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Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling

Mariluz Bagnoud-Velásquez[a,b,*,1], Martin Brandenberger[b,1], Frédéric Vogel[b,c], Christian Ludwig[a,b]

[a] École Polytechnique Fédérale de Lausanne (EPFL), School of Architecture, Civil and Environmental Engineering (ENAC-IIE), 1015 Lausanne, Switzerland
[b] Paul Scherrer Institute (PSI), General Energy Research Department (ENE-LBK), CH-5232 Villigen PSI, Switzerland
[c] University of Applied Sciences and Arts Northwestern Switzerland (FHNW), Klosterzelgstrasse 2, 5210 Windisch, Switzerland

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ABSTRACT

A novel process named SunCHem has been proposed to produce methane via catalytic hydrothermal gasification of microalgae [1–3]. The process is innovative because it is designed as a closed-cycle system with respect to water, nutrients and some of the CO_2, which are recycled and reused for the growth of microalgae. However, this recycled hydrothermal input is a matter of concern because upon continuous operation, it may become enriched in potential toxicants for algae. This study concerns the investigation of (1) the continuous catalytic hydrothermal gasification of the microalgae *Phaeodactylum tricornutum*, and (2) the influence of aluminum on microalgae growth, as traces of this metal are expected in the hydrothermal effluent. Experiments with the algae *P. tricornutum*, demonstrated the technical feasibility of pumping algae slurry (6.5 wt.%) through the continuous pilot plant with simultaneous gasification for several hours. The carbon gasification efficiency, C_{Gas}/C_{Feed}, was ca. 31% at steady state. The catalyst was rapidly deactivated during the continuous gasification experiment, due to sulfur poisoning and coking. Concerning the study on the effect of soluble Al on freshwater microalgae, it was demonstrated that at alkaline conditions, the Al hydroxides had a negative effect on algae growth even at concentrations as low as 0.025 mg L^{-1}.

1. Introduction

To meet future energy demands is a pressing issue for the world community and most probably one of the most challenging ones in the near future. The choice of the energy conversion technology will have a significant impact on our natural resources, our lifestyle and on future generations. Future energy technology should thus satisfy several points in order to minimize impact on the environment and society [4]:

- The fuel resource needs to be renewable.
- The fuel produced should be free of toxic and potentially environmental harmful materials.
- Material cycles and flows should be closed to increase resource efficiency.
- Fuel production should be scalable.
- The fuel should be distributable via existing infrastructure.
- The fuel production should be technically and economically feasible.

Liquid or gaseous fuels made from biomass were put forward in recent years to satisfy the above mentioned sustainability criteria. Waste biomass or energy crops are a renewable source of fuel production because biomass is produced through photosynthesis and requires CO_2 for growth. A total amount of 49 EJ was provided from biomass in 2007, thus contributing to almost 10% of the total global primary energy demand (503 EJ) [5]. Energy crops are estimated to have the potential to cover between 200 and 600 EJ y^{-1} and residual biomass between 62 and 325 EJ y^{-1} of the global primary energy supply in 2050 [5,6].

However, biofuels do not necessarily mean environmental friendly fuels. Biomass production, if not obtained from residues, requires arable land, fertilizers and water. Agro-biofuels place a heavy burden on the environment by emitting greenhouse gases

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* Corresponding author at: EPFL ENAC IIE GR-LUD, CH B2 397 (CH Building), Station 6, CH-1015 Lausanne, Switzerland. Tel.: +41 0216936284.
E-mail addresses: mariluz.bagnoud@epfl.ch (M. Bagnoud-Velásquez), martin.brandenberger@gmail.com (M. Brandenberger), frederic.vogel@psi.ch (F. Vogel), christian.ludwig@psi.ch (C. Ludwig).

[1] These authors equally contributed to this work.

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like NO_x to the atmosphere, soil degradation, eutrophication of water sources and land change [7–9]. Furthermore, if appropriate policies are not implemented prior to large scale biofuel production, rural populations in developing countries may be affected seriously by adverse impacts on food production and food prices as well as uneven distribution of benefits and harmful consequences on the quality of life [10].

Nevertheless, biomass conversion technologies of the 2nd and 3rd generation are expected to convert large quantities of biomass with high-energy yield into biofuels, but presently are mostly at the demonstration scale and still need significant development with respect to logistics and economics [11].

In this article, the production of synthetic natural gas (SNG), a methane rich gas, from algal biomass through catalytic hydrothermal gasification is presented based on PSI's catalytic hydrothermal process with a focus on how catalytic hydrothermal gasification may contribute to sustainable energy carrier production from biomass in the future. Our first experimental results on the continuous catalytic hydrothermal gasification of algal biomass presented here illustrate well the difficulties faced in converting algal biomass into synthetic natural gas (SNG). The process and its features have been described in earlier publications [1–3]. Noteworthy that published results with respect to the supercritical water gasification of microalgae were mostly obtained in unstirred batch experiments [3,12–14] and only one further article has been published recently at the scale of a continuous laboratory plant but without further characterization of the spent catalyst [15].

Efforts are also concentrated on the process optimization to achieve an efficient recycling of the nutrient solutions recovered from the hydrothermal system. This includes the determination of the tolerance of microalgae cultures to potentially toxic trace metals in the effluent due to corrosion under the harsh hydrothermal conditions.

1.1. Nutrient recovery and the influence of aluminum on microalgae

The recycled input from the hydrothermal process is a matter of concern because trace contaminants might be present due to reactor wall corrosion and catalyst leaching. Our first results demonstrated the importance of monitoring the metal concentration in the recycled hydrothermal effluent used for the growth of microalgae [3]. Too high levels of potentially harmful compounds could negatively affect the growth of microalgae. Aluminum is one of metals not studied yet and expected in the hydrothermal effluent as the salt separator is made of Ti–6Al–4V alloy material. The solubility of Al at supercritical conditions was already addressed in prior studies. Schacht et al. [16] showed that reactor walls containing Al will undergo supercritical corrosion when their feed is alkaline. The weight losses observed were explained by oxidation to $Al(OH)_3$ soluble species. The Ti alloy used in the salt separator unit has been for now the most suitable and resistant material for supercritical water conditions.

Despite the fact that aluminum is the third most abundant crustal element, no biological role is known [17]. Inorganic aluminum exists as monomeric species (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2{}^+$, $Al(OH)_3{}^\circ$ and $Al(OH)_4{}^-$), amorphous $Al(OH)_3$ and as polynuclear species. As solubility of Al is dependent on pH and the neutral pH responsible for insoluble forms, aluminum is less bioavailable to aquatic organisms. However, Al has the ability to form complexes relatively inert and strong such as the dinuclear $Al_2(OH)_2{}^{4+}$ and in particular the polynuclear $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ that can potentially interfere with the cellular metabolism [18,19]. Important chemical complexing agents for Al are fluoride, silicon, phosphate and organic compounds, helping to decrease its toxicity but, in the case of aquatic biota, the consumption of essential nutrients is an issue (e.g. Si and P). P becomes unavailable for enzymatic transport when complexed with Al in particular at circum-neutral pH [20]. Aluminum likely reduces the intracellular acid phosphatase activity. ATP metabolism is also affected by complexation with Al as being unavailable in this form [21].

Organic compounds released by algae solubilize Al from minerals, then aluminum binds to dissolved organic matter (DOM), reduces the amount of inorganic Al available to interact at biological membranes [17]. However, organic acids in the cell membrane could mobilize Al from the Al-hydroxo complexes and enhance the intracellular uptake.

The effects of Al on freshwater microalgae have been studied extensively, though they concentrated on effects at low pH. It appears that growth rates are more inhibited by Al than physiological processes (e.g. photosynthesis) [17]. pH is the dominant controlling factor in Al toxicity to microalgae, other factors include cation competition (e.g. Ca) and complex formation (with DOM and P). Al hydroxides were rarely considered in toxicity studies because of the assumption that only the Al^{3+} has the potential to be toxic to algae. Our motivation in this study is to keep an alkaline pH for two main reasons: (1) The hydrothermal effluent is rather alkaline, and (2) the possibility to increase the efficiency of CO_2 transfers in the microalgae culture when operating the system at alkaline pH [22].

2. Materials and methods

2.1. Catalytic supercritical water gasification

A laboratory plant for the continuous hydrothermal gasification of wet biomass described by Waldner [23] and Schubert et al. [24] was used for the glycerol/microalgae gasification experiment. The laboratory plant consists of seven sections: a feeding section, pre-heating, salt separator, catalytic reactor, cooling, pressure control and a gas–liquid phase separation. The temperature setpoints for the preheater, salt separator and catalytic reactor were 360 °C, 470 °C and 420 °C respectively. The plant pressure was 323 ± 6 bars. The catalytic reactor was filled with 118 g dry weight (DW) of 2 wt.% Ru/C microporous catalyst from BASF.

A 5 wt.% glycerol–water mixture was pumped with a weight hour space velocity (WHSV) = $0.34\ g_{Gly}\ g_{Cat}{}^{-1}\ h^{-1}$ through the continuous laboratory plant during the first 110 min, followed by a 6.5 wt.% *Phaeodactylum tricornutum*[2]–water mixture (WHSV = $0.42\ g_{Algae}\ g_{Cat}{}^{-1}\ h^{-1}$) for the remaining experimental time. The measured values and an overview of the performed experiments are given in Table 1.

The gas samples were analyzed on-line with a gas chromatograph (Agilent Technologies 6890N) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Total organic carbon was determined using a vario TOC Cube from Elementar. The specific surface area (BET) and active metal surface area (ASA) measurements of the fresh and spent catalyst samples were performed with a Quantachrome Autosorb AS1. H_2 chemisorption was used to determine the ASA after the method developed by Schubert [24]. Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) was used for elemental mapping. The measurements were performed on a Zeiss Ultra 55 microscope. No sputtering was applied to the samples. All measurements were carried out at an accelerating voltage of 30 kV. Transmission emission microscopy (TEM) samples were prepared in two ways. Fresh catalyst samples were embedded in Epotek® 523 resin, polished by ion milling (tripod method) on a Teflon support and embedded in a second resin (Epon® 812). Finally, 60–80 nm

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[2] *P. tricornutum* was obtained from a commercial microalgae producer (Subitec, Germany) as a concentrated algae paste.