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Combined algal processing: A novel integrated biorefinery process to produce algal biofuels and bioproducts

Tao Dong, Eric P. Knoshaug, Ryan Davis, Lieve M.L. Laurens, Stefanie Van Wychen, Philip T. Pienkos *, Nick Nagle

National Bioenergy Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO, USA

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ABSTRACT

The development of an integrated biorefinery process capable of producing multiple products is crucial for commercialization of microalgal biofuel production. Dilute acid pretreatment has been demonstrated as an efficient approach to utilize algal biomass more fully, by hydrolyzing microalgal carbohydrates into fermentable sugars, while making the lipids more extractable, and a protein fraction available for other products. Previously, we have shown that sugar-rich liquor could be separated from solid residue by solid–liquid separation (SLS) to produce ethanol via fermentation. However, process modeling has revealed that approximately 37% of the soluble sugars were lost in the solid cake after the SLS. Herein, a Combined Algal Processing (CAP) approach with a simplified configuration has been developed to improve the total energy yield. In CAP, whole algal slurry after acid pretreatment is directly used for ethanol fermentation. The ethanol and microalgal lipids can be sequentially recovered from the fermentation broth by thermal treatment and solvent extraction. Almost all the monomeric fermentable sugars can be utilized for ethanol production without compromising the lipid recovery. The techno-economic analysis (TEA) indicates that the CAP can reduce microalgal biofuel cost by $0.95 per gallon gasoline equivalent (GGE), which is a 9% reduction compared to the previous biorefinery scenario.

1. Introduction

Oleaginous microalgae are well known as promising candidates for renewable energy production mainly because of high biomass productivity and lipid content [1]. Microalgal biofuel research is generally centered on two distinct conversion pathways: algal lipid upgrading (ALU) and hydrothermal liquefaction (HTL). Both pathways target hydrocarbon fuel products [2,3,4,5,6]. It has been realized that the high cost of algal biomass is a major obstacle that impedes the commercialization of algal biofuel production [7]. Reducing the costs for algal biofuel production is a significant goal for the Department of Energy (DOE) that is outlined in the outlook presented in the multi-year program plan [8].

Currently, increases in lipid productivity, achieved primarily through improved growth rates or lipid content, are unlikely to reduce production costs to prices competitive with petroleum-based fuels. Improvements in cultivation capital expenditures (CAPEX) and in harvest costs can also help reduce costs, but further reductions in costs can be achieved by more complete utilization and valorization of all algal cellular components rather than relying solely on the lipid fraction [2,7]. Likewise efficient conversion and upgrading for all of the algal components into fuels and value-added chemicals can significantly reduce both production costs for algal biofuels and risks to stakeholders.

By applying mild processing conditions, microalgal biomass can be fractionated into three major streams: lipid, carbohydrate and protein, which can be converted into respective (co-)products with added-value. Previously, we successfully demonstrated an acid-based fractionation process for algal biomass in a Parallel Algal Processing (PAP) schematic [2] (and Fig. 1a). We previously demonstrated that dilute acid pretreatment can effectively hydrolyze algal structural and storage polysaccharides to release monomeric sugars (primarily glucose and mannose) into an aqueous stream, which was separated from solid residue (rich in lipids and protein) by solid/liquid separation (SLS). The sugars released in the liquor phase could be fermented to ethanol (or higher value co-products), while lipids could be recovered from the solid fraction using hexane extraction leaving a residue stream enriched in protein. The value of the sugar and lipid streams has been previously calculated based on sugar fermentation to ethanol and hydrodeoxygenation of lipids to a renewable diesel blendstock [2]. The value of amino acids in the protein stream can be valorized by conversion to branch-chained higher alcohols [9], anaerobic digestion [10], or other applications [11]. These cellular components can be upgraded into fit-for-use hydrocarbon based fuels and value-added co-products.

In the previous processing design approach [5], it has been indicated through process modeling that the liquor entrapped in the solid cake after SLS contains a considerable amount of sugars that cannot be

* Corresponding author at: National Bioenergy Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA.
E-mail address: philip.pienkos@nrel.gov (P.T. Pienkos).

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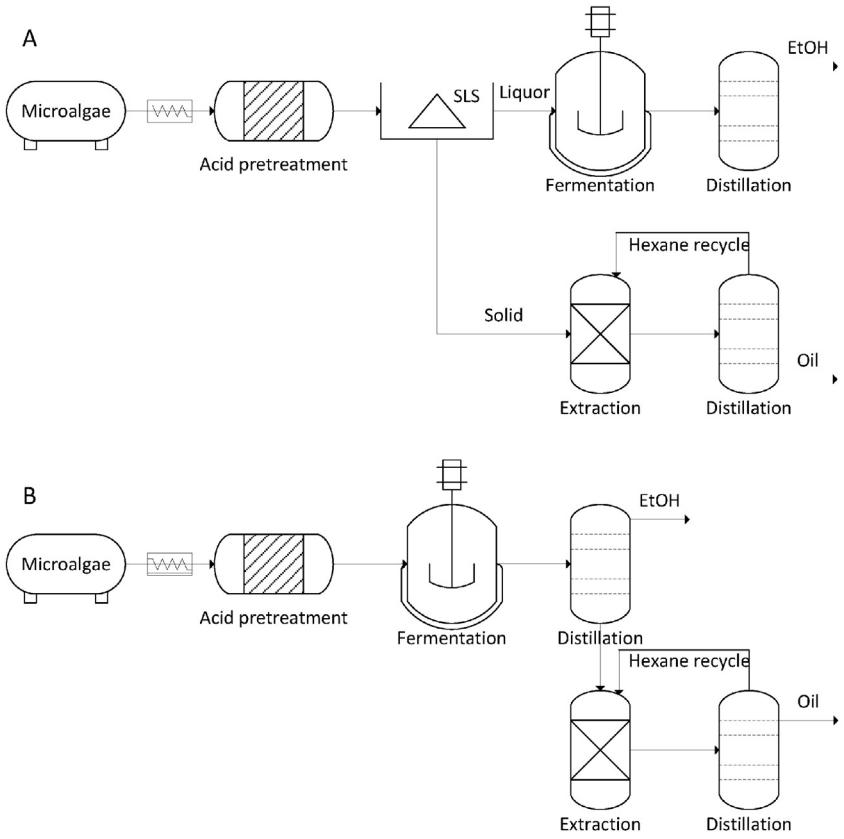

Fig. 1. Process flow diagrams for Parallel Algal Processing (PAP) and Combined Algal Processing (CAP) (A): PAP and (B): CAP.

used for fermentation without a costly washing step, resulting in a loss of overall fuel yield. To fully recover the hydrolyzed sugar for fermentation, a cost-effective approach is needed to improve the valorization of the carbohydrate stream to further reduce the cost of microalgal biofuel production.

The objective of this work is to investigate experimentally the process yields and cost impact of integrating a fermentation approach with subsequent lipid extraction using a Combined Algal Processing (CAP) configuration (Fig. 1b). In the dry-grind corn ethanol industry, whole grains are ground, starch is hydrolyzed enzymatically, and the resulting slurry is used as a feedstock for ethanol fermentation. Ethanol is distilled from the fermentation beer which contains oil and other nonvolatile residues. Then, oil can be recovered from the stillage [12,13]. This process was rapidly adopted by a significant number of corn biorefineries, providing inspiration for us to modify our benchmark PAP scheme. In the integrated CAP configuration, by skipping the SLS unit, the whole slurry will be directly used for fermentation, after which ethanol and lipids can be recovered sequentially from the post-fermented broth. Our hypothesis is that the ethanol yield could be significantly improved by simplifying the processing. In addition, the capital and operating costs for SLS can also be avoided to reduce overall fuel cost. Our goal is to demonstrate that the highly integrated CAP configuration will lead to a higher total energy yield to fuels and a lower cost for algal biofuel production.

2. Materials and methods

2.1. Materials

Scenedesmus acutus (LRB-AP 0401) biomass was provided by Dr. J. McGowen at the Arizona State University. In brief, biomass was obtained in a controlled fashion in outdoor flat panel (650 L) photobioreactors in nitrate deplete cultivation media. Cultivation time after reaching nutrient deplete conditions depended on final target biomass composition desired, which, depending on the season, typically was 6 to 9 days for lipid accumulation under nutrient deplete conditions to reach the targets of ~40% each of carbohydrate and lipid content (batch number B.0401_1102012PBR2, 4–8 and B.0401_10242012_PBR3, Harvest#75). Harvesting the biomass was accomplished using centrifugation (Alfa Laval, Lund, Sweden) and the material was frozen until needed [14].

2.2. Biomass pretreatment

Pretreatment of the microalgal biomass was performed in a batch-type reactor, a 4-L (2-L working volume) ZipperClave® (ZC) reactor (Autoclave Engineers) previously described [2,15,16]. Steam was directly injected into the bottom of the reactor through ports in a rotary-plow type agitator and constant temperature was achieved by controlling the steam pressure in the reactor. The ZC reactor is also equipped with an electrical heating blanket set at reaction temperature to lessen steam condensation due to heat losses through the reactor wall. The contents within the ZC reactor typically reached reaction temperature within 5 to 10 s of starting the steam flow as measured by two thermocouples, one inserted into the bottom and one near the middle of the reactor. At the end of pretreatment, the steam pressure was slowly released through a condenser over a period of 15 to 30 s to eliminate boil-over while still allowing for steam escape to reduce slurry dilution by condensate. The ZC is able to pretreat biomass at high solid concentrations using direct steam injection for rapid heating and mixing, which are all important process parameters for an economical commercial reactor.

A total solid content of starting biomass paste was determined at 105 °C using a Mettler-Toledo SP precision infrared balance (Columbus, OH). Wet algal paste (300 g), H_2SO_4 and water were sequentially added to the sample canister achieving a final solids loading of 25% (*w*/*w*) and

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