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PARAMETERIZATION OF CSTR AND PFR REACTORS IN THE LIQUEFACTION OF MICROALGAE FOR BIO-OIL PRODUCTION

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Highlights:

- Using microalgae cultivated in wastewater to produce bio-oil is a potential technology for biofuel production.
- Optimizing the operating conditions and reactor design can improve the economic viability of the process.

Keywords: Algae; Biorefineries; Optimization.

INTRODUCTION

The transition towards a more sustainable energy matrix that generates less environmental impact is a global goal, motivated by the need to reduce greenhouse gas emissions and diversify the energy matrix. In this context, biorefineries stand as key elements in efficiently converting renewable biomass into high-value-added products, especially biofuels. Additionally, microalgae are emerging as a source for biofuel production, due to their rapid growth, high photosynthetic efficiency, and carbon dioxide (CO_2) absorption during growth. A key technology in this field is hydrothermal liquefaction (HTL) of microalgae, which converts proteins, carbohydrates, and lipids in microalgae into bio-oil without pre-treatment (Chen & Quinn, 2021). In addition to bio-oil, gaseous, aqueous, and solid (biochar) phases are formed. The gaseous and aqueous phases have the potential to be reused in the microalgae cultivation system in order to reduce the demand for resources (Chen et al., 2017). While biochar is usually produced in small quantities, it can be a source of carbon credits (Kwapinski, 2019). Although HTL technology using microalgae has the potential to be implemented at an industrial level, the high investment required for the HTL process represents a significant barrier to its competitiveness with conventional fuels (Chen & Quinn, 2021). In this regard, this study focuses on optimizing the operational and dimensional parameters of the HTL reactor to reduce the cost of bio-oil by considering feedstock, equipment, and energy costs, alongside the revenue from the final products.

METHODOLOGY

The HTL process converting microalgae into bio-oil was simulated using Aspen Plus software (version 14, Aspen Technology Inc., USA) for a Continuous Stirred Tank Reactor (CSTR) and a Plug Flow Reactor (PFR). Thermodynamic properties of the involved components were estimated using the Soave-

Redlich-Kwong (SRK) equation of state (Borazjani et al., 2023). A kinetic model proposed by Borazjani et al. (2023) was employed, based on the reaction pathways illustrated in Figure 1.

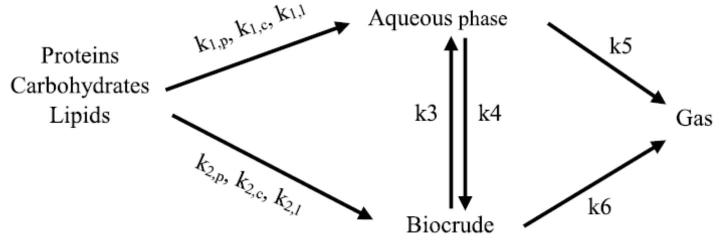

Figure 1. Reaction pathways for HTL of microalgal biomass. Proteins, carbohydrates, and lipids are converted into the aqueous phase ($k_{1,p}$, $k_{1,c}$,$k_{1,l}$) or biocrude ($k_{2,p}$, $k_{2,c}$, $k_{2,l}$). Interconversion between the aqueous phase and biocrude is represented by k_3 and k_4. Gas formation occurs from the aqueous phase (k_5) and from biocrude (k_6).

This model considers first-order reactions for the conversion of proteins, lipids, and carbohydrates into aqueous, oil, and gas phases. The activation energies ($E_{a,i}$) and pre-exponential factors ($A_{0,i}$) for each reaction step were calculated using the Arrhenius equation (Equation 1) and are detailed in Table 1.

$$k_i=A_{0,i} \exp\left[-\frac{E_{a,i}}{RT}\right] \qquad \text{Eq 1}$$

Where, k_i is the rate constant for reaction i, $A_{0,i}$ is the pre-exponential factor, $E_{a,i}$ is the activation energy, R is the universal gas constant, T is the temperature in Kelvin.

Table 1. Kinetic parameters for the conversion of microalgal biomolecules into biocrude, aqueous phase, and gas, as described in Figure 1.

Reactions	$E_{a,i}$(kJ/mol)	Ln A (1/min)	Reactions	$E_{a,i}$(kJ/mol)	Ln A (1/min)
Protein → Aq	17.00	3.21	Carbohydrate → Oil	73.28	7.11
Lipid → Aq	14.01	2.06	Oil → Aq	28.56	4.61
Carbohydrate → Aq	15.00	2.99	Aq → Oil	22.14	3.55
Protein → Oil	49.98	6.32	Aq → Gas	62.99	8.51
Lipid → Oil	41.98	4.38	Oil → Gas	118.75	7.99

A FORTRAN subroutine was integrated into the simulation to optimize operational and design parameters, specifically temperature (250–400 °C), feed flow rate (54,571.45–89,285.45 kg/h), and reactor volume (0.5-3.5 m^3). The objective was to maximize profit from bio-oil production, defined as the difference between the revenue from selling the bio-oil and the cost of purchasing the reactor. The profit function (Z) is represented in Equations 2 and 3 for the PFR and CSTR, respectively.

$$Z_{PFR} = 7920(0{,}59OBC) - 1{,}5((10\verb|^|(3{,}3496 + 0.7235\log10(V) + 0{,}0025(\log10(V))\verb|^|2)))/7 \qquad \text{Eq 2}$$

$$Z_{CSTR} = 7920(0{,}59OBC) - 1{,}5((10\verb|^|(4.1052 + 0.5320\log10(V) - 0.0005(\log10(V))\verb|^|2)))/7 \qquad \text{Eq 3}$$

In these equations, OBC is the bio-oil production capacity (L/h), V is the reactor volume (m^3), 7,920 represents the total operating hours per year (330 days/year × 24 hours/day), the factor of 1.5 accounts for additional costs, the division by 7 reflects equipment depreciation over a 7-year period.

The acquisition cost of the reactors was calculated using the method outlined by Turton et al. (2018), adjusted for inflation using the Chemical Engineering Plant Cost Index (CEPCI) for 2021 (761.4). Bio-oil production was assessed under continuous operation, assuming 24-hour shifts for 330 days annually, totaling 7,920 operational hours per year.

RESULTS AND CONCLUSIONS

Simulation results show that, after optimizing the operational and design parameters for HTL of microalgae into bio-oil (Figure 2), CSTR configuration yields a maximum profit of USD 8.91 million, approximately four times higher than the USD 2.22 million achieved with PFR. The optimal conditions for the CSTR were a reactor volume of 3.5 m³, a feed flow rate of 71,428.57 kg/h, and an operating temperature of 400 °C. In contrast, the PFR reached maximum profitability with a reactor volume of 0.5 m³, a feed flow rate of 89,285.75 kg/h, and a temperature of 372 °C.

These findings suggest that the CSTR is more economically favorable for large-scale bio-oil production via HTL of microalgae. The higher profit associated with the CSTR can be attributed to its larger reactor volume and higher operating temperature, which enhance conversion efficiency and bio-oil yield. Although the PFR operates at a higher feed flow rate, its smaller volume and lower temperature may limit its profitability.

Despite these promising results, challenges remain in scaling up bio-oil production from microalgae via HTL. The complexity of the HTL process and limited comprehensive kinetic data introduce uncertainties in the simulations. Further experimental studies are necessary to validate the kinetic models and optimize reactor designs.

In conclusion, this study identified improved operational conditions and reactor designs that maximize the profitability of bio-oil production from microalgae using HTL. The comparative analysis demonstrates that under the simulated conditions, the CSTR offers superior economic benefits over the PFR. Optimizing variables such as temperature, feed flow rate, and reactor volume is crucial for enhancing the process's economic viability. This work contributes to this field of research by developing efforts in scaling up bio-oil production from microalgae, thereby supporting the advancement of sustainable biofuel technologies.

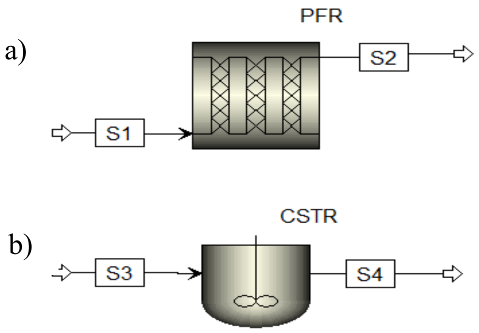

Figure 2. Reactors used in the parametric study for the conversion of microalgae to bio-oil. (a) Plug Flow Reactor (PFR)**:** The feed stream (S1) enters the reactor, where the reaction progresses along the length of the reactor, and the product stream (S2) exits. (b) Continuous Stirred Tank Reactor (CSTR): The feed stream (S3) is introduced into the reactor, which maintains uniform mixing throughout, and the product stream (S4) exits.

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