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Green macroalgae for biomitigation of nutrients, purification of biogas and energy production

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Abstract

The green macroalgae *Ulva lactuca* and *Ulvaria splendens* are two species particularly interesting in an algal biorefinery concept including biofuel production in Denmark and Greenland, respectively. The possibility of using digested pig manure (DPM) as nutrient source for the cultivation of the two species was investigated, and the macroalgae were also used as substrate for anaerobic thermophilic digestion with DPM as inoculum. Half the algal fronds were washed with fresh water in order to investigate the effect of sea salt in the anaerobic digestion. In addition, biogas was investigated as carbon source for algal biomass production. Diluted DPM was suitable as nutrient source. However, growth rate 27% lower (0.16 d^{-1}) than the maximum achieved (0.22 d^{-1} with NO_3^- culture medium (F/2)). *Ulva lactuca* had higher growth rates compared to *U. splendens* ($p < 0.05$). The specific growth rates of *U. lactuca* were not significantly different when using diluted DPM or standard medium (F/2), both with biogas

and CO_2 as bubbled gas. Both species could be used for biogas production with a yield of approx. $0.2 \text{ L-CH}_4/\text{gVS}$. The CH_4 yields were 21-29% higher when the macroalgae was washed, removing salt on surface ($p < 0.05$). Especially, the biogas yield from *U. splendens*, growing under more saline conditions, benefited from this treatment.

These results suggest that CO_2 from biogas and biogas effluents can be used for respectively carbon and nutrients supply for cultivation of algae, which can further be used for possible extraction of high added value products and bioenergy. This will, in addition to algal biomass, result in purification of nutrient rich waste waters, and purification of biogas. This study showed the two green macroalgae as promising candidates for future algal biorefineries.

Aims

- Determine the growth rate of *U. lactuca* and *U. splendens* cultivated under different nutrient regimes.
- Investigate digested pig manure (DPM) as nutrient source candidate for algal growth.
- Investigate biogas as a carbon source for cultivation of *U. lactuca*
- Quantify the biogas potential production of *U. lactuca* and *U. splendens*.
- Investigate the possible inhibition of the biogas process, by the marine sea salt contained in the superficial seawater present on the algal fronds.

Results

- High growth rates (0.22 d^{-1} with NO_3^- culture medium) and high yields (10 x corn yield).
- *U. lactuca* had higher growth rates for all treatments compared to *U. splendens* ($p < 0.05$).
- Diluted DPM was suitable as nutrient source, however growth rate 27% lower (0.16 d^{-1}) than the maximum achieved (Figure 1).
- No significant difference in specific growth rates of *U. lactuca* when using diluted DPM or standard medium (F/2), both with biogas and CO_2 as bubbled gas (Figure 2).
- Both *U. splendens* and *U. lactuca* could be used for biogas production with a yield of approx. $0.2 \text{ L-CH}_4/\text{gVS}$. The CH_4 yields were 21-29% higher when the macroalgae was washed.
- The Na^+ and K^+ concentrations of $< 1 \text{ g/L}$ should not be inhibiting the biogas process (Figure 3).

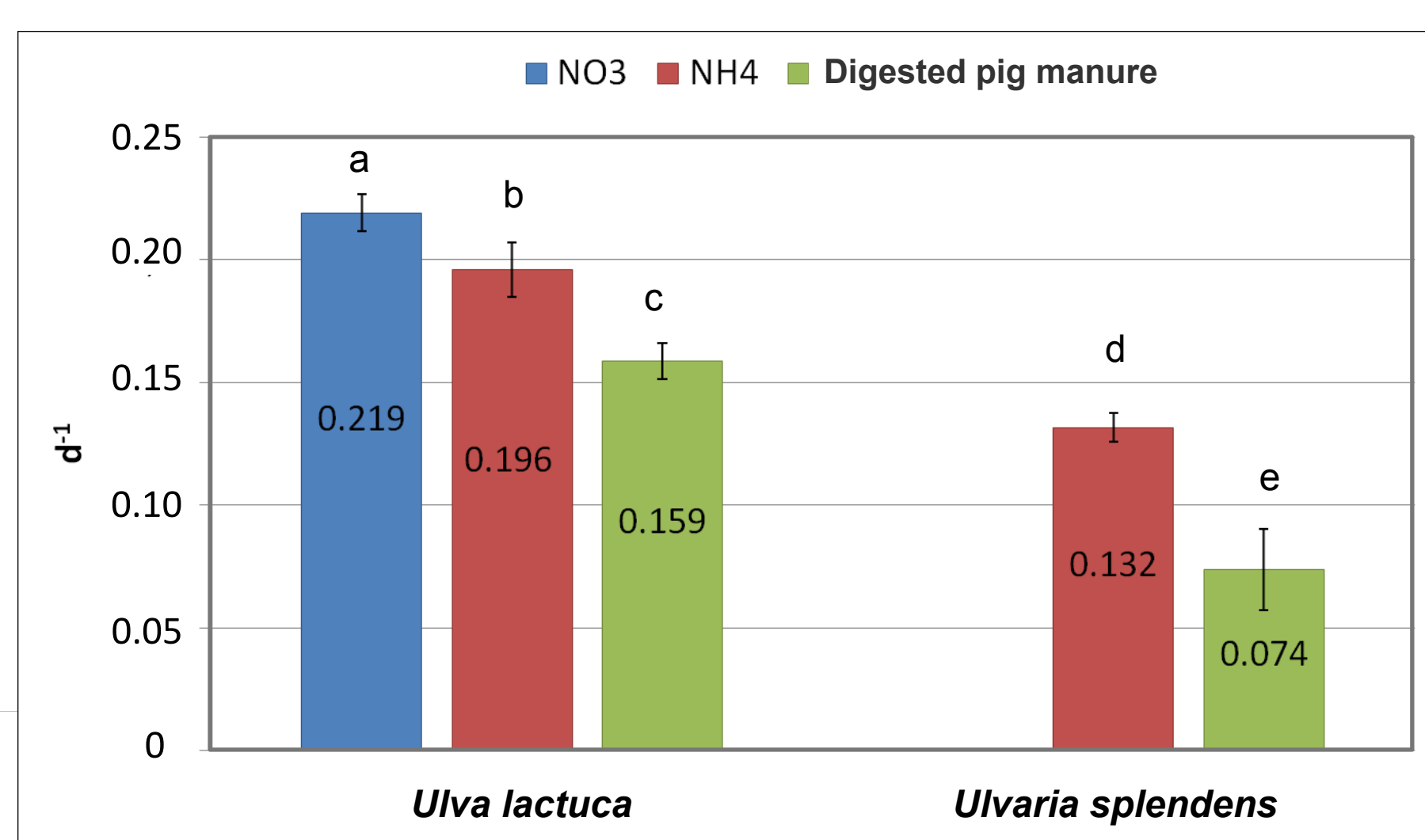


Figure 1: Specific growth rates of *U. lactuca* and *U. splendens* cultivated under different nutrient regimes corresponding to 12.35 mgN/L . *U. splendens* died after 4 days of cultivation in NO_3^- . Different letters represent results of significant difference ($n=3$, $p < 0.05$)

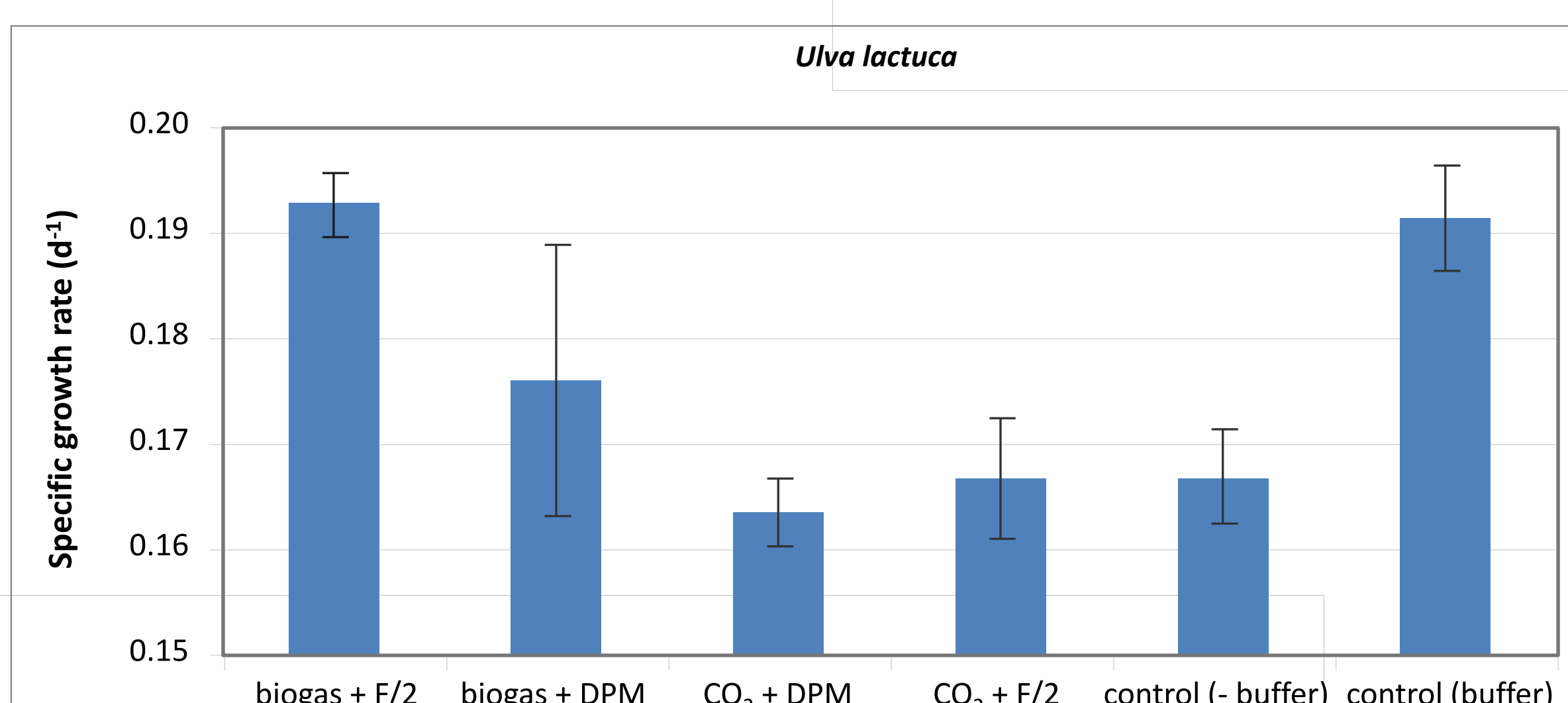


Figure 2: Specific growth rates of *U. lactuca* cultivated under different nutrient regimes (corresponding to 12.35 mgN/L) and sparging of CO_2 or biogas as carbon source. Buffer (K_2HPO_4) was added in all treatments except control (- buffer). Error bars represent standard errors ($n=3$).

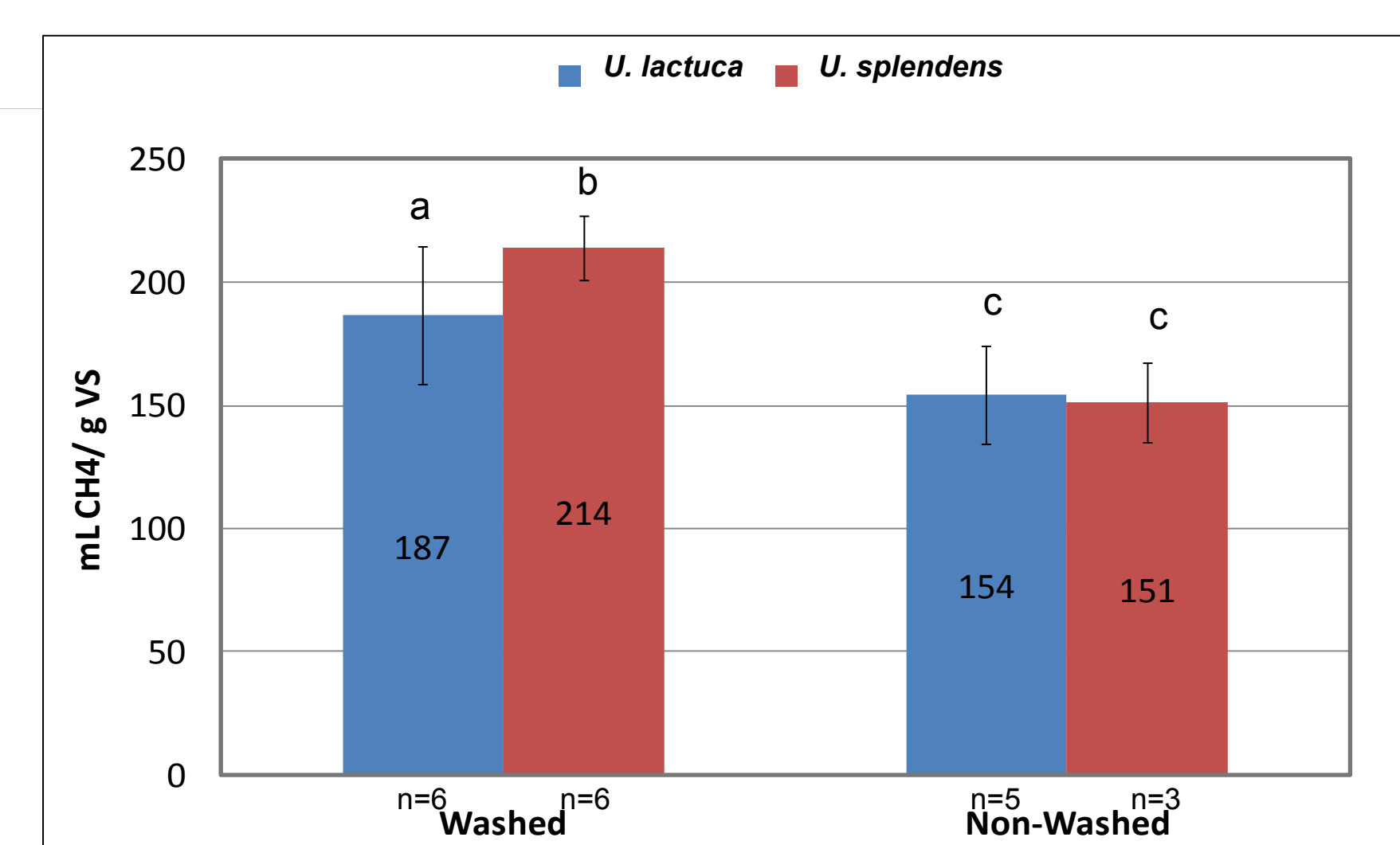


Figure 3: Average methane production of *U. lactuca* and *U. splendens* digested under batch thermophilic conditions. Fresh refers to washed and salt to non-washed samples prior to incubation. Different letters represent results of significant difference ($p < 0.05$)

Materials and methods

Natural populations of *Ulva lactuca* and *Ulvaria splendens* were collected at Danish and Greenlandic shores, respectively, and cultivated in 300 mL aerated seawater enriched with with NO_3^- (F/2), NH_4^+ (standard algal medium) and diluted (1:200) digested pig manure (mainly NH_4^+) as nitrogen source corresponding to 12.35 mg N/L . Light was provided 24 hours daily with intensity of $48 \mu\text{mol photons/s/m}^2$ temperature of 15°C , salinity 13 ppt (*U. lactuca*) and 35 ppt (*U. splendens*) and experiment duration was 21 d. Another experiment was setup with *U. lactuca* using the same variables but sparging with CO_2 or biogas. CO_2 was added using an electronic valve connected to the gas bubble allowing a puls of 1 min at intervals of 1 hour. Biogas (artificial mixture of 30% CO_2 , 30% nitrogen (N_2), and 40% methane (CH_4)) was added at a rate of 5 mL/min in pulses of 15 min with intervals of 45 min, using a peristaltic pump connected to a bag reservoir. A buffer (1% of K_2HPO_4 , 1M solution) was added to media to prevent pH changes below pH6. Buffer (K_2HPO_4) was added in all treatments except control (- buffer). For experiments of biogas potential 550 mL bottles were used with organic loading of 1, 2, and 4 g VS/L macerated algal biomass (*U. lactuca* and *U. splendens*; washed with fresh water or left with sea water on surface), water and inoculated with digested pig manure (DPM) to volume of 200 mL. The biogas was measured by GC after 34 days.

The algal biorefinery concept

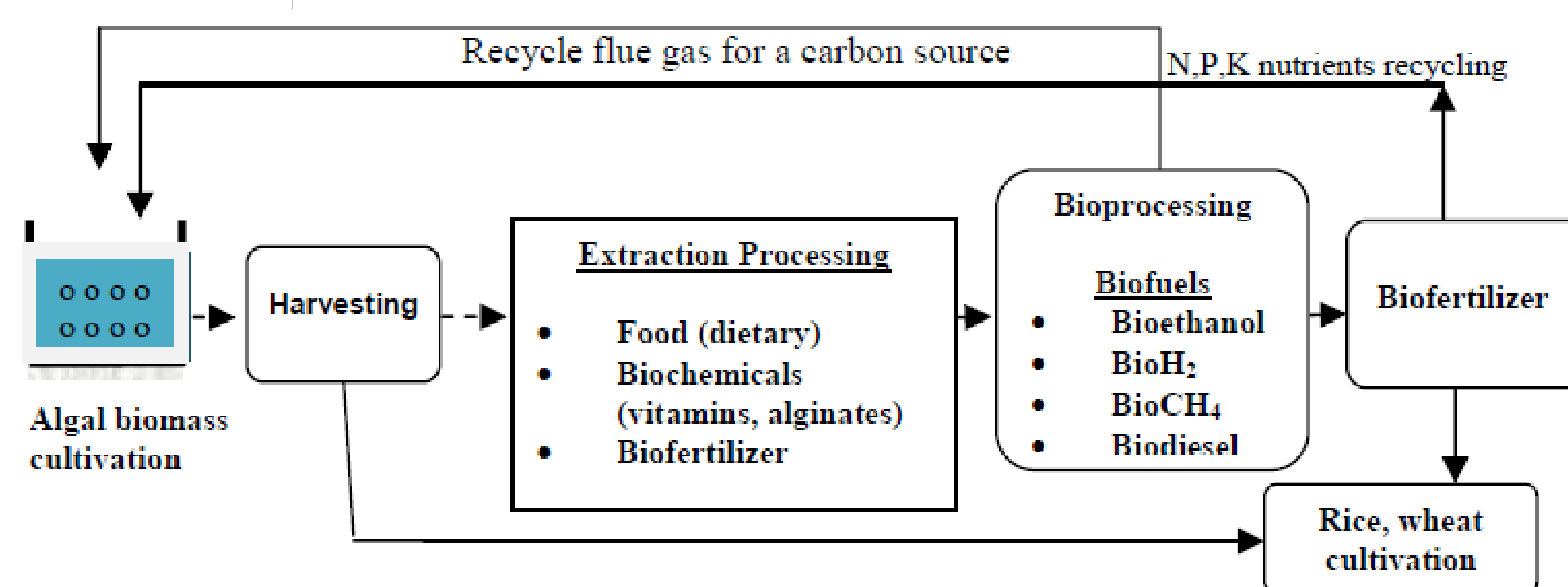


Figure 4: The algal biorefinery concept: Algal biomass cultivated and harvested are utilized for several extracted high value-added products, and biomass waste are converted to biofuels. Waste effluent from biofuel processes, such as digested pig manure are rich in nutrients and may be used for crop or algal cultivation. Flue gas may be recycled as carbon source for algal cultivation. Biogas may be purified when sparged through algal cultivation system.

Conclusions

Ulva lactuca and *Ulvaria splendens* could both be cultivated on diluted DPM as growth medium, and experiments with *U. lactuca* showed that sparged biogas was suitable for cultivation. The biogas potentials are comparable to other well-known feedstocks incl. Manure. Higher biogas potentials were reached in the washed *U. splendens*. This species natural habitat in Greenland and in the experimental setup were remarkably more saline.

These results suggest that CO_2 from biogas and biogas effluents can be used for respectively carbon and nutrients supply for cultivation of algae, which can further be used for possible extraction of high added value products and bioenergy. This will, in addition to algal biomass, result in purification of nutrient rich waste waters, and purification of biogas. Further studies are needed to describe the process of biogas purification.

