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Design of an optimal process for enhanced production of bioethanol and biodiesel from algae oil via glycerol fermentation

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HIGHLIGHTS

- Algae are used to produce simultaneously ethanol, biodiesel.
- Glycerol is a byproduct that can be further used to increase the yield to fuels.
- Glycerol fermentation to ethanol almost doubles its yield.
- The integrated facility is competitive with other uses of glycerol to produce methanol or ethers.

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ABSTRACT

In this paper, we optimize a process that integrates the use of glycerol to produce ethanol via fermentation within the simultaneous production of biodiesel and bioethanol from algae. The process consists of growing the algae, determining the optimal fraction of oil vs. starch, followed by oil extraction, starch liquefaction and saccharification, to sugars, oil transesterification, for which we consider two transesterification technologies (enzymes and alkali) and the fermentation of sugars and glycerol. The advantage of this process is that the dehydration technologies are common for the products of the glucose and glycerol fermentation. Simultaneous optimization and heat integration is performed using Duran and Grossmann's model. The fermentation of glycerol to ethanol increases the production of bioethanol by at least 50%. The energy and water consumptions are competitive with other processes that either sell the glycerol or use it to obtain methanol. However, the price for the biofuels is only competitive if glycerol cannot be sold to the market.

1. Introduction

The use of the byproducts from biorefineries has become very important for their profitability since first generation biofuels. In particular, the production cost of biodiesel is highly dependent on the price of glycerol. For some time, the wide range of uses of the glycerol and its limited production conferred it a reasonably high price. However, the increase in the production of biodiesel has created an excess saturating the market [1] and reducing the price of glycerol to values of $0.102/lb [2]. Based on the previous work by the authors [3,4], the production cost of biodiesel would increase $0.15/gal if the glycerol drops to this price. There are a number of alternative uses for the glycerol within the biorefinery. On the one hand we can generate syngas and later methanol so that we can reduce the dependency on fossil based raw materials of the current biodiesel production processes [5]. Another feasible alternative is the transformation of glycerol into fuel oxygenates by means of etherification and esterification reactions enhancing the production of diesels substitutes [6–15]. However, there is an even simpler integration option, the fermentation of glycerol to ethanol [16–19]. In this way we already have most of the technologies in place and we can use it for the production of biodiesel through ethanolysis. Furthermore, we enhance the production of bioethanol from algae [20]. Alternatively, we could use glycerol as a source of carbon for the algae growing [21].

The challenge is to integrate the fermentation of glycerol within the biodiesel production facilities. Even though we can produce ethanol out of the glycerol for the plants that involve methanolysis or ethanolysis, the residue of methanol in the glycerol may complicate the purification process. Therefore, we focus on the integration of the ethanol obtained from the fermentation of

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Nomenclature

Ci	concentration of the chemical I in the reactor (mol/L)
Cpi	heat capacity
fc (j,unit1, unit2)	individual mass flow rate (kg/s)
F (unit1,unit2)	mass flow rate (kg/s)
Pi	partial pressure of component i (bar)
T (unit1,unit2)	temperature of the stream from unit 1 to unit 2 (°C)
x (J,unit1,unit2)	mass fraction of stream from unit 1 to unit 2
λ	vaporization heat (kJ/kg)

glycerol with the processes that simultaneously produces bioethanol and biodiesel from algae. The algae processing to bioethanol and biodiesel is based on previous papers by the authors [3,4,20].

The aim of this paper is to optimize a process that starting with algae, produces ethanol and biodiesel using the glycerol to enhance the production of ethanol. We compare the results of this study with the different integration alternatives that have been presented so far, namely, the use of glycerol to produce methanol, to produce fuel oxygenates or considering the production of glycerol as it is [5,15,20]. Therefore, the work also allows a discussion on the best use of glycerol. For the design of such an integrated plant we use mathematical programming techniques that allow us to account for the trade offs in the transesterification reaction related for instance to the excess of alcohol needed for the operation of the reactor. We divide the paper into 4 sections. First, we describe the process flowsheet. Next, we comment on the main modeling issues highlighting the glycerol fermentation to ethanol. Subsequently, we present the results and the comparison with different integration alternatives. Finally, we draw some conclusions.

2. Overall process description

We divide the process into four sections, algae oil production, ethanol production from starch, biodiesel production from oil, and finally glycerol fermentation to ethanol, which will be recycled to the dehydration step. Interesting reviews on the different stages are available in the literature [22].

The first stage includes the production of biomass (oil, starch, protein), see Martín and Grossmann [3] for further details. Algae are grown by injecting CO_2 into the water, which can be saline water so that the consumption of freshwater is reduced, together with air and fertilizers. The amount of water needed, the concentration of fertilizers is taken from the report by Pate [23], while the consumption of CO_2 depends on the growth rate, typically 50 g/m^2 d [24] and is given by the experimental results by Sazdanoff [25]. We assume that the dry algae biomass is composed of oil, up to a maximum of 60%w/w, starch and protein with a minimum of 10%w/w to be conservative [20,22,26]. Together with the algae, oxygen is produced and water is evaporated [23]. The energy consumed by the pond system is calculated based on the results by Sazdanoff [25]. Next, the algae are harvested from the pond. Recently, Univenture Inc. has presented an innovative technology capable of integrating harvesting and drying the algae with low energy consumption. It is based on the use of capillarity, membrane systems and paint drying to obtain 5% wet algae with a consumption of 40 W per 500 L/h. The biomass is mixed with cyclo-hexane and compressed so that oil is extracted and the biomass (starch and protein) is separated from the oil.

On the other hand, the starch follows liquefaction (85 °C) and saccharification (65 °C) to break down the polymers into glucose. Next, the glucose is fermented into ethanol at 38 °C. The solid phase, mainly protein, is separated from the liquid phase and is sold. The liquid phase, mainly ethanol and water, but containing other products in small amounts such as glycerol, succinic acid, lactic acid, is distilled in a multi-effect distillation column to reduce the consumption of energy and cooling needs in the purification of ethanol. The last stage for the production of ethanol is the final dehydration using molecular sieves. This section is common for the ethanol produced from the starch, as well as for that obtained from the fermentation of glycerol. Part of this ethanol will be used in the transesterification of the oil and the rest can be sold as biofuel. Details on the process can be found in Martín and Grossmann [20].

The production of biodiesel via ethanolysis of algae oil was described in Severson et al. [4]. Two interesting catalysis were identified, enzymes and KOH. Surface response models for the reactors were developed to evaluate the trade-offs related to the operating variables at the reactor, namely, temperature, excess of ethanol, catalysis load and composition, and its effect on the yield. Next, the mixture of ethanol, glycerol and biodiesel is distilled to recover and recycle the excess of ethanol used. The polar phase containing glycerol is separated from the non polar phase containing the biodiesel, and while the biodiesel is purified in a distillation column to remove mainly the oil remaining, the glycerol is sent to etherification. The main process constraints can be seen in Table 1.

Recently, it has been reported that glycerol can be fermented anaerobically to ethanol as main product using *Escherichia coli* [17–19,27]. Therefore, the byproduct of the synthesis of biodiesel from oil can be further converted to ethanol, increasing the liquid fuels production from algae following as main reaction Eq. (1)

$$C_3H_8O_3 \rightarrow C_2H_6O + H_2 + CO_2 \quad (1)$$

The gas phase is recovered separately and the liquid phase containing the ethanol, biomass and traces of other organic chemicals is purified. This liquid phase is similar to the one that is obtained from the fermentation of glucose, and thus we can use the same purification and dehydration scheme. We mix the liquid phases from both fermentors, and after the recovery of the biomass and protein, we dehydrate the ethanol using a three effect multi-effect distillation column and molecular sieves. In Fig. 1 we present a general flowsheet for the entire superstructure of the process.

3. Mathematical modeling

All the unit operations in the production process of liquid fuels and hydrogen from glycerol are modeled using surrogate models,

Table 1
Main operating constraints [3,4].

Equipment	Temperature limit
Alcohol separation column	Bottoms: < 150 °C Reflux ratio: 2–3
Biodiesel purification column	Top: <250 °C Bottoms: <350–375 °C Reflux ratio: 2–3
Phase separation	30–40 °C