to produce biogas in climates with cold winters [231,245]. Our design is modified reference digester suggested by Adebayo *et al*. [269]. To make the household digester attractive it must integrate features such as good maintenance capability, simple operation, relatively inexpensive design, using locally available materials. From the simple structure digesters, plug flow digesters best meet the criteria needed but also ensures its place to live acid and methanogenic producing bacteria. The inclined position produces a two-phase system making it possible to separate acidogenesis and methanogenesis longitudinally [269].

Characteristics of the bioreactor and solar components are shown in Table 3.10. It is possible that in some of the reactor components other materials can be used. It may be possible that some of the reactor components are not needed if it is found that during the construction of the prototype component is interfering with the system, easing system operation, and operational costs.

TABLE 3.10.

Characteristics of the Bioreactor and Solar Components

Component	Details
Digester type	Plug flow digester
Digester volume (for one household)	4 m^3 (2 m^3 to 15 m^3)
Length to width ratio	3.5 : 1
Process	Two-phase system
Gas collecting	The upper part of the digester or balloon
Portability	Portable
Operation	Semi-continuously
Hydraulic retention time	30–60 days
Solid content	7–14 %
Digester temperature range	15–35 °C
Inoculum source	Wastewater treatment plant or cow manure
Digestion unit	Plastic
Feed tank	Metal with pre-treatment unit
Mixing	No
Digestate storage tank	Metal/concreate
Tubes	Plastic, insulated metal
Digester unit heating jacket	Metal tubes/wiring
Insulation	Composite material, rock or glass wool, organic
Feedstock	
Water source	Rainwater tank/underground
Heating source	No heating or solar collector/heat accumulator
Pre-treatment	Milling, boiling, chemical, drying
Co-substrates Food waste (FW) Fish waste (FIW) Garden waste (GW) Cow manure (CM)	Methane potential in volatile solids (VS) or total solids (TS) Co-digestion with other substrates was 0.27–0.86 m^3 CH_4/ kg VS [270] Biomethane production potential of 0.2 to 0.9 CH_4 m^3/kg VS [272] 0.10 ± 0.02 biogas (m^3/kg VS) [272] 0.6–0.8 m^3/kg TS CH_4/g TS [273]
Slurry storage, organics content	Digestate storage tank, organics content after digestion is variable depending on reactor temperature and specific activity of microorganisms and other complex factors
Solar collector type	Flat plate collector
Solar irradiation, annual	950–1050 kWh/m^2
Flat plate collector, model	Optional
Gross area of collectors	20 m^3
Inclination angle to horizontal	34°
System type	Closed loop system
Oriental angle	0°, south
Storage tank	Cylindrical tank

Heat exchanger	Helical coil heat exchanger
Heat transfer fluid	Water + glycol (for freeze protection)
Collector interconnection	Parallel-connected collector array
Control systems	Pumps, controllers, temperature control
Portable	Yes
Solar heat application	Heating of water for different uses

Technology has different potential applications, however, one example of the possible use of technology will be briefly described below. As declared in the above paragraphs the idea is suggested for household environments, on a larger or smaller scale with or without related production that generates biodegradable residues. Technology can be used, for example, a small producer of bio-based goods. This small producer which generates a variety of food products generates 47 tons of biodegradables a year. Generating 47 tons of waste means that daily production is up to 130 kg of food waste. Results show biomethane production in a low-temperature biogas reactor (average temperature 20 °C) has a retention time of 53 days, in a co-digestion mode, with a maximum bioreactor size of 14 m^3. Theoretical calculated OLR is 1.72 kg VS/m^3 per day. Considering that plug flow digesters can withstand ORL up to 10 kg VS/m^3 per day [136]. Therefore, the maximum size of the bioreactor is reduced three times to 4 m^3, with OLR 6.88 kg VS /m^3 per day.

TABLE 3.11.

Characteristics of the Technology Studied

Characteristic	Value
Biomass quantity, annually	47 000 kg
Biomass volume, annually	~95 m^3
Biogas yield for food waste	0.4 m^3/kg TS
Average FW feedstock density	510 kg/ m^3
Reactor temperature, average	20 °C
Biomethane concentration in biogas	60 %
Organic loading rate	6.88 kg VS /m^3day
Hydraulic retention time	~53 days
Reactor size, m^3	4–15 m^3
Solar collector, area	20.2 m^2
Usable solar heat produced, year	~3000 kW
The amount of biomethane produced	4230–14 800 CH_4/m^3

The average yield of biomethane in the co-digestion of food waste and activated sludge, at low temperatures with substrate retention of 28 days, is from 90 to 200 m^3 of CH_4/t of food residue, depending on the type and water content [259,265,274]. The production unit of this size theoretically could produce an equivalent of ~20 000 m^3 of biogas a year if the

biomass is digested with maximal efficiency. Depending on the feedstock used and its volatile solids, biomethane content it is from 4230 m^3 to 14 800 m^3 a year (Table 2). In best case scenario, system of this size in the maximum effective mode would produce 27.5–96.2 MWh of heat per year. The thermal energy of the hybrid-system can be used for heating living and production premises, drying wood or food, sprouting grains, growing vegetables and mushrooms, growing insects, earthworms, and similar solutions. Considering a small-scale the costs may vary depending on the type and quality of the selected materials and scale. The payback time for digester with solar collector, control system, heat storage, needs to be determined by market analysis of the offers, and it depends on the reactor, collector technology, heat accumulator capacity and increase of component price.

The importance of social approval for decentralized energy systems plays an important role for broad consumer use. Development of suggested renewable technology and modifications in the long term will make significant impact. Implementation of technologies will move industry towards a heterogeneous energy. In the long run it increases (1) energy resilience; (2) decreases the volatility of energy prices and the (3) introduction of a block-chain (market); (4) minimizes the environmental impact on human health by promoting industry connectivity to the integration of renewable energy. Linking electricity, heat, and transport to the infrastructure and stored energy carriers, could be achieved. It is necessary to develop decentralized systems because there are a large number of, for example, bioreactor owners, then the system is much more integrated – from supply to demand, and horizontally – between different energy vectors – electricity, heat, gas. Decentralized energy systems can reduce transmission costs and centralized energy capacity. At the current level of technology, fully autonomous regions are economically impossible due to the need for large energy storage capacities [276,277]. Use of biogas as a renewable energy source will help to reduce negative external effects (emissions of CO_2, methane and thereby global warming, and polluted air, water, and soil) and by that reducing social costs of energy production. Biomethane as energy source gives positive overall economic effects – reduction of fossil energy import, saving of foreign exchange, less dependency upon foreign energy supply, less price volatility, improvement of electrical energy supply. Biogas as a renewable energy source is a good investment opportunity because planning, construction, and operation are not way too complicated. There will be good effects of increased biomass use. If waste biomass is used it will result in waste reduction, reduced costs of waste treatment, reduced environmental risks and groundwater pollution, unpleasant smell, health and sanitation problems. The exploitation of renewable energy produced from anaerobic digestion leads to direct and indirect benefits for the producer and the community – environmental benefits, improved living standards and revenue from sales of energy.

It is crucial to improve public awareness by introducing society to biogas production as an easy and convenient way to manage biodegradable residues. Development of household biogas may lead to community biogas as a way of treatment of biowaste and producing energy, and later probably a business. To ensure the regional investment potential of the energy sector, it is necessary to diversify renewable energy resources. And one way of doing this is to increase the share of biogas (biomethane) in the final energy consumption of renewable energy. The anaerobic digestion application rate for biodegradable waste management could be increased in two main ways. First, in the context of knowledge

transfer by increasing the resonance of the biogas production on its extraction, use and positive aspects for society. Second, technologically – increasing the number of feedstocks used and diversifying technological solutions so that they are more widely available for households, companies, farms. Environmental and economic valuation of system will be carried out to estimate the cost of energy and the initial investment for this type of solution.

Kowalczyk-Juśko et al., 2019 analysed spatial and social conditions of agricultural biogas plants in Poland. More than 80% of respondents believe that the building of a biogas plant will help the commune by safeguarding the environment, providing people with cheaper power, and delivering cash to farmers by creating additional employment and crop sales. Concerns regarding the construction of biogas plants include unpleasant odors, loudness, increased pollution, and the possibility of an explosion. The size of the land on which the agricultural biogas plant will be built, as well as the condition of the roads, connectivity to the power grid, distances from possible substrate suppliers, and distances from human habitats, are all important considerations. Choosing the appropriate site entails taking into account a number of technological, legal, environmental, and social issues [336].

Small-scale agricultural biogas facilities, geared to small amounts of feedstock and farm energy requirements, should become increasingly popular in Europe. The capacity provided in such units must be sufficient to cover the energy needs of one residence. Czubaszek et al., 2022 draws attention to careful calculations and correct recognition of the nature of feedstock and parameters in small biogas plants. According to technical considerations, the approach would lower the cost of modifying the reactor to the feedstock to be utilized. Small agricultural biogas plants' feeding systems might be more complicated, according to research. Due to the variable physical characteristics of the feedstock that the operators utilize, such stations need to be adaptable in terms of technology and equipment. Additional research is required to determine an affordable pre-treatment method that will improve the efficiency of anaerobic digestion in small reactors [337]. For pilot plant development at temperate climate use mixture of psychrophilic and mesophilic bacteria are suggested [338]. According to the research findings of Prvulovic et al., 2022, based on the estimated energy requirements anaerobic digesters requires less energy from June to August, and more from November to March. An average of 16% of the generated combined heat and power engineheat is required yearly to heat the fermenter. Most thermal energy is required in January and December (20%), and the least in July (12%) [339]. Anaerobic digestion on a small scale is a promising method for treatment of organic part of municipal waste. It applies to the European agriculture industry, and adoption of installation is predicted to rise considerably [340].

3.3. Managing aquatic biomass residue issue

3.3.1. Analysis of production of bioproducts from fishery waste

Fish processing by-products are considered low value and disposed of in the easiest possible way – buried in a landfill, incinerated, or used in the production of biogas, or low value products. Nowadays, there is an increase in fish catches in capture fisheries and in aquaculture, which in addition leads to the growing use of the surplus. Most of the so-called waste is used

for fish meal production because, in the last decade, worldwide aquaculture fish production has doubled. Fish waste is used for fish meal, sauce, silage, or other low value product production. Lately, the main attention is on the development of new products with high added value. In some regions, where political and economic circumstances permit, industrial-scale production of a variety of fish bio-products, has started. In this list of products there are protein powders, cosmetics, and enzymes, which have an incomparably higher added value compared to traditional products [3], in addition, depending on the technology, waste can still be used. Fish processing waste can serve as raw materials for other industries, this practice contributes to better fisheries processing by-products recovery and utilizing in food, pharmaceutical, nutraceutical, and biotechnological applications [278]. European Union has determined landfills are not sustainable. The re-use of waste should be encouraged to prevent unnecessary biomass to be wasted. To improve the governance of biological resources, large-scale bio-economy research and innovation are necessary. The development of the bioeconomy is not only the unnecessary use of biomass. This will create new markets for both food additives and other bio-based products. The European Commission stresses the need for continued and increased in public funding and private investments into bioeconomic research and development. A good example of the use of biological resources, research, and its funding is the Nordic Bioeconomy – the cooperation of Norway, Finland, Iceland, Faroe Islands, Greenland, Sweden, and Denmark. Norway is quite developed in this context notably in the use of marine fisheries and aquaculture by products [3].

One of the main problems that restrict the use of this waste is its variable nature. The composition depends on the fish species, pre-treatment, storage, and processing methods Choosing the best fisheries production waste application reduces the industries impact on the environment and can create products for human consumption[279], [280].

The bioprocessing industry waste generated can be used for a variety of indicators that help to compare different areas and parts of the world with each other. For example, value added (% of GDP), the environmental and sustainability indicators (CO_2 emissions per unit of generated product waste (kg) per unit of the product obtained), production indicators (chemical consumption per unit of product, the number of man hours invested in each unit of production), and quality indicators (impurities in the final product, % or g), etc. Often the lack of data in some parts of the world limits the possibility of obtaining high-quality information. For this reason, qualitative indicators can be used that can be based on conclusions, expert opinions, assessments, and opinions, and information that cannot be expressed numerically. One thing that is particularly difficult and time-consuming is to comprehensively assess innovative experimental products. For this reason, experts' views on the obtainable products from fish waste.

New products or new method development does not happen in an instant but requires a long time. After analysing literature and experimental research carried out over several years, the first step to move towards larger-scale production is a laboratory research scale-up in the form of a pilot project. A pilot project, or a test project, is the preceding small-scale study to assess the feasibility, costs, adverse events, effect size (statistical variability), and the time trying to predict the likely size of the sample, and to improve the design of the study before making a full-scale research project [281]. However, this type of goal-oriented research project requires substantial resources, it takes many years, and there are many equally significant political and

economic factors (changes in power, economic priorities, redistribution of educational reform, i.e. the higher education funding changes) and what delays its (the selected product) development to be a finished locally, or regionally, produced product.

Examining the theoretical possibilities in the context of product production in Latvia, nine intermediates are directed for further development and consideration of production possibilities, because there is a logical basis and they do not require the use of specific fish species for product production. These products are oils [282,283], proteins [177,284] including collagen [285] and gelatine [286], enzymes [287], minerals [288], and bioproducts with specific characteristics peptide cryoprotectants [289], peptide antioxidants [290], adsorbents [291]. From mixed waste, it is almost always possible to exude oil and produce biodiesel but to produce high-quality fish oil it is necessary for raw material that is relatively clean or a method to separate the specific density of fish parts from the rest of the mass. It is also possible to produce protein hydrolysates from unsorted mass relatively easily, but its quality and purity will be much lower than if they were produced from roe or fish fillets [177]. However, other products need a particular type of waste. To produce collagen and gelatine, waste with a high content of connective tissue structural protein is needed, like fish skin and bones, to a lesser extent scales [285,286]. In turn, to produce proteolytic enzymes a particular type of waste from fish internal organs (viscera) is required [287]. For the manufacture of adsorbent and hydroxyapatite, fish bones and scales are required. Adsorbents obtained from residues of carbonized fish are theoretically suitable for all types of composite fish waste.

The literature review indicates that the resulting product quality is dependent on both the raw materials used and the specific acquisition methods. Pharmaceuticals, cosmetics, and food, which are obtained from fish waste, should be of high quality and the end product should be without impurities. It is very hard to ensure a high quality because the waste quality and composition is very variable. The best way to get high-quality products is to use high-quality raw materials, instead of using the available raw materials, which are of poor and questionable quality. Low-quality raw materials make the process of substance separation and purification more expensive. To develop different kinds of products some essential conditions about raw material and product development must be considered: (1) Raw material quality is one of the main factors determining the possibility to manufacture. (2) Biomass and product transport are expensive, which is why processing plants must be strategically placed. (3) High-added value product production development is a difficult and time-consuming process. (4) A lot of unforeseen problems appear because of scale-ups and scale-up, process demonstrations, and product commercialization is a high-risk business that is difficult to finance. (5) It is necessary to improve the governments' regulations and support for the bioeconomy [3].

Research work done in context with the Thesis shows that comprehensive and systemic research in both technological and economic sectors are needed for further by-product processing analysis. Available information indicates that for the production to start, the most important components are technical criteria, which are what is the amount of the fish resource, how complicated is the technological scheme for product acquisition and economic criteria, equipment operating costs, and cost of raw materials and then only the environmental factors.

In the context of European fisheries, added value is usually associated with the processing of salmon or cod into food and the processing of residues into fish meal. And these residues also tend to contain more added value. A study analysing the use of Scottish salmon production

to produce value-added products stated that use of discards can increase value by up to eight times [42].

3.3.2. Technological clues and recommendations for pilot development

The concept of biorefining in the quest for sustainability thrives on using the entire substrate to obtain products for use in various industries while stopping the extraction of a single product. Research focuses on the use of innovative, economically, and ecologically sustainable extraction methods to preserve the biological activity of molecules and to respond to increasing consumer awareness of product-related issues. Innovative techniques can transform waste into value-added by-products through an efficient and viable economic strategy [45]. The functional unit of a bioeconomy is called a biorefinery. Biorefining of marine compounds ensures the continuous application of technology to reduce risks to the environment and human health. The extraction efficiency process depends on food matrices and the chemistry of target compounds. Aspects to be considered in extraction procedure are particle size of biomass, pre-treatment, compatibility, and interactions of components in a matrix, nutritional, organoleptic quality of recovered components, and safety of the product. Biorefining by green technology's most notable advantage over traditional methods is minimizing losses of functional properties of the bioactive compounds extracted from marine by-products. As a result of literature research, several key aspects of the path are highlighted which should be paid attention to and which would help use aquatic biomass to produce products ensuring higher added value. The general processing framework for bioresources consists of several large blocks each of which has its own specifics. When developing any framework, it should be considered that the blocks are contextually and informatively different in terms of importance and can be mutually subordinated. Development of a detailed framework requires a great deal of involvement from both industry and related companies, as well as public and labour participation in the process. Although the marine processing sector is characterized by a large amount of data in the primary processing sector and traceability, the use of aquatic waste can be improved. Accurate and sufficient amount of information in the planning process and operation of the biorefinery ensures successful and smooth operation of the system. Analysis carried out in this work shows that a peripheral but quintessential example of the main blocks of marine bioprocessing can be organized into following groups:

1. Fishery – method, target species and population, catch, by-catch, catch area, vessel, vessel capacities and sizes, fishing intensity, catch reports, current, temperature, wave data, wind, costal waves, sonar data; in the case of aquaculture (species, region and climate, water physical-chemical parameters, type of feed, external energy consumption, etc.) [1].
2. Logistics – throughout the processing cycle in food production, distribution, transport, utilization of residues, sourcing of biomass.
3. Bioresources and descriptive – chemical characteristics of marine resources, including characteristics of residues.
4. Processing technology in food – fresh or preserved, number and types of stages.
5. Processing technology in added value products – type of processing – food, feed, energy, etc.

6. The niche of products – uses, applications, diversity and flexibility, relevant market characteristics.
7. Residue processing technology between or in the final product, including methods of purification or improvement.
8. Product and by-product packaging – type, material, quantity used per product unit.
9. Long-term storage of products – storage environmental conditions i.e. temperature, air circulation.
10. Appliances – type and material of equipment, additional supplies, energy, human resources.
11. Legislation and safety – relevant legislative acts for each block and other applicable regulations, international agreements, or other recommendations.
12. Feedback – sustainability indicators, economic indicators, safety indicators, recycling, residual utilization indicators etc.
13. Driving forces behind industry – exogenous – market, biosciences, technology and innovation, climate change and threats to ecology; and endogenous – science policy and science diplomacy [292].
14. Planning and information throughout the production of products – meteorological conditions, species availability, price and availability of additives, price of energy, new legislations, change in taxes, the funding of infrastructure winding up and its expected impact. Forecasting yield, prices, expenses, other indicators by suitable mathematical models.

Within the framework of the Thesis, the aspects of processing three aquatic waste biomass feedstocks, possible technologies, and obtainable products were studied. The results show that the sector of this "aquatic bioresources" is given relatively little emphasis on raising the added value and creative use of residues, mainly due to the low quality of resources, the fragmentation of resource provision for economically based economic activity, the low level of investments and high initial costs in innovative processing methods. From these four substrates, it is possible to obtain very high value-added products (mentioned in the previous chapters of the work), which are in demand in the global market, but in these latitudes there is a marked seasonality and there are months when the raw materials for the production of the product are not available. Therefore, resource storage and recycling planning is necessary. Storing of resources increases the marginal cost of production.

The main task of the biorefinery in the processing of aquatic bioresources is to reduce costs and the amount of low-value residues by ensuring the extraction of several products from several feedstocks in one place. For processing in the biorefinery to be possible, the continuity of electricity is very important, and in case of interruptions – additional backup energy sources, because in biotechnology, the manipulation of plant or animal biomass is carried out at a certain temperature, and pre-treatment and extraction methods may require electricity to be used. Engineering solutions in the application of innovative methods in practice are usually hidden behind patents, and in laboratory research they consist of several separate stages. The use of technologies and equipment, their specific solution in industrial processing requires electronic and mechanical engineering, chemical engineering, engineering teams, and research to ensure the error-free operation of the refinery. Human resource expertise and creativity in technology solutions provide an opportunity for bioresource processing industries to develop and

development of biorefining is also linked to logistics and supply chains of biomass and additional resources, shortages of materials, and energy can render the production system ineffective.

Choice of feedstock is a significant part of biorefining. Analysis of the literature shows that the price of raw materials is the biggest contributor to the final price of product. Therefore, it is important that the raw material is inexpensive and available, with a high content of substances and sufficient yield and quality for the process to be economically competitive. The best is residual biomass and biomass considered as a by-product. This biorefinery description includes three researched groups of aquatic biomass: mixed fish waste, algae waste and reed waste. Regardless of other factors, aquatic biomass usually has different origins. Fish and algae come either from wild harvest or aquaculture, reed biomass from green biomass management in wetlands or from special wastewater processing reed growing stations. Pre-treatment, extraction, separation and purification in one word is called processing, and diverse approaches are used, purification highly depends on further use of intermediate. The goal of pre-treatment is to make slurry suitable to be used as feed in batch or continuous system. Concentration of solids in slurry depends on further extraction process, but it is necessary to ensure fluidity so that the mass can be easily moved through the pipes. To obtain the desired solids loading, the dry matter content of the feedstock had to be determined first. Materials are homogenized to ease the formation of slurry and to destroy larger particles. Animal and plant biomass have different pre-treatment options.

Biorefining takes advantage of the favourable properties of specific biomass. Extraction of products can be done one batch at the time run-to-run or continuous process depending on feedstock availability. Seasonality factor plays important role in year-round processing in the east part of the Baltic Sea region. Co-treatment of mixed biomass is also possible if pre-treatment was done right. Yield of the product and defining characteristics are indicators of extraction procedures efficiency. General key-stages for three feedstock pathways, extraction procedure and other relevant information of theoretical biorefinery are showed in Table 3.12.

Table 3.12.

Theoretical by-product biorefinery processing stages for each feedstock

Stage	**Feedstock**		
	Fish waste *Neogobius melanostomus* biomass	Red algae *Furcellaria lumbricalis* biomass	Dried reed *Phragmites australis* biomass
1.Sourcing of feedstock	Quantity. Fresh or stored. Description of the raw material – temperature, pH, water content, protein, lipids. carbohydrates. C/N ratio. Colour, odour. Impurities. Microbiological inoculation [293].		
	Place of origin, processing plant, species, processing method, residue type and description, storage method. Feedstock – fish waste. Substance – protein.	Place of harvest or cultivation, salinity, temperature, wave regime, ratio of species in mixed mass, species, residue type and description, storage method [294].	Place of growth, harvesting time, method and conditions, composition, storage method, duration of storage [295]. Feedstock – reed biomass

		Feedstock – red algae. Substance – furcellaran.	Substance – fibre for production of ethanol.
2.Pre-treatment	Improvement of substrate structure. Immobilization of substrate. Processing or fermentation pathway. Addition or removal of water, addition of chemicals.		
	Fish biomass →Mincing → Protein isolation (pH shift, defatting) → Homogenisation [296] [100]	Drying → Storing → Washing [297][298]	Liquid hot water (LHW) 170 °C, 60 min [299] → Na_2CO_3 16 % w/w, 0.8 MPa O_2. 160 °C 60 min [300] Alternative pre-treatment for extraction of cellulose, lignin, hemicellulose. [301]
3. Extraction and separation	Target compound extraction from matrix, extraction stages, other characteristics of process, separation method.		
	Hydrolysis Temperature and pressure adjustment → Chemical hydrolysis with alkaline solution or equivalent → Terminating hydrolysis by suspending heat treatment and pressure [296].	Hot extraction Boiling in water → Filtering the extract → Drying with on roller-driers [297] An alternative extraction process with aqueous KOH solution, 2% (w/w) [302]	Semi-simultaneous saccharification and fermentation (Fed-batch S-SSF) 20 FPU/g-PS and 0,2 mL yeast → Fed-batch S-SSF 36 °C 18 h, 50 °C 48 h →Bioethanol solution [300]
4. Refinement of extract	Methods of purification, concentration, preparation, addition of preservatives.		
	Centrifugation, filtration (nano, ultra, ion exchange chromatography) → Drying (spray drying, lyophilization, evaporation) → Fish protein hydrolysate [296], [303] Preservation [304]	Furcellaran washing → treatment with KCl and washing → Drying and milling → Packing → Storing 2 – 8 °C [297]	Solution → Distillation → Bioethanol [300].
5. Storage, packaging, distribution	Storage environment and temperature. Refrigerated storage in frozen form for in days or in refrigerated form for in days. Storage of bulk extract in an inert environment in a vacuum or in a nitrogen atmosphere in sealed polymer material package. Transportation in cardboard or plastic container with loose insulation.		

6. Product laboratory testing and process efficiency	Laboratory extraction with multiple disposable bioreactors [305], protein content analysis [306], amino-acid analysis with MS-LC, HPLC [307] [308]; elemental composition analysis with atomic absorption spectrometry [309]; yield calculation and moisture content.	Laboratory extraction with multiple disposable bioreactors [305], structural properties (FTIR analysis), moisture, solubility, yield [302]. Functional properties of gel – viscosity, hardness, rheology [310]. Extraction residue elemental, carbohydrate and protein analysis for energy recovery assessment [311].	Laboratory extraction with multiple disposable bioreactors [305], kinetic modelling and mass balance. Substate concentration, cellulase loading. Yield calculation [300].
7.Treatment of residual biomass and effluents	Extraction and refinement process gas condensation and mixing with secondary liquid waste (stick-water, lipids, residual peptides) [312], sludge and effluents [313] for production of biogas [314]. Drying and homogenisation of mineral waste (scale, bones), to produce fertilizer [315] [316]. Estimation of primary and secondary feedstock quality, bioenergy sustainability [317].	A perspective on the use of residuals [318] – energy recovery from the leftovers with low-temperature mixing of biomass for enhanced methane production [319]. Estimate of macroalgae biogas production and sustainability [320].	Residual xylan and lignin use as solid biofuel by pyrolysis [321].
8. Evaluation of mass and energy inputs and outputs	Biomass substrate stream and other resources tonnes/year→ Full-fledged and effective use of waste and resources → Provision to zero-residue production. Fossil and renewable energy demand for all biorefinery → Biorefinery extraction unit energy consumption → Energy recovery where possible in joules /year.		
9. Costs and sustainability monitoring	Costs: Land, total equipment, direct and indirect installation costs. Operating capital, and annual operating cost – feedstock, operating labor, utilities, other variable costs. Sales, taxes, payback period. Sustainability monitoring: Renewable energy, cost ratio of raw-materials; biotechnological-valorization potential; material consumption; fraction of revenue for raw materials, gross margin, sustainable land use, employment, community investment. Environmental impact categories and reduction targets, reduction of water use and emissions [322].		

10. Retail price of extract and application	3 – 30 EUR/kg [323] for non-research purposes, feed or food.	90 – 165 EUR/kg [324] for research and development. Use in coatings, edible films, food, cosmetics.	0,70 – 3 EUR/L [325] for chemical manufacturing, fuel, disinfectant, food, cosmetics.

Global fish processing waste is increasing, so effort to develop an effective environmentally friendly treatment technology still plays important role in sustainable biomass waste management. Fishery co-streams are volarized by traditional or innovative technologies or combination of technologies. Economically and technologically justified sustainable zero residue process is needed for added value and mitigation of environmental impacts. Scientific research on environment and food shows that food-grade fish protein hydrolysate and fish oil recovery have the biggest economic benefit. Full use of waste streams includes two-stages. First, nutrient recovery operations, then, energy and fertilizer production. More likely in reality this means that there is a value chain network of fisheries-biomass associated processing companies where intermediates are purchased at a certain price. Quality of waste streams should be defined as the main indicator when utilizing fish resources because it changes the final yield of target compound. Detailed design research and increase in data information can further elevate utility and aid decision-making process [315]. Nutrient recovery from food waste or biomass waste streams in most cases is a straightforward process of extracting proteins from protein rich by-products. Technology for feed grade protein recovery from seafood wastewater is still being developed and membrane separation, adsorption, and microbe-assisted recovery are the methods that show promising results, but there is a delay in development of new technologies for large-scale manufacturing [326]. Production of energy and fertilizer takes place in one system – anaerobic digestion process of fish waste where digestible by-products are co-fermented into gaseous forms – methane, carbon dioxide, and digestate – liquid mineral and solid fertilizer, and water. Anaerobic digestion is promising energy recycling technology for biorefinery system, as it may be used for decentralized conversion of large-volume fish waste. Research shows that pre-treatment, anaerobic digestion, and combustion of gas have TRL9 and overall fish waste biorefinery reaches minimum TRL7 because limitation of operational capacity in separate distinctive parts of biorefinery. It should be emphasized that for this well-known technology to be economically profitable, system requires certain conditions in biomass prices, quality and product sales prices, as well as favorable local policy and legislative conditions [327].

The processing of macroalgae has also become more relevant for manufacturing of value-added products. *Furcellaria lumbricalis* are naturally harvested in the Baltic Sea and as a beach wrack for manufacturing of various products. Commercially viable aquaculture options have also been considered. Low salinity in the middle part of Baltic sea is the main limiting factor for increased utilization [294]. Interesting and profitable compound extracted from red seaweed is furcellaran, which is naturally sulfated anionic polysaccharide that is used in edible films, food, and cosmetics [297]. Furcellaran is a promising new alternative to plastics in food packaging industry because of non-toxicity and biodegradability and it is now researched for the production of new modified coatings in food industry [302]. Residue of furcellaran production is also used for methane production using co-digestion and shows profitable results [328].

Processing of reed biomass into ethanol is a promising option – ethanol concentration of 66.5 g/L is achieved [300]. For this technology to be cost-effective using the four-stage ethanol extraction technology, cheap sustainable electricity for pre-treatment and extraction are required. Better treatment operations of reed lignocellulose fraction in future can result in profitable industrial scale reed ethanol production [300]. Remaining fibres are used in the production of biofuels. Pyrolysis of common reed produces gases and volatile materials that are valuable for their energy content. Composition of the products and their energy value are largely influenced by the temperature of pyrolysis [321,329].

Advanced biorefinery aims at valorisation of variety of biomass into products and energy. The concept has different stages of technological maturity, and biorefinery is subject to constant flux and change. This leads to challenges in assessment and standardization of concepts. Based on the overview of Federal Government of Germany on technology readiness level (TRL), marine biorefineries have TRL of 5–6 for seaweed and 5–8 for green and lignocellulosic biorefineries. Implementation of biorefinery at a commercial scale necessitates dependable feedstock processing and presents technological, strategic, and sustainability concerns. Most technical hurdles are related to biomass supply and manufacturing costs. Because biomass heterogeneity necessitates distinct pre-treatment and extraction techniques, a multi-feedstock biorefinery with optional variable substrates and creative processing is advised. Biorefinery biomass cascading demonstrates greater usage of primary biomass and may overcome feedstock rivalry for food and feed. Nevertheless, problems may arise when defining the functional unit, often the functional unit reflects material flows. Also, multifunctional biorefinery causes problems for allocating the environmental impacts to various outputs. Life cycle approach of biobased product makes premise for assisted decision-making for finding the best solution within several scenarios. Further research in marine and green biorefineries is needed because it shows the lowest TRL compared to other biorefineries. Regardless of TRL, technical, economic and environmental assessment of exact biorefinery are needed for better use of biomass [330]. Manufacturing of intermediates from aquatic biomass and value improvement of residues is a technology-intensive process. Techno-economic analysis assessing capital and operational cost factors lead to sustainable biomass utilization [331]. A blue feedstock biorefinery at plant level includes biomass treatment and pre-treatment units followed by main processing facilities and are based on thermochemical or biochemical conversion. Unwanted by-products are removed, and remaining components are made into the desired end-products. Operation of the biorefinery will depend on the equipment and the selected operating parameters that determine the biomass yield to product and the energy and mass balance of the plant. It is also important to be aware of the investment costs of the plant as well as the costs of integrating the plant into location. Techno-economic evaluations are needed to assess yield, energy efficiency and production costs [332]. In regional context it is vital to investigate how the Baltic nations might overcome the "Bioeconomy valley of death" (TRL 6) [333] in the manufacture of additional goods and energy from blue wastes and biomass, as well as the ideal scale of the biorefinery. Performing of extensive research and creating individual scale-up plants to make confident and fact-based decisions on future growth directions is also advised. In the traditional industries – textile, construction and energy-intensive industries have higher TRLs both in processing and communication technologies because of the characteristics of circular technologies for different industrial ecosystems,

coupled with the need to address the full life cycles of circular products in specific value chains [334].

However, both traditional industrial and bioresource processing sectors can improve the use of residues, promoting more complete recycling and reducing volume of waste in landfills. Sustainable and multi-level development of the seafood processing sector is crucial to build economy with smaller carbon footprint. Diversification of production not producers will strengthen the value chains and sustain enterprises. Clear terminology will aid communication through downscaling the messages from global scientific literature array and upscaling information and data for individual networks.

Recommendations and further research for the development of a biorefinery prototype

- Integrate a national decision-making support tool based on bioeconomy research data, economic and technological analysis in the development of the next national bioeconomy strategy.
- Establish national guidelines for the exploitation of aquatic bioresources for energy generation.
- Define possible support mechanisms and the scope for expanding bioresource processing based on scientific study of bioresource availability and technological yield.
- Find out how and whether it is feasible to develop bioeconomy goods through social entrepreneurship, as well as operational and financing methods needed.
- Calculate the best site for the aquatic biomass biorefinery using mathematical modelling and geographical analysis, including an evaluation of the level of civil protection.
- Define possible future marine and inland uses of aquatic bioresources through cross-sector and academic cooperation.
- Increase the disciplines of science engaged in the research of aquatic bioresources and promote how to cope with socio-economic problems linked to blue industries.

CONCLUSIONS

Published data on the most prevalent seafood species shows that a relatively small number of species dominate worldwide catches and aquaculture. Capture fisheries include 14 finfish, 8 crustaceans, 7 mollusk species, and 6 other aquatic animal species of importance. A higher number of species are grown in aquaculture, which is split into six groups. The top 15 species in inland and marine finfish aquaculture account for more than 75% of total biomass. Crustacean, mollusk, and macroalgae aquaculture account for more than 80% of total biomass in each category. In key aquaculture regions the main species have already been defined and significant changes in species and volume are not expected in near future either. However, there are opportunities to grow these species in other regions in suitable artificial or natural water bodies. In the context of natural catch in the Republic of Latvia, the main sea fish species are herring and sprat, and likewise significant changes in the catch of these species are not expected under favorable conditions, nor is a significant increase of other fish species is expected. Which means that in seafood processing industry it is necessary to promote more complete processing of by-products in higher value-added products. If the quality and availability of the raw materials remains unchanged, then it is the efficiency of processing technologies and the quality of processing that determine the purity, value, and industry of secondary products.

Like terrestrial resources, aquatic bioresources, marine and inland aquatic by-products are already being processed into value-added intermediates and end products, and fuel, or energy, using a wide range of commercially approved traditional and developing innovative environmentally friendly technologies. The suitability and appropriateness of technologies depends on the type of feedstock and regardless of which treatment methodology is used, it is important to monitor the processes and apply analytical techniques where possible, at the same time ensure biological activity of target products and prevent degradation. Aquatic biomass processing supports a sustainable approach, the use of low-toxic chemicals, biological processes, and the use of renewable energy resources, providing the consumer with a product that is safe to use and of good quality. Theoretical assessment of the processing suitability of local aquatic bioresources fish waste, macroalgae, reed shows how these resources have reasonable potential as feedstock to produce bioproducts and energy by different technological approaches. However, it is important to ensure sustainable use of resources in the long term – define feedstock availability and condition, technological-economic justification for the specific situation, product market and retail price. Biorefinery, a processing plant where green principles and bioeconomy concepts are applied, will facilitate the use of financial, technological and land resources. Scientific literature indicates that the biological fraction of aquatic bioresources by-products can be processed using anaerobic digestion and shows good results. When processing secondary residues into bioenergy, the cascade principle is applied, and the added value chain is extended. As part of the Thesis, aspects of processing three types of aquatic waste biomass feedstocks, possible technologies and products were studied, results showed that theoretical aquatic by-product biorefinery could process three different feedstocks using technologically uncomplicated extraction methods, but further multidisciplinary research and cross-sectoral cooperation is needed to provide a circular economy of aquatic natural resources with little added value.

The results of round goby waste anaerobic digestion show that biogas production at low temperature (23 °C) takes twice the time, thus prolonging the hydraulic retention time, which means increased size of biodigester to produce same volume of biogas. Also, 23% decrease in total produced biomethane was noticed. The best available technique for successful treatment is biomethane production in co-digestion regime with high carbon substrate, e.g., garden waste. Additional experimental data from the batch tests and continuous systems, and parallel, modelling of fish waste treatment process will assist reaching overall sustainability of fish waste digestion and favourable digester size in costal rural areas. Undeniably technologic and economic analysis and supply chain strength should be assessed when optimizing energetic waste treatment options of seafood processing industry.

A review of the literature on green fish oil extraction methods shows that supercritical fluid extraction with carbon dioxide is an excellent way to obtain high-yield, high-purity fish oil at relatively low temperatures that does not contain polar compounds, but the equipment has increased production start-up and operating costs compared to traditional methods. A by-product of supercritical extraction is partially hydrolysed fish protein. The results of the laboratory research of the round goby, found in the coastal waters of Latvia, show that the species is not promising for use in fish oil extraction, because the oil concentration in the fish biomass is only 1%, but the total protein concentration is 16%, therefore, in order to fully use the biomass, it is preferable to process it into hydrolysed protein, which can be used to produce food additives, animal feed. Liquid residues of hydrolysate production can be digested into biogas and the solid residues processed into fertilizer.

Literature analysis indicates that Easter Baltic macroalgae species biomass can be processed in variety of products – polysaccharides, proteins, lipids, pigments, minerals using novel more environmentally friendly extraction methods, and macroalgae growth conditions, availability, quality, and quantity determine whether it is possible to scale-up extraction. Innovative multi-phase processing system analysis and scale-up should be assessed. Limited technologies, unpredictable amounts and quality of seaweed biomass, scalability still could be serious problem limiting production of extracts.

Multi-criteria analysis of reed biomass management options shows that production of value-added products is being implemented. From environmental and economic point of view the highest value products are construction materials insulation panels and roofing which have been harvested in winter. Literature suggests that manufacturing of ethanol on a small scale from reed could be possible using hot water sodium carbonate pre-treatment and semi-simultaneous saccharification and fermentation. Fibre residues from ethanol production are recommended to be used for pyrolysis fuel production. Resource availability is also important factor to consider.

Feasibility analysis of low-temperature biogas reactor with solar panel support as a management tool for household-to-small business biodegradable waste was performed. Literature confirms solar assistance to biogas increases production of biogas, efficiency of production, costs and decreases toxicity of digestate. There is socio-economical value of technology in two contexts – a renewable technology reduces waste and produces energy and serves as bottom-up integrator of renewable energy. Investigation showed that multilocality of biogas must be taken in consideration when the policy of the renewable energy sector is developed, particularly in rural areas. Implementation of a functioning system requires additional research for small-scale renewable energy hybrid systems – system modelling,

techno-economic analysis, identification of specific technical parameters of the workable system in precise location, defining the boundaries of the hybrid system.

Even when researching the resources of a single nation or region, the issue of the use and processing of water bioresources is too large and complex to be handled in a single project or PhD thesis. The industry covers a variety of geographic areas and variable types. The development of the doctoral thesis demonstrates that, as in other areas of science, it was critical to conduct a feasibility analysis of a substantial body of literature and identify the most crucial research objectives to make the best possible analytical contribution and produce results that could be applied to scientific inquiry. The research covered in the work directly and strongly relates to the aquatic environment's marketed components, such as aquatic biomass resources, their processing technologies, and available consumables. A part of the blue economy, which is a much bigger and more complex system is the blue bioeconomy. On a larger scale, these industries are in various phases of growth, therefore even relatively straightforward research in the form of scientific studies or other initiatives is crucial to the development of the blue economy.

The vocabulary has become more precise when discussing the blue economy. The new vocabulary used in scientific journals can help developed countries better comprehend the maritime sector conditions of less developed countries and help them have discussions about how to support their sustainability initiatives and protect natural resources. The use of terminology in research is recommended since it will benefit both countries that launch the commercialization of research-based products as well as smaller, less developed pelagic fisheries. In both science and politics, achieving the long-term strategic goals of sustainability and nature preservation necessitates making choices today and taking steps tomorrow to guarantee that there will be resources and a functioning society.

It should be stated that the growth in publications in the fields of the marine economy and marine biotechnology, as well as the bioeconomy, indicates that things are now moving in the proper path. In the EU, the number of projects is steady, there are more interested parties, and the scientific and project call themes are becoming more specialized. Successful collaboration and synergy have also increased, because of developments in the other sectors. The requirements for projects that must be met to qualify for funding have been more apparent because of project feedback. It's also essential to develop action programs/development strategies in particular sub-sectors and have clearly defined national government goals for the blue bioeconomy business to advance. It calls for thorough understanding of and keen interest in particular crucial subjects in the growth of the aquatic bioresources technology industry from universities and research institutions. Also, it is crucial to ensure international cooperation to undertake research, train young scientists, develop technologies with the potential for commercialization, and create new beneficial goods and services.

The author's research examined the use of Latvian water bioresources in the creation of products using various processing techniques. It also examined the resource composition in resources that have not previously been researched. The thesis compiles information that is currently accessible regarding the primary categories and makeup of resources and residues, processing techniques, and products that can be obtained, as well as the processing of secondary biomass residues.

Based on scientific data, a conceptual review of the integration of three distinct resources (fish, algae, and marcophytes) was performed. Because the technical readiness of these methods for extracting products from fish biomass varies, experiments in extraction using small-scale bioreactors are required to gather data about the factors that need to be optimized in the extraction process, costs, etc., to develop products on a larger scale and safeguard cross-over TRL 6.

Whenever resource availability varies owing to natural factors or anthropogenic impacts, research into the processing of aquatic bioresources, is crucial to ensure the viability of various future scenarios in the context of biomass management. In developed countries, the technical level for using macrospecies is currently very high, but there are chances to build integrated multi-trophic aquaculture, boost processing efficiency, and increase consumer acceptability of the products. Biotechnology offers more opportunities to produce specialized products since it allows for the use of state of art modern techniques for studying microorganisms and the ability to develop products in bioreactors that are tailored to specific needs. Although these microbial technologies typically do not operate on an industrial scale, funding and successful operation of such initiatives are nonetheless achievable.

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PUBLICATIONS ARISING FROM THESIS

Paper I: Ivanovs, K., Spalviņš, K., Blumberga, D. Approach for Modelling Anaerobic Digestion Processes of Fish Waste. Energy Procedia, 2018, Vol.147, 390.-396.lpp. ISSN 1876-6102.

Paper II: Gruduls, A., Bāliņa, K., Ivanovs, K., Romagnoli, F. Low Temperature BMP Tests Using Fish Waste from Invasive Round Goby of the Baltic Sea. Agronomy Research, 2018, 16 (2), 398.-409.lpp.

Paper III: Ivanovs, K., Blumberga, D. Extraction of Fish Oil Using Green Extraction Methods: a Short Review. Energy Procedia, 2017, Vol.128, 477.-483.lpp.

Paper IV: Melvere, M., Ivanovs, K., Pubule, J., Blumberga, D. Use of Round Goby (Neogobius Melanostomus) Processing Waste in Bioeconomy. Energy Procedia, 2017, Vol.128, 484.-490.lpp. ISSN 1876-6102.

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APPROACH FOR MODELLING ANAEROBIC DIGESTION PROCESSES OF FISH WASTE

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Approach for modelling anaerobic digestion processes of fish waste

Kaspars Ivanovs*, Kriss Spalvins, Dagnija Blumberga

Institute of Energy Systems and Environment, Riga Technical University, Azenes iela 12/1, Riga, LV-1048, Latvia

Abstract

This paper proposes to identify matters to be considered when modelling anaerobic digestion processes of fish waste. The design of the model takes into account the specific features of fish waste as substrate. Previous research shows that the anaerobic digestion and co-digestion of fish waste has significant potential for biomethane production – from 0.2 up to 0.9 CH_4 m^3/kg VS added. Generally, anaerobic digestion processes are modelled in two ways – using both micro-organism growth kinetics and chemical reactions in the system. The production of biogas using anaerobic digestion involves the use of different substrates with different properties. However, waste from fish processing poses distinct technological problems because it releases high levels of ammonia when digested. This can later reduce or inhibit the digestion of substrates.

Keywords: anaerobic digestion; fish waste; biomethane potential; modelling; biogas

1. Introduction

The sustainable management of fish waste generated from the seafood processing is a worldwide problem. Fins, scales, viscera, heads and carcasses are parts of the fish which are wasted during processing. Global fish production was ~167 million tons in live weight in 2014. Of this 87.5 % were intended for human consumption and the remaining 12.5 % for fish oil and meal production. Fish from both the sea and from inland accounts for about 55 % of the total world fish production, aquaculture accounts for the remaining 45 % [1]. About 70 % of fish are

* Corresponding author.
E-mail address: kaspars.ivanovs@rtu.lv

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processed before being sold. 20 % to 80 % of this total is fish waste, depending on the type of processing and the species processed [2]. This waste has significant potential for the production of biogas through anaerobic digestion.

Anaerobic digestion is a complicated, but naturally occurring biochemical process in which anaerobic bacteria breaks down organic matter in the absence of oxygen. Biogas and digested substrate (digestate) are the products of anaerobic digestion. The biogas usually contains 55–65 % CH_4, 35–45 % CO_2, 0–3 % N, 0–1 % H_2, and 0–1 % H_2S [3]. The sustainable production of biogas is also one of the ways to reduce the use of fossil fuels and by that reduce carbon dioxide emissions. For years, this process has been applied to municipal and agricultural waste streams to reduce environmental impact. The anaerobic digestion process depends on a specific microorganism consortium to break down biomass. Anaerobic digestion consists of four main stages: hydrolysis, acidogenesis, acetogenesis, methanogenesis. The biogasification process is highly dependent on environmental and/or ambient conditions such as temperature, pH, C/N ratio, C/P ratio, particle size, inhibitors, and type of substrate [4].

The emergence in the 70's, of mathematical models of anaerobic digestion were the result of a need for increased efficiencies in anaerobic systems. Scientific models in anaerobic digestion processes have thus been developing for almost 40 years. Generally, anaerobic digestion processes are modeled in two ways: by the use of microorganism growth kinetics to predict system behavior and by the use of chemical reactions in the system. The complexity of the process means that each model developed is designed for a specific purpose. As a result, there is currently a range of models that vary according to their intended use. Among them are relatively simple models designed to calculate the maximum biogas amount that is theoretically obtained in the anaerobic digestion process. Other models estimate the amount of biogas production taking into consideration the degradation rate of different substrates and their components. Many of the models are limited and do not show the dynamic nature of macromolecular degradation. The most complex of these is the growth of kinetics of microorganisms – activity, death rate and washout of microorganisms through different mechanisms. The developed models are designed for a specific substrate or a small number of substrates with very similar compositions and therefore are not suitable for other types of substrates [5]. The aim of this paper is to present a brief approach for the anaerobic digestion of fish waste taking into account the specificity of substrate composition.

2. Fish waste as substrate in anaerobic digestion

The composition of solid and liquid fish processing waste depends on the composition of the fish species used, which in turn depends on the sex, feeding habits, season and health of fish. Fish waste is a mixture of solid and liquid wastes. The solid matter consists of the fish tissues and the bones; the liquid phase consists of blood-water and stick-water, which are high in both proteins and oils. One of the major problems that limit the use of this kind of biological waste is its variable nature. These wastes contain protein (up to 60 %), fat (up to 20 %) and minerals (calcium and hydroxyapatite from bones and scales). Palmitic acid, oleic acid, and monosaturated acids are also abundant in fish waste streams (22 %) [6]. At the beginning of 2018, literature on the anaerobic digestion of fish and fish waste was still rather sparse – about 20 research papers on this issue. Existing studies show that digestion and co-digestion of fish waste both have considerable potential for producing biomethane. Studies on the anaerobic digestion of fish waste show a biomethane production potential of 0.2 to 0.9 CH_4 m^3/kg VS added. Fish waste is also used in anaerobic digestion experiments as a substrate in pure form and as silage, as well as in co-digestion with cow manure, sisal pulp, Jerusalem artichoke, water hyacinth, and waste from strawberry processing (Table 1).

The production of biogas using anaerobic digestion involves the use of different substrates with different properties, however, waste from fish processing poses a distinct technological problem. Fish waste releases high levels of ammonia when digested, which inhibits the digestion of substrates [7]. High concentrations of ammonia can result in the accumulation of VFAs (acetic acid as the main type in the batch tests). And depending on reactor type and organic loading rate, this can inhibit the process especially if the substrate is very high in oils [8]. Co-digestion of two different substrates is a possible technological solution or at least one that has a mitigating effect on this problem. In current practice, co-digestion is used, where two different substrates (co-substrates) are combined in the reactor to increase the organic matter content and thus achieve higher rates of biogas production. The composition and yield of biogas depend on the raw materials and co-substrate type, pretreatment methods used, etc. Substrates with high levels of lipid and easily degradable carbohydrates show higher methane production potential, while lignocellulosic materials show lower methane concentrations in biogas. Co-digestion also reduces or

diffuses the content of heavy metals in the digestate and generally improves the composition of the digestate to ensure that it can be used without treatment as a biofertilizer.

To avoid process failures, best practices require pre-treatment of raw materials. This would include e.g. concentration of stick-water to increase solid content, and the hydrolysis of fish material with high protein content. The application of pre-treatment methods improves the intensity of substrate degradation and thus increases the efficiency of the process. Chemical, thermal, mechanical or enzymatic processes can be used to accelerate the decomposition process, although this does not always result in an increase in the amount of biogas [9]. In our previous work, we tested the anaerobic digestion of round goby *Neogobius melanostomus* residues in both mesophilic and thermophilic conditions. The results obtained show considerable biomethane production potential [10] (Table 1). Further comprehensive research is needed on various factors in the anaerobic digestion of fish waste to further justify the use of fish as a potential substrate in biomethane production. One of best ways to co-digest fish waste is with agricultural waste. As this has been very little studied, experimental data are very limited. Agricultural waste streams have immense potential for energy production both by using dry residues in direct incineration and by using dry or wet residues in anaerobic digestion for biomethane production. The global production of agricultural residues from barley, bread, rice, soybean, sugar cane and wheat is estimated to a total of $3.7^{+1.3}_{-1.0}$ Pg dry matter yr^{-1} [11].

Table 1. Anaerobic digestion of fish waste.

Type of waste (Substrate)	Incubation time, days	BMP	Reference
Salmon heads	33	0.828 ± 0.15 CH_4 m^3/kg VS added	[12]
FW	36	F/M ratio 0.2 with a total maximum methane yield 0.165 CH4 m^3/kg VS added COD_{Mn}	[13]
FW	25	0.39 CH_4 m^3/kg VS added	[14]
Nile Perch waste	42	0.50–61 CH_4 m^3/kg VS added	[15]
FW	15	180 mL/kg of waste	[16]
Jellyfish *Aurelia aurita*	-	121.35 mL/g and 870.12 mL/g	[17]
Tuna, sardine, mackerel waste	67	0.47–0.59 g COD-CH4/g COD added	[18]
FW	67	0.53–0.554CH_4 m^3/kg VS added	[19]
FW	-	0.380–0.920 CH_4 m^3/kg VS added	[20]
Round goby waste	-	0.520–0.922 CH_4 m^3/kg VS added	[10]
Co-digestion of fish waste with other material			
Type substrate	BMP		Reference
FWS: JA	0.531 CH_4 m^3/kg VS added		[12]
1:1			
SE:FCIW	0.205 CH_4 m^3/kg VS added		[21]
94:6			
FW:SP 33:67	0.62 CH_4 m^3/kg VS added		[14]
FW: CM 1:1.2	1950 ml CH_4/kg of waste (biogas)		[16]
FW: WH 1:2	0.408 CH_4 m^3/kg VS added		[22]
FW: BWS 20:80 (%, TS)	0.482 CH_4 m^3/kg VS added		[23]
CM:CI:FS 45:22:33	0.533 CH_4 m^3/kg VS added		[24]
FWS:CM2 16:86	0.400 CH_4 m^3/kg VS added		[25]

FW – fish waste; FWS – fish waste silage; CM – Cod meat; CI – cod intestine; WH – water hyacinth; SP – sisal pulp; CD – cow dung; SE – strawberry extraduate; JA – Jerusalem artichoke; FCIW – fish canning industry waste; CM2 – cow manure; BWS –bread waste silage

3. Modelling of the anaerobic digestion of fish waste

The need for the development of models was determined by the fact that anaerobic digestion is itself an intricate group of processes and there is no universal model for predicting/analyzing the anaerobic digestion of different substrates. The closest to a universal model is the International Water Association (IWA) developed "anaerobic digestion model number 1" (ADM-1). It was developed between 1997 and 2002. This model has been widely applied, modified and validated in simulating the digestion of various types of organic waste. The model includes several phases describing physiochemical and biochemical processes. ADM-1 consists of complex reaction kinetics and a large number of concurrent and sequential reactions, which are primarily classed as physicochemical or biochemical [5]. The complexity of such a model necessitates many input parameters. This ultimately results in a great number of stoichiometric and kinetic equations, for which precise identification and manipulation may prove challenging. Due to the fact that the models set out in ADM-1 and other kinetic models described in Kythreotou et al. [5] require a large amount of specialized data, they are not available to farmers and other interested parties with limited scientific knowledge of anaerobic digestion. In view of the growing interest in anaerobic digestion, it is necessary to increase the range of substrates and the number of biogas plants to use in waste recycling, renewable energy generation and reduction of greenhouse gas emissions.

This approach to the development of a model for the anaerobic digestion of fish waste has arisen from the fact that the fisheries sector in Latvia has a high energy consumption to produce one unit of product. This is because of the outdated equipment base and infrastructure used. Integrating biogas production with fish processing could increase production efficiency by, for example, using the heat from biogas combustion to dry wood chips and/or to heat the production premises, or by using combined heat and power to generate heat and electricity. Integration of biogas production by anaerobic digestion in the fisheries sector would also ensure greater buffering capacity in the regional energy sector. One of the ways to diversify renewable energy is by increasing the share of biomethane in the final consumption of renewable energy. In Latvia, biomethane production is limited to about 60 existing biogas plants, of which 83 % are agricultural biogas plants, 12 % municipal waste landfills and 5 % biogas plants for municipal wastewater and food waste. However, there are no biogas plants that produce biomethane as one of the main substrates using fish waste [11]. Our goal is to develop an anaerobic digestion model for fish waste to increase the efficiency of biomethane production and in that way integrate fish waste anaerobic digestion into the national economy. The development of the model involves modelling the biochemical and physical processes, incorporation of the experimental data, comparing results from the deterministic model and the empirical data, developing a prototype, and then validating the developed model based on the available empirical data.

Modelling the biochemical and physicochemical processes includes creating a mathematical model for the anaerobic digestion processes, defining the components of the system including microorganism groups, fisheries waste and the traditional agricultural substrates of high C/N ratio. After that validation and simulation of each model component, the analysis of pretreatment and other system operating factors (mixing, temperature, pH, etc.) are all needed. The next task is to test and evaluate anaerobic digestion processes in a single anaerobic digestion bioreactor system. After this, the defining the benchmarks for assessing the performance of a system is needed.

A very important part of developing a mathematical model is the collection of accurate data in different configurations or arrangements. This requires planning experiments and designing an experimental plan by analyzing and determining the relative importance of factors and parameters in order to reduce the number of further experiments to obtain reliable results. To obtain an empirical model, a laboratory for experiments to test various factors influencing the process in bioreactor system is required. Data from tests will be used to compare the deterministic model (theoretical model based on literature and assumptions) and to develop an empirical mode (based on experiments). The last step is building a prototype and validation of the model by performing simulations under different conditions. The simulation model will be validated against data containing different measurements of CH_4 yield and production, VS (volatile solids), TS (total solids), and NH-4 concentrations. The simulation of anaerobic digestion is not only very useful when predicting process results, it can also aid in avoiding (or at least reducing the possibility of) production failures. This, along with optimization (of the preceding processes), makes it possible to gain improved profitability.

Our vision of the model is described in the following paragraph. This model allows the biomethane potential of the substrate to be predicted – the production of CH_4 in the generated models will be simulated with a low

percentage of deviation. This model will handle the TS and VS concentrations accurately and it will improve the prediction of NH_4-N compared to other models. The model allows us also to predict whether ammonium induced inhibition is possible. The model will be capable of simulating conditions where the system crashes, and it will offer a better overview of what may occur in those circumstances. In some cases, the model will be based on estimates, which means output will be affected. The first developed semi-validated models will be later rearranged, and new co-substrates and equipment will be tested to improve the quality of the model. This model combined with the right measurement data could function as a powerful tool for estimating how an industrial-scale plant would function, as well for predicting biomethane production potential (BMP), immobilization, and optimizing the overall anaerobic fermentation process in bioreactors. Knowledge of how to utilize fish waste combined with carbon rich substrates to reach the best CH_4 yields will also benefit the national economy (notably fish processors) in the long term. Experimental data of anaerobic digestion of fish waste is limited, which means that the collection of additional data is required. Laboratory experiments will result in data on:

- The main composition of commercial fish species in the Baltic Sea, composition of the processing residues (TS, VS, proteins, lipids) and the impact of various pretreatment methods of fish waste on biomethane production potential;
- The biomethane production potential in thermophilic and mesophilic conditions;
- The effect of ensiling (as a storage method) on the biomethane production potential of fish waste;
- The main composition of the digestate (including heavy metals).

All of this can later be used to acquire further knowledge of process control, monitoring and development and testing of individual potential real-time process control solutions.

The first step in designing a model for the anaerobic digestion of fish waste is to analyze and evaluate the existing literature on theoretical models. The first stage is the mathematical description of relatively simple degradation reactions. The potential biogas yield from the anaerobic digestion of a particular type of substrate and the composition of the gas can be determined theoretically from the chemical composition of the used substrates. The production of methane depends on the nutrient content of mainly organic substrates (crude fiber, crude protein, crude protein, N-free extracts), which can be degraded to CH_4 and CO_2. Nutrient content determines the degradability and hence the methane yield that can be obtained by anaerobic digestion. There is a difference between these nutrients in specific methane yields – crude fat (850 l kg VS), crude protein (490 l kg VS) and carbohydrates (crude fiber and N-free extracts, 395 l kg VS) [26]. According to Buswell and Mueller [27], methane and carbon dioxide yields can be calculated within a range of error of about 5 % (Eq. (1)), assuming that the chemical composition of the organic matter used is known. Eq. (1) does not take into account microbial metabolism – the synthesis of cell biomass and energy for growth and nourishment. Accordingly Eq. (1), the methane fraction of fully degraded glucose is 50 % $C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$.

$$C_aH_bO_c + (a - \frac{b}{4} - \frac{c}{2})H_2O \rightarrow (\frac{a}{2} + \frac{b}{8} + \frac{c}{4})CH_4 + (\frac{a}{2} + \frac{b}{8} + \frac{c}{4})CO_2 \quad (1)$$

Known organic matter does not consist solely of carbon, hydrogen and oxygen. Twenty-five years after Buswell and Mueller, Boyle [28] presented a modified relation of Eq. (1), which included nitrogen and sulphur in the composition of organic matter. This allowed the calculation of the ammonia and hydrogen sulphide fraction in the produced biogas, which should be evaluated by ratio, Eq. (2):

$$C_aH_bO_cN_dS_e + (a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2})H_2O \rightarrow (\frac{a}{2} + \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4})CH_4 + (\frac{a}{2} + \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4})CO_2 + dNH_3 + eH_2S \quad (2)$$

Amon et al. [29] offers a model that was developed by carrying out a multifunctional analysis of full regression models, which assessed methane yield from the composition of substrates of energy crops in mono-fermentation via regression models. Basically, it considers the impact of the content of crude fiber, protein, fat, N-free extracts on the methane formation with the following equation:

$$MEV = x_1 \cdot XP + x_2 \cdot XL + x_3 \cdot XF + x_4 \cdot XX \quad (3)$$

where

MEV	methane energy value in $1_N CH_4$/kg VS;
XP	crude protein content, dry matter, %;
XL	crude fat content, dry matter, %;
XF	crude fiber content, dry matter, %;
XX	N-free extracts content, dry matter, %;
x_1, x_2, x_3, x_4	coefficients of regression that will be determined through the batch experiments [29].

The next stage in the development of the model is to analyze the anaerobic hydrolysis kinetics, taking into account the growth of microorganisms, substrate degradation and product formation. The process set can be divided into continuous and discontinuous, depending on the supply of substrate. In continuous processes, the substrate continuously flows and exits from the system, resulting in a process with constant substrate flow and gas production (equilibrium). Therefore, the growth requirements of microorganisms over time are unchanged. The process of molecular degradation is controlled by bacterial growth kinetics and to a large extent depends on the growth medium. Consequently, gas production and substrate degradation change depending on retention time during which growth requirements for microorganisms change permanently. The substrate balance of a continuous or a discontinuous process can be expressed as:

$$\frac{dS}{dt} = D \cdot S_0 - D \cdot S + (\frac{dS}{dt})_r \quad (4)$$

where

D	dilution rate (flow per reactor volume, in 1/h);
S	substrate concentration;
S_0	initial substrate concentration;
$D \cdot S_0 – D \cdot S + (dS/dt)_r$	input output reaction;
$(dS/dt)_r$	reaction rate;
(dS/dt)	accumulation rate (change of substrate concentration over change in time) [5].

4. Conclusions

This paper briefly outlined the initial stage of modelling the anaerobic digestion of fish waste taking into account the specificity of substrate composition. In view of the complexity of mathematical equations for the development of an anaerobic digestion model for fish, there is a need for additional experimental data, both from batch tests and continuous systems. Further work should also include a comprehensive review of anaerobic digestion and co-digestion of fish waste. This would be essential for planning experiments for data acquisition. The information obtained will help define the model's limits and its values.

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LOW TEMPERATURE BMP TESTS USING FISH WASTE FROM INVASIVE ROUND GOBY OF THE BALTIC SEA

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Low temperature BMP tests using fish waste from invasive Round goby of the Baltic Sea

A. Gruduls*, K. Balina, K. Ivanovs and F. Romagnoli

[1]Riga Technical University, Institute of Energy Systems and Environment, Azenes street 12-K1, LV-1048 Riga, Latvia
*Correspondence: Arturs.Gruduls@rtu.lv

Abstract. Round goby *(Neogobius melanostomus*) is an invasive fish species in the Baltic Sea. While meat can be used for human consumption, fish processing residues are considered as a waste. Within circular economy and bio-economy perspectives fish waste could be used as a valuable feedstock for biogas production. However, the research is mostly focused on evaluating biogas yield at mesophilic conditions (i.e. 37 °C). In this study the impact of low temperature on Biochemical Methane Potential (BMP) tests has been investigated. Round goby's processing leftovers - heads, intestines and skin/bone mixture were tested in codigestion with sewage sludge. Anaerobic digestion (AD) was carried out in 100 mL batch tests at low temperature 23 °C and 37 °C conditions, over an incubation period of 31 days. The results show that AD at low temperature occurs twice as slowly as under 37 °C conditions. However, after 31 days the BMP values for 23 °C samples were only 2% lower than for high temperature samples. Heads and skins showed similar BMP values reaching on average 502 L CH_4 kg_{VS}^{-1} and 556 L CH_4 kg_{VS}^{-1} respectively. BMP for fish intestines was higher, reaching on average 870 L CH_4 kg_{VS}^{-1}. Average BMP for mixes of fish heads, skins, intestines and bones was 660 L CH_4 kg_{VS}^{-1}. Acquired BMPs were further compared with the theoretical BMPs from Buswell's formula. Research results suggests that anaerobic digestion of fish waste under low temperature conditions could be feasible as the process still efficiently occurs, in fact opening a new opportunity to explore the overall sustainability of technologies based on these conversion processes.

Key words: Biomethane, low temperature, fish waste, anaerobic digestion, Neogobius melanostomus.

INTRODUCTION

In last decades' the population of round goby (*Neogobius melanostomus*) has spread into the Baltic Sea. Coming from Caspian Sea, this fish in Latvian coastline has been firstly observed in 2004 and since then, the amount of it has increased significantly reaching 25 tons in the year 2013 and more than 700 tons in year 2017 (Riekstiņš, 2014; 2017). Currently in the nearshore waters of the Baltic Sea this is the second most caught fish species after the Baltic herring. Distribution area is still expanding and has become a huge problem regarding both environmental and economic aspects. This fish species has become invasive in Latvia due to easy adaption to surrounding environment (Charlebois et al., 2001). Since the amount of fish has been growing, it can represent a valuable economic opportunity.

Physiology of round goby allows using only 40% of it as a meat for food, creating large amounts of waste. Waste biomass includes parts like skin, head, bones, fins and intestines (Eiroa et al., 2012). In recent years potential use of this fish waste has become a popular research topic. Melvere et al. (2017) describe many options for use of round goby's processing waste in bioeconomy. The author suggests using it as raw material to produce a wide range of products including also high value-added end products like enzymes, proteins and fish oil. Salam et al. (2009) claims that fish waste can also be successfully used for energy production producing biogas in anaerobic fermentation processes. However the high content of ammonia nitrogen might negatively affect fermentation processes thus one of the best ways for fish waste biomethanation is co-digestion (Tomczak-Wandzel et al., 2013).

Anaerobic fermentation has been used for waste treatment and biogas recovery from many types of organic waste. Its numerous advantages, such as the recovery of a renewable energy, waste volume and odour reduction are well documented (Gunaseelan, 1997; Wu et al., 2009). Anaerobic treatment of fish waste not only reduces unpleasant odour but also gives the opportunity to regain some energy used for the production processes. However, until recently, research has mainly been focused on anaerobic digestion (AD) at mesophilic (25–45 °C) or thermophilic (45–65 °C) temperatures. It is believed that a lower temperature in the psychrophilic range (< 25 °C) reduces microbial activity and in fact is lowering the biogas yield (Connaughton et al., 2006; Saady & Massé, 2013). One of the main advantages of psychrophilic temperatures would be the lower energy input required for heating the reactor, consequently reducing the overall operating cost (Smith et al., 2013). The most recent results on microbiological activity in psychrophilic conditions show that lower temperatures require a longer fermentation time and lead to higher methane content and lower accumulation of volatile fatty acids compared to mesophilic conditions, although still keeping a similar cumulative biomethane yield in both conditions (Wei & Guo, 2018).

In this study experiments on biogas production at mesophilic and lower temperatures were carried out and the data have been compared. The aim of this study was to assess the process performance of two BMP test setups inoculated with the same sewage sludge for treatment of fish waste. One setup of 100 mL bioreactors was operated at 37 °C, while the second was maintained at room temperature 21–23 °C. Comparative investigations of biomethane production in both temperature ranges would allow evaluation of the overall economic feasibility. In fact, it would be a key aspect to assess the potential benefits in operational costs in terms of lower energy input required for heating, reduction of the amount of waste in fish processing plants, energy recovery capability within the production processes, although bigger digester volume may be necessary.

MATERIALS AND METHODS

Substrate (collection, pre-treatment, and storage)

The *Neogobius melanostomus* used within the batch tests for the BMP evaluation were freshly caught on Baltic sea costal area in August 2015 (biomass 2) and April 2017 (biomass 1), near the city of Liepaja, West Latvia. Whole fish samples were transported within plastic bags to the Biosystem Laboratory at the Riga Technical University, separated in smaller portions and then frozen at –18 °C. Prior experiments biomass was

defrosted at room temperature. Then fish were skinned, gutted, deboned and beheaded. Processing waste products – heads, intestines and skin/bone mixture were used for further BMP testing. Each fish waste fraction was separately homogenized using 1,500 W kitchen blender and given to total solids (TS) and volatile solids (VS) content analyses. Homogenized samples were frozen again at –18 °C, and defrosted a day before the start of BMP tests.

TS and VS values were determined prior to the experiments based on ISO Standards (ISO 14780:2017, ISO 18134–2:2017, ISO 18134–3:2015). TS were obtained by placing a sample into an oven for 18 hours at 105 °C, and then the dry sample was finely ground and placed into an oven for 5 hours at 105 °C. VS were obtained by placing 5g of totally dry sample into an oven for 11 hours with a heating step 50 °C h^{-1} and then kept at 550 °C for 3 hours to be able to obtain the VS content as a fraction of TS (% of TS). The results are presented in Table 1.

Table 1. TS and VS content of inoculum and fish waste fractions

Substrate	TS, %	VS, % of TS
Inoculum 1	2.0	60.5
Inoculum 2	1.9	60.5
Inoculum 3	1.9	60.5
Heads[1]	20.5	76.5
Skin/bone mix[1]	22.2	75.3
Intestines[1]	36.7	82.6
Heads[2]	19.8	76.5
Skin/bone mix[2]	19.4	75.3
Intestines[2]	30.1	82.6

Inoculums 1, 2, 3 – inoculums for experiment 1, 2 and 3; [1] – biomass 1; [2] – biomass 2.

Inoculum

Sewage sludge was collected from local waste water treatment plant 'Daugavgriva' (Riga district, Latvia) directly from biogas bioreactors. Prior to the BMP experiments, the inoculum was incubated for 6 days at 37 °C, with regular degassing. Inoculum was always evaluated for TS and VS content using ISO standards (ISO 14780:2017, ISO 18134–2:2017, ISO 18134–3:2015, ISO 18122:2015).

BMP test method

BMP tests were used to define the amount of methane produced per kilogram of VS, for an inoculum to substrate ratio (ISR) equal to 3 based on a TS basis. Generally, BMP measuring methods are based on liquid displacement or the displacement of a syringe piston. An alkaline solution for cleaning the biogas (by absorbing the CO_2 fraction) is added in both methods. The method is a well-known approach, but still lacking true standardization (Esposito et al., 2012; Edward et al., 2015). A pH range from 6.5 to 8.2 (Ağdağ & Sponza, 2005; Chandra et al., 2012; Esposito et al., 2012) is optimal for most anaerobic bacteria, including methanogens. Therefore, an alkaline compound is normally added within the solution as a buffer capacity (i.e. sodium hydroxide, sodium (bi)carbonate or sodium sulphide) (Chynoweth et al., 2000), in our case a 0.7M $NaHCO_3$ solution was specifically prepared.

BMP is a sensitive method, influenced by the conditions for the anaerobic bacteria to grow. In this light, the analysis of the results can be difficult due to the amount of potentially influential factors, resulting in likely possible errors and/or inaccuracies (Angelidaki & Sanders, 2004, Wellinger et al., 2013). Moreover, sometimes the same substrates don't show the same BMPs based on the tests' conditions (Del Borghi et al., 1999).

Experimental set-up

BMP tests were conducted in a batch mode using 100 mL crimp neck ND20 vials with a working volume of 50 mL. Each bottle was filled with 30 mL of distilled water, 20 mL of inoculum and 1mL of 0.7M $NaHCO_3$ buffer basal solution to maintain neutral the pH. Different amount (fresh weight) of different fish waste fraction was added to specific samples based on TS content and to maintain ISR around 3. Additionally, reference samples (blanks) containing only inoculum were prepared both for high and low temperature conditions to account for the methane production solely from the fish waste biodegradation. Sample headspace was flushed with N_2 for 30 seconds at flow rate around 2 L min^{-1} before sealing them with butyl rubber stoppers and aluminium crimps. The tests were carried out in dark conditions at a mesophilic temperature (37 °C) in the EcoCell LSIS-B2V / EC 111 incubator and at 23 °C, and lasted for 31 days. The batches were manually shaken one time per day on average. All batch tests were prepared in triplicates.

In total, three experiments were performed. In first experiment fish waste from year 2017 (biomass 1) was used. Tested samples contained heads, skin/bone mixture and intestines. For second and third experiment fish waste from year 2015 (biomass 2) was used. These samples also contained heads, skin/bone mixture, intestines and additional biomass mixes (consisting of all waste fractions in different shares). First mix (M1) contained all waste fractions in equal share based on TS. Second mix (M2) contained all waste fractions in equal share based on wet weight. Third mix (M3) contained all waste fractions in wet weight ratios: 2 parts heads, 2 parts skin/bone mixture, 1part intestines (based on practical fish processing approach when intestines make up only one fifth of total waste amount). Experiments were performed with one-month time shift between them, thus also having slightly different inoculum for each test setup. In total 90 samples were analysed for 6 different feedstock's and two AD temperature conditions.

A volumetric measuring method was used by measuring the biomethane amount through the displacement of a 20 mL syringe piston connected to a batch bottle. For triplicates three best syringes were selected (with lowest friction) and slightly modified (cutting off excess piston rubber to minimize friction). Each syringe was dedicated to specific triplicate in consistent order, thus giving opportunity to see if piston friction changes and affects measurements. To determine the methane concentration without the CO_2 fraction, 5 mL of 3M NaOH alkaline solution was filled into the measuring syringes before each measurement. For extra confidence some of measured samples periodically were left overnight in closed syringes to see if all CO_2 has been absorbed during measurement.

Theoretical BMP according to Buswell's formula

Depending on the type of biomass, the assessment of BMP can eventually require time of up to 90 days (Hansen et al., 2004; Angelidaki et al., 2009; Kafle & Kim, 2013). For a more rapid estimation, a theoretical biomethane potential (BMP_{theo}) can be used from the Buswell equation (Allen et al., 2013) – see formula 1. Once the biomass' chemical compositions of C, H, O are known, it is possible to calculate the BMP_{theo} (Angelidaki & Sanders, 2004) and the correspondent CH_4 fraction as BMP_{theo}.

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 \qquad (1)$$

where n – carbon atoms in biomass; a – hydrogen atoms in biomass; b – oxygen atoms in biomass.

The methane yield (BMP_{theo}) from the Buswell's equation can be recalculated with a reference to the unit of gram (i.e. g-VS) in standard condition (i.e. STP) (Raposo et al., 2011), see Formula 2.

$$BMP_{theo,yield} = \frac{\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right) \cdot 22.4}{12n + a + 16b} \cdot \left(STP\frac{lCH_4}{g - VS}\right) \qquad (2)$$

where n – carbon atoms in biomass; a – hydrogen atoms in biomass; b – oxygen atoms in biomass.

Experimental yields are usually lower but knowing the theoretical yield value allows to calculate the efficiency of digestion.

Chemical composition of fish waste fractions was analysed by a Latvian State Institute of Wood Chemistry. Results are presented in Table 2.

RESULTS AND DISCUSSION

Inoculum and substrate characterization

TS and VS content for all three inocula were similar, however, slightly different methanogenic activity was observed referring to the methane volume produced from the blanks (data not shown) and the total accumulated methane amount from samples. Sludge was most active in the second experiment and especially at high temperature conditions. However, that did not have a relevant impact on the final BMP values acquired from batch tests.

Table 2. Chemical composition of different fish waste fractions (for biomass 2)

Substrate	% of TS					
	Carbon (C)	Hydrogen (H)	Oxygen (O)	Nitrogen (N)	Sulphur (S)	Ash
Heads	37.82	4.72	22.51	11.14	0.29	23.51
Skin/bone mix	40.30	5.06	17.37	12.16	0.35	24.75
Intestines	57.17	6.78	12.12	6.17	0.34	17.43
M1	43.55	5.44	19.32	9.53	0.32	21.85
M2	46.89	5.83	16.09	9.64	0.33	21.22
M3	41.51	5.51	20.62	9.77	0.32	22.27

TS and VS content for fish heads and skin/bone mixture (furthermore also referred as 'skins') was similar both for the biomass 1 and biomass 2 (Table 1). TS were around 20% and VS were 75–76% of TS. Although homogenized intestine samples seemed more liquid, they showed the highest TS content varying between 36% for biomass 1 and 30% for biomass 2. This could be explained with high lipid content that is not lost during TS drying operation.

Furthermore, this high lipid concentration is affecting BMP test results, showing the highest methane yield for samples with intestines both for high and low temperature conditions. Similar effect was observed by Nges et al., 2012. VS content for round goby's intestines was similar for both biomass sources reaching 82.6% of TS.

Biochemical methane potential

BMP testing was done with slightly modified 20 mL rubber piston syringes containing 5 mL of 3M NaOH solution for CO_2 absorption. Piston's friction was constantly monitored and no significant change was detected during all three experiments. Periodically, accumulated gas samples were left overnight in closed syringes to check NaOH solution's CO_2 absorption efficiency during slow biogas collection. Fortunately, no visible change in gas volume was ever detected. Consequently, the measured biogas values pertain to the methane content produced.

Regarding to **total accumulated** biomethane volume per test vial, significant difference can be seen between low temperature and high temperature batch samples. Overall, for the samples that were incubated at 23 °C an average 23% reduction can be observed in total accumulated biomethane volumes (Fig. 1, A). This matches with trends reported in literature stating that lowering temperature by 10 °C biogas production slows down approximately two times (Seadi et al., 2008; Zhu & Kumar, 2014).

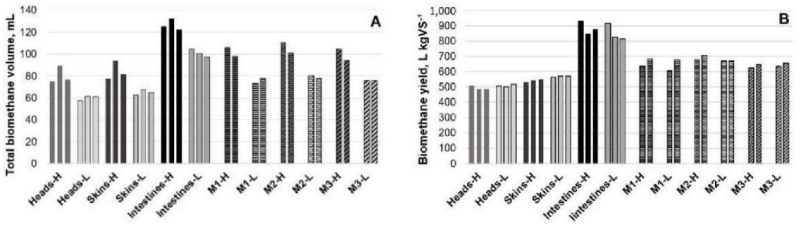

Figure 1. Total accumulated biomethane amount (A) and BMP per 1 kg VS (B) during experiments 1, 2, and 3. Index –H stands for 37 °C, –L stands for 23 °C.

After calculating the net biomethane volumes (by subtracting blank sample volumes from the total accumulated biomethane volumes), the difference between low and high temperature samples occurs to be very low. Furthermore, after calculating the final BMP values (always based on the net biomethane volumes) per kg of VS, the overall average BMP results for low temperature samples are only 2% lower than for 37 °C (Fig. 1, B).

In total, the BMP difference per 1 kg of VS among the two sets of temperature conditions was only 2%. Nevertheless, it must be clarified that the overall difference in total accumulated biomethane amount is 23% (see Fig. 1, A). This result may be due to an extra 23% of total biomethane volume that was contributed by the sewage sludge inoculum at higher temperature. Methanogenic bacteria activity and growth is much lower at low incubation temperature conditions, thus resulting in a slower augmentation and decay (dead biomass methanation) of the microorganism consortium, thereby lowering the amounts of total produced biomethane. This should be taken into account when designing bioreactor for fish waste and sewage sludge co-digestion at low temperature conditions in terms of bigger digester's size. Nevertheless, results of this study suggest that lowered temperature does not have a strong impact on fish waste digestion efficiency and final BMP, however, it affects digestion kinetics.

During all three experiments the highest BMP values were obtained from batch samples containing fish intestines both for high and low temperature conditions (Fig. 1, B). Average biomethane yield from all three experiments at 37 °C was 887 L CH_4 $kgVS^{-1}$ and 853 L CH_4 $kgVS^{-1}$ at 23 °C. These high values are reached because of high lipid and protein content, especially in gonads and fish eggs that were present in Round Goby's abdomens. The theoretical BMP yield for lipids is about 1000 L CH_4 $kgVS^{-1}$, while the theoretical yield for protein is about 490 L CH_4 $kgVS^{-1}$ (Nges et al., 2012). BMP values of first experiment are higher than those of second and third, reaching 933 L CH_4 $kgVS^{-1}$ at 37 °C and 917 L CH_4 $kgVS^{-1}$ at 23 °C. In comparison, results from second and third experiment were only 850–878 L CH_4 $kgVS^{-1}$ for high and 816–826 L CH_4 $kgVS^{-1}$ for low temperature. Despite similar VS content (82.6%) of round goby's both biomasses this difference in results could be explained due to the fact that for first experiment used fish biomass was caught in spring season (April). In spring time fish are ready for new spawning season and have larger gonads and contain more mature fish eggs, thus increasing overall lipid and protein relative share in viscera.

These results are slightly higher than reported 500 L CH_4 $kgVS^{-1}$ for perch (*Perca fluviatilis*) intestines (Tomczak-Wandzel et al., 2013), however, this could be attributed to the fact that relative share of gonads in perch abdomen is much smaller (if present at all in different seasons).

The overall average BMPs acquired from three experiments for fish heads at high temperature and low temperature was 494 L CH_4 $kgVS^{-1}$ and 508 L CH_4 $kgVS^{-1}$ respectively. Skin and bone mix showed slightly higher results, therefore average BMP at 37 °C was 542 L CH_4 $kgVS^{-1}$ but at 23 °C was 570 L CH_4 $kgVS^{-1}$. It can be seen that at lower temperatures average BMP values are slightly higher than at 37 °C both for heads and skin/bone mixture. This could be explained due to the fact that for several high temperature samples after 20 days' biomethane production was delayed and a slight inhibition of methane production was observable, as blank reference samples on daily basis produced more gas than samples containing fish waste. This in fact resulted in negative daily net biomethane values, indicating the start of inhibition which is consequential after digestion of high organic content substrates and rapid VFA accumulation, as can be observed also during dairy product anaerobic digestion (Labatut et al., 2011). This also is in line with literature where it is suggested that AD under lower temperature conditions is more stable and less volatile fatty acids are accumulated

(Appels et al., 2008). However, no great change in pH was observed at the end of all experiments, only for few samples lowering from pH8 to pH 7.7.

Summary of BMP values acquired during this research for different fish waste samples can be seen in Table 3.

Table 3. Summary of estimated yields from Buswell's equation and experimental CH_4 yields

Substrate	BMP_{theo} (L CH_4 $kgVS^{-1}$)	BMP at 37 °C (L CH_4 $kgVS^{-1}$)	BMP at 23 °C (L CH_4 $kgVS^{-1}$)
Heads[1]	–	509.2 ± 29.5	506.3 ± 1.0
Skin/bone mix[1]	–	533.0 ± 17.8	565.4 ± 110.8
Intestines[1]	–	933.1 ± 60.9	916.9 ± 39.7
Heads[2]	625.0	485.4 ± 20.2	500.8 ± 14.9
Skin/bone mix[2]	728.9	544.9 ± 25.5	572.6 ± 26.3
Intestines[2]	895.7	849.8 ± 15.4	826.1 ± 26.0
M1[2]	719.4	639.1 ± 4.8	609.2 ± 11.6
M2[2]	791.8	677.6 ± 18.0	672.4 ± 11.0
M3[2]	769.0	626.3 ± 24.5	636.7 ± 2.5
Heads[3]	625.0	488.8 ± 18.6	519.6 ± 19.1
Skin/bone mix[3]	728.9	548.8 ± 24.4	572.2 ± 22.9
Intestines[3]	895.7	877.7 ± 41.8	816.3 ± 51.9
M1[3]	719.4	685.7 ± 17.4	676.5 ± 27.0
M2[3]	791.8	709.2 ± 37.5	668.6 ± 30.7
M3[3]	769.0	649.5 ± 10.3	657.6 ± 18.4

[1] – experiment 1 (biomass 1); [2] – experiment 2 (biomass 2); 3 – experiment 3 (biomass 2).

Three different fish waste fraction mixes were also prepared. First mix (M1) contained all waste fractions in equal share based on TS. Second mix (M2) contained all waste fractions in equal share based on wet weight. Third mix (M3) contained all waste fractions in wet weight ratios: 2 parts heads, 2 parts skin/bone mixture, 1part intestines (based on practical fish processing approach). M1 average BMP at 37 °C and 23 °C was 662 L CH_4 $kgVS^{-1}$ and 642 L CH_4 $kgVS^{-1}$ respectively. M2 average BMP at high temperature was 693 L CH_4 $kgVS^{-1}$ and 670 L CH_4 $kgVS^{-1}$ at low temperature. M3 average BMP at high temperature was 638 L CH_4 $kgVS^{-1}$ and 647 L CH_4 $kgVS^{-1}$ at 23 °C. No significant difference can be seen regarding to anaerobic digestion of these three mixes, thus any of these three compositions can be successfully used for biomethane production. As expected, average BMP was around 660 L CH_4 $kgVS^{-1}$, that is similar to mathematical average from heads, skins and intestines BMPs'. Other authors report similar results for Pacific saury, Nile perch, mackerel and cuttlefish wastes, ranging between 562–777 L CH_4 $kgVS^{-1}$ (Kassuwi et al., 2012; Kafle et al., 2013). BMP for cod meat and intestine mix was reported to be 503–533 L CH_4 $kgVS^{-1}$ after 14 days long incubation period (Almkvist, 2012; Shi, 2012). Regarding to 14-day period BMP from round goby's waste mix is slightly higher reaching approximately 640 L CH_4 $kgVS^{-1}$. In this light, it would be advisable to measure BMP for more extended time period, as far as it is reasonable, to obtain fully total BMP of biomass.

Dynamics of biomethane production

Cumulative curves and dynamics of biomethane production are shown in Fig. 2. For high temperature samples the main production was observed during the first 7–9 days, accounting for 95% of the total BMP. In turn for low temperature conditions main biomethane production was observed during first 14–16 days, accounting for 94% of the total BMP.

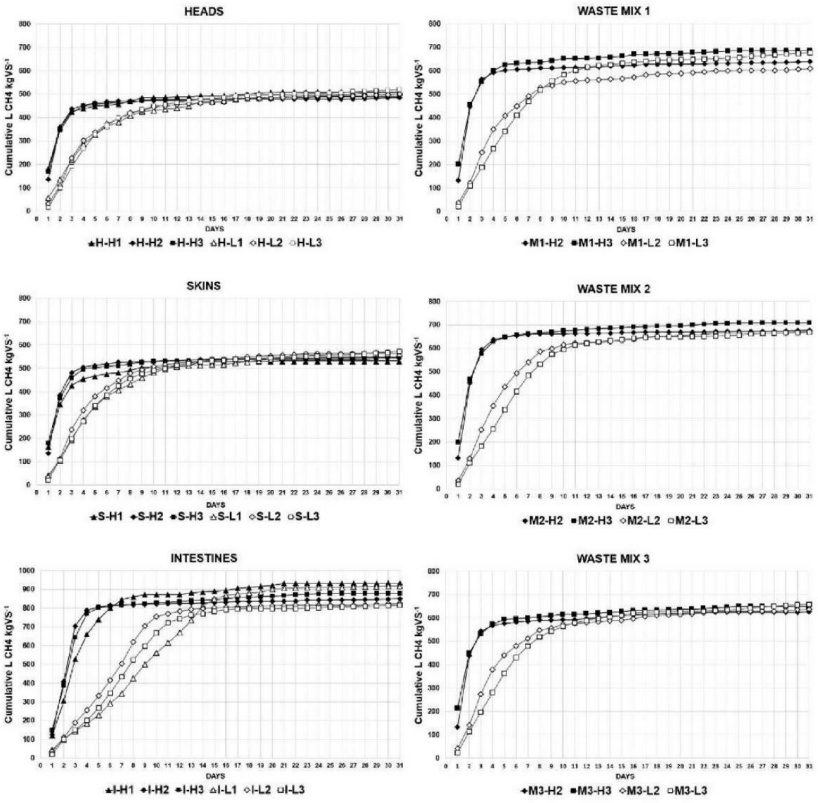

Figure 2. Averaged triplicate methane production dynamics trough experiments 1, 2, and 3. Indexes –H stands for 37 °C; –L stands for 23 °C; 1, 2, 3 stands for experiments 1, 2, 3.

Similar pattern regarding to fish waste highest production rate time shift was reported by (Chen et al., 2010), where highest biogas production rate under thermophilic conditions (50 °C) was achieved on day 10, in comparison to 17 days at mesophilic (35 °C) conditions. Moreover, this great difference could be also attributed to type of inoculum that was used in this research, because sewage sludge was gathered from bioreactors that normally operate at 37 °C. Shift to low temperature conditions put extra

stress on microorganism consortium. It is also suggested that more appropriate microbial consortium can be developed and adapted for fish waste AD by sequential addition of fish based feedstock, thus making optimized inoculum for substrates with low C:N ratios (Quinn et al., 2016).

Nevertheless, slower biomethane production rate had no significant impact on final BMP results. In addition, slower digestion time means that substrate needs longer hydraulic retention time (HRT) in digester (Dhaked et al., 2010; Zhu et al., 2014), thus slowing down biogas production or forcing to increase digesters size. On average, lowering fermentation temperature by 10 °C required anaerobic digester's size increases 2–2.5 times (Balasubramaniyam et al., 2008). However, digester's size can be reduced if shorter HRT is selected. In respect to this research results, it would be more reasonable to use a HRT of 15 days instead of 30 days for low temperature fish waste anaerobic digestion, as more than 94% of BMP is achieved during this short time.

CONCLUSIONS

The results of this research show that AD of round goby's processing waste at 23 °C is twice as slow as under 37 °C conditions. Thus prolonging hydraulic retention time (HRT) needed for complete biomethanation of feedstock, in turn increasing necessary size of digester. However, costs of digesters size increase should be compared to savings on insulation materials and heat energy input. Thus most feasible approach regarding to ratios of digesters size, HRT and fermentation temperature could be found.

For low temperature conditions an overall 23% reduction in total produced biomethane volume was observed. However, this difference is attributable to the inoculums specific activity at different temperatures and counteracting the contribution to the total biomethane volume, rather than to feedstock's biomethanation efficiency. Despite the fact, that several fish waste fractions such as heads and skins showed higher BMP values at lower temperature, based on overall averaged results, in general only a 2% reduction in total BMP outcome was observed for low temperature samples after 25 days, thus showing that biomethanation is still efficient also at lowered temperatures.

Round goby's processing wastes could be successfully used for biogas production in co-digestion, especially if containing intestines, however in-depth research is still needed to find out possible inhibitory effects and mechanisms. Also volatile fatty acid accumulation and inhibitory effect during continuous low temperature fermentation should be researched. Furthermore, AD of *Neogobius melanostomus* under psychrophilic conditions should be explored.

Research results suggests that anaerobic digestion of fish waste under low temperature conditions could be feasible as the process still occurs with 98% efficiency in respect to 37°C, in fact opening a new opportunity to explore the overall sustainability of technologies based on these conversion processes.

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EXTRACTION OF FISH OIL USING GREEN EXTRACTION METHODS: A SHORT REVIEW

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Extraction of fish oil using green extraction methods: a short review

Kaspars Ivanovs*, Dagnija Blumberga

Institute of Energy Systems and Environment, Riga Technical University, Azenes iela 12/1, Riga, LV−1048, Latvia

Abstract

This article describes green extraction methods: Supercritical fluid extraction using CO_2 (SCF-CO_2), ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) and enzymatic hydrolysis, their process, the main disadvantages and advantages in the use in fish oil extraction from fish or fisheries processing waste briefly compared to traditional methods. Green extraction methods allows to improve oil extraction yied, optimize and innovate in pretreatment and extraction procedures. Based on reviewed scientific papers the most promising green extraction method is extraction of oil using supercritical CO_2, other methods described are still being developed.

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Keywords: green extraction; fish oil; enzymatic; supercritical fluid; ultrasound; microwave

1. Introduction

Green extraction is based on findings and the development of the extraction process that reduces energy consumption, allows the use of alternative solvents, renewable natural substances, and provides secure high-quality extract/product, thus fulfilling the circular bioeconomy principles [1−7]. To develop and deliver a green extraction laboratory or offer green extraction on an industrial scale three main solutions have been identified as an approach for optimal raw material consumption, solvents and energy: (1) the existing process optimization and improvement, (2)

* Corresponding author. Tel.: +371-29331243.
E-mail address: kaspars.ivanovs@rtu.lv

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the use of non-specific facilities, (3) innovations in processes and procedures, including the discovery of alternative solvents [8].

Fish oil is the primary natural long-chain (LC) Omega-3 fatty acid source containing two human health beneficial fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) [9]. It is scientifically proven that EPA and DHA have a positive impact on human health, they reduce the chance of heart and vascular disease, cancer, diabetes, decrease the risk of depression, as well as affect the immune system, and ensure the proper neural development. Since the beginning of biochemical and biomedical research more than 31,000 reviewed scientific articles have been published about Omega-3 fatty acids [10].

Fish oil accounts for about 2 % of world consumption of fats and oils. Traditionally, the fish oil is obtained as a by-product of the fish meal industry. But currently smaller fish with a relatively high fat content – anchovies, sardines, herring, eels are in the centre of attention as a raw material in the fish oil industry. Already historically fish oil has played a significant role in the human diet, and currently, the demand for fish oil is still growing thanks to its curative properties [9]. Fish oil is mainly used in food and pharmaceutical industry, agriculture and aquaculture as a feed additive. Around the world from 25−30 million tons of healthy fish and fish cuttings approximately 1.1 million tons of fish oil are produced [9]. While only 5 % of it is used to extract the Omega-3 fatty acids, the remaining is used in the aquaculture industry [11]. Although in some regions of Europe and the rest of the world, fisheries sector still has a great place for growth and resource optimization [34], analysis of the current situation shows that fish oil production is relatively static and the future projections show that the available fish oil sources will not be able to provide the increasing demand [9]. Therefore, the last decade has emphasized the research of a new source or species in different parts of the world, the environmental impact reduction of the extraction methods and the integration of green extraction methods in an industrial scale. This article is intended to summarize the information available on the green fish oil extraction methods, to give a brief introduction of method and define main advantages and drawbacks, and parameters influencing extraction.

2. Green extraction methods for fish oil extraction

In fish oil extraction from whole fish or fisheries waste both traditional − hydraulic pressing, heat extraction, solvent extraction, and relatively new, innovative and environmentally friendly methods – supercritical fluid extraction, enzyme extraction, microwave-assisted extraction, and ultrasound assisted extraction can be used [12, 13]. The main disadvantage of traditional methods from the quality of the product is that the high temperatures degrade heat-sensitive and labile natural compounds, and toxic solvents are used, which remains are present in the final product. Also, traditional methods often have a greater impact on the environment because the extraction process requires a significant amount of heat, there is a risk of organic solvents leaking into the environment [13]. In the last 20 years, the green extraction methods are recognized as a promising alternative to the organic solvents and oil extraction grease. Mostly it is the supercritical fluid extraction using CO_2, but also other green methods keep up with the SCF-CO_2 regarding extraction yield, product quality, the content of Omega-3 Fatty acids EPA and DHA [14]. Although the green extraction methods can ensure the same quality or product, the green methods like traditional ones also have their drawbacks (Table 1).

Table 1. Overview of green extraction methods for fish oil extraction.

Name of extraction method	Brief introduction	Advantages (A) and drawbacks (D)	Main influencing parameters (P) and conditions (C) for extraction	References
Supercritical fluid extraction (SCF-CO_2)	Uses supercritacal fluids to seperate extractant from matrix using SC-CO_2 as solvent.	(A) Fast. No need for organic solvent and hence extract is very pure. Free of heavy metals and inorganic salts. No chance of polar substances forming polymers. High yield. Lipids can be used for further analysis immediately. Low operating temperatures (40–80 C°) (D) Very pricey and complex equipment operating at elevated pressures. CO_2 is highly selective – no polar substances are extracted. Supply of clean CO_2 needed. High power consumption	(P) Water content, temperature, pressure. Flow of CO_2. Extraction type: continuous, co-solvent, soaking, pressure swing (C) Pressure 25−40 MPa, T = 40–80 °C, > 2 mL CO_2/min, soaking time 45 min − 6 h.	[13, 14, 16, 18–20]
Microwave assisted extraction (MAE)	Uses microwaves to warm the solvents in contact with the solid matrix to extract the contents from the sample solution.	(A) Decreased extraction time and solvent consumption; higher penetration of chosen solvent into cellular material and enchanced release of cell content in medium. Loses insufficient heat into the surrounding environment. Higher extraction rates, lower temperatures (D) High power consumption. Heating affects only polar solvents and/or materials. Difficult to scale up. Heat generation, which can lead to unsaturated fatty acid oxidation; low efficiency when using volatile solvents	(P) Particle size, the used solvent, time, capacity, and frequency of microwaves (C) 110–2450 W, medium – water or organic solvent	[13, 15, 27−29, 39]
Ultrasound assisted extraction (UAE)	Uses ultrasound to penetrate the solvents in contact with the solid matrix to extract the content from the sample solution.	(A) Decreased extraction time and solvent consumption; higher penetration of chosen solvent into cellular material and enchanced release of cell content in medium (D) High power consumption. Difficult to scale up	(P) Ultrasonic frequency, power, time and medium (C) 25 kHz, 200–2450 W, 30–60 min sonication time. Medium – ethanol, cyclohexane other organic solvents	[23, 31–34]
Enzymatic hydrolysis	Uses exogenous proteolytic enzymes to digest material to extract oil.	(A) No need for organic solvent. Using commercial low cost protease provides an attractive alternative (D) Expensive/difficult to scale up	(P) Type, activity and amount of protease. pH. Endogenous enzymes absence. (C) Time 1−4 h at temperature 40−60 °C The ratio of enzyme to substrate (E/S) ~ 0.5–5 %	[35, 36, 38, 40]

As mentioned above the most famous green extraction method is supercritical fluid extraction (SFE) mostly using CO_2 as a solvent. Supercritical fluid extraction is used to produce high added-value products from plants, e.g. micro-algae [15], and animal tissue, e.g. fish and fish by-products [16, 17]. This method has several advantages, it uses no toxic solvents, the extraction and separation are faster, and thermal process at lower temperatures is much safer (as well as its benefits regarding the flexibility of the process thanks to the ability to change the solvent power or supercritical solution selectivity) [16]. Except for CO_2 also other compounds are researched for use in the SCF, such as fluorinated hydrocarbons, sulfur, nitrogen oxides, hexafluorides, butane, pentane, hexane [13]. Carbon dioxide is the most traditional SCF solvent because it is easily available at a low price, it is not burning and has low toxicity, high diffusivity with tunable solvent power. The fact that CO_2 at a room temperature is a gas ensures that the solvent is easily detachable from the extraction chamber. Relative to other solvents CO_2 has mild critical conditions (Tc = 303.9 K Pc = 7.38 MPa) [18]. The four major factors that affect the SCF-CO_2 extraction is pressure, temperature,

time and CO_2 extraction flow rate [15, 19−21]) as well as the extraction type: continuous, co-solvent, soaking, pressure swing [22]. The main limitation of the SCF-CO_2 extraction is its low polarity. CO_2 is a good solvent for non-polar (lipophilic) compounds. Moisture in the sample reduces the contact time between the solvent and solute. The water acts as a barrier against CO_2 diffusion in the sample and the release of lipids from cells. Therefore, before the extraction, it is necessary to dry the sample [21, 23].

Analysis of the literature suggests that SCF-CO_2 method is used in the fish oil extraction in industrial scale for already about 20 years. Extraction yields are similar or even higher than those of traditional extraction methods, and yield of extraction is logically dependent on fish species and part used for extraction. For example, processing scraps of a hake (Merluccius Merluccius − Merluccius paradoxus) can provide around 10 g of oil/100 g of dry raw materials, but the fatty fish species, e.g. salmon *Salmo Salar* and orange roughly *Hoplostethus atlanticus* offcut provide greater quantities of 40 g and 50 g of oil respectively and 100 g dry raw material [18], African Catfish *Clarias gariepinus* − 67 g dry raw material [14], Tuna *Thunnus tonggol* 36.2 g [17]), Indian mackerel 52.3 g oil/100 g dry raw material [24] Longtail Tuna *Thunnus tonggol* head 35.6 % [25, 26] and about 10 g oil /100 g dry raw material in different parts of sardine [21, 19]. As mentioned above, the biomass of fish requires pre-treatment – moisture content reduction below 20 %. A freeze-drying method in temperature below – 40 °C is used to reduce the moisture, although the particle size reduction does not make a marked difference in the extraction yield [20]. Optimum extraction parameters: pressure 25−40 MPa, T = 40−80 °C, > 2 mL CO_2/min, soaking time 45 min − 6 h [14, 18, 19, 21].

Microwave-assisted extraction (MAE) uses the microwaves to warm the solvents in contact with the solid matrix to extract the contents from the sample solution. This extraction process is still in development and it should be improved, and tested on a broad spectrum of sample matrices [13, 27]. Microwave extraction is based on the principle that microwave heating system is very selective, and it loses very little heat into the surrounding environment. Direct heating affects polar solvents and/or materials. If it is used for biomass samples, the moisture is reduced, and it results in a considerable pressure generation, which breaks the cell membranes of the animal or plant cell walls freeing up in cells existing materials [15]. Microwave extraction is considered better than traditional solvent extraction methods because it has several advantages − higher extraction rates, lower temperatures, automatization, and a resource to simultaneously produce different samples [28]. However, microwave extraction has two major drawbacks: the heat generation, which can lead to unsaturated fatty acid oxidation and its low efficiency when using volatile solvents [29]. Many factors influence the extraction efficiency: sample particle size, the used solvent, time, capacity, and frequency of microwaves. Microwave extraction method is not widely used. Also, the number of publications about this method in fish oil extraction is relatively small. However, there are some articles that have discussed the oil extraction from fish using MAE. A study that analysed the fat content of frozen fish found that fish oil extraction using MAE gives a similar or even greater yield than traditional extraction methods. For example, Ramalhosa et al. [27] used the CEM MARS-X 1500 W extraction unit to extract oil from Chub mackerel, sardine, and Horse mackerel using petroleum ether:acetone (2:1, v/v) as a solvent, extraction yield (raw material) ranged from 4.5 % for sardine to 9 % for chub mackerel. Prior the extraction fish were homogenized in a blender. In other work, Chimsook and Wannalangka, 2015 used MAE (110 W Microwave power, 60 s) prior to extraction of oil from waste of hybrid strain *Pangasianodon gigas* x *Pangasianodon* hypothalamus, this yielded at 9.25 % of raw material. Shativel et al. used Sharp Carousel 1000–2450 W microwave oven to extract catfish liver oil, in this study it was concluded that in comparison to conventional methods the microwave treatment reduces the amount of certain fatty acids in the extract [30].

More recent studies have shown that ultrasonic assisted extraction using acoustic cavitation and mechanical impact can improve the efficiency of extraction. Acoustic cavitation can disrupt cell wall facilitating the solvent penetration into plant material and allowing the cell to release the product. Ultrasonic mechanical impact offers greater penetration of solvents in the sample matrix because it increases the surface area of contact between the solvent and the extractable compounds. The ultrasonic-assisted extraction (UAE) requires less extraction time and reduced solvent consumption and can be performed at low temperatures, which can reduce the temperature caused damage and minimize the loss of bio-active substances [31]. Ultrasound is in frequencies above the human's hearing levels ranging from 20 kHz to 10 MHz. Ultrasound is classified by several criteria: the amount of energy generated characterized by the sound power (W), sound intensity (W/m^2), or sound power density (W/m^3). The use of ultrasound can be divided into two types: high intensity and low intensity. Low-intensity ultrasound has a high frequency (100 kHz to 1 MHz), and low-power < 1 W/cm^2, it is used in non-destructive analyses and as an analytical method for assessing the quality to provide information on physical and chemical properties of food products (such as firmness, readiness, sugar content,

acidity). While high-intensity ultrasound has a low frequency (100 kHz –16 kHz) and high power (10−1000 W/cm^2) [32]. High-intensity ultrasound is used to speed up and improve the efficiency of sample preparation, as it can change food physical or chemical properties. Ultrasonic extraction is generally recognized as an effective method of extraction, which significantly reduces the time required to increase the productivity and often the quality of the product. Several studies have critically assessed a variety of ultrasonic applications in the industrial extraction of bio-active materials [33]. Although MAE and UAE are quite widely used in bio-active material extraction, in fish oil extraction it is almost not used, and there are very few scientific articles on this topic. Abdullah et al. [23] used UAE in ethanol medium for extracting oil from Asian swamp eel Monopterus albus fillets. Before the extraction, the material had to be dried (60 °C) and homogenised in a blender. Optimal extraction parameters are 25 kHz, 200 W, 25 kHz, 200 W, 60 min sonication time, and 500 ml of ethanol. The final production − 7.2 % of dried fillet material. In another work, Xiao et al. [34], extracted 94.82 % of total lipids using cyclohexane medium, optimal extraction parameters 4:1 liquid-to-solid ratio at 50 °C within 57 min and 400 W extraction power.

Another method that the authors find debatable as a green extraction method is an enzymatic hydrolysis. In comparison with the other methods discussed here, it is much more studied. Enzymatic hydrolysis is a term that is used if the enzymes are derived from other sources. Adding exogenous enzymes makes digestion process better controllable and reproducible. Thus, enzymatic hydrolysis is an ideal way to recover oil and protein from fish and fishery processing waste. The enzymes and the fish that are used in the process have one thing in common − they must be in food quality, and if the enzymes are of microbial origin they must not be pathogens. In most cases, alkaline/neutral proteases are used for the hydrolysis because they produce better results than the acidic proteases. [35−37]. Before the extraction, it is necessary to deactivate the exogenous enzymes by heating in about 80−90 °C temperature and adjusting the pH. Oil regain yield depends on the used protease, its activity, concentration, pH, temperature, and particle size. It is reported that compared with the traditional thermal extraction enzymatic hydrolysis is better in oil regaining and it competes with the solvent extraction (Table 2) [35−38].

Table 2. Pretreatment method, optimum extraction parametrs and yield of enzymatic extraction methods.

Fish species and parts	Green extraction technique	Material pre-treatment	Yield	Optimum extraction parameters	Reference
Different parts of Mackerel	Enzymatic etraction	Homogenized, heated to deactivate endogenous enzymes, pH was adjusted	Whole fish 7.96 g, head – 9.80 g, frame 5.96 g, fin, tail, skin and gut – 11.98 g oil/100 g raw material	2 % Alcalase enzyme 1 h	[35]
Cultured salmon *Salmo salar*	Enzymatic etraction	Homogenization, heating at 90 °C for 5 min to inactivate the enzymes	Gut – 13.1 g Head − 59.9 g Frame 78.58 g oil/100 g raw material	240 min, 30 °C, 0.5 % Sea-B Zyme L200 enzume	[38]
Catla *Catla catla* and rohu *Labeo rohita* visceral waste	Enzymatic etraction	Homogenization, 85 °C for 20 min to deactivate endogenous enzymes	From 42 % to 74 % depending of protease used, highest yield P-amano 74.9 % of extractable oil	0.5 %, w/w, 2 h at 40 °C with shaking after every 10 min	
Salmon *Salmo Salar* heads	Enzymatic exraction	Homogenization with grinder, heated to deactivate endogenous enzymes	Neutrase 17.2 %, Flavourzyme 17 %, Alcalase 17.4 % of raw material	The ratio of enzyme to substrate (E/S) was set at 0.05, 2 h at 55 °C,	[40]
Salmon *Salmo Salar* heads	Enzymatic extraction	Homogenization with grinder, heated to deactivate endogenous enzymes	Neutrase 14.4 % Protamex 14.6 % Alcalase 19.6 % Oil of wet weight basis	2 h at 50−55 °C The ratio of enzyme to substrate (E/S) was set at 5 %	[36]

3. Conclusions

Laboratory studies shows that green extraction methods provide an excellent alternative to traditional methods – the amount of fish oil produced and the quality is similar or even better. However, these methods require additional research. It is necessary to improve the pre-processing technology and the process of extraction itself. On the basis of reviewed scientific papers, it is concluded that the most promising green extraction method is extraction of oil using supercritical CO_2, other described methods are still under development.

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USE OF ROUND GOBY (NEOGOBIUS MELANOSTOMUS) PROCESSING WASTE IN BIOECONOMY

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Use of round goby (*Neogobius melanostomus*) processing waste in bioeconomy

Maira Melvere*, Kaspars Ivanovs, Jelena Pubule, Dagnija Blumberga

Institute of Energy Systems and Environment, Riga Technical University, Azenes iela 12/1, Riga, LV-1048, Latvia

Abstract

Round goby (*Neogobius melanostomus*) in Baltic Sea is an invasive species, which over the past decade spreads rapidly. Round goby was indirectly introduced from Black or Caspian Sea. During these years catch reaches several thousand tons. Fishermans acquire these fish sourcing but appears problems with implementation. The development plan of Latvia establish to use these species of fish for human consumption and that is why in research have been considered possibility of fish processing residue (internal organs, head, bones etc.). In accordance to bioeconomic principles, processing waste is considered to be raw material for the production of high added value products. Evaluating the use of round goby processing waste from the economic and technical viewpoint in the context of Latvia we examine the extraction of fish oil. During the research fish's total amount lipids has been determined while using Bligh/Dyer method. The oil has several quality indicators – amount of free fatty acids, acid value and saponification value. Content of protein, moisture, ashes and carbohydrates in the fish has been determined. Round goby's head consists of 81.18 ± 1.10 % water, 4.24 ± 0.10 % ash 1.00 ± 0.13 % fat, 16.60 ± 0.40 % protein, 0.0 ± 1.00 % carbohydrates. The body consists of 83.68 ± 12.86 % water, 3.75 ± 0.01 % ash, 0.67 ± 0.07 % fat, 16.60 ± 0.40 % protein, and 0 ± 1.00 % carbohydrates. While assessing production capabilities, attempts were made to obtain oil through heat extraction and microwave extraction methods. After numerous applications of centrifugation using the heat extraction method fish gelatin was acquired, there were no findings of oil in the upper part of the liquid layer. Similar results were obtained using the microwave extraction.

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Keywords: fish; extraction; fish oil; bio-products; high–value products

* Corresponding author. Tel.: +371-29384024.
E-mail address: mairamelvere@inbox.lv

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1. Introduction

Round goby (*Neogobius melanostomus*) is indirectly way introduced from Black or Caspian Sea. Round goby first time in Baltic Sea recognized in Poland, Gdansk by approximately in 1991. First time in Latvia this fish recognized approximately in 2004 in Liepaja coast. Fish prevalence repeatedly investigated in scientific literature. Average fish prevalence speed is about 30 km per year. Currently round goby are in all coast of Latvia. In addition, species spread also provides in fresh-water [1−7].

Exploring the reasons for the spread of fish determined that mostly impact is from human activity. One of the main reason for spread is sailing and human activity near coast. These fish species easily adapts surrounding conditions and in imported place they continue feed and reproduce. Therefore changes the current environment, food cycle and species of fish population. Viewing fresh − water goby prevalence in fresh-water concluded that zander changes food chain becoming aggressive. Bigger zanders eat small ones about 1.2 %−7.7 % often. It is related with lack of traditional feed. Similar tendency expected in result of round goby prevalence. Observed that turbot population in the sea now is decreasing rapidly – even twice. Number of fish and nutrition tendency should continue to research to fully understand the situation [4−11].

Fish processing residues makes approximately 60 % of fish total weight. In the last years researches are trying to understand what kind of high added value product could be made from this processing residues. One of version is obtaining industrial enzymes. They are obtained from fish internal organs which constitute average 5 % from fish total weight. Obtained trypsin from other species of fish keeps activity in alkaline environment at approximately 50 °C−60 °C temperature and catalyze the chemical reaction. This kind of enzyme could be used as washer for clothing, as skin treatment, for food processing, in chemical industry and in many other processes [9−15].

To improve quality of animal food and quantity of valuable essential amino acids can produce fish protein hydrolasate. In that way could significantly improve the nutritional value of fish meal. Amino acids concentration in hydrolasate could double [16].

Biofuel producing from fish oil are known last 20 years but now people are researching to get higher quality material and solving storage and logistics problems. By the fuel processing it is possible to obtain biofuel which accord American Society for Testing and Materials (ASTM) standard requirements [14−19].

Fish processing residues could be raw material for cosmetic products for example for sun tan cream, face cream or serum which accelerates wound healing [17−21].

In non-food industry fish oil can use for lubricant, washing products, pesticides, fungicides, polyurethane foam and many other products production. From bio-economy perspective are researches how to get fish oil from processing residue. In this case main important thing is quality of oil and Omega 3 unsaturated fatty acid composition [21−23].

2. Methodology

2.1. Material preparation

For the laboratorial research round goby is used, caught on April 5, 2017 at 12:00 on the coast of the Baltic Sea (coordinates: 56,516325; 20,946526). Fishing nets where employed. This specific day is considered to be the first day when round goby appeared on the coast of the Baltic Sea. Fishing for the round goby was initiated. The experiment began after approximately 40 h.

The average length of the fish is 19.53 ± 0.05 cm. ¼ of the length of the body is the head. Fish's body weighs 77.46 g ± 2.00 g, however the head weighs 20.83 g ± 2.00 g. For further research the body and the head are used separately. In this experiment the internal organs are removed and discarded.

Homogenisation is done before acquiring the oil. Prior to homogenisation the fish specimen is rinsed under running cold water. Blender is used for the homogenisation process, maximum power output 750 W. The fish heads are diced to fractions of 1– 2.5 mm on average. Before homogenisation the rest of the fish's body is mixed with distilled water (ratio of 1:5) and diced until 0.2–0.7 fraction size.

2.2. Assessing total lipid content

Total lipid content determination is done using the Bligh/Dyer methods. Before hand prepared fish specimen is repeatedly cleaned from any hard particles – skin, fins and scales. The specimen is weighed (100 g) and solvents are added – chloroform 100 ml and methanol 200 ml. The mass is added to the blender on maximum power output 750 W for 2 min to ensure even distribution. Again chloroform 100 ml is added and the mass is evenly mixed (30 s). After that 100 ml of distilled water is added. The mass is mixed for 30 s in room temperature [24–28].

The resulting mixture is poured in 50 ml test tubes which are then placed in a centrifuge. Centrifugation takes 15 min at 7500 rpm. Supernatant is separated from liquid portion. 10 ml of chloroform and 10ml of methanol is added to the supernatant. It is then once again centrifugated for 10 min at 7500 rpm. Again the supernatant is separated [24, 25].

Mixture of methanol and chloroform that is gathered after centrifugation is added to a separating funnel which is left to stand for 15 min to settle. Methanol settles in upper part, chloroform in the lower. Lower layer is carefully separated and filtered through filtering paper which contains anhydrous sodium sulphate (Na_2SO_4). Filtering is done twice, the second time using filtering paper without anhydrous sodium sulphate. Filtrate is transferred into a round-bottomed flask and at 60 °C evaporation of chloroform is carried out until oil without solvent is obtained. The oil is cooled and in a sealed container placed into a freezer at – 18 °C until further analysis. Experiment is repeated three times using fish body and separately fish head [24, 25].

2.2. Indicators of oil quality

To attain a complete quality check round goby's body/head moisture and ash contents are determined. Date is acquired according to standards – LVS EN ISO 18134-2, LVS EN ISO 18134-3, LVS CEN/TS 14780, LVS EN ISO 18122, LVS EN 14775. Moisture content in the fish is determined by calculating body mass changes before and after heating. Overall the test was conducted for 20 h, a temperature of 105 °C was sustained for drying [24].

Ash content was obtained in accordance to a method by the AMC (Analytical Methods Committee of the Royal Society of Chemistry) (1979), modifying it without adding magnesium acetate [25].

Saponification value is an important factor which needs to be addressed while assessing the further manufacturing process. Fish oil saponification value is determined in accordance to American Oil Chemists' Society (AOCS) oficial methodology (AOCS, 1992) [25].

Free fatty acid content (%) and acid value is determined in accordance to AOCS official method Ca 5a-40. Protein content is determined using the Kjeldahl method. Method was developed by scientist Johan Kjeldahl in 1883 and it conists of heating a substance with sulphuric acid, which decomposes the organic substance by oxidation to liberate the reduced nitrogen as ammonium sulphate. By determining protein, fat and also water and ash content in the fish it is also possible to calculate the amount of carbohydrates. This calculation is done in accordance to AOAC, 2002 official methodology [25–28].

2.3. Oil extraction methods

Mechanical and microwave method is used and compared to determine the most effective oil extraction method. Extraction schemes are portrayed in the Fig. 1.

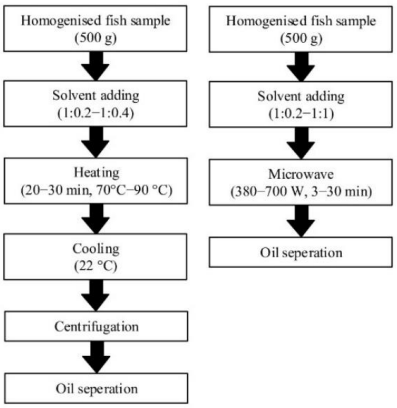

Fig. 1. Heat extraction (to the left) and microwave extraction (to the right) schemes.

While using Taguchi experiment methodology three different variables are chosen which can affect the result when using the mechanical extraction method – temperature, time and solvent ration. Taguchi methodology is statistical method that gives the best possible results in as few experiments as possible. Using three different variable parameters it is necessary to make nine experiments in a certain order to determine the most effective combination. Temperature is determined while keeping in mind that the boiling point of water is 100 °C. To avoid the boiling point maximum temperature is set to 90 °C, however the lowest temperature is – 70 °C which is assessed from various sources of scientific literature. The optimal heating period is on average 20–30 min, which is used while obtaining oil from various fishes, these values are also used as a minimal and maximum value [26–28].

Distilled water is used a solvent for microwave extraction. It is possible to vary it to increase the amount or the quality of the oil. Microwave oven power output is varied within 380 W to 700 W, the time is varied from 3 min to 30 min, however the solvent ration is varied within 1:0.4 to 1:1.

3. Results and discussions

The obtained quantitative and qualitative figures are compiled to the acquired oil (Table 1) while using total lipid content determination.

Initially mechanical centrifugation is done at 7500 g for 15 min (relative centrifuge speed considering the radius of the rotor). The specimen is removed, however there is no oil in the upper layer of the liquid part. The process is repeated for the next specimen increasing the centrifugation speed to 10 000 g, this attempt also yields no oil. Similarly centrifugation was done with two other specimens, using 15 000 g and 18 000 g with no appearance of oil.

The liquid part is separated from the supernatant in every specimen. Fluid is divided in separate test tubes while not mixing the specimens with different variable figures. This acquired liquid part is added to a centrifuge and centrifugation according to the figures that where used in the first centrifugation process, i.e., if the first specimen was centrifuged at 7500 g then the separated mass will also be centrifuged at 7500 g for 15 min.

A thick, paste-like substance – gelatin (Fig. 2) is obtained after the centrifugation of the liquid part. It is obtained from the collagen that is the structural protein in the connective tissue of fish. In the result of previously conducted thermal treatment this collagen turns into gelatin [26–28].

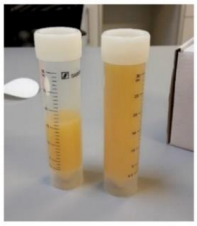

Fig. 2. Heat extraction (to the left) and microwave extraction (to the right) schemes.

Likewise, after the microwave extraction method there was no fish oil in the upper later of the liquid part. After the total lipid content determination the highest oil content is found in the round goby's head 1.00 % ± 0.13 %, oil content in the body is lower − 0.67 % ± 0.07 %.

Round goby's head consists of 81.18 % ± 1.10 % water, 4.24 % ± 0.10 % ash 1.00 % ± 0.13 % fat, 16.60 % ± 0.40 % protein, 0.0 % ± 1.00 % carbohydrates. The body consists of 83.68 % ± 12.86 % water, 3.75 % ± 0.01 % ash, 0.67 % ± 0.07 % fat, 16.60 % ± 0.40 % protein, and 0 % ± 1.00 % carbohydrates.

Comparatively low acid value and low free fatty acid content points to the fact that the obtained raw material is fresh and usable in edibles. Acid value from the head (2 mg KOH/g ± 0.47 mg KOH/g) and the body (1.90 mg KOH/g ± 0.06 mg KOH/g) in the obtained fish oil is with accordance to the fish oil quality standards (< 3 mg KOH/g). Free fatty acid content (FFA %) in the oil the of round goby head is 1.03 % ± 0.24 %, in the body 0.96 % ± 0.03 %.

Saponification value of the oil is 233.4 mg KOH/g ± 15.84 mg KOH/g (head) and 244.65 mg KOH/g ± 54.94 mg KOH/g (body). This shows that the oil contains high ratios of large molecular weight fatty acids.

Table 1. Qualitative indicators of different fish oils.

Fish	Moisture, %	Ash, %	Lipids, %	Protein, %	Free fatty acids, %	Acid value, mgKOH/g	Saponification, mg KHO/g	Refer.
Marine fish								
Salmon (head)	63.36	3.52	21.86	11.31	0.17	0.59	-	[29]
Salmon (corpus)	57.19	3.65	22.65	10.39	0.33	1.17	-	[29]
Herring (edible part)	64.60	-	16.40	16.70	0.38	-	-	[30]
Herring (waste)	68.60	-	16.20	11.70	0.71	-	-	[31]
Sardinella							211.90	[32]
Round goby (head)	81.18 ± 1.10	4.24 ± 0.10	1.00 ± 0.13	16.60 ± 0.40	1.03 ± 0.24	2.00 ± 0.47	233.4 ± 15.84	-
Round goby (corpus)	83.68 ± 12.86	3.75 ± 0.01	0.67 ± 0.07	16.60 ± 0.40	0.96 ± 0.03	1.90 ± 0.06	244.65 ± 54.94	-
Fresh water fish								
Perch	70.30	0.70	4.40	13.90	-	-	-	[33]
Goby	81.30	1.00	0.10	12.90	-	-	-	[33]

Comparing the total lipid determination method when using the mechanical and microwave extraction it was established that at 1 % total lipid content fish oil extraction is not possible with these methods. Relatively small amount of extracted oil is attributable to the specific time of the specimen collection and the research object's physiological

and feeding peculiarities. Regarding that the acquired amount of oil is low it is necessary to carry out an additional research with round goby's which are caught in various seasons. Fat content in fish is dependent on the metabolic activity which is reduced in the beginning of the fishing season (spring).

Relatively high protein content shows a potential utilization of the researched object. That is why it is necessary to do an in-depth research of the content and amount of protein amino acids. Experimentally obtained oil quality value give a general notion about goby fish oil. More complex experiments have to be conducted in which the amount and content of fatty acids in the oil is determined. Also the qualitatively characterized size and fatty acid content and amount in fish with a different storing time period.

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COMPREHENSIVE LITERATURE REVIEW ON VALUABLE COMPOUNDS AND EXTRACTION TECHNOLOGIES: THE EASTERN BALTIC SEA SEAWEEDS

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Comprehensive Literature Review on Valuable Compounds and Extraction Technologies: The Eastern Baltic Sea Seaweeds

Karīna BĀLIŅA[1]*, Kaspars IVANOVS[2], Francesco ROMAGNOLI[3], Dagnija BLUMBERGA[4]

[1, 3, 4] *Institute of Energy Systems and Environment, Riga Technical University, Āzenes iela 12/1, Riga, LV1048, Latvia*

[2] *Institute of Food Safety, Animal Health and Environment "BIOR", Lejupes iela 3 Riga, LV1076, Latvia*

***Abstract* – Seaweed valuables have been researched a lot in the last decades but there is a lack of information on brackish seaweed at the eastern part of the Baltic Sea. Previous research shows that Baltic seaweed can be used as a source for phycocolloids as well as for bioenergy. The amount of available usable biomass is not clear, also seaweed in brackish seawater does not reach the dimensions such as the same species in Western parts of the Baltic Sea where the salinity is higher. Therefore, the use of this biomass must be smart to create economic benefit. Three abundant Baltic brackish seaweed species were chosen, to represent green, brown and red seaweed groups and an in-depth information analysis was made to clarify possible focus substances that could be extracted from these species. In this paper we summarize literature of common seaweed components, traditional extraction technology, and potential amount in seaweed and give an overview of novel methods for extraction of seaweed bioactive compounds.**

Keywords* – Bioeconomy; extraction; *Fucus vesiculosus; Furcellaria lumbricalis;* macroalgae; phytobenthos; *Ulva sp.

1. INTRODUCTION

Biorefinery is an important part of the biobased economy and biotechonomy integrating different biomass conversion processes to produce energy and value-added products into a single facility. Biotechonomy is the sustainable conversion of a biomass to produce energy, food, feed, pharmaceuticals and other materials [1]–[3]. The production of these products through a biorefinery concept and in compliance with the biotechonomy approach make the cultivation and seaweed processing economically and environmentally feasible, respecting social and policy angles. Nowadays the global biorefinery concept mainly includes terrestrial biomass with plants and forest on top and only a small part has recently been devoted to algae [4].

Marine macroalgae or seaweed have the potential to partly replace terrestrial biomass. With current research going on in this field it is already declared that algae are a third generation bioresource and do not compete with food and feed plants, nor do they use resources for their growth. Valuable substances that can be found in algae can be a way to promising low-carbon

* Corresponding author.
E-mail address: kbalina88@gmail.com

economy. Seaweed aquaculture is already popular in Asian countries [5], but seaweed natural distribution area covers the world, including Europe and the Baltic Sea [6]. Recently seaweed products have become popular in Europe as a source of polysaccharides for food and pharmaceutical use [7], [8]. The seaweed mineral content is higher than the mineral level in terrestrial plants and animal products [9], [10]. High mineral and low-fat content makes seaweed a suitable feedstock for food and feed.

Even though seaweed compounds have recently been widely researched, there has been lack of information on brackish seaweed naturally growing on the eastern part of the Baltic Sea. In any case, the amount of available biomass is not clear, but it is known that specimens do not develop to a great size as the same species in the Western parts of the Baltic Sea. To gain the maximum benefit from a minimum amount of biomass, a smart biorefinery strategy has to be used.

In this review, a summary of seaweed biorefinery potential compiling the most common seaweed compounds and their contents have been developed. Three Baltic Sea brackish seaweed species were chosen to represent green, brown, and red seaweed groups and an in-depth information analysis was conducted to clarify possible focus substances that could be extracted from these species. Extraction techniques that would allow to use leftover biomass from extraction processes were summarized and discussed.

This review focuses on seaweeds abundant in Eastern Baltic Sea region, where salinity ranges from 5 % to 7 %. A comprehensive literature review was done to investigate the potential added value compounds contained in three Eastern Baltic typical seaweed species and their extraction technologies to build the analytical basis for prediction and planning of Baltic seaweed application pathways under the biorefinery concept. An in-depth literature search was done to summarize the research performed on seaweed extraction, and relevant quantitative and qualitative data on seaweed extraction was summarized and combined in tables.

2. EASTERN BALTIC SEAWEED POTENTIAL

2.1. Seaweed Components

Seaweed is composed of a special composition of substances. Even though it is often considered as a close ancestor to terrestrial plants, substances found in seaweed are different [11]. Known for their high nutritional and pharmaceutical value, they are widely consumed as food and as herbal remedies to cure health problems like eczema, psoriasis, renal disorders, digestive system problems, heart and cardiovascular diseases and are even mentioned as a treatment for cancer [12]–[15]. Seaweed use as feed, food, fertilizer, fungicide, herbicide has developed a demand for seaweed as a valuable resource [15]–[17].

Nutrient composition in seaweed varies, depending on the species, time of collection, geographic location and environmental conditions such as temperature, light and nutrient concentration in water. Even the same seaweed genus can have great differences in their nutritional composition.

Seaweed biomass has a high polysaccharide amount (Table 1) that exists in the cell wall structures and has numerous commercial applications in products such as stabilisers, thickeners, emulsifiers, food, feed, beverages, etc [18], [19]. The total amount of polysaccharides can range from 4 % to 76 % of dry weight.

TABLE 1. MAJOR SACCHARIDES AND POLYSACCHARIDES FOUND IN EACH OF THE THREE TYPES OF SEAWEED [20]

Green algae	Brown algae	Red algae
Cellulose	Cellulose	Cellulose
Starch	Laminarin starch	Floridean starch
Mannan or galactan	Mannitol (monomer)	Agar
Heteroglycan	Alginic acid	Carrageenan
Ulvan	Fucoidans	Xylan
Xylan		Galactan

Structural features of polysaccharides give them the ability to bind water up to 20 times their weight to give hydrogel, which qualifies them to be referred to as hydrocolloids or phycocolloids. The formation of gel involves non-covalent interaction, such as hydrogen bonding, hydrophobic and ionic interaction among the constituents and are formed from cooling of heated solutions of polymers. Many polysaccharides can form hydrogels by either heating or cooling. The gel is composed of at least two components, where a polymer forms a three-dimensional network in a liquid medium such as water.

The amount of proteins in seaweed varies in relation to surrounding environmental factors and species [21]. Highest protein concentrations are reported in winter and early spring months and lowest concentrations regarding to nitrogen concentrations have been observed from July to October. In general, red and green seaweed have relatively high protein concentrations (10 %–30 % dry matter), while brown seaweed contains an average of 3 %–15 % of dry weight [22]. Brackish red seaweed *Furcellaria lumbricalis* sometimes is assimilated to *Palmaria palmata* for which protein content can represent even up to 35 % and 47 % of the dry mass. That is higher protein amount than legumes, like soybean with 35 % of protein in dry mass, meaning it can be alternative dietary addition for vegetarian and vegan diet. The amino acid composition of seaweeds can be compared to other protein sources such as eggs and soybean. For most seaweed, glutamic acid and aspartic acids together make a large part of the total amount of amino acids [21].

As photosynthetic organisms, seaweed contains pigments that are responsible for the variety of colours observed in brown, green and red seaweed. These pigments allow seaweed to absorb the light necessary for photosynthesis at depths that have various degrees of light intensity. These pigments can be divided into three main groups which include chlorophylls, phycobiliproteins and carotenoids and have various health benefits (Table 2).

TABLE 2. DOMINANT PIGMENTS REPRESENTING THE THREE MACROALGAE GROUPS

Pigment Class	Green Algae	Brown Algae	Red Algae	Reference
Chlorophylls	Chlorophyll a, Chlorophyll b, derivatives	Chlorophyll a Chlorophyll b Chlorophyll c derivatives	Chlorophylls a Chlorophyll d derivatives	[23]
Carotenoids	α, β, γ-carotene, Xanthophylls	Fucoxanthin Xanthophylls β-carotene	Xanthophylls α, β-carotene	[20], [23]–[25]
Phycobiliproteins	–	–	Phycoerythrin Phycocyanin	[23], [24]

Chlorophyll and its derivatives are associated with a number of health benefits including antioxidant and anti-mutagenic activities which may help to prevent cancer [26]. Carotenoids found in seaweed include β-carotene, fucoxanthin, astaxanthin, violaxanthin, tocopherol,

zeaxanthin and lutein [19]. Fucoxanthin is another carotenoid present in brown seaweed such as *Ascophyllum nodosum* and *Laminaria digitata* [27]. Phycobiliproteins are water-soluble pigments that are found in red seaweed and include phycoerythrin, phycocyanin and allophycocyanin. Previous scientific studies have reported that this group of proteins possess anti-inflammatory, liver protecting, anti-viral, anti-tumour, serum lipid reducing and anti-oxidant properties [14]. Phycobiliproteins are found in red seaweed such as *Chondrus chrispus* and *Furcellaria lumbricalis* and are responsible for the red-brown colour of these species [28].

Lipids represent only 1–5 % of seaweed dry matter and show a valuable polyunsaturated fatty acid (PUFA) composition particularly regarding with omega-3 and omega-6 acids which play a role in the prevention of cardio-vascular diseases, osteoarthritis and diabetes. The green algae show interesting levels of alpha linolenic acid. The lipid content in seaweed is very sensitive and has significant differences between species, it also varies by geographical location, season, temperature, salinity and light intensity [29]. Although oxidative stability of PUFAs in brown seaweed lipids is not clear yet, these lipids could be applied to nutraceuticals and functional foods as an oxidative stable omega-3 source.

The mineral composition varies according to genera as well as various other factors such as seasonal, environmental, geographical and physiological variations, as well as the seaweed type such as wild type and cultivated type [15]. Seaweed contains significant amounts of essential minerals (Na, K, Ca, and Mg) and trace elements (Fe, Zn, Mn, and Cu), which play an important role in building human tissues and regulating vital reactions as related elements of many metalloenzymes due to their cell surface polysaccharides (e.g., agar, carrageenan, alginic acid, alginate, salt of alginate acids, and cellulose), enabling them to absorb inorganic substances from the ambient environment [15]. The mineral content in the form of ash of the seaweed reaches levels of up to 55 % on a dry weight basis.

Phenolic compounds are a group of secondary metabolites comprising a wide variety of compounds produced by both terrestrial and aquatic plants, which include seaweed [30]. One of their most outstanding features is their antioxidant properties, as they prevent the formation of many free radicals because of their metal ion chelating capacity [20], [31]. Phenolic compounds include: flavonoids – that are associated with various bioactivities, including the antioxidant and radical scavenging activity, lignans, tannins, tocopherols, and phenolic acids [32]. Flavonoids that are known as safe and non-toxic antioxidants, have an important function to protect the plant against UV radiation [33]. The capacity of flavonoids to act as antioxidants depends on their molecular structure. The position of hydroxyl groups and other features in the chemical structure of flavonoids are important for their antioxidant and free radical scavenging activities [34].

2.2. Eastern Baltic Seaweed Biorefinery Potential

To estimate Baltic seaweed biorefinery potential, the most abundant species were chosen and in-depth literature research was carried out to seek for possible compositions. Findings from researched scientific literature were summarized in Table 3. It must be mentioned that data summarized in this table is not only from seaweed from the Baltic Sea but also from the same species of algae growing around the world. In this way, we can evaluate all potential quantities that could be extracted from these species of seaweed. As mentioned before, seaweed composition can change from season, location, depth and other factors both biotic and abiotic. This table shows all concentrations of the substances that can be expected from these types of biomass. Before commencing any kind of production, it is necessary to carry

out in-depth composition analysis for locally available seaweed, and repeat analysis 2–4 times through the year to see the composition dynamics during the seasons.

TABLE 3. EASTERN BALTIC SEAWEED BIOREFINERY POTENTIAL

	Green algae (*Ulva intestinalis*)		**Brown algae (*Fucus vesiculosus*)**		**Red algae (*Furcellaria lumbricalis*)**	
Carbohydrates (% DW)	31.34–92	[35]–[39]	65.7	[7]	55.4	
Polysacchrides	4.9–59	[35], [38], [40]–[42]	2.31–22	[43]		
Agar					19–28	[44]
Alginate	2–59	[38]				
Furcellaran					40–50	
Cellulose					3.4–5.7	[28], [45]
Proteins (% DW)	9.49–20.60	[35], [37]–[39], [41], [42], [46], [47]	1.4–11.3	[9], [48]	13.1–28	[28], [49]–[51]
Pigments (% of total pigments)						
Chl a	0.394	[52]	0.157–5	[52], [53]	0.228	[52]
Chl b					0.078	
Chl c			0.035	[52]		
B carotenoids			0.2	[53]	13.3–28.6	[28], [52]
Fucoxantin			1			
R-phycoerythrin					0.1	[28]
Xantophyll (mg/kg)					32.8	[50]
Phenolic compounds (% ww water extracts)			18.4	[20], [53], [54]	2.25–4.6	[28], [52]
Lipids (% DW)	1.16–22.0	[9], [39], [47], [55]–[57]	3.95–4.8	[48], [58]	1 %	[49], [50]
Fatty acids (FA)		[9], [55], [56], [59]		[9], [48], [60]		[50], [51], [60]
SFA (% of total FA)	25.0–60.6		24.3		38	
C10:0			2.8–18.8			
C14:0	1.8–5.38		7.5–13.9		5.07	
C16:0	17.9–23.2		9.6–12.1		29.36	
MUFA (% of total FA)	21.81–24.8		47.1		28.80	
C16:1, n7	1.8–6.56		46.9–31.9		8.54	
C18:1, n7	7.6–15.2				4.80	
C18:1. n9	1.5–5.4		46.0		10.22	

PUFA (% of total FA)	14.8–37.1		25.8		14.45	
C16:4. n3	4.8–10.0					
C18:2. n6	4.6–5.8		7.5–10		2.48	
C18:3. n3	8.55–24.1		2.7–3.4		2.05	
C18:4. n3	4.39–14.4		2.2		0.92	
C20:4. n6	1.4–1.5		7.4		1.63	
C20:5. n3	0.8–5.43		3.7–6.7		3.26	
Minerals (mg/100g)		[47], [60]	[6], [7], [70], [76]			[60]
Mg	11		6.7		8.9	
K	12		25		42	
Ca	29		30		3.7	
Na	8.5		18		10	
P	1.7		1		1.2	
Cu	5.7		3.7		6.2	
Fe	5800		290		130	
I	130		260		84	
Mn	180		37		7.5	
Se	0.76		0.08		0.1	
Zn	21		28		23	
Total ASH (% DW)	5.42–29.4	[38], [42], [46], [47], [61]	18.74–30.30	[7], [9], [10], [54]	9–41	[45], [50], [51]

As illustrated in the table, green algae can be rich with carbohydrates, therefore can be used as a source for cellulose and alginate. Red algae are rich with pigments, that also are valuable antioxidants, therefore can be used for nutritional and pharmaceutical purposes. Values of minerals and phenolic compounds in brown algae show that those could be potential use pathways for these types of seaweed. The amount of the substances detected in the biomass depends mainly on the extraction technologies used.

3. TECHNOLOGICAL SCHEME OF SEAWEED EXTRACTION

3.1. Selection of Criteria for Seaweed Biomass Extraction

To determine extraction parameters for an application of seaweed extracts it is necessary to define its field of application before using the macroalgae. The degree of purity of the product and impurities are co-factors that determine the national economy sector in which the extract is to be used. In context of biorefinery, the field of application also determines the number of extraction steps, theoretical structure of the plant and technological steps [62], [63]. Seaweed composition varies significantly between species depending on nutrient availability, seasonality and other environmental factors [63], [64]**.** The choice of species of algae for the desired production is an important factor as it affects not only the ability to produce large-scale biomass but also the composition of valuable compounds under relevant environmental conditions. Although each species of algae offers a unique proportion of proteins, carbohydrates and lipids, some are high in lipids while others are high in protein or

carbohydrates. Selection criteria should be based on their nutrient content as well as their specific use requirements [65].

The following criteria should be considered when selecting the appropriate algae for food, feed and fuel production:

- Constantly and steadily growing (open pond/sea);
- Produce large-scale biomass;
- Produce high quality and relatively constant ingredients of desirable nutritional value;
- Survive and grow seasonally and with daily climate change;
- Exhibit high photosynthesis efficiency and energy conversion rate;
- Provide minimal dirt from attachment to environment;
- Easy to collect and extract substances [66].

Selection of criteria also includes seaweed harvest, pre-treatment and storage methods [67]. According to the Baltic Marine Environment Protection Commission (HELCOM), the following seaweed species are available for biomass extraction in the Baltic Sea: *Furcellaria lumbricalis, Fucus vesiculosus, Cladophora aegagrophila, Laminaria digitata, Chorda filum, Fucus serratus, Chorda tomentosa, Fucus spiralis, Laminaria sacchari* [68]. This list includes two of the Eastern Baltic seaweed species used in this research: *Furcellaria lumbricalis* and *Fucus vesiculosus*.

In order to obtain the highest quality product, there are several steps to increase efficiency of seaweed extraction (Fig. 1).

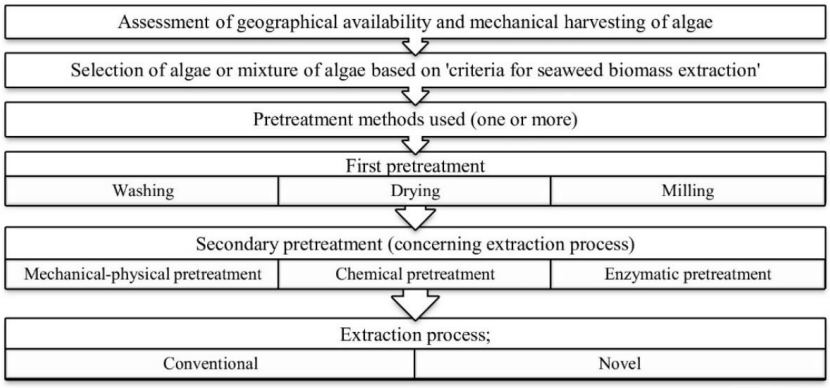

Fig. 1. Scheme of seaweed handling before extraction.

Extraction process of seaweed can be done in different ways depending on product quality parameters and specific biomolecules needed. Based on previous work [62], it is clear that the use of biorefinery principles is needed to ensure the economical and sustainable extraction of algae products. The conceptual model proposed in the previous work states that a high added value product is obtained and biomass is used with maximum efficiency meaning that physical, chemical and biological transformation processes must operate in a sequential system and in a symbiotic operation to ensure efficient, and hence more profitable, product production [62].

Existing scientific literature offers two perspectives on extraction. The first approach is: (a) based on the treatment of substrates under defined conditions with conventional extraction methods, in this case, seaweed extraction to obtain biomolecules, (b) second approach is based on novel extraction techniques and methods that reduce the cost of extraction, reduce the number of extraction steps and increase the yield of biomolecules.

Traditional and innovative methods can be combined to get the best extraction yield at the lowest cost and least impact on the environment. Traditional extraction methods are based on thermomechanical effects and chemical hydrolysis processes, while novel techniques are a significant improvement on existing technologies and are based on the use of physical phenomena (pressure, electric field, ultrasound, microwaves) and biological (enzymes) effects on the matrix [69], [70]. This review article does not address groups of substances or compounds that are relatively unexplored and commercially insignificant.

Just before the extraction of the bioactive substances, it is necessary to process the biomass in order to obtain maximum yield. Secondary pre-treatment methods are divided into three groups of methods that can be used to extract different bioactive substances – lipids, Pigments and sugars [71]:

- Mechanical-physical pre-treatment methods e.g. autoclaving, bead-beating, microwave, sonication, freeze-drying, mechanical crushing, lyophilization and pulsed electric field technology.
- Chemical pre-treatment methods e.g. liquid nitrogen, nitric acid, acetic acid, hydrolysis by NaOH, HCl, H_2SO_4, NaCl solution, nitrous acid.
- Enzymatic pre-treatment methods e.g. cellulase, protease K, driselase, alginate lyase S.

3.2. Conventional Extraction Techniques

Conventional extraction methods use organic solvents (i.e. petroleum ether, hexane, cyclohexane, isooctane, toluene, benzene, diethyl ether, dichloromethane, isopropanol, chloroform, acetone, methanol, ethanol etc.) and acids or alkalis, and water. The main purpose of these aggressive substances is to disrupt cell membranes and allow substances contained in the algae to enter the extraction matrix. According to current trends, the solvent used in the extraction process should be cheap and non-toxic [71].

Several types of extraction methods have been used based on the literature on extraction of bioactive compounds from various matrices. Existing conventional extraction methods include:

1. Hydrodistillation;
2. Soxhlet extraction;
3. Maceration;
4. Percolation;
5. Infusion;
6. Decoction; hot continuous extraction [72].

Effectiveness of these methods depends on various influencing parameters, such as solvent properties (polarity, toxicity, volatility, viscosity, and purity), sample size and concentration, particle size, time, polarity of extractant [73], [74]. Drawbacks of conventional techniques are long extraction time, need for very high purity solvents, energy consumption associated with evaporation of a large amount of solvent, relatively low extraction yield, selective and thermolabile degradation of the components used [75]. Traditional extraction methods are relatively well described in scientific literature (lab scale). Environmental policy and resource

consumption, scientific research viewpoint has advanced green extraction methods (innovative - modern - non-conventional) [69], [70], [75], [76].

Seaweed carbohydrate extraction methods: 1) Food grade – agar, alginate, carrageenan, mannitol; 2) Nonfood grade polysaccharides – fucose-containing sulfated polysaccharides/fucoidan, laminaran, ulvan; their sources, structures and physical properties and uses are well described in Rioux and Turgeon, 2015 [77], in context of hydrocolloids [78] and dietary fibers [76]. Generally, seaweed carbohydrate compounds are extracted using the following methods: i) heating in water; ii) by heating in water with an alkali compound (e.g., sodium bicarbonate) followed by cooling, separation and purification. One of the major drawbacks of the current industrial extraction of seaweed hydrocolloids is the huge time, energy and water consumption. Extraction of seaweed hydrocolloids usually takes 3 hours to achieve optimum yield, depending on the type of hydrocolloids involved. Basically, agar, alginate, and carrageenan extraction should take 2 to 4 hours, but with green methods, it may take up to a few minutes [63], [77], [78]. Seaweed cellulose also belongs to this product group but is not mentioned because existing land-based biomass is a much more accessible and easily obtainable source of cellulose.

Extraction of seaweed proteins, peptides, and amino acids is mainly done on a laboratory scale. Main methods for extracting seaweed protein fractions in the context of traditional methods are solvent extraction, proteolytic hydrolysis (enzymes from microorganisms, plants), hydrolysis by proteolytic microorganisms during fermentation. The overall view of protein in seaweed and extraction methods, is well considered in Pangestuti and Kim, 2015; Bleakley and Hayes, 2017; Kazir *et al*., 2019 [79]–[81]. Algae proteins are extracted by water, acid and alkali methods followed by several centrifugations, dialysis and recovery steps using methods such as ultrafiltration, precipitation or chromatography. Successful extraction of algae proteins can be greatly influenced by the availability of protein molecules, which are significantly inhibited by high viscosity and anion cell wall polysaccharides such as alginates and carrageenans [80].

Macroalgae are generally considered unsuitable for the production of oil-based products since most species have a low total lipid content <5 % by weight [64], [82]. Oils from algae, plant biomass are extracted through a variety of methods including organic solvents and water [83]. However, the green extraction process is better suited for low oil oxidation and high yield [84]. The most common traditional lipid extraction methods are water vapour extraction or solvent extraction, such as soxhlet [72].

Seaweed contains a large amount of minerals, up to 30 % of dry weight. Minerals include Na, Ca, Mg, K, Cl, S and P and trace elements (Fe, Zn, Mn, Cu). Mineral content of seaweed is generally high (8–40 %). Minerals and trace elements essential for human consumption are predominantly in brown and red algae [64], [82]. Part of the minerals from the algae biomass can be extracted by incineration and acid treatment of the resulting material [85].

3.3. Novel Extraction Techniques

Extraction of biologically active compounds from macroalgae can be conducted through novel methods. These methods are often qualified as green methods. Green methods have several advantages over conventional, including reduced amount of solvent used (including its recovery), shorter time of extraction, and technological performance at lower temperatures. These methods also include improved selectivity for isolation of the desired compounds while avoiding the formation of by-products during extraction and adverse reactions [86]. Most of the extraction methods listed below are considered “green” because they meet the standards that have crystallized in green extraction [87], [88]. Compared to

conventional extraction methods, the main advantages of innovative extraction methods are higher efficiency, use of water, renewable raw materials, more environmentally friendly treatment conditions, significantly reduced use of hazardous chemicals, safer co-solvents, energy efficiency, reduced derivatives [72]. Based on the reviewed papers and others, there are six novel techniques for biomolecule extraction from seaweed [67], [71], [72], [74], [75], [86], [89]:

- Supercritical fluid extraction (SFE) – SC-CO_2;
- Microwave-assisted extraction (MAE);
- Ultrasound-assisted extraction (UAE);
- High-pressure methods (HPM);
- Ionic liquids extraction (ILE);
- Enzymes-assisted extraction (EAE);
- Pulsed electric field extraction (PEF) (see Annex Table 1).

Supercritical fluid extraction (SCF-CO_2) applies supercritical fluids to separate compound from matrix using SC-CO_2 as solvent. The most important factors affecting the extraction are pressure, temperature, time and SC-CO_2 flow rate. The prerequisite for the method is extraction in a dry environment where humidity is below 20 % in the extraction matrix. As a result, SCF-CO_2 extracts non-polar materials. The co-solvents used, such as methanol or ethanol, make the spectrum and method of extraction more efficient (for polar materials).

Microwave-assisted extraction (MAE) uses microwaves to warm the solvents in contact with solid matrix to extract contents from the solution. The solvents used, the temperature range, the time of extraction and the power used affect the MAE. This method makes it easier to obtain a spectrum of different polar compounds. The selectivity is affected by the solvent used.

Ultrasound-assisted extraction (UAE) utilizes ultrasound to penetrate solvents in contact with the solid matrix to extract content from the solution. The advantages of the UAE method are the low operating temperatures, efficient cell disruption and various extraction media. Disadvantages are high energy consumption and low extraction volumes, which significantly complicate the technology scale-up.

Enzymatic hydrolysis uses exogenous enzymes to digest material. The efficiency of the method is influenced by the enzyme used, its activity and concentration, temperature, pH. The method is ineffective at elevated temperatures due to enzyme denaturation. Hydrolysis is stopped by heating the material.

High-pressure methods use solvents under critical conditions (increased temperature and/or pressure) to speed up extraction rate of solvents used. There are different variations of high-pressure methods. For example, "Subcritical Water Extraction (SWE)" and "Accelerated Solvent Extraction (ASE)". The influencing parameters are pressure, extraction temperature, solvent concentration and time. In the case of water as a solvent and other solvents, these parameters differ significantly (see Annex Table A1).

Ionic liquid extraction uses specially designed ionic liquids to extract a wide range of compounds. Applied extraction conditions strongly depends on target compound. Pulsed electric field extraction utilizes an electric field to disintegrate cell matrix.

4. CONCLUSION

Literature analysis shows several reviews on extraction of biomolecules from biomass in different contexts, like conventional and novel extraction, as well as pre-treatment of algae

biomass, compounds from other marine organisms such as fish and crustacean. Our review shows there are many differences in bioactive compounds between Baltic seaweed species. It is possible to extract main seaweed polysaccharides, proteins, lipids, pigments, minerals using novel methods. The studies referred to in this review show the possibility of using eastern Baltic seaweed biomass to extract different kinds of valuables. Even though the quantities of valuables can change a lot due to environmental parameters, this analysis can be used to predict and plan Baltic seaweed application pathways. Novel methods are characterized by more environmentally friendly extraction conditions, high power consumption, need for ongoing optimization of processes. Availability and quality of algae species play an important role in integrating these extraction methods (scale-up). Seaweed biorefinery focuses on single product extraction, newer literature shows increase in products and extraction techniques. For development of more than single phase extraction system, further research in different directions, regarding optimal process parameters, consumption of chemicals (co-solvents), biotechnology and extraction vessels is needed. Our analysis also shows that most extraction processes and results are obtained from laboratory-scale experiments and there is a need for industrial scale data. Limited technologies and unpredictable amounts and quality of seaweed biomass still could be serious problems to limit extraction. This review can be used as a tool to consider ways to apply cascade principle to extraction process.

Still many challenges remain with respect to use of Baltic seaweed for chemical production, such as seaweed availability and large seasonal variation in the chemical and nutritional composition of the seaweed. Seaweed biomass varies between species, locations, season and the yields and type of products obtained are highly dependent on the processing technologies. Further research is suggested to analyse seaweed biomass and change of biomass composition during the different seasons and locations.

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ANNEX

TABLE A1. OVERVIEW OF NOVEL METHODS FOR SEAWEED BIOACTIVE COMPOUND EXTRACTION

Extraction technique Conditions (C) and influencing parameters (IP)	Seaweed species under investigation	Extracted bioactive compounds	Application outlook	References
Supercritical CO_2 (SC-CO_2) (C) Pressure 9.1–40 MPa, Temp. 25–75 °C, Time 50–360 min, >2 mL CO_2/min Co-solvents: EtOH 0.5–15 % Sunflower, soybean, canola oil 0.5–2 %. (IP) Water %, T °C, pressure. Flow of CO_2; Extraction type: continuous, co-solvent, soaking.	*Cladophora glomerata, Chara fragilis, Chondrus crispus, Dictyopteris membranacea, Fucus serratus, Gracilaria mammillaris, Hypnea charoides, Hypnea spinella, Halopytis incurvus, Porphyra sp., Laminaria digitata, Sargassum muticum, Sargassum vulgare, Ulva clathrata* *Undaria pinnatifida, Polysiphoniucoides, Saccharina japonica, Sargassum horneri,* *Undaria pinnatifida, Ulva flexuosa,*	Fucoxanthin, polyphenols, phlorotannins, carotenoids, pigments, fatty acids, cytokinins, auxins, microelements, macroelements	High investment cost; Operates in elevated pressure (safety); High power consumption.	[84], [86], [90]–[93]
Microwave-assisted extraction (MAE) (C) Power 300–1000 W; Frequency – 2450 MHz; Temperature – 10–185 °C; Solvents – EtOH, H_2O, acetone, propanol, ethyl acetate, 0.1 M HCl, petroleum ether, ethyl acetate; Time – 2–30 min. (IP) Particle size, solvent used, time, capacity, and frequency of microwave	*Ascophyllum nodosum, Carpophyllum flexuosum, Carpophyllum plumosum, Caulerpa racemose, Carpophyllum flexuosum, Ecklonia radiata, Enteromorpha prolifera, Fucus vesiculosus, Padina pavonica, Sargassum thunbergii, Monostroma latissimum, Ulva meridionalis, Ulva ohnoi, Ulva prolifera, Undaria pinnatifida,*	Polysaccharides, alkaline, galactans, carrageenans, agar, phlorotannins, phloroglucinol, iodine, bromine, phenols, phytosterols, phytol	Hard to scale up; Generation of heat leads to degradation of thermolabile compounds; Low efficiency when using volatile solvents.	[86], [94]–[98]
Ultrasound-assisted extraction (UAE)	*Hormosira banksia, Ascophyllum nodosum, Ascophyllum nodosum, Laminaria hyperborean, Ecklonia cava, Gelidium*	Polyphenols, laminarin, phycobili-proteins, taurine,	High power consumption and difficult to scale up.	[99]–[103]

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(C) Ultrasound Equipment – Ultrasonic bath, Ultrasound probe; Frequency – 20–60 kHz; Power – 100–750 W; Temperature – 20–60 °C; Time – 2–720 min; Solvents: ethanol, 0,03 M HCl, methanol, water; Small sample – 1–10 g. (IP) Ultrasonic frequency, power, time and medium.	*pusillum, Sargassum muticum, Osmundea pinnatifida, Codium tomentosum, Laurencia obtuse, Porphyra yezoensis*	fucose, uronic acid, antioxidants, prebiotic compounds		
High pressure methods "Subcritical Water Extraction (SWE)" "Pressurized liquid extraction (PLE)" "Accelerated solvent extraction (ASE)" (C) Water extraction: Pressure – 1.3–52 MPa; Temperature – 50–420 °C; Time – 5–25 min; Solvent Extraction: 50–200 °C; 3.5–20 MPa (IP) Temperature (°C), solvent concentration (%), static time (min), pressure (psi), weight of sample (g), and flush volume (%).	*Ascophyllum nodosum, Fucus spiralis, Codium fragile, Cystoseira abies-marina, Sargassum muticum, Padina pavonica, Fucus serratus, Laminaria digitata, Gracilaria gracilis, Porphyra spp., Sargassum vulgare, Undaria pinnatifida, Halopitys incurvus, Himanthalia elongate, Pelvetia canaliculata, Ulva intestinalis. Saccharina japonica, Ulva lactuca, Fucus vesiculosus, Dictyota dichotoma, Cystoseira baccata, Himanthalia elongate*	Polyphenols, phlorotannins, fucoidan, total organic carbon, minerals, monosaccharides, amino acids, polar compounds; fatty acids	Not suitable for thermolabile compounds; Less selective than SFE.	[86], [104]–[106]
Enzyme-assisted extraction (EAE) (C) Time 1–4 h Temperature 40–60 °C The ratio of enzyme to substrate ~ 0.5–5 % (IP) Type, activity and amount of enzyme used, pH. Absence of endogenous enzymes.	*Sargassum horneri,brown seaweeds, Undaria pinnatifida, Sargassum coreanum*	Antioxidants, fucoxanthin, fatty acids, polysaccharides	Costs of enzymes are very high; Selectivity of enzymes.	[107], [108]

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Ionic liquids extraction (ILE) (C) Chemicals: For phenolic extraction 0.5 M [C4C1im][BF4], 1:32 w/v mixing ratio; time 24 h, stirring at 500 rpm; Optional extraction vessel and pressure. Extraction conditions (ionic liquids used) strongly depends on target compound. (IP) Chemicals, vessel, pressure used.	*Kappaphycus alvarezii,* *S. japonica*	Phenolic compounds, polysaccharides, carrageenan, terpenoids, alkaloids	Some ILEs require purification process	[109]–[111]
Pulsed electric fields (PEFs) (C) field strength of 0.5–1.0 kV/cm treatment time 100–10,000 µs or 1–10 kV/cm and shorter time (5–100 µs) (IP) Field strength, time, conductivity of intact and disintegrated cells	–	Phenols, proteins	Optimization of process by using different parameters is needed. These include pulse duration, pulse interval, electric field strength, or other electrical pulse shapes.	[74], [112]

EVALUATION OF REED BIOMASS USE FOR MANUFACTURING PRODUCTS, TAKING INTO ACCOUNT ENVIRONMENTAL PROTECTION REQUIREMENTS

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Evaluation of reed biomass use for manufacturing products, taking into account environmental protection requirements

I. Muizniece*, V. Kazulis, L. Zihare, L. Lupkina, K. Ivanovs and D. Blumberga

Riga Technical University, Institute of Energy Systems and Environment, Azenes iela 12/1, LV-1048 Riga, Latvia
*Correspondence: indra.muizniece@rtu.lv

Abstract. In many countries reed is considered as invasive or unnecessary plant, because it is spreading rapidly, causing decrease in biodiversity and creating unacceptable living conditions for many bird species in their natural habitats. Due to environmental considerations it is necessary to cut reed, to decrease their over exceeding growth. Reed burning or leaving for decomposition on fields, that has been practiced until now, creates additional carbon dioxide air pollution. Therefore, the question on what to do with cut reed has become vital from environmental protection perspective. In addition, this question applies to bioeconomy principles in compliance with their use in national economy, which makes it clear, that solutions for the use of reed biomass for production have to be found. But any production process can leave a negative effect on surrounding environment. Further to product production, economic motivation, possible market and availability of resources are primarily essential to see whether it is worth to produce the product at all. Therefore, reed biomass use possibilities in production have to be analysed as a complex question, taking into account environmental and climate, economic and technological aspects. In this study, solutions to perspective reed biomass use are evaluated, considering environmental protection requirements. For this task, multi-criteria analysis method TOPSIS is used, which includes 11 environmental and climate, economic and technological criteria. Evaluation includes both – already existing and new products that are divided in 3 sectors: power industry, construction and other products. Results of the research clearly state, which of reed biomass made products are perspective, taking into account not only traditional economic and technological aspects, but also environmental and climate aspects.

Key words: reed, multi-criteria analysis, TOPSIS, bioeconomy.

INTRODUCTION

Reed *(Phragmites)* is a perennial grasses herb that forms a dense and broad crops. Reed is found in wetlands, in standing water, in coastal areas and even as floating islands in the water. Reed is very adaptable to changes in the environment and can grow in many ecosystems and plant communities, including wetlands, coastal swamps, inland lakes and rivers, mountains, deserts and cities (Meyerson et al., 2016). In ecological succession water bodies and wetlands overgrow with reed and, when reed stands are gradually aging, they produce sufficient fertilizer and waste, draining the area with time and creating the possibility of developing bushes and trees in this environment. Reed is considered as one of the most invasive plant species in the world (Uddin et al., 2017).

Over the past 150 years, reed has grown exponentially and most reed stands form a dense monoculture because reed is monodominant (Dubrovskis & Adamovics, 2012). Reed provides cover for fish and invertebrates in lakes and rivers, produces oxygen, and is a nutrient for individual fish and other animals.

Changes in the chemical composition of the soil which are caused by human intervention (e.g. agriculture, livestock farming, industrialization, nutrient deposition, etc.) can create conditions that favor the introduction of reed in this ecosystem (Uddin & Robbinson, 2018). The expansion of invasive plant species can have dramatic effects on local ecosystems (Gordon, 1998). Changes in reed volume can also be considered as an indicator of the health of water bodies. Also the number of reduced reed can be related to water quality problems – pollution and herbicides. From 1,170,000 measurement sites in 33 European surveyed countries was determined that 35% of soil and groundwater pollution was made up of heavy metals (Panagos et al., 2013). Reed absorbs not only nutrients from the water body, but also polluting elements. The reed absorbs nitrogen (N) and phosphorus (N) which are dissolved in water, as well as heavy metals, therefore reed can be used to purify water bodies from these elements which increasingly come into water bodies as a result of human activities from agricultural land fertilization, waste, scum, overflows etc. (Cicero-Fernandez et al., 2017). Reed is intensified due to agricultural fertilizers that enter into the soil. Reed best absorbs nutrients up to 3-year age, because in this period reed are growing very fast (Adler et al., 2008). Reed indirectly affects the nitrogen cycle, because on the roots of reed certain denitrifying bacteria can grow. Reed promotes the sedimentation of suspended solids by reducing the rate of flow (Zhu et al., 2015), prevents erosion by stabilizing the soil (Horpilla et al., 2013). Although reed, on the one hand, competes with other plants, they can also contribute to the diversity of the biotope by increasing the wealth of fish and invertebrate taxonomy (Thomaz et al., 2007).

Reed can compete and occupy another plant site, as they have several benefit:

- reed can reach nutrients with rhizomes where they are not available to other plants;
- reed can reach nutrients with rhizomes where they are not available to other plants;
- they can change the soil by creating favorable conditions for them (Windham & Lathrop, 1999);
- reed genetically identical stalks can be interconnected with rhizomes, thus forming a single plant and it is not known how big and the old reed clone can develop. Stems that grow under unfavorable conditions can get nutrients from the rhizomes;
- reed can easier survive at rising water levels than other plants;
- increased levels of nitrogen contribute to reed reproduction;
- the rise of the CO2 level in the atmosphere is promoted by plants such as reed with C3 photosynthesis pathway.

Up to now reed is mainly perceived as an invasive plant, whose further spread should be limited to preserve biodiversity. Rather than as a valuable, so far not fully used and undervalued bioresource which could be used to produce a variety of products, including high value added products. On the issue of reed management and utilization, its dual nature appears – on the one hand, the requirements of environmental protection, which restrict the area of reed, and, on the other, business interests, where the economic justification and long-term availability of the resource are the most important. Therefore, this issue needs to be seen as a complex system in which one process has an impact on

the other in order to find a compromise solution for the sustainable use of reed in the national economy, while respecting environmental protection requirements.

Currently, the use of reed in the national economy has the following positive aspects:

- do not have to be cultivated (no planting and fertilization required);
- grow in water bodies (places that are not suitable for the production of other crops and do not compete with the food industry);
- the use of reed in the national economy reduces the emissions of CO^2 and CH_4 in the atmosphere;
- clean up sediment of water bodies from nitrogen, phosphorus and the content of heavy metals if they are harvested.

By studying the distribution of reed, the possibility of using reed biomass in the national economy for the production of various products and its environmental impact, the dual nature of the investigated issue has been revealed:

1. it is necessary to restrict the spread of reed to prevent the overgrowth of the water bodies and to preserve the biodiversity what best to do in the summer when reed is green;
2. in order to use reed biomass as a raw material to production, entrepreneurs are primarily interested in the economic justification of this product, the long-term availability of the market and raw materials.

The first point is mainly for municipal and lake operators, while the second one is for entrepreneurs. In order to achieve a sustainable solution in the long term, it is necessary to find a compromise between these two sides, and only then will it be possible to ensure that the reed area does not uncontrolled increase and does not become an invasive plant that reduces biodiversity, while at the same time benefiting from its economic and social benefits.

Therefore, the research subject of this study is: Which products are prospective from reed to observe the environmental protection requirements?

By analyzing literature on the various products from reed biomass and from discussions with environmental protection requirements, it was concluded that in order to combine the interests of nature conservation and business, the most problematic issues are:

- **reed mowing time**

To reduce the area of reed, they need to be mowed in the summer when they are green, but for most products is required dry reed that is mowed in winter, because the transportation and drying of green reed is not economically viable. Till now there are no information about experience about possibility to mow reeds during the summer and then dry mowed reeds naturally in the field, as it is done with hay. But that would be possibility how to get and transport dry reed and also reduce its areas. If reed was only mowed in winter for product production, it would not affect the further spread of these areas, only reducing the size of the decomposition of reed biomass and pollution and emissions.

- **long-term stable and predictable reed biomass availability**

In order to start commercial production of a product using reed biomass, it will be essential for any entrepreneur to have the resources available in the required amount and in the long-term. At present, there are no research reports available to report developers that would clearly demonstrate the specific volumes of reed biomass that will be

available now and in the future in a specific area. In addition, starting the production, where the raw material is biomass of reed, the necessary amount should be available near the production site. Also, the diverse management of reed does not guarantee the availability of this resource. As a limiting factor, the seasonal nature of reed production should also be mentioned.

Therefore, the authors of this study came to the conclusion that for using reed biomass in the national economy is recommended to produce products for which:

- **reed biomass would be an alternative to the use of any other biomass in whole or in part**

If reed biomass could be used to produce products for which currently is used another biomass or replace part of another biomass, then the availability of resources would not be so significant. In this case, the use of reeds would depend solely on their relevance to the particular product and on the economic justification for their purchase and use, which might be even more advantageous in some cases if it is compared to other types of biomass. As well as the seasonal nature of reed extraction would no longer be decisive for them to not to be used when it is economically viable.

- **the moisture content of reed biomass is not significant**

In this case, there is a greater chance of getting raw material from the reed areas that are mown both in summer and winter. There will only be a difference between the cost of transportation of green and dry reed.

In addition, the principles of bioeconomy must also take into account in the economic development, which include the rational and efficient use of science-based local bioresources (European Commission, 2012; Blumberga et al., 2016). The use of reed for the production of products is absolutely in line with the principles of biotechonomy, because it has so far been incomplete used and undervalued resource, which was mostly considered to be cumbersome and associated with the extra costs of managing it. Although in this study is examined the possibility of using reed biomass for the production of various products, including products with low added value (direct energy combustion), it is clear that biomass of reed can also be used to produce products with higher added value (e.g., an extract that can be used in pharmaceutical industry and cosmetics).

The above-mentioned restrictive factors and many others have to be taken into account in order to determine the prospective use of reed biomass for the production of products in order to promote not only development of national economy and the use of a bioresource that is so far not fully exploited in accordance with the principles of bioeconomy but also to comply with environmental protection requirements.

Therefore, the aim of the study is to carry out a feasibility study on the use of reed in the national economy, observing environmental protection requirements. A multicriteria analysis method was used to achieve the goal, which allows for the consideration of different, mutually incomparable factors, also taking into account the importance of each of them in this case.

MATERIALS AND METHODS

In this study, the multi-criteria analysis (MCA) – TOPSIS (*Technique for Order Preference by Similarity to Ideal Solution*) method – was used (Jahan et al., 2016). It is a type of analysis that takes into account the influence of several factors. An analysis of

MCA TOPSIS provides an assessment of the situation as close as possible to the real situation. With this method it is possible to compare several alternatives and identify the best of the considered options, taking into account the various influencing criteria. In this study, alternatives are various products from reed biomass, which are not mutually compatible without an analytical approach. Multi-criteria analysis in the TOPSIS method evaluates the alternatives in relation to the ideal possible solution. The alternative which is closest to the ideal variant is considered as the best. The TOPSIS method is based on five calculation steps. The first step is to gather information about alternatives and selected criteria. In the second step of the calculation, these data are normalized. The next step is to normalize the data with the weight values and calculate the distance from the maximum and minimum values (distance from the ideal variant) (Lu et al., 2007; Doumpos & Grigoroudis, 2013; Ishizaka & Nemery, 2013).

To use this method (Fig. 1), information and data from scientific literature and other reliable sources of information (project reports, information which is provided by related industries, project data, etc.) were used to compare products from reed biomass. In the case of lack of data, an environmental engineering assessment, which is based on information on similar products, was taken into account.

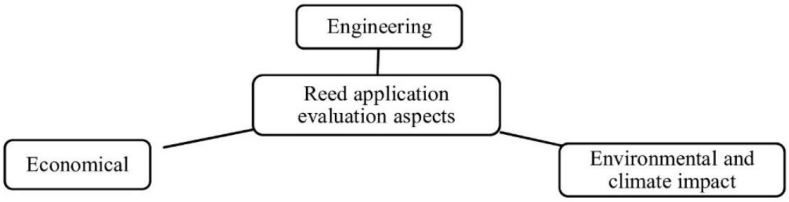

Figure 1. Grouping of evaluation aspects of reed application.

The used method – MCA TOPSIS – has proved itself in a similar study which was carried out by the Institute of Energy Systems and Environment of RTU 'Forest biomass – new products and technologies' in 2016 where was analyzed the potential for commercialization in Latvia of various innovative products that can be made from low-value forest biomass (RTU, 2017).

In this study, in order to determine the most promising products from reeds in the TOPSIS method in accordance with the requirements of environmental protection, the main factors, which are affecting the research issue, were defined as 11 indicators (Table 1).

To determine the significance or weight of each of the raised factors, the assessment of nature conservation experts was used. Using this method to evaluate the product, the subjectivity of the evaluators is reduced because it is based on reasonable numbers or expert judgment.

Table 1. Indicators which are included in the multi-criteria analysis

Indicators of engineering index	Indicators of the climate and environmental impacts	Economic Indicators
• The stage of manufacture of the product; • used amount of reed resources (%) in the final product; • the complexity of the technological process; • the possibility to replace other biomass with reed biomass which so far is used to produce the particular product	• The amount of CO_2 emissions which is arisen in the production process of product; • the consumption of resources (energy, water, chemicals) in the production process of the product; • the impact of raw material extraction and production processes on the environment (air, water, soil, living organisms); • the impact of the product on human health	• product outlet market; the necessary investments for launching the product; • product added value

RESULTS AND DISCUSSION

Within the framework of this study, using the TOPSIS multi-criteria analysis, 11 products were analyzed in order to identify the most promising products from reed, observing environmental protection requirements: thermal insulation panel of reed, sound insulation panel of reed, roofing of reed, fuel from reed for direct combustion, reed composite material (with clay), reed composite material (binder of fossil origin), biogas, extract, bioethanol, activated carbon, paper and cardboard. First of all, the selected products were evaluated in terms of sectors: construction, energy and other products that are not relevant to the two sectors which are mentioned above.

The weight which is given by experts in the field of nature protection to the included indicators in the multi-criteria analysis is summarized in Table 2. The weight of all indicators should be 100. As it can be seen, according to experts, the most significant indicator is the impact of the raw material extraction and production process on the environment (air, water, soil, living organisms) and the consumption of resources (energy, water, chemicals) in the production process of the product.

Table 2. Results of determining the weight of multi-criteria analysis indicators

Criterion	Weight
The stage of manufacture of the product	11
Used amount of reed resources (%) in the final product	6
Outlet market of product	11
The complexity of the technological process	8
The amount of CO_2 emissions which is arisen in the production process of product	5
The consumption of resources (energy, water, chemicals) in the production process of the product	12
The impact of raw material extraction and production processes on the environment (air, water, soil, living organisms)	17
The impact of the product on human health	9

The possibility to replace other biomass with reed biomass which so far is used to produce the particular product	7
The necessary investments for launching the product	8
Product added value	6

The results of the multi-criteria analysis are summarized in Table 3.

For the construction industry, five products were analyzed, from which sound or thermal insulation panels of reed were equally well and promising, and the most ancient and most commonly used type of reed – the product – roofing of reed. The production of reed composite material with binder of fossil origin is definitely not supported because the production of this product does not match the requirements of environmental protection.

Table 3. Results of the evaluation of the product from reed using a multi-criteria analysis

Product	Result of Multi-Criteria Analysis	Place
Thermal insulation panel of reed	0.826	1
Sound insulation panel of reed	0.826	2
Roofing of reed	0.789	3
Direct combustion	0.685	4
Reed composite material (with clay)	0.628	5
Biogas	0.578	6
Extract	0.559	7
Bioethanol	0.538	8
Reed composite material (binder of fossil origin)	0.469	9
Activated carbon	0.393	10
Paper and cardboard	0.343	11

For the energy sector, three products were analyzed, of which the best result was fuel from reed for direct combustion. This is mainly due to the fact that the launch of this product requires relatively less investment because the production process is simpler.

In the 'other products' category were included only three products. Of the analyzed, the greatest potential has extract from reed. In this case, for reed extract production, extraction in water technology without any chemical adding is used. So it is environment friendly production process. It should be noted that this product has the highest added value of all analyzed, since it can be used in pharmaceutical and cosmetic production, and its production corresponds to the principles of bioeconomy.

By comparing all of the eleven analyzed products from reed, the most promising products, in compliance with environmental protection requirements, are reed panels for thermal insulation and sound insulation and roofs from reed (Table 3). The first three products with the highest ratings in the multi-criteria analysis are products from the construction industry. These are not products with the highest added value, but in any case, from the environmental and climate point of view, are better than products for energy sector, as they can replace the products which are made from fossil fuels and temporarily store carbon so that it does not enter the environment and does not contribute to climate change.

The results which are obtained in this study are considered as a feasibility study in order to have a clear direction for future research. In order to more fully assess the compliance of the most promising products with the requirements of environmental

protection, it would be necessary to make and compare their life cycle analysis to determine their long-term impact on climate and environment. From a business perspective, for the most promising products is also required detailed economic and market analysis.

The results show that, in view of environmental protection requirements, the most promising products are those whose production is required dry, winter-mown reed. Which, in turn, does not coincide with the interests of managers of reed areas who want to reduce these areas and therefore mowing is done in the summer when the reeds are green. In order to find a solution to this controversial situation, planed and well-considered management of reed area is needed, which would include those areas where it is necessary to eliminate reed stands, mow in summer, and the rest in winter, in order to ensure availability of the resource in the long term.

CONCLUSIONS

Reed is a widespread invasive plant, the management and control of reed is complex and resource-intensive. From an environmental point of view, reed areas should be reduced. But from the point of view of the bioeconomy and sustainable use of resources, reed is little used and undervalued bioresource that could be used to produce products and get economic benefits. There is a number of inconsistencies between the two sides in terms of availability and quality of resources, which is why it is best to use reed as an alternative to other bioresources for the production of products.

A multi-criteria analysis has been conducted to determine which products can be promising from reed biomass with respect to environmental protection requirements. The obtained results show that the most promising are products related to the construction industry – thermal insulation and sound insulation panels and roofing from reed. However, for the production of these products is required dry, winter-mown reed, the harvest of which would not affect the spread of reed areas. Therefore, for the management of reed areas is required planned and prudent management that would include areas where it is necessary to eliminate reed stands, mow in summer, and the rest in winter, in order to ensure the availability of reed biomass resources for long-term production of products and to prevent uncontrolled reed areas.

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PLUG FLOW DIGESTER WITH ASSISTED SOLAR HEAT: FEASIBILITY OF SMALL-SCALE SYSTEM

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Psychrophilic plug-flow digester with assisted solar heat – small-scale system feasibility

K. Ivanovs[1,2*], D. Blumberga[1]

[1]Riga Technical University, Institute of Energy Systems and Environment, Āzenes iela 12/1, LV-1048 Riga, Latvia
[2]Liepaja University, Institute of Science and Innovative Technologies, Lielā iela 14, LV-3401 Liepaja, Latvia
[*]Correspondence: kaspars.ivanovs@hotmail.com

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Abstract. Paper discusses using a low-temperature biogas reactor with a solar support system technology as a management tool of biodegradable waste in small scale. A feasibility study looks at primary factors affecting anaerobic digestion process and solar heat production, design examination of a solar heating for anaerobic digester and possible technology application, also defines the multilocality of biogas, illustrates diffusion of innovation for diversification of biogas production. Analysis confirms solar heat increases efficiency and production of biogas, decreases costs and toxicity of digestate. Results show that for implementation of technology in rural areas further research in socio-economic, sourcing of feedstock and customization is needed.

Key words: plug-flow, anaerobic digester, solar heat, low-temperature, multilocal.

INTRODUCTION

Energy is a fundamental constituent in development since it stimulates and aids economic growth (Omer, 2018). The need to provide affordable energy to underprivileged communities is crucial in a global context. It is also essential for less developed European countries. Finding substitute, clean and cost-effective energy sources today has become a crucial challenge for households and national economies. One of the main factors determining this is the rising price of fossil fuels and taxes on energy sources. Economic welfare and quality of life in most countries are linked to consumption of energy, a prime factor of economic development and a traditional development indicator. Energy demand is a major source of climate change, resource use, and limiter of people's living conditions. The deployment of renewable energy on a large scale has great potential to mitigate several challenges related to ecological imbalances, significant fuel demand, health and quality of life in rural and urban areas. Energy sector stability and sufficiency are crucial for the growth of developing countries, economically less developed regions and for raising society's standard of living. The country's energy development can be met by several renewable energy sources. Renewable energy sources are energy sources that have less negative impact on the environment than conventional fossil energy. Most of the investments in the

renewable energy sector are spent on materials and personnel, on building and maintaining equipment, not on expensive energy import (Balasubramaniyam et al., 2008; Rajendran et al., 2012; Shahzad, 2012). One of the promising forms of renewable energy that can help promote additional energy production is biogas production by anaerobic digestion process. Anaerobic digestion can be locally used for integration of sustainable renewable energy source solutions. Biogas is energy source that can be used as a substitute for natural gas (Mccabe and Schmidt, 2018). Also, biogas has the potential to meet the energy demand of the rural community, it can be used as a substitute for firewood or manure. Anaerobic digestion is a solid waste management tool (Bruno et al., 2009).

The production of the biogas takes place in mainly three ways, due to these needs: (1) biogas is produced in small reactors (households) in developing countries for biodegradable waste treatment and the production of gas primarily for cooking or heating applications (Gupta et al., 2012; Karanja and Kiruiro, 2003); 2) manufacturers in developed countries produce electricity and syngas from waste and energy crops (Korres et al., 2013; Miltner et al., 2017); 3) manufacturers use the anaerobic digestion process as a waste management tool and the energy produced is used to promote the company's energy self-sufficiency (Achinas et al., 2017; Nnali and Oke, 2013).

In the anaerobic digestion process, organic material is degraded by bacteria in an anoxic environment, transforming substrates (feedstock) into a blend of CH_4 and CO_2 with a few other gases such as H_2S, water vapor, and digestate – material remaining after the anaerobic digestion of feedstock. Methane formation in anaerobic digestion consists of four different processes, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Anaerobic digestion has been used for waste treatment and biogas recovery from many types of organic waste. Its numerous benefits, such as recovery of renewable energy, waste volume reduction, and reduction of odor, are well documented (Wellinger et al., 2013). Biomethane can be produced by psychrophilic (0–25 °C), mesophilic (25–45 °C) and thermophilic (45–70 °C) bacteria. In the production of industrial-scale biogas temperature is chosen from 37 °C to 70 °C, because in high-temperature conditions anaerobic digestion is faster and digestate is better disinfected (Seadi et al., 2008). This approach produces more gas in a shorter time, and retention time of the feedstock in the bioreactor is reduced. Such a method applies to a biogas plant for commercial gain. However, this approach involves some drawbacks in the context of efficient use biomass, such as inefficient processing (digestion) of raw materials, process instability (inhibition), a potential decline in biogas production and stoppage of the process. In-depth knowledge about microorganism community dynamics are needed for more understanding of and controlling the process. The formation of biomethane at low temperatures (10–20 °C) is approximately twice as slow as in the mesophilic (25–42 °C) conditions. In general, such a biomethane production process is slower, but the process is more stable. Feedstock in bioreactor require twice as much retention time and the amount of biomethane produced per day is lower. Longer hydraulic retention time provides better recycling efficiency of biomass and biomethane concentration in biogas is higher (Gruduls et al., 2017). And less likely inhibition of bacteria because of volatile fatty acids, ammonium, heavy metals. Based on the basic principles of bioeconomy, the production of biomass in psychrophilic conditions is

the most suitable technology for recycling biomass waste. Biogas production can be carried out from 100 ml to 10 000 m^3 bioreactors (Venkata Mohan et al., 2016; Sol-sánchez and Zúniga-gonzález, 2018).

The solar collector is a special heat exchanger that converts solar irradiation energy to the thermal energy of the working fluid in solar thermal applications. To use solar heat, the solar collector absorbs solar radiation as heat that is then transferred to the working fluid (air, water or oil). Solar collectors are usually divided into two categories according to concentration factors: non-concentrating collectors and concentration collectors. The non-concentrating collector has the same intercept zone as its absorbing zone, while the solar collecting concentrating solar collector usually has concave reflective surfaces to intercept and concentrate solar radiation on a much smaller capture zone, resulting in increased heat flow so that the thermodynamic cycle can achieve a higher Carnot efficiency working at higher temperatures. The flat-plate collector is a non-concentrating solar collector, the simplest and most widely used. To prevent overheating of the system, the heat absorbed by the suction plate must be quickly transferred to the working fluid. After the solar collectors have collected the heat, it must be efficiently stored. Thus, it is very important to create an economical energy storage system (Tian and Zhao, 2013). Absorbent plate, usually a metal, is connected to a series of risers (or tubes) which are connected to the upper and lower tubes of larger diameter, called headers. Solar energy generated on the absorption plate is transferred to the fluid flowing through the pipes. Cooled water gets to the lower header and the heated water leaves the top header. Receiver is usually located in an isolated box with a transparent lid. The flat plate collectors have a temperature range of about 30–80 °C. Flat collectors can be made of different materials and different construction methods are possible. As a result, they are designed for different applications, they may have different performance and costs. For example, two layers of glazing are sometimes used to improve thermal performance (MPMSAA, 2009).

Regardless of what temperature anaerobic digestion takes place, energy is needed to keep the process at a reasonable temperature and time to produce biogas. Researchers need to find a way to provide the necessary energy for a minimal cost. If the temperature is below 15 °C in anaerobic digestion biogas production become insignificant. This problem can be overcome by using solar energy to support a biogas reactor or plant (Alkhamis et al., 2000; Chamoli et al., 2011) or by using electricity or heat from grid. Heat in biogas digester is required in three aspects: 1) the heat required to raise feedstock temperature; 2) to compensate for heat losses within the digester; 3) to compensate for losses that could occur in the pipelines between the heat source and the bioreactor. The heat required is provided by a collector that absorbs solar radiation and transforms it into the heat absorbed by the heat transfer fluid passing through the collector (Gupta, 2010a).

Unequivocally mini-scale psychrophilic biogas production is disadvantageous from an economic point of view but there are pros for such a system – the production of biogas in mini-scale low-temperature digestion allows it to use the opportunity to produce energy for self-consumption with relatively small financial investment. Also reduce the amount of bio-waste to manage, the negative environmental impact of both waste disposal and climate change, and reduce costs associated with management of waste (Anyaoku and Baroutian, 2018; Balasubramaniyam et al.,

2008; Rajendran et al., 2012). The combination of renewable energy sources in a hybrid system provides more efficient energy production and facilitates market entry of such systems (Agarkar and Barve, 2011). A shift to distributed renewable energy resource are useful way to increase overall energy grid resilience.

A feasibility study is an investigation of the viability of a project idea. It was employed to assess potential and determine if proceeding with it would be advantageous. Techno-economic, environmental, and legal aspects of the project are often reviewed, along with any potential challenges that could arise. Renewable energy system discussed are considered for temperate region biowaste treatment to produce heat. Developing of bioenergy in small scale production will facilitate transition to self-sustaining full cycle biosystem. Approach would invigorate management of household, horticulture and farm biodegradable residues and will reduce problems associated with the release of these residues into the environment, while the produced biogas can be used for heating and cooking applications of households. Also, the hybrid biogas digester unit is a tool for renewable energy integration as it is diffuser of renewable energy sources and techniques. The main aim of the paper is to do a feasibility study for a psychrophilic to mesophilic anaerobic digestion reactor with solar system support for biogas and heat production.

MATERIALS AND METHODS

Assumptions for Analysis

Various assumptions about the state of the system were made to simplify the system for a feasibility study. System components and their functions were based on references from the literature. Biogas yield is assumed to be determined only by the digester temperature and feedstock used. Heat produced by solar collectors are sufficient to heat digester to get the desired temperature; heat exchangers are adiabatic meaning heat loss with the environment can be avoided.

Reactor volume

Individual parameters for reactor size and solar support system were calculated for quantification purpose of technology. The volume of the reactor was chosen to be adapted with the daily amount of feedstock and the degradation rate of the feedstock. Amount of biodegradable waste is equivalent to 130 kg of food waste per day. Two parameters were used to calculate the volume of the digester – organic loading rate (OLR) and the hydraulic retention time (HRT), to achieve the right balance for reactor volume (Gupta, 2014).

The OLR describes as the amount of feed processed per unit of the reactor volume per day, expressed in kilograms of total volatile solids (TVS) per day and per cubic meter of the digester (kg TVS/m^3day) (Khoiyangbam et al., 2014). The ORL was calculated by Eq. (1). To calculate the organic loading rate, TS and TVS values were adapted from Mhandete *et al.* (Mshandete et al., 2004). The higher the OLR, the more sensitive the system becomes and monitoring system is required to ensure process efficiency. Plug-flow digesters function with a higher OLR than traditional digesters, up to 10 kg VS/m^3day (Nathalie Bachmann, 2013). Therefore, OLR was increased three times.

$$OLR = \frac{SI \cdot TS \cdot TVS}{DV}, \quad (1)$$

where,SI – substrate input, kg/day, TS – total solids %, TVS – total volatile solids %, DV – digester volume, m^3.

The HRT is the theoretical time period that the substrate stays in the digester (Nathalie Bachmann, 2013). The HRT was calculated from Eq. (2):

$$HRT = \frac{NDV}{SI}, \quad (2)$$

where, NDV – net digester volume, m^3, SI – substrate input, m^3.

It describes the mean retention time. HRT deviates from this value. HRT must be chosen to allow adequate degradation of substrates without increasing the digester volume.

Energy production

To evaluate the potential energy produced in from the biogas system the energy production in this study was observed. Biogas is directly used for heating as a substitute for natural gas, according to (Khoiyangbam et al., 2014) one cubic meter of biogas with 60 % methane is equivalent to 4713 kcal or 4.698 kWh electricity. The amount of energy from those aggregates was calculated by Eq. (3) The calorific value of 1 m3 of the biogas (KJ) is:

$$4713\,\text{kcal} \cdot \text{Total biogas volume } m^3/\text{year} \cdot 4.18\,\text{KJ/kcal} \quad (3)$$

Required Solar Collector Area

Solar collector yield or the useful thermal output of the collectors depends on the total irradiation onto collector area and the collector efficiency. For estimating the required solar collector area Zijdemans (Zijdemans, 2012) provides a simple calculation method:

$$A_{abs} = \frac{Q_{demand} \cdot SF}{Q_{sol}}, \quad (4)$$

where, A_{abs} - collector absorber area; Q_{demand} – total heat demand; SF – desired solar fraction;Q_{sol} – Collector yield (Jakobsons, 2015).

RESULTS AND DISCUSSION

The Framework and Concept of Technology

In northern Europe production of biogas developed in the middle of the last century as an instrument for wastewater treatment, reducing the bulk of sludge and biogas is used for wastewater station heating. But at the end of the last century, because of the change in the political system in Eastern Europe, biogas production declined to almost zero. In Sweden this was the period when biogas shifted from by-product to the desired energy carrier – it became possible to create a profitable company and

entrepreneurs and municipalities worked together to produce vehicle gas and to increase energy efficiency. Since the end of the last century, with the advent of technology and the diversification of different technological styles increased the efficiency of the process technology (Centre et al., 2008). Main objective of the technology being studied is to increase the amount of renewable energy at the national level to ensure regional investment potential of the energy sector by increasing the share of biomethane and solar energy in the final energy consumption of renewable energy sector of Latvia. The main importance of a technological solution is to maximize digestion of organic residues by getting higher concentrations of methane in biogas and digestate with less organic material. Psychrophilic anaerobic digestion with assisted solar heat is a way how to maximize methane content and decrease organics in digestate. Technology is intended for non-profit and autarky, later for economic benefit of biogas plant owners. In this work, we combine biogas production in the mini to small-scale as the main renewable energy resource with solar collector as assisted heat. This is offered as a more efficient and faster alternative for composting of waste and better management of biodegradable residues.

Potential target audience of technology are households, households with farms, small-scale producers of bioproducts with residual biomass. Combining the state of art biogas production technology with the solar collectors (considering the price-performance ratio) can reduce probable costs of heating reactor. Later optimization performance and operation of a hybrid system can result in even greater energy savings when the solar heating system is used and at the given type of reactor to ensure a stable production of biogas throughout the year despite changing seasons (Balasubramaniyam et al., 2008; Vinoth Kumar and Kasturi Bai, 2008). System comprises of five major components: biomass – pre-treatment and feedstock, digestate, psychrophilic plug flow digester, solar collector unit, use of gas. (Fig. 1). Solar collector heat will heat the reactor, if unnecessary, for the heating of accumulator. If it is necessary firewood boiler can be used for heating the bioreactor.

There are few reasons why we such hybrid-system must be supported. Solar heat-assisted biogas production is essential because a) almost everywhere in the world there are biomass and sun; b) solar heat energy (Suman et al., 2015; Tian and Zhao, 2013), and anaerobic digestion of biomass (Hagos et al., 2017; Jingura and Kamusoko, 2017; Mata-Alvarez et al., 2014; Patil and Tathe, 2019) are sufficiently long studied technologies; c) technology can produce both heat and power, and fuel – this enables sector coupling (European Parliament, 2018). Additional consideration for the development of technology is that hybrid solar assisted biogas in the micro to small scale serves as a socio-economic integrator of renewable energy sources. It is also a driver of innovative renewable technologies (IRT) and helps the diffusion of knowledge about technologies by bottom-up integration, meaning community initiated and supported.

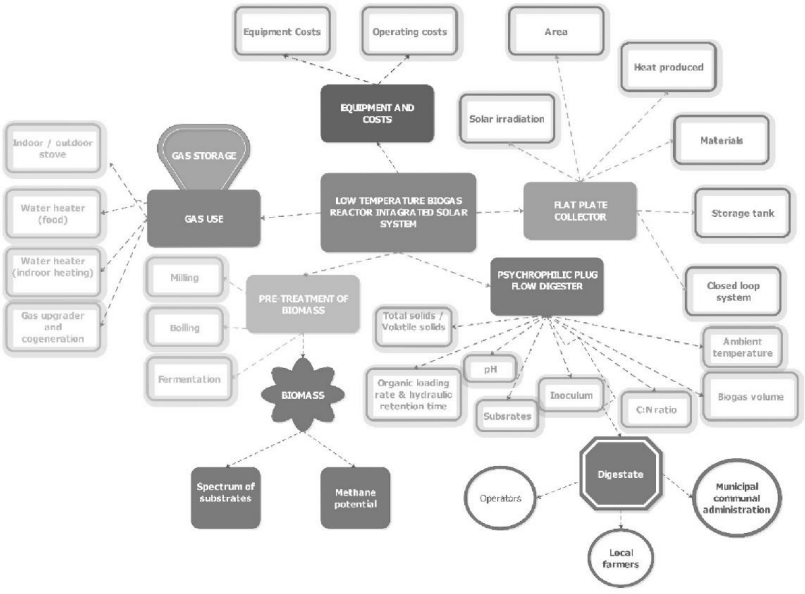

Fig. 1. The framework of low-temperature biogas production system with integrated solar heat.

Solar heat will be used in several ways to assist the anaerobic digestion process, for pre-treatment of the feedstock, heating digester and reducing moisture in biogas produced. Several studies have been conducted on solar assisted biogas e.g. (Chamoli et al., 2011; Dai et al., 2009, 2007; Dong and Lu, 2013; Gupta, 2010a; Karimov and Abid, 2013; Nirunsin et al., 2017). Regional disparities in the availability and form of feedstock, solar intensity, serve as a barrier to technology transfer. Research is compulsory to facilitate the diversification of renewable energy and the development of hybrid systems for energy efficiency (Østergaard, 2012; Schaber, 2013; Shahzad, 2012; Soshinskaya, 2013; Lannoye, 2015). Development is needed in this topic to increase knowledge and later instinctively integrate technology in the regional renewable energy sector.

Multi-Locality of Biogas

Anaerobic digestion is complex and optimization is still ongoing, literature review shows that in the production and use of biogas there is no universal solution suitable for all interested parties. Temperature conditions, types and quantities of feedstock, economic situation, the level of education, vary regionally. Researchers agree that the biogas development and innovation process require an active network of heterogeneous peers (Muller and Peres, 2018). In addition, biogas policy is often national. Thus, there is a tendency to consider biogas as one homogeneous and a nationwide system but it is not. Over the years several technological styles have evolved and continue to operate. Production of biogas is because of various motivations. Technology transfer takes place, for example, between the farms, thus creating new opportunities for cooperation. With biorefineries, there is also an

extension of the scope to include more participants and feedstocks. This means that biogas is not just one system as it is usually perceived but several local ones. Problem is that the politics of resilience are developed in such a way it has only one system – one type of production and one kind of use. Therefore, the benefits of diversity of technologies in the medium and long term are lost and hinder the development of the renewable energy industry. To increase biogas production, the diversity of biogas production needs to be recognized and promoted in the research and policy-making process. Diversification of production are essential factor for further development of the renewable energy industry. In the long term, in the European region, diversification of production would promote the flexibility of energy resources, moving towards regional energy autonomy (Olabi et al., 2015; Olsson and Fallde, 2015; Shahzad, 2012; Shmelev and Van Den Bergh, 2016).

Biogas producers and users are in a multi-local system. The authors use term multi-local (multilocality) to denote a variety of technologies, solutions, applications and scales of technology in a certain area or region. Development of biorefinery concepts will contribute to integration of biogas – the expansion of the scope, increase in a number of actors and feedstocks. Research that determines potential of gas production, technological and economic conditions are considered but are vaguely related to the social conditions. Thus, these studies can be very subjective in scientific sense and cannot be used as a basis for political decision making. Researchers should reckon with many technological styles to develop industry policies, research into biogas systems. (Almeida and Báscolo, 2006).

Development of renewable energy sector policies and support mechanisms require implementation of diversified biogas production, interdisciplinary and applicable scientific research including comprehensive (social) and sectoral (economic) preconditions. The potential for production and uses of biogas globally is very high. At the moment a tiny part of the available resources is used and it needs to be changed. Diversifying the production of biogas with the solar collector support system is a way to promote and improve biogas production and, overall, renewable energies in the region (Fig. 2) (Olsson and Fallde, 2015; Owen, 2018).

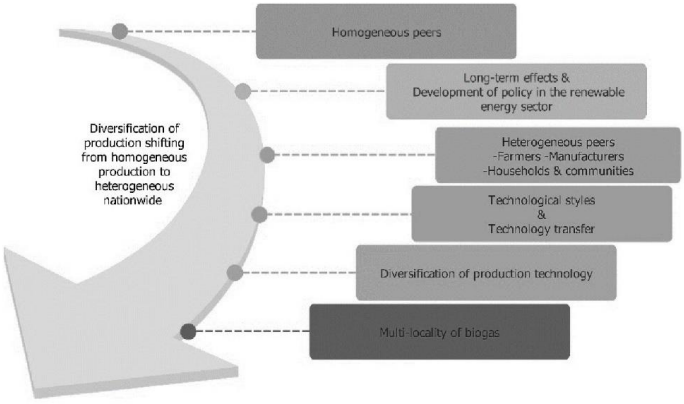

Fig. 2. Diffusion of innovation for diversification and increase of biogas production.

Small-scale anaerobic digestion system with solar heat support – influencing factors and design investigation

Optimal performance of anaerobic digestion depends on several parameters. Various groups of bacteria are engaged in the production of methane and appropriate conditions must be created to ensure that all microorganisms are in balance. As the complexity of the process is high for anaerobic digestion factors affecting the yield of produced methane is quite large. Absolutely, the temperature matters in biogas production it substantially determines the activity of microorganisms, other key factors are C/N ratio, pH, blending, feedstock, HRT. Anaerobic digestion is a protracted process and the adaptation of microorganisms to a new state when the feedstock or temperature changes is about three weeks. Thus, it is essential to provide a more constant temperature and homogeneous easy to degrade feedstock. Vast majority of the hydrogen-consuming methanogens grow in of 6.7 to 7.5 pH, meaning the neutral pH is beneficial for biogas production. Acid-forming microorganisms grow under mesophilic conditions, but methanogens at higher temperatures. Mixing is also an important for biogas production, too much stresses bacteria and without mixing foam appears. Methane-producing microorganisms grow gradually, with a doubling time of about 5 to 16 days. Accordingly, the hydraulic retention time in the psychrophilic range should be at least 30–60 days. Also important is the feedstock used, its carbon balance with other nutrients, primarily nitrogen, and phosphorus and sulfur. Digestion needs to be done slowly in different circumstances easily disintegrated substrates can cause escalation in acid and inhibition of the process. The carbon to nitrogen proportion needed to be approximately 16:1 to 25:1. Too much carbon or nitrogen increase or decrease biogas production. The concentration of solids in the bioreactor should be between 7 % and 14 %. The size of the particle of the substrate is less important than temperature and pH. However, the size of the particles affects the rate of deterioration and ultimately generation rate of the biogas (Achinas et al., 2017; Deublein and Steinhauser, 2010.; Rajendran et al., 2012).

Production of the most efficient biogas takes place in the co-fermentation mode with the addition of high carbon substrate to high nitrogen substrate. Depending on the location of the technology, the processing plant can choose a feedstock, for example, sewage treatment activated sludge, manure, plant biomass, silage, damaged fish feed, cereal products, and other food/feed residues can be used (Hagos et al., 2017; Mata-Alvarez et al., 2014). The psychrophilic reactor is more stable than mesophilic or thermophilic (Wei and Guo, 2018), and then the main control parameter is the pH value. When increasing the pH of the reactor, more raw materials with high carbon content should be added. The total dry matter content of the bioreactor should not be greater than 14 % for plug flow digester. This reduces the energy consumption of the mixing system. Required dry matter content of the bioreactor is ensured by diluting feedstock with water. The main advantages of psychrophilic temperatures for anaerobic digestion would be the lower energy input required for heating the reactor, consequently reducing the overall operating cost. Most recent results on microbiological activity in psychrophilic conditions show that lower temperatures require a longer digestion time and lead to higher methane content and lower accumulation of volatile fatty acids compared to mesophilic

conditions, although still keeping a similar cumulative biomethane yield in both conditions (Gruduls et al., 2017).

Main factors that influence heat produced by solar collector is intensity of sun, type of solar collector generation used, solar collector area, angle, position, height, the height of the surroundings, rotating and rotating rate, capacity, flow rate, material's thermal conductivity, color, insulating and consuming rate. Heat loss from the collector plate depends on several factors. Such as (1) absorption plate temperature, (2) spectral properties of the collector plate, including absorption and emission capacity, (3) air temperature; ambient air and sky conditions; (4) number and characteristics of glass panes and their spacing; (5) the physical properties of the heat for the insulation material used at the edges and at the back; (6) the horizontal inclination of the collector; and (7) the wind speed above the absorber (Garg and Rani, 1980).

When solar heat is produced there is a need for heat accumulation. There are few materials used as heat energy storage media, for example, sand-rock minerals, reinforced concrete, cast iron, salt (NaCl), cast steel, silica fire bricks. But the cheapest and most commonly used is water (Lázaro et al., 2009). Water has a high heat capacity (about 4180 $kJ \cdot m^{-3} \cdot K^{-1}$) but is limited to 100 °C unless there is increased pressure. Most materials used for intelligent heat storage range from 900 to 3000 $kJ \cdot m^{-3} \cdot K^{-1}$. Heat conductivity of the following materials ranges from 0.5 to 4 $W \cdot m^{-1} \cdot K^{-1}$ (Stutz et al., 2017). Main factors that ensure the technical feasibility of a solar thermal storage system are superb technical features. First, high sensible heat storage capacity is essential to reduce the volume and increase the efficiency of the system. Second, a good heat transfer rate should be maintained between the heat storage material and the heat transfer fluid to ensure that the heat energy can be released/absorbed at the desired rate. Third, the storage material should have good stability to avoid degradation (chemical or mechanical) by a specific number of thermal cycles. The cost of a solar thermal storage system consists mainly of three parts: storage material, heat exchanger and land costs. Cost efficiency is usually associated with technical characteristics. High heat storage power and exceptional heat transfer performance can substantially decrease the size of the system (Tian and Zhao, 2013).

To build a solar heating system for Latvia, weather data for specific location must be collected. First necessary to acquire data on the sun radiation (global, diffuse, and direct), other environmental factors, such as the outside temperature, the relative humidity of the atmosphere, and the wind speed. Due to temperate meteorological conditions, reactor outages are possible during winter when external heating are required, most likely, the break could be from the beginning of January to March. It should be mentioned that low temperature operation is mainly to avoid the need for electric heating of the reactor during the spring and autumn months, it also ensures a more stable process. Previous studies on solar energy and temperature in Latvia show that from 2015 to 2020 in Riga, Latvia yearly total solar radiance was 1017 kWh/m^2. Planning for energy production rates and heat demand is quite challenging in due to the local climate. Trend indicates that weather in Latvia is erratic, for instance, the maximum ambient air temperature in 2020 was 30.8°C, but by 2021, it had already risen to 37°C in several parts of the country, the lowest ambient air temperature in 2020 was – 10.3°C, but by 2021, – 31°C (Polikarpova et al., 2021).

Meteorological conditions, region, topography, season, daytime or night, changes vary considerably in different climatic conditions. When developing a solar system, to magnify the use of solar energy, it must be ensured that the system has high heat exchange efficiency and energy recovery. This requires a temperature control system to keep the temperature constant. Heat is stored to match temperature between day and night, sunny or cloudy (Ren et al., 2012).

It is necessary to achieve the most suitable solution for the solar heating component for the system (MPMSAA, 2009). The system contains a collector, a heat transfer control pool and a temperature control system. Solar energy is collected by collectors to heat media material for heat transfer. The heated transfer control pool is connected to the heating manifold through the pipelines. Pipelines in a heated transfer basin should be constructed as uniformly as possible to assist in heat transfer (if there is a larger pool, blenders are required). To reduce heat loss, the basin and pipe casing must be insulated. The temperature control system includes a temperature probe. The probe can keep track of the pool temperature and provide a timely response to the controller connected to the pump to control the amount of heat to reach the reaction temperature. Characteristics of the solar component are shown in Table 1.

Practice shows that a successful reactor must be capable of taking a sufficient amount of biomass. The reactor as microbiological growth and replication ecosystem of different micro-organisms must be stable, the flow of materials and energy smooth and efficient. It is problematic for a household to choose one appropriate type of digester. Design depends on geographic location, feedstock availability and climatic conditions and other circumstances. From all the distinct digesters, the dome developed by China and the floating drum developed by India continues to operate until today. Plug flow digesters gain attention because of ease of operation and portability (Rajendran et al., 2012). What materials will be used for the construction of the biogas digester depends on the local conditions – geological, hydrological, and locally available materials (Shian et al., 2003). In recent years, as a result of technological advances, there has been a proliferation of materials with improved properties and lower costs (Rajendran et al., 2012). For the construction of this type of digester stones and bricks are used as a building material. With the advancement of technology, PVC and polyethylene are used because they are comparatively inexpensive (An et al., 1997). From different materials used for the construction of mini-digesters most promising in the case of East Europe are bricks and concrete and plastic – polyvinyl chloride, polyethylene, with or without modifications. Main advantages of plastic are less weight, easily portable, relatively cheap, bricks and concrete have an advantage over maintenance cost and the material is everlasting. Disadvantages of plastic – relatively short life span, disadvantages of bricks and concrete – difficulty to clean, built underground, the possibility of gas escaping through concrete when pressure increases. As research in household biogas digesters shows the psychrophilic biogas reactor in its simplest form may be a plastic or concrete tank, in which anaerobic environments undergo degradation of organics and the formation of biomethane. The decision of the reactor elements is determined by the availability of materials and price. Smaller households or household communities are more suitable small-sized reactors that can be installed in the territory of household and run at ambient temperatures or with solar heating support. Larger farms are better suited for production capacities with concreted large-volume

reactors that are insulated or partly below ground level to provide reactor operation in winter (Rajendran et al., 2012).

Biogas system comprises the following components:

- Pre-treatment tank consists of electrical miller – homogenizer and is used for the feedstock particle size reduction and mixing with water. Feedstock inlet comprises of a container for organic waste and a tube with a diameter of at least 10 cm,
- Psychrophilic anaerobic digester – organic waste reservoir in which the feedstock is degraded by anaerobic microorganisms to produce biogas,
- Gas storage/reservoir depending on the design can be just a room above the digester or a durable rubber balloon,
- Exhaust pipe is a tube of similar size with an inlet pipe connected to the surface at a slightly lower level than the intake pipe to facilitate digester discharge;
- Digestate storage is tank made from the impermeable layer for dehydration of digestate or storage,
- Gas burner – modified burner for cooking or water heating.

Digester design is adapted to the situational aspects outlined in this paper. Literature review shows it is possible to produce biogas in climates with cold winters (Balasubramaniyam et al., 2008; Gupta, 2010a). Our design is modified reference digester suggested by Adebayo *et al.* (Adebayo et al., 2014). To make the household digester attractive it must integrate features such as good maintenance capability, simple operation, relatively inexpensive design, using locally available materials. From the simple structure digesters, plug flow digesters best meet the criteria needed but also ensures its place to live acid and methanogenic producing bacteria. The inclined position produces a two-phase system making it possible to separate acidogenesis and methanogenesis longitudinally (Adebayo et al., 2014).

Characteristics of the bioreactor and solar components are shown in Table 1. It is possible that in some of the reactor components other materials can be used. It may be possible that some of the reactor components are not needed if it is found that during the construction of the prototype component is interfering with the system, easing system operation, and operational costs.

TABLE 1. CHARACTERISTICS OF THE BIOREACTOR AND SOLAR COMPONENTS

Component	Detail
Digester type	Plug flow digester
Digester volume (for one household)	4 m^3 (2 m^3 to 15 m^3)
Length to width ratio	3.5:1
Process	Two-phase system
Gas collecting	The upper part of the digester or balloon
Portability	Portable
Operation	Semi-continuously
Hydraulic retention time	30–60 days
Solid content	7–14 %
Digester temperature range	15–35 °C

Inoculum source	Wastewater treatment plant or cow manure
Digestion unit	Plastic
Feed tank	Metal with pre-treatment unit
Mixing	No
Digestate storage tank	Metal/concreate
Tubes	Plastic, insulated metal
Digester unit heating jacket	Metal tubes/wiring
Insulation	Composite material, rock or glass wool, organic – reed, or other
Feedstock	
Water source	Rainwater tank/underground
Heating source	No heating or solar collector/heat accumulator
Pre-treatment	Milling, boiling, chemical, drying
Co-substrates	Methane potential in volatile solids (VS) or total solids (TS)
Food waste (FW)	Co-digestion with other substrates was 0.27–0.86 m^3 CH_4/ kg VS (Bong et al., 2018)
Fish waste (FIW)	Biomethane production potential of 0.2 to 0.9 CH_4 m^3/kg VS (Bücker et al., 2020; Ivanovs et al., 2018)
Garden waste (GW)	0.10 ± 0.02 biogas (m^3/kg VS) [8], (Getahun et al., 2014)
Cow manure (CM)	0.6–0.8 m^3/kg TS CH_4/g TS (Ferrer et al., 2011)
Slurry storage, organics content	Digestate storage tank, organics content after digestion is variable depending on reactor temperature and specific activity of microorganisms and other complex factors
Solar collector type	Flat plate collector
Solar irradiation, annual	950–1050 kWh/m^2
Flat plate collector, model	Optional
Gross area of collectors	20 m^3
Inclination angle to horizontal	34°
System type	Closed loop system
Oriental angle	0°, south
Storage tank	Cylindrical tank
Heat exchanger	Helical coil heat exchanger
Heat transfer fluid	Water + glycol (for freeze protection)
Collector interconnection	Parallel-connected collector array
Control systems	Pumps, controllers, temperature control
Portable	Yes
Solar heat application	Heating of water for different uses

Technology has different potential applications, however, one example of the possible use of technology will be briefly described below. As declared in the above paragraphs the idea is suggested for household environments, on a larger or smaller

scale with or without related production that generates biodegradable residues. Technology can be used, for example, a small producer of bio-based goods. This small producer which generates a variety of food products generates 47 tons of biodegradables a year. Generating 47 tons of waste means that daily production is up to 130 kg of food waste. Results show biomethane production in a low-temperature biogas reactor (average temperature 20 °C) has a retention time of 53 days, in a co-digestion mode, with a maximum bioreactor size of 14 m^3. Theoretical calculated OLR is 1.72 kg VS/m^3 day. Considering that plug flow digesters can withstand ORL up to 10 kg VS/m^3 day (Nathalie Bachmann, 2013). Therefore, the maximum size of the bioreactor is reduced three times to 4 m^3, with OLR 6,88 kg VS /m^3 day.

TABLE 2. CHARACTERISTICS OF THE TECHNOLOGY STUDIED

Characteristic	Value
Biomass quantity, annually	47 000 kg
Biomass volume, annually	~95 m^3
Biogas yield for food waste	0.4 m^3/kg TS
Average FW feedstock density	510 kg/ m^3
Reactor temperature, average	20 °C
Biomethane concentration in biogas	60 %
Organic loading rate	6.88 kg VS/m^3day
Hydraulic retention time	~53 days
Reactor size, m^3	4 – 15 m^3
Solar collector, area	20.2 m^2
Usable solar heat produced, year	~3000 kW
The amount of biomethane produced	4230 –14 800 CH_4/m^3

The average yield of biomethane in the co-digestion of food waste and activated sludge, at low temperatures with substrate retention of 28 days, is from 90 to 200 m^3 of CH_4/t of food residue, depending on the type and water content (Chen et al., 2010; Rajendran et al., 2012; Zhang et al., 2014). The production unit of this size theoretically could produce an equivalent of ~20 000 m^3 of biogas a year if the biomass is digested with maximal efficiency. Depending on the feedstock used and its volatile solids, biomethane content it is from 4230 m^3 to 14 800 m^3 a year (Table 2). In best case scenario, system of this size in the maximum effective mode would produce 27.5–96.2 MWh of heat per year. The thermal energy of the hybrid-system can be used for heating living and production premises, drying wood or food, sprouting grains, growing vegetables and mushrooms, growing insects, earthworms, and similar solutions. Considering a small-scale the costs may vary depending on the type and quality of the selected materials and scale. The payback time for digester with solar collector, control system, heat storage, needs to be determined by market

analysis of the offers, and it depends on the reactor, collector technology, heat accumulator capacity and increase of component price.

The importance of social approval for decentralized energy systems plays an important role for broad consumer use. Development of suggested renewable technology and modifications in the long term will make significant impact. Implementation of technologies will move industry towards a heterogeneous energy. In the long run it increases (1) energy resilience; (2) decreases the volatility of energy prices and the (3) introduction of a block-chain (market); (4) minimizes the environmental impact on human health by promoting industry connectivity to the integration of renewable energy. Linking electricity, heat, and transport to the infrastructure and stored energy carriers, could be achieved. It is necessary to develop decentralized systems because there are a large number of, for example, bioreactor owners, then the system is much more integrated – from supply to demand, and horizontally – between different energy vectors – electricity, heat, gas. Decentralized energy systems can reduce transmission costs and centralized energy capacity. At the current level of technology, fully autonomous regions are economically impossible due to the need for large energy storage capacities (Anyaoku and Baroutian, 2018; Pierie et al., 2016). Use of biogas as a renewable energy source will help to reduce negative external effects (emissions of CO_2, methane and thereby global warming, and polluted air, water, and soil) and by that reducing social costs of energy production. Biomethane as energy source gives positive overall economic effects – reduction of fossil energy import, saving of foreign exchange, less dependency upon foreign energy supply, less price volatility, improvement of electrical energy supply. Biogas as a renewable energy source is a good investment opportunity because planning, construction, and operation are not way too complicated. There will be good effects of increased biomass use. If waste biomass is used it will result in waste reduction, reduced costs of waste treatment, reduced environmental risks and groundwater pollution, unpleasant smell, health and sanitation problems. The exploitation of renewable energy produced from anaerobic digestion leads to direct and indirect benefits for the producer and the community – environmental benefits, improved living standards and revenue from sales of energy.

It is crucial to improve public awareness by introducing society to biogas production as an easy and convenient way to manage biodegradable residues. Development of household biogas may lead to community biogas as a way of treatment of biowaste and producing energy, and later probably a business. To ensure the regional investment potential of the energy sector, it is necessary to diversify renewable energy resources. And one way of doing this is to increase the share of biogas (biomethane) in the final energy consumption of renewable energy. The anaerobic digestion application rate for biodegradable waste management could be increased in two main ways. First, in the context of knowledge transfer by increasing the resonance of the biogas production on its extraction, use and positive aspects for society. Second, technologically – increasing the number of feedstocks used and diversifying technological solutions so that they are more widely available for households, companies, farms. Environmental and economic valuation of system will be carried out to estimate the cost of energy and the initial investment for this type of solution.

Kowalczyk-Juśko et al., 2019 analysed spatial and social conditions of agricultural biogas plants in Poland. More than 80% of respondents believe that the building of a biogas plant will help the commune by safeguarding the environment, providing people with cheaper power, and delivering cash to farmers by creating additional employment and crop sales. Concerns regarding the construction of biogas plants include unpleasant odors, loudness, increased pollution, and the possibility of an explosion. The size of the land on which the agricultural biogas plant will be built, as well as the condition of the roads, connectivity to the power grid, distances from possible substrate suppliers, and distances from human habitats, are all important considerations. Choosing the appropriate site entails taking into account a number of technological, legal, environmental, and social issues (Kowalczyk-Juśko et al., 2019).

Small-scale agricultural biogas facilities, geared to small amounts of feedstock and farm energy requirements, should become increasingly popular in Europe. The capacity provided in such units must be sufficient to cover the energy needs of one residence. Czubaszek et al., 2022 draws attention to careful calculations and correct recognition of the nature of feedstock and parameters in small biogas plants. According to technical considerations, the approach would lower the cost of modifying the reactor to the feedstock to be utilized. Small agricultural biogas plants' feeding systems might be more complicated, according to research. Due to the variable physical characteristics of the feedstock that the operators utilize, such stations need to be adaptable in terms of technology and equipment. Additional research is required to determine an affordable pre-treatment method that will improve the efficiency of anaerobic digestion in small reactors. (Czubaszek et al., 2022). For pilot plant development at temperate climate use mixture of psychrophilic and mesophilic bacteria are suggested (Jaimes-Estévez et al., 2020). According to the research findings of Prvulovic et al., 2022, based on the estimated energy requirements anaerobic digesters requires less energy from June to August, and more from November to March. An average of 16% of the generated combined heat and power engineheat is required yearly to heat the fermenter. Most thermal energy is required in January and December (20%), and the least in July (12%) (Prvulovic et al., 2022). Anaerobic digestion on a small scale is a promising method for treatment of organic part of municipal waste. It applies to the European agriculture industry, and adoption of installation is predicted to rise considerably (O'Connor et al., 2021)

CONCLUSIONS

This article concisely discusses the possibility of using a low-temperature biogas reactor with solar support as a management tool for household-to-small business biodegradable waste. Literature review confirms solar assistance to biogas increases production of biogas, efficiency of production, costs and decreases toxicity of digestate. Literature analysis highlighted the socio-economical value of technology in two contexts, a renewable technology reduce waste and produce energy and serves as bottom-up integrator of renewable energy, and that multilocality of biogas must be considered when the policy of the renewable energy sector is developed. Feasibility study shows that such small-scale systems can reduce the amount of greenhouse gases and contribute to progress towards the EU Green Deal. Design

examination of a solar heat support was suggested in this paper to provide logical basis for further research. Research is needed in different directions – socio-economic, identification of specific technical parameters of the workable system, defining size boundaries of hybrid system, sourcing of feedstock.

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Kaspars Ivanovs was born in 1992 in Jēkabpils, Latvia. He holds a Bachelor's and Master's degree in Environmental Science from the University of Latvia. He has worked as an inspector in the Marine Control Department of Fisheries Control Department of State Environmental Service of the Republic of Latvia, as a researcher at the Institute of Environmental Protection and Heat Systems of RTU EVIF and at the Scientific Institute of Food Safety, Animal Health and Environment "BIOR". He is currently an expert at the Department of Higher Education, Science and Innovation of the Ministry of Education and Science of the Republic of Latvia. His research interests are biomass management for efficient production of products with higher added value.