# Process Optimization for the hydrothermal production of algae fuels

**Andres Taimbú[a], Mariano Martín[a 1], Ignacio E. Grossmann[b]**

[a]Departamento de Ingeniería Química y Textil, Universidad de Salamanca, Plz caídos 1-5, 37008.

[b]Department of Chemical Engineering. Carnegie Mellon University, Pittsburgh, PA, 15213

## Abstract.

In this work of the production of liquid fuels from algae via hydrothermal liquefaction has been analyzed. The process consists of algae growing and harvesting, the biomass liquefaction, hydrocracking of the biocrude and the separation of the products into fuels. Surrogate models for all the units are developed to evaluate the optimal operating conditions including the nutrients and light effect on algae growth rate, the yield and distribution of the products of the hydrothermal liquefaction (HTL) and the hydrocracker, using kinetic and yield data, and the operation of the column using both rules of thumb and experimental data. The model is optimized aiming at selecting the algae composition, the HTL and hydrocracking product distribution. The algae should have 53% lipids, 30% protein, 15% carbohydrates for the production of a mass with 51% biocrude that is cracked into 18% Kerosene, 24% Gasoline and 59% Diesel. The facility investment costs add up to 130 M€ with a production cost for fuels of 0.64 €/gal. These results are competitive with renewable based FT fluids and biodiesel.

Keywords: Energy, Biofuels, Alternative fuels, Diesel, Fisher – Tropsch

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[1] Corresponding author. Email address: mariano.m3@usal.es

## 1.-Introduccion

Biomass transformation into fuels and chemicals can follow different paths. Among them the use of gasification and hydrolysis have focused the attention to process lignocellulosic materials. Gasification is a high temperature partial oxidation process that produces a versatile intermediate, syngas, that allows the production of a large number of chemicals including ethanol (Piccolo and Bezzo, 2009,Martin and Grossmann, 2011), DME (Peral and Martin, 2015) and FT-liquids (Martín and Grossmann, 2011). On the contrary, Hydrolysis of biomass is a moderate temperate and pressure process to breakdown the structure of the raw material to produce C5 and C6 sugars. The main use of them has been the production of ethanol (Piccolo and Bezzo, 2009; Kazi et al 2011, Martín and Grossmann, 2012), but they are useful for the production of other chemicals such as i-butene (Van Leeuwen, 2012; Martín and Grossmann, 2014), and recently platform chemicals such as DMF and HMF (Roman-Leshkov et al 2007; Binder et al 2010; Chheda et al 2007, Martin and Grossmann, 2015). If instead of lignocellulosic raw materials algae are the available biomass, the studies have focused on the transesterification of the oil within towards biodiesel production evaluating different catalysts and following a simulation( Zhang et al 2013) or a mathematical optimization approach (Martin and Grossmann, 2012). Lately the algae starch has also been used to ethanol (Martín and Grossmann, 2013), ibutene (Martin and Grossmann, 2014) or DMF production (Martín and Grossmann, 2015) as well as higher added value products like carotenoids (Psycha et al 2014). One of the main disadvantages related to algae processing is the large amount of water involved in its growing. As a result, a large consumption of energy (Sandaroz 2006) or complex designs are required (Martin and Grossmann, 2012) to harvest the algae and technologies such as gasification or pyrolysis have not been applied to algae.

Thermochemical processes for wet biomass can be a promising alternative to obtain fuels and chemicals from biomass including hydrothermal gasification, liquefaction or carbonization. Among them hydrothermal liquefaction has the advantage of not requiring drying since the wet biomass is fully used as well as it acts as solvent and reactant to hydrolyze the algae biomass. The drawback is the energy required to heat up the entire mass for its processing. Hydrothermal liquefaction (HTL) is a process based on applying high-temperature (>250 ºC) and high-pressure (>4 MPa) to convert wet biomass, including algae, into a biocrude oil as well as aqueous and gaseous byproducts (Amin, 2009). The biooil presents lower oxygen content and higher heating value than the one produced by fast pyrolysis of biomass (Peterson et al., 2008) so that it has been classified as similar to heavy crude (Ross et al 2010) which simplifies the upgrading process to be similar to crude oil fractionation. Valdez and Savage, (2013) developed a kinetic model to represent the hydrothermal process of a particular algae species and it was later extended for generality (Valdez et al 2014). Lately, surface of response models have been also developed to predict the yield of biooil production as a function of the temperature, heating rate and residence time (Yang et al. 2019). However, these models only focus on oil not providing results on the other products. The resulting biooil must be upgraded to fuel specifications for which hydrocracking (Speight, 1991) and crude distillation (Gadalla et al 2003) are the typical processes.

In this work the production of synthetic fuels from algae biomass using HTL is evaluated. Mathematical optimization techniques have been used for the optimal design of the facility providing guidelines on the algae composition and the operating conditions of the units involved. Surrogate models based on experimental data and rigorous kinetic ones have been developed to simulate the entire process from algae growing to green gasoline and diesel production. The rest of the paper is organized as follows. Section 2 describes the process. Section 3 shows the modelling effort. Section 4 presents the main results of the operation of the facility an section 5 draws some conclusions.

## 2. Overall Process Description

The process consists of the growing of the algae and its harvesting to partially remove water. The excess is recycled to the ponds. Next, the wet biomass is hydrotreated to produce an aqueous phase, a gas phase and bio-oil. The three phases are separated. Subsequently, the bio-oil is hydrocracked to produce fuel quality products and finally a crude distillation unit, modelled as a series of thermally coupled columns is used to produce naphtha, diesel and kerosene. The residue is recycled to the hydrocracker to increase the yield towards products. Figure 1 presents a the flowsheet of the process.

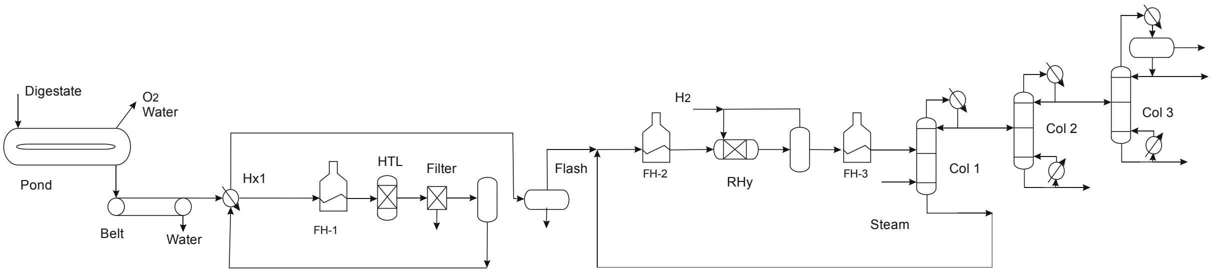

Figure 1.- Algae bio oil production and upgrading

## 3.-Mathematical modelling.

All the unit operations in the hydrothermal liquefaction of algae are modelled using first principles including mass and energy balances and phase equilibrium. Special units such as the algae ponds, the HTL or the hydrocracking reactors are modelled using surrogates based on experimental data and yields, while the hydrothermal liquefaction is modelled using detail kinetics. The entire process model is written in terms of the total mass and component flows and stream temperatures that are the main decision variables for the optimization. $J$ = { water, $CO_2$, $O_2$, algae, protein, lipids, carbohydrates, aqueous phase, biocrude, gas, gasoline, kerosene, diesel, residue, $CH_4$, slurry, nitrogen, phosphorus, $H_2$}.

### 3.1.-Algae growing production

Algae growth depends on a number of parameters such as carbon source, water, nutrients or light. In particular, nutrients concentration in terms of total nitrogen and total phosphorous determine the algae growth rate together with the light incidence that the algae receive and the temperature. A surrogate to predict for the effect of these four variables on the algae growth using data from several studies is developed. We first take the model developed in a previous paper (Hernández and Martín, 2016) where the effect of the nutrients was already considered, eq (1). This previous model is corrected to include effect of the light and temperature (Amini et al 2016) as follows. The experimental data for the algae growth yield used to develop the original model, from Xin et al (2010), were measured at 25ºC, 60 $\mu$mol/m$^2$s and we assume a pH of 7.4. We used those to provide a reference and correct the growth model as follows:

$$\mathrm{Growth}_N\left(\frac{g}{m^2 d}\right) = 0.418528\cdot\mathrm{TotP} + 0.52762\cdot\mathrm{TotN} + 0.225013\cdot\mathrm{TotN}\cdot\mathrm{TotP} - 0.20754\cdot\mathrm{TotP}^2 - 0.03026\cdot\mathrm{TotN}^2 \quad (1)$$

$$\begin{aligned}
&\mathrm{Growth}\left(\frac{g}{m^2 d}\right) = \mathrm{Growth}_N \frac{f(T, Light, pH)}{f_{ref}(25^{\circ}C, 60\mu mol/m^2/s, 7.4)} \\
&f(T, Light, pH) = -156.77 + 0.21\cdot T(^{\circ}C) + 0.23\cdot Light + 41.45\cdot pH + \\
&0.00000339\cdot T(^{\circ}C)\cdot Light + 0.022\cdot pH + 0.0000181\cdot pH\cdot Light - 0.00863\cdot T(^{\circ}C)^2 \\
&-0.0000509\cdot Light^2 - 2.84\cdot pH^2
\end{aligned} \quad (2)$$

The total phosphorus and the total nitrogen are given in mg per L, and temperature is in ºC. The light is included in μmol/m²s. However, the weather information is typically given in kWh/m² d. Approximately, 4.57 μmol/m²s is equivalent to 1 W/m² (Sager and McFarlane, 2017) and 1 kWh/m² d is equal to 41.7 W/m²

Apart from nutrients and light, $CO_2$ is also consumed. The consumption rate depends on the growth rate of the algae as given by eq. (3), Sazdanoff (2006)

$$\mathrm{CO_2}\left(\frac{\mathrm{m}^3}{d}\right) = 0.6565\cdot\mathrm{Growth}\left(\frac{g}{m^2 d}\right) + 5.0784 \tag{3}$$

The algae are grown in ponds that operate only during day light. To secure a production of 10kg/s of dry biomass, the number of ponds is to be estimated based on the growth time in the ponds and the growth rate. Water is fed to secure 1% of dry biomass by the end of the growth period.

$$\mathrm{Algae} = \mathrm{Growth}\cdot\mathrm{Area\_Pond}\cdot(1/1000)\cdot N_{\mathrm{Ponds}} \tag{4}$$

Since the algae only grow during the sun hours, to secure an average production rate

$$\mathrm{Algae} = \mathrm{Feed}\cdot\mathrm{Biomass}_{\mathrm{Fraction}}; \tag{5}$$

Where we assume 1% biomass in water ($\mathrm{Biomass}_{\mathrm{Fraction}}$). The energy consumed for the operation of the ponds is computed following Sazdanoff's (2008) data as pumping needs. Next, algae are harvested and dried up to 20% dry mass in the stream. We assume that the water can be recycled to the pond so that water is lost only by evaporation. The amount of evaporated water is 6.2 m³/d pond.

The actual composition of the algae consists mainly of carbohydrates, lipids and proteins (http://www.oilgae.com/algae/comp/comp.html). We assume as upper bounds for each of the three to be up to 30% Protein, up to 55% lipids and up to 15% carbohydrates. The growth also determines the accumulation of oil. Here, the content of each of the three components is a variable to be optimized. In this way, not only the best product distribution but also the optimal algae composition for the production of the fuels via thermal liquefaction can be identified resulting in a process and product design problem.

### 3.2.- Hydrothermal liquefaction (HTL) process

The HTL process is modeled based on the work by Valdez y Savage (2013) that considers a network of reactions that transforms the biomass into a set of products including an aqueous phase, a gas phase and bio-oil.

Figure 2 shows the mechanism of reaction including the intermediates and the final products. Eqs (6)-(7) show the kinetic equations for the five species involved, the solids (algae), light biocrude, and the three main products, the aqueous phase, the biocrude and the gas. In Table 1 the values for the activation energies and preexponential factors are presented.

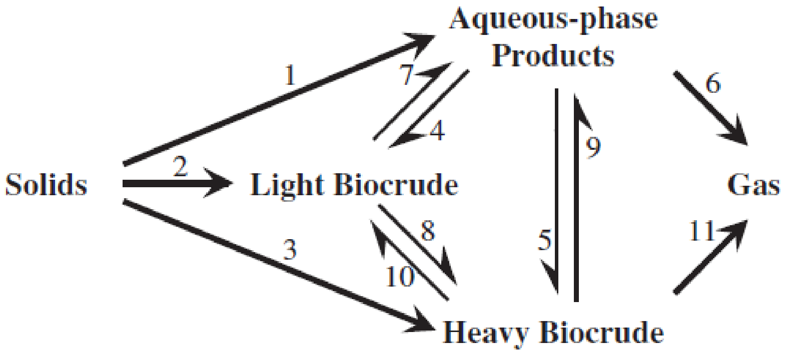

Figure 2.- Decomposiion mechanism.

$$
\begin{aligned}
\frac{dx_1}{dt} &= -(k_1 + k_2 + k_3) \cdot x_1 \\
\frac{dx_2}{dt} &= -(k_4 + k_5 + k_6) \cdot x_2 + k_1 \cdot x_1 + k_7 \cdot x_3 + k_9 \cdot x_4 \\
\frac{dx_3}{dt} &= -(k_7 + k_8) \cdot x_3 + k_2 \cdot x_1 + k_4 \cdot x_2 + k_{10} \cdot x_4 \\
\frac{dx_4}{dt} &= -(k_9 + k_{10} + k_{11}) \cdot x_4 + k_3 \cdot x_1 + k_5 \cdot x_2 + k_8 \cdot x_3 \\
\frac{dx_5}{dt} &= k_6 \cdot x_2 + k_{11} \cdot x_4
\end{aligned}
\qquad (6)
$$

where

$$
k\left(\min^{-1}\right) = A \cdot e^{-\frac{E_a}{R \cdot T}} \qquad (7)
$$

Table 1.- Kinetic parameters for the liquefaction process.

| Reaction | $E_{a,j}$ (kJ/mol) | Ln ($A_j$) |
|---|---|---|
| 1 | 27 ± 12 | 2.8 ± 2.4 |
| 2 | 15 ± 5 | -0.2 ± 1 |
| 3 | 41 ± 14 | 6 ± 2.8 |
| 4 | 26 ± 5 | 1.8 ± 1 |
| 5 | 2.9 ± 0.8 | -2.2 ± 0.2 |
| 6 | 66 ± 19 | 4 ± 3.6 |
| 7 | 17000 ± 10 | 1.2 ± 2 |
| 8 | 33 ± 10 | 0.9 ± 2.1 |
| 9 | 4.8 ± 2,7 | -0.8 ± 0.5 |
| 10 | 45 ± 27 | 4.7 ± 5.4 |

| | | |
|---|---|---|
| 11 | 80 ± 6 | 10 ± 1 |

The reactor operates adiabatically and we assume that, based on literature data, by heating up the feed up to the reaction temperature, the reactor can self-sustain (Ibbett et al 2011; Magdeldin et al, 2018). The data on the heat of reaction is scarce and inconsistent reporting either endothermic or slightly exothermic reactions (Lee et al, 2016). We assume negligible averaged heat of reaction.

### 3.3.-Hydrocracking.

The three phases obtained in the previous reactor are separated in a flash and a liquid-liquid decanter. The gas can be a source of energy to the process. The water phase contains organics and will be sent to water treatment. Finally the biocrude is to be processed towards fuels. Hydrocracking is the best option in order to produce liquid fuels. The yield to different fuels depends on the operating conditions.

The hydrocracking reactor is modelled using experimental data on the conversion and selectivity as a function of the temperature from the paper by Bezergianni et al. (2009). Note that in that paper the selectivities to the three products do not add to 1, because the range of boiling points of the three main fractions, gasoline, kerosene and diesel, overlap. The typical ranges are 40 to 200 for gasoline, 170 to 220 for kerosene and 180 to 360 for diesel. Considering the full range, the composition is adjusted assuming almost linear distribution of the products in the temperature range. In this way, the selectivities are decoupled based on typical distillation curves that consider that gasoline distillates up to 150 ºC, and diesel from 220 ºC onwards leaving kerosene in between. Figure 3 shows the profiles used to developed the surrogate model of the unit, for the conversion, eq. (8) and the selectivities to diesel, kerosene, gasoline, eq. (9)

$$\mathrm{X} = 0.000185714 \cdot (\mathrm{T}_{HC})^2 - 0.128829 \cdot \mathrm{T}_{HC} 3 + 22.6931 \tag{8}$$

$$\begin{aligned} S\_D &= -1.2232 \cdot 10^{-04} \mathrm{T}_{HC}^2 + 8.2418 \cdot 10^{-02} \mathrm{T}_{HC} - 1.2951 \cdot 10^1 \\ S\_K &= -2.5000 \cdot 10^{-05} \mathrm{T}_{HC}^2 + 2.165010^{-02} T_{HC} - 4.465 \\ S\_G &= 1.4732 \cdot 10^{-04} \mathrm{T}_{HC}^2 - 1.0407 \cdot 10^{-01} \mathrm{T}_{HC} + 1.8416 \cdot 10^1 \end{aligned} \tag{9}$$

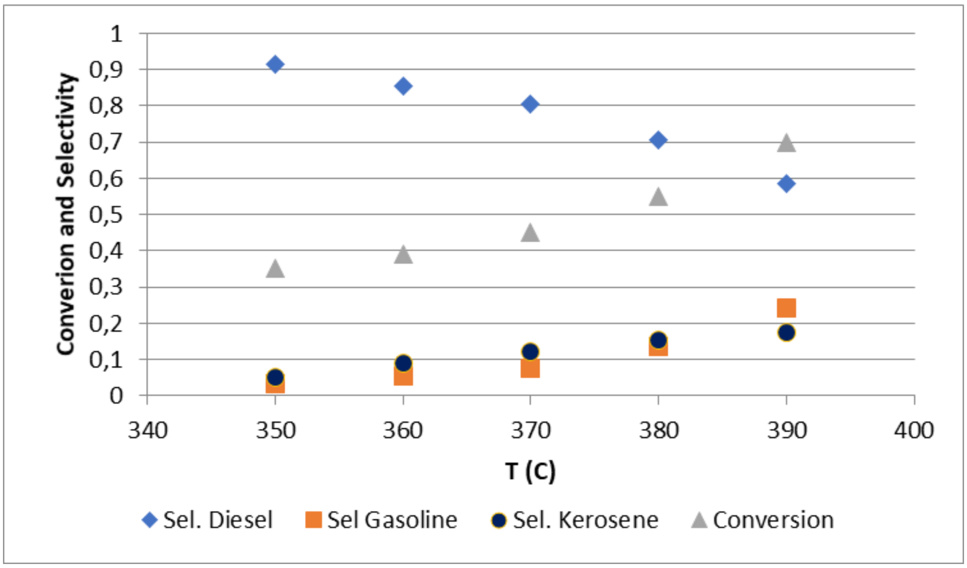

Figure 3.- Conversion profiles for the hydrocracking reactor

The reactor also requires a flow of hydrogen. Typically 600-1150 $ft^3$ of hydrogen per bbl to be left with the products. Other results show that 0.039 kg of $H_2$ per kg of crude for hydrocraking (mines.edu), and this represents around 7.5% of the total hydrogen fed to the hydrocracker and up to 23% (Watking 1979). These values depend on the composition of the feed, the catalyst and operating conditions; a range is available in the literature. Eqs. (10)-(15) models the total mass of fuels obtained from the reaction..

$$\text{masshydro} = 1.039 \cdot \text{fc}\left(Heavy\right) \tag{10}$$

Thus, the products from the reactor will be, considering the hydrogen not reacted:

$$\text{fc}\left(\text{Diesel}\right) = \text{X} \cdot \text{S\_D} \cdot \text{masshydro} \tag{11}$$

$$\text{fc}\left(\text{Gasoline}\right) = \text{X} \cdot \left(\text{S\_G}\right) \cdot \text{masshydro} \tag{12}$$

$$\text{fc}\left(\text{Kerosene}\right) = \text{X} \cdot \left(\text{S\_K}\right) \cdot \text{masshydro} \tag{13}$$

$$\text{fc}\left(Heavy\right) = \left(1 - \text{X}\right) \cdot \text{masshydro} \tag{14}$$

$$0.15 \cdot \text{fc}\left(Heavy\right) \le \text{fc}\left(\text{H2}\right) \le 0.52 \cdot \text{fc}\left(Heavy\right) \tag{15}$$

The excess of $H_2$ is recovered and recycled. Meanwhile, the liquids (Gasoline, Kerosene, Diesel and heavy residue) are sent to the column to be separated. The heat of reaction is 77.53 kJ per kmol (50 BTU/scf) of hydrogen consumed (Coker 2018),

### 3.4.-Separation

The separation of the hydrocarbons is a well-known practice in the petrochemical industry. The most important issue is the fact that a mixture instead of single species is processed. The model presented by Gadalla et al. (2003) is used to simulate the distillation column as a series of distillation columns, see Figure 4. We assume 4 products, gasoline (G), kerosene (K), diesel (D) and heavy (H). Therefore, we have three columns. For simplicity the separation of each species is complete. Note that in fact since we separate mixtures of fuels, this assumption holds. Thus, the gasoline obtained in the hydrocracking is the distillate of the three columns.

$$fc_{i,out} = fc_{i,in} \forall i = \{G, K, D, H, W\} \tag{16}$$

Based on the results by Gadalla et al (2013) we formulate the energy balance to the reboilers and the condensers involved. Columns 2 and 3 have condenser and reboiler.

$$\begin{aligned}
&Q_{dist,3} = fc(Gasoline)(R_3)\lambda_G + W\lambda_W \\
&Q_{\mathrm{Re}b,3} = fc(Gasoline)(1+R_3)\lambda_G + W\lambda_W \\
&Q_{dist,2} = [fc(Gasoline)\lambda_G + fc(Kerosene)\lambda_K + W\lambda_W](R_2) \\
&Q_{\mathrm{Re}b,2} = [fc(Gasoline)\lambda_G + fc(Kerosene)\lambda_K + W\lambda_W](1+R_2) \\
&Q_{dist,1} = [fc(Gasoline)\lambda_G + fc(Kerosene)\lambda_K + fc(Diesel)\cdot\lambda_K + W\lambda_W](R_1)
\end{aligned} \tag{17}$$

In fact, these columns do not have reboiler. The heating to the column is provided by steam that is directly injected. The steam required is assumed to be from 0.043 kg/kg of residue (Watking 1979, Gorak (2014)) to 0.18 kg of steam per kg of residue based on the results by Jonas & Pujado (2006). Over the time, more efficient columns have been designed and therefore smaller steam needs are required. A value of 0.043 kg/kg of residue is used. We also assume that we recover the steam used and recycle it after heating it up again, and thus, the energy consumption of the column is given by the furnace to heat up the condensed water as well as the reboilers.

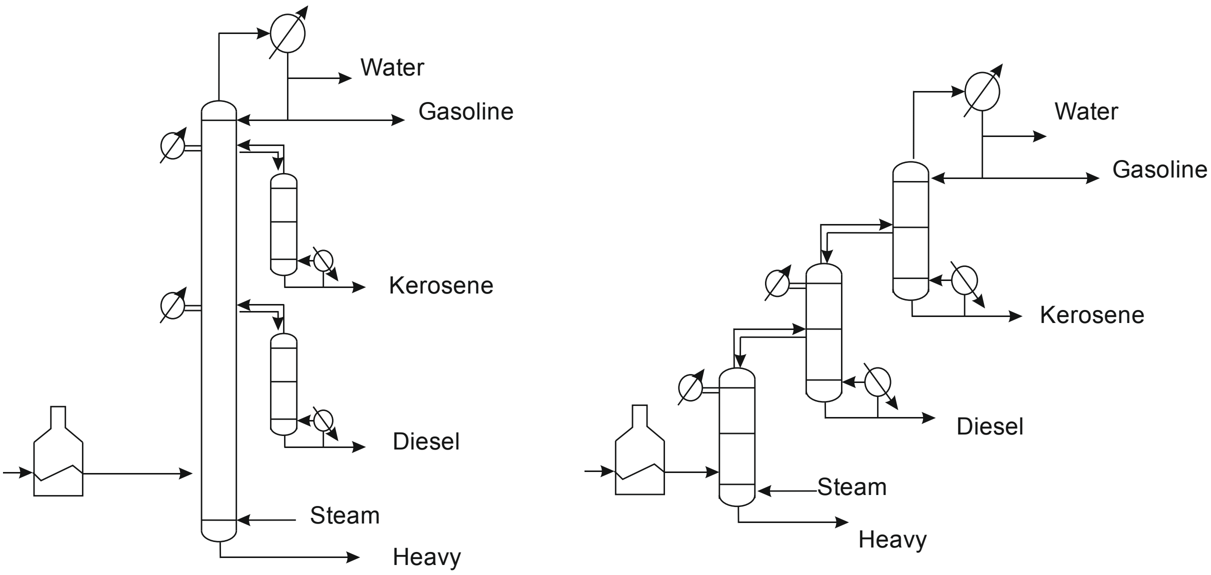

Figure 4.- Scheme of the model for the biocrude separation

The reflux ratios of columns 1, 2 and 3 are taken from the literature as 0.41, 1.47 and 4.77 that have been obtained from the optimization of the separation of crude oil Gadalla et al (2013). The temperatures of the product streams are computed based on the number of carbons of the organics as follows. We assume that the temperature of condensation of the water is the same as that of gasoline. According to Speight (1991), the typical distillation towers for crude oil have 30 trays and the typical temperatures are 110 ºC for the top (Gasoline),160ºC for Kerosene, 245 ºC for the diesel and 372 ºC at the bottom for the heavier components. (Watkins 1979; Riazi, and Esser, 2013)

### 3.9.-Solution procedure.

The process is modelled as a dynamic optimization problem using orthogonal collocation for the hydrothermal reactor and the surrogate models for each of the units as discussed along section 3. It consists of 4751 equations and 4810 variables. We solve the model maximizing a simplified annual cost, eq.(18), for the average operation over a year using a multistart optimization approach with CONOPT as the preferred solver. Table 2 shows the cost coefficients Alternatively, the model can be used for a particular allocation since the algae growth includes the solar incidence

$$Z = \left( \sum_{i \in Products} C_{Product} \cdot f_{Product,i} + \frac{C_{naturalgas}}{LHV} \sum_{i \in Heaters} Q_i - C_{Steam} \cdot f_{steam} - C_{Nutiernts} \sum_{i \in Nutrients} f_{Nutrients} \right) \tau - \frac{1}{K} C_{Ponds} \cdot N_{Ponds} \quad (18)$$

Table 2.- Cost coefficients for the objective function

| Coefficient | Cost | Reference |
|---|---|---|
| $C_{Steam}$ | 0.019 €/kg, | Uresti et al 2019 |
| $C_{Nitrogen}$ | 0.45€/kg, | (Hernández et al 2016) |
| $C_{Phosphorus}$ | 0.32€/kg, | (Hernández et al 2016) |
| $C_{Natural\ gas}$ | 1.15 €/kg | EIA 2019 |
| $C_{Gasoline}$ | 2.03€/kg, | |
| $C_{Diesel}$ | 1.44€/kg, | |
| $C_{Kerosene}$ | 0.54€/kg, | |

## 4.-Results.

### 4.1.- Plant operation

Table 3 shows the main features of the units involved in the process including operating temperatures and products yield. Among the results it is important to highlight the algae composition, consisting of 30% Protein, 53% lipids and 15% carbohydrates, with 2% other species. Note that both the protein and the carbohydrates are at the upper bound of the composition provided. Next, in the HTL reactor, the product distribution is basically 51% biocrude, 44 % aqueous phase and 5% gas. The aqueous phase is not useful but it can be considered as a source of carbon or even nutrients. The biocrude is cracked at 623 K with a conversion of 70% where 59% of the product is diesel, 19 % Kerosene and 24% gasoline based on the cost and the operating conditions diesel is favoured. Finally, the products are fractionated in a crude distillation units consuming 0.65 kg/s of steam and 6 MW of thermal energy in reboilers. The two fire heaters used, there is no need for additional heating to feed the distillation column, require 34 MW of thermal energy

Table 3.- Main operating conditions major units

| **Feature/Unit** | **Pond** | **HTL reactor** | **Hydrocracker** | **Columns** |
|---|---|---|---|---|
| | 17280 Ponds<br>1.442 mg/L P<br>2.931 mg/L N<br>**Algae composition**<br>0.3 Protein<br>0.53 Lipids<br>0.15 Carbohydrates | 557 K<br><br>**Products**<br>0.44 Aqueous phase<br>0.51 biocrude<br>0.05 gas | 623 K<br>$H_2$: 0.59 kg/s<br><br>**Product distribution:**<br>0.59Diesel<br>0.18 Kerosene<br>0.24 Gasoline<br>Conversion: 0.70 | Steam: 0.65 kg/s |

### 4.2.-Economic evaluation

For the evaluation of the investment cost we use the factorial method (Sinnot and Towler, 2009) that is based on estimating the unit costs. The cost of the ponds is assumed to be 0.61€/m$^2$ , as in previous works (Martín and Grossmann, 2012) for comparison. The hydrocracker and the crude distillation units cost are estimated using (https://www.ogj.com). The Matche web page is used to estimate the cost of the common chemical processing equipment such as heat exchangers, furnaces and centrifuges. The details on the procedure for the cost estimation for these typical units is available in the supplementary material of Almena and Martín (2015). The units cost adds up to 27 M€. Algae growing represents the largest share with around 50% of the cost. The breakdown of the units cost by type can be seen in Figure 5, where the reactors include the heat exchangers. The factors provided in Sinnot and Towler (2009) are used to estimate the investment cost of the entire facility assuming that it processes fluids and solids. The investment cost adds up to 130 M€ for the production of 74 Mgal of fuels a year, similar to biodiesel production facilities.

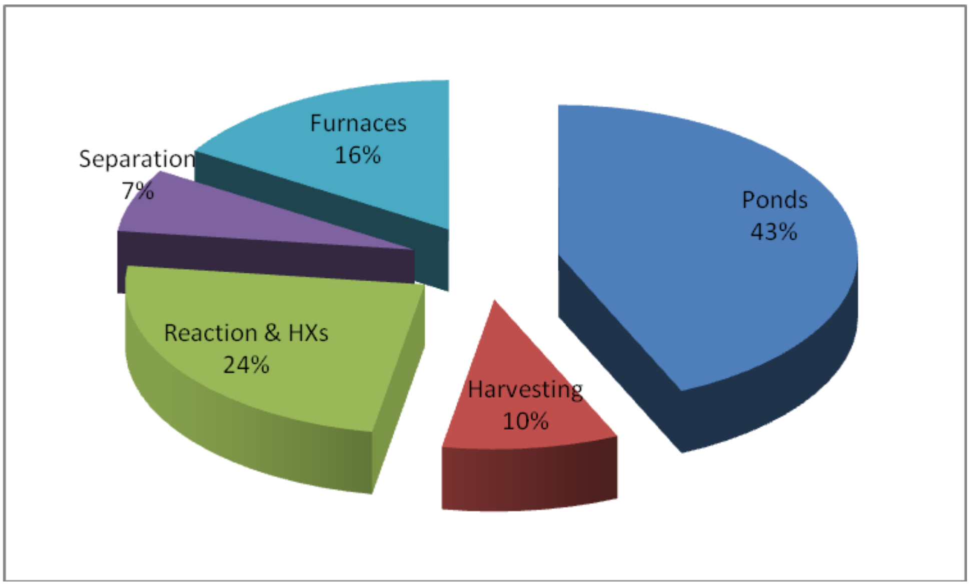

Figure 5.- Breakdown of units costs

To estimate the production cost of HTL fuels, we consider labour, taxes, administration, utilities and equipment maintenance. Utilities and chemicals are computed from the mass and energy balances as summarized in section 4.1. Salaries are assumed to be 2.5 M€. Taxes, and administration represent around 2.4 M€. Figure 6 presents the distribution of the production costs into items for a total of 47.5 M€ a year for a production of around 74 Mgal a year of fuels. Chemicals, where nutrients and hydrogen (1.6€/kg) are the largest share, represent 62% of the production cost. Note that the $CO_2$ fed to the ponds is assumed to be at zero cost.

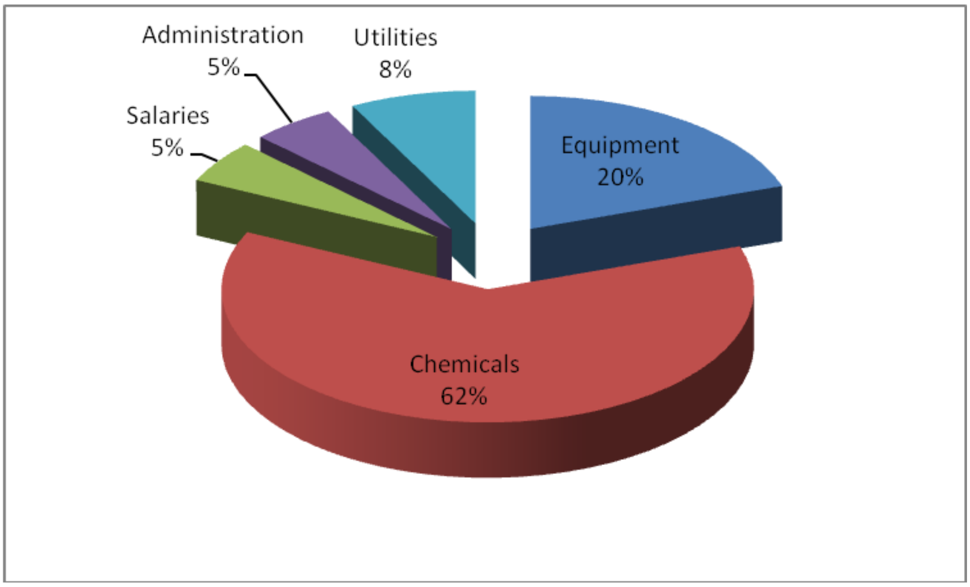

Figure 6.- breakdown of porduction costs

### 4.3.- Comparison with other bio/green fuels production

Maybe the most clear comparison is the one that can be established with FT- processes because of the similarity of the products. However, we also present here several results of the use of algae to obtain biodiesel too, see Table 4. The investment cost of the FT-plant following Sinnot and Towler (2009) method is $216 million (based on the equipment cost of $47.9M), that it is almost 50% higher the cost of the facility described in this work. The production costs of HTL fuels are similar to FT fuels, 0.64 vs 0.71 €/gal, but larger than biodiesel in all cases. In addition, the FT-fuels produce power, while the HTL process requires utilities. If we compare both facilities with biodiesel production facilities, either with external feed of the alcohols or self production, we see that although in most cases the production costs are lower in case of biodiesel (Martín and Grossmann, 2012,2013, 2016) and only for solar /wind based methanol the investment and production costs are closer, even though the energy required for the HTL process is 6 times larger. When using wastes (Hernández and Martin, 2017), carbohydrates within the algae to produce ethanol (Martín and Grossmann, 2013) or producing methanol via gasification, the investment costs are 50% larger due to the complex biomass processing into its constitutives.

However, the mild operating temperatures of the entire process result in the reduced consumption of energy from 4 to 15 times cheaper than the HTL process.

Table 4. Comparison of the production costs and investment for different biofuels production processes

| | FT-Diesel | Biodiesel Martin and Grossmann (2012) | Biodiesel Self Martin and Grossmann (2013) | Biodiesel Self Martin and Grosssmann (2016) | Biodiesel Self Martin and Grossmann (2017) | Biodiesel Self Hernández and Martín (2017) | **HTL** |
|---|---|---|---|---|---|---|---|
| Total investment ($MM) | 216 | 105 | 170 | 180 | 144 | 193 | **130** |
| Energy consumption (MJ/gal) | -63.0 | 1.94 | 4.0 | 1.27 | 4.05 | 1.5 | **17.7** |
| Production cost ($/gal) | 0.71 | 0.42 | 0.33 | 0.53 | 0.76 | 0.31 | **0.64** |

## 6.-Conclusions

In this paper, a mathematical optimization approach is developed for the analysis of the hydrothermal liquefaction of algae. The facility is modeled units by unit using surrogate models for the main units including detailed kinetics of the hydrothermal liquefaction, surface of response model for the algae growth rate, empirical correlations for the product yield of the hydrocracking and rules of thumb for the crude distillation unit. The framework allows determining the optimal algae composition, operating conditions at the HTL reactor and Hydrocracker and optimal product/fuels distribution. The model is optimized as a dynamic optimization one

The algae composition suggested results in 53% lipids, 30% protein, 15% carbohydrates. This species generates a biocrude that represents 51% of the hydrothermal liquefied mass. After cracking and separation, 74Mgal/year of fuels are produced with an optimal distribution of 18% Kerosene, 24% Gasoline and 59% Diesel. The facility investment costs add up to 130 M€ with a production cost for fuels of 0.64 €/gal. These results are competitive with renewable based FT fluids and biodiesel.

## Acknowledgments

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## 7.-Nomenclature.

| | |
|---|---|
| A | Preexponential factor |

| | |
|---|---|
| Ea: | Activation energy (kJ/mol) |
| fc(j,) | individual mass flow rate of component j (kg/s) |
| growth | Algae growth rate (g/m$^2$ d) |
| $k_i$ | Kinetic constant |
| light | Light intensity ($\mu$mol/m$^2$ s) |
| Masshydro | Mass flow of hydrogenated mass (kg/s) |
| N Ponds | Number of ponds |
| S_D | Selectivity to diesel |
| S_G | Selectivity to gasoline |
| S_K | Selectivity to kerosene |
| pH | pH of the algae pond |
| Q | Thermal energy flow (kW) |
| $R_i$ | Reflux ration of column i |
| R: | Gas constant (kJ/kmol K) |
| T: | Temperature (ºC/K) |
| $T_{HC}$ | Temperature of the hydrocracker (ºC) |
| TotP | Phosphorous nutrients (mg/L) |
| TotN | Nitrogen nutrients (mg/L) |
| W | Flow of water/steam in the crude distillation unit |
| X | Conversion of Hydrocracking |
| $x_i$ | Mass fraction of component i= i{lipids,carbphydrates,protein, aqueous, biocrude, gas} |
| $\lambda$: | heat of evaporation (kJ/kg) |

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