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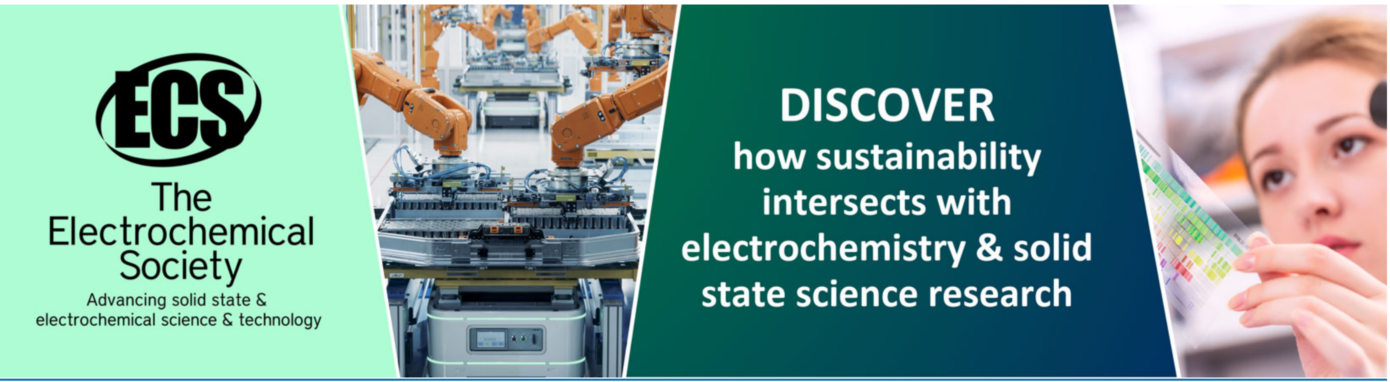

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Life-Cycle Assessment of Kelp in Biofuel Production

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Abstract. The study is devoted to the life cycle assessment and perspectives of the kelp seaweed of the Russian Federation northern seas water areas usage for the biogas, bioethanol and biodiesel production. The article presents the stages of seaweed growth, its harvesting (including environmental impact of different types), transportation, dewatering and three types of biofuel processing. Conclusions are made on the potential use of kelp seaweed as a feedstock for biofuel production for the northern regions of Russia (on the example of Arkhangelsk region). A diagram of the biofuel production from kelp seaweed life cycle is also presented.

1. Introduction

Over the past decade renewable energy has become an integral part of the energy strategies of many countries of the world, including the "Energy Strategy of Russia until 2035". Energy produced from combustible renewable energy sources has the highest potential among other renewable sources and will play an increasingly important role in the nearest future for further diversification of global energy resources, which should have a positive effect on the number of jobs. However, by 2025, the number of famishing people will increase to 1.2 billion people because of the harsh competition for agricultural lands in the production of biofuels from plant biomass.

Liquid biofuels economic efficiency providing requires high-quality agricultural lands, application of significant amounts of fertilizers and pesticides to the soil, and irrigation. Moreover, it means the competition for resources between energy and food crops. This competition can be eliminated via the algae based third generation biofuel technologies.

Most of the researches concern the production of biofuels from microalgae [for example, 1,2], while macroalgae have lots of environmental benefits. They are: the complete absence of the surface demand and irrigation. This research studies the life cycle peculiarities of biofuel production from macroalgae, in particular from Russian seas kelp.

The relevance of the article is determined by the insufficient knowledge of the kelp biofuel production process in Russia. The subject of the research is kelp harvested in the seas and coasts of the North and the Far East of Russia. The life cycle analysis is based on the open sources data, including the information from the kelp fishery in the Khabarovsk and Kamchatka Territories, the Komi Republic, Arkhangelsk and Murmansk regions.

2. The problem study of biofuel production from kelp

Kelp is a valuable marine biological resource. It is used to extract useful products necessary for food, cosmetic, pharmaceutical industries and agriculture.

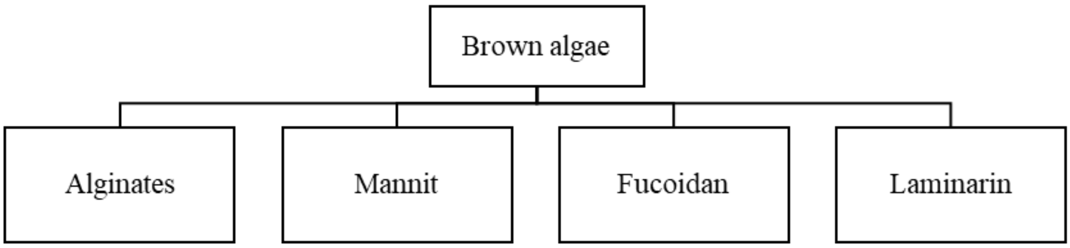

Figure 1. Useful components issued from brown algae.

The largest species of brown algae are found in the seas of temperate and northern latitudes. Brown algae harvesting and the useful goods production have been carried out in the USA, Norway, South America, Southeast Asia and Russia for many years. In 2014, *Laminaria japonica* accounted for almost half of the seaweed production in China, which is currently the largest producing country [3]. In Russia, the largest part of commercial brown algae is found in the White, Barents, Okhotsk and Japanese seas. Only in 2013, the commercial stock of kelp in the White Sea was estimated at about 531.000 tons [4], and off the coast of Sakhalin and the Kuriles – about 600.000 tons [5], according to some unpublished data, the commercial stock of kelp in the Russian northern seas is more than 2 million tons.

The area of biofuel production from algae in Russia, is not widely studied yet. The most probable reason is that our country is one of the leading producers of fossil fuel, and the main emphasis in the economy is placed on the export of oil and gas. However, the commercial reserves of seaweed in Russia are huge, and this type of biomass needs to be investigated as a potential source of raw materials for biofuel production in the country.

3. Methodological basis of the research

To solve this problem, the algorithm for the life cycle assessment in accordance with GOST R ISO 14040-2010 [6] is taken as a basis. It allows to analyze the impact of products on the environment from the time of cultivation, harvesting or acquisition of raw materials until the final disposal of products and waste products in accordance with the established goal and area of study. The boundaries of this study are the commercial kelp algae of the North Seas of Russia - *Laminaria saccharina* and *Laminaria digitata* [7] and the Far East - Japanese kelp (*Laminaria japonica*), as well as the processes of biogas, bioethanol and biodiesel production.

The analysis is carried out at each technological stage of the biofuel algae production, which involves the cultivation of algae, its harvest, transportation and processing into biofuel.

We propose to organize the process of biofuel production by means of anaerobic digestion (to obtain biogas), fermentation (to obtain bioethanol) and hydrothermal liquefication (to obtain bio-oil and biodiesel).

4. Results and discussion

4.1. Cultivation of kelp

In Russia, kelp have been cultivated in the south of the Far East since 1972. The yield was near 80–90 tons of wet weight per hectare [7, 8]. After the collapse of the Soviet Union, technologies for the cultivation of brown algae practically was ceased, as it became economically unprofitable. Presently wild-growing kelp is used in Russia, which grow in the littoral zone at a depth of 3-7 meters. Kelp of temperate latitudes grow most actively in spring and summer months. The growth rate is also influenced by illumination, currents and wave heights [7].

Table 1. Characteristics of kelp as objects of fishing and cultivation in the White and Barents seas.

Algae type	***Laminaria saccharina***	***Laminaria digitata***
The period of intensive growth of the thallus	January-July	The Same
Slowdown of thallus growth	September-December	The Same
Sporophyte life span	6-8 years	4-5 years (Onega bay) 10-12 years (Kandalaksha Bay)
Thallus weight, g	760-1309	1000-1100
Thallus weight, g	1,82	0,9-0,95

We think that it is possible to use storm caused seaweed washing ashore. During the whole year, about 100 thousand tons (3-8 tons per 10 m of the coast) of benthic plants are thrown onto the shores of the White Sea [9]. Information on “storm seaweeds” as a raw material for the production of useful components and biofuels is practically absent, since until now they have been mainly studied from a scientific point of view to obtain information on the species composition [9].

The value of seaweed raw materials from storm washing ashore depends on the time of their exposure to air, weather conditions, the presence of mechanical impurities (sand, shells, etc.) and storage time (no more than 2-3 days; then viscous mucus is released on their surface, which contributes to the development of euryhaline microorganisms and fungi that consume seaweed sugars, polysaccharides, mannitol and alginic acid). Partial decomposition of seaweed makes storm washing ashore especially valuable for soil fertilization and biogas production [9].

4.2. Kelp harvesting

The collection of wild kelp is carried out selectively in the fields, where it is at the stage of commercial maturity.

Harvesting can be done in three ways: manual, underwater and mechanical. In the manual method, braids, dredges, kabea (three-pronged pitchfork on a long handle) are used. The cost of 1 kg of wet raw materials is approximately 1.5 - 2 US dollars [9]. A team of pickers of 3 people per season (from May to October) can collect 1-1.5 tons of algae and get 4 million rubles for their work. Excluding transportation (1.5–2 million rubles) and taxes (13%), the brigade's income may amount to 700 thousand rubles [9, 10].

In underwater mining, the diver cuts off algae at a specified height from the bottom. The cut algae are sucked up by the airlift and fed on board the floating equipment at a speed of 2 t/h. From the point of view of the subsequent reproduction of algae, this method of extraction is the most rational and less traumatic for the algae population.

The mechanical method takes place using a mechanical dredge. It is currently used in Norway and once it was used in the former Soviet Union on the Solovetsky Islands and the Far East. However, for Russia this method is unacceptable today, since the machine harvest of kelp destroys also the substrate on which the seaweed grows, and the population revives slowly in six years [10].

Harvesting of storm-washed ashore seaweeds on the territory of the Russian North is allowed in accordance with issue 77.1 of the Order of the Ministry of Agriculture of the Russian Federation dated to10/30/14 [11]. Anyhow there is a difficulty in harvesting. It is the inaccessibility of the coastal strip for both land transport and sea vessels. But manual gathering mainly is carried out. However, there is a patented technology using a platform on air-supported tracks with a hydraulic crane [12].

Harvesting kelp has a number of environmental consequences, among which are the slow growth of the algae after cutting; the probability of damage to the growth point (at the junction of the thallus and the leg) and, as a result, the death of the seaweed; in the case of cutting the seaweed above the stem, during decomposition, substances are released that prevent the germination of spores and the growth of seedlings; a limestone film forms on the surface of the substrates, which is not strong enough to support larger plants, which then break off during storms or strong currents; the predominance of younger plants, which can lead to a decrease in the complexity of the habitat, biomass and diversity of the territory; increasing the potential for coastal erosion; deposits of drifting kelp on beaches are an important source of nutrients for dune plants that stabilize coastal sediments, so harvesting drifting macroalgae can indirectly affect coastal protection by negatively impacting coastal plant growth and therefore dune formation; harvesting seaweed can reduce the release of stored carbon back into the atmosphere by reducing microbial degradation.

4.3. Algae drying
Dehydration to 20-30% of the water content stabilizes the biomass, allows transporting with less water contain and reduces the energy required for any subsequent drying stage. Kelp drying is carried out on hangers, netting or using hot air.

4.4. Algae transportation
The development of the kelp processing industry in Russia is hampered by the raw material transportation system. For example, for the Arkhangelsk seaweed plant, kelp is harvested in the area of the Solovetsky Islands. The distance by water from the gathering point to the city of Arkhangelsk is about 250 km, the ship's capacity is 1.5 tons. The price of diesel fuel is about 49 rubles /liter, the power of the diesel generator karbass is 20 kW, the operating time is 8 hours at a load of 75%. According to calculations, the average fuel consumption is 4.15-4.57 l/h, the total fuel consumption is 33.06-36.54 l [13].

4.5. Processing macroalgae into biofuel
One of the most optimal economical approaches for biofuel production can be the combined production of bioactive materials, including the production of several types of biofuels. There are groups of processes that make it possible to obtain different types of biofuels from dry and wet algal biomass. For dry algae, direct combustion, pyrolysis, gasification, transesterification can be used. Wet biomass is subjected to anaerobic digestion, hydrothermal liquefaction and fermentation to bioethanol. Since the process of drying algae is a rather labor-intensive and energy-intensive process, it is proposed to analyze the production of biofuel from liquid biomass of kelp.

4.5.1. Biomethane. The most direct way to obtain biofuel from macroalgae is its anaerobic digestion into biogas (~ 60% methane). Compared to terrestrial biomass crops, macroalgae contain little fiber and do not contain lignin, and therefore undergo more complete hydrolysis [14]. There are no serious technical obstacles to the process of anaerobic fermentation of kelp, especially as an additional feedstock for existing plants, however, the presence of salts, polyphenols and sulfated polysaccharides must be carefully controlled to avoid inhibiting the process of anaerobic fermentation and reduce the yield of methane [15]. Maximum yields of biomethane from kelp ranged from 0.209 to 0.26 m^3/kg volatile solids (VS).

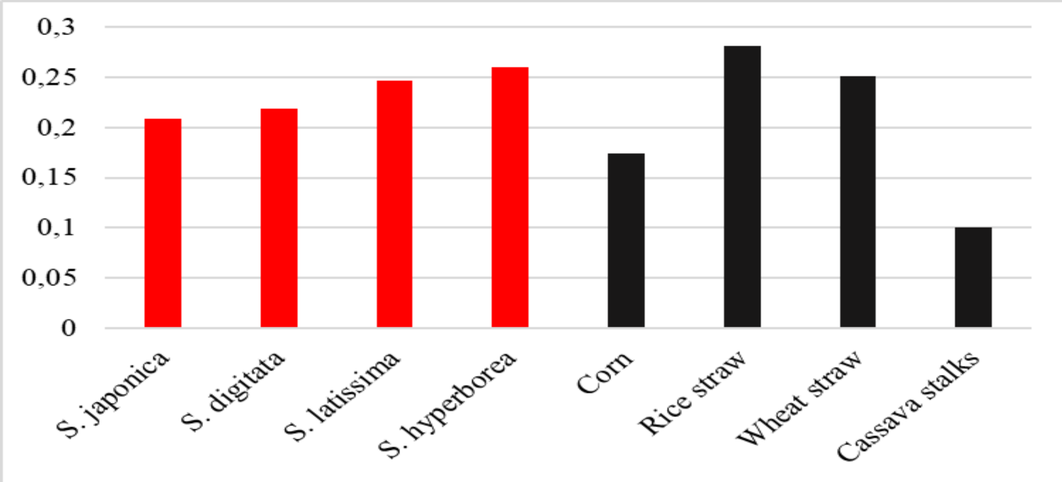

Figure 2. Biomethane yield (m^3 CH_4/kg VS).

Analysis of biomethane production during the entire life cycle of macroalgae showed a 69% reduction in fossil fuel use compared to natural gas, a 54% reduction in greenhouse gas emissions and an improvement in the sea eutrophication index [14].

4.5.2 Bioethanol. Sugar kelp is the most widespread seaweed studied for the production of various types of biofuels, with bioethanol being the most studied [16]. Kelp practically does not contain lignin, unlike lignocellulosic plants, they have a high carbohydrate content and can be easily grown in bulk with modern agricultural technology.

The maximum yields of bioethanol production from polysaccharides such as mannitol and glucan are from 0.152 to 0.196 kg ethanol/kg dry seaweed biomass, and they are lower compared to glucose from sugar crops and lignocellulosic biomass (from 0.219 to 0.337 kg ethanol/kg dry raw materials) . It is believed that the energy balance for fermentation and distillation of seaweed in ethanol is similar to that for terrestrial crops, with energy consumption accounting for approximately 70% of the calorific value of ethanol produced [17].

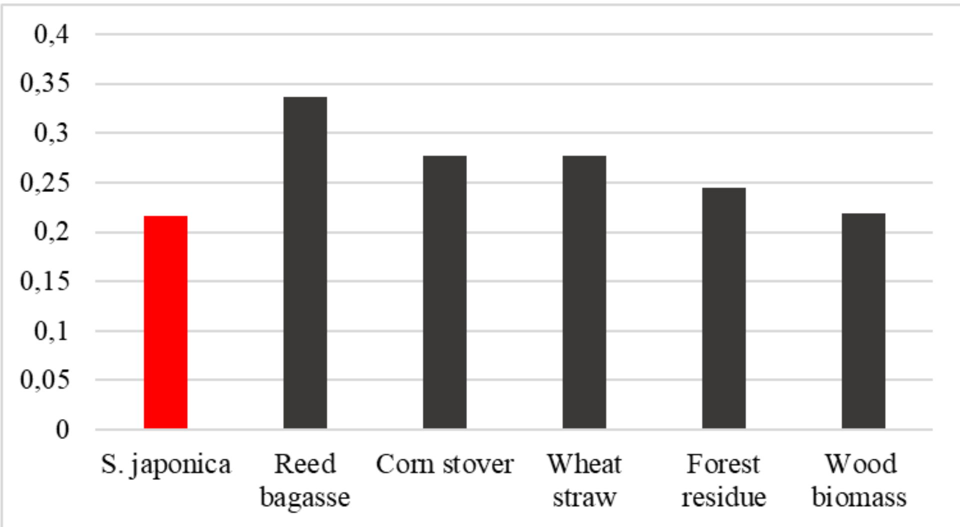

Figure 3. Bioethanol yield (kg ethanol kg feedstock).

4.5.3 Bio oil. Thermochemical conversion technology such as hydrothermal liquefaction (HTL) is a promising option for converting a variety of plant biomass into stable concentrated biomass (bio-raw or bio-crude) that can be directly burned or converted into oil substitutes [18] It can be assumed that HTL has some advantages for the use of moist brown algae containing about 10–20 wet % solids and for the treatment of brown algae with a low lipid content, which convert some proteins and carbohydrates into oil [19].

The yield of macroalgae bio-oil using HTL is up to 23% [20], while energy extraction from the initial biomass of macroalgae is 63% for *L. saccharina* 79% [21].

The biological oil of brown algae obtained by using HTL may contain such useful products as phenols, carboxylic acids, CO, ammonia, and organic bases [22]. Oil obtained by HTL from brown algae usually has a lower oxygen content and a higher energy density than oils obtained as a result of rapid pyrolysis [21], however, significant amounts of oxygen, nitrogen and sulfur due to the high content in raw materials must undergo further processing.

Comparison of the energy yield between the products of thermochemical treatment and products of biochemical conversion, such as fermentation and anaerobic digestion (AD), shows that thermochemical treatment (34 MJ/kg kelp) has a higher energy yield than biochemical conversions (7.9 MJ / kg kelp for fermentation and 8.3 MJ/kg kelp for AD) [21].

4.5.4 Biodiesel. A large amount of unsaturated fatty acids (up to 25% of the total amount of fatty acids) allow kelp to be used as a raw material for biodiesel production. Consequently, biodiesel from algae can ensure the operation of vehicles in winter conditions. [23]. At the same time, the cost of raw materials from kelp will be 5 times lower in comparison with rapeseed and soybeans, and the cost of the final product is 2.5-3.0 times lower, that is, approximately 0.2 US $/l. [23]. Algal biodiesel is a neutral carbon fuel, which means that it absorbs about the same amount of CO_2 during the growth of algae as it is released during fuel combustion [24]. The oxygen content in biodiesel in the amount of 10–11% allows to reduce net carbon dioxide emissions by 78% during the life cycle compared to conventional diesel fuel and reduces the concentration of soot in emissions [25]. Algal biodiesel fuel complies with the International Standard for Biodiesel for Vehicles [26, 27].

4.5.5 General life cycle diagram of the biofuel production from kelp. This diagram is based on the analysis of the stages of the kelp life cycle as a potential source of biogas and liquid biofuels, and created with incoming and outgoing flows.

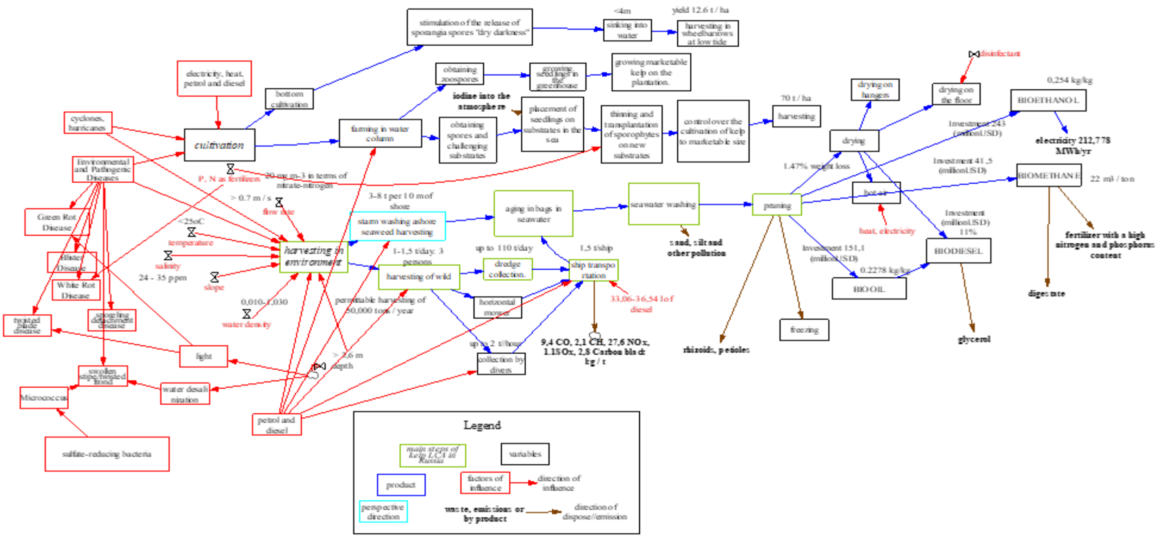

Figure 4. Diagram of the kelp life cycle assessment.

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5. Conclusions

1. Since the kelp drying is a labor- and energy-intensive process and is subject to the influence of weather conditions (fresh rain water leaches valuable components from seaweed), it is most rational to pay attention to the methods of obtaining biofuels from wet biomass. The most rational are the process of anaerobic digestion to obtain biogas, enzymatic decomposition to obtain bioethanol, and hydrothermal liquefaction to obtain bio-oil, followed by transesterification to obtain biodiesel.

2. One of the factors that hinder the use of kelp algae as a biofuel is their seasonal harvesting, however, this problem can be solved by harvesting storm seaweed washing ashore. Decaying storm seaweed can be used, for example, in digesters to produce biogas.

3. The hydrothermal liquefaction of kelp (HTL) has a higher energy yield than biogas and bioethanol. However, the HTL of kelp is at the initial stage of research, and so far the results are given at an experimental level and have not been introduced into industrial development. But already at the experimental level, the results of using HTL show the high potential of this method for the further production of biodiesel for vehicles.

4. Today, the most rational process is biogas production. This is due to the collection of a large amount of seaweed as a commercial resource of the northern regions of Russia and the possibility of using the obtained gas in local heat and power generators. This will reduce the cost of purchasing and transporting natural gas to the hard-to-reach regions of the Russian North.

5. Research on the production of bioethanol was mainly carried out at Japanese Kelp. For its production, polysaccharides such as mannitol and glucan are used, and parallelly they are available for the pharmaceutical and cosmetic industries. Bioethanol yield is lower than that of biogas compared to corn or wheat straw. There is a potential for bioethanol production, but Japanese kelp practically does not grow in the northern regions of Russia, and its amount will not be enough for the production of bioethanol in this region.

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