Cluster On Anaerobic digestion, environmental Services and NuTrient

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D4.2 A

Energy Recovery from Contaminated Marine Biomass

https://www.coastal-biogas.eu/

Preface

The project receives funding by the Interreg South Baltic Programme 2014-2020 under the project “Cluster On Anaerobic digestion, environmental Services and nuTrients removAL (COASTAL Biogas)“, STHB.02.02.00-DE-0129/17.

Cover photo

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2. Gdańsk University of Technology (GUT), Poland – project partner
3. Baltic Energy Innovation Centre (BEIC), Sweden – project partner
4. Roskilde University (RUC), Denmark – project partner
5. University of Rostock (UROS), Germany – project partner
6. Lithuanian Energy Institute (LEI), Lithuania – project partner

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Abbreviations/Glossary

Δt	-	period over which the average volume of biogas production per reactor used volume unit is determined	days
A	-	Coefficient of the disintegration kinetic equation	%
a	-	certain number of charges in a steady state of the anaerobic process	dm^3/dm^3 per day
A_{COD}	-	Degree of algae biomass disintegration measured COD method	%
AD	-	Anaerobic digestion	
B	-	Coefficient of the disintegration kinetic equation	-
BAT	-	Best available technology	
b_{dt}	-	the amount of biogas produced during the period *dt*	dm^3
b_i	-	the amount of biogas stored in the collection tank	dm^3
BPM	-	Bio-methane potential measurement	
b_V	-	comparative average biogas production rate per reactor working volume per day	dm^3/dm^3 day
B_V	-	average biogas production rate per reactor operated volume unit over the whole biomass sample period	dm^3/dm^3 day
b_{Vd}	-	comparative average biogas production rate per reactor used volume unit during Δt	dm^3/dm^3 day
b_{Vm}	-	comparative instantaneous biogas production rate per reactor volume unit per time	dm^3/dm^3 day
B_{Vn}	-	average single-charge biogas production rate per reactor operating volume unit, after	-
C_B	-	Heat capacity of feedstock	$kJ\ kg^{-1}K^{-1}$
C_{CH4}	-	Methane concertation at i-th cycle	V/V
COD_0	-	Chemical oxygen demand of untreated sample	$mgO_2\ dm^{-3}$
COD_{NaOH}	-	Chemical oxygen demand of an alkaline hydrolysed sample	$mgO_2\ dm^{-3}$
COD_X	-	Chemical oxygen demand disintegrated sample	$mgO_2\ dm^{-3}$
d	-	number of days the biomass is stored in the reactor until it is completely biodegraded	-
dt	-	a period of time	days
E_T	-	Energy used for transportation	MJ
e_t	-	Energy needed for transport 1 t of wet biomass per 1 km	$MJ\ t^{-1`}km^{-1}$
F	-	Heat exchange surfaces	m^2
HHV	-	Heat of combustion when the product of water being in liquid form	$MJ\ kgTS^{-1}$
H_i	-	concentration of methane in the biogas contained in the collection tank	%
K	-	Heat transfer coefficient	$W\ m^{-2}K^{-1}$
k	-	number of charges to reach the steady-state of the anaerobic process	
LHV	-	Heat of combustion when the product of water being in vapour form	$MJ\ kgTS^{-1}$
m	-	amount of recycling biomass	kg
m_0	-	Mass of the aluminium evaporating dish	g
m_1	-	Mass of the aluminium dish and the sample before drying	g
m_2	-	Mass of the aluminium dish and the sample after drying	g
m_b	-	Mass of wet biomass	t
m_c	-	Mass of the crucible	g
m_{DM}	-	dry matter content in the recycled biomass	kg

m_F	-	Mass of feedstock	kg
m_s	-	Mass of the crucible and sample before calcination	g
n	-	the number of pulses per day recorded in the biogas accounting system	-
n_d	-	number of pulses recorded in the biogas accounting system over the period Δt	-
P	-	Pressure in the OxiTop bioreactor	Pa
Q_{FH}	-	Energy for feedstock heating	kJ
Q_{HL}	-	Bioreactor heat lost	kJ
Q_T	-	Total energy necessary for biogas plant operation	kJ
R	-	Gas constant	J mol K^{-1}
S	-	Distant for transportation	km
SC	-	Sand content	%
t	-	Time	s
T	-	Temperature	K
T_A	-	Ambient temperature	K
T_B	-	Temperature of bioreactor	K
TS	-	Total solids	%
T_S	-	Initial temperature of the feedstock	K
TS_1	-	Total solids before washing	%
TS_2	-	Total solids after washing	%
V	-	Volume of the headspace in the OxiTop bioreactor	m^3
V_{bg}	-	Biogas production	m^3
V_{rd}	-	used reactor volume	dm^3
VS	-	Volatile solids	%
z	-	number of biogas collection tanks filled during the whole experimental period	-
α	-	Mixing factor	-
η_{net}	-	Energy efficiency of the process	%

Summary

The COASTAL Biogas project revolves around the co-digestion of cast seaweed and the utilisation of digestate as an organic fertiliser as means to mitigate eutrophication. Due to high levels of contaminants it is not always possible to directly use the cast seaweed as a substrate, e.g. for biogas production. For example, in Denmark the biogas production requires that the cadmium content in a raw substrate must be below a certain threshold before it enters the bioreactor. Otherwise, other treatment methods must be used. In this report, thermal treatment of contaminated seaweed and digestate is investigated to find out how much energy can be recovered. This includes recovery of nutrients such as nitrogen and phosphorus, which are present in the by-products of the pyrolysis process.

The anaerobic digestion of seaweed biomass can be used to produce electricity, heat and biofuels (biogas, methane). However, after the anaerobic digestion process in the bioreactor, an energy-rich residue (digestate) remains. Ideally, it can be used as a fertiliser for agricultural fields as it contains useful nutrients. However, if the remaining digestate cannot be utilised due to an elevated heavy metal content, it can be reprocessed to obtain the maximum amount of energy instead of being landfilled or left on the beach. Seaweed absorbs not only minerals and beneficial substances during its life cycle, but also pollutants. As a result, marine biomass can be contaminated with heavy metals, which makes its use for crop fertilisation impossible. One of the most popular and promising methods to extract its energy is through pyrolysis. Bio-oil, gas and carbon are formed as products of this process.

In the quest to produce sustainable renewable resources, seaweed and macroalgae have proven to be a remarkably suitable and efficient resource, and immensely productive for the third-generation circular economy. The European Commission strives to reach robust aquaculture in the EU in order to increase potential renewable resources such as seaweed, which could be used in the biogas production and are also seen as exciting renewable feedstock for the production of biofuels in Europe. Within the COASTAL Biogas project, experiments were conducted by utilising two merged technologies, anaerobic digestion and pyrolysis, in order to assess the captured energy from the digestate (assuming it is contaminated).

The energy balance for the whole value chain (from the collection of the seaweed to its energetic utilisation) was analysed. In this context, three different pathways (presented in Figure 2 - Figure 4 of marine biomass utilisation were considered.

In each of the analysed cases, the total energy balance was positive, and guarantees generating energy from the processed marine biomass. The most energy-efficient process is the anaerobic digestion of marine biomass and the lowest energetically effective is the plasma induced gasification of digestate.

Introduction

The excessive nutrient content of surface waters results in explosive growth of algae, which causes disruptive changes to the biological equilibrium (including fish deaths). This is true both, for inland waters (ditches, rivers and lakes) as well as for coastal waters.

The goal of the COSTAL BIOGAS project (Cluster On Anaerobic digestion, environmental Services and nuTrients removAL) is to utilise seaweed to fertilise soil in order to contribute to a reduced use of artificial fertilisers, while simultaneously decreasing the eutrophication problem in the Baltic Sea.

The analysis of nutrients recovery from marine biomass for soil fertilisation was presented in report D4.2 B.

The amounts of cast seaweed presented in Table 1 show how big a problem the excess marine biomass in the Baltic Sea basin is.

Table 1. Basic information about casted seaweeds in project partner countries

Parameter	Poland	Denmark	Germany	Sweden	Lithuania
Type of seaweed	Green, brown and red algae	Green, brown algae	Green algae	Green, brown and red algae	Green, brown and red algae
Seaweed collection dates	May –October	1 May - 1 September	April-October	15 May – 15 September	May-September
Reason for the collection of seaweed	purification of beaches	biogas production/ purification of beaches	purification of beaches	biogas production is not the primary target but mitigation of eutrophication	purification of beaches
Quantities of collected seaweed	9 500 tons/year [1]	42 000 tons/year	11 595 tons/year	63 628 tons/year	54 tons/year

In the present study, an analysis of the energy balance of marine biomass utilisation in the anaerobic digestion process will be presented, taking into account two pathways of the digestate usage. The first pathway covers the direct use of digestate as fertiliser. Alternatively, in the case of heavy metals (mainly cadmium and nickel) exceeding thresholds content, the digestate or directly cast seaweed can be used for a gasification process, which represents the second pathway. The diagram of the proposed marine biomass treatments is shown in Figure 1.

The preferred way of marine biomass utilisation is the digestion process, in which it is possible to recover energy in the form of biogas as well as nutrients in the form of digestate. However, due to possible contamination of the algae an alternative utilisation of excess marine biomass has been proposed, in which biomass is not used for fertilisation purposes, but instead its mass is reduced as much as possible by pyrolysis to ash.

In case contaminated seaweed is collected at a coastal region, pyrolysis of either the raw material or of the digestate could be used for energy recovery. These two possible pathways are presented in the block diagrams Figure 2 and Figure 3. In the first one, the direct pyrolysis of marine biomass was carried out after drying and sand removal. In the second case, the pyrolysis of the digestate of marine biomass was conducted, where, next to pyrolysis products, also biogas was obtained from the digestion process.

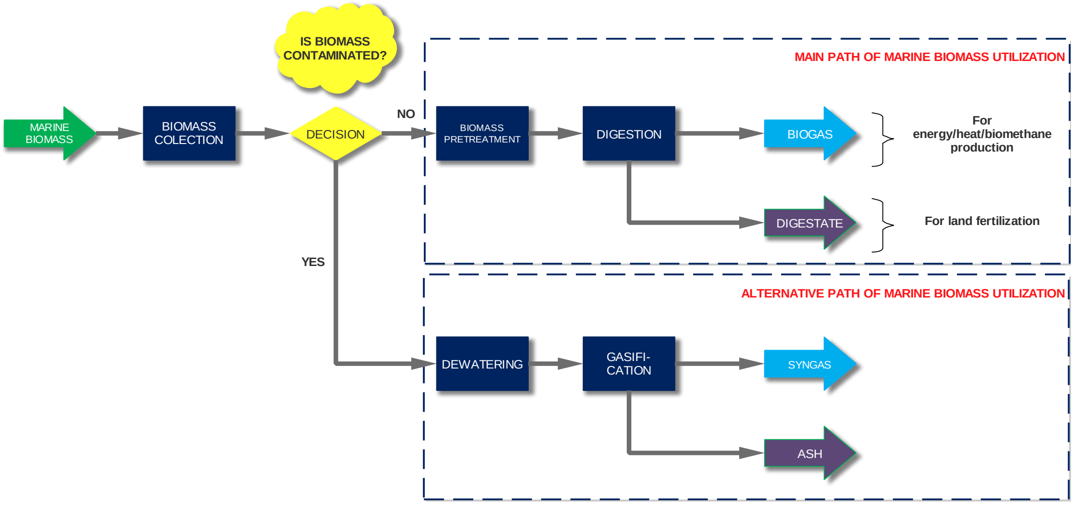

Figure 1. Diagram of marine biomass handling chain proposed in the COASTAL Biogas project

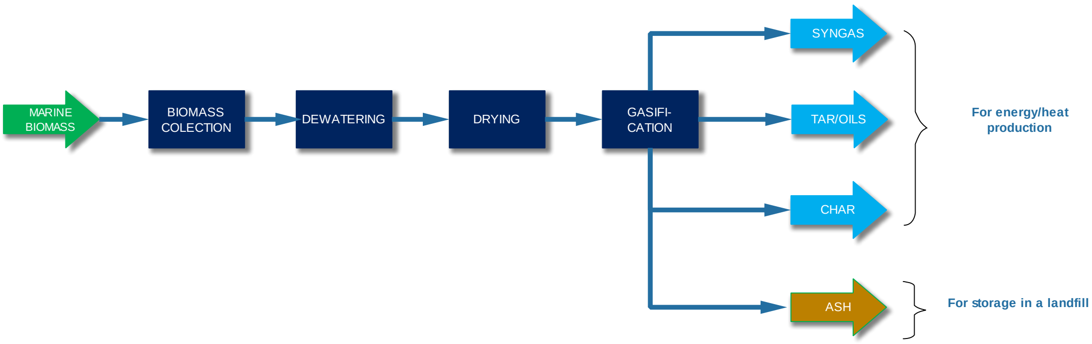

Figure 2. Block diagram of contaminated marine biomass utilisation directly in pyrolysis process

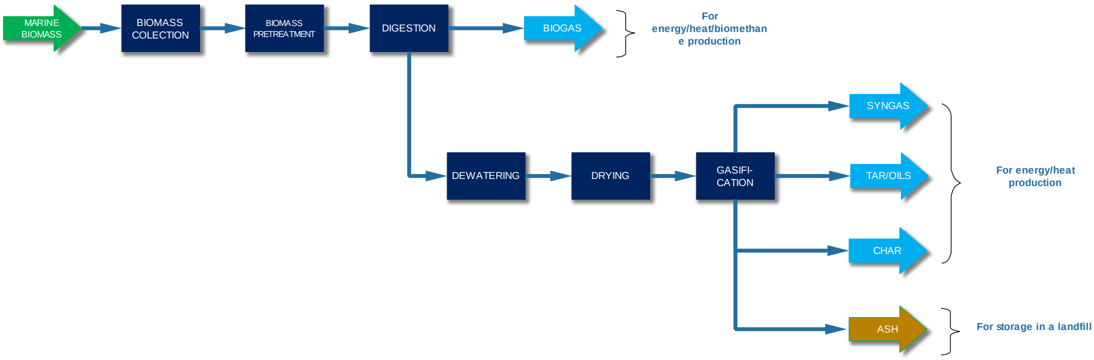

Figure 3. Block diagram of contaminated marine biomass utilisation in pyrolysis process of digestate

For the direct gasification of dried marine biomass, a plasma-induced method was applied. The following block diagram in Figure 4 shows the whole process of plasma induced gasification of contaminated marine biomass .

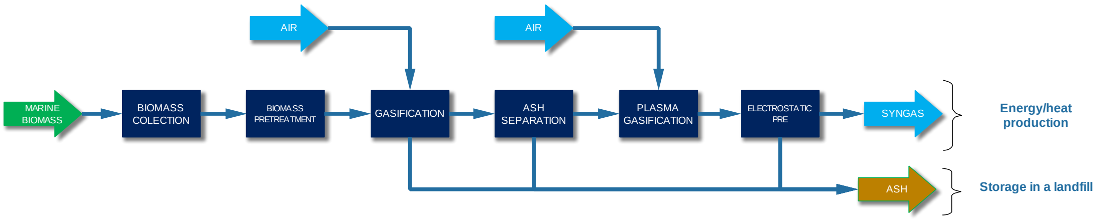

Figure 4. Block diagram of contaminated marine biomass utilisation in plasma induced gasification process

The energy balance presented in this report is not a thermodynamic energy balance, however, it shows almost all calculable or predictable input and output flows in the seaweed treatment process.

The report is divided into ten chapters. The first chapter is related to the characterisation of the biomass used in the biomethane potential measurements and pyrolysis test. In the next chapter, the contamination of heavy metals that may occur in the collected biomass is discussed. The following chapters are related to the methodology of digestion process measurements, pyrolysis and plasma assisted gasification of marine biomass. Chapter 7 contains the analysis of the energy balance of anaerobic digestion of marine biomass in different pre-treatment methods (scenario first presented in Figure 1 and Figure 2). In the chapters 8 and 10 energy recovery in pyrolysis and plasma assisted gasification of the seaweed (second scenario presented in Figure 4) are described. Chapter 9 presents an analysis of the energy balance of the marine biomass digestate utilised in scenario three presented in Figure 3.

1 Marine Biomass characteristic

The seaweed for the anaerobic digestion and pyrolysis experiments was collected from Melnrage beach (Figure 5), which is part of Klaipeda city and north of the Curonian Lagoon (Klaipeda channel). In the South, Melnrage reaches the northern breakwater and the access of Klaipeda port; in the East it is surrounded by Klaipeda Forest. The decision to collect the seaweeds from Melnrage beach was taken due to very high biomass availability at this location.

Figure 5. Location of seaweeds collection place by Lithuanian Energy Institute (Eimontas, 2020)

Biomass (Figure 6) was collected during wintertime when seaweeds had a high variation in chemical composition between the species. In contrast, shores were dominated by nutrient-poor algae during the summertime [2].

The collected seaweeds had a high amount of sand and other troublesome contaminations. In order to use it for anaerobic digestion or thermochemical processing, it should be washed to avoid excessive wear of equipment and to reduce dead useless volume in the bioreactor.

Marine biomass can contain high percentage of minerals (up to 3% of fresh weight) that can affect the activity of microorganisms in the anaerobic digestion process. The mineral salts mainly include light metal ions, such as sodium, potassium, calcium, and magnesium. At low concentrations, these metal ions are necessary nutrient sources for microbial growth and reproduction. When concentrations of sodium, potassium, and calcium is less than 350, 400, and 200 mg/dm^3, respectively, the microbial growth and cellular metabolism in microorganisms is stimulated, but when the concentration of the salts is higher than 3-5 g/dm^3 anaerobic digestion can be inhibited [3].

For that both reasons, algae was washed with tap water in order to reduce sand contents in the feedstock and the influence of salinity on the anaerobic digestion process.

The laboratory-based washing experiments were conducted at Gdańsk University of Technology (GUT) and Lithuanian Energy Institute (LEI).

A sample of the collected algae biomass was divided into two parts, one of which was mixed with tap water in a beaker with a volume of about 1 dm^3. The beaker was then set aside until the particles of a higher density than water were completely sedimented. Next, biomass was decanted and filtered on a paper filter. The process was repeated twice. Subsequently, the total solids were determined for both samples (washed and unwashed).

The sand content was determined as the loss of total solids after washing the sample with fresh water:

$$SC = \frac{\mathrm{TS}_1 - \mathrm{TS}_2}{\mathrm{TS}_1} \cdot 100 \qquad (1)$$

Legend:

TS_1 – total solids before washing
TS_2 – total solids after washing

Figure 6. Red seaweeds (Rhodophyta) collected at Melnrage beach, Lithuania

As it can be seen from the results presented on Table 2, the location of biomass collection is crucial in terms of the sand content in seaweed. When the algae is collected from the beach, the sand content is much higher compared to when it is collected from shallow water. It has also been found that sand removing is easier to conduct if the algae are fresh. It is much more difficult to wash off the sand from the biomass if it was lying on the beach for 1-3 days.

After washing a part of the seaweed was dried in a laboratory dryer in accordance with ISO 579 standard and was used for thermal analysis. The basic biomass parameters (TS, VS and elemental analysis) are presented in the Table 3. The total solids of samples were determined in accordance with the requirements of LST CEN / TS 15414-1: 2010 and LST EN 14774-1 [4,5] as the mass change of the sample during drying at 105 ± 2°C and expressed as a percentage by mass.

Table 2. Sand content in marine biomass

Type of algae	Sand content, [%]	Place of sampling
Enteromorpha compressa	11.65	Shallow water
Enteromorpha plumosa	4.96	Shallow water
Potamogeton pectinatus	4.00	Shallow water
Zostera marina	20.88	Beach
Pheaophyta	7.80	Shallow water

The ash tests of the biomass samples were performed in accordance with the methods described in LST EN 15403: 2011 and LST EN 14775: 2010 [6,7] as the mass loss of the sample during oxidised in air atmosphere at 550°C. The fixed carbon content was calculated as the percentage difference in humidity, volatile matter, and ash.

Table 3. Feedstock parameters (seaweeds, washed seaweeds and sewage sludge) used in BPM experiments at Lithuanian Energy Institute

Biomass	TS [%]	VS [%]	C [%]	H [%]	O [%]	N [%]	S [%]	Cl [%]	C/N
Enteromorpha compressa[1]	8.86	83.83	24.30	3.97	n.d.	2.32	n.d.	n.d.	10.5
Enteromorpha plumose[1]	7.19	79.71	19.48	3.19	n.d.	1.48	n.d.	n.d.	13.2
Potamogeton pectinatus[1]	13.07	61.39	15.27	2.31	n.d.	1.74	n.d.	n.d.	8.8
Zostera marina[1]	12.56	79.63	24.28	3.17	n.d.	1.62	n.d.	n.d.	15.0
Red algae[1]	17.23	63.87	13.74	1.88	n.d.	1.37	n.d.	n.d.	10.0
Unwashed Red seaweeds (Rhodophyta)[2]	42.68	53.83	34.58	5.16	6.79	3.65	3.54	0.43	9.5
Washed Red seaweeds (Rhodophyta)[2]	37.44	90.53	46.93	4.73	29.61	4.13	5.13	0.05	11.4
Sewage sludge[2]	4.19	55.60	29.89	3.87	14.41	2.99	1.08	0.24	10.0

n.d. – not investigated

Determination of C, H, N content in biomass samples have been carried out in accordance with the requirements of LST EN 15407: 2011 and LST EN 15104: 2011 [8],[9]. An elemental analyser (Thermo scientific Flash 2000) was used to determine the basic chemical elements (C, H, N, S) of seaweed, sewage sludge and digestate. The sulphur content was also determined by the Flash 2000 analyser but using a non-standardised method. Dried, crushed, and homogenised samples were analysed using a laboratory-developed device test procedure. The biomass samples were completely oxidised in an oxygen containing environment to determine carbon, hydrogen, nitrogen and sulphur content. The oxygen (O) content of the samples was calculated by difference.

The determination of chlorine content in seaweed, sewage sludge, and digestate was carried out in accordance with the requirements of LST EN 15408: 2011 and LST EN15289:

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[1] Algae collected by Gdańsk University of Technology at Gdansk Bay coast

[2] Algae collected by Lithuanian Energy Institute at Melnrage beach, Lithuania

2010 standard [10],[11] using an ion chromatograph (Dionex ISC 5000). The homogeneous biomass samples were burning dry, crushed and in a sealed container (bomb) at an oxygen pressure of 35 bar. After incineration, the gas was dissolved in deionised water. The resulting solution was analysed by DIONEX ISC-5000 ion chromatograph. The amount of chlorine in the sewage sludge samples was determined from the signal curve calibrated by the conductivity detector.

For determination of volatile matter (VM) dry samples were placed in the ceramic heating crucible of known mass. The sample in crucible was placed in the oven, which was preheated to 900 ± 10°C. The air environment was used. After the experiment, the crucible with the sample is removed from the oven and allowed to cool at the room temperature. The experiment takes 420 ± 5 sec. Volatile compounds are calculated from weight loss. Experiments were carried out in accordance with the requirements of LST EN ISO 18123:2015 [12]

The calorific value of marine biomass was determined in accordance with the requirements of LST EN 15400: 2011 and LST EN 14918: 2010 standards [13],[14] by an automated calorimeter (IKA C5000).

Metals and minerals were determined using the following standards: LST EN 15410: 2011, LST EN 15290: 2011 (Ca, K, Mg, P), LST EN 15411: 2011 and LST EN 15297: 2011 (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, V, and Zn) [15–18]. A Plasma Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Optima 8000) was used to determine the amounts of metals and minerals present in the biomass samples. The content of metals and minerals in seaweeds, sewage sludge, and digestate was determined by mineralisation using a mixture of hydrofluoric acid (HF), HNO_3 and $B(OH)_3$ acids in a ratio of 1:3:10. The resulting solution was diluted to 50 cm^3 and analysed using an induced plasma optical emission spectrometer.

For efficient operation of an anaerobic digester, a balanced supply of nutrients and trace elements is necessary, as these components are the building ingredients for microbial cells as also provide a suitable physico-chemical condition for optimum growth of microorganisms. In the literature the optimal C/N ratio for different biomass is reported as a value between 20 and 30 [19], but as described in many publications, the high biogas productivity can be also obtained when the value is in range 9 – 50 [20].

How can be seen in Table 3, the C/N ratios for all investigated algae except *Potamogeton pectinatus* were above 9.0, which means that the collected marine biomass can be an appropriate input for methane fermentation. In the case of *Potamogeton pectinatus*, the value was only 0.2 lower than the recommended which is within the limits of the standard deviation error range of the measure parameters.

2 Methane Potential of Algae

Anaerobic digestion is an environmental friendly technology that can utilise cast seaweed as a substrate for energy recovery. In order to obtain satisfying results, the co-digestion processes should be applied. That means that for optimising the process it is advised to use different feedstock sources as substrate. It can improve the C/N ratio and balance of the dry matter content.

To enhance the methane yield the algal biomass could be co-digested with sludge, cattle manure or other organic matter. This procedure results in synergistic effects on microorganisms increasing methane yields per unit of digester volume and biodegradability level [21].

Table 4 presents methane yields for different pure marine species. In Table 5, methane and biogas potential of different feedstocks in co-digestion are presented.

In general, algae have a lower methane potential than biomass sources like manure, though there are some species that in the optimum process condition could give comparable results like *Dunaliella salina, Euglena gracilis* and other examples. However, when considering *Dunaliella* genus as a feedstock, it can be seen that depending on the species the results can be dramatically different, from 24 to 323 SPTdm^3 CH$_4$/kg VS for *salina* and *tertiolecta*, respectively. Some species do not contain enough carbon in their composition, whereas the C/N ratio is a key parameter of the anaerobic digestion process for obtaining a satisfying performance. In order to provide the optimal carbon/nitrogen ratio, co-digestion with different other feedstocks with good bioavailability can be used. Nevertheless, it is essential to perform basic tests on the biogas and methane potential to get a knowledge on possibly achievable results.

Table 4. Methane potential for different algae species (n.d. – no data)

Algae species	Methane yield [SPTdm^{3}CH$_4$/kg VS]	Biogas yield [SPTdm^3/kg VS]	C:N ratio	Reference
A. esculenta	226	N/R	15.5	[22]
Arthrospira maxima	173	N/R	4.3-5.33	[23]
A. nodosum *- fresh* *- silage* *- effluent*	185.7 239.3 218.3	N/R	30.3 27.7 N/R	[24]
A. nodosum	166	N/R	26.0	[22]
Arthrospira platensis	283.4	481.0	N/R	[25]
Blue green algae	366	N/R	N/R	[26]
Chlamydomonas reinhardtii	387.4	587		[25]
Chlorella kessleri	217.8	335	N/R	[25]
Chlamydomonas reinhardtii and Pseudokirchneriella subcapitata	320	490	N/R	[27]
Chlorella sorokiniana	212	248	N/R	[28]
Chlorella vulgaris	286	N/R	N/R	[29]
Dunaliella salina	323.2	505	N/R	[25]
Dunaliella tertiolecta	24	N/R	N/R	[29]
Euglena gracilis	324.9	485	N/R	[25]

Algae species	Methane yield $[\text{SPTdm}^3\text{CH}_4/\text{kg VS}]$	Biogas yield $[\text{SPTdm}^3/\text{kg VS}]$	C:N ratio	Reference
F. serratus	101	N/R	15.5	[22]
F. spiralis	235	N/R	17.3	
F. vesiclosus	126	N/R	17.6	
H. elongate	260	N/R	21.4	
L. digitata *-fresh* *-silage* *-effluent*	340.8 371.4 376.1	N/R	37.3 31.1 N/R	[24]
L. digitata	218	N/R	22.3	[22]
Macroystis pyrifera and Durvillea Antartica (50% blend)	298	426	21.9	[24–30]
D. Antarctica	255	393	23.4	
Macroystis pyrifera	267	381	24.6	
Microcystis sp.	94.42 - 140.48	111.50 - 145.87	32.8	[31]
Nannochloropsis oculata	242	N/R	N/R	[32]
Scenedesmus obliquus	177.9	287	N/R	[25]
Scenedesmus sp. (single stage process)	309.5	N/R	N/R	[33]
Scenedesmus sp. (two stage process)	383	N/R	N/R	
S. latissima *-fresh* *-silage* *-effluent*	329.5 353.4 422.5	N/R	29.7 25.9 N/R	[24]
S. latissima	342	N/R	24.0	[22]
Spirulina maxima	350	N/R	4.16	[34]
S. polyschides *-fresh* *-silage* *-effluent*	358.8 294.9 273.1	N/R	38.7 31.9 N/R	[24]
S. polyschides	263	N/R	23.2	[22]
Tetraselmis	250–310	N/R	N/R	[35]
U. lactuca *-fresh* *-silage* *-effluent*	247.2 314.1 220.3	N/R	19.9 27.6 N/R	[24]
U. lactuca	190	N/R	8.5	[22]
Seaweed	102±25	152	N/R	[36]
Brown algae	179±35	232		
Green algae	256±28	425		
Fish viscera	127±20	244		
Brown seaweed: *- Undaria pinnatifida* *- Saccorhiza polyschides* *- Sargassum muticum* *- Saccharina latissimi* *- Himanthalia elongata*	242 ± 41 216 ± 16 130 ± 10 209 ± 15 202 ± 28	N/R	12.2 20.1 11.9 20.6 15.8	[37]
Red seaweed: *- Gracilaria verrucosa* *- Palmaria palmata*	139 ± 5 279 ± 1	N/R	11.2 19.1	[37]
Green algae *- Codium tomentosum* *- Ulva lactuca*	144 ± 14 241 ± 10	N/R	8.8 15.1	

Algae species	Methane yield [SPTdm^{3}CH$_4$/kg VS]	Biogas yield [SPTdm^3/kg VS]	C:N ratio	Reference
40% Chlamydomonas, 20% Scenedesmus and 40% of an unknown microalgae tentatively characterized as Nannocloropsis	400.0	571.0	N/R	[38]
58% Acutodesmus obliquus, 36% Oocystis sp., 1% Phormidium and 5% Nitzschia	200.0	277.8	N/R	
Microspora	300.0	500.0	N/R	
Seaweed (mixture of brown and red seaweed) *- raw* *- hydrolysis leachate* *- post-treatment leachate* *-hydrolysis leachate/post-treatment leachate*	120 ± 10 150 ± 10 110 ± 20 340 ± 20	N/R	N/R	[39]

Table 5. Methane potential for different feedstock compositions

Feedstock	Methane yield [Sdm^{3}CH$_4$/kg VS]	Biogas yield [Sdm^3/kg VS]	C:N ratio	Reference
Algal sludge	143.3 ± 7.0	N/R	6.7	[40]
(25%) of waste paper + algal sludge	242.0 ± 18.3	N/R	11.8	
(50%) of waste paper + algal sludge	292.5 ± 18.8	N/R	18.0	
(75%) of waste paper + algal sludge	79.3 ± 28.5	N/R	36.4	
(100%) of waste paper	113.0 ± 9.0	N/R	21.5	
100% MS (mixed sludge)	335 ± 27	744±30	N/R	[41]
15% U (Ulva sp.) + 85% MS	296 ± 19	710±21	N/R	
30% U + 70% MS	285 ± 19	663±20	N/R	
60% U + 40% MS	257 ± 4	598±12	N/R	
80% U + 20% MS	229 ± 3	521±5	N/R	
100% U	196 ± 9	456±9	N/R	
Mono-digestion *-A. platensis* *-Barley straw* *-Beet silage* *-L. digitata*	357.1 196.8 393.5 306.5	N/R	4.3 145.5 41.7 28.7	[42]
85% A. platensis, 15% barley straw	347.8	N/R	N/R	
45% A. platensis, 55% beet silage	360.9	N/R	N/R	
15% A. platensis, 85% L. digitata	311.5	N/R	N/R	
Mono-digestion *-U. lactuca* *-Manure*	152 ± 19 262 ± 20	N/R	N/R	[43]

Feedstock	Methane yield [Sdm^{3}CH$_4$/kg VS]	Biogas yield [Sdm^3/kg VS]	C:N ratio	Reference
80% manure: 20% Ulva	259 ± 8	N/R	N/R	
60% manure: 40% Ulva	238 ± 23	N/R	N/R	
50% manure: 50% Ulva	206 ± 11	N/R	N/R	
Pig manure	350	N/R	<10	[44]
Raw algae	150	N/R	<10	
Lipid extracted algae	200	N/R	N/R	
Protein extracted algae	180	N/R	N/R	
100% of algae	155	225	6	[45]
80% of algae + 20% of corn straw	200	308	15	
65% of algae + 35% of corn straw	230	369	20	
50% of algae + 50% of corn straw	160	270	25	
100% of corn straw	80	145	71	
50% Algae+50% raw sludge	360	N/R	N/R	[46]
100% waste activated sludge+0% Chlorella	304	485	N/R	[47]
96% waste activated sludge+4% Chlorella	310	481	N/R	
89% waste activated sludge+11% Chlorella	286	476	N/R	[47]
59% waste activated sludge+41% Chlorella	303	479	N/R	[47]
0% waste activated sludge+100% Chlorella	135	285	N/R	[48]
Microalgae (Chlorella vulgaris and Scenedesmus obliquus) 0%+ Food waste 100%	342	N/R	N/R	[48]
Microalgae (Chlorella vulgaris and Scenedesmus obliquus) 12%+ Food waste 88%	287	N/R	N/R	
Microalgae (Chlorella vulgaris and Scenedesmus obliquus) 25%+ Food waste 75%	230	N/R	N/R	
Microalgae (Chlorella vulgaris and Scenedesmus obliquus) 37%+ Food waste 63%	225	N/R	N/R	
-Seaweed *-Solid cow manure* *-Seaweed/solid cow manure*	170 ± 10 90 ± 10 13 0± 10	350± 10 240± 10 270± 10	9.3 16.9 N/R	[49]
0:10 chicken manure to raw Chlorella	95.93	N/R	4.65 ± 0.37	[50]
2:8 chicken manure to raw Chlorella	111.99	N/R	N/R	

Feedstock	Methane yield [Sdm^{3}CH$_4$/kg VS]	Biogas yield [Sdm^3/kg VS]	C:N ratio	Reference
4:6 chicken manure to raw Chlorella	120.88	N/R	N/R	
6:4 chicken manure to raw Chlorella	125.12	N/R	N/R	
8:2 chicken manure to raw Chlorella	169.66	N/R	N/R	
10:0 chicken manure to raw Chlorella	148.57	N/R	12.28 ± 0.14	
100% cattle manure *- mesophilic* *- thermophilic*	143 ± 20 154 ± 21	N/R	N/R	[51]
85% cattle manure *15% Laminaria* *- mesophilic* *- thermophilic*	139 ± 42 119.6 ± 35	N/R	N/R	
76% cattle manure *24% Laminaria* *- mesophilic* *- thermophilic*	136 ± 11 165.6 ± 13.5	N/R	N/R	
59% cattle manure *41% Laminaria* *- mesophilic* *- thermophilic*	136 ± 11 185.7 ± 23	N/R	N/R	
Chlorella post transesterified residues+ Glycerol	308	446	8.53	[52]
Algae+ Swine manure [ISR- inoculum to substrate ratio] 3.0	190.90	N/R	N/R	[53]
Algae+ Swine manure (ISR 2.0)	219.99	N/R	N/R	
Algae+ Swine manure (ISR 1.0)	96.23	N/R	N/R	
Algae+ Swine manure (ISR 0.5)	47.59	N/R	N/R	
100% WAS (waste activated sludge)	350	N/R	N/R	[54]
75% WAS-25% C. sorokiniana	442	N/R	N/R	
50%WAS-50%C. sorokiniana	345	N/R	N/R	
25% WAS-75% C. sorokiniana	320	N/R	N/R	
100% C. sorokiniana	300	N/R	N/R	
100:0 algae to sewage sludge ratio	310	512	10.8	[55]
90:10 algae to sewage sludge ratio	332	568	10.6	
80:20 algae to sewage sludge ratio	355	589	10.3	
65:35 algae to sewage sludge ratio	359	581	9.82	
50:50 algae to sewage sludge ratio	380	600	9.35	

Feedstock	Methane yield $[Sdm^3CH_4/kg\ VS]$	Biogas yield $[Sdm^3/kg\ VS]$	C:N ratio	Reference
35:65 algae to sewage sludge ratio	389	599	9.39	
20:80 algae to sewage sludge ratio	402	623	8.43	
10:90 algae to sewage sludge ratio	400	608	8.12	
0:100 algae to sewage sludge ratio	390	573	7.81	
Nannochloropsis salina biomass	220	280	6.5 -12.2	[56]
Corn silage	390	600	32.6 -44.5	
Corn-cob-mix	390	570	26.2	
2:1 Nannochloropsis salina biomass to corn silage ratio	310	440	N/R	
1:2 Nannochloropsis salina biomass to corn silage ratio	370	580	N/R	
1:6 Nannochloropsis salina biomass to corn silage ratio	410	650	N/R	
1:3 Nannochloropsis salina biomass to corn-cob-mix	370	600	N/R	
O. tenuis fermented with pig manure mixing ratio 3.0	183	N/R	N/R	[57]
O. tenuis fermented with pig manure mixing ratio 2.0	191	N/R	N/R	
O. tenuis fermented with pig manure mixing ratio 1.0	84	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *1.0:0.0*	106.9	N/R	N/R	[58]
$VS_{microalgae}$: $VS_{food\ waste}$ *0.8:0.2*	285.2	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *0.6:0.4*	381.6	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *0.5:0.5*	525.1	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *0.4:0.6*	549.1	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *0.2:0.8*	639.8	N/R	N/R	
$VS_{microalgae}$: $VS_{food\ waste}$ *0.0:1.0*	575.7	`N/R	N/R	
Control microalgae *-Untreated* *-Pretreated*	264 ± 3 287 ± 9	N/R	7.4	[59]
80% microalgae + 20% wheat straw *-Untreated* *-Pretreated*	279 ± 6 289 ± 15	N/R	8.9	

Feedstock	Methane yield [Sdm^{3}CH$_4$/kg VS]	Biogas yield [Sdm^3/kg VS]	C:N ratio	Reference
50% microalgae + 50% wheat straw *-Untreated* *-Pretreated*	289 ± 3 299 ± 15	N/R	13.1	
20% microalgae + 80% wheat straw *-Untreated* *-Pretreated*	289 ± 4 315 ± 7	N/R	26.4	
Control wheat straw *-Untreated* *-Pretreated*	279 ± 9 304 ± 7	N/R	95.4	
100% Cattle Manure *-35°C* *-50°C*	143.6 154.1	229.4 267.5	N/R	[60]
11% Ulva *sp.* *89%c cattle manure (50°C)*	157.6	262.7	N/R	
24% Ulva *sp.* *76% cattle manure (50°C)*	133.5	237.5	N/R	
37% Ulva *sp.* *63% cattle manure (50°C)*	70.8	153.9	N/R	
15% Laminaria *-35°C* *-50°C*	139.2 119.6	231.2 12.9	N/R	
24% Laminaria *-35°C* *-50°C*	136 165.6	234.5 292.1	N/R	
41% Laminaria *-35°C* *-50°C*	139 185.7	246.5 326.0	N/R	

The chemical composition of seaweed plays a significant role in the fermentation process. According to Chynoweth et al. the nutrients required for anaerobic digestion follow the order of importance: nitrogen, sulphur, phosphorus, iron, cobalt, nickel, molybdenum and selenium [61]. However, the knowledge of the C, N, and O content makes possible to calculate the theoretical bio-methane potential. The elemental composition of different algal species is presented in Table 6.

Table 6. Elemental composition of different algae species

Algae	Organic element [%TS]						Notes	Reference
	C	H	O	N	S	P		
Fucus Vesiculosus	36.98	5.12	35.98	2.02	2.82	0.14	Collected in October 2014 in the Gulf of Riga (56o 59' N and 23o 51'E) characterised by shallow depths, low salinity level and high nutrient level. The biomass was cut to a size of 2cm and then	[62]

Algae	Organic element [%TS]						Notes	Refe-rence
	C	H	O	N	S	P		
							reduced with a mortar to <2mm	
Cladophora Sp.	31.5±1.23	4.29±0.09	61.3±1.53	2.88±0.19	-	-	Collected in summer of 2016 near the city of Liepaja (West Latvia). The biomass was cut to a size of 0,5cm and then reduced with a mortar to <1mm	[63]
Ulva Intestinalis	34.6±0.19	5.28±0.04	59.1±0.28	1.18±0.06	-	-		
Ulva Intestinalis	26.43			1.97		0.16	Collected in summer of 2012 on the Sopot beach	[64]
Fucus Vesiculosus	35.56			1.42		0.16		
Furcellaria Lumbricalis	31.48			2.41		0.12		
Macrophyte Mixture	29.32			1.93		0.22	Collected in Sopot In Trelleborg from 02.06.2011 to 20.05.2012. Among found species there were: brown filamentous macroalgae (Ectocarpus siliculosus, Pilayella littoralis and F. vesiculosus, green macroalgae (Cladophora sp., Enteromorpha sp.), red macroalga P. fucoides, F. lumbricalis,) and Z. marina (a vascular plant).	[64]
Ulva Spp.	34.38±3.2			2.89±1.6		0.23±0.01	Was grown artificially on a polyethylene substrata in two locations in the northern Baltic Sea near Hämmärö and Tvärminne. Most of the formed biomass (more than 94%) were invertebrates. Among major algal species there were found: Ulva spp., Cladophora glomerate, Ceramium tenuicorne, Polysiphonia fibrillose, Pylaiella littoralis and Ectocarpus siliculosus. The measurements were made in autumn 2011 and summer 2012	[65]]
Cladophora Glomerata	26.44±5.6			2.38±0.8		0.28±0.08		
Polysiphonia Fibrillose	32.23±5.5			4.12±1.1		0.22±0.05		
Ceramium Tenuicorne	28.66±4.9			3.04±0.5		0.27±0.07		
Filamentous Brown Algae	23.76±3.9			2.54±0.61		0.3±0.07		
Enteromorpha Compressa	24.30	3.97		2.32			Collected within COASTAL Biogas project	
Enteromorpha Plumosa	19.48	3.19		1.48				
Potamogeton Pectinatus	15.27	2.31		1.74				
Zostera Marina	24.28	3.17		1.62				

Algae	Organic element [%TS]						Notes	Reference
	C	H	O	N	S	P		
Red Algae	13.74	1.88		1.37			Collected within COASTAL Biogas project	

3 Heavy Metal Content in the Digestate and Marine Biomass

Although seaweeds seem to have a great potential as a feedstock in anaerobic digestion due to high biomass yields and lack of competition with terrestrial plants on limited agricultural land, their potentially high heavy metals content creates significant problems for the digestion process, but also for the further use of the digestate. The micro and macro elements uptake by algae strongly depends on factors as water salinity [66], characteristics of habitats (e.g. presence of an nearby industrial area or existence of an estuary whose waters might carry additional nutrient loads from urban and agriculture areas). The main limiting factor of digestate utilisation as an organic fertiliser is the heavy metals concentration. Table 7 presents the heavy metal and Table 9 nutrients contents in some algae species at different Baltic Sea regions.

A more detailed analysis of heavy metal pollution of marine biomass and periods and areas of occurrence in the Baltic Sea region is presented in report D4.2 Part B.

In the COASTAL Biogas project, contents of selected heavy metals (Cd, Cu, Ni, Fe, Cr, Hg) in algae samples used for biogas potential measurement as well as biomass used for co-fermentation (cattle slurry) were analysed.

The analyses of heavy metal content were also carried out in experiments conducted by the Lithuanian Energy Institute, using the following standards: LST EN 15410: 2011, LST EN 15290: 2011 (Ca, K, Mg, P), LST EN 15411: 2011 and LST EN 15297: 2011 (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, V, and Zn) [15–18]. The inductively coupled plasma optical emission spectrometry technique (ICP-OES) was used to determine the number of metals and minerals present in the samples (Optima 8000 apparatus). At Gdańsk University of Technology measurements of heavy metals in biomass were provided using the inductively coupled plasma mass spectrometry (ICP-MS) on PerkinElmer NexION 300D apparatus.

The seaweed, sewage sludge, and digestate were mineralised by oxidising with strong oxidants (mineral oxidising acids, potassium permanganate, perhydrol, fluoric acid). If the sample was very concentrated or contained organic compounds difficult to decompose, concentrated nitric acid was used together with perchloric acid.

Table 10 shows the heavy metal and mineral contents in the following biomass samples: collected algae, sewage sludge and digestate of algae and marine biomass measured at Lithuanian Energy Institute.

Table 8 shows the heavy metals and total phosphorus contents in the following biomass samples: collected algae, cattle slurry and digestate of algae and marine biomass measured at Gdańsk University of Technology.

Among the collected algae species in the Pomerania region, the highest concentration of heavy metals (Cu-12.8±0.03, Fe-2830±6.23, Cr-3.47±0.01, Ni-4.3±0.01, Cd-0.49±0.01, Hg-1.39±0.01 mg/kg TS) was found in mixed seaweed from Gdańsk beach. This was also confirmed with digestate results where the highest concentration of heavy metals (Cu-5.66±0.03, Fe-262±1.16, Cr-0.56±0.01, Ni-0.78±0.01, Cd-0.05±0.01, Hg-1.2±0.01) was found in 25% mixed seaweed from Gdańsk beach and cattle slurry digestate. It should be also noted that cattle slurry is characterized by relatively low heavy metals (only concentration of Cu is relatively high) and the highest P level (1,070±5.35 mg/kg TS).

Table 7. Heavy metal contents in some algae species at different Baltic Sea regions

Species	Place of collection	Year of collection	Heavy metals [mg/kg TS]										
			Cd	Cu	Pb	Ni	Zn	Mn	Fe	Sr	Cr	Se	As
Enteromorpha sp. [67]	Southern Baltic	2000-2003	not detected	3.78 ± 0.87	2.61 ± 0.71	3.84 ± 1.17	53.1 ± 16.5	151.0 ± 58.6	-	-	-	-	-
Enteromorpha sp. [67]	Gulf of Gdansk	2000-2003	0.44 ± 0.24	4.92 ± 2.33	3.77 ± 2.17	3.61 ± 1.71	64.1 ± 40.5	172.7 ± 86.3	-	-	-	-	-
Enteromorpha sp. [67]	Vistula Lagoon	2000-2003	0.24 ± 0.18	4.61 ± 1.37	3.56 ± 0.83	8.20 ± 1.61	32.1 ± 12.0	361.5 ± 111.0	-	-	-	-	-
Cladophora sp. [68]	Southern Baltic	2000-2003	not detected	5.15 ± 1.28	4.35 ± 1.35	6.36 ± 2.21	67.5 ± 18.2	253.3 ± 104	-	-	-	-	-
Cladophora sp. [68]	Gulf of Gdansk	2000-2003	0.29 ± 0.12	5.32 ± 1.99	5.11 ± 2.69	3.50 ± 1.87	63.0 ± 33.3	298 ± 161	-	-	-	-	-
Cladophora sp. [68]	Vistula Lagoon	2000-2003	0.19 ± 0.09	8.36 ± 3.09	7.46 ± 3.76	11.42 ± 3.99	73.1 ± 27.6	1185 ± 450	-	-	-	-	-
Fucus vesiculosus [62]	Gulf of Riga	October 2014	-	12,7	11	-	89	1680	490	930	10	0,1	-
Ulva spp. [69]	Rymättylä	2011	0.18 ± 0.01	16.4 ± 7.6	0.615 ± 0.04	-	35.5 ± 6.5	-	-	-	-	-	-
Ulva spp. [69]	Rymättylä	2012	0.24	6	0.65	-	24	-	-	-	-	-	2.7
Cladophora glomerata [69]	Rymättylä	2011	0.75 ± 0.16	18.67 ± 2.62	7.4 ± 0.5	-	119 ± 15.56	-	-	-	-	-	8.23 ± 0.87
Cladophora glomerata [69]	Rymättylä	2012	1.25 ± 0.05	16 ± 1	4.65 ± 0.85	-	90 ± 8	-	-	-	-	-	7.9 ± 2.1
Polysiphonia fibrillosa [69]	Rymättylä	2011	4.93 ± 3.59	17.67 ± 2.49	3.7 ± 0.22	-	230 ± 106.77	-	-	-	-	-	5.53 ± 0.34
Polysiphonia fibrillosa [69]	Rymättylä	2012	5.97 ± 1.72	22.33 ± 0.94	4.43 ± 2.4	-	206.67 ± 4.71	-	-	-	-	-	5.27 ± 1.52
Ceramium tenuicorne [69]	Rymättylä	2012	1.5 ± 0.5	22 ± 1.63	5 ± 1.78	-	99.67 ± 29.17	-	-	-	-	-	7.03 ± 0.85
Filamentous brown algae [69]	Rymättylä	2012	3.85 ± 0.75	21.5 ± 2.5	7.15 ± 2.45	-	185 ± 25	-	-	-	-	-	11.4 ± 4.6
Ulva spp. [69]	Tvärminne	2011	0.1 ± 0.01	6.35 ± 0.35	0.35 ± 0.08	-	24.5 ± 0.5	-	-	-	-	-	2.5 ± 0.1
Ulva spp. [69]	Tvärminne	2012	0.06	4.5	0.61	-	12	-	-	-	-	-	1.4
Cladophora glomerata [69]	Tvärminne	2012	0.34 ± 0.03	10.67 ± 0.47	6.73 ± 0.53	-	64.33 ± 4.11	-	-	-	-	-	6.03 ± 0.75
Filamentous brown algae [69]	Tvärminne	2012	0.55 ± 0.16	13.67 ± 0.47	10.63 ± 1.29	-	83.33 ± 9.84	-	-	-	-	-	12.67 ± 1.25

Table 8. Heavy metal contents in biomass samples used in bio-potential measurement experiments made at Gdańsk University of Technology

Sample	Place of collection	Year of collection	Heavy metals [mg/kg TS]						P_{Total} [mg/kg TS]
			Cu	Fe	Cr	Ni	Cd	Hg	
Cattle slurry	Barkoczyn	10.05.2019	6.64 ± 0.04	87.3 ± 0.44	0.27 ± 0.01	0.68 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	1070 ± 5.35
Enteromorpha Compressa	Rzucewo	10.05.2019	0.5 ± 0.01	117 ± 1.13	0.16 ± 0.01	0.17 ± 0.01	0.03 ± 0.01	0.31 ± 0.01	745 ± 7.16
Enteromorpha Plumosa	Rzucewo	10.05.2019	0.47 ± 0.01	211 ± 1.27	0.23 ± 0.01	0.2 ± 0.01	0.03 ± 0.01	0.13 ± 0.01	248 ± 1.49
Mix of *Zostera Marina* and *Enteromorpha Plumosa*	Rzucewo	10.05.2019	0.92 ± 0.01	402 ± 2.34	0.72 ± 0.01	0.51 ± 0.01	0.1 ± 0.01	0.27 ± 0.01	425 ± 2.47
Zostera Marina	Rzucewo	10.05.2019	1.33 ± 0.01	396 ± 0.44	0.64 ± 0.01	0.65 ± 0.01	0.14 ± 0.01	0.34 ± 0.01	734 ± 0.81
Mix of algae mainly Phaeophyta	Brzezno, Gdansk	10.05.2019	12.8 ± 0.03	2830 ± 6.23	3.47 ± 0.01	4.3 ± 0.01	0.49 ± 0.01	1.39 ± 0.01	881 ± 1.94
(25% Enteromorpha Compressa) Digestate	GUT laboratory	10.06.2020	4.52 ± 0.02	66 ± 0.19	0.19 ± 0.01	0.56 ± 0.01	0.02 ± 0.01	0.26 ± 0.01	817 ± 2.29
(25% Enteromorpha Compressa) Digestate	GUT laboratory	10.06.2020	3.71 ± 0.01	157 ± 0.19	0.2 ± 0.01	0.88 ± 0.01	0.01 ± 0.01	0.23 ± 0.01	692 ± 0.84
(25% Mix of Zostera Mmarina and Enteromorpha Plumosa) Digestate	GUT laboratory	10.06.2020	4.52 ± 0.03	119 ± 0.77	0.3 ± 0.01	0.54 ± 0.01	0.02 ± 0.01	0.3 ± 0.01	818 ± 5.24
(25% Mix of Zostera Mmarina and Enteromorpha Plumosa) Digestate	GUT laboratory	10.06.2020	3.67 ± 0.01	101 ± 0.12	0.27 ± 0.01	0.47 ± 0.01	0.03 ± 0.01	0.29 ± 0.01	686 ± 0.76
(25% Mix of Zostera Mmarina and Enteromorpha Plumosa) Digestate	GUT laboratory	10.06.2020	5.66 ± 0.03	262 ± 1.16	0.56 ± 0.01	0.78 ± 0.01	0.05 ± 0.01	1.2 ± 0.01	879 ± 3.87

Table 9. Nutrients contents in some algae species at different Baltic Sea regions

Species	Place of collection	Year of collection	Macroelements [mg/g TS]			
			K	Na	Mg	Ca
Enteromorpha sp. [67]	Southern Baltic	2000-2003	52.7 ± 6.7	35.0 ± 10.5	14.7 ± 3.0	6.5 ± 2.8
Enteromorpha sp. [67]	Gulf of Gdańsk	2000-2003	35.8 ± 10.9	25.7 ± 7.7	18.0 ± 3.6	6.4 ± 3.1
Enteromorpha sp. [67]	Vistula Lagoon	2000-2003	26.4 ± 6.2	20.5 ± 6.5	19.5 ± 5.4	5.5 ± 1.0
Cladophora sp. [68]	Southern Baltic	2000-2003	53.4 ± 11.7	37.3 ± 7.2	19.4 ± 5.7	4.5 ± 1.3
Cladophora sp. [68]	Gulf of Gdańsk	2000-2003	52.7 ± 6.7	35.0 ± 10.5	14.7 ± 3.0	6.5 ± 2.8
Cladophora sp. [68]	Vistula Lagoon	2000-2003	35.8 ± 10.9	25.7 ± 7.7	18.0 ± 3.6	6.4 ± 3.1
Fucus vesiculosus [70]	Gulf of Riga	October 2014	26.4 ± 6.2	20.5 ± 6.5	19.5 ± 5.4	5.5 ± 1.0
Ulva spp. [69]	Rymättylä	2011	53.4 ± 11.7	37.3 ± 7.2	19.4 ± 5.7	4.5 ± 1.3

As it can be seen in the given data from Lithuanian Energy Institute measurements, the highest concentrations of Zn and Mn elements were determined in almost all feedstocks. The lowest concentration of Zn and Mn (8.4 and 88.2 mg/kg TS) was obtained for the washed seaweed, while the highest of 1,475 and 859.1 mg/kg TS for the sewage sludge, respectively. The highest and the lowest concentration of P (46,512 and 11,952 mg/kg) was obtained for the digestate #1 (described in paragraph **Fehler! Verweisquelle konnte nicht gefunden werden.**) and the washed seaweed, while the highest and the lowest concentration of nitrogen (41,300 and 25,600 mg/kg) for the washed seaweed and the digestate #3, respectively.

Table 10. Heavy metal contents in biomass samples used in bio-potential measurement experiments provided at LEI

Sample		Unwashed seaweeds	Washed seaweeds	Sewage sludge	Digestate #1**)	Digestate #2**)	Digestate #3**)
Heavy metals [mg/kg TS]	As	n.d.*)	n.d.*)	n.d.*)	1.5	0.88	n.d.*)
	Cd	n.d.*)	n.d.*)	n.d.*)	n.d.*)	n.d.*)	n.d.*)
	Co	n.d.*)	n.d. *	4.56	3.44	2.27	5.29
	Cr	9.11	2.87	100.25	93.72	93.59	127.2
	Cu	8.15	8.19	246.25	231.47	209.58	318.85
	Mn	183.09	88.16	859.1	645.5	579.18	580.2
	Ni	7.41	2.49	56.43	52.07	49.54	56.82
	Pb	n.d.*)	n.d.*)	25.13	25.84	25.68	20.32
	Sb	n.d.*)	n.d.*)	2.1	0.68	0.54	n.d.*)
	V	n.d.*)	n.d.*)	14.71	n.d.*)	n.d.*)	n.d.*)
	Zn	40.91	8.42	1475.83	770.67	746.05	704.7
PTotal [mg/kg TS]		23373.31	11952.63	41622.99	46512.03	43207.29	34843.21
K [mg/kg TS]		12737.94	10286.94	9042.71	7407.79	8934.35	7983.90
Ca [mg/kg TS]		10163.31	6532.63	6910.05	9838.75	10020.04	5797.19
Mg [mg/kg TS]		1451.90	1063.83	24212.30	15630.55	13898.13	14574.07

*)n.d. – not detected

**) obtained in the semi-continuous digestion process described in paragraph Fehler! Verweisquelle konnte nicht gefunden werden.

4 Methodology and Measurements

4.1 Methodology of Biomethane Potential Measurements

To determine the biomethane potential of seaweeds, a single-charge test was performed using 15 pieces of 500 cm^3 volume vessels (Figure 7). In the thermostatic reservoir (Figure 7 A) mesophilic temperature (37 ± 0.2°C) was controlled. To absorb carbon dioxide (CO_2) released gases passes through sodium hydroxide solution (Figure 7 B) while methane penetrates straight to the accounting system of methane (Figure 7 C). Methane production is continuously recorded and automatically adjusted according to standard (1 bar and 0°C) conditions.

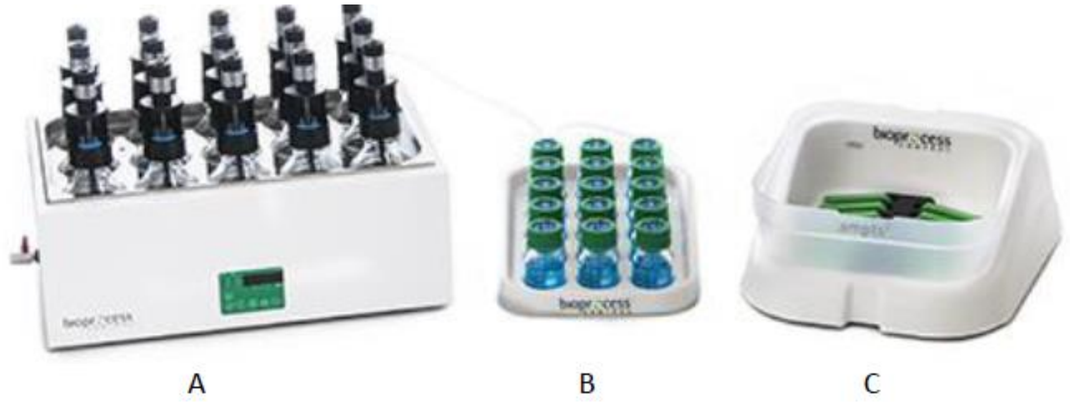

Figure 7. Biomethane Potential Bench: A-Thermostatic Reservoir; B- CO_2 absorption device; C - meter for measuring the amount of methane

4.2 Methodology of the Experiments in Semi-continuum Digestion Process

Anaerobic digestion experiments in a semi-continuum process were performed in vertical lab-scale bioreactors equipped with data acquisition system. The work volume of the stainless-steel reactor was 20 dm^3, which was equipped in adjustable rotation speed agitator, pH-meter, biogas flowmeter, biogas storage tank and composition analyser of biogas. Temperature sensors control the temperature in the bioreactor. The bioreactor mixing cycle and temperature are controlled automatically. Reactor temperature, substrate acidity, biogas amount and composition are recorded by a programmed logical widget.

Released biogas accumulates in the upper part of the reactor chamber, passes through the pipe and reach a volumetric biogas analyser. Biogas is collected in a plastic bag (“Tedlar bag”). Collected biogas is analysed by the Awite AwiFlex analyser. It can detect amounts of hydrogen sulfide (H_2S), carbon dioxide (CO_2), methane (CH_4) and oxygen (O_2) in the biogas. During the experiment, methane (CH_4) and hydrogen sulfide (H_2S) concentrations were measured with an accuracy of ±3%. Mesophilic temperature (37 ± 0.5°C) was controlled during the whole process.

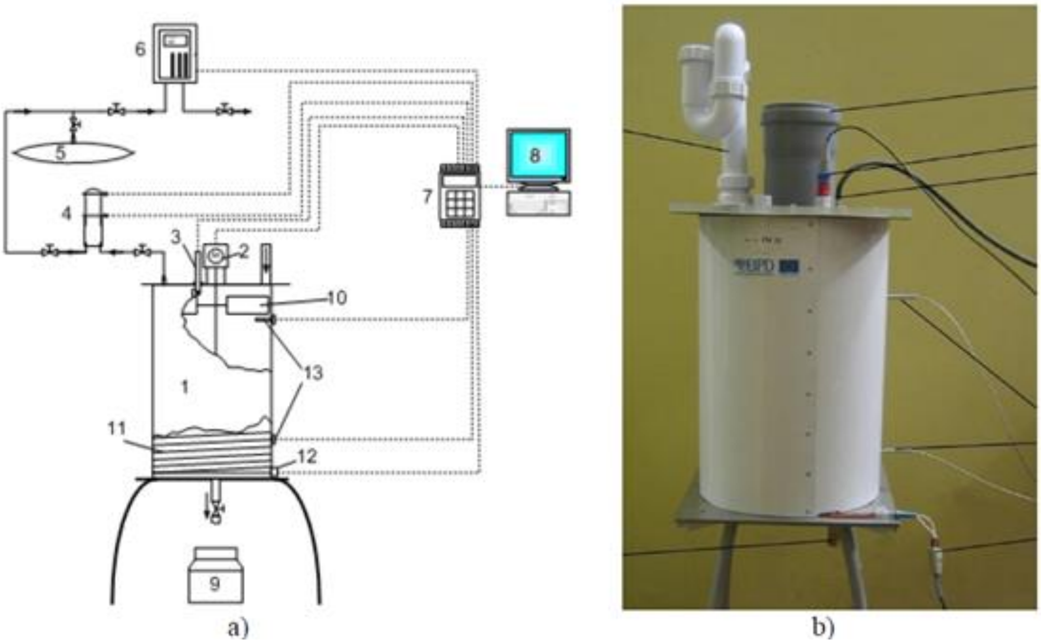

Figure 8. Bioreactor for anaerobic treatment a) schematic view; b) real view. 1-Bioreactor, 2- electronic gear shifting system, 3- pH meter, 4- biogas meter, 5- biogas tank, 6- biogas composition analyser, 7- programmed logical widget, 8 - computer, 9 – tank for recycled substrate; 10 - mixer, 11 - heating element, 12 - heating element control, 13 - temperature sensors.

4.3 Determination of biogas yield and energy value

The results of studies on the conversion of raw materials into biogas can be evaluated using several indicators: biogas production rate (b), biogas production yield from recycled biomass mass unit (B_M), biogas yield from dry matter (B_{DM}) and biogas yield from dry organic matter (B_{OM}). The intensity of biogas production represents duration of the biodegradation of a single charge of biomass. The comparative instantaneous biogas production rate per bioreactor operated volume unit per time unit is determined from the instantaneous biogas production values (b_{DT}), which are obtained by experimentally measuring the amount of biogas produced over time interval (dt). In the case at hand, the volume of biogas is determined by means of a volumetric meter, which generates an impulse corresponding to 200 cm^3 of biogas in the biogas accounting system. Daily biogas production data and changes of biogas production intensity throughout the sample study period until full biodegradation of biomass are used in this work. The comparative instantaneous biogas production rate per operated reactor volume per unit time is given by the following equation:

$$b_{Vm} = \frac{b_{dt}}{V_{rd} \cdot dt} \tag{2}$$

b_{Vm} - comparative instantaneous biogas production rate per reactor volume unit per time [dm^3/dm^3 day]
b_{dt} - the amount of biogas produced during the period dt [dm^3]
V_{rd} - used reactor volume [dm^3]
dt - a period of time [days]

The comparative average biogas production rate per reactor used volume unit over a period of one day is determined using the following expression:

$$b_V = \frac{n \cdot b_{dt}}{V_{rd}} \quad (3)$$

b_V - comparative average biogas production rate per reactor working volume per day [dm^3/dm^3 day]
n - the number of pulses per day recorded in the biogas accounting system

The average biogas production rate per reactor used volume unit over the whole biomass sample period is determined from the following equation:

$$B_V = \frac{\sum_{i=1}^{i=d} n_i \cdot b_{dt}}{V_{rd} \cdot d} \quad (4)$$

B_V - average biogas production rate per reactor operated volume unit over the whole biomass sample period [dm^3/dm^3 day]
d - number of days the biomass is stored in the reactor until it is completely biodegraded

The biogas yields per mass unit of recycled biomass (B_M), dry matter and dry organic matter per day (B_{DM}) are calculated from the following expressions:

$$b_M = \frac{n \cdot b_{dt}}{m} \quad (5)$$

$$b_{DM} = \frac{n \cdot b_{dt}}{m_{DM}} \quad (6)$$

m - amount of recycling biomass [kg]
m_{DM} - dry matter content in the recycled biomass [kg]

The biogas yields per mass unit of recycled biomass (B_M), dry matter (B_{DM}) and dry organic matter (B_{OM}) obtained during the whole study period are determined by the following equations:

$$B_M = \frac{\sum_{i=1}^{i=d} n_i \cdot b_{dt}}{m} \quad (7)$$

$$B_{DM} = \frac{\sum_{i=1}^{i=d} n_i \cdot b_{dt}}{m_{DM}} \quad (8)$$

Energy value of biogas is calculated using the following formula:

$$e_b = 10.0 \cdot \frac{CH_4\%}{100} \quad (9)$$

The concentration of methane in anaerobic biogas evolves over the study period. In one biomass sample study, several biogas capture tanks were filled with biogas and the composition of these biogases was analysed. The methane concentration in the biogas over the whole study period was determined by calculating the arithmetic mean of the methane concentrations measured in the biogas storage tanks and by estimating the quantities of biogas collected for analysis:

$$CH_4\% = \frac{\sum_{i=1}^{i=z} b_i \cdot H_i}{\sum_{i=1}^{i=z} b_i} \quad (10)$$

b_i - the amount of biogas stored in the collection tank [dm^3],
H_i - concentration of methane in the biogas contained in the collection tank [%],
z - number of biogas collection tanks filled during the whole experimental period.

4.4 Investigation of periodic charge process

Investigations of the technological process of biogas production were carried out using a periodic charge of feedstocks. The laboratory reactor was used, and the mesophilic environment was maintained. The comparative average biogas production rate per reactor [volume per day] was determined in the same way as in the case of a single charge, using equation (11). To estimate the dynamic course of the anaerobic biomass decomposition process, the one-day period (from one batch to the next one) is divided into time intervals. The comparative average biogas production rate per reactor volume unit over the period Δt is determined by the following expression:

$$\mathrm{b_{Vd}}=\frac{\mathrm{n_d}\cdot \mathrm{b_{dt}}}{\mathrm{V_{rd}}\cdot \Delta \mathrm{t}} \tag{11}$$

b_{Vd} - comparative average biogas production rate per reactor used volume unit during Δt [dm^3/dm^3 day]

n_d - number of pulses recorded in the biogas accounting system over the period Δt

Δt - period over which the average volume of biogas production per reactor used volume unit is determined [days]

The average single-charge biogas production rate per reactor operating volume per day, with a given number of charges in a steady state of the anaerobic process is calculated by the given equation:

$$\mathrm{B_{Vn}} = \frac{\sum_{\mathrm{i=1}}^{\mathrm{i=k}} \mathrm{b_{Vi}}}{\mathrm{k}} \tag{12}$$

B_{Vn} - average single-charge biogas production rate per reactor operating volume unit, after a certain number of charges in a steady state of the anaerobic process [dm^3/dm^3 per day]

k - number of charges to reach the steady-state of the anaerobic process

The biogas yields per unit mass of recycled biomass (b_M), dry matter (b_{DM}) and dry organic matter (b_{DOM}) per day are calculated in the same way as for a single charge using equations (7) to (8).

To evaluate the dynamics of the anaerobic process, the biogas yields of the recycled biomass (b_{Md}), dry matter (b_{DMd}) and dry organic matter mass per time period unit (Δt) is determined by the following expressions:

$$\mathrm{B_{Md}} = \frac{\mathrm{n_d} \cdot \mathrm{b_{dt}}}{\mathrm{m}} \tag{13}$$

$$B_{sMd} = \frac{n_d \cdot b_{dt}}{m_{DM}} \tag{14}$$

The average single charge biogas yields per unit mass of recycled biomass B_{Mn}, dry matter B_{DMn} and dry organic matter in the well-established anaerobic process mode are given by the formulas:

$$B_{Mn} = \frac{\sum_{i=1}^{i=k} b_{Mi}}{k} \tag{15}$$

$$B_{DMn} = \frac{\sum_{i=1}^{i=k} b_{DMi}}{k} \tag{16}$$

In the periodic-charge mode, the energy conversion factors for biomass e_{Mn}, e_{DMn} for each batch are calculated from the following expressions:

$$\mathrm{e_{Mn}} = \mathrm{B_M} \cdot \mathrm{e_b} \tag{17}$$

$$\mathrm{e_{DMn}} = \mathrm{B_{DM}} \cdot \mathrm{e_b} \tag{18}$$

The average energy conversion factors of single-charge biomass into biogas in the steady-state anaerobic process mode E_{Mn}, E_{DMn} are calculating by these equations:

$$E_{Mn} = \frac{\sum_{i=1}^{i=z} e_{Mni}}{k} \tag{19}$$

$$E_{DMn} = \frac{\sum_{i=1}^{i=z} e_{DMni}}{k} \tag{20}$$

The above methodology for determining the biomethane potential and energy efficiency was used to determine energy recovery in the fermentation and pyrolysis process presented in chapters 7-9.

5 Pyrolysis of Biomass

In case contaminated seaweed is collected at a coastal region, there are two ways in which to utilise it for energy recovery. The first one is a direct use of the pre-treated seaweed via thermochemical processing and obtaining various valuable products: gas, tar and char. The second way uses a synergistic approach by applying co-digestion with other contaminated material, such as sewage sludge, and only then treat the obtained digestate using thermochemical processes. The second way of contaminated biomass utilisation is widely used for biogas production at wastewater treatment plants.

5.1 Methodology of Pyrolysis Test

The pyrolysis experiments were performed under a nitrogen atmosphere. Three different types of biomass – namely seaweed, sewage sludge and digestate were used in the thermal treatment analysis. Digestates (#1, #2, #3) characterisation showed that despite the fact that they were collected in different periods, their composition was very similar (Table 11). Therefore, a mixture of equal proportions of these three digestates were used for further pyrolysis experiments. The products obtained during the pyrolysis process were liquid tar, gases and biochar. The obtained results are described in the next paragraph.

Figure 9 **Fehler! Verweisquelle konnte nicht gefunden werden.**shows the laboratory setup for the pyrolysis test. The pyrolysis process was run using three different materials: pre-treated seaweed, sewage sludge and digestate obtained after co-digestion of seaweed and sewage sludge mixture. Each feedstock batch was comprised of 50 g with a heating rate of 20°C min^{-1} and gas 5 $STPdm^3$ min^{-1} carrier N_2.

The reactor consists of three main sections: the first section consists of the main pyrolysis reactor with a cylindrical form with a diameter of 45 mm and a length of 600 mm. The reactor chamber is linked to two inlet channels (nitrogen flow and feedstock loading) and is connected to one outlet channel designed for the release of formed gases and liquid fraction. The solid residue char formed during the final stage of pyrolysis is further investigated for characteristic parameters.

The second section of the reactor is designed for the accumulation and purification of produced gases and tar. The release of gases and liquids (tar) from the reactor starts at the beginning of the process. The heavy hydrocarbons are immediately collected at the bottom of the reactor during the process of tar condensation. The lighter hydrocarbon and other gases are transmitted through five gas washing flasks containing 75 cm^3 isopropanol. Such condensation process allows for the separation of the formed lighter hydrocarbons from the non-condensable gases namely H_2, CO_2, O_2, CO, CH_4.

The last segment is designated for the direct evaluation of the produced gases, principally H_2, CO, CH_4, CO_2, O_2, and N_2. An online portable gas analyser (Visit 03H) was used for the determination of the composition of formed gases. In addition, there is an opening for separating sampling of gases in specific gasbags (Tedlar bags) for the sole purpose of sampling at a definite point at any given temperature. The gas samples from Tedlar bags were analysed with the help of a gas chromatograph device (Agilent 7890A). This instrument has two carrier routes connected to a thermal conductivity detector (TCD) and a required valve: the first carrier medium separates gases such as O_2, CH_4, N_2, CO, CO_2 and lighter hydrocarbon (C_2H_2, C_2H_6) and the second channel is chosen for the separation of hydrogen. The carrier gas flow operated at 5 cm^3 min^{-1}. The detector temperature reads 200°C at the beginning of the program, with a column temperature of 40°C, which is retained for 13 minutes. Later, the temperature is raised to 160°C and maintained for 45 minutes. The tar obtained with a quadrupole mass spectrometer detector (GC-MS) at the process are examined using a gas chromatograph (Agilent 7890A). The dimensions of the column length, inner diameter, and outer diameters were 30 meters, 0.25 µm and 0.25 mm respectively. The column HP-5Ms induced with 5% phenyl-methyl-siloxane filler was used for the derivative isolation.

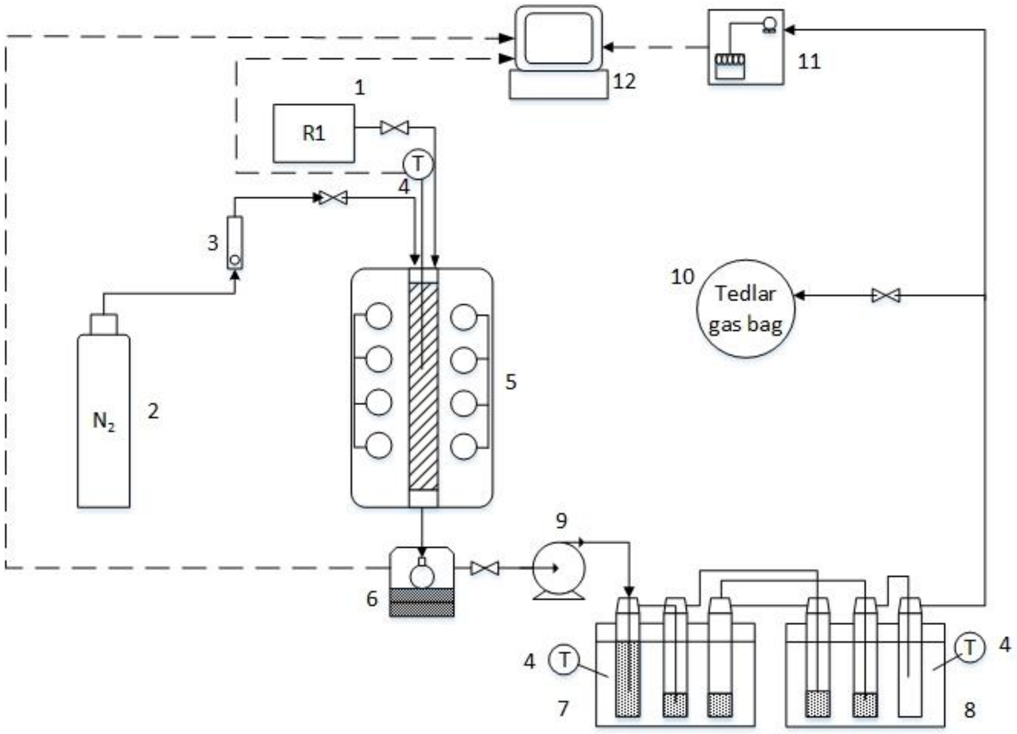

Figure 9. Scheme of pyrolysis thermochemical system. 1 – biomass tank; 2 – nitrogen gas tank; 3 – flow meter; 4 – thermocouple; 5 – biomass pyrolysis reactor; 6 – scales; 7 - heated bath; 8 – cooled bath; 9 – peristaltic pump; 10 – Tedlar gas bag; 11 - gas analyser “Visit 03H “; 12 – personal computer for data analysis

5.2 Characteristics of Biomass Used in Pyrolysis Test

The pyrolysis of the seaweed biomass was conducted at the Lithuanian Energy Institute. The pyrolysis experiments were performed under nitrogen atmosphere.

Three different types of biomass were used as feedstock for the pyrolysis tests. For the first test, the collected and pre-treated seaweed was used. To simulate the second case, a digestate obtained after co-digestion of seaweeds with sewage sludge was used. The digestate was obtained at different times during the co-digestion process: #1 after 18 days of co-digestion, #2 after 30 days, and #3 after 52 days. Finally, in order to compare how the addition of seaweeds affects the digestate composition, the sewage sludge was pyrolysed as well.

Digestate characterisation showed that despite the fact that they were collected in different periods, their composition was very similar (Table 11). Therefore, a mixture of equal proportions of these three digestates was used for further pyrolysis experiments. The products obtained during the pyrolysis process were liquid tar, gases and biochar. The obtained results are described in the next paragraph.

Table 11 presents the characteristics of all mentioned feedstocks. The most distinguished parameter that occurred during the analysis of seaweed is the ash content. As it can be seen from the data in the table, the washing procedure of seaweed reduced the residual mass by five times. This indicates that a high share of the collected raw seaweed actually consists of sand and other obstructive particles adhered to the feedstock. The sewage sludge and the digestate had very similar characteristics as well. However, after the thermal processing, the high ash content in the char indicated that the biggest part of heavy metals and minerals remained in the ashes.

The C, H, N, S data analysis showed different tendencies between the samples. As it can be seen in the Table 11, the highest amount of C (46.93% TS) was detected in the washed seaweed, while the lowest (28.68% TS) was found in the digestate #2. The sulphur content was also higher for the seaweed which constitute of 5.13% TS, while for the digestate ranged from 0.88 to 1.22% TS. The chlorine content in the raw seaweed was obtained to be of 0.43% TS, but after washing and drying it reduced to approximately 0.05% TS. The chlorine content in the sewage sludge and digestate was in the range of 0.24 - 0.39% TS.

Heavy metal and mineral contents in the feedstocks are presented in Table 11. The highest concentrations of Zn and Mn elements were determined in almost all feedstocks. The lowest concentration of Zn and Mn (8.4 and 88.2 mg/kg) was obtained by the washed seaweed, while the highest of 1,475 and 859.1 mg/kg was obtained by the sewage sludge, respectively. It should be noted that elemental cadmium was not detected during the investigation of seaweeds.

The highest and the lowest concentration of P (46,512and 11,952 mg/kg) was obtained for the digestate #1 and the washed seaweed, while the highest and the lowest concentration of N (41,300 and 25,600 mg/kg) for the washed seaweed and the digestate #3, respectively.

The highest and the lowest concentration of K (12,737 and 7,407 mg/kg) was obtained for the unwashed seaweed and the digestate #1. The highest and the lowest concentration of Ca (10,020 and 5,797 mg/kg) was obtained for the digestate #2 and digestate #3, while the highest and the lowest concentration of Mg (24,212 and 1,063 mg/kg) for the sewage sludge and the washed seaweed, respectively.

The highest concentration of major metals, such as Cu, Mn and Zn (246.3, 859.1 and 1,475 mg/kg) was obtained for the sewage sludge, respectively. These elements in the washed and unwashed seaweed were detected in minor concentrations if compared with the sewage sludge and the digestate.

The conducted research aimed at showing the method of analysing contaminated marine biomass with heavy metals or other pollutants (e.g. plastics). However, the contamination content of the collected marine biomass was lower than of the co-substrate used. Table 11 shows that the content of heavy metals in the sewage sludge is higher than in the collected seaweed and constitutes the main contamination of the digestate. Washing marine biomass by tap water decreases the concentration of pollutants in most cases. In the case of chlorine content, this decrease was almost eightfold.

Table 11. Feedstocks ultimate, proximate and elemental composition

Parameter	Unwashed seaweed	Washed seaweed	Sewage sludge	Digestate #1	Digestate #2	Digestate #3
Carbon, % TS	34.58	46.93	29.89	32.14	28.68	31.14
Hydrogen. % (TS)	5.16	4.73	3.87	4.5	3.84	4.6
Oxygen, % (by diff.)	6.79	29.61	14.41	19.62	23.37	17.77
Nitrogen, % (TS)	3.65	4.13	2.99	2.91	2.61	2.56
Sulphur, % (TS)	3.54	5.13	1.08	1.12	1.22	0.88
Chlorine, % (TS)	0.43	0.05	0.24	0.28	0.39	0.35
Moisture, % (a.r.)	57.32	62.56	95.79	96.79	95.49	95.27
Moisture, % (Uptake)	2.27	0.60	3.36	2.02	1.85	1.94
Volatiles, % (TS)	41.82	58.30	47.15	51.70	49.91	49.63
Fixed carbon, % (TS)	12.01	32.23	8.45	8.59	9.81	8.32
Ash, % (TS)	43.90	8.87	44.40	37.69	38.43	41.11
HHV (MJ/kg) (TS)	17.21	17.54	12.31	13.44	12.78	13.13
LHV (MJ/kg) (TS)	16.43	16.51	11.47	12.46	11.94	12.20
As mg/kg	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *
Cd mg/kg	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *
Co mg/kg	n.d. *	n.d. *	4.6	3.4	2.3	5.3
Cr mg/kg	9.1	2.9	100.3	93.7	93.6	127.2
Cu mg/kg	8.1	8.2	246.3	231.5	209.6	318.9
Mn mg/kg	183.1	88.2	859.1	645.5	579.2	580.2
Ni mg/kg	7.41	2.5	56.4	52.1	49.5	56.8
Pb mg/kg	n.d. *	n.d. *	25.1	25.8	25.7	20.3
Sb mg/kg	n.d. *	n.d. *	2.1	0.9	0.5	n.d. *
V mg/kg	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *
Zn mg/kg	40.9	8.4	1475	770.6	746.1	704.7
P mg/kg	23373	11952	25622	46512	43207	34843
K mg/kg	12737	10286	9042	7407	8934	7983
Ca mg/kg	10163	6532	6910	9838	10020	5797
Mg mg/kg	1451	1063	24212	15630	13898	14574

*n.d. – not detected; a.r. – as received

5.3 Results of Pyrolysis Test

In order to determine the behaviour of the selected three feedstocks under high-temperature conditions, thermal analysis TG-DTG-FTIR using NETZSCH STA 449 F3 Jupiter was carried out. The results are shown in Figure 10**Fehler! Verweisquelle konnte nicht gefunden werden.**. As can be seen, the TGA analysis was performed running two processes: the pyrolysis process under N_2 atmosphere and the oxidation of residual char under N_2-O_2 atmosphere. During the pyrolysis process, it is easy to identify three stages of thermal decomposition. At the beginning of the process (stage I), all absorbed humidity evaporates from the samples making the mass loss of 0.1 to 2.9% wt. for the seaweed and the sewage sludge, respectively. The highest mass loss rate for the seaweed was observed at 302.4°C and 693.6°C, respectively. The lower temperature shows thermal degradation of cellulose and hemicellulose (stage II), while the higher temperature shows a fraction of lignin decomposition (stage III). The stages II and III represent a volatile fraction, which amounts to 58.7% wt. for the seaweed.

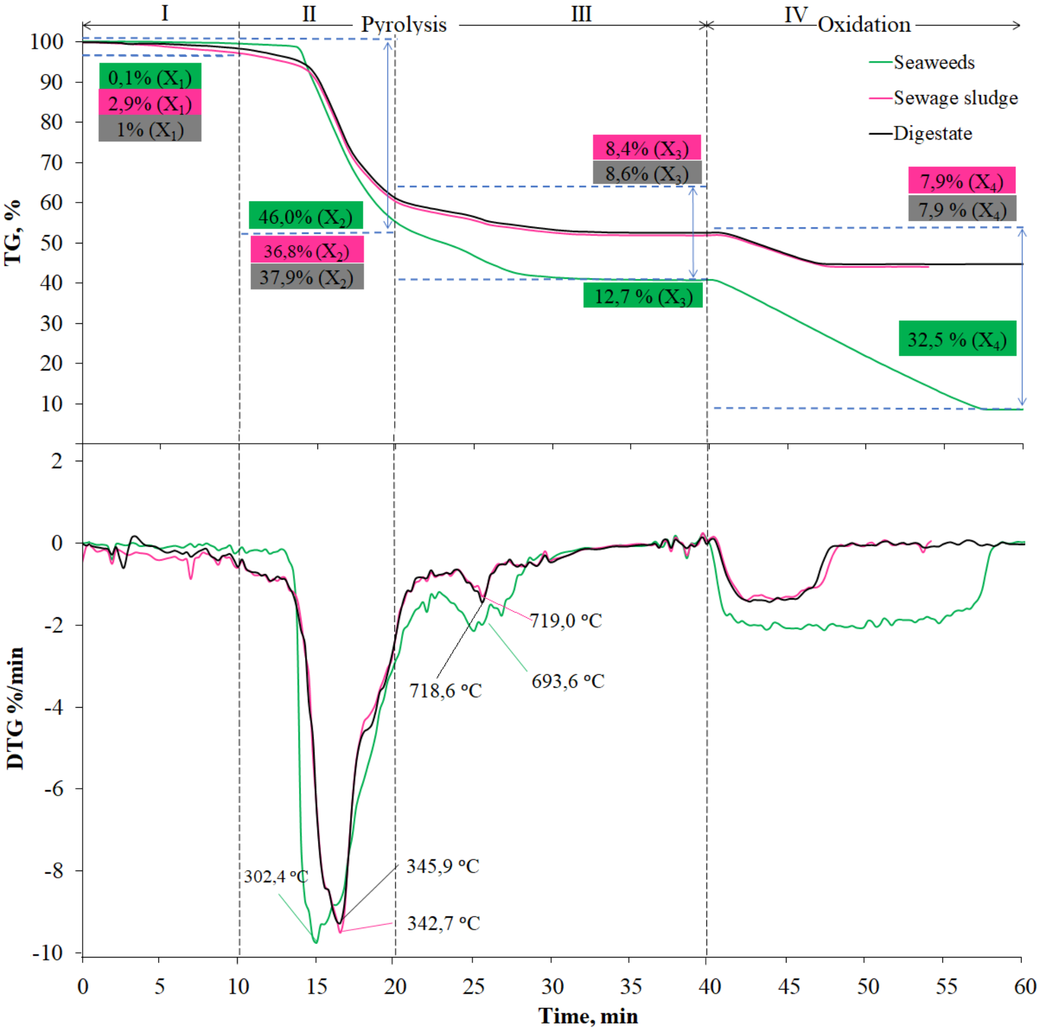

Figure 10. Thermal analysis of seaweed (Green), sewage sludge (Pink) and digestate (Black)

The thermal degradation behaviour of the sewage sludge and the digestate are very similar to that of the seaweed. The highest difference between these samples is the mass loss. During the oxidation process (stage IV), a 32.5% wt. of fixed carbon was determined in the seaweed. The residual mass was 8.7% wt. Analysing the TG data of the sewage sludge it was found that the highest mass loss rate occur in the temperature range of 342.7 °C and 719.0 °C and the volatile matter of 45.2% wt. The amount of fixed carbon was 7.9% wt. and the residual mass was 44% wt. For the digestate, the highest mass loss during thermal decomposition was at 345.9°C and 718.6°C, respectively. The detected amount of volatile matter was 46.5% wt. and the fixed carbon accounted for 8.6% wt. The residual mass was 43.9% wt.

Summarising the microthermal analysis, it was determined that all samples behaved similarly during the thermal treatment process. Two stages of volatile releases were indicated. The first one at 320±30°C and the second one at 705±15°C. Different materials in samples, i.e. hemicellulose and cellulose, which brake at 320 ± 30°C, and bonds in lignin, which brake at 705±15°C.

The composition of gaseous products released during the thermal analysis was investigated by a Bruker Tensor 27 FTIR spectrometer combined with TGA. The obtained spectra curves are shown in Figure 11**Fehler! Verweisquelle konnte nicht gefunden werden.**.

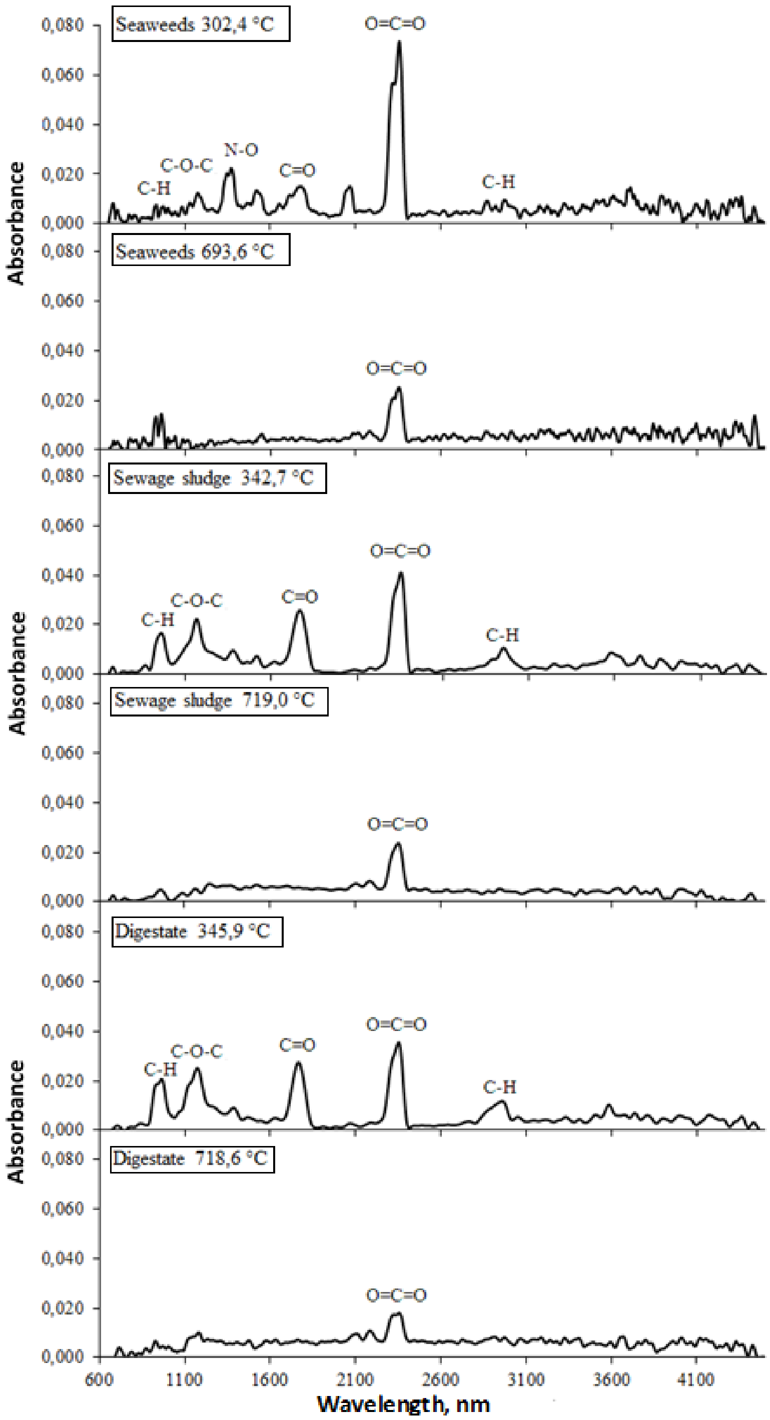

Figure 11. FTIR analysis of seaweeds, sewage sludge and digestate at different temperature

The temperatures were selected from the differential thermal gravimetric (DTG) curve. A comparison of data obtained during an experiment at approximately 300°C showed that it is possible to identify the C-H group at 3,000 cm^{-1} that belongs to aromatic and aliphatic compounds. According to the intensive peaks from the fingerprints zone (600 – 1,000 cm^{-1})

stated that there are some aromatic derivatives. At 3,600 cm^{-1} wavelengths there are minor stretching oscillations, which typically belong to amine (N-H) or hydroxyl (O-H) groups. It is difficult to identify the form of peak and therefore both groups are likely. At 2,300 cm^{-1} a high-intensity, stretching vibration peak was detected. It is a typical place for carbon dioxide (O=C=O). At 1,700 cm^{-1} a medium intensity stretching vibration peak was observed, which belongs to a carbonyl group. This wavelength is typical for ketone, ester or aldehyde. The ether (C-O-C) group could be identified at 1,100 cm^{-1} wavelength. Some of the peaks had different intensities in the seaweed and the sewage sludge/digestate samples. For the seaweed, obertonic oscillations were captured at 2,100 cm^{-1} so it could confirm benzene derivatives present. Also, the nitro N-O group was detected, which is confirmed by two peaks at 1,300 cm^{-1} and 1,500 cm^{-1} wavelengths. A low-intensity peak at 1,900 cm^{-1} shows the presence of cyclic quaternary or pentagonal ester. At approximately 700°C, no big changes were observed. The peak at 2,300 cm-1 wavelength, showed the presence of carbon dioxide. Moreover, low-intensity peaks occurred at the fingerprint zone, but it was difficult to assign to a functional group.

After the FTIR analysis, it could be summarised that different biomasses showed similar compounds or functional groups in released gases, such as methane, carbon dioxide, esters, ketones, phenols or light hydrocarbons. After the treatment, these compounds could be processed to gain valuable energy, chemicals or fuel carriers.

5.3.1 Gaseous Products

The formation of pyrolysis gases heavily depend on the heating rate, process temperature and raw material used, as depicted in Figure 12.

The principal gases released from pyrolysis were methane (CH_4), carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and several other light hydrocarbons, such as ethyne, ethene, or ethane. During the pyrolysis at around 300°C, the gases evolve and progress until the sample undergoes complete conversion. The peak of CO_2, CO, CH_4 and H_2 were assessed at 530°C, 670°C, 560°C and 750°C, respectively. Light hydrocarbons, such as C_2H_6, C_2H_2 and C_3H_8, were also detected at lower concentrations and were up to 1 percent by volume. As it is seen in the given figure, the highest gas composition of CO, CO_2 and CH_4 (26.2, 73.8 and 27.4%) was obtained from the sewage sludge sample, while the lowest of 4.7, 19.7 and 7.6 % for the digestate. Hydrogen was obtained in all three samples at the same quantities, but from the sewage sludge, it started releasing at 330°C and from the seaweed and the digestate at 500°C.

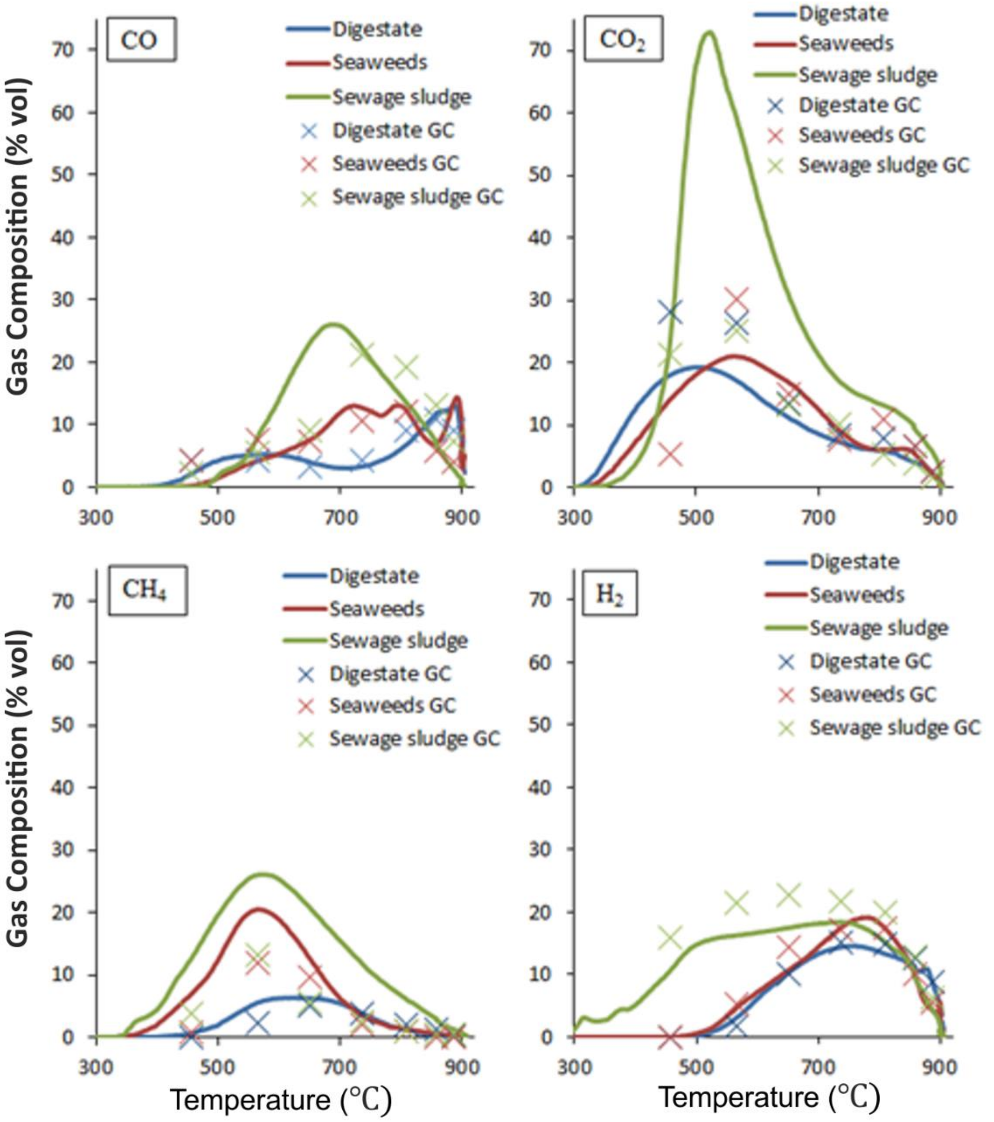

Figure 12. Evolution of gaseous products during pyrolysis at different process temperature

5.3.2 Light Tar

In order to determine the compounds formed in a liquid state, the tar analysis was performed and the results are presented in Figure 13. Similar results were obtained for the three different samples. The feedstock preference marks the minor differences between each sample. Toluene was found to be the dominant compound in these performed tests with the concentration ranging between 20 to 49% wt. of the obtained solution. Benzene derivatives such as styrene, phenol, ethenone, and ethylbenzene were also produced. The raw material composition had the biggest impact on the toluene compound concentration as it varied from 10 to 20% wt. The compounds with lower molecular weight were formed in the products of the digestate pyrolysis process. This resulted in the deterioration of toluene due to lighter hydrocarbons because of the diverse constituents of biomass, which breaks bonds in cyclic compounds. The GC/MS results revealed that the light tar samples were obtained and the pyrolysis seaweed had more high intensity peaks corresponding occurrence of various compounds than that in the case of the sewage sludge and the digestate.

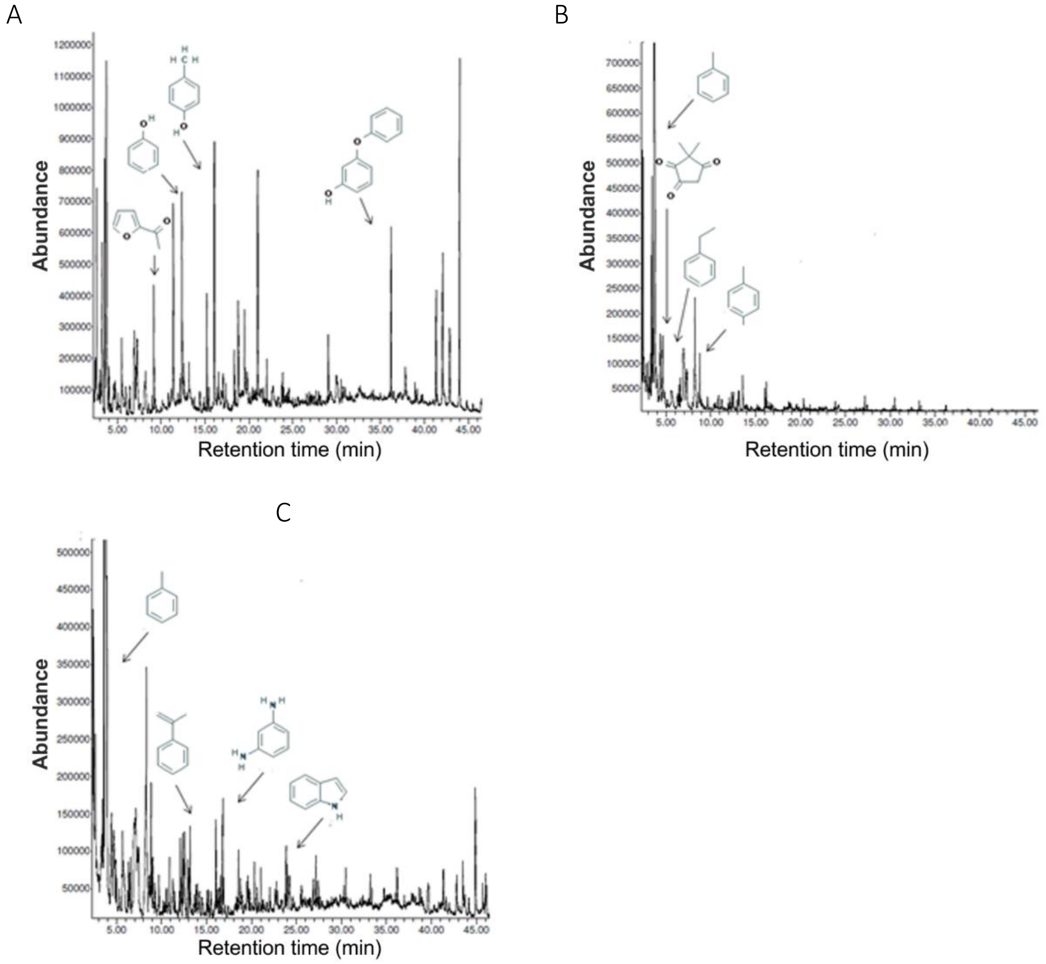

Figure 13. Qualitative GC/MS analysis of light tar samples obtained during pyrolysis: A - Seaweeds, B - Sewage sludge, C - Digestate

5.3.3 Heavy Tar

The heavy tar produced during the pyrolysis experiments of the selected feedstock and were analysed with the GC/MS. The results are shown in Figure 14. Considerable amounts of bio-resin compounds, for instance, phenolic compounds (2-methyl, 4-methyl), alcohols, pyridine and benzyl nitriles, were discovered in the collected samples. The amount of toluene in heavy tar of sewage sludge, digestate and seaweed was 10% wt., 5% wt., and 20% wt., respectively. It should be noted that in the current study, the percentage of phenolic compounds present in the tar varied between 2.5% wt. to 9% wt. In heavy tar samples of the sewage sludge and the digestate the occurrence of styrene, about 3.5% wt. to 4.5% wt. was determined, although styrene was not observed in the sample during the seaweed pyrolysis. About 1% wt. of hydrocarbon (light and aliphatic) was found. A few other compounds such as cholestane and their respective derivatives were identified. Their presence indicates various thermochemical reactions by heterocyclic compounds with polysubstituted derivate, which can be generated from animals and human bio waste [71]. The seaweed samples did not show any existence of such compounds.

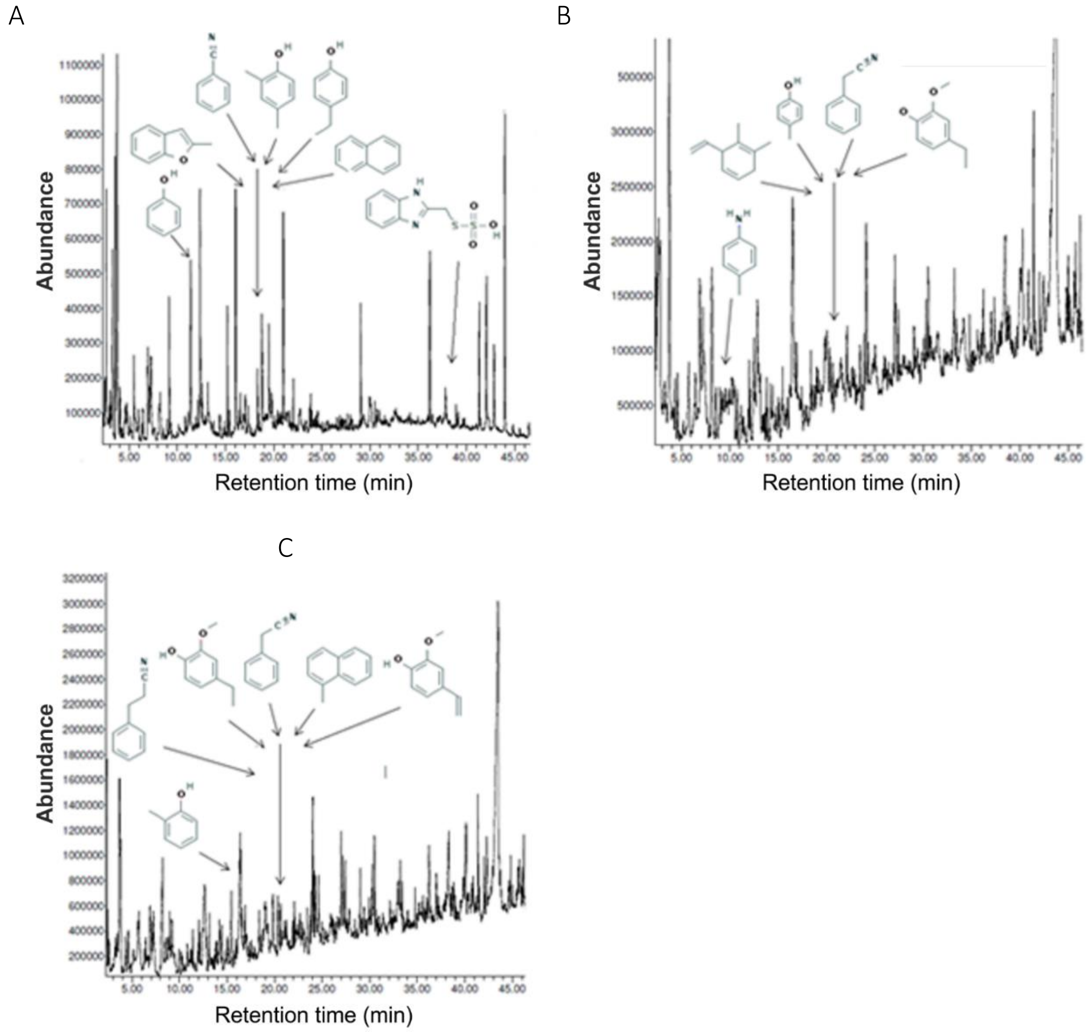

Figure 14. Qualitative GC/MS analysis of heavy tar samples obtained during pyrolysis: A - Seaweeds, B - Sewage sludge, C - Digestate

5.3.4 Elemental Characterization of Char and Tar

Gaseous, liquid (tar) and solid (char) products were obtained during the pyrolysis process. In order to investigate the fate of elements coming with a feedstock and their distribution within the products, ultimate, proximate and elemental analysis was performed (Table 3). The analysis showed that the char formed from the seaweed had the highest carbon amount and the lowest ash content compared to the char from other investigated feedstocks. This occurrence could be explained by a high metal content in the sewage sludge and the digestate char. Some metals remained in the char, thus lowering the quantity of carbon and increasing the ash content. In the char get from different feedstocks (seaweed, sewage sludge and digestate), Cu varies from 41.4 to 492.3 mg/kg, Mn from 569.7 to 1,687 mg/kg, and Zn from 146.8 to 517.1 mg/kg, respectively. It should be noted that a part of phosphorus could be recovered from the formed char. The concentration of it in the seaweed char reached 25,750 mg/kg, in the sewage sludge char 54,352 mg/kg and in the digestate char 50,437 mg/kg.

Table 12. Ultimate, proximate, heavy metals and minerals analysis of pyrolysis products (char and tar)

	Seaweeds char	Sewage sludge char	Digestate char	Seaweed tar	Sewage sludge tar	Digestate tar
Carbon, % (TS)	60.10	17.66	22.04	50.50	50.81	51.29
Hydrogen. % (TS)	0.52	0.14	0.20	11.69	11.91	12.25
Oxygen, %[3]	1.90	1.69	0.28	22.58	20.38	18.49
Nitrogen, % (TS)	2.66	0.80	0.74	2.59	3.75	3.02
Sulphur, % (TS)	2.79	0.26	0.70	1.98	1.57	1.33
Chlorine, % (TS)	0.08	0.09	0.30	0.10	0.08	0.29
Moisture, % (a.r.)	-	-	-	-	-	-
Moisture, % (Uptake)	2.42	1.31	1.48	10.43**	11.21**	13.17**
Volatiles, % (TS)	11.28	6.32	10.34	89.34	88.42	86.38
Fixed carbon, % (TS)	56.69	15.54	13.62	-	-	-
Ash %, (TS)	29.61	78.14	74.56	0.23	0.37	0.45
HHV (MJ/kg) (TS)	22.35	6.63	7.42	29.31	29.89	30.61
LHV (MJ/kg) (TS)	22.21	6.60	7.38	26.93	27.46	28.13
As mg/kg	n.d.	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *
Cd mg/kg	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *	n.d. *
Co mg/kg	n.d. *	13.4	10.60	n.d. *	n.d. *	n.d. *
Cr mg/kg	n.d. *	149.1	166.1	n.d. *	n.d. *	n.d. *
Cu mg/kg	41.4	492.3	464.4	0.7	24.6	2.5
Mn mg/kg	569.7	1687.5	1083.7	n.d. *	n.d. *	n.d. *
Ni mg/kg	n.d. *	76.6	80.1	n.d. *	3.2	n.d. *
Pb mg/kg	n.d. *	n.d. *	4.5	1.2	1.1	3.1
Sb mg/kg	n.d. *	2.2	3.9	n.d. *	n.d. *	n.d. *
V mg/kg	n.d. *	7.1	7.8	n.d. *	n.d. *	n.d. *
Zn mg/kg	146.8	268.4	517.1	12.6	10.4	16.7
P mg/kg	25750	54352	50437	4.8	5.9	15.6
K mg/kg	8841	20431	17443	n.d. *	29.4	n.d. *
Ca mg/kg	17364	6725	7484	n.d. *	9.7	n.d. *
Mg mg/kg	2533	45953	29503	n.d. *	n.d. *	n.d. *

*n.d. – not detected; ** - moisture and isopropanol.

The analysis of the tar obtained from different feedstocks (seaweed, sewage sludge and digestate) revealed that it contained lesser elements compared with the char from the same feedstocks. The carbon, hydrogen, nitrogen and sulphur was in the range of 50.50 to 51.29% wt., 11.69 to 12.25% wt., 2.59 to 3.75% wt. and 1.33 to 1.98% wt., respectively. This distribution of elements explains the formation of lighter or heavier hydrocarbon compounds. In addition, during the sampling the tar was dissolved in isopropanol, thus the calorific value

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[3] calculated as the difference between total solids and all other elements

was in the range of 29.31 to 30.61 MJ/kg (HHV), which can be explained by a high carbon content.

The fate of the selected metals in liquid and solid products during the pyrolysis process was also analysed. The metal concentrations of the feedstock are presented in Table 12. The repeated measurements of metal concentrations in three different experiments and the calculation of the arithmetic average of their values showed the occurrence of mass imbalance between the metals found in the liquid and solid products, and the ones found in the feedstock samples. This confirms that part of the species is accumulated in the system or might be emitted with gaseous products. A longer time of analysis is required in order to determine a complete mass balance of the elements in this process.

Naturally, after the thermal processing, the concentrations of almost all elements found in the char were higher than that in the raw material. The accumulation of metals in char is a typical process. It is due to the gradual reduction of organic compounds during pyrolysis. In this process, the main chemical elements C, H and O were released with formed volatile compounds. Thus, the concentrations of metals in pyrolysis tar and oils were significantly lower than that in the pyrolysis char. The performed analysis showed that the vast amount of heavy metals and minerals remained in the pyrolysis char. Only a small amount of heavy metals was obtained in the tar sample. By assessment of the physical and chemical properties of certain metals shows that the boiling point, for example of Cu or Zn, is relatively high and reaches 2,567°C and 1,391°C, respectively. Therefore, they are attributed to the non-volatile metals. However, it can be found in the literature that if such metals can form metal chloride, thus the boiling point can be reduced significantly. The melting and boiling points of copper chloride, depending on their forms, can range from 430°C to 1,490°C [71], while the boiling point of zinc chloride decreases to approximately 750°C. The melting point of chromium chloride can start approximately at 850°C. It is probably that during the thermochemical reactions some metals formed the compounds with chlorine, which can lead to the reduction of its melting/boiling points and are removed together with volatile products or could accumulate in the pipelines of the device.

As it was mentioned before, the presence of metals in the tar and oils was very low compared to the presence in the char. The amounts of heavy metals, such as Zn and Pb, were detected to be in the range from 0.59 to 9.77% wt. Some of the elements determined in the feedstock were not detected because concentrations were lower than the detection limit of the equipment. The quantity of alkaline earth and alkaline metals in pyrolysis oils and tar were extremely low compared to the amounts of heavy metals in the feedstock or char. The total amount of these elements was lower than 1% wt. Significant changes compared to chars and tar composition occurred with Cu, Mn, Zn, K and Ca. The amounts of these elements in the char were much higher than in the tar. It can be stated that an insignificant quantity of these elements entered the liquid fraction during the pyrolysis process.

The elemental analysis showed that the largest discrepancies in the mass balance was occurred for the elements Pb (93.97%), Zn (84.11%) and V (67.51%). Other elements, such as Ni, Cr, Mn and Cu, also showed some disparities, but it could be explained by the formation of chlorides or their accumulation on the reactor pipelines.

6 Plasma Assisted Gasification of Marine Biomass

6.1 Theoretical evaluation of plasma assisted gasification

The plasma-assisted gasification and its application to the current project were evaluated based on work presented in article [72]. The main idea is to incorporate the plasma-chemical reactor after the downdraft gasifier system and investigate product composition and yields before and after introducing of plasma-assisted gasification. The installation of plasma into gasification systems is presented in Figure 15. The main components of evaluating system units are the gasification reactor, the plasma reactor, the gas cooler, the electrostatic precipitator (ESP) and the boiler.

For the further investigation was selected to analyse digestate as a primary feedstock in order to utilize the contaminated seaweed and its substrate, which was obtained after AD and drying processes. Moreover, in the sections **Fehler! Verweisquelle konnte nicht gefunden werden.** and **Fehler! Verweisquelle konnte nicht gefunden werden.** it was assumed, that digestate is a potential feedstock for additional energy products recovery.

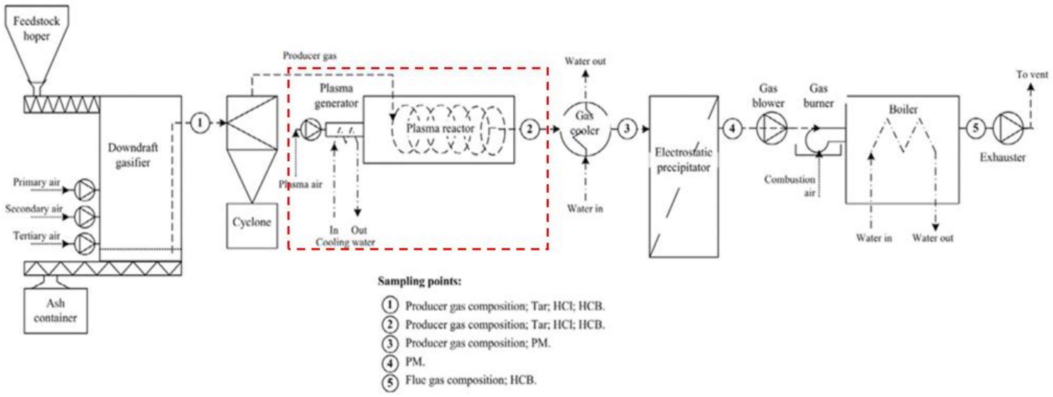

Figure 15. Plasma assisted gasification principle scheme

6.2 Gasification of the biomass

The gasification experiments were performed under a nitrogen-oxygen atmosphere using a single-batch load (about 50 g). For that reason, gathered products composition might be a bit different in comparison with a continuous mode load [73]. The obtained results are presented in the paragraph 6.3. The amount of oxygen from air (V) required for gasification per 40 minutes was calculated based on the following equations and reaches 1.8 dm^3 min^{-1} (for seaweed) and 1.2 dm^3 min^{-1} (for sewage sludge and digestate).

$$Vc = \frac{0.0889 * (C + 0.375 * S) + 0.265 * H - 0.0333 * O}{t} \tag{21}$$

Vc – amount of the air which is required for complete combustion, (m^3/min)/kg;
C, S, H, O – raw material composition (carbon, sulphur, hydrogen, oxygen respectively);
t – time of combustion.

$$V = \frac{Vco * SR}{m} \tag{22}$$

V – amount of air required for gasification, (m^3/min);

m – mass of feedstock for gasification, g;
SR – stoichiometric fuel to air ratio for gasification - (0.3);

6.3 Gaseous products analysis

The main process parameters and characteristics, which were used in this report, were taken from the previous work [72]. According to the obtained parameters, the theoretical investigation of possibly obtained products and yields were estimated, and results are depicted in Table 13Fehler! Verweisquelle konnte nicht gefunden werden.. The average gaseous product composition is obtained by calculation of a mean value of the results of different gaseous samples (maximum values) analysed by continuous analyser and gas chromatography. As could be seen (Table 14) from the given parameters, the gas composition at the outlet from the gasifier is not typical and standard for downdraft gasification systems [74]. It could be explained by the small-scale gasification experiments with a single batch load, which was processed and described in paragraph 5.3.1. Moreover, the experiments were carried out with a continuous carrying flow of nitrogen, so for that reason composition might be affected.

Table 13. Comparison of gasification performance with and without plasma reactor

Parameter	After gasifier	After plasma reactor
Fuel load, kg/h	1	1
Plasma power, kW	-	2.30
Air flow, m^3/h	1.63	3.67
Produced gas yield, m^3/kg	1.57	2.11
Produced gas LHV, MJ/m^3	1.87	2.52
Produced liquids in gas yield, g/m^3	62.92	0.14
Produced liquids in gas LHV, MJ/m^3	29.2	-

The major composition of the gaseous products changes as it passes through the plasma reactor: H_2 concentration increased on average from 2.6 to 8.0 vol.%. That of CO from 7.1 to 12.6 vol.%, CH_4 decreased from 1.5 to 0.2 vol.%, CO_2 from 9.3 to 7.1 vol.%, and the other identified light hydrocarbons practically vanished. With the change increasing in the gas yield and change in composition, the concentration of nitrogen decreases from 79.0 to 72.1 vol.%. This distribution and changes after plasma reactor are explained by partial oxidation of the produced gaseous products and additional thermal destruction of light hydrocarbons due to heat generated by the plasma. Moreover, tar constituent hydrocarbons also are decomposed, forming certain gaseous products and increasing energetic values. Additional evaluation without nitrogen was also included in Table 15, which could be used for estimating the real system parameters.

Table 14. Average produced gas composition in plasma induced gasification

Compound	Average produced gas composition, vol.% (dry)			
	Measured (paragraph 5.3.1)	Recalculated without nitrogen	Evaluated (based on previous studies [73])	Recalculated without nitrogen
CO_2	9.3	44.9	7.1	25.6
CH_4	1.5	7.2	0.2	0.7

Compound	Average produced gas composition, vol.% (dry)			
	Measured (paragraph 5.3.1)	Recalculated without nitrogen	Evaluated (based on previous studies [73])	Recalculated without nitrogen
H_2	2.6	12.3	8.0	28.6
CO	7.1	34.4	12.6	45.1
C_2H_2	0.0	0.0	0.0	0.0
C_2H_6	0.3	1.2	0.0	0.0
C_3H_8	0.0	0.0	0.0	0.0
N_2	79.2	-	72.1	-

7 Energy Recovery in Digestion Process of Seaweeds

If the content of heavy metals in marine biomass is below the permissible limits, it is possible to use seaweed directly in the digestion process. In this case, it is possible to obtain energy from the produced biogas as well as digestate, which is an excellent substitute for artificial fertilisers. The diagram of the process steps of using marine biomass in anaerobic digestion is presented in Figure 16.

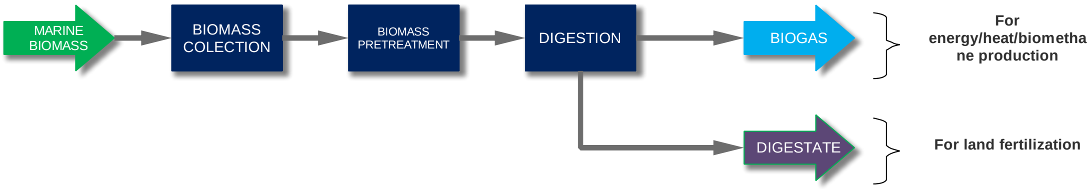

Figure 16. The diagram of marine biomass treatment when the heavy metals concentration is below limits for the utilisation digestate as fertiliser

As can be seen in the energy diagram shown in the Figure 17, the greatest energy demand is for biomass heating and pre-treatment, which is 51.84% and 25.81% of the total energy demand, respectively.

Nevertheless, it should be mentioned that when using marine biomass for methane production, a positive energy effect of about 54.59% is still obtained. The energy efficiency of the process was calculated base of the equation below:

$$\eta_{\mathrm{net}} = \frac{\text{net energy in the products}}{\text{total energy input}} = \frac{\mathrm{Q}_B + \mathrm{Q_D}}{\mathrm{Q_T} + \mathrm{Q_{PT}} + \mathrm{Q_{DP}}} \cdot 100\% \qquad (23)$$

Where,

Q_T - energy of biomass transportation [MJ],
Q_{PT} - energy for pre-treatment of biomass [MJ],
Q_{DP} - energy input to digestion process [MJ],
Q_B - heat of biogas combustion [MJ]
Q_D - the energy equivalent of the production of artificial fertiliser [MJ]

7.1 Energy for Biomass Collection

Depending on the macroalgaes occurrence, the biomass might be collected offshore, in the shallow waters near the coast or directly from the beach. One study estimated that the energy use of harvesting *Polysiphonia fuciodes,* as drifting algae directly from the water, was around 24 MJ/t wet biomass [75]. For the seaweed located on the coast, a grating bucket could be used. Assuming a capture efficiency of around 30 t/h and power of 75 to 130 kW this process would need around 9 to 15.6 MJ/t of wet biomass [76].

The calculation of average work for the collection of biomass is presented in Table 15.

Table 15. Energy efficiency of biomass collection [76]

Algae		Enteromorpha compressa	Enteromorpha plumosa	Mix of Zostera marina and Enteromorpha plumose	Zostera marina	Mixed seaweed from Gdansk beach (Phaeophyta)	Average
Place of collection		Rzucewo	Rzucewo	Rzucewo	Rzucewo	Brzezno, Gdansk	
TS [%]		8.86	7.19	7.65	12.56	17.42	10.74
Collecting by grating bucket	Energy efficiency [MJ t^{-1}]	Energy efficiency [MJ tTS^{-1}]					
Low performance	9.0	101.58	125.17	117.64	71.65	51.66	83.83
High performance	15.6	176.07	216.96	203.92	124.20	89.55	145.30
Average	12.3	138.82	171.07	160.78	97.93	70.61	**114.57**

7.2 Energy for Biomass Transportation

Transportation of biomass plays a significant role in a biogas production chain. The places of seaweed collection might differ due to the seasonal variations as well as due to the local infrastructure and can influence considerably the actual transport distance. The energy used for transport would be highly dependent on factors such as truck efficiency, total load of a truck and the condition of the infrastructure. After taking into consideration data from different European countries from 2000-2010, it is possible to conclude that the energy need of both, heavy and light trucking, reaches from 1.8 to 3.0 MJ/t km [77]. Other studies suggest that light trucks' or vans' energy use is around 1.5 MJ/t km and declines strongly with heavy trucks to around 1 MJ/t km [78].

Table 16. Energy efficiency of biomass transportation [77]

Algae		Enteromorpha compressa	Enteromorpha plumosa	Mix of Zostera marina and Enteromorpha plumose	Zostera marina	Mixed seaweed from Gdansk beach (Phaeophyta)	Average
Place of collection		Rzucewo	Rzucewo	Rzucewo	Rzucewo	Brzezno, Gdansk	
TS [%]		8.86	7.19	7.65	12.56	17.42	10.74
Transport by light and heavy trucks	Energy efficiency [MJ t^{-1}]	Energy efficiency [MJ tTS^{-1}]					
Low performance	1.8	20.31	25.03	23.53	14.33	10.33	16.77
High performance	3	33.86	41.72	39.21	23.88	17.22	27.94
Average	2.4	27.08	33.38	31.37	19.11	13.78	**22.35**

When we assume the average energy needed for the transportation of 1 t of wet biomass is 2.2 MJ/t km, and the distance of transportation is 15 km, while the average TS of seaweed is 50%, we can calculate the energy for transportation 1 t of TS of seaweed by equation (25) which is equal to 66 MJ/t TS km.

$$E_T = \mathrm{S} \cdot m_b \cdot e_t \cdot TS^{-1} \tag{24}$$

Where:

S - distant for transportation [km]
m_b - mass of wet biomass [t]
TS - total solids [%m/m]
e_t - energy needed for transport 1 t of wet biomass per 1 km [MJ/t km]

7.3 Energy for Pre-treatment

Usually for feedstocks for methane fermentation, different pre-treatment processes need to be used. One of the most commonly used forms is mechanical size reduction that increases the size to volume ratio and helps the fermentation with instance intercellular substance release. It is estimated that energy use of this method would be around 113 MJ/t wet biomass [79]. A similar value was found in another study where grinding required 136.8 MJ/t wet algae [80]. Ensiling is another way of pre-treatment mostly used for preventing the quality of the biomass through the storage time. Estimated energy needed for this process is around 24 MJ/t wet biomass [81]. Other study gathered different data on energy consumption from various chemo-mechanical and physic-chemical pre-treatments and are shown on Table 17.

Table 17. Specific energy consumed with various pre-treatment [82]

No.	Pre-treatment method	Energy consumption [MJ/t TS]
1	Disperser + alkali	4544.00
2	Thermo chemo disperser	3360.94
3	Chemo disperser	5013.00
4	Sono alkaline	4172.00
5	Thermo chemo sonic	5290.50
6	Citric acid + ultrasonic	171.90
7	Fenton + ultrasonic	641.00
8	Thermo-chemo-sonic	5500.00
9	Disperser + microwave	18000.00
10	Chemo mechanical	7377.00
11	Sonic mediated biological	2.45
12	Chemo-thermo disperser	174.00
13	Surfactant sonic	5120.00
14	Chemo disperser	3312.60
15	Surfactant + sonic	5400.00
16	Disperser + bacterial	9.50
17	Ultrasound + microwave	16700.00
18	Surfactant + sonic	9600.00
19	Microwave	1844.00
20	Microwave + citric acid	1400.00
21	Microwave + surfactant	14000.00
22	Microwave + H_2O_2	18600.00

7.4 Energy for Conducting Digestion Process of Marine Biomass

For a good performance of the digestion process, it is required to keep a constant temperature of the bioreactor. For the thermophilic process, the optimal temperature range is 48-52°C and for the mesophilic process 35-37°C.

To calculate the heat necessary for the biogas plant operation, we should calculate the energy needed to heat the feed for the bioreactor and energy to keep a constant temperature in the bioreactor, which is equal to the loss of the heat:

$$\mathrm{Q}_{T} = \mathrm{Q}_{FH} + \mathrm{Q}_{HL} \tag{25}$$

Where:
Q_T – total energy necessary for biogas plant operation [kJ],
Q_{FH} – energy for feedstock heating [kJ],
Q_{HL} – bioreactor heat lost [kJ],

$$\mathrm{Q}_{FH} = \mathrm{m}_F \cdot (\mathrm{T_S} + \mathrm{T}_B) C_B \tag{26}$$

Where:
m_F – mass of feedstock [kg],
T_S – initial temperature of the feedstock [K],
T_B – temperature of bioreactor [K],
C_B – heat capacity of feedstock [kJ/kg K],

$$\mathrm{Q}_{HL} = 24 \cdot \mathrm{K} \cdot \mathrm{F} \cdot \alpha \cdot (\mathrm{T_B} + \mathrm{T}_A) \tag{27}$$

Where:
K – heat transfer coefficient [W/m^2 K],
F – heat exchange surfaces [m^2],
T_B – temperature of bioreactor [K],
T_A – ambient temperature [K],
α – mixing factor[-].

Table 18 presents the average ambient temperatures in the 1991-2016, energy necessary to heat the feedstock and heat loss during the digestion process in each project partner countries. For a calculation, the following assumptions have been made: The volume of the digester 1,200.00 m^3, bioreactor filling factor 0.70, diameter to high of the digester ratio 1.00, average heat transfer coefficient 0.123 W m^{-2} K^{-1}, mixing factor 0.5, digester temperature 37°C and hydraulic retention time 20 days.

Table 18. Average ambient temperature in project partner countries in 1991-2016 [83]

Parameter	Poland	Germany	Lithuania	Denmark	Sweden
Temperature [^{o}C]	8,24	9,62	7,44	8,30	2,50
Heat loss of digester [MJ tTS^{-1}]	33.77	32,15	34,71	33,70	40,51
Energy necessary for heat feedstock [MJ tTS^{-1}]	1122.41	1068.55	1153.63	1120.06	1346.42
Total heat [MJ tTS^{-1}]	**1156.18**	**1068.55**	**1153.63**	**1120.06**	**1346.42**

The energy necessary for conducting digestion processes is strongly dependent on the ambient temperature. Much more heat is needed in winter than in summer (sometime the cooling of the bioreactors is needed for the proper operation during summer).

7.5 Energy Equivalent of Digestate

Unfermented parts of biomass, which are organic compounds, bacterial biomass and minerals, are the residues from the anaerobic digestion process – the so-called digestate. Its characteristics are dependent on the substrates used for the process. Generally, the main components of the feedstock consists of plant biomass, natural fertilisers, manure and wastes from food industry. The COASTAL Biogas project investigates the utilisation of maritime biomass for recovering nutrients from the Baltic Sea. During the anaerobic digestion carbon sources easily degradable are removed with remaining more resistant carbon compounds, colloids are degraded, nitrogen compounds are transformed to ammonia, pathogens are disabled and carbon/nitrogen ration is changes in comparison to the source.

Typically, the amount of digestate is about 95% of the feed mass. The large part of it is water. The amount of digestate used is dependent on the nitrogen concentration though it cannot exceed 170 kg of nitrogen per hectare. Digestate from co-digestion of cattle manure and maritime biomass contained about 2% of nitrogen and 25% of carbon in the remaining solids, whereas the total solids content was about 6%. This gives about 1.2 kg of nitrogen per 1 m^3 of raw digestate and implies utilization of about 140 tons of digestate per 1 hectare of the crop. In comparison, commonly used urea contains 47% of nitrogen and is used in amounts of 360 kg/ha.

The minimal energy consumption (after a BAT recommendation [84]) for producing 1 t of artificial nitrogen fertiliser (urea) calculating for pure nitrogen can be estimated at about 22 GJ/t N [85].

7.6 Energy Balance for Digestion of Marine Biomass

In Table 19, the energy balance of using 1 t of marine biomass is presented. The net energy that could possibly be retrieved from seaweed using the co-digestion process is about 257.44 MJ per 1 t of wet marine biomass. Figure 17 shows the Sankey diagram of the energy recovery. The red arrows represent the consumed (lost) work/energy during all the value chain steps – from collection of marine biomass up to obtaining the products of the digestion process.

Table 19. Energy balance base on 1 t of marine biomass

		Energy	
		[MJ]	%
1.	**Energy generated**		
1.1	Energy of biogas	247.91	75.45%
1.2	Energy equivalent of digestate	80.66	24.55%
1.3	**Energy generated in total**	328.57	
2.	**Energy consumed**		
2.1	Work used for collecting seaweed	12.30	17.29%
2.2	Energy for transportation	2.40	3.37%

		Energy	
		[MJ]	%
2.3	Energy for pre-treatment	18.80	26.43%
2.4	**Energy for digestion**	*37.63*	*52.90%*
2.4.1	Energy lost	4.06	5.71%
2.4.2	Energy for biomass heating	33.57	47.19%
2.7	**Energy consumed in total**	71.13	
3.	**Total net energy**	257.44	

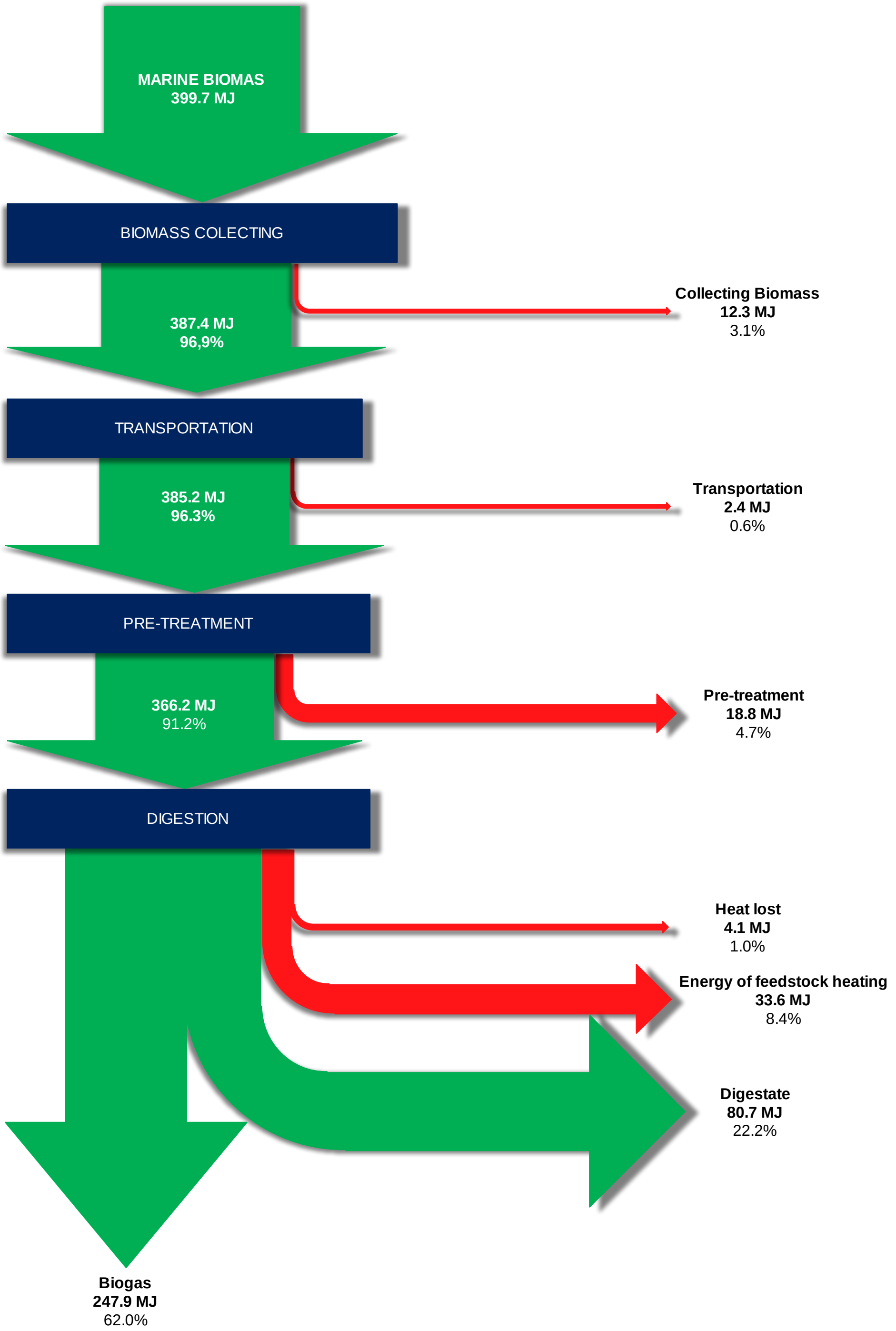

Figure 17. Sankey diagram of energy recover in digestion process of marine biomass

8 Energy balance of Seaweeds Pyrolysis

The gasification process produces char, tars and synthesis gas. The highest product formation rate was achieved at 900°C maximum temperature. Gaseous and liquid phase products estimated the rate of conversion. Product yields and conversion rates are shown in Table 20.

Table 20. Product yields and conversion rates

Sample	Seaweed	Digestate
Oil, %	17.22	15.58
Gases, %	43.69	35.65
Biochar, %	39.09	48.77
Conversion rate, %	60.91	51.23

According to Table 20, seaweed has the highest yield of oil (17.22%) whereas digestate a bit lower (15.58%). Seaweed has the highest yield of gaseous products (43.69%) and the lowest biochar yield (39.09%). The amount of biochar is higher for digestate (50.16%). Seaweed has the highest conversion rate (60.91%). In case to utilize formed digestate after AD, a 51.23% conversion rate could be achieved. Conversion rate calculated as oil and gas percentages sum.

On **Fehler! Verweisquelle konnte nicht gefunden werden.**a detailed result of energy and nutrient balance during utilisation of contaminated seaweed by pyrolysis process is shown. For this case, the feed supply consisted of 100 kg seaweed with 194.4 kWh of energy.

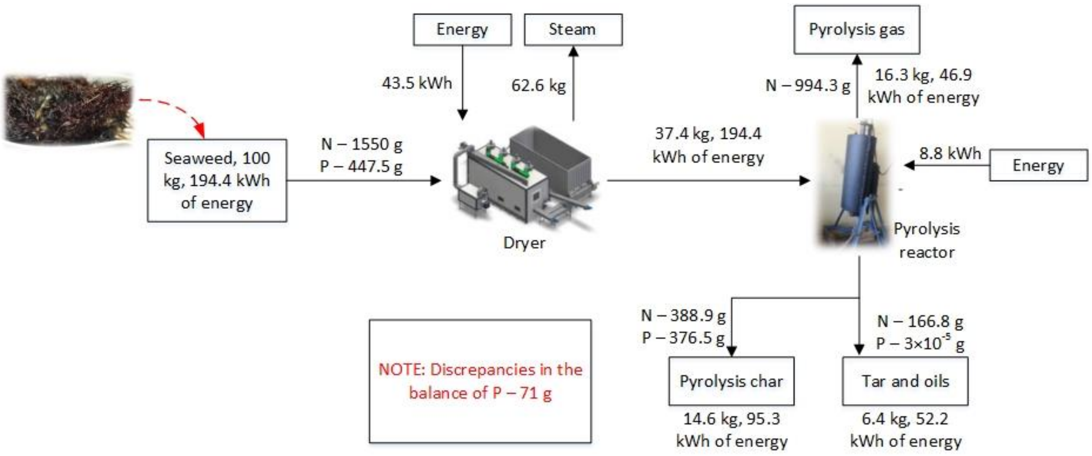

Figure 18. Energy and nutrient balance of the seaweed pyrolysis

The total amount of N in the feedstock was 1,550 g, and 447.5 g of P. To eliminate the moisture content (62.5%), the biomass was dried in a dryer with 43.5 kWh energy consumption. The remaining dry feedstock was used in the pyrolysis reactor to obtain three types of different products. The pyrolysis had conserved the energy content of 46.9 kWh in the pyrolysis gas, 52.2 kWh in the tar and 95.3 kWh in the char. The analysis of nutrient distribution showed the same tendencies as in the digestate pyrolysis case (Figure 21). The recovered P from the pyrolysis char reached approximately 84% of the total content, while the highest part of N of 65% was emitted with the pyrolysis gas. However, a much higher part remained in the char if compared with the pyrolysis of digestate. In addition, the analysis showed that this particular case was more energy efficient enabling to recover 42% of energy.

Based on the results obtained in the marine biomass pyrolysis tests an energy balance was drawn up, including energy for transport, pre-treatment, dewatering, drying and pyrolysis, which is presented in Table 21 and Figure 19.

Table 21. Energy balance of seaweed pyrolysis

		Energy	
		[MJ]	%
1.	**Energy generated**		
1.1	Energy of pyrolysis gas	639.00	99.50%
1.2	Energy of pyrolysis char	2.88	0.45%
1.3	Energy of tar and oil	0.36	0.06%
1.4	**Energy generated in total**	642.24	
2.	**Energy consumed**		
2.1	Work used for collecting seaweed	12.30	6.29%
2.2	Energy for transportation	2.40	1.23%
2.3	Energy for pre-treatment	162.66	83.24%
2.4	Energy for biomass drying		
2.5	Energy for pyrolysis		
2.6	**Energy consumed in total**	195.40	
3.	**Total energy**	446.84	

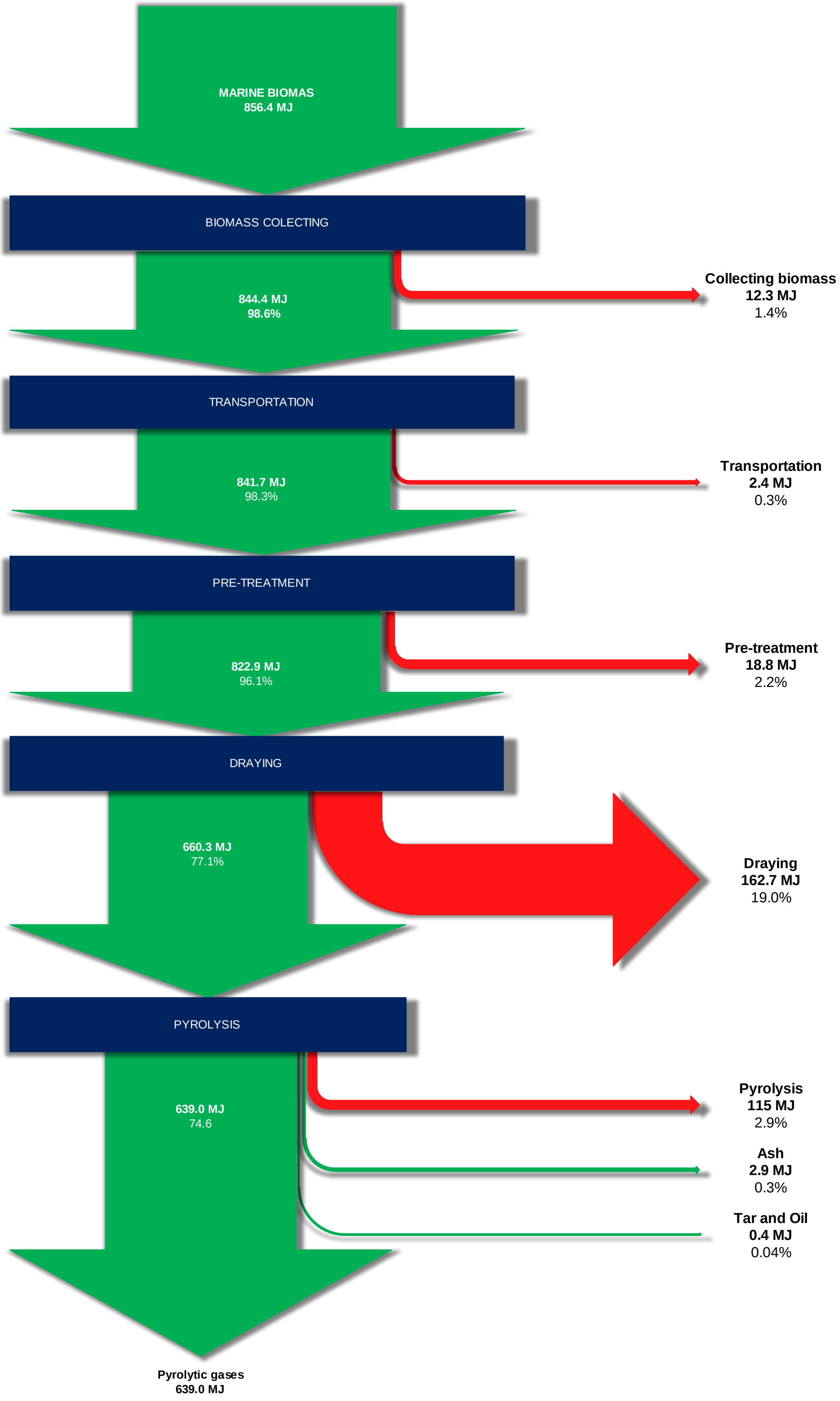

Figure 19. Sankey diagram of energy recover in pyrolysis process of marine biomass

9 Energy Recovery of Seaweeds Digestate in Pyrolysis Process

In the third scenario, marine biomass was co-digestated with sewage sludge, and then the digestate was pyrolised (flowsheet diagram is presented in Figure 20. A simplified energy balance of the seaweed utilization by the combined digestion and pyrolysis process was analysed. This case represents the possible routes of contaminated seaweed and other biomass (e.g. sewage sludge) utilization for recovering of valuable energy products.

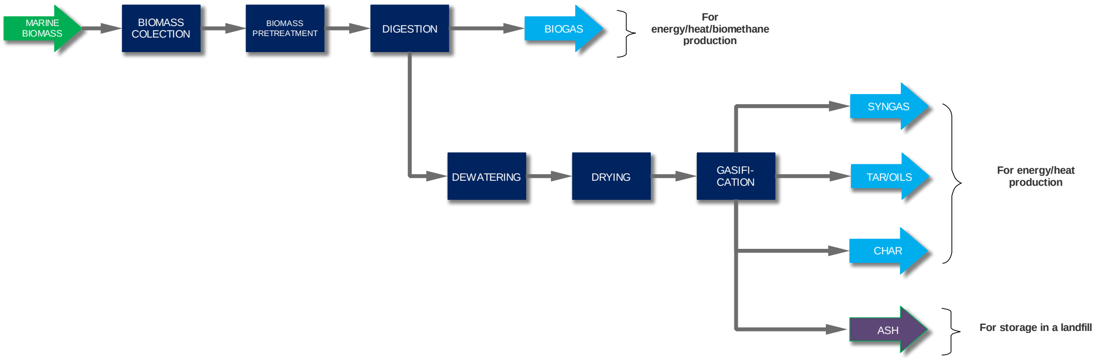

Figure 20. The diagram of marine biomass digestate pyrolysis (when the heavy metals concentration is above limits for the utilisation digestate as fertiliser)

Figure 21 shows a detailed result of energy and nutrient balance for the digestate pyrolysis. For this case, the feed supply consists of 10.0% wt. of seaweed which has about 19.4 kWh of energy calculated on LHV basis and 90.0% wt. of sewage sludge with 14.5 kWh of energy. The total amount of N of this mixture is 272 g and 141.8 g of P. The amount of biogas after AD was calculated in accordance with the obtained results for as received feedstock. Thus, in this reference case, the amount of biogas is about 4.5 kg along with 21.7 kWh of energy, which corresponds to 95.5 kg of raw digestate including 12.2 kWh energy remaining in it.

The mass and energy balance distribution were conducted for the initial feedstock and products obtained such as biogas, oils, tars, and chars. In this conservation, 100 kg of biomass is taken as a reference for the production of bio-methane. The in-feed supply consists of 5.0% wt. of seaweed with 22.9 kWh of energy and 95.0% wt. of sewage sludge with 30.3 kWh of energy. The calculated amount of biogas yield after anaerobic digestion is 0.2 m^3 per 1 kg of feedstock. Thus, in this reference case, the amount of biogas yield is 23.4 kg along with 40.3 kWh of energy, which corresponds to 76.6 kg of raw digestate including 12.9 kWh energy remaining in the bioreactor. It should be noted that the remaining digestate contains 5 wt. % of dry matter content. After the drying process, this dried digestate weights around 4.2 kg with 10% moisture still intact. Subsequently, dried digestate is subjected to the pyrolysis process, which releases three different energy products, identified as oil, gas and biochar. These end products of pyrolysis constitute 3.8 kWh energy for pyrolysis gas, 5.5 kWh of energy for oils and tars along with 3.6 kWh of energy for chars.

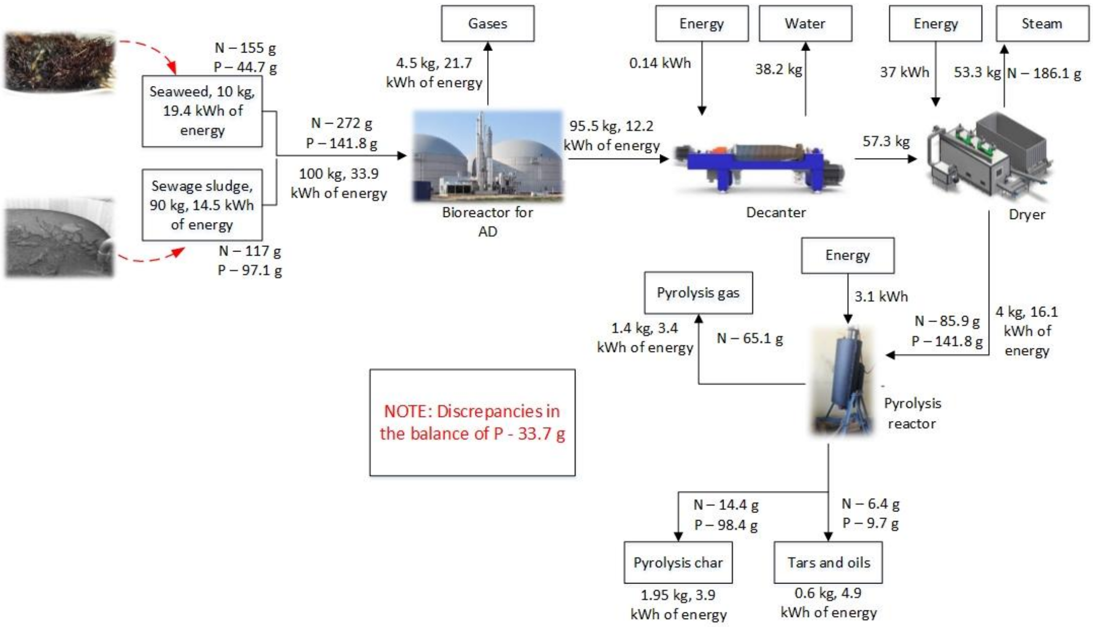

Figure 21. Energy and nutrient balance of the digestate pyrolysis in Lithuanian Energy Institute experiments

After AD, a dewatering system, such as a decanter, could be used to reduce energy consumption for drying. Generally, dewatered digestate has the moisture content of about 60% by weight. As the digestate still contains a lot of water, thermal drying is used to remove the remaining moisture to appropriate level suitable for pyrolysis process. This energy intense process consumes up to 37 kWh of energy to fully dry the remained digestate. After the thermal drying process, dried digestate weights around 4 kg. The performed nutrient analysis after the dryer showed high loss of N. Based on the literature [86], about 70% of total N in AD reactors is mineralized to ammonium NH_4^+ and free ammonia NH_3 and, therefore, during the thermal drying process can be easily emitted with other gases [87]. Subsequently, the dried digestate is subjected to the pyrolysis process, which produced three different energy products, identified as oil, gas, and biochar. These end pyrolysis products constitute 3.4 kWh energy for gas, 4.9 kWh of energy for oils and tar along with 3.9 kWh of energy for chars. The obtained pyrolysis products can be further processed, as an example, gases can be used for the pyrolysis process to maintain reaction heat; oils can be converted to alternative biofuels via catalytic hydro processing units; and biochar can be used for soil remediation.

The analysis of nutrient recovery revealed that in the gathered liquid and solid products 6.4 g and 14.4 g of N, and 9.7 g and 98.4 g of P remained, respectively. This means that approximately 92.3% of total N is removed during thermal processing and vice versa approximately 76% of total P retain in pyrolysis products with the main part in the char.

Based on the results obtained in the marine biomass pyrolysis tests carried out by Lithuanian Energy Institute, an energy balance was drawn up, including energy for transportation, pre-treatment, digestion, dewatering and drying of digestate and pyrolysis. The results are presented in Table 22 and Figure 22. The energetic efficiency in total in the process is about 24%, which was determined from below equation (28).

$$\eta_{\mathrm{net}} = \frac{\text{net energy in the products}}{\text{total energy input}} = \frac{\mathrm{Q}_B + \mathrm{Q}_{\mathrm{PG}} + \mathrm{Q}_{\mathrm{PC}} + \mathrm{Q}_{\mathrm{PO}}}{\mathrm{Q}_{\mathrm{T}} + \mathrm{Q}_{\mathrm{PT}} + \mathrm{Q}_{\mathrm{DP}} + Q_P} \cdot 100\% \tag{28}$$

Where:

Q_T –energy of biomass transportation [MJ],
Q_{PT} – energy for pre-treatment of biomass [MJ],
Q_{DP} – energy input to digestion process [MJ],
Q_P – energy input to pyrolysis process [MJ],
Q_B - heat of biogas combustion [MJ]
Q_D - the energy equivalent of the production of artificial fertiliser [MJ]
Q_{PG} - heat of pyrolytic gas combustion [MJ]
Q_{PC} - heat of pyrolytic char combustion [MJ]
Q_{PO} - heat of pyrolytic tars and oils combustion [MJ]

Table 22. Energy balance of seaweed digestate pyrolysis

		Energy	
		[MJ]	**%**
1.	**Energy generated**		
1.1	Energy of biogas	247.91	90.92%
1.2	Energy of pyrolysis gas	23.80	8.73%
1.3	Energy of pyrolysis char	0.93	0.34%
1.4	Energy of tar and oil	0.04	0.02%
1.5	**Energy generated in total**	272.67	
2.	**Energy consumed**		
2.1	Work used for collecting seaweed	12.30	9.68%
2.2	Energy for transportation	2.40	1.89%
2.3	Energy for pre-treatment	18.80	14.79%
2.4	**Energy for digestion**	*37.63*	***29.61%***
2.4.1	Energy lost	4.06	3.20%
2.4.2	Energy for biomass heating	33.57	26.41%
2.5	Energy for dewatering	2.88	2.27%
2.6	Energy for draying	53.07	41.76%
2.7	Energy for pyrolysis		0.00%
2.8	**Energy consumed in total**	127.08	
3.	**Total energy**	145.59	

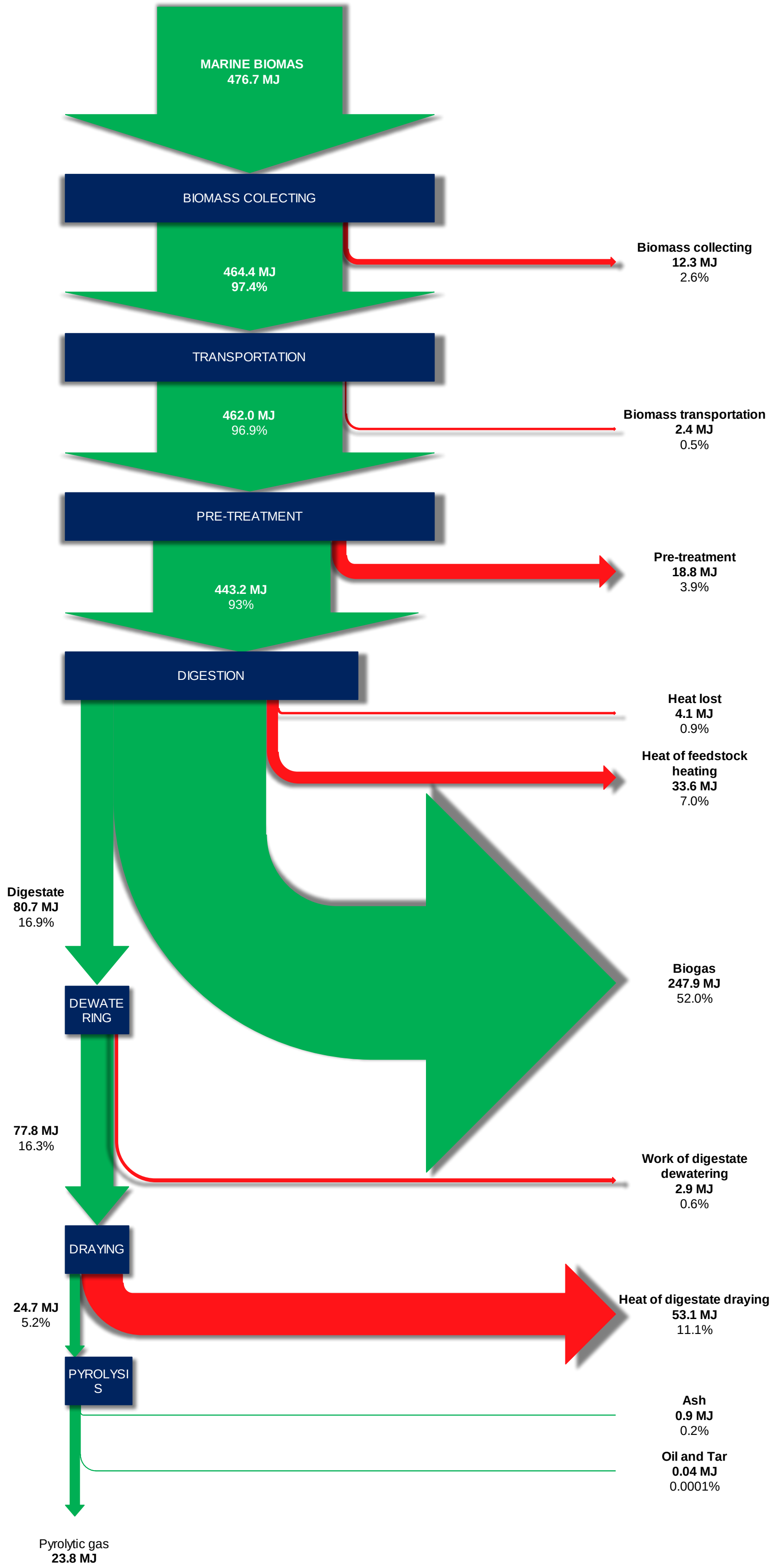

Figure 22. Diagram of energy recover in pyrolysis process of marine biomass digestate

10 Energy Recovery of Plasma Assisted Gasification of Marine Biomass

An analysis of energy and mass balances was carried out according to the same study [72]. The mentioned balances were calculated to evaluate the possible performance of the air plasma-assisted gasification of the digested seaweed. The diagram presented in Figure 23 **Fehler! Verweisquelle konnte nicht gefunden werden.**shows the possible distribution of mass and energy in separate nodes of the installation. The calculations were maintained for a 1 kg/h of biomass feed to gasification to produce condensable and non-condensable products containing 2.5 kWh of energy, and the temperature around 550°C. The parameters of feedstock (digestate) were presented in Table 11 (paragraph section 5.2).

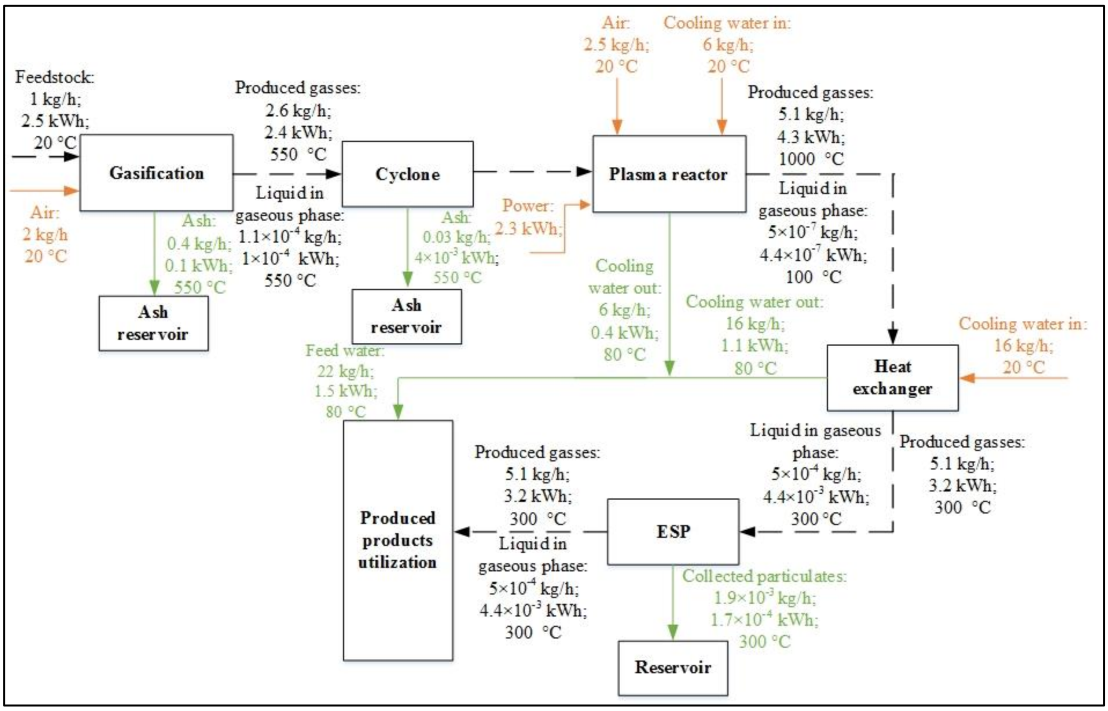

Figure 23. Energy and mass balance of the digestate plasma assisted gasification

Major gasification product composition was taken from paragraph 6.2. Downstream from the gasifier gases pass through a cyclone which is installed trapping a part of the particulates. There, about 0.1 kWh of heat energy was lost with emitting char with the temperature of 550°C. After exiting the cyclone, the gaseous products with tars enter the plasma-chemical reactor, where additional electrical energy of approximately 2.3 kWh for 1 kg of feedstock is used for plasma flow generation and treatment of produced gases. It is worth to mention, that about 81% of supplied electrical energy is transmitted to the syngas flow, while other part leaves plasma-reactor as heat with hot water, which is needed for the cooling of the plasma torch. Therefore, the energy content of the produced gaseous products after the plasma reactor increases to 4.3 kWh. This is mostly related to an increase in gas flow with the conversion of liquid products to gas and the heat content due to an increase in gas temperature from 550 to 1,000°C. The predicted gas composition of the gases after the plasma reactor is presented in **Fehler! Verweisquelle konnte nicht gefunden werden.**. Downstream of the plasma reactor, the produced gases are cooled down to 300°C before the treatment system to remove any residual particulates and other contaminants.

In the system examined here, not all of the required gas treatment system components (scrubbers, absorbents, etc.) were installed, only a dry type ESP (electrostatic precipitator) was used for collecting the particles.

The fate of the metals and minerals was not evaluated, but according to the literature [74], it can be seen, that the situation might be very similar, as it was in the pyrolysis case (paragraph 5.3.4, Table 12). Major part of metals and minerals remains in solid products. It means that this type of product was not additionally processed and any changes should not be observed.

In addition, the analysis showed that this particular case was enabling to the recovery of 6% of energy.

$$\eta_{net} = \frac{net\ energy\ in\ the\ products}{total\ energy\ input} = \frac{Q_{gaseous\ products} + Q_{liquid\ products\ in\ gaseous\ phase}}{Q_{feedstock} + Q_{plasma}} \cdot 100\% \tag{29}$$

11 The potential of nutrient recovery in the partner countries

One of the specific goals of the Coastal Biogas project is nutrient recovery from cast seaweed. Thus, it was valuable to approximately estimate the potential amounts of N and P, which can be recovered at least in the project partner countries. Table 23 presents the potential annual amounts of cast seaweeds per project partner country with potential nitrogen and phosphorus recovery per ton from the collected seaweed. The data was provided by the project partner Roskilde University, Denmark. The estimation was based on the measured concentrations of nutrients and the amount of the potentially collected seaweed in the mentioned countries. Moreover, it needs to be mentioned that the amounts of recovered nutrients should be the same in all evaluated cases (pyrolysis, gasification, and plasma assisted gasification). For that reason, only one case (pyrolysis) is presented in this section.

The mass balance shows the possible amounts of nutrients, which can be recovered from the seaweed by applying thermal treatment. As described in the section above, the main part of nutrient remains in the pyrolysis char. In order to close life cycle and contribute to the circular economy, the recovered nitrogen and phosphorus in the form of biochar could be used in farmlands as fertilisers for remediation of poor soils. Table 24 presents the evaluated amounts of nutrients according to the tests performed for two different analysed cases: i) pyrolysis of digestate obtained after co-digestation of seaweed with sewage sludge, and ii) standalone pyrolysis of seaweed. A visualisation of the provided data is shown in Figure 24.

Table 23. Estimated amount of cast seaweed and N and P in selected countries

Country	Seaweed t/a	Nitrogen, t/a	Phosphorus, t/a
Sweden	1143952	1034	156
Denmark	607467	549	83
Lithuania	76003	68.7	10
Germany	140279	127	19
Poland	184790	167	25
Total			

Table 24. The potential amount of nutrient recovered from collected cast seaweed applying different thermal treatment processes

Country	Seaweed pyrolysis char (d.b.)		Digestate pyrolysis char (d.b.)	
	Nitrogen, t/a	Phosphorus, t/a	Nitrogen, t/a	Phosphorus, t/a
Sweden	259	131	75	119
Denmark	137	70	40	63
Lithuania	17	9	5	8
Germany	32	16	9	15
Poland	42	21	12	19
Total				

It could be seen from the data that the highest amount of N (259 t/a) and P (131 t/a) can be recovered in Sweden, while the lowest in Lithuania (17 t/a and 9 t/a respectively). The same tendencies observed for the digestate char: the highest amount of N and P (75 t/a and 119 t/a) can be recovered in Sweden, while the lowest in Lithuania (5 t/a and 8 t/a), respectively.

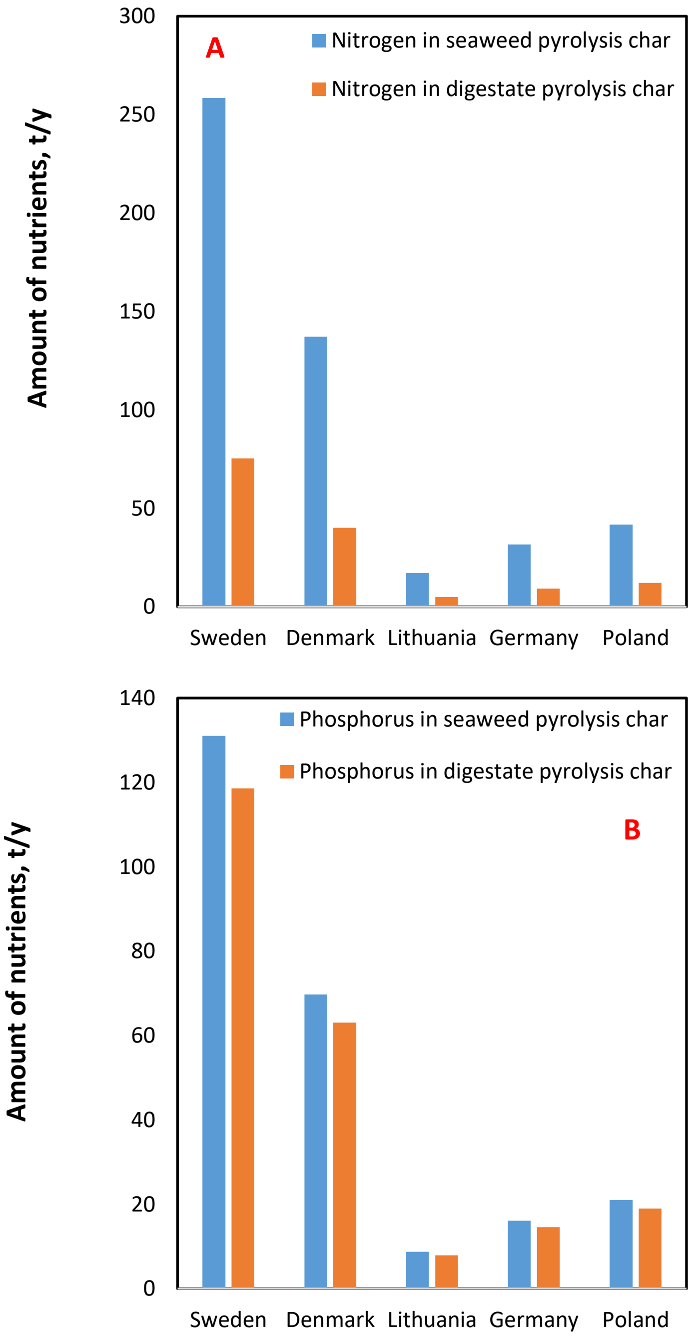

Figure 24. Amount of nutrients which could be potentially recovered in selected countries from. A – Nitrogen, B – Phosphorus

Concluding Remarks

The main objective of this report was to determine the energy balance of the use of marine biomass in anaerobic digestion and pyrolysis processes, and to investigate the possibility of nutrients recovery from digestate that is contaminated with heavy metals and is not usable as a fertiliser on farmland. For that reason, thermochemical gasification of digestate on micro- and pilot-scales has been used.

Digestate is a valuable source of nutrients and can be used as a fertiliser in agriculture as a natural substitute for mineral fertilisers. Such a solution contributes to the development of a circular bioeconomy, where surplus nutrients are taken from the sea and are transferred to the land. However, in case the used seaweed contains high amounts of heavy metals its use as fertiliser on farmland is prohibited to avoid crop contamination. The digestate is then considered as waste. Different assessments have shown that the heavy metal content of seaweed is related to specific locations of the Baltic Sea and to the time of the year when it is being washed ashore. However, it can still be used as a resource for generating energy by gasification.

In each of the analysed cases, the total energy balance was positive, and guarantees generating energy from the processed marine biomass. The most energy-efficient process is the anaerobic digestion of marine biomass (energy efficiency coefficient 54.59%) and the lowest energetically effective is the plasma induced gasification of digestate (energy efficiency coefficient 6%). If only the digestion of marine biomass is conducted, the energy efficiency coefficient is about 42%, but in this case, the utilisation of nutrients presented in the biomass as a fertiliser is fully possible. The energetic effectiveness of digestate of seaweed pyrolysis is about 24%.

References

[1] K. Kuligowski, A. Kozak, Rośliny słodkowodne i makroglony morskie jako substrat w produkcji biogazu, Gdańsk, 2011.

[2] L. Pastare, I. Aleksandrovs, D. Lauka, F. Romagnoli, Mechanical Pre-treatment Effect on Biological Methane Potential from Marine Macro Algae: Results from Batch Tests of Fucus Vesiculosus, Energy Procedia. 95 (2016) 351–357. https://doi.org/10.1016/j.egypro.2016.09.021.

[3] Y. Zhang, M.A. Alam, X. Kong, Z. Wang, L. Li, Y. Sun, Z. Yuan, Effect of salinity on the microbial community and performance on anaerobic digestion of marine macroalgae, J. Chem. Technol. Biotechnol. 92 (2017) 2392–2399. https://doi.org/10.1002/jctb.5246.

[4] LST CEN/TS 15414-1:2010, Kietasis atgautasis kuras. Drėgmės kiekio nustatymas. Džiovinimo krosnyje metodas. 1 dalis. Visuminio drėgmės kiekio nustatymas pamatiniu metodu, (n.d.).

[5] LST EN 14774-1:2010, Kietasis biokuras. Drėgmės kiekio nustatymas. Džiovinimo krosnyje metodas. 1 dalis. Visuminė drėgmė. Pamatinis metodas, (n.d.).

[6] L. 15403:2011 EN, Kietasis atgautasis kuras. Pelenų kiekio nustatymas, (n.d.).

[7] LST EN 14775:2010, Kietasis biokuras. Pelningumo nustatymas, (n.d.).

[8] LST EN 15407:2011, Kietasis atgautasis kuras. Anglies (C), vandenilio (H) ir azoto (N) kiekio nustatymo metodai, (n.d.).

[9] LST EN 15104:2011, Kietasis biokuras. Visuminio anglies, vandenilio ir azoto kiekio nustatymas. Instrumentiniai metodai., (n.d.).

[10] LST EN 15408:2011, Kietasis atgautasis kuras. Sieros (S), chloro, (Cl), fluoro, (F) ir bromo (Br) kiekio nustatymo metodai., (n.d.).

[11] LST EN 15289:2011, Kietasis biokuras. Visuminio sieros ir chloro kiekio nustatymas., (n.d.).

[12] EN 15148:2009, Solid biofuels - Determination of the content of volatile matter, (n.d.).

[13] LST EN 15400:2011, Kietasis atgautasis kuras. Šilumingumo nustatymas, (n.d.).

[14] LST EN 14918:2010, Kietasis biokuras. Šilumingumo nustatymas, (n.d.).

[15] LST EN 15410:2011, Kietasis atgautasis kuras. Pagrindinių elementų (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) kiekio nustatymo metodai., n.d.

[16] LST EN 15290:2011, Kietasis biokuras. Pagrindinių elementų – Al, Ca, Fe, Mg, P, K, Si, Na ir Ti – nustatymas, (n.d.).

[17] LST EN 15411:2011, Kietasis atgautasis kuras. Mikroelementų (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Se, Tl, V ir Zn) kiekio nustatymo metodai., n.d.

[18] LST EN 15297:2011, Kietasis biokuras. Šalutinių elementų - As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V ir Zn – nustatymas., n.d.

[19] S.K. Khanal, T.G.T. Nindhia, S. Nitayavardhana, Biogas from wastes: Processes and applications, Elsevier B.V., 2019. https://doi.org/10.1016/B978-0-444-64200-4.00011-6.

[20] G. Guarino, C. Carotenuto, F. Di Cristofaro, S. Papa, B. Morrone, M. Minale, Does the C/N ratio really affect the bio-methane yield? a three years investigation of buffalo manure digestion, Chem. Eng. Trans. 49 (2016) 463–468. https://doi.org/10.3303/CET1649078.

[21] I. Angelidaki, D. Karakashev, M. Alvarado-Morales, Anaerobic Co-digestion of Cast Seaweed and Organic Residues, 2017. https://energiforskning.dk/sites/energiteknologi.dk/files/slutrapporter/12097_slutrapport-12097.pdf.

[22] M.R. Tabassum, A. Xia, J.D. Murphy, Potential of seaweed as a feedstock for renewable gaseous fuel production in Ireland, Renew. Sustain. Energy Rev. 68 (2017) 136–146. https://doi.org/10.1016/j.rser.2016.09.111.

[23] A.E. Inglesby, A.C. Fisher, Enhanced methane yields from anaerobic digestion of Arthrospira maxima biomass in an advanced flow-through reactor with an integrated recirculation loop microbial fuel cell, Energy Environ. Sci. 5 (2012) 7996–8006. https://doi.org/10.1039/c2ee21659k.

[24] C. Herrmann, J. FitzGerald, R. O'Shea, A. Xia, P. O'Kiely, J.D. Murphy, Ensiling of seaweed for a seaweed biofuel industry, Bioresour. Technol. 196 (2015) 301–313. https://doi.org/10.1016/j.biortech.2015.07.098.

[25] J.H. Mussgnug, V. Klassen, A. Schlüter, O. Kruse, Microalgae as substrates for fermentative biogas production in a combined biorefinery concept, J. Biotechnol. Xxx. (2010). https://doi.org/10.1016/j.jbiotec.2010.07.030.

[26] X. Rui, E. Pay, G. Tianrong, Y. Fang, W. Zhang, The Potential of Blue-Green Algae for Producing Methane in Biogas Fermentation, Proc. ISES World Congr. 2007. (2009) 2426–2429.

[27] L. De Schamphelaire, W. Verstraete, Revival of the biological sunlight-to-biogas energy conversion system, Biotechnol. Bioeng. 103 (2009) 296–304. https://doi.org/10.1002/bit.22257.

[28] G. Polakovičová, P. Kušnír, S. Nagyová, J. Mikulec, Process integration of algae production and anaerobic digestion, in: Chem. Eng. Trans., Italian Association of Chemical Engineering - AIDIC, 2012: pp. 1129–1134. https://doi.org/10.3303/CET1229189.

[29] A.M. Lakaniemi, C.J. Hulatt, D.N. Thomas, O.H. Tuovinen, J.A. Puhakka, Biogenic hydrogen and methane production from Chlorella vulgaris and Dunaliella tertiolecta biomass, Biotechnol. Biofuels. 4 (2011) 34. https://doi.org/10.1186/1754-6834-4-34.

[30] A. Vergara-Fernández, G. Vargas, N. Alarcón, A. Velasco, Evaluation of marine algae as a source of biogas in a two-stage anaerobic reactor system, Biomass and Bioenergy. 32 (2008) 338–344. https://doi.org/10.1016/j.biombioe.2007.10.005.

[31] S. Zeng, X. Yuan, X. Shi, Y. Qiu, Effect of inoculum/substrate ratio on methane yield and orthophosphate release from anaerobic digestion of Microcystis spp., J. Hazard. Mater. 178 (2010) 89–93. https://doi.org/10.1016/j.jhazmat.2010.01.047.

[32] S. Buxy, R. Diltz, P. Pullammanappallil, Biogasification of Marine Algae Nannochloropsis Oculata, in: Ceram. Trans., American Ceramic Society, 2013: pp. 59–67. https://doi.org/10.1002/9781118585160.ch6.

[33] J. Wang, Y. Yin, Fermentative hydrogen production using pretreated microalgal biomass as feedstock, Microb. Cell Fact. 17 (2018) 22.

https://doi.org/10.1186/s12934-018-0871-5.

[34] R. Samson, A. Leduyt, Detailed study of anaerobic digestion of Spirulina maxima algal biomass, Biotechnol. Bioeng. 28 (1986) 1014–1023. https://doi.org/10.1002/bit.260280712.

[35] A.C.M. Di San Marzano, A. Legros, H.P. Naveau, E.J. Nyns, Biomethanation of the marine algae tetraselmis, Int. J. Sol. Energy. 1 (1982) 263–272. https://doi.org/10.1080/01425918208909891.

[36] A. Gurung, S.W. Van Ginkel, W.C. Kang, N.A. Qambrani, S.E. Oh, Evaluation of marine biomass as a source of methane in batch tests: A lab-scale study, Energy. 43 (2012) 396–401. https://doi.org/10.1016/j.energy.2012.04.005.

[37] G. Jard, H. Marfaing, H. Carrère, J.P. Delgenes, J.P. Steyer, C. Dumas, French Brittany macroalgae screening: Composition and methane potential for potential alternative sources of energy and products, Bioresour. Technol. 144 (2013) 492–498. https://doi.org/10.1016/j.biortech.2013.06.114.

[38] M.E. Alzate, R. Muñoz, F. Rogalla, F. Fdz-Polanco, S.I. Pérez-Elvira, Biochemical methane potential of microalgae: Influence of substrate to inoculum ratio, biomass concentration and pretreatment, Bioresour. Technol. 123 (2012) 488–494. https://doi.org/10.1016/j.biortech.2012.06.113.

[39] V.N. Nkemka, M. Murto, Exploring strategies for seaweed hydrolysis: Effect on methane potential and heavy metal mobilisation, Process Biochem. 47 (2012) 2523–2526. https://doi.org/10.1016/j.procbio.2012.06.022.

[40] H.W. Yen, D.E. Brune, Anaerobic co-digestion of algal sludge and waste paper to produce methane, Bioresour. Technol. 98 (2007) 130–134. https://doi.org/10.1016/j.biortech.2005.11.010.

[41] J.C. Costa, P.R. Gonçalves, A. Nobre, M.M. Alves, Biomethanation potential of macroalgae Ulva spp. and Gracilaria spp. and in co-digestion with waste activated sludge, Bioresour. Technol. 114 (2012) 320–326. https://doi.org/10.1016/j.biortech.2012.03.011.

[42] C. Herrmann, N. Kalita, D. Wall, A. Xia, J.D. Murphy, Optimised biogas production from microalgae through co-digestion with carbon-rich co-substrates, Bioresour. Technol. 214 (2016) 328–337. https://doi.org/10.1016/j.biortech.2016.04.119.

[43] H.B. Nielsen, S. Heiske, Anaerobic digestion of macroalgae: Methane potentials, pre-treatment, inhibition and co-digestion, Water Sci. Technol. 64 (2011) 1723–1729. https://doi.org/10.2166/wst.2011.654.

[44] S. Astals, R.S. Musenze, X. Bai, S. Tannock, S. Tait, S. Pratt, P.D. Jensen, Anaerobic co-digestion of pig manure and algae: Impact of intracellular algal products recovery on co-digestion performance, Bioresour. Technol. 181 (2015) 97–104. https://doi.org/10.1016/j.biortech.2015.01.039.

[45] W. Zhong, L. Chi, Y. Luo, Z. Zhang, Z. Zhang, W.M. Wu, Enhanced methane production from Taihu Lake blue algae by anaerobic co-digestion with corn straw in continuous feed digesters, Bioresour. Technol. 134 (2013) 264–270. https://doi.org/10.1016/j.biortech.2013.02.060.

[46] R. Samson, A. LeDuy, Improved performance of anaerobic digestion of Spirulinamaxima algal biomass by addition of carbon-rich wastes, Biotechnol. Lett. 5 (1983) 677–682. https://doi.org/10.1007/BF01386361.

[47] M. Wang, A.K. Sahu, B. Rusten, C. Park, Anaerobic co-digestion of microalgae Chlorella sp. and waste activated sludge, Bioresour. Technol. 142 (2013) 585–590. https://doi.org/10.1016/j.biortech.2013.05.096.

[48] I. Krustok, E. Nehrenheim, M. Odlare, X. Liu, S. Li, F. Energy, Cultivation of Indigenous Algae for Increased Biogas Production, Int. Conf. Appl. Energy. 1 (2013) 1–7.

[49] V.N. Nkemka, M. Murto, Two-stage anaerobic dry digestion of blue mussel and reed, Renew. Energy. 50 (2013) 359–364. https://doi.org/10.1016/j.renene.2012.06.041.

[50] R. Li, N. Duan, Y. Zhang, Z. Liu, B. Li, D. Zhang, T. Dong, Anaerobic co-digestion of chicken manure and microalgae Chlorella sp.: Methane potential, microbial diversity and synergistic impact evaluation, Waste Manag. 68 (2017) 120–127. https://doi.org/10.1016/j.wasman.2017.06.028.

[51] S. Sarker, H.B. Møller, A. Bruhn, Influence of variable feeding on mesophilic and thermophilic co-digestion of Laminaria digitata and cattle manure, Energy Convers. Manag. 87 (2014) 513–520. https://doi.org/10.1016/j.enconman.2014.07.039.

[52] E.A. Ehimen, Z.F. Sun, C.G. Carrington, E.J. Birch, J.J. Eaton-Rye, Anaerobic digestion of microalgae residues resulting from the biodiesel production process, Appl. Energy. 88 (2011) 3454–3463. https://doi.org/10.1016/j.apenergy.2010.10.020.

[53] H. Miao, S. Wang, M. Zhao, Z. Huang, H. Ren, Q. Yan, W. Ruan, Codigestion of Taihu blue algae with swine manure for biogas production, Energy Convers. Manag. 77 (2014) 643–649. https://doi.org/10.1016/j.enconman.2013.10.025.

[54] C. Beltrán, D. Jeison, F.G. Fermoso, R. Borja, Batch anaerobic co-digestion of waste activated sludge and microalgae (Chlorella sorokiniana) at mesophilic temperature, J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 51 (2016) 847–850. https://doi.org/10.1080/10934529.2016.1181456.

[55] P. Bohutskyi, T.A. Keller, D. Phan, M.L. Parris, M. Li, L. Richardson, A.M. Kopachevsky, Co-digestion of Wastewater-Grown Filamentous Algae With Sewage Sludge Improves Biomethane Production and Energy Balance Compared to Thermal, Chemical, or Thermochemical Pretreatments, Front. Energy Res. 7 (2019) 47. https://doi.org/10.3389/fenrg.2019.00047.

[56] S. Schwede, A. Kowalczyk, M. Gerber, R. Span, Anaerobic co-digestion of the marine microalga Nannochloropsis salina with energy crops, Bioresour. Technol. 148 (2013) 428–435. https://doi.org/10.1016/j.biortech.2013.08.157.

[57] Q. Cheng, F. Deng, H. Li, Z.H. Qin, M. Wang, J. Li, Nutrients removal from the secondary effluents of municipal domestic wastewater by Oscillatoria tenuis and subsequent co-digestion with pig manure, Environ. Technol. (United Kingdom). 39 (2018) 3127–3134. https://doi.org/10.1080/09593330.2017.1375020.

[58] G. Zhen, X. Lu, T. Kobayashi, G. Kumar, K. Xu, Anaerobic co-digestion on improving methane production from mixed microalgae (Scenedesmus sp., Chlorella sp.) and food waste: Kinetic modeling and synergistic impact evaluation, Chem. Eng. J. 299 (2016) 332–341. https://doi.org/10.1016/j.cej.2016.04.118.

[59] M. Solé-Bundó, C. Eskicioglu, M. Garfí, H. Carrère, I. Ferrer, Anaerobic co-digestion of microalgal biomass and wheat straw with and without thermo-alkaline pretreatment, Bioresour. Technol. 237 (2017) 89–98. https://doi.org/10.1016/j.biortech.2017.03.151.

[60] S. Sarker, A. Bruhn, A.J. Ward, H.B. Moller, Bio-fuel from anaerobic co-digestion of the

macro-algae Ulva lactuca and Laminaria digitata., Renew. Energy Energy Effic. Proc. Int. Sci. Conf. Jelgava, Latv. 28-30 May 2012. 3 (2012) 86–90.

[61] A.D. Hughes, M.S. Kelly, K.D. Black, M.S. Stanley, Biogas from Macroalgae: Is it time to revisit the idea?, Biotechnol. Biofuels. 5 (2012) 86. https://doi.org/10.1186/1754-6834-5-86.

[62] F. Romagnoli, L. Pastare, A. Sabūnas, K. Bāliņa, D. Blumberga, Effects of pre-treatment on Biochemical Methane Potential (BMP) testing using Baltic Sea Fucus vesiculosus feedstock, Biomass and Bioenergy. 105 (2017) 23–31. https://doi.org/10.1016/j.biombioe.2017.06.013.

[63] F. Romagnoli, M. Dorella, A. Gruduls, M. Collotta, G. Tomasoni, Anaerobic co-digestion of Baltic seaweeds with wheat straw and straw pellets: Synergetic effects on biomethane yield and kinetic biodegradability constant, in: Energy Procedia, Elsevier Ltd, 2019: pp. 854–860. https://doi.org/10.1016/j.egypro.2019.01.221.

[64] K. Bucholc, M. Szymczak-Zyła, L. Lubecki, A. Zamojska, P. Hapter, E. Tjernström, G. Kowalewska, Nutrient content in macrophyta collected from southern Baltic Sea beaches in relation to eutrophication and biogas production, Sci. Total Environ. 473–474 (2014) 298–307. https://doi.org/10.1016/j.scitotenv.2013.12.044.

[65] M. Suutari, E. Leskinen, K. Spilling, K. Kostamo, J. Seppälä, Nutrient removal by biomass accumulation on artificial substrata in the northern Baltic Sea, J. Appl. Phycol. 29 (2017) 1707–1720. https://doi.org/10.1007/s10811-016-1023-0.

[66] B.D. Struck, R. Pelzer, P. Ostapczuk, H. Emons, C. Mohl, Statistical evaluation of ecosystem properties influencing the uptake of As, Cd, Co, Cu, Hg, Mn, Ni, Pb and Zn in seaweed (Fucus vesiculosus) and common mussel (Mytilus edulis), Sci. Total Environ. 207 (1997) 29–42. https://doi.org/10.1016/S0048-9697(97)00246-5.

[67] R. Zbikowski, P. Szefer, A. Latała, Distribution and relationships between selected chemical elements in green alga Enteromorpha sp. from the southern Baltic, Environ. Pollut. 143 (2006) 435–448. https://doi.org/10.1016/j.envpol.2005.12.007.

[68] R. Zbikowski, P. Szefer, A. Latała, Comparison of green algae Cladophora sp. and Enteromorpha sp. as potential biomonitors of chemical elements in the southern Baltic, Sci. Total Environ. 387 (2007) 320–332. https://doi.org/10.1016/j.scitotenv.2007.07.017.

[69] M. Suutari, E. Leskinen, K. Spilling, K. Kostamo, J. Seppälä, Nutrient removal by biomass accumulation on artificial substrata in the northern Baltic Sea, J. Appl. Phycol. 29 (2017) 1707–1720. https://doi.org/10.1007/s10811-016-1023-0.

[70] F. Romagnoli, L. Pastare, A. Sabūnas, K. Bāliņa, D. Blumberga, Effects of pre-treatment on Biochemical Methane Potential (BMP) testing using Baltic Sea Fucus vesiculosus feedstock, Biomass and Bioenergy. 105 (2017) 23–31. https://doi.org/10.1016/j.biombioe.2017.06.013.

[71] C. Zörb, M. Senbayram, E. Peiter, Potassium in agriculture - Status and perspectives, J. Plant Physiol. 171 (2014) 656–669. https://doi.org/10.1016/j.jplph.2013.08.008.

[72] N. Striūgas, V. Valinčius, N. Pedišius, R. Poškas, K. Zakarauskas, Investigation of sewage sludge treatment using air plasma assisted gasification, Waste Manag. 64 (2017) 149–160. https://doi.org/https://doi.org/10.1016/j.wasman.2017.03.024.

[73] N. Striūgas, V. Valinčius, N. Pedišius, R. Poškas, K. Zakarauskas, Investigation of sewage sludge treatment using air plasma assisted gasification, Waste Manag. 64 (2017) 149–

160. https://doi.org/10.1016/j.wasman.2017.03.024.

[74] N. Striugas, K. Zakarauskas, A. Džiugys, R. Navakas, R. Paulauskas, An evaluation of performance of automatically operated multi-fuel downdraft gasifier for energy production, Appl. Therm. Eng. 73 (2014) 1151–1159. https://doi.org/10.1016/j.applthermaleng.2014.09.007.

[75] E. Risén, O. Tatarchenko, F. Gröndahl, M.E. Malmström, Harvesting of drifting filamentous macroalgae in the Baltic Sea: An energy assessment, in: J. Renew. Sustain. Energy, American Institute of Physics Inc., 2014: p. 013116. https://doi.org/10.1063/1.4862783.

[76] Technological Solutions for the Collection and Removal of Algae from the Beach, Sea and Coastal Strip in Trelleborg Municipality, n.d. http://wabproject.pl/files/Technological solutions for the collection and removal of algae from the beach, sea and coastal strip in Trelleborg Municipality ENGLISH.pdf.

[77] J. Eom, L. Schipper, L. Thompson, We keep on truckin': Trends in freight energy use and carbon emissions in 11 IEA countries, Energy Policy. 45 (2012) 327–341. https://doi.org/10.1016/j.enpol.2012.02.040.

[78] M. Gucwa, A. Schäfer, The impact of scale on energy intensity in freight transportation, Transp. Res. Part D Transp. Environ. 23 (2013) 41–49. https://doi.org/10.1016/j.trd.2013.03.008.

[79] L. Cadoche, G.D. López, Assessment of size reduction as a preliminary step in the production of ethanol from lignocellulosic wastes, Biol. Wastes. 30 (1989) 153–157. https://doi.org/10.1016/0269-7483(89)90069-4.

[80] M. Alvarado-Morales, A. Boldrin, D.B. Karakashev, S.L. Holdt, I. Angelidaki, T. Astrup, Life cycle assessment of biofuel production from brown seaweed in Nordic conditions, Bioresour. Technol. 129 (2013) 92–99. https://doi.org/10.1016/j.biortech.2012.11.029.

[81] M. Pöschl, S. Ward, P. Owende, Evaluation of energy efficiency of various biogas production and utilization pathways, Appl. Energy. 87 (2010) 3305–3321. https://doi.org/http://dx.doi.org/10.1016/j.apenergy.2010.05.011.

[82] T. Karuppiah, V. Ebenezer Azariah, Biomass Pretreatment for Enhancement of Biogas Production, in: Anaerob. Dig., IntechOpen, 2019. https://doi.org/10.5772/intechopen.82088.

[83] https://climateknowledgeportal.worldbank.org/ (accessed 20.08.2020), (n.d.).

[84] K. Kermeli, Energy Efficiency and Cost Saving Opportunities for Ammonia and Nitrogenous Fertilizer Production: An ENERGY STAR® Guide for Energy & Plant Managers, 2017.

[85] P. Baboo, Ammonia & Urea Plant Energy Consumtion Calculation, Vijaipur, India, 2015.

[86] L. Shi, W.S. Simplicio, G. Wu, Z. Hu, H. Hu, X. Zhan, Nutrient Recovery from Digestate of Anaerobic Digestion of Livestock Manure: a Review, Curr. Pollut. Reports. 4 (2018) 74–83. https://doi.org/10.1007/s40726-018-0082-z.

[87] W. Liu, J. Xu, J. Liu, H. Cao, X.F. Huang, G. Li, Characteristics of ammonia emission during thermal drying of lime sludge for co-combustion in cement kilns, Environ. Technol. (United Kingdom). 36 (2015) 226–236. https://doi.org/10.1080/09593330.2014.942705.

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