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Biorefinery process for hydrothermal liquefaction of microalgae powered by a concentrating solar plant: A conceptual study

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HIGHLIGHTS

- A concentrating solar plant drives the hydrothermal liquefaction of microalgae.
- Conventional chemical units can be coupled with solar heat.
- Costs of the solar plant marginally affect the cost of biocrude.
- Proposed strategy seems promising to store solar energy in biofuels.

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ABSTRACT

A conceptual analysis of coupling a concentrating solar power plant with a biorefinery process consisting in the hydrothermal liquefaction (HTL) of microalgae to biocrude was performed. The configuration of the CSP-HTL plant was designed to allow continuous operation considering 10 kT of microalgae processed each year using, for the first time, a ternary nitrate mixture as heat transfer fluid and storage medium in the temperature range of 340–410 °C.

With adopted models, the capital and operating costs of the solar plant marginally affect the minimum fuel selling prize (MFSP) of biocrude that decreases with the size of the solar field and of the thermal storage system provided that the scale of CS plant is large enough.

A MFSP of the biocrude of 2.19 US$/kg was estimated that is quite similar to that reported in the literature for more conventional processes of HTL of microalgae with capability similar to that considered in this study. This value for the MFSP is lower than that calculated for the same HTL plant in which part of the produced biocrude is used as bio-fuel to drive the process. These results indicate that the utilization of solar heat in an indirect solar reactor could be an interesting option to improve sustainability of the processes and to store solar energy in biofuels.

1. Introduction

The industrial sector accounted for 27% of the total global energy use in 2005 and the chemical and petrochemical industry shared 29% of this amount [1]. The concept of biorefinery has been proposed to make possible the utilization of biomass as source of renewable energy and chemicals in substitution of crude oil. In this context, the conversion of wet biomass into biofuels would be highly interesting but it is made unfavorable by the high heat demand to dry the raw material that, in conventional processes, cannot be recovered by heat integration, thus being a loss term in the global energetic balance of the process.

A possible solution to the aforementioned drawback is the utilization of hydrothermal (HT) processes which can be carried out in aqueous environment without the need of drying the feed. The hydrothermal liquefaction (HTL) of microalgae, generally carried out between 200 and 380 °C at pressures from 7 to 30 MPa, has been an object of significant investigation as reported in several reviews [2–8]. Its main product is a viscous organic liquid, called biocrude, having a heating value in the range 30–36 MJ/kg and characterized by high

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heteroatom contents, mainly oxygen and nitrogen that must be upgraded to meet standards to fuel modern engines.

Other products of the HTL process are a water-soluble phase, a gaseous stream primarily composed of carbon dioxide and a solid residue in which residual inorganic salts and chars accumulate. The CO_2 rich gaseous stream and the aqueous phase, that is characterized by high nitrogen and phosphorus content and by a significant concentration of soluble organics, can be recycled to the microalgae growth section of the plant provided that the latter is properly diluted using water recovered from the concentration steps of microalgae cultivation broth and that macro and micronutrients are added [9].

One major disadvantage of HTL processes is the large enthalpy required to raise the temperature of the aqueous biomass slurry [10,11]. Heat integration between inlet and outlet streams from the HTL reactor is reported to be a mandatory strategy to make the process net energy producer [12]. Regardless, an external heat source is always necessary and it can be obtained using a fraction of the produced biocrude as fuel but this strategy reduces the net biocrude production rate and the overall process efficiency.

From aforementioned considerations it seems reasonable to hypothesize that the sustainability of HTL would be improved if the enthalpy necessary to perform the process could be obtained from solar heat using an economical affordable plant configuration.

In this context, an interesting option is to use CS plant that operates at temperatures lower than 500 °C [13] i.e. compatible with the operating conditions of HTL of microalgae. These solar plants are equipped with suitable optical systems to collect and concentrate solar radiation onto a component, the receiver or solar absorber, where a heat transfer fluid (HTF) circulates. To satisfy the heat demand also during cloudy periods and overnight, thermal energy storage (TES) systems can be used. The integration of CS plants with TES systems maximizes the productivity, often called "capacity factor", of the solar plant and makes it possible to provide solar heat "on demand" and at the desired rate regardless of the natural variability of the solar source [14,15]. Therefore, the HTF removes the high temperature solar heat from the receiver and it is afterwards stored into an insulated heat storage tank (hot tank). The hot fluid is pumped, on demand, to the thermal load where it releases sensible heat, to produce electricity and/or to drive chemical processes. After the heat exchange, the cold HTF is stored into a lower temperature tank (cold tank), ready to restart the solar heat collection loop. Besides the adoption of TES systems, CS plants can be "hybridized" with a back-up source to enhance their capability of satisfying the heat requirement in the absence of solar radiation with satisfactory results. Thus, it is possible to drive steadily a continuous chemical process with solar energy avoiding daily start-up and shut down operations. Clearly, for a given site (i.e. a given solar radiation profile), and heat load (i.e. the process heat load), the solar field area, the heat storage capacity and the back-up fuel rates are three dependent parameters that must be optimized in the CS plant design.

Solar heat is an interesting option to drive chemical processes. Most of the researches on this topic were devoted to the solar assisted production of hydrogen or syngas from methane, ethanol or biomass. [16–19] Azadi studied the hydrothermal gasification of glycerol, chosen as a biomass model compound, in a double pipe tubular catalytic reactor using a binary "solar salt" mixture (60% $NaNO_3$ and 40% KNO_3) heated by solar heat. He found that molten salts are effective HTFs for hydrothermal gasification reactions due to their fast heating rates. Moreover the integration of the solar heat in the process decreased the use of fossil fuels and the overall greenhouse gas emission of the plant and allowed a better utilization of the solar energy stored in the HTF with respect to power generation by steam turbines. [20].

To our knowledge only one study is reported in the literature on the possibility of integrating solar energy in the HTL of microalgae [21]. In that study, the basic idea was to use the aqueous slurry of microalgae as HTF in parabolic through concentrators to bring the mixture at the reaction temperature. The liquefaction reaction is then completed in a batch adiabatic reactor. Due to the simple configuration of the plant a quite low minimum fuel selling price of 1.23 US$/kg was estimated. However, the long term operability of solar concentrators, challenged by the precipitation of the salt content of the aqueous slurry owing to the low dielectric constant of hot compressed water at near critical conditions [22], was not assessed. Moreover the plant has no storage system and can process batchwise a limited amount of microalgae every day (0.2 T/d) leading to a quite limited productivity for the bio-crude fuel. Hence, further studies are necessary to assess a process of HTL of microalgae to biocrude coupled with a CSP and characterized by high productivities and continuous operations.

In this study, we have investigated a different process configuration that couples a CS plant based on parabolic through technology with a plant for hydrothermal liquefaction of microalgae under the constraint of maximizing the thermal recovery from the hot reactor effluent. A ternary molten salt mixture, $NaNO_3$-KNO_3-$Ca(NO_3)_2$ 15/43/42 w/w, working in the temperature range of 290–420 °C, was considered as a HTF in the linear parabolic collectors and as a heat storage medium in a two-tank TES system. Compared to thermal oils, the ternary molten salts mixture is environmental friendly and cheaper; additionally, it has a lower freezing temperature (lower than 140 °C) than traditional binary "solar salt" mixtures (with freezing temperature higher than 220 °C) thus leading to easier management and higher performance of the linear CS plant.

The process configuration proposed in this study is based on the concept of indirect solar reactor i.e. a conventional chemical reactor that is heated by solar heat through the intermediacy of the HTF. This strategy makes possible to optimize independently the performances of the solar and of the chemical plant and it is compatible with large scale continuous operation of the chemical plant despite the transient behavior of solar radiation. Another important feature is that it can be applied to any chemical process whose operating temperature is compatible with the stability interval of the molten salt mixture.

The conceptual analysis was performed to decrease as much as possible capital and operating expenses and it allowed us to assess the most critical sections of the combined plants from the techno-economic point of view. With this strategy, we could estimate the minimum selling price of the produced biocrude, which resulted comparable with the cost of biocrude produced by more conventional biorefinery processes thus showing that the use of the solar plant, with the configuration proposed in this study, does not affect negatively the economic sustainability of the process.

2. Materials and methodology

2.1. Process layout

In this study, an integrated CS-HTL plant sized to process 10 kT of microalgae is considered. The schematic layout of the process is presented in Fig. 1. The proposed plant configuration is based on the equipments used in experimental studies on the hydrothermal conversion of microalgae and ligno-cellulosic biomass in continuous lab scale reaction systems [23–26]. Two feeding streams, pure water at 25 °C and 0.1 MPa (stream 1, mass flow rate 1.07 kg/s) and a concentrated microalgae aqueous slurry at 30% w/w (stream 2, mass flow rate 1.07 kg/s) were considered.

Both streams are compressed to 23 MPa at room temperature by pumps 1 and 2. Heat exchangers were configured to maximize the heat recovery from the hot stream from the reactor thus minimizing the size of the solar field. Stream 1 is heated in two consecutive heat exchangers, HX2 using the hot effluent from the cyclone as heating medium, and HX1 using molten salts heated by the solar field. Stream 2 is sent to heat exchanger HX3 to be pre-heated by the residual enthalpy stored in the effluent from HX2. After compression and heating, streams 1 and 2 are rapidly mixed to obtain a 15% w/w microalgae slurry at 350 °C which is sent to the reactor. According to the literature