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PHOSPHORUS RECOVERY IN ALGAE-BASED BIOFUELS

Report from an f3 project

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PREFACE

This report is the result of a collaborative project within the Swedish Knowledge Centre for Renewable Transportation Fuels (f3). f3 is a networking organization, which focuses on development of environmentally, economically and socially sustainable renewable fuels, and

- Provides a broad, scientifically based and trustworthy source of knowledge for industry, governments and public authorities,
- Carries through system oriented research related to the entire renewable fuels value chain,
- Acts as national platform stimulating interaction nationally and internationally.

f3 partners include Sweden's most active universities and research institutes within the field, as well as a broad range of industry companies with high relevance. f3 has no political agenda and does not conduct lobbying activities for specific fuels or systems, nor for the f3 partners' respective areas of interest.

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SUMMARY

Replacing fossil fuels with sustainable fuel from biomass requires both innovative technological solutions and a feedstock that does not put too much strain on food production and land use. Hy-drothermal liquefaction is a technology for producing biofuels that has been gathering increasing interest, and by using seaweed (macroalgae) as a feedstock it is a promising option that fulfils both previously mentioned criteria. Using macroalgae has the added benefit of remediating eutrophic coastal waters since the macroalgae during marine cultivation absorb some of the excess nutrients from the surroundings. The main culprit in eutrophication is phosphorus, which is primarily used in fertilizers and ends up in the environment from agricultural runoff. After the hydrothermal liquefaction of the macroalgae, the phosphorus can be recovered and used to produce struvite, a natural fertilizer that can replace the conventional mineral fertilizer. The purpose of this study was to identify profitable and environmentally friendly technological solutions connecting phosphorous recovery with macroalgae processed with hydrothermal liquefaction (HTL) and at the same time diversify the products outcome of biofuel production.

The project consisted of a comprehensive analysis of available P recovery technologies through a literature review and citation network analysis as well as modelling of one P recovery technology. Three different options of the chosen P recovery were assessed where the economic performance was evaluated by comparing the operating cost for the different options and the environmental impact was evaluated by comparing cumulative energy demand (CED), global warming potential (GWP) and eco-indicator99 (EI99).

"Option 1" consists of HTL, catalytic hydrothermal gasification (CHG) of HTL aqueous phase, biocrude upgrading through hydrotreatment, incineration of HTL solid phase followed by acidic leaching of the ashes and precipitation of phosphorus in form of struvite from the mixture of CHG aqueous phase and the ash leachate. The gas produced by CHG and off-gas from the biocrude upgrading was used to produce hydrogen through steam reforming and water-gas shift reaction, which was then used for the biocrude upgrading itself. In Option 2, leaching is not performed, and incineration ashes are instead disposed of, the landfilling of the ashes being outside system boundaries. In Option 3 neither leaching nor CHG is performed, ash is disposed of and HTL aqueous phase is directly fed to the precipitation step.

The costs of all the options are highly sensitive to the price of dried algae, which accounts for nearly 60 % of the total operating costs. Without considering capital costs, option 2 seems the best scenario by enjoying highest net revenue at \$21.17 based on 1 ton of dried algae, closely followed by option 1. In option 3 the residual organic carbon in the wastewater is significantly higher than in option 1 and 2, due to the exclusion of CHG. This causes the cost and environmental impact of the wastewater treatment (WWT) to increase, leading to a net revenue of less than \$13.59 for the same amount of alga. Apart from reducing the need for WWT, CHG also produces a methane rich gas that can be used to produce hydrogen necessary for increasing the quality of the biofuel, resulting in added benefits for the process.

It is important to note that the environmental assessment does not account for the CO_2 absorbed during the cultivation of the algae, nor the emissions from the end use of the products, but only considers and compares the production of fuel and fertilizer with the production of conventional products. The combustion of a conventional petroleum based fuel would have a significantly higher impact than that of a renewable fuel. Wastewater treatment and methane, used both for heating and as a raw material in hydrogen production, are the two largest contributors to the CED and GWP of the process. All options have a CED lower than what conventional production of equivalent products would have, around 34 MJeq/kg product compared to 48.8 MJ-eq/kg product. Meanwhile none of the options manage to obtain a reduction in GWP; in fact, even the lowest GWP is six times as high as that of conventional production which is 0.29 kg CO2-eq/kg product. The largest drawback of CHG becomes evident when looking at the EI99; only option 3, which excludes CHG, has a lower impact than conventional production, 0.10 points compared to 0.18. The catalyst used in the CHG, ruthenium, comprises around 70 % of the indicator value for option 1 and 2, both at 0.34.

Finally, more than 90 % of the revenues come from the fuel, which means that the struvite production has a marginal impact on the net revenue and it might be interesting to consider recovering P in the form of a different product with a higher value. Macroalgae based biofuel production can help towards becoming independent on fossil fuels and establish energy security, meanwhile, some socio-economic factors outside of the technological scope shall be also paid attention to, such as negative public perception and conflicts with shipping lanes and anchorage space caused by algae cultivation.

SAMMANFATTNING

Att byta ut fossila bränslen mot hållbara bränslen från biomassa kräver både innovativa teknologiska lösningar samt ett råmaterial som inte lägger för stor belastning på matproduktion och landanvändning. Hydrotermisk förvätskning (hydrothermal liquefaction, HTL) är en teknik för att producera biobränslen som har genererat ett ökat intresse, och genom att använda sjögräs (makroalger) som råvara är det ett lovande alternativ som uppfyller båda de tidigare nämnda kriterierna. Användandet av makroalger medför ytterligare en fördel genom att avhjälpa övergödningen av kustvatten, eftersom makroalger vid marin odling tar upp överflödiga näringsämnen från omgivningen. Den huvudsakliga orsaken till övergödning är fosfor, vars främsta användningsområde är i gödningsmedel, och tillslut hamnar i omgivningen genom avrinning från jordbruk. Efter den hydrotermiska förvätskningen av makroalgerna kan fosforn återvinnas och användas till att producera struvit, ett naturligt gödningsmedel som kan ersätta traditionella mineralgödningsmedel. Syftet med den här studien var att identifiera lönsamma och miljövänliga tekniska lösningar som sammankopplar fosforåtervinning med makroalger bearbetade med HTL, och samtidigt bredda produktutfallet från biobränsleproduktion.

Projektet bestod av en omfattande analys av tillgängliga fosforåtervinningstekniker genom en litteraturstudie och en analys av referensnätverk såväl som modellering av en fosforåtervinningsteknik. Tre olika alternativ av den valda fosforåtervinningen granskades där den ekonomiska prestandan utvärderades genom att jämföra driftskostnaderna för de olika alternativen och miljöpåverkan utvärderades genom att jämföra kumulativt energibehov (cumulative energy demand, CED), global uppvärmningspotential (global warming potential, GWP) och eco-indicator99 (EI99).

"Alternativ 1" består av HTL, katalytisk hydrotermisk förgasning (catalytic hydrothermal gasification, CHG) av vattenfasen från HTL, uppbearbetning av biooljan genom hydrobehandling, förbränning av den fasta fasen från HTL följt av lakning av askan med syra och därefter utfällning av fosfor i form av struvit från en blandning av vattenfasen från CHG samt lakvattnet från asklakningen. Gasen som produceras av CHG samt restgaser från uppbearbetningen av biooljan användes till att producera vätgas genom ångreformering och vatten-gas skift-reaktion, som i sin tur sedan kunde användas i uppbearbetningen av biooljan. I alternativ 2 utförs ingen lakning, utan förbränningsaskan läggs istället på deponi, vilket anses vara utanför systemgränserna. I alternativ 3 utförs varken lakning eller CHG, askan forslas bort och HTL-vattenfasen tillförs direkt till utfällningssteget.

Kostnaderna för alla processalternativ är ytterst känsliga för priset på algerna, vilken utgör nästan 60 % av de totala driftskostnaderna. Utan att ta hänsyn till kapitalkostnad verkar alternativ 2 vara det bästa scenariot med den högsta nettointäkten på \$21.17 per ton torrmassa alger, tätt följt av alternativ 1. I alternativ 3 är återstoden av organiskt kol i avloppsvattnet betydligt högre är i alternativ 1 och 2, på grund av uteslutandet av ett processteg kallat katalytisk hydrotermisk förgasning (catalytic hydrothermal gasification, CHG). Som en följd av detta ökar kostnaderna för och miljöpåverkan av avloppsvattenreningen (WWT), vilket leder till en nettointäkt på \$13.59 för samma mängd alger. Förutom att minska behovet av vattenrening medför CHG också en produktion av en metanrik gas som kan användas till att producera vätgas som behövs för att öka kvaliteten av biobränslet, vilket resulterar i ytterligare en fördel för processen.

Det viktigt att notera att utvärderingen av miljöpåverkan varken inkluderar absorptionen av koldioxid från odlingen av makroalgerna eller utsläppen som genereras av det slutliga användandet av produkterna, utan endast tar hänsyn till och jämför produktionen av bränsle och gödningsmedel med produktionen av konventionella produkter. Förbränningen av ett konventionellt petroleumbaserat bränsle skulle ha betydligt högre påverkan än den från ett förnyelsebart bränsle.

Avloppsvattenreningen och metan som används till både uppvärmning och som råmaterial i vätgastillverkningen är de två största bidragande orsakerna till det totala CED och GWP för processerna. Alla alternativ har ett CED som är lägre än vad konventionell produktion av ekvivalenta produkter skulle ha, runt 34 MJ-ekvivalenter/kg produkt jämfört med 48.8 MJ-ekvivalenter/kg produkt. Samtidigt lyckas inget av alternativen uppnå en minskning av GWP, i själva verket är tillochmed det lägsta värdet av GWP för de tre alternativen sex gånger så hög som för konventionell produktion som är 0.29 kg CO2-ekvivalenter/kg produkt. Den största nackdelen med CHG blir uppenbar vid närmare granskning av EI99; endast alternativ 3, som exkluderar CHG, har en lägre påverkan än konventionell produktion, 0.10 jämfört med 0.18. Katalysatorn som används i CHG, rutenium, står för runt 70 % av EI99-värdet för alternativ 1 och 2, båda vid 0.34.

Mer än 90 % av de totala intäkterna kommer från bränslet, vilket betyder att struvitproduktionen endast har en marginell påverkan på nettointäkterna och det kan därför vara intressant att överväga att återvinna fosforn i form av en annan produkt med ett högre ekonomiskt värde. Biobränsleproduktion baserad på makroalger kan bidra till att bli oberoende av fossila bränslen och etablera energisäkerhet. Samtidigt finns det socio-ekonomiska faktorer som inte omfattas av det tekniska perspektivet men som ändå bör beaktas, såsom eventuell negativ allmän uppfattning och konflikter med sjöfartsleder och ankringsutrymmen som orsakas av algodling.

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1 INTRODUCTION

Replacing fossil fuels with sustainable fuels from biomass is a difficult and important challenge that require new and innovative technologies to be solved. One such technology is hydrothermal liquefaction (HTL), a process where the feedstock is treated in an aqueous solution at elevated temperature and pressure to produce biofuel. The feedstock in this process can range from sewage sludge and other wastes to different kinds of biomass, and seaweed (macroalgae) is one possible feedstock that can be used to produce biofuels (Tian et al., 2014). To increase the profitability, reduce the environmental impact and diversify the products outcome of macroalgae based hydrothermal liquefaction, recovery of phosphorus (P) as a fertilizer is considered. The aim of this work is to identify profitable and environmentally friendly technological paths connecting P recovery with macroalgae based HTL.

1.1 BACKGROUND

P is an element that is essential for life and it is produced for industrial use from mined phosphate rock (Desmidt et al., 2014). The largest consumer of P is the agricultural industry where it is primarily used for fertilizer production. The regeneration rate of mineral P is negligible compared with its current and future expected exploitation, moreover phosphorus rich waste streams release in nature causes eutrophication of aquatic environments, motivating the integration of P recovery technologies for a phosphorus closed loop. Furthermore, P is an unevenly distributed resource as more than 70 % of world phosphate rock natural reserves are found in Morocco and Western Sahara (Desmidt et al., 2014), making P an important element also for the strategies of geopolitics to ensure security of supply.

As a result, technologies for recovering and recycling P from various industrial streams is of increasing interest. Marine cultivation of macroalgae helps remediate eutrophic coastal waters by removing excessive nutrients (Andersson, 2016) and can at the same time provide biofuel production with a feedstock that does not compete with food production or land use. If P is recovered from the biofuel production it can be sold as a natural fertilizer and thus reduce the need for mining of phosphate rock. P recovery is both implemented at large scales and well documented for municipal wastewater treatment (WWT) (Egle, 2015). Scientific literature offers a wide range of technologies investigations applied on waste waters treatment plants for several purposes such as struvite scaling prevention or nutrients recovery. On the other hand, the technological maturity of hydrothermal liquefaction, HTL, is not as advanced, and phosphorus recovery from HTL waste streams is a poorly analyzed topic in scientific literature although HTL waste streams could be suitable for the same phosphorus recovery strategies performed in waste waters treatment plants. One of the driving forces of this study was to investigate the possibilities and the challenges of applying the documented technologies of phosphorus recovery to HTL.

2 METHOD

2.1 PROCEDURE

The major procedure followed in the project is shown in Figure 1. The first step was to identify technological pathways that are environmentally friendly and profitable, and connect phosphorus (P) recovery with macroalgae based hydrothermal liquefaction (HTL). This was done by performing an extensive review of literature concerning relevant technologies in various fields of application. In the second step citation network analysis (CNA) of the gathered literature was carried out and thereafter technologies that could potentially be involved were compiled into a comprehensive list. For these technologies a framework of quantitative and qualitative information about process conditions, the significance of said process and material and energy flows was developed. Based on this information framework, processes were combined into a superstructure of options for P-recovery from macroalgae based HTL. From the superstructure, different sub processes were combined into a custom process that was then evaluated based on criteria such as technology maturity and severity of process conditions. If more data was required, additional literature was gathered and the first part of the procedure repeated, otherwise a process layout was created and modelled through energy and material balances, and finally the results were interpreted.



Figure 1. General representation of the procedure followed in the project.

2.2 LITERATURE REVIEW

The fate of P during HTL of macroalgae was initially unknown and thus the main effort of the literature study was identifying technologies for recovery of P from either of the three possible phases P could be distributed in; the biocrude, the aqueous phase and the solid phase. As various technologies were found some important aspects of the processes were emphasized, such as typical process conditions, P recovery efficiency or type and purity of the recovered P-containing product. Another way of categorizing the P recovery technologies is by what principle the P recovery is based on, e.g. mechanical, chemical, thermal or biological. Since these processes all concern P recovery from a wide range of feedstocks they often contain stages for e.g. increasing the P concentration and/or removing heavy metals before obtaining the final product. Figure 2 shows an overview of the different process steps included in the studied P recovery technologies.



[a] precipiation of dissolved interfering ions (primarily iron) can be acheived by pH increase using NaOH and Na2S or by complexation with citric acid [b] microbially induced precipitation, requires presence of NH4 and Mg for struvite biomineralisation or Fe and Si for marine biomineralisation

[c] Unsatisfactory results

[d] Exothermic process (Heat can be recovered)

[e] Produce also ashes rich in P which can be further released

[f] Heavy Metal Precipitation occurs during Intermediate Stages Through pH adjustments

Figure 2. Overview of process steps comprising the studied P recovery technologies.

The distinguishing factor between recovery and removal of P could be inferred from the form of final P product in a process; P recovery results in a product which can have further use, such as a fertilizer, whereas P removal results in a product with very low to no worth. Since the major use of P is in fertilizers, processes that result in a bioavailable product with a fertilizer potential were favoured over other processes. Heavy metals content, presence of pathogens and phosphorus concentration are other factors that affect the choice of process and product. One form of P that has particularly attracted attention is magnesium ammonium phosphate, also known as struvite. Struvite is a solid fertilizer that can be recovered from an aqueous phase through crystallization and precipitation. It is considered a slow releasing fertilizer (Desmidt et.al., 2014), meaning that its nutrient potential is not easily washed away with the runoff water, and it is also a valid nitrogen and magnesium supplement. Struvite production does not require too expensive or severe process conditions, it is precipitated through pH adjustments to around or slightly above a pH of 8, and addition of magnesium and/or ammonium if necessary (Liu et.al., 2012).

To choose a suitable method for producing struvite it was important to know the P distribution in the output streams from the HTL. This was a contributing factor to the literature review being expanded to include research of HTL. The additional literature showed that HTL aqueous phase can contain up to around 50 % of the original feedstock phosphorus (Valdez et.al., 2012) whereas the solid phase in some cases contain as much as 90 % of the total P (Jones et al., 2014). The biocrude usually has a low P content, but up to 26 % of the P has been observed in the biocrude from HTL (Valdez et.al., 2012). The distribution of P depends on several factors such as process temperature, residence time, solid or dry mass content in the HTL process and obviously on the feedstock P-content. P recovery from the biocrude was dismissed in favour of recovery from both the aqueous and solid phase.

2.3 CITATION NETWORK ANALYSIS

Through citation network analysis (CNA) of the reviewed literature information sources were prioritized. The CNA was done by first creating a citation matrix where any citation between two of the gathered sources was recorded, classifying the literature sources based on their topic and the information presented in them, and then creating a plot for visualization of the data. Examples of how to interpret the CNA is given in Figure 3a and 3b. Each circle represents a literature source, and its size is proportional to the number of times it has been cited (i.e. an indicator of its relevance for the analysis). The technological maturity of each process was assessed by considering the temporal distribution of the sources, whereas possible technological affinities within the process superstructure were indicated by studies shared by more than one classification and the citations across sources of different fields. Direct use of the HTL aqueous phase as a nutrients supplement for microalgae cultivation medium was initially considered as a valid option and successively discarded for its high costs and its poor affinity with P-recovery shown in

Figure 3a. Figure 3b shows there is a high affinity between HTL and catalytic hydrothermal gasification (CHG), which supported the decision of including CHG as a process step in the treatment of the aqueous phase. It is also apparent that the literature on the two processes is quite recent, implying that it is in fact state-of-the-art technologies.



Figure 3a. Citation network analysis of algae cultivation (top), P recovery (middle) and a combination of the two (bottom). Gray lines represent citations within the same field, whereas green lines represent inter-citations between the two fields.



Figure 3b. Citation network analysis of HTL (top), CHG (middle) and a combination of the two (bottom). Gray lines represent citations within the same field, whereas green lines represent inter-citations between the two fields.

2.4 PROCESS SUPERSTRUCTURE

Apart from processes directly related to P recovery, the literature review also identified other technologies involving the HTL product streams. Concerning the HTL aqueous phase, one such approach consists of utilizing the residual carbon content of the stream. The two main strategies of the HTL aqueous phase "carbon approach" are:

- Recirculating the aqueous phase into the HTL process to enhance its biocrude yield.
- Convert the organic carbon of the HTL aqueous phase into valuable gas (such as methane) through catalytic hydrothermal gasification (CHG).

This latter process is particularly appealing because of its synergies with the upgrading biocrude treatments; methane produced with CHG can be used for hydrogen production through steam reforming, and hydrogen is required for the upgrading treatments of the biocrude to enhance its properties as a combustion fuel. The carbon and the P recovery approaches are not mutually exclusive, it is indeed possible to for example use CHG aqueous phase for phosphorus precipitation or as supplement for microalgae growth medium, and vice versa, is it possible to use the precipitation effluent for CHG.

It is now clear that there is a large variety of processes and technologies that can be applied to HTL product streams. Figure 4 was obtained by gathering all these processes into a superstructure.



Figure 4. Superstructure of processes and technologies suitable for application on HTL streams.

In Figure 4, rectangles represent materials whereas ovals represent processes. The colours of the materials indicate feedstocks (green), final products (red) or non-final products (yellow). The arrows represent the possible process paths and the red arrows represent the path that was evaluated in this project. The final process option was decided on with the help of the CNA and by assessing the superstructure according to severity of process conditions, technology maturity, potential revenues, energy integration and other synergies.

This process system was labelled "Option 1" and consists of HTL, CHG of HTL aqueous phase, biocrude upgrading through hydrotreatment, incineration of HTL solid phase followed by acidic leaching of the ashes and precipitation of phosphorus in form of struvite from the mixture of CHG aqueous phase and the ash leachate. The gas produced by CHG and off-gas from the biocrude upgrading was used to produce hydrogen through steam reforming and water-gas shift reaction, which was then used for the biocrude upgrading itself. Besides Option 1 two other process options were modelled:

- Option 2, where leaching is not performed, and incineration ashes are instead disposed of. (The landfilling of the ashes is outside system boundaries.)
- Option 3, where neither leaching nor CHG is performed, ash is disposed of and HTL aqueous phase is directly fed to the precipitation step.

As mentioned above, a way of using the aqueous phase (with or without previous CHG) that was discarded yet is worth mentioning, is as a nutrient supplement to microalgae growth medium. Low temperature excess heat is suitable for integration in microalgae cultivation systems and one the positive aspect of this method is that excess carbon dioxide could be supplied to the cultivation systems and consumed by the microalgae. Additionally, harvested microalgae could be reused in HTL towards a closed nutrient loop (Garcia Alba et al., 2013). Nevertheless, there are two major reasons for why this option was discarded; microalgae growth is highly affected by solar radiation and weather conditions (which is not really promising from a Swedish perspective), and even the most productive cultivation systems have a relatively low yield per area ratio.

2.5 MODELLING

The HTL is the core process of the superstructure, and its performances is highly affected by the feedstock composition and by the process conditions (López Barreiro et al., 2013). Therefore, the modelling of HTL of a specific macroalgae strain was difficult to simplify with average literature data from experiments using different feedstocks or limited process settings. To overcome this obstacle a kinetic model to predict the HTL yields was developed. This model was based on a reaction framework proposed by Valdez et al. (2014), experimental data was collected from several sources and the reaction kinetic constants were calculated to minimize the error with the experimental results. Since the model was not able to provide reliable results for HTL residence times shorter than 15 minutes, two different sets of kinetic constants were calculated; for residence times shorter, and longer than 15 minutes.

The results obtained using the two different sets of kinetic constants were then merged according to Eq. (A)

$$Y = Y_{k,\theta < 15} f(\theta, T) + Y_{k,\theta > 15} (1 - f(\theta, T))$$
 Eq. (A)

Where Y_k is the result calculated from the respective set of kinetic constants, and f is a function of θ and T (HTL residence time in minutes and temperature expressed °C respectively) bounded between 0 and 1. f is used for weighting the results according to the pertinent HTL setting and its mathematical expression is given in Eq.(B).

$$f(T,\theta) = \left[1 - \frac{1}{1 + \left(\frac{T}{400}\right)^{0,6}}\right] \cdot \frac{1}{1 + \left(\frac{\theta}{90}\right)^{0,6}}$$
Eq. (B)

Apart from the HTL, the other processes were modelled with material and energy balances using typical or average performances and process data according to the literature. Energy consumption and potential energy recovery strategies were included in the model.

Heat integration was studied through pinch analysis. Each stream was characterized with its specific heat, inlet and outlet temperatures. Specific heat of aqueous phases was assumed to be equal to the specific heat of water, whereas the specific heats of gases were calculated with the help of the ASPEN Plus software. Specific heat of biomass was retrieved from literature, while specific heat of biocrude and upgraded oil were calculated again with Aspen Plus by assuming their compositions as a mix of hydrocarbons of the same length of the typical hydrocarbons composing biocrude and upgraded oil according to the literature, and elemental composition (C/H/O) so to match the model atom balance as close as possible.

The energy consumption of compressors was also calculated through ASPEN Plus, while the energy consumption of pumps, W, was estimated with the expression given in Eq. (C).

$$W = \frac{m\Delta p}{\rho \eta_{pump}}$$
 Eq. (C)

Where m is the mass in kg of the fluid being pumped, Δp is the pressure difference in Pa, ρ is the density of the fluid in kg/m³, and η_{pump} is the electrical efficiency of the pump.

Energy required to sustain each process (both heat supplied to endothermic processes and heat removed from exothermic processes) was calculated either according to exact heats of reaction or, when the reactions were undefined, through energy balances between inlet and outlet streams with data from ASPEN Plus, assuming isothermal and isobaric conditions and neglecting external heat losses. Given the high temperature required in some process (as high as 800 °C) a gas furnace (using natural gas) was considered as hot utility.

All process parameters are given in Table A1.

2.6 ECONOMIC AND ENVIRONMENTAL ASSESSMENT

The economic profitability of running the process at industrial scale, based on three options mentioned in section 2.4, was assessed by considering only the materials and energy operating costs. As for assessing the environmental footprint, three indicators, namely cumulative energy demand (CED), global warming potential (GWP) and eco-indicator 99 (EI99) were analyzed for each option separately. Data on price and environmental impact of most of feedstock, material and utility energy were acquired from ecoinvent database v3.3, except for catalyst prices which were obtained from online suppliers, and for the environmental information of the CHG ruthenium catalyst which was found in Nuss et al. (2014). Cost and environmental impact of wastewater treatment are calculated according to Rerat et al. (2013). The background data are listed in Table A2.

3 MODELLING RESULTS AND DISCUSSION

3.1 MODELLING RESULTS

The results of the HTL model for the macroalgae Ulva Lactuca assumed to have the biochemical composition of Ulva sp. given by Neveux et al. (2013) are shown in Figure 5. These results were validated by comparison with the experimental HTL results provided by Raikova et al. (2017).



Figure 5. Predicted HTL yields as a percentage of the original dry, ash free feedstock mass.

The combination of low temperatures and high residence times favours the feedstock matter to be dissolved into the aqueous phase, whereas high temperatures and long residence times together lead to an increase of the gas phase yield. For short residence times, especially at low temperatures, the feedstock matter has not had enough time to be converted and stays in the solid phase, while for medium-high temperatures and residence times above 20 minutes the best crude yield is achieved.

3.2 ECONOMIC EVALUATION

Figure 6 shows the calculated materials and energy operation costs and revenues. Costs are shown as negative values and the revenues of the final products (upgraded oil and struvite) are positive. The costs of all the options are highly sensitive to the price of dried algae, which accounts for nearly 60 % of the total shares. It is also noteworthy that WWT and purchase of methane account for another 30 % of the total costs. The category "Others" include sulfuric acid, process water, so-dium hydroxide, magnesium chloride, catalysts and electricity; this group takes the rest cost.

Option 2 has higher net revenues than option 1 (\$21.17/t dry macroalgae and \$18.88/t dry macroalgae respectively), which means that the ash leaching in option 1 is not worth the additional struvite produced. Nevertheless, this assessment highly depends on the phosphorus content of the ashes and the price of the struvite. Generally, the produced struvite should always pay back its production costs. Option 3 showed a sensibly lower net revenue (approximately 1/3 lower than the other options), mainly because of high wastewater treatment costs. Indeed, excluding the CHG causes the organic carbon to remain unconverted and dissolved into the aqueous phase, which burdens the WWT. On the other hand, option 3 is expected to have a lower investment cost.

The struvite production peaks at 7.2 kg/t dry macroalgae, corresponding to 75.5 % of the P input, which only marginally affects the total profits unless the P market price significantly increases. The international market prices of fuel on the other hand has a more significant impact on the net revenues. Heavy metals contamination of struvite was not considered, but depending on the HM content of the feedstock a removal step could be necessary prior the precipitation by increasing capital investment, operating costs and environmental impact.



Others Methane Wastewater treatment Dried Algae Upgraded oil Struvite

Figure 6. Feedstock and raw material costs, product revenues and net revenues for the three process options.

3.3 ENVIRONMENTAL IMPACT ASSESSMENT

After performing life cycle analysis, results of CED, GWP and EI99 are illustrated in Figure 7, Figure 8 andFigure 9, respectively. It should be mentioned that the positive and negative impacts of the P-recovery options on biodiversity are not considered, while positive eutrophication impacts of the technology are only partially considered as part of the EI99. Each indicator is grouped by five categories, na-mely feedstock plus material, catalysts, electricity, wastewater treatment and methane, and the red reference line stands for the conventional production of 1 kg of products, of which 98 % is petro-leum and 2 % is triple superphosphate. There are two ways of utilizing methane, methane 1 is used for producing heat through combustion (CO₂ emitted from burning methane is considered in LCA) and methane 2 for hydrogen production through steam reforming. Figure 7 shows that the total energy demand required by all three options is stably below 34 MJ-eq/kg product, which is much less than the conventional production (48.8 MJ-eq/kg product), saving between 14.9 and 15.5 MJ equi-valent energy for producing 1 kg of products. Option 3 requires slightly lower energy than option 1 and 2 since the energy for the steps of CHG and leaching is saved. Methane is the biggest contri-butor to the CED for all the options, followed by

wastewater treatment, while the remaining three groups together account for circa 10 % of the total energy demand.

Similar trends as for CED can be seen for the GWP shown in Figure 8, option 3 has slightly lower emission than the other two, and unfortunately none of the options is competitive with the conventional production and exceeds the reference line by nearly 1.5 kg CO2 for producing 1 kg of products. In option 1 and 2, more than half of the total CO2 equivalent comes from burning methane 1 as hot utility, while the second largest share is from the WWT. While under the absence of CHG, WWT of option 3 is the biggest contributor by requiring high energy with high CO₂ emissions. Noticeably, the CO₂ generated during the process accounts for around 10 to 12 % of total shares in each option.

The situation changes when it comes to EI99, as illustrated in Figure 9. The choice of ruthenium catalyst used for CHG step causes option 1 and 2 being above the conventional production level by approximately 0.16 points, while option 3 is 0.08 points lower than the reference line owing to exclusion of the rare metal.



Figure 7. Cumulative energy demand (CED) composition and comparison for the three process options. Ref. line refers to the conventional production of 1 kg of products, of which 98 % is petroleum and 2 % is triple superphosphate.



Figure 8. Global warming potential (GWP) composition and comparison for the three process options <u>without considering the CO₂ absorbed for the algae cultivation</u>. Ref. line refers to the conventional production of 1 kg of products, of which 98 % is petroleum and 2 % is triple superphosphate.



Figure 9. Eco-indicator99 (EI99) composition and comparison for the three process options <u>without</u> <u>considering the CO₂ absorbed for the algae cultivation</u>. Ref. line refers to the conventional production of 1 kg of products, of which 98 % is petroleum and 2 % is triple superphosphate.

3.4 INTEGRATION WITH PETROLEUM REFINERY

The grand composite curve (GCC) of option 1 is shown in Figure 10. As mentioned before, the hot utility is provided by burning methane in a gas furnace. This choice originated from the original heat demand; high pressure steam above 350 °C is not convenient for heating purposes and furthermore, temperatures higher than 800 °C were required to sustain the steam reforming process.



Grand Composite

Figure 10. Grand composite curve of process option 1. The red area indicates heat demand that could be covered by excess heat from a petroleum refinery.

Analyzing the GCC of a petroleum refinery, possibilities of further heat integration were addressed. For example, the heat demand indicated in the red area in Figure 10 could be easily provided by a nearby situated refinery where the heat available at 400 °C is around 1.33 MW, as described by Andersson (2016). This would potentially reduce the heat supplied through the natural gas furnace related to the indicated area, with both economic and environmental benefits.

3.5 SOCIO-ECONOMIC FACTORS

Much like other renewable energies, in addition to techno-economic aspects, there are some socioeconomic factors that could also affect the price setting for P-recovery by algae-based fuel production. Main benefits include reducing reliance on fossil fuels, terrestrial biomass and enhancing energy independence. Meanwhile, factors such as early use of immature technology, general negative public perception and conflicts with shipping lanes and anchorage space caused by algae cultivation, may put the obstacles on the promotion of the industrial process of algae-based fuel. More detailed factors are presented in Table 1, where they are listed on two levels (supply chain level and external stakeholder level) in the aspects of benefits and challenges for the sake of stakeholders.

Stakeholders	Benefits	Challenges				
Bio-refinery plant operators	Reduction of reliance on fossil fuels and territorial biomass.					
Processing companies (Bio-economy)	Extraction of value-added products (i.e., skincare products, antioxidant compounds, polyunsaturated fatty acids). Reduction of phosphate import for fertilizers.					
Technology providers			chain level			
Seaweed farmers	Regular employment. Increase of incomes. Improvements in housing and purchasing assets. Economic independence of women farmers in developing countries.	Seasonal jobs. Variable income being easily affected by the global price.				
Government (policy makers, ad- ministration, regulators)	More revenues. More administration and office jobs. Enhancement of energy security and independence. Alleviation of carbon emissions in the seawater.	Lacking standards and certificates. Requiring implemental regulations, licensing. Requiring funding, incentives and innovation directives for ecological protection, conservation of biodiversity and access of emerging market. Requiring global operation. Monitoring and management in the aspects of algae growing area, algae blooms. Finding solutions towards public resistance to algae harvesting.				
NGOS	Encourage and assist environmental and communication progra- jects and the preservation of environmentally sensitive areas.	ams, expertise transfer among countries, research and monitoring, restoration pro-				
Tourism and recreation operators		Reduction in recreational fishers, amusement experiences of visitors, lodging and restaurants due to algae cultivation. Creating new tourism seasons for alleviating the impact of algae harvesting period.	External stakeholder level			
Universities and other research institutions	Lead research programs for working on the diversifying biofuel Conduct restoration projects and provide educational program	production. s to improve understanding and appreciation of lake/sea ecosystems.				
Local coastal communities	Improvements in the benthic ecosystem. Water purification through nutrient removal. Water de-acidification through carbon absorption. Removal and alleviation of harmful algae deposition. Reverse of rural depopulation in developing countries.					
Fishery farmers	Increase of some fish species.	Some local fish catches may reduce due to harvest of wild seaweed, which is used to be their food resources.				

Table 1. Socio-economic benefits and challenges for different stakeholders of cultivation of macroalgae and its use for biofuel production.

4 CONCLUSION AND FUTURE PROJECTS

A deep literature review and its citation network analysis (CNA) were carried out to investigate the possibility of integrating phosphorus (P) recovery with biofuel production from macroalgae hydrothermal liquefaction (HTL). Many processes and technologies concerning phosphorus recovery from different waste products and streams were studied together with their potential synergies with hydrothermal liquefaction and with other HTL related waste streams treatments. Any process was assessed according to its technological maturity, complexity, material and energy requirements, cost and environmental impacts.

A P recovery superstructure was outlined this way, and a system layout was preferred according to the above-mentioned features and according to internal synergies evaluated with the help of the CNA. Beside macroalgae HTL, the system included catalytic hydrothermal gasification (CHG) of HTL aqueous phase, incineration of HTL solid phase and acidic leaching of incineration residual ashes, phosphorus recovery in form of magnesium ammonium phosphate (struvite) via precipitation of CHG aqueous phase and leachate, recirculation of precipitation effluent of the ash leaching, hydrogen production through steam reforming of CHG and biocrude upgrading gas, biofuel upgrading through hydrodeoxygenation of biocrude. The chosen system was then modelled together with other 2 possible variations.

Results shows that P recovery could be effectively achieved from HTL waste streams treatments, diversifying the HTL product outputs. All the evaluated options resulted to generate a positive material and energy costs and revenues with net balance peaking around 20\$/kg of dry feedstock. Nevertheless, the revenues were highly affected by the price of the feedstock macroalgae (which should be therefore further verified) accounting for more than 60% of the total costs.

The struvite production, peaking at 7.2 kg/t dry macroalgae, has a marginal impact on the profits, but pays back its related operating costs.

The cost of performing the leaching was equal or even higher than the value of the additional struvite produced (even though this assessment strongly depends on the amount of phosphorus in the ashes), whereas not performing the catalytic hydrothermal gasification resulted in a net revenue loss (even if probably counterbalanced by an investment cost reduction) mainly because the total organic carbon of the HTL aqueous phase becomes a cost burden on the waste water treatment of the precipitation effluent.

Besides the phosphorous content and price of HTL feedstock, also the heavy metal content plays a key role in the economic and environmental assessment. To get more reliable results, it will be important to include a capital cost analysis, indeed according to the developed HTL kinetic model results, for the same feedstock flow and type, a shorter HTL residence time would penalize the biocrude production but could substantially reduce the capital investment.

From the LCA results, all the options stand out in the cumulative energy demand indicator by saving 30 % of energy from conventional production, whereas, none of them is competitive in the GWP and EI99 indicators (only option 3 is below the reference line in EI99). One thing that needs to be noted is that environmental impact during algae cultivation is considered within life cycle analysis, however the CO_2 in the atmosphere absorbed by the algae during cultivation is excluded

in the calculation. It means that the combustion of a conventional petroleum based fuel would have a significantly higher impact than that of a renewable fuel when coming to the end use of fuel.

According to the original project proposal, the following guideline targets have been fulfilled:

- A technical system study of how the phosphorus recovery works was performed through the literature review and the P-recovery process modelling.
- A stand-alone plant was compared with a plant integrated with Preemraff Lysekil and possibilities of heat integration have been highlighted.
- A knowledge synthesis on how to set reasonable price on how much phosphorus recovery may cost has been provided by the net revenues balance estimation for three different option layouts.
- The HTL kinetic model could be used to encourage future joint research studies with the University of Bath.
- Finding alternative catalysts.

Macro-algae based biofuel production could help replacing fossil fuels and establishing energy security. More experimental studies from lab to pilot scale are necessary to investigate the HTL optimal reaction conditions, yields and accurate scale-up factors using different macroalgae species. This will provide additional data to further screen the downstream superstructure options for P-recovery technologies. Besides this, socio-economic factors outside of the technological scope should also be paid attention to, such as negative public perception and conflicts with shipping lanes and anchorage space caused by algae cultivation. This will require more detailed social network analysis s including multiple actors and game theoretic approaches to enhance the multi criteria analysis of this study. This step requires a bigger consortium to work closely together in a bigger project in terms of duration, resources and support from industrial partners.

REFERENCES

[1] Tian, C., Li, B., Liu, Z., Zhang, Y., & Lu, H. (2014). Hydrothermal liquefaction for algal biorefinery: A critical review. *Renewable And Sustainable Energy Reviews*, *38*, 933-950. <u>http://dx.doi.org/10.1016/j.rser.2014.07.030</u>

[2] Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., & Verstraete, W.
 (2014). Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. *Critical Reviews In Environmental Science And Technology*, 45(4), 336-384.
 http://dx.doi.org/10.1080/10643389.2013.866531

[3] Andersson, V. (2016), Excess Heat Utilisation in Oil Refineries - CCS and Algae-Based Biofuels, Doctoral thesis, Chalmers University of Technology, Available at: <u>http://publications.lib.chalmers.se/publication/241955-excess-heat-utilisation-in-oil-refineries-ccs-</u> <u>and-algae-based-biofuels</u>

[4] Egle, L., Rechberger, H., & Zessner, M. (2015). Overview and description of technologies for recovering phosphorus from municipal wastewater. *Resources, Conservation and Recycling, 105,* 325-346. <u>http://dx.doi.org/10.1016/j.resconrec.2015.09.016</u>

[5] Liu, Y., Kumar, S., Kwag, J., & Ra, C. (2012). Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review. *Journal of Chemical Technology & Biotechnology*, 88(2), 181-189. <u>http://dx.doi.org/10.1002/jctb.3936</u>

[6] Valdez, P., Nelson, M., Wang, H., Lin, X., & Savage, P. (2012). Hydrothermal liquefaction of Nannochloropsis sp.: Systematic study of process variables and analysis of the product fractions. *Biomass And Bioenergy*, *46*, 317-331. <u>http://dx.doi.org/10.1016/j.biombioe.2012.08.009</u>

[7] Jones, S.B., Zhu, Y., Snowden-Swan, L.J., Anderson, D.B., Hallen, R.T., Schmidt, A.J., Albrecht, K.A., & Elliot, D.C. (2014). Whole Algae Hydrothermal Liquefaction: 2014 State of Technology, Pacific Northwest National Laboratory, United States of America.

[8] Garcia Alba, L., Torri, C., Fabbri, D., Kersten, S. & Brilman, D.W.F (Wim). (2013). Microalgae growth on the aqueous phase from Hydrothermal Liquefaction of the same microalgae. Chemical Engineering Journal, 228, 214-223. <u>http://dx.doi.org/10.1016/j.cej.2013.04.097</u>

[9] López Barreiro, D., Zamalloa, C., Boon, N., Vyverman, W., Ronsse, F., Brilman, W., & Prins, W. (2013). Influence of strain-specific parameters on hydrothermal liquefaction of microalgae.
Bioresource Technology, 146, 463-471. <u>http://dx.doi.org/10.1016/j.biortech.2013.07.123</u>

[10] Valdez, P., Tocco, V., & amp; Savage, P. (2014). A general kinetic model for the hydrothermal liquefaction of microalgae. Bioresource Technology, 163, 123-127. http://dx.doi.org/10.1016/j.biortech.2014.04.013

[11] Nuss, P., Eckelman, Matthew J. (2014). Life cycle assessment of metals: a scientific synthesis. Belgian Nuclear Research Centre SCK•CEN, Belgium.

[12] Rerat, C., Papadokonstantakis, S., Hungerbühler, K. (2013). Integrated waste management in batch chemical industry based on multi-objective optimization. Air \& Waste Management Association, 63(3):349-66).

[13] Neveux, N., Yuen, A., Jazrawi, C., Magnusson, M., Haynes, B., & Masters, A. et al. (2014).
Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae. Bioresource Technology, 155, 334-341.
<u>http://dx.doi.org/10.1016/j.biortech.2013.12.083</u>

[14] Maehre, H., Malde, M., Eilertsen, K., & Elvevoll, E. (2014). Characterization of protein, lipid and mineral contents in common Norwegian seaweeds and evaluation of their potential as food and feed. Journal Of The Science Of Food And Agriculture, 94(15), 3281-3290. http://dx.doi.org/10.1002/jsfa.6681

[15] Jena, U., Vaidyanathan, N., Chinnasamy, S., & Das, K. (2011). Evaluation of microalgae cultivation using recovered aqueous co-product from thermochemical liquefaction of algal biomass.
 Bioresource Technology, 102(3), 3380-3387. <u>http://dx.doi.org/10.1016/j.biortech.2010.09.111</u>

[16] López Barreiro, D., Bauer, M., Hornung, U., Posten, C., Kruse, A., & Prins, W. (2015). Cultivation of microalgae with recovered nutrients after hydrothermal liquefaction. Algal Research, 9, 99-106. <u>http://dx.doi.org/10.1016/j.algal.2015.03.007</u>

[17] Dupont, C., Chiriac, R., Gauthier, G., & Toche, F. (2014). Heat capacity measurements of various biomass types and pyrolysis residues. Fuel, 115, 644-651. http://dx.doi.org/10.1016/j.fuel.2013.07.086

[18] Petzet, S., Peplinski, B., & Cornel, P. (2012). On wet chemical phosphorus recovery from sewage sludge ash by acidic or alkaline leaching and an optimized combination of both. Water Research, 46(12), 3769-3780. <u>http://dx.doi.org/10.1016/j.watres.2012.03.068</u>

[19] Elliott, D., Hart, T., Schmidt, A., Neuenschwander, G., Rotness, L., & Olarte, M. et al. (2013). Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. Algal Research, 2(4), 445-454. <u>http://dx.doi.org/10.1016/j.algal.2013.08.005</u>

[20] Rahman, M., Salleh, M., Rashid, U., Ahsan, A., Hossain, M., & Ra, C. (2014). Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review. Arabian Journal Of Chemistry, 7(1), 139-155. <u>http://dx.doi.org/10.1016/j.arabjc.2013.10.007</u>

[21] Gallucci, F., Comite, A., Capannelli, G., & Basile, A. (2006). Steam Reforming of Methane in a Membrane Reactor: An Industrial Case Study. Industrial & Engineering Chemistry Research, 45(9), 2994-3000. <u>http://dx.doi.org/10.1021/ie058063j</u>

[22] Chen, W., Hsieh, T., & Jiang, T. (2008). An experimental study on carbon monoxide conversion and hydrogen generation from water gas shift reaction. Energy Conversion and Management, 49(10), 2801-2808. <u>http://dx.doi.org/10.1016/j.enconman.2008.03.020</u>

[23] Luberti, M., Friedrich, D., Brandani, S., & Ahn, H. (2013). Design of a H2 PSA for cogeneration of ultrapure hydrogen and power at an advanced integrated gasification combined cycle with pre-combustion capture. Adsorption, 20(2-3), 511-524. <u>http://dx.doi.org/10.1007/s10450-013-9598-0</u>

[24] Barthe, P., Chaugny, M., Roudier, S., & Delgado Sancho, L. (2015). Applied Processes and Techniques, Best available techniques (BAT) reference document for the refining of mineral oil and gas industrial emissions, 88-91, Publications Office of the European Union, Luxembourg

[25] The Linde Group. Hydrogen Recovery by Pressure Swing Adsorption. Linde Engineering, Retrieved: 14 Dec. 2017, Available at: <u>www.linde-</u>

engineering.com/internet.global.lindeengineering.global/en/images/HA_H_1_1_e_09_150dpi_NB1 9_6130.pdf?v=3.0

[26] Ecoinvent database, Life cycle inventory database.

APPENDIX

Table A1.	Parameter	values and	settings	used in	the pro	ocess mo	delling.

Model settings								
Parameter	Value	Unit	Source					
Macroalgae feedstock	Ulva Lactuca	-						
Dry feedstock	1000	kg	Reference amount					
Ash content	30,7	w%	Neveux et al. (2014) *					
Water content	92,38	w%	Maehre et al. (2014)					
Phosphorus content	1200	mg/kg _{dry feedstock}	Maehre et al. (2014) *					
Magnesium content	15000	mg/kg _{dry feedstock}	Maehre et al. (2014)					
Calcium content	5500	mg/kg _{dry feedstock}	Maehre et al. (2014) *					
Proteins content	26,3	W% (dry ash free)	Neveux et al. (2014) normalized	Feedstock				
Lipids content	3	W% (dry ash free)	Neveux et al. (2014) normalized					
Carbohydrates content	70,7	W% (dry ash free)	Neveux et al. (2014) normalized					
Carbon (C)	46,9	W% (dry ash free)	Normalized*					
Hydrogen (H)	7	W% (dry ash free)	Normalized*					
Oxygen (O)	34,8	W% (dry ash free)	Normalized*					
Nitrogen (N)	10,7	W% (dry ash free)	Normalized*					
Sulphur (S)	0,5	w% (dry ash free)	Normalized*					
Dry biomass heat capacity	1,65	kJ/kgK	Dupont et al. (2014)					
Process pressure	220	bar	Below critical point					
Process temperature	323	°C	Optimization					
Residence time	87	min	Optimization					
Total solid	20	w%	Optimization					
Aqueous phase TOC	15,8	g/l	Atom balance					
Aqueous phase TN	12	g/l	Atom balance					
Aqueous phase phosphorus	56	W% (feedstock P)	Maximum expected value					
Aqueous phase magnesium	0,5	W% (feedstock Mg)	Data averaging, Jena et al. (2011), López Barreiro et al. (2015)	HTL				
Aqueous phase calcium	0,5	W% (feedstock Ca)	Data averaging, Jena et al. (2011), López Barreiro et al. (2015)					
Solid phase phosphorus	30	W% (feedstock P)	Valdez et al. (2012), Jones et al. (2014)					
Solid phase magnesium	99,5	W% (feedstock Mg)	Assumed, by difference					
Solid phase calcium	99,5	w% (feedstock Ca)	Assumed, by difference					
Ash free solid phase HHV	4	MJ/kg	Neveux et al. (2014)					
Biocrude Carbon (C)	73,5	w%	Atom balance					
Biocrude Hydrogen (H)	8,3	w%	Atom balance					

Biocrude Oxygen (O)	11,1		w%	Atom balance		
Biocrude Nitrogen (N)	7		w%	Atom balance		
Crude-to-Fuel η	0,75		kg/kg _{inlet}	Jones et al. (2014)		
Crude-to-Aqueous phase η	0,07		kg/kg inlet	Jones et al. (2014)		
Crude-to-Gas η	0,18		kg/kg _{inlet}	Jones et al. (2014)		
	CO 0		vol%			
	CO ₂	0	vol%			
Biocrude upgrading gas com- position	CH ₄ 47		vol%	Jones et al. (2014)	Biocrude	
	C_2H_6	43	vol%		opgrading	
	NH_3	10	vol%			
Process temperature	400		°C	Jones et al. (2014)		
Process pressure	105		bar	Jones et al. (2014)		
Residence time	255		min	Calculated from Jones et al. (2014)		
Air-to-fuel α	1,15		mol/mol stochiometric	Optimization	Incineration	
Flue gas specific heat	40		kJ/kmolK	Calculated	incineration	
Leaching P efficiency	0,9		-	Petzet et al. (2012)	Leaching	
Leaching Mg efficiency	0,9		-	Assumed		
Soild content	20		w%	Optimized		
рН	1,95		-	Petzet et al. (2012)		
Acid-to-Ash ratio	0,0518		-	Calculated		
Process temperature	350		°C	Jones et al. (2014)		
Process pressure	206		bar	Jones et al. (2014)		
TOC conversion efficiency	98		% total organic carbon	Assumed, Jones et al. (2014)		
Carbon-to-Gas efficiency	34,5		% _{carbon}	Jones et al. (2014)		
	СО	0	vol%			
	CO ₂	34	vol%		CHG	
	H ₂	2	vol%			
Output gas composition	CH ₄	59	vol%	Jones et al. (2014), Elliott et al. (2013)		
	C_2H_6	1	vol%			
	NH_3	3	vol%			
	H ₂ O 2		vol%			
Aqueous phase pH	8		-	Data averaging		
рН	8		-	Liu et al. (2012), Rahman et al. (2014)		
Struvite efficiency	90		% inlet P	Liu et al. (2012), Rahman et al. (2014)	Precipitation Crystallization	
Mg-to-PO ₄ ratio	≥1		-	Liu et al. (2012)		
NH ₄ -to-PO ₄ ratio	≥1		-	Assumed		

Steam reforming efficiency	75	% hydrocarbon conversion	Gallucci et al. (2006)	
Water gas shift efficiency	90	% CO conversion	Chen et al. (2008)	
PSA efficiency	80	% hydrogen recovered	Luberti et al. (2013)	Hydrogen
Hydrogen purity	~100	%	Barthe et al. (2015)	
Steam reforming tempera- ture	800	°C	Barthe et al. (2015)	
Water gas shift temperature	220	°C Chen et al. (2008)		production
PSA temperature	30	°C	The Linde Group	
Steam reforming pressure	20	bar	Barthe et al. (2015)	
Water gas shift pressure	20	bar	Chen et al. (2008)	
Steam-to-Hydrocarbon(C)	4	mol-ratio	Gallucci et al. (2006)	
Inlet temperature	25	°C	Assumed	
Flue gas outlet temperature (min)	100	°C	Assumed	
Natural gas HHV	55	MJ/kg	NIST	Hot utility
Flue gas specific heat	40	kJ/kmolK	Assumed	
Air-to-Fuel ratio	1,15	mol/mol stochiometric	Optimization	

*Experimental data from University of Bath.

Name	Source	Allocation method	Description	Formula unit	Price [\$]	Tot-CED [MJeq]	GWP(100a) [kg-CO2-eq]	EI99(H,A) [points]	
Macroalgae	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. Energy demand and environ- mental impact of harvesting macroalgae.	kg	0.093	0.056	0.004	0.0004	
Sulfuric Acid	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. Market for sulfuric acid.	kg	0.049	1.688	0.116	0.035	
Process Water	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. Market for water, completely softened.	t	0.852	0.307	0.026	0.002	Feedstock + Material
NaOH	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. Market for NaOH, without water, in 50% solution state.	kg	0.299	25.199	1.543	0.231	
MgCl2	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. Market for MgCl2.	kg	0.235	5.911	0.400	0.049	
Methane 1	Ecoinvent v3.3	Substitution, consequential, long-term	GLO. For producing heat.	MJ	0.241	1.240	0.069	0.004	Methane
Methane 2	Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. For extracting natural gas.	MJ	0.241	1.240	0.012	0.004	
Co/Mo/Al2O3(3.6%/15%/81.4%) (biocrude upgrading)	^a Online supplier ^b Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. For production.	kg	4.8 ^a	34.572 ^b	2.474 ^b	6.128 ^b	Catalysts
Ru/Carbon(8%/92%) (CHG)	^a Online supplier ^b Ecoinvent v3.3 ^c Ref.	Substitution, consequen- tial, long-term	For production.	kg	27.2	3370.977	171.112	459.125	
Ni/Al2O3(15%/85%) (steam reforming 1)	^a Online supplier ^b Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. For production.	kg	6.5ª	23.323 ^b	1.737 ^b	0.237 ^b	
CuO/ZnO/Al2O3(36%/34%/30%) (steam reforming 2)	^a Online supplier ^b Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. For production.	kg	4.25ª	52.010 ^b	3.255 ^b	4.639 ^b	
Electricity	Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. Market for electricity, high voltage.	kWh	0.097	10.389	0.762	0.058	Utility-El.

Table A2. Prices and environmental impact indicators used in the assessment.

Name	Source	Allocation method	Description	Formula unit	Price [\$]	Tot-CED [MJeq]	GWP(100a) [kg-CO2-eq]	EI99(H,A) [points]	
Effluent (option 1)	Rerat et al (2013).			kg	0.006	0.293	0.017	0.001	Wastewater
Effluent (option 2)	Rerat et al (2013).			kg	0.006	0.370	0.022	0.001	treatment
Effluent (option 3)	Rerat et al (2013).			kg	0.009	0.764	0.058	0.002	
Petroleum	Ecoinvent v3.3	Substitution, consequen- tial, long-term	GLO. Market for petroleum.	kg	0.664	49.287	0.258	0.173	Conventional production of
Triple superphosphate	Ecoinvent v3.3	Substitution, consequential, long-term	RER Triple superphosphate production. Refers to 1 kg P2O5, resp. 2.08 kg triple superphos- phate with a P2O5-content of 48.0%.	kg	0.3	24.390	1.433	0.270	fuel and ferti- lizer

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