International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 79

Optimal Design For The Utilization And Conversion Of Macroalgae Into Energy And Value-Added Chemicals

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ABSTRACT

A novel superstructure is developed for the biochemical conversion of macroalgae to mixed alcohols (MAs). Microalgae production processes as well as wastewater treatment networks are integrated into the process synthesis framework to improve the environmental performance of the MAs manufacturing process. Based on the superstructure, techno-economic mixed integer linear programming model was formulated. The objective function was the maximization of the net present value (NPV). The results indicated that biofuel production from macroalgae is economically viable, at minimum ethanol selling price (MESP) of $1.26 $/gal. Furthermore, the optimal design has achieved a 90% reduction in CO_2 emissions (CE). Sensitivity analysis indicated that the selling price of heavier alcohols and purchasing price of macroalgae are the most sensitive parameters to MESP.

Keywords: Superstructure optimization, process synthesis, macroalgae, biofuels, mixed alcohols.

1. INTRODUCTION

With the rapid depletion of fossil fuels and increasing demand for transportation fuel, it is anticipated that by the year 2030 the world is projected to consume two-thirds more fossil fuels than today. To address energy challenges, development of biofuel production from renewable sources like biomass has gained significant attention. Among various biomass feedstocks, brown algae, as a 3rd generation feedstock, is considered as a promising candidate due to its sustainable cultivation, high carbohydrates contents (32-60 wt.%), lack of lignin, high sequestration efficiency, and absence of ethical issues such as food competition [1]. Taking into consideration the benefits of brown algae and its versatile chemical composition, this study will focus on biofuel production from brown alga *Saccharina japonica* (SJ) as a potential feedstock.

In general, biochemical pathway can produce MAs including ethanol, propanol, and butanol. The biochemical pathway is divided into two alternative pathways: volatile fatty acid platform (VFAP) and sugar platform (SP). VFAP is superior to SP due to higher yields, lower CO_2 emissions, no enzymes requirements, and its ability to convert all components of the biomass including carbohydrates, proteins, and lipids [2]. Whereas SP only focuses on carbohydrates content of biomass and therefore has lower yields and higher pollutants such as unreacted biomass and CO_2 emissions. Dickson et al. [3] used a superstructure-based approach to evaluate the economics of bioethanol production from SJ through SP. They estimated the MESP of 1.97 $/gal at a plant scale of 612 kt/y. Studies on the process economics evaluation and determination of the optimal design for VFAP are very limited and requires further investigation.

One of the biggest challenges to the industrial scale application of VFAP is the effective and economically viable separation technologies for dehydration of the aqueous VFAs and MAs due to the formation of the azeotrope. Another challenge associated with the VFAP is the massive production of CO_2 during AD. A potential method to mitigate direct CE from VFAP is microalgae-based biological utilization. According to Davis et al. [4,5], 1 kg of microalgae consumes 1.93 kg of CO_2, which make it a suitable candidate to reduce CE from MAs manufacturing process.

Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

Based on the presented arguments, this study introduces an optimization-based process synthesis framework for MAs processes that will directly analyze the techno-economic, and environmental trade-offs using a large-scale mixed-integer linear programming model. The proposed framework simultaneously optimizes the topology of MAs manufacturing process as well as determine the optimal strategy to utilize CE produced during fermentation.

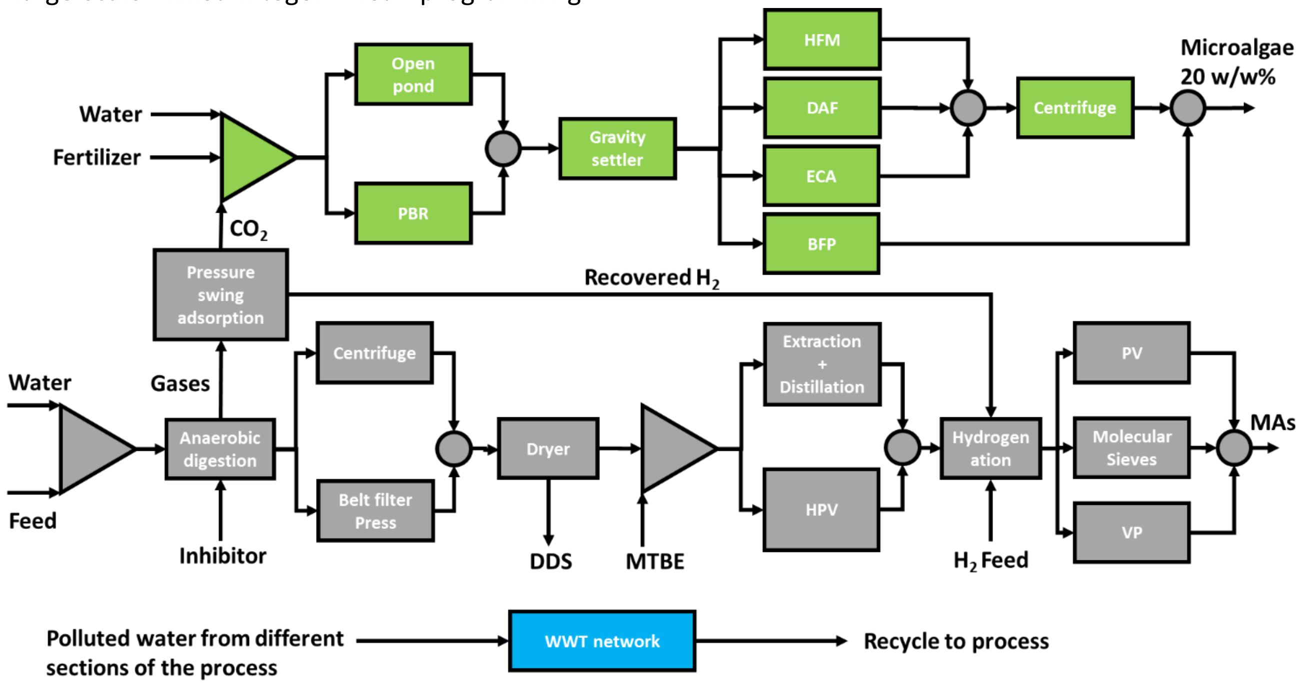

Fig. 1. Superstructure for the mixed alcohols manufacturing process.

2. Methodology

2.1 Problem statement

The optimization problem is defined as determining the topology of the MAs manufacturing process, which has maximum process economic potential as well as minimum determinantal effects on the environment.

2.2 Overall process

MAs can be produced from the partial AD of brown algae. AD consists of four stages hydrolysis, acidogenesis, acetogenesis, and methanogenesis. To produce the MAs methanogenesis stage must be prevented. This is achieved by adding inhibitors such as iodoform, at 30 PPM concentration [6]. The operating conditions of AD are 5 days of retention time at 13 wt.% solid loading and 35 °C [7]. The overall efficiency ranges from 0.307-0.412 g VFAs/ g dry feed. The outlet stream from the digester consists of solid, liquid, and gaseous products. Solid and gaseous products are separated from the liquid products. Separated Solid and gaseous products can be further processed to form value-added products such as dry distillery solids and hydrogen. The liquid stream is sent to VFAs recovery section, where VFAs are recovered at 99.9 wt.% using extraction column, rectification column, decanter, and stripping column. The concentrated VFAs are then hydrogenated for the synthesis of mixed alcohols. The hot effluent of the hydrogenation reactor is cooled, and vapors are separated from the liquid products and are recycled to the reactor. The liquid stream consists of 25 wt.% water, 42 wt.% ethanol, 19 wt.% propanol, and 12 wt.% butanol, and is sent to the alcohol recovery unit. Herein, MAs are dehydrated by the molecular sieves and sent to the alcohol distillation column to separate ethanol from butanol and propanol. The 99.9 wt.% purity of ethanol is obtained in the overhead stream of the distillation column. Propanol and butanol are obtained in the bottom stream of the column and considered as co-products.

2.3 Superstructure development

Design alternatives are added in the previously mentioned baseline process to develop a superstructure. The proposed superst[4]ructure is shown in Fig. 1 and contains fourteen design alternatives at various processing stages. The general mathematical model is similar to one reported in our previous work [3]. The design alternatives for solid processing include mechanical separator and centrifuge. As dehydration is energy intensive, five design alternatives are considered for recovering VFAs and MAs. VFAs can be recovered either by classical extraction/distillation processes or hybrid pervaporation (HPV). The classical methods for recovering VFAs are similar to those described in Section 2.2. In HPV, pervaporator is integrated into the classical process, which increases the concentration of VFAs from 5 wt.% to 10 wt.% by removing ~50 wt.% of the total water flow. Removal of this large amount of water directly impacts the process economics. Likewise, MAs can be dehydrated by three design alternatives to achieve the desired level of purity for their applications as a fuel. Dehydration can be performed by either molecular sieves, pervaporator (PV), or vapor permeation (VP). In all design alternatives, the target purity of ethanol is 99.5 wt.%.

To reduce CE, seven design alternatives are considered for microalgae cultivation and harvesting. Microalgae can be cultivated either in open ponds or photobioreactors (PBR). For its harvesting and dewatering, five design alternatives are considered. The microalgae are harvested in gravity settler, which can be dewatered either by hallow filter membranes (HFM), diffused air flocculation (DAF), or electrocoagulation (ECA) followed by centrifugation. Alternatively, belt filter press (BFP) can be implemented at the outlet stream of gravity settler. The final concentration of microalgae from all dewatering alternative is 20 wt.%. The operating data and equipment costs considered for microalgae production are based on the work of Davis et al [4].

A complete wastewater treatment network is incorporated that will treat and recycle wastewater from various process units including distillation columns, blowdown from the cooling tower as well as boilers. Process wastewater is treated using anaerobic digestion, aerobic digestion, and reverse osmosis. The treated water is assumed to be pure and is recycled to the process.

2.4 Objective function and assumptions

The objective function used for this optimization problem is maximization of the NPV and given in Eq. (1)

$$NPV = \sum_{n=0}^{20} \frac{NCF_n}{(1+r)^n}, \quad (1)$$

where NCF_n is non-discounted cash flow for the year n, and r is the discount rate. Various assumptions considered in techno-economic analysis include: 20 years of project life, 10% discount rate, straight-line depreciation method over 7 years, 30% tax rate, and two-year construction time. The chemical composition of SJ reported by Roesijadi et al. [1] was used in the simulation. An efficiency of 0.35 g VFA/g of dry biomass is considered in AD. The selling prices of products such as ethanol, heavier alcohols, DDS, and microalgae considered in this study to calculate process revenue were 0.72 \$/kg, 1.13 \$/kg, 0.13\$/kg, and 0.5 \$/kg, respectively. Likewise, costs of raw materials such as brown algae, MTBE, cooling H_2O, chilled H_2O, H_2, LP steam, and electricity were 68 \$/t, 1100 \$/t, 0.013 \$/t, 1 \$/t, 1.5 \$/t, 12.68 \$/t, and 0.0622 \$/kWh, respectively.

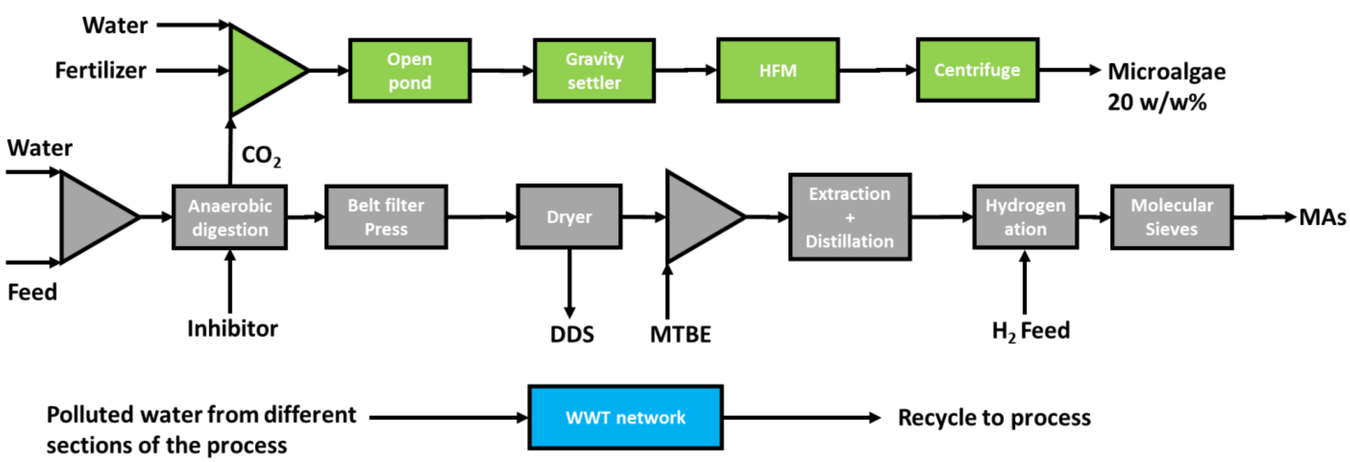

Fig. 2. Optimal design for the mixed alcohols manufacturing process.

3. Results and Discussion

The proposed process synthesis framework was implemented in GAMS (25.0.2) to determine optimal process design for MAs production process and CE utilization. The digester receives 612 kt/y dry feed for biofuel production. The optimal manufacturing process for MAs synthesis shown in Fig. 2 consists of AD, solid separation by belt filter press and dryer, VFAs dehydration by the extraction followed by distillation, hydrogenation, and MAs dehydration by molecular sieves followed by distillation. For CO_2 utilization, microalgae cultivation in open pond, harvesting by gravity settler, and dewatering by hollow filter membranes followed by centrifugation were selected as an optimal strategy. The products obtained from the biorefinery are ethanol, butanol, propanol, DDS, and microalgae. Their production rates are 32 mgal/y, 8 mgal/y, 14 mgal/y, 258 kt/y, and 49 kt/t, respectively. The installed cost breakdown is given in Fig. 3 The NPV, TCI, TCOM, and utilities costs are $124.7 MM, $328 MM, $31 MM, $141.7 MM, respectively. By integrating microalgae process to MAs manufacturing process, CE are decreased from 117 kt/y to 11kt/y. The cost of integration of microalgae process into the MAs manufacturing is $72 MM.

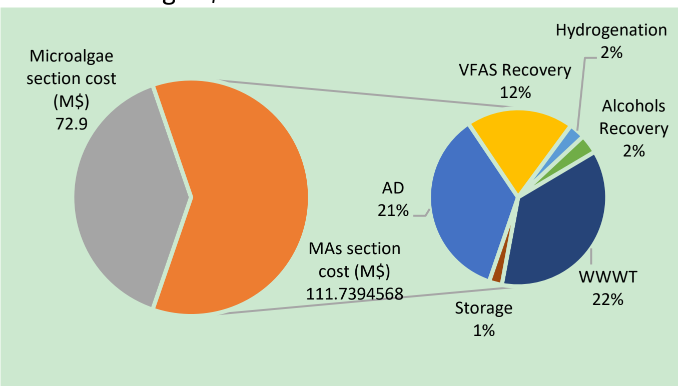

Fig. 3. Installed cost breakdown

3.1 Minimum and maximum price of products and seaweed

The minimum selling price of products can be defined as the selling price of products that makes the NPV equal to zero. The estimated MESP of optimal design is 1.26 $/gal at the current wholesale price of all products. Similarly, the minimum selling price of higher alcohols, DDS, and microalgae are 2.3 $/gal, 0.05 $/kg, and 0.114 $/kg.

The maximum seaweed price (MSP) can be defined as the purchasing price of seaweed that makes the NPV equal to zero. The estimated MSP of optimal design is 111 $/ton.

3.2 Sensitivity analysis

Sensitivity analysis was performed to evaluate the effect of selling and purchasing prices of products and seaweed, respectively. Each sensitivity parameter was varied by ± 10% from the base value. The result of sensitivity analysis is presented as a tornado chars in Fig. *4*. The result indicated selling price of heavier alcohols and seaweed price are the most dominant parameters that effect MESP.

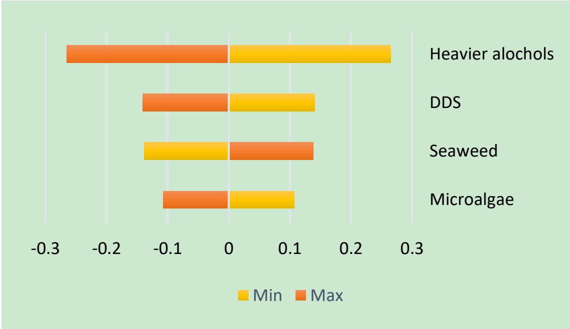

Fig. 4. Sensitivity analysis for MESP

4. Conclusion

An optimization-based framework for the MAs process synthesis as well as optimization of CE was proposed in this study. A rigorous techno-economic objective function (NPV) was used to investigate various economic parameters such as minimum selling price of products and MSP. The result indicated that biofuel production by VFAs route is viable; however, some challenges such as biomass price and its availability should be addressed before implementation of such biorefineries.

5. Acknowledgment

This research was supported through the Basic Science Research Program of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2017R1A2B4004500).

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