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Design and economic analysis of a macroalgae-to-butanol process via a thermochemical route

Chinedu O. Okoli [a], Thomas A. Adams II [a,*], Boris Brigljević [b], Jay J. Liu [b]

[a] Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4L7, Canada
[b] Department of Chemical Engineering, Pukyong National University, 365 Sinseon-ro, Nam-gu, Busan 608-739, Republic of Korea

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ABSTRACT

In this work, a first of its kind assessment of butanol production from macroalgae through a thermochemical route is carried out. Different process configurations were designed and simulated in Aspen Plus to quantify their mass and energy balances. Furthermore, economic and environmental metrics such as the minimum butanol selling price (MBSP), and cost of CO_2 equivalent emissions (CO_2e) avoided were used to assess the potential of the different configurations under different market scenarios, with comparisons carried out amongst the configurations as well as against standard literature references of similar processes. Finally, a sensitivity analysis was used to assess the impact that changes in key parameters have on the considered metrics. The results show that configurations which import natural gas and electricity as utility sources alongside the macroalgae feedstock offer the lowest MBSP, however they do poorly when cost of CO_2e avoided is considered. On the other hand, the configurations which utilize only macroalgae offer the best potential for cost of CO_2e avoided but have the poorest values for MBSP. In addition, the cost of CO_2e avoided obtained for the best configurations are in line with literature references. However, the MBSP values are higher than literature references for butanol derived from cellulosic feedstock primarily due to the high ash content in seaweed. The sensitivity analyses results show that changes in gasoline prices have a very significant effect on the plant configurations in the South Korean market, but not as significantly in the United States market.

1. Introduction

Macroalgae or seaweed is a term used to describe non-vascular large aquatic photosynthetic plants, thus they differ from microalgae which are unicellular [1,2]. Globally in 2012, seaweed production was estimated to be about 24.9 million wet-metric tonnes (85–90% moisture content) with 96% coming from aquaculture production [3]. Most of the world's farmed macroalgae is produced in Asia, with 99% of the world's production coming from that region [4]. Macroalgae has traditionally been grown for use as edible food, or as a raw material from which hydrocolloids utilized in the pharmaceutical and food industries are extracted.

Recently, there has been an increased interest in growing macroalgae for use in biofuel production. This is because macroalgae, which is a feedstock for third generation biofuels, have fast growth rates with up to 4–6 harvest cycles per year. Unlike first and second generation biofuel feedstocks, macroalgae can be grown in the sea thus eliminating issues relating to land use and irrigation water [4]. Furthermore, macroalgae is preferable to microalgae (also a third generation biofuel feedstock) for biofuel production because its plant-like characteristics make it easier to harvest, and its high concentration of carbohydrates in comparison to microalgae make it a potentially better biofuel feedstock [2,5,6].

Several studies have been conducted by government research institutes around the world investigating the potential of macroalgae as a biofuel feedstock. One such preliminary study by the Energy Research Center of the Netherlands (ECN) investigated the feasibility of producing biofuels from macroalgae cultivated offshore in the North Sea [7]. The study recommended carrying out a pilot scale seaweed cultivation experiment in the North Sea to improve the technological and ecological know-how of seaweed production, and also endorses the development of biorefinery technologies for seaweed utilization including its conversion to chemicals and fuels. The Sustainable Energy Authority of Ireland also carried out a study which concluded that priority should be given to the large scale cultivation of macroalgae to ensure sufficient feedstock for biofuel production and avoid the negative impact that could occur on marine biodiversity by exploiting wild seaweed [8]. In another study carried out in the United States (U.S.)

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[*] Corresponding author.
E-mail address: tadams@mcmaster.ca (T.A. Adams II).

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by the Pacific Northwest National Laboratory, it was concluded that the U.S. has a high potential for producing macroalgae biomass based on the very high surface area of U.S. coastal waters and known rates of macroalgae production in other parts of the world [4]. However, the authors note that additional research into macroalgae cultivation, harvesting and conversion into fuel is needed. In South Korea, research into macroalgae biomass has been funded by the Ministry of Oceans and Fisheries since 2009 and has focused on offshore systems for large scale growth of macroalgae and their conversion to energy [9].

In the peer-reviewed literature several recent review studies have been carried out by researchers into the potential of macroalgae use for fuel or chemicals production. Lehahn et al. [10] used a modeling approach to investigate the global potential for macroalgae growth as identify areas for growth. They estimate that 98 gigatonnes per year dry weight of macroalgae can be grown globally over a surface area of approximately 10^8 km^2 and conclude that with near-future aquaculture technologies, offshore cultivation of macroalgae has huge potential to significantly provide fuels and chemicals for humans. Another point noted by some of these review studies was that despite the potential for macroalgae based biorefineries, technological improvements in the whole supply chain of macroalgae based biorefineries (such as seaweed cultivation, harvesting and transporting, pretreatment, and fuel conversion technologies) are needed for economically feasible macroalgae fuel and chemical processes [5,11,12].

Based on the conclusions from all these studies, there is a high motivation to conduct research into the technological and economical aspects of macroalgae conversion to fuels.

Currently, research efforts into biofuels suitable for gasoline replacement have shifted focus to butanol instead of ethanol because of advantages such as lower miscibility with water, higher heating value (HHV), and better compatibility with existing gasoline engines and fuel pipeline infrastructure [13,14]. Similar to first and second generation biofuel feedstocks such as corn and agricultural residue, butanol can be produced from macroalgae using either a biochemical or thermochemical route.

The conversion of macroalgae to butanol through the biochemical route is done via the acetone, butanol and ethanol (ABE) process where species of *Clostridium* bacteria are used to convert sugars such as hexoses and pentoses to acetone, butanol and ethanol. Nikolaison et al. [15] fermented the macroalgae *Ulva lactuta* with *Clostridium* strains to produce butanol with a yield of 0.16 g butanol/g sugars, which was lower than that of ethanol produced under similar conditions. Using *Clostridium beijerinckii* as the fermentation ogranism Van Der Wal et al. [16] obtained butanol yields of 0.23 g butanol/g sugars from *Ulva lactuta*. Potts et al. [17] showed through a pilot study in which *Ulva lactuta* grown in Jamaica Bay, New York City was used as a fermentation substrate that a butanol yield of 0.29 g butanol/g sugars was obtainable. This value corresponds to a 22.4% deviation from the theoretical yield of 0.37 g butanol/g sugars [18]. Huesemann et al. [19] carried out a study of butanol fermentation from brown algae (*Saccharina*), but obtained very low butanol yields of 0.12 g butanol/g sugars. One challenge of current ABE fermentation strains is the difficulty in effectively converting some glucose-based polysaccharides, such as mannitol which constitutes up to 12% of brown algae [7], thus leading to slow reaction rates and productivity [6,20], thus progress in the area of metabolic engineering of fermentation organisms is required to improve butanol yields at the laboratory scale [6,11]. This has led to the conclusion that significant improvements at the laboratory scale are still required before economically feasible butanol production from fermentation of seaweed can be achieved on the industrial scale [16,21]. In fact no conceptual studies on the techno-economics of macroalgae-to-butanol processes via the biochemical route have been carried out in the peer reviewed literature.

In this regard the thermochemical route might be of considerable interest to study as past research on first and second generation biomass to butanol processes have shown that the thermochemical route has a number of more technologically mature processing steps such as the gasification, syngas cleanup and separation steps [22,23], and thus might be closer to commercial implementation than the biochemical route. However, though past work [24] has shown that economically competitive butanol can be produced from second generation biofuel feedstock using a thermochemical route, no such studies have been carried out on a macroalgae-to-butanol process in the peer reviewed literature to the best of the authors' knowledge.

As a first step in building an understanding of the process design and economics of macroalgae to butanol processes, this work will focus on developing a macroalgae-to-butanol process using a thermochemical conversion route and assessing its economics with future work focusing on the biochemical route. The research will aim to develop different design configurations for producing butanol from seaweed and address questions regarding the overall efficiency and butanol yields that are possible from these designs. Furthermore the different configurations will be compared amongst themselves and against other biofuels by using standard metrics such as the cost of CO_2 equivalent emissions (CO_2e) avoided as well as the minimum butanol selling price (MBSP). These metrics are also assessed for different market scenarios, and along with sensitivity analyses on key economic parameters help give a robust assessment on the potential for butanol production from seaweed using the thermochemical route.

2. Materials and methods

2.1. Macroalgae

The macroalgae selected for this study is the brown macroalgae *Laminara Japonica. L. Japonica* is chosen for this study because it is the most widely produced macroalgae with a production rate of 5 million wet tons per year, making up 33% of the world's yearly production [6]. Table 1 shows the plant gate characteristics of the *L. Japonica* that is used for this study [25], noting that the chemical composition of brown macroalgae changes somewhat depending on the season, growing habitat, and species [12,20]. In general, carbohydrates are consumed in the dark season and produced in the light season [26]. On a moisture free basis, the biochemical composition of brown macroalgae consist of 30–50% minerals, 30–60% carbohydrates, 10–13% cellulose, 6–20% proteins and 1–3% lipids [27].

2.2. Process simulation and description

2.2.1. Process and simulation overview

This paper considers and assesses three design configurations for the thermochemical conversion of macroalgae to butanol. All of the design configurations adhere to a similar approach. First, macroalgae is gasified to produce syngas (CO and H_2). The syngas is then cleaned before being sent to the mixed alcohol synthesis

Table 1
Ultimate and proximate analysis of *L. Japonica* used in this study [25].

Ultimate analysis	wt% dry basis	Proximate analysis	wt%
Carbon	32.41	Moisture	2.79
Hydrogen	3.37	Volatile matter	70.90
Nitrogen	1.18	Fixed Carbon	3.32
Sulphur	0.31	Ash	22.99
Oxygen	39.74		
Ash	22.99		
HHV (MJ/kg)	14.05		