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Conceptual Study of the Coupling of a Biorefinery Process for Hydrothermal Liquefaction of Microalgae with a Concentrating Solar Power Plant

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Abstract. A conceptual analysis of the coupling of a concentrating solar power plant with a chemical process for hydrothermal liquefaction (HTL) of microalgae to biocrude was performed. The two plants were considered coupled by molten salt recirculation that granted energetic supply to the chemical process. Preliminary estimations have been done considering a solar field constituted by 3 linear parabolic solar collectors rows, each 200 m long, using a ternary molten salts mixture as heat transfer fluid, and a chemical plant sized to process 10 kT/y of microalgae. Under adopted conditions, we have estimated a minimum selling prize of the biocrude that is similar to that achieved in non-solar HTL processes.

INTRODUCTION

The environmental issues associated with the utilization of fossil fuels and the strong dependence of modern society on their imports to power economic activities is promoting the search for more clean and environmental friendly alternatives.

Among the different considered alternatives, biofuels represent an objective of great research efforts since several decades. Non-oil derived renewable liquid fuels can be obtained by different thermal, thermo-catalytic and biological routes, using as feedstock several kinds of biomass such as ligno-cellulosic biomass, sewage sludge, manure waste, microalgae, vegetable and waste cooking oil.

A hot topic in this context is the utilization of wet biomass whose conversion to biofuels is made energetically unfavorable by the high energetic costs associated to drying of the raw material. In conventional processes, heat used to power this unit operation cannot be recovered by heat integration and it negatively affects the sustainability of the process.

A possible solution of the aforementioned drawback is the utilization of hydrothermal (HT) processes, that can be performed in aqueous environment without need of drying of the feedstock. HT processes have several potential advantages over more conventional biofuel production routes: they could be carried out at high production rates in continuous reaction systems in which heat wastes can be minimized by heat integration between hot products and cold reactants. Reaction section can be easily integrated with efficient separation sections and the versatility of the continuous plant makes possible the utilization of mixed feedstocks.

Three main categories of HT processes can be considered, depending on the adopted operative temperature and pressure. Carbonization allows one to obtain a solid fuel at temperature ranging from 150 to 250°C and pressure lower than 2.5 MPa, liquefaction (temperature in the range 280-380 °C and pressures between 7 and 30 MPa) that

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brings to a biocrude oil and gasification that can be catalytic (from 370 to 500 °C) or thermally activated (T higher than 500 °C) and gives as a product a hydrogen rich syngas.

Particularly relevant for this study are hydrothermal liquefaction (HTL) processes performed under temperature condition compatible with the coupling of the chemical process with a concentrating solar (CS) plant.

HTL of microalgae is a promising process to produce third generation biofuels based on the treatment of the biomass in an aqueous environment in conditions approaching the critical point of water (22.1 MPa, 374 °C), i.e. at temperature and pressure in the ranges of 280-380 °C and 7-30 MPa, respectively. Alkaline compounds can be added as catalysts and reaction times can change from 10 to 60 min. During the treatment, the organic molecules are broken and rearranged, by decomposition and polymerization reactions. The final product is a viscous, water-insoluble, organic mixture, called biocrude or bio-oil, having a heating value ranging in the interval 30 to 40 MJ/kg and characterized by high heteroatom contents, notably oxygen and nitrogen, which must be removed to make the product suitable as a fuel. In particular, biocrude recovered from HTL processes has an oxygen content of 10 to 20% w/w that is significantly lower than that found in biocrude oil produced by fast pyrolysis of biomass at room pressure, where oxygen content is generally close to 50% (1).

Other products of HTL are: a water-soluble phase, a gaseous stream in which CO_2 and CO have a volume fraction of 93 and 4% respectively the rest being constituted by hydrogen and methane, and a solid residue containing inorganic salts and chars.

Conversely, one of the disadvantages of HTL processes is the elevated power required to heat a slurry with high water content to reaction temperatures (2, 3). The net amount of power required can be reduced by heat integration between inlet and outlet streams, but an external energy source is always necessary.

One of the possible sources of thermal energy is the sun, by using solar radiation to heat the slurry at operative temperature. The concept of solar chemistry (chemical processes in which the energy required to run the reactions is obtained from the solar radiation, both directly and indirectly) has been recently considered a promising route to synthesize environmentally friendly chemicals whose production is independent from fossil fuels. An interesting possibility in this sense is to use concentrating solar (CS) systems to direct solar radiation to the HTL process streams. The CS systems basically consists of solar collectors, focusing the solar radiation over solar receivers, and a heat transfer fluid to collect the high temperature heat and transfer it to the heat demanding process units. A suitable heat storage system is also required to maximize the "capacity factor" (productivity) of the solar plant, and to provide solar heat at the desired rate regardless the instantaneous solar radiation availability and fluctuations. More in detail, the mirrors of the solar field concentrate the direct solar radiation on the solar receiver set at the focal point (if point concentrators are adopted) or at the focal line (if linear concentrators are used). The heat transfer fluid removes the high temperature solar heat from the receiver and it is afterwards collected into an insulated heat storage tank to be pumped, on demand, to the heat users where it releases its sensible heat. Finally, the heat carrier fluid is stored into a lower temperature tank ready to restart the solar heat collection loop. A proper dimensioning of the heat storage system allows to drive the HTL process continuously at the designed working conditions independently on the intermittent nature of the solar radiation.

In this study, the utilization as heat transfer fluid (HTF) of a ternary mixture of $Ca(NO_3)_2/KNO_3/NaNO_3$ 43/42/15 w/w molten salts was considered. It can work in the temperature range 180-420 °C that is quite compatible with the temperature adopted for HTL processes and is characterized by a melting temperature as low as 120 °C which allows more economic operation and management of the solar plant.

The coupling of a CS plant, using molten salts as heat transfer fluids and storage medium, with a plant for hydrothermal liquefaction of microalgae has been studied. The general objectives of the study were the maximization of the thermal recovery from the hot reactor effluent, the estimation of the minimum selling price of the produced biocrude to compare it with the cost of similar streams produced in conventional processes.

MATERIALS AND METHODOLOGY

Process Layout

The HTL plant had to process 10 kT/y of microalgae and its schematic layout is depicted in Fig. 1. Two feeding streams, a concentrated microalgae aqueous slurry at 30% w/w of biomass (stream 1, mass flow rate 1.07 kg/s) and a pure water stream at 25 °C and 0.1 MPa (stream 2, mass flow rate 1.07 kg/s) were considered. Both streams are first compressed to 23 MPa at room temperature. The adopted heat exchanger configuration allowed one tomaximize the heat recovery from hot stream from the reactor thus minimizing the size of the solar field. Stream 2 is heated in two consecutive heat exchangers, HX2 using the hot cyclone effluent as heating medium, and HX1 using molten salts heated by the solar field as HTF. Stream 1 is sent to heat exchanger HX3 to be pre-heated by the residual heat stored in the stream effluent from HX2. Compressed and heated streams 1 and 2 are rapidly mixed to obtain a 15% w/w microalgae slurry at 350 °C, which is sent to the reactor. Heat effects inside the reactor were considered negligible according to the literature (2-4) and the reactor itself was modeled as a single tube adiabatic tubular reactor.

Inside the reactor microalgae are converted into the products: biocrude, aqueous phase products, gas and solid residue. The stream exiting the reactor is sent to a cyclone, considered adiabatic too, where the solid fraction is removed. The purified stream is then sent to HX2 and HX3 where it is cooled by heating stream 2 and 1 respectively. Stream recovered from HX3 was at 145°C and 23 MPa. Under this condition the dielectric constant of water is about 46 and biocrude demixing was considered to be completed so that a biphasic compressed mixture was sent to the flash valve SX to be expanded to the vapor pressure of water at the expansion temperature.

The cooled products are finally expanded to atmospheric pressure and conveyed to a sedimentation vessel where the three phases, biocrude, aqueous phase and gas, are separated by gravity. The gas phase is sent to a catalytic combustion step in order to completely oxidize it, the solids are disposed, the aqueous phase is recycled back to the microalgae cultivation system as it contains water soluble compounds suitable to be reused as nutrient.

The energy necessary to heat the system is provided by a solar field composed by parabolic linear collectors. The collectors are arranged in different rows connected in parallel to provide the desired power during solar radiation hours. The fluid flowing inside the collectors is a molten salts mixture called Hitec XL® (ternary mixture of $Ca(NO_3)_2/KNO_3/NaNO_3$ 43/42/15 w/w). The molten salts flow from the cold storage tank of the solar plant, at the nominal temperature of 340 °C, in the solar field, with a flow rate suitable to reach the nominal outlet temperature of 410 °C. Then, the hot molten salts are conveyed to the hot storage that allows to store the surplus of energy collected by the solar field during high insulation periods.

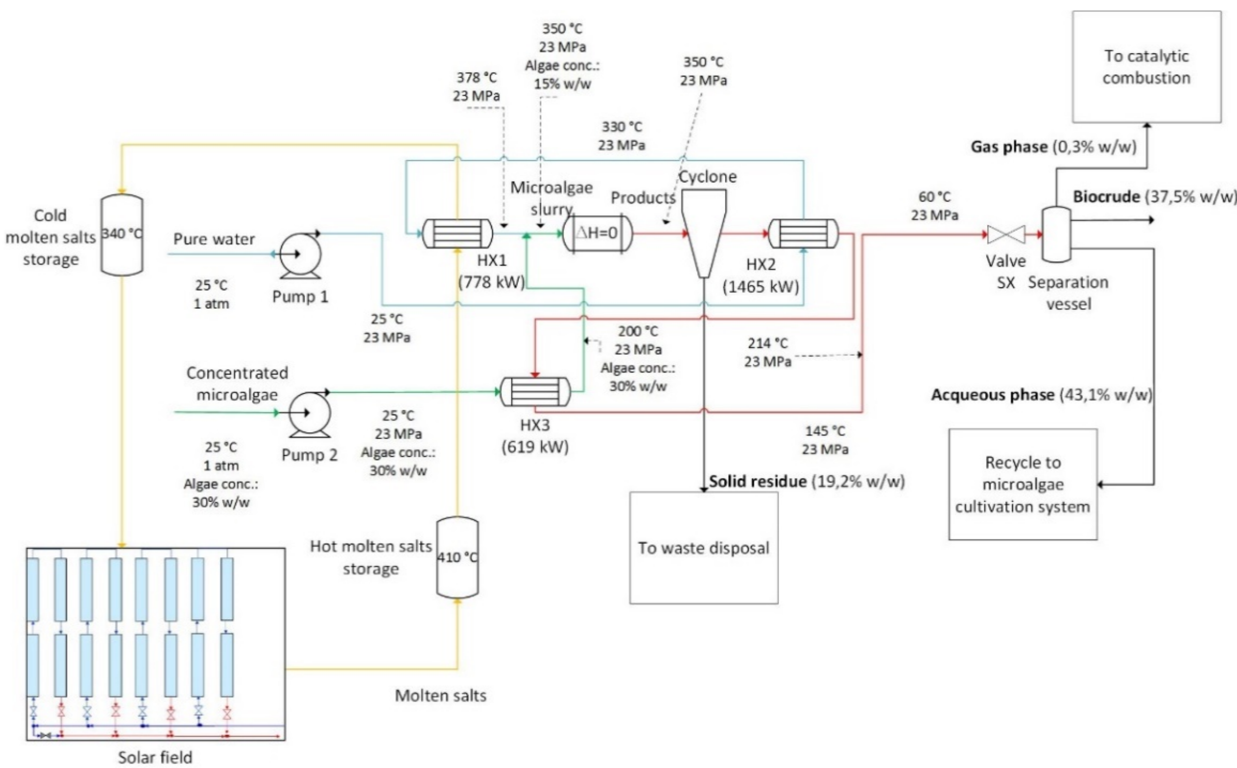

FIGURE 1. Schematic description of the solar HTL plant.

Kinetic Model and Reactor Design

All calculations were performed using Matlab® and Microsoft Excel® software. Thermodynamic and transport properties of water were obtained through the use of XSteam software. Mass and energy balances were performed in order to determine the energy inputs and outputs of the process, these information were used to design the main equipments (reactor and heat exchangers). The required power, the chemico-physical and transport properties of the thermal fluid and its temperature variation between inlet and outlet of the solar field were used to calculate the number of solar collectors and their layout.

The yields of the products of microalgae HTL were estimated with the kinetic model proposed by Valdez and Savage that consider the biomass as a mixture of the three main biochemical constituents (proteins, carbohydrates, and lipids) and ashes, the latter being considered as an inert (5). The model parameters were obtained from the fitting of experimental data of yields obtained from HTL of three different microalga strains, *Scenedesmus sp.*, *C. Prothecoides* and *Nannochloropsis sp*. In our study we selected *Scenedesmus sp.* as model feedstock whose composition can be summarized as follows: proteins 50% w/w, carbohydrates 31% w/w, lipids 8% w/w and ashes 11% w/w (5).

The kinetic model was numerically integrated using the finite difference method with a time step of 0.001 min. Any temperature change inside the reactor was neglected as, it was considered, that the heat absorbed by HTL reaction is negligible compared to the enthalpy required to heat the aqueous slurry (2, 3).

From the integration of the equations of the aforementioned kinetic model under considered operative conditions, an asymptotic behavior of biocrude yield was observed that is typical of a first order kinetic process. In order to find a good compromise between biocrude yield and reactor volume, the optimal value of reaction time was considered as that necessary to reach a yield corresponding to 95% of the maximum value. By this approach an average residence time of 4 minwas estimated to obtain yields of biocrude, aqueous soluble products, gas and solid residue of 37.5%, 43%, 0.5% and 19% respectively The volume V of the HTL reactor was estimated considering the aforementioned residence time and the volumetric flow rate of the fed slurry. Given the limited concentration of microalgae in the combined feed obtained from the mixing of streams 1 and 2, the density of pure water was used to perform calculations.

The internal diameter D and the total length L of the high-pressure tubular HTL reactor were fixed in order to have a thickness of the reactor wall smaller than 5 cm to limit the cost of apparatus. Pressure drops inside the reactor were estimated using the Colebrook equation under the assumption that transport properties of the feed are the same of pure water neglecting the presence of the biomass whose mass fraction in the slurry is lower than 5% w/w. The values were always very low with respect to the working pressure because of the rather low linear velocity (33.3 cm/s) necessary to have 4 min residence time in the reactor.

The cost of the reactor was estimated calculating its weight W_v from the volume of the shell considering a value of 7833 kg/m^3 for the density of carbon steel (6). The unit mass cost C_v of the apparatus was estimated by the following equation in which carbon steel is considered as material:

$$C_v=73(W_v)^{-0.34}$$

The bare module cost was estimated multiplying C_v by the total weight W_v and applying correction factor from carbon steel to AISI 316 that was considered as construction material in all parts of the HTL plant.

Economic Analysis

The estimation of capital cost for the HTL section of the plant was performed using Guthrie method (7), where the capital expenditure (CAPEX) is computed as a function of the cost of each single equipment of the plant. The price of each equipment was estimated from correlations found in the literature (6, 7), that relates the equipment cost with its size. The bare module cost (BMC), i.e. the total cost to be afforded to install each equipment taking in consideration labor cost, insurance, general expenses, etc., was obtained by multiplying the purchased equipment cost by a suitable correction factor that also considers that apparatuses are made of AISI 316 stainless steel and rated to work at high pressure.

In order to actualize the cost of the equipment, a value of the Chemical Engineering Plant Cost Index (CEPCI) of 579.7, referring to October 2014, vas used (8).

The cost of the solar field was calculated by ENEA staff, the estimated value was considered as the CAPEX for the solar field. The CAPEX of the HTL section and of the solar field were summed to obtain the value for the whole plant.

The operating expenses (OPEX) comprehend the costs associated with raw materials, waste disposal, utilities, labor and other. They were estimated from correlations present in (7) using the CAPEX, the number of equipment pieces and mass and energy flows. The purchase cost of microalgae was considered to be 0.3 €/kg (3), and the cost of electric energy was considered to be 0.1727 €/kWh (9) the cost of disposal of aqueous phase products was neglected, as it was assumed that these products were recycled back to the microalgae cultivation system. The working capital (WK), i.e. the amount of money required to make operative the plant, was assumed to be 20% of the CAPEX.

In order to estimate the minimum fuel selling price (MFSP) of the biocrude, a cash flow analysis was performed. It was taken in consideration a plant life of 25 years, the interest rate on the investment was considered to be 10% and the taxation rate on revenue 40%. The minimum selling price was calculated through the use of the Excel solver by imposing the net present value (NPV) of the project at the end of its life to be equal to zero.

RESULTS AND DISCUSSION

Streams 1 and 2, whose flowrates are 1.07 kg/s each, must be compressed from atmospheric pressure to 23 MPa. Under the assumption that density of microalgae in the slurry is the same as water, and considering an overall pumping efficiency of 0.9, the power required to compress the streams was calculated to be 72.6 kW.

Heating 2.14 kg/s microalgae slurry at 15% w/w from 25 to 350 °C requires 2800 kW of thermal power, most of which can be recovered by heat integration with the product stream that exits from the reactor at 350 °C. As the process is considered isothermal, the pure water stream is preheated in the shell of HX2 by the hot products circulating in the tubes. Temperature of pure water increases from 25 to 330 °C considering a minimum temperature difference between the streams of 20 °C. In this step 1465 kW are transferred between the currents and the products are cooled to 214 °C. Another step is the preheating of the 30% w/w microalgae slurry from 25 to 200 °C using residual sensible heat in the products (HX3). During this heating step, the kinetics of HTL process can be neglected since residence time in HX3 is lower than 15 s. The power transferred in this unit is 619 kW and product stream is further cooled to 145 °C. To obtain a 15% w/w slurry at 350 °C by mixing the pure water and the concentrated slurry pre-heated at 200 °C, the former must be further heated from 330 to 378 °C providing it 778 kW of thermal power by heat exchange in HX1 with the HTF from the solar field.
Heat exchangers were sized using the Kern method and their features are summarized in Tab. 1.

TABLE 1. Heat exchangers design specifics

	HX1	**HX2**	**HX3**
Exchange area [m^2]	88	18	17
N° of tubes	1100	450	420
Tube diameter [mm]	4.6	4.6	4.6
Tube thickness [mm]	0.89	0.89	0.89
Tube length [m]	4	2	2
T^{tube}_{in} [°C]	330	350	25
T^{tube}_{out} [°C]	378	214	200
T^{shell}_{in} [°C]	410	25	214
T^{shell}_{out} [°C]	340	330	145
W^{tube} [kg/s]	1.07	2.04	1.07
W^{shell} [kg/s]	7.8	1.07	2.04
Q [kW]	778	1465	619

High pressure hydrocyclone was sized using correlations reported in the literature (10).

Bare module cost of the tubular reactor and hydrocyclone were estimated using the design procedure for pressure vessels reported in (6). Costs of all other equipments were estimated by the Gutrie methods (7). AISI 316 was considered as construction materials and all units contacted with high pressure streams were sized to operate at 23 MPa.

The grass root cost of the HTL plant (Tab. 2) was obtained using equation:

$$C_{GR} = 1.18 \sum C_{BM} + 0.5 \sum C_{BM}^{0} \quad (1)$$

Where C_{BM}^{0} is the bare module cost of the equipment at room pressure considering carbon steel as construction material.

By hypothesizing a temperature difference of 30 and 10 °C for the outlet and inlet section of HX1 respectively, molten salts inlet temperature in the solar field is 340 °C and the mixture must be heated up to 410 °C. Calculations performed considering a solar plant constituted by 3 parallel rows of linear parabolic solar collectors, each 200 m long, gave a solar fraction of power consumed to drive the process of about 47% and about 10% of the synthesized biocrude must be consumed as internal energy back-up.

Under these conditions a minimum selling price of the biocrude of 2.8 €/kg was estimated that is quite similar to that of biocrude obtained in not solar processes (11).

TABLE 2. Bare module cost of process equipment constituting the HTL plant.

Equipment	C_{BM} (USD) [2]
HX1	334000
HX2	255000
HX3	257000
Slurry pump (2 units)	262000
Pure water pump (2 units)	422000
Reactor	634000
Cyclone	177000
Separation vessel	184000
Total HTL Plant	3235000

[2]Bare module cost of the equipment referred to 2014 in USD, chemical engineering plant cost index CEPCI=579.8 (8).

CONCLUSIONS

A conceptual analysis of the coupling of a concentrating solar power plant with a chemical process for the hydrothermal liquefaction of 10 kT/y of microalgae was performed. The two plants were considered coupled by molten salt recirculation that granted energetic supply to the chemical process. Preliminary estimations considering a solar field constituted by 3 linear parabolic solar collector rows, 200 m long each, using a ternary molten salts mixture as heat transfer fluid led to a minimum selling price of biocrude of 2.8 €/kg that is quite similar to that of biocrude obtained in not solar processes. This result shows that solar driven HTL of biomass can be an interesting option for solar biofuel production, especially in countries with high direct solar radiation values: the application of a concentrating solar plant allows maximization of the biomass conversion to biofuel without any significant increase of the cost.

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