Annex 4:

Catalytic Supercritical Water Gasification of *Ulva lactuca*

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Ulva Lactuca Catalytic supercritical water gasification (SCWG) of *Ulva lactuca* for biomethane production – Preliminary tests and results

Experimental procedure

Water and biomass were mixed to yield the desired feed concentration (2.6 and 4.5 wt.%, respectively). The amount of catalyst corresponding to the desired ratio of catalyst to biomass was then added, and the mixture was transferred into the reactor. The reactor tube (see figure 1) was closed tightly with the help of a torque wrench and connected to the capillary tube. Air was removed by evacuating the apparatus with a vacuum pump and the reactor was flushed twice with argon before each experiment. Before starting the gasification experiments, the reactor was pressurized with 2.0–4.2 MPa of argon to avoid water evaporation and drying out of the biomass slurry during heat-up. Argon also served as a leak test. The reaction was initiated by the immersion of the reactor assembly into a preheated fluidized sand bath (Techne SBL-2D). The desired reaction temperature T_{end} was reached in less than 10 min after immersion. To stop the reaction after a predetermined time, the reactor was lifted out of the fluidized sand bath and quenched in a cold water bath. The pressure inside the reactor and the temperatures were measured and recorded at intervals of 1 s using a LabView™-based data acquisition system. At the end of the experiment, the gas phase was taken from the reactor with a gas sampling bag (volume 1 L, SKC) for further off-line gas chromatograh analysis (Agilent 6890). The liquid/solide phase was removed from the reactor, extracted with water, hexane and methanol and finally filtrated.

Figure 1: High-pressure 316 stainless steel reactor with total internal volume of 54 ml.

Result and discussion

The gasification of *Ulva Lactuca* was performed at supercritical water conditions (400 °C, ~ 30 MPa) for 60 min over 2 wt.% Ru/C. Prior experiments in our lab with other algae have shown that such conditions are enough to yield full conversion of the organic fraction to biogas. The results of the gasification of *Ulva Lactuca* are illustrated in figure 2.

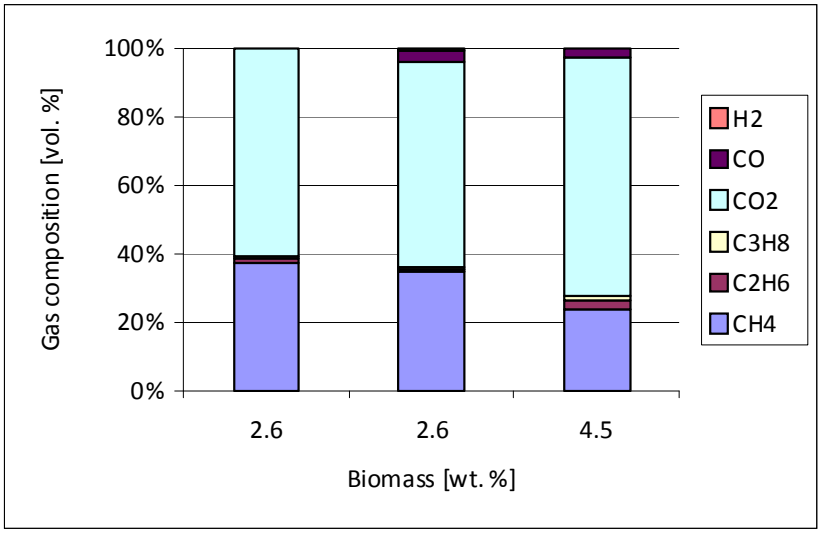
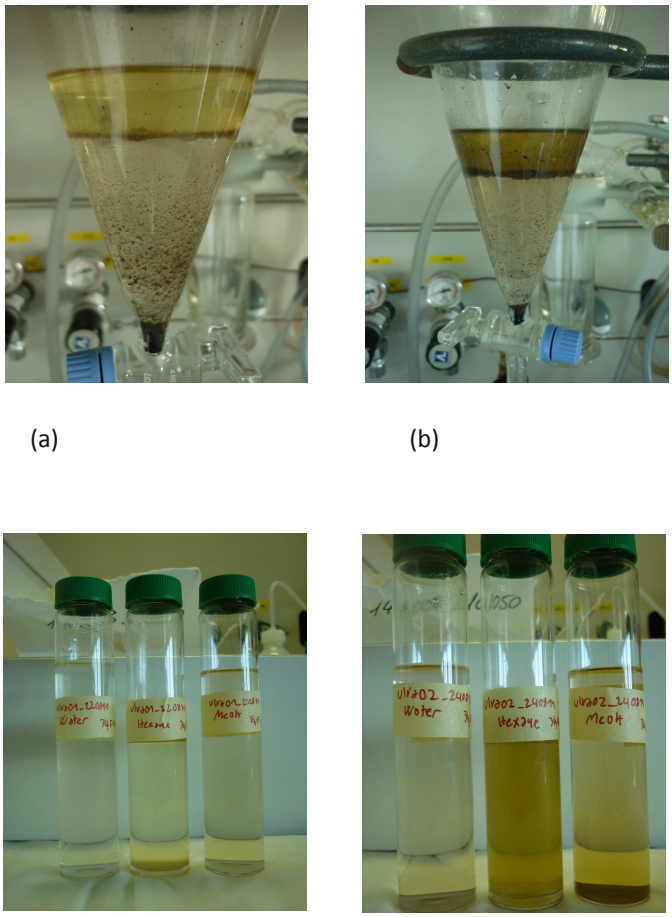


Figure 2: Gas composition obtained after the gasification of *Ulva Lactuca* in SCW conditions (400 °C, ~30 MPa) for 60 min over 2 wt.% Ru/C.

First of all, it could be seen that the macroalgae was successfully gasified (mostly to CH_4 and CO_2). Moreover, low CO and H_2 content are expected if gasification of biomass was efficient. For the samples containing 2.6 wt.% of biomass, the methane volume fraction is close to 40 %, whereas it is only 25 vol.% for the 4.5 wt. % biomass. Such an observation could be easily explained by the catalyst poisoning due to the presence of sulfur. In fact, algae contain sulfur in low amount (about 2 wt.% for *Ulva Lactuca*). So one critical parameter, when gasification experiments are carried out, is to ensure a high ruthenium to sulfur ratio (Ru/S) in order to avoid the poisoning of all the active sites. Usually, an extra of ruthenium is added as a sulfur adsorbent. In our case, the Ru/S ratio was 1 (rather low) for the 2.6 wt.% biomass and only 0.5 for the 4.5 wt.% biomass. By working with a Ru/S ratio > 1, we may expect full conversion of biomass and a methane composition close to the thermodynamically equilibrium. For instance, another gasification experiment with *P. tricornutum* (microalgae) with Ru/S = 1.25 gave a methane percentage volume of 45.

In addition to the gas analysis, the liquid phase analysis provides also informations about the algae gasification efficiency. Figure 3(a) and 3(b) show the aqueous, the organic and the solid phases for the 2.6 wt.% biomass (on the left) and for the 4.5 wt.% biomass (on the right) prior the filtration. Figure 3(c) and 3(d) represent 3(a) and 3(b) after filtration and extraction with methanol.



(a) (b)

(c) (d)

Figure 3: (a) and (b): Aqueous, organic and solid phases after *Ulva Lactuca* gasification in SCW. Left picture corresponds to the 2.6 wt. % biomass and right picture to the 4.5 wt. % biomass. (c) and (d) refer to (a) and (b) after filtration and extraction with methanol. The upper layer in (a) and (b) is hexane, whereas below is the aqueous phase.

Visually, it's already possible to confirm that the gasification with the lower biomass content was better than that with the higher biomass content. The reason for that is, that the clearer aqueous and organic phase obtained for the 2.6 wt.%., which means that both phases contained lower amount of unreacted organic carbon. Hence the carbon conversion from algae to biogas seems to be less complete for 4.5 wt.% biomass comparing to 2.6 wt.% biomass experiment. To confirm quantitatively this assumption further TOC/TIC analysis should be carried out. It's also worth to know that if the carbon conversion had been complete, both aqueous and organic phase would have been transparent which is not the case for both samples.

Conclusions

These preliminary batch experiments gave an inidication that the catalytic supercritical water gasification of *Ulva lactuca* is feasible and a methane rich gas can be obtained. The gasification behavior of the macroalgae is similar to the ones observed with other algal biomass in preliminary batch tests. However, only in a continuously operated plant such as “PSI’s hydrothermal process” with integrated salt separator (in order to remove the catalyst poison sulphur) it may be possible to convert *Ulva lactuca* fully to biomethane without the presence of unreacted carbon in the aqueous phase.