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Algae processing for energy production: development of waste pyrolysis technology

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Abstract. Waste processing accordingly to waste-to-energy concept remains a major challenge to deal with growing amounts of different waste types. The aim of the study is to expand the knowledge base for biomass waste thermochemical processing into syngas and biochar on example of algae waste treatment. In accordance to this concept, waste pyrolysis technology is further advanced by evaluating, studying and adapting the most technologically and economically feasible approach and by developing a pilot scale facility with the aim to demonstrate its potential to offer the industry an innovative solution for solid waste processing. The study includes theoretical background for thermal recovery of organic waste, with application of specifics of algae waste (beach wrack). Algae waste thermochemical processing and gas analysis are tested both for process of torrefied material and with full ash content characterisation. Additional algae waste proximate/ultimate analysis were done. The synthesis gas produced by the pyrolysis process contain 30–60% CH_4, 5–12% H_2, 20–40% CO (remaining CO_2, N_2) and thus can be used for heating purposes. The another algae waste pyrolysis product - biochar is enriched with mineral components thus increasing its application potential in agriculture, however in can be used also for energy production purposes. Thermal analytics of beach wreck undertaken on different type of samples to be common for the Baltic Sea area and projections on application of gasification technology for upscale at municipality level is analysed with a view to application for municipality larger amount material.

Key words: algae waste, biomass waste, biochar, gasification, syngas.

INTRODUCTION

Marine biomass, at first primary producers - algae, represents a cheap biomass source with a great diversity in composition and functional properties due to the presence of different bioactive compounds (Ibañez & Cifuentes, 2013; Hamed, 2016; Khoo et al., 2019). Seaweeds have been harvested and used locally in small quantities for feed, food and fertilizer for centuries, however large-scale cultivation of recently is expanding very rapidly (Buschmann et al., 2017). Limitations of terrestrial resources, the fast global growth and ageing population requires alternative energy and food sources as well as novel medicines and thus algae biomass seems to be a promising alternative to solve main challenges of contemporary society. Processing of algae supports progress of 'Blue

Bioeconomy' and new initiatives of climate neutral development (Vieira et al., 2020). Different technologies can be used for the production of biofuels from algae: anaerobic digestion to produce biogas, fermentation to obtain bioethanol, chemical processing, to get biodiesel as well as direct combustion, gasification or pyrolysis (Rastogi et al., 2018; Kamani et al., 2019; Aravind et al., 2020; Tang et al., 2020). After algae biomass processing significant amount of algae wastes are left requiring solutions for their utilisation and further processign to exclude adverse impacts on the environment. Another major source of algae waste is beach-cast sea wrack - an organic material consisting from fresh and decaying algae biomass, various other marine organisms, as well as manmade litter (Suursaar et al., 2014), that accumulates on beaches due to the action of waves, tides and aperiodic water level fluctuations. In spite to the natural origin of the beach wreck have significant environmental impact (Dugan et al., 2011, Chubarenko et al., 2020), if accumulated in excessive amounts. Anthropogenic pressures, such as shoreline changes, eutrophication, and climate change stimulates accumulation of algae biomass onshore and makes mentioned problems even worse (Barreiro et al., 2011; Misson et al., 2020). Furthermore, marine eutrophication and climate changes not only affects accumulation of algae biomass on shorelines but as well may be affected by the products of its aerobic decomposition. It is estimated that the annual global carbon flux from algae wrack to atmosphere is between 1.31 and 19.04 Tg C yr^{-1} (Liu et al. 2019) thus significantly contributing to greenhouse gas emissions. Algae biomass processing waste and beach wreck in common have depleted composition in respect to valuable, carbon (energy) rich or biologically valuable components and thus further biorefinery have severe limitations.

As a prospective solution of algae biomass processing waste and beach wreck can be considered torrefaction. Torrefaction, also known as destructive drying and slow pyrolysis, is a mild pyrolytic process that recently received a wide attention of scientific community as both the method of the pre-treatment and upgrade of low quality fuels (Gong et al., 2019; Mamvura & Danha, 2020), as well as for the production of soil amendment, called biochar (Heikkinen, 2019). This process may be organised at scales ranging from large industrial facilities down to the individual farm (Pathy et al., 2020), and even at the domestic level (Yan et al., 2020), making it applicable to a variety of socioeconomic situations. The study of Macreadie et al., 2017 provided the clear evidence that the conversion of beach wrack to biochar could be a viable environmental solution for dealing with unwanted wrack, offsetting carbon emissions, and providing a commercially valuable product. The use of algal biomass for biochar production, with energy co-generation potential, provides a value-driven model to sequester C and recycle nutrients (Ross et al., 2008; Bird et al., 2011). Biochar has demonstrated applications as a soil ameliorant capable of improving water holding capacity, nutrient status and microbial ecology of many soils (Lehmann, 2007; Lehmann et al., 2011). Results of Bird et al. (2011) showed that microalgae biochar has properties that provide direct nutrient benefits to soils and stimulate crop productivity and will be especially useful for the application on acidic soils. (Bird et al., 2011). In contrast to bioenergy, in which all CO_2 that is fixed in the biomass by photosynthesis is returned to the atmosphere quickly as fossil carbon emissions are offset, biochar has the potential for even greater impact on climate through its enhancement of the productivity of infertile soils and its effects on soil GHG fluxes (Woolf et al., 2010).

The aim of the study is to demonstrate potential of use of elaborated and consstructed pyrolysis facility for processing of algae waste on example of beach wreck into biochar and syngas, their composition and application potential.

MATERIALS AND METHODS

Sampling of algae waste (beach wreck)

Samples of algae waste (beach wreck) were sampled in Latvia (Riga Gulf and Baltic sea coastline near Liepaja) at the end of the vegetation season – in September, October 2019, 2020. The studied samples consisted from species dominant in coastal areas in the Baltic Sea. To characterise the studied algae, biomass of *Fucus vesiculosus* were used. After sampling, the obtained mass were air dried and stored in dry not longer than 1 month.

Analysis of algae waste composition

The dominant species of the beach wreck were estimated after hand-sorting and identification. The biomasses of algae were weighed after separation of identified species and drying at 60 °C to constant weight (Suursaar et al., 2014). Amount of plastics were estimated after separation from other wreck components, washing with demineralised water, drying at 60 °C to constant weight and weighing. The los-on-ignition method was employed to estimate the content of mineral matter (Heiri et al., 2001) incinerating the samples for 2 h at 950 °C.

Characterisation of the composition of samples

Ultimate analysis performed using thermogravimetric method described by Agrawal (1988). Carbon, nitrogen and hydrogen content determined using EN ISO 16948 (Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen) standard method. Chlorine and sulphur content determined using ISO 16994 (Solid biofuels - Determination of total content of sulphur and chlorine) standard method. Calorific values of algae biomass samples determined using standard method: EN ISO 18125 in a bomb calorimeter: AC-350, LECO, USA. For analysis of algae and algae char samples (1.00 g) were weighed into Teflon tubes followed by addition of 8 mL 65% HNO_3 (Sigma Aldrich, ≥ 65%) and 2 mL 30% H_2O_2 (Enola, Latvia). The tubes were closed (to provide high pressure) prior to sample digestion using a microwave system (Milestone Advanced Microwave digestion system, Ethos Easy) at 200 °C for 30 min. The resulting samples were diluted to 50 mL with deionised water (Millipore). The concentrations of inorganic elements were determined by inductively coupled plasma spectrometry with optical emission detection (Thermo Scientific iCAP 700 series ICP spectrometer). The elements determined were Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn. The detection limit was 1–10 ppb for Al, Ca, and Fe, 0.1–1 ppb for Mg, K, and Na, and 0.1 ppb for all other elements. The concentrations were expressed per dry weight of sample.

Thermogravimetric analysis

Thermogravimetric analysis performed with heating rate 20 °C min^{-1}, under dynamic flow of nitrogen (100 mL min^{-1}) on about 10 mg of a solid powder sample using TA instruments SDT-Q600 thermogravimetric device. TG and DTG curves recorded.

Synthesis gas composition analysis

For the online analysis of syngas composition ETG MCA 100 Syn, biogas, multigas analyser (ETG, Italy). For measuremtn of CH_4, CO_2, CO, O_2 non-dispersive infrared (NDIR) gas with a single optical path platform were used, but for measurement of H_2 TCD principle (thermal conductivity) was used. Internal calibration were used for gas concentration analysis was used and the accuracy of measurement was confirmed using synthetic has mixtures: H_2: CH_4, N_2:CO (Linde, Latvia).

RESULTS AND DISCUSSION

Dominant algae species in the studied samples (Fig. 1) were filamentous algae *Cladophora glomerata* (L.), *Fucus vesiculosus* (L.) and *Furcellaria lumbricalis* (Hudson).

Figure 1. Beach-cast algae deposits (sea wrack) in Lapmežciems, Ragaciems, Jaunkemeri and Bigauņciems, Latvia (July, 2019).

These results were similar as in previous study on Baltic Sea beach wreck (Suursaar et al., 2014). As the largest peaces of the plastic waste (bottles, packaging residues etc) was removed during the sampling and preparation for the torrefication process, but the microplastic amount per gram would be expected to be less than 1% as suggested in other studies (Suursaar et al., 2014) the found amounts were found to be $< 3 \pm 0.5\%$. Also wood debris were found to be in similar amounts. However main admixture to algae was mineral material (sand) in highly variable amounts, starting from 5% from the beach wreck mass up to15%. As main factor affecting the amount of sand in the algae beach wreck sems to be storms (after storms sand amount increases), rain (helps to remove sand particles) as well as age (with decay of algae the amount of sand admixtures seems to increase. Of the 1,300 kg collected algae waste, 219 kg of algae biomass was obtained after drying.

The studied beach wreck samples do have reasonably high heating values: lower heating value 7.55 ± 0.10 MJ kg^{-1} (1,804 ± 12 kCal kg^{-1}) and higher heating value 8.96 ± 0.15 MJ kg^{-1} (2,140 ± 12 kCal kg^{-1}). These heating values are comparable to heating values of other types of biofuel: wheat straw have higher heating value14.86 MJ kg^{-1} (Montero et al., 2016), 24 types of biomass with higher heating values ranging from 5.63 to 23.46 MJ kg^{-1} (Nhuchhen & Salam, 2012). The algae biomass contain 21.5 ± 5.5% of carbon and 40.0 ± 5.0 oxygen, but the S concentration is < 0.7% and Cl concentration < 0.2%.

In the elemental composition of the algae beach wreck (Table 1) dominates elements, such as Al, K, Ca, Na, Mg but also concentrations of P and Fe are relatively high. At the same time concentrations of toxic trace elements are low. Thermal decomposition character of waste algae (Fig. 2) demonstrates, that major part of the biomassis decomposing in the interval 180–380 °C.

Table 1. Elemental composition of the beach wrack and biochar after torrefaction (mg kg^{-1} of beach wrack/ algae biochar)

Element	Concentration of elements in the beach wreck, mg kg^{-1}	Concentration of elements in biochar after torrefication mg kg^{-1}
Al	1,551.89 ± 18.50	2,689.43 ± 19.50
K	2,692.10 ± 12.32	21,211.56 ± 13.55
Ca	9,727.68 ± 25.32	33,597.90 ± 20.29
Na	6,432.23 ± 16.34	10,168.73 ± 17.60
Mg	3,234.80 ± 15.32	8,059.73 ± 20.25
P	1,150.47 ± 34.20	3,281.32 ± 29.49
Fe	1,829.38 ± 21.89	6,156.03 ± 18.57
Sr	279.75 ± 5.48	739.72 ± 6.03
Mn	60.53 ± 3.48	3,948.72 ± 4.82
Si	64.59 ± 5.27	233.58 ± 6.90
Zn	53.24 ± 15.18	74.20 ± 5.91
Ti	60.36 ± 5.26	73.82 ± 4.83
Ba	54.32 ± 4.21	264.59 ± 4.31
Cr	23.72 ± 3.82	24.62 ± 4.02
Ni	11.33 ± 2.95	171.13 ± 11.89
Cu	7.91 ± 0.83	8.97 ± 1.03
As	2.64 ± 0.72	8.10 ± 0.55
Pb	2.34 ± 0.32	2.44 ± 0.18
V	2.76 ± 0.16	1.88 ± 0.17
Cd	1.56 ± 0.11	1.92 ± 0.08
Co	1.01 ± 0.08	3.08 ± 0.07
Mo	1.32 ± 0.11	1.92 ± 0.02

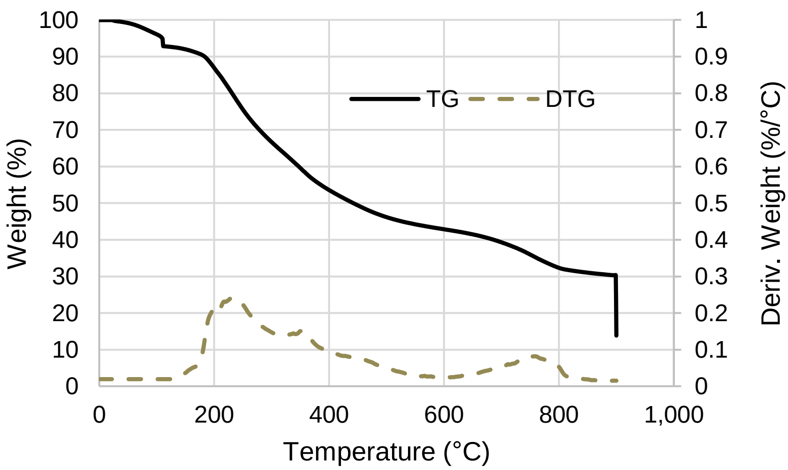
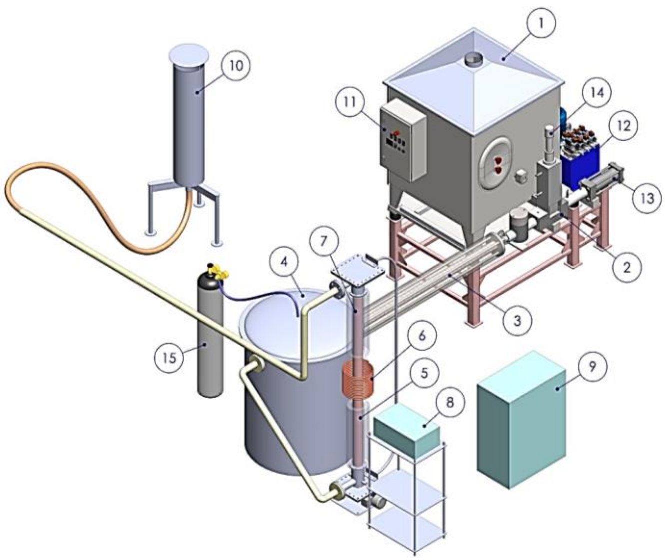


Figure 2. Thermal decomposition character of algae mass representing beach wreck.

Beach wrack pyrolysis/gasification tests were performed on an innovative facility for pyrolysis of various wastes and thermal cracking of pyrolysis gas products (Fig. 3). The concept of the design of the gasification is to split the thermal transformation of wastes into 2 processes: 1) torrefication of the waste or biomass into waste char (in case of biomass – biochar); 2) high temperature treatment of the pyrolysis gas to destroy tars and transform the pyrolysis has into syngas. The apparatus consists of an extruder-type pyrolizer/gasifier, a pyrolysis product separation chamber, a thermal cracker for gaseous pyrolysis products. The gasification process does not use air or oxygen as a gasification agent. The plant has an allothermal gasification process using an external heat source, but nitrogen is used for inerting the plant and for process safety. The machine is functioning in semi-continuous operation mode as the off-loading of the biochar periodically is needed.



1 – feedstock bunker;
2 – hydrolic press feeder;
3 – heated extruder;
4 – gas and char accumulation tank;
5 – secondary gas cracking;
6 – external inductive heater;
7 – gas cooler;
8 – inductive heater resonator;
9 – inductive heater power box;
10 – flare;
11 – control cabinet;
12 – hydrostation;
13 – hydrocilinder;
14 – prior hydropresser box;
15 – nitrogen balloon.

Figure 3. Experimental waste gasification plant.

In the extruder-type pyrolizer (3), the algae waste is compacted in a continuous 42 mm diameter briquette blast, which is pressed into a heated extruder by means of a hydraulic piston. The operating temperature of the extruder was set and automatically adjusted to desired temperature from 300 °C to 600 °C. The primary reforming of the algae waste into pyrolysis gas and char is carried out in the extruder and at temperatures 350–600° biochar formation takes place, forming pyrolysis gas.

In the pyrolysis product separation chamber (4), the pyrolysis gas is separated from the char. The biochar is stored in an airtight container (4) and after cooling, the biochar can be unloaded from the container. During torrefication the transformation of algae waste mass in inert atmosphere takes place. The yield of biochar depending on the temperature is from 75 till 90% from the original algae waste mass. The biochar is enriched with mineral components (Table 1) thus increasing its application potential in agriculture, however in can be used also for energy production purposes.

The pyrolysis gas is fed to a secondary high temperature reformer (6) where the pyrolysis gas is heated to 800–1,200 °C. At elevated temperature, high turbulence thermal tar cracking takes place and the heavy organic gaseous substances are reformed into the synthesis gas components H_2, CO, CO_2. At the output of the secondary reformer, the gas is cooled and the heat consumed in the process is recovered. The resulting synthesis gas samples are analyzed on site with a portable gas analyzer. The synthesis gas produced by the gasification process contain 30–60% CH_4, 5–12% H_2, 20–40% CO (remaining CO_2, N_2) and thus can be used for heating purposes (10).

CONCLUSIONS

Algae waste (beach wreck) gasification was undertaken to transform the algae biomass into biochar and synthesis gas (syngas). Elaborated thermal processing technology provides possibility to split the thermal transformation of algae biomass into 2 processes: 1) torrefication of the waste or biomass into waste char (in case of biomass – biochar); 2) high temperature treatment of the pyrolysis gas to destroy tars and transform the pyrolysis has into syngas. Both processes yield valuable products: biochar for application as fuel or in agriculture and synthesis gas.

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