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Impact of volatile fatty acid recovery on economics of ethanol production from brown algae via mixed alcohol synthesis

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ABSTRACT

This study evaluates the economics of production of mixed alcohols from brown algae. Mixed alcohols (MA) were generated by hydrogenation of volatile fatty acids (VFA) that were produced by anaerobic digestion (AD) of brown algae. The process units including AD, VFA recovery, hydrogenation, and MA recovery were simulated in Aspen plus v.8.4. Two alternative processes, i.e., extraction/distillation (case 1) and hybrid pervaporation (PV) combined with extraction/distillation (case 2), were considered for recovery of VFAs from the dilute fermentation broth. Techno-economic models were developed to evaluate the plant economics and calculate a minimum ethanol-selling price (MESP). Sensitivity analysis of the economic and process parameters was performed to rigorously explore the uncertainties and main parameters affecting the MESP. The respective MESPs for cases 1 and 2 were calculated to be 1.24 and 3.61 $/gal. The results of the study showed that application of PV for dilute streams results in higher capital and energy costs primarily because of increased refrigeration, heating, and membrane costs.

1. Introduction

Global warming, escalating oil prices, depletion of fossil fuels, and the security of energy supply concerns have stimulated global interest in renewable energy sources. Carbon-neutral biobased fuels such as ethanol, butanol, and biodiesel are promising candidates for transportation purposes. Generation of bioethanol from lignocellulosic biomass has already reached the industrial scale in countries like the USA and Brazil (RFA, 2013). However, the development of this industry in other countries is limited by feedstock availability due to land and water limitations (IPCC, 2011). Aquatic biomass, including microalgae and macroalgae, are promising alternative biomass sources that have recently become focal (Reith et al., 2005; Roesijadi et al., 2008; Bruton et al., 2009; IEA, 2010; US DOE, 2010). Brown algae, regarded as third generation biomass, offer several advantages over lignocellulosic biomass. They do not require land, fertilizers, or irrigation water for cultivation. In addition, in comparison with lignocellulosic biomass, brown algae have a higher harvest cycle (4–6 times/year) and simpler processing requirements due to lack of lignin (Reith et al., 2005; Roesijadi et al., 2008). The culture of seaweed is a growing industry worldwide, with a production of 14.5 million tons (wet weight) worth US$ 7.54 billion in 2007 (FAO, 2009). Therefore, it is anticipated that biofuel production from macroalgae should emerge as a major contributor to sustainable world biofuel production.

Mixed alcohols (MAs) can be produced from biomass by biochemical pathways. In the biochemical pathway, MAs are produced through a volatile fatty acid platform (VFAP) or sugar platform (SP). In the VFAP, volatile fatty acids (VFA), including acetic acid, propionic acid, and butyric acid, are produced

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by anaerobic digestion of biomass using a mixed culture bacterial ecosystem. Subsequently, VFAs are hydrogenated to produce MA (Chang et al., 2010; Holtzapple and Granda, 2009; Holtzapple et al., 1999). The SP uses hexose and pentose sugars extracted or converted from plant bodies (Humbird et al., 2011; Aden et al., 2002). Fasahati et al. (2015) evaluated the economics of bioethanol production from brown algae through SP. They calculated a minimum ethanol-selling price of 2.33 and 2.08 $/gal at a plant scale of 400,000 ton/year dry seaweed for acid thermal hydrolysis and hot water wash pretreatments, respectively. The VFAP is proven to have a higher carbon yield (g alcohol/g dry biomass) in comparison to the SP (Chang et al., 2010; Feng et al., 2009; Qi et al., 2003). This is primarily due to the low release of CO_2 during fermentation and the fact that mixed anaerobic bacteria are capable of utilizing all non-lignin parts of biomass, including proteins, lipids, and carbohydrates, whereas in the case of SP, only the carbohydrate portion of the biomass is converted to ethanol. In addition, because of the low release of CO_2 during anaerobic fermentation, mixed VFA fermentation provides a higher carbon yield than direct ethanol fermentation using yeast or *Zymomonas mobilis* (Bolzonella et al., 2005; Chang et al., 2008). Thus, if VFAs can be converted to fuels and chemicals such as ethanol and butanol via economical processes, mixed VFA fermentation could provide a new platform with versatile applications for the production of biofuels.

However, effective and energy-efficient separation technologies for dehydration of the aqueous VFAs are a major hurdle to large-scale application. Separation of acetic acid from water using distillation is difficult and energy-intensive due to the close boiling points of water and acetic acid; this leads to a large number of trays in the distillation column to accomplish the separation, which increases the associated costs (Chien et al., 2004). Therefore, in practice, azeotropic rectification has proven useful and can operate either with or without the extraction stage, depending on the acetic acid concentration. The addition of an auxiliary substance may be employed to increase the volatility of the water, and thus, separation can be achieved with lower energy consumption. Therefore, the state-of-the-art technology for recovering acetic acid at concentrations lower than 40 wt% involves initial extraction of acetic acid from the aqueous solution with a suitable extraction agent prior to recovery of the pure product during rectification of the azeotropic mixture (De Dietrich, 2014).

Recently, pervaporation (PV) has gained attention as a new-generation technology over classical separation processes (Hinchliffe and Porter, 2000). PV requires a vacuum downstream of the membrane to allow separation by partial vaporization through a dense and selective membrane. A variety of membrane materials have been evaluated for possible application in dehydration and recovery of acetic acid, including inorganic membranes (Masuda et al., 2003; Cui et al., 2004; Teli et al., 2007; Asaeda et al., 2005; Sommer and Melin, 2005; Sato et al., 2011), organic membranes (Jullok et al., 2011; Tanaka et al., 2011), modified PVA membranes (Asman and Sanli, 2003; Isiklan and Sanli, 2005; Huang and Yeom, 1991; Hilmioglu et al., 2001; Alghezawi et al., 2005), charged membranes (Kusumocahyo and Sudoh, 1999; Semenova et al., 1997), PVC membranes (Koops et al., 1993; Okuno et al., 1993), and composite membranes (Lee and Lai, 1994; Wang, 2000; Wang et al., 2002; Chen et al., 2008, 2013; Toti and Aminabhavi, 2004; Zhang et al., 2014). However, despite all the experimental studies, the economics of the application of PV to dehydration of dilute acetic acid streams has not yet been evaluated. Economic assessments are helpful tools for identification of the strengths, weaknesses, and bottlenecks of a process.

In this study, the economics of MAs production from brown algae via VFAP were evaluated for the first time. In addition, economic comparison of two alternative VFA recovery methods (i.e., a classical extraction/distillation (case 1) and an integrated PV and extraction/distillation (case 2)) is presented. Based on a thorough literature survey, the state-of-the-art membrane technology for acetic acid dehydration is identified, and Aspen plus v.8.4 software is used to rigorously model the processes. Techno-economic models are developed in order to calculate the MESP of each process, identify the main cost drivers, and to assess the impact of several key parameters on plant economics.

2. Methodology

2.1. *Process description*

Mixed alcohols can be produced by hydrogenating volatile fatty acids produced from anaerobic digestion of brown algae. Fig. 1 shows a block flow diagram of the process. The process requires two dehydration units, one for the VFAs and the other for the mixed alcohols. The process is divided into four areas including: Fermentation (A), VFA recovery (B and C), Hydrogenation (D), and MA recovery (E). As shown in Fig. 1, two alternative processes were considered for VFA recovery, i.e., classical extraction/distillation (B) and hybrid PV and extraction/distillation (C).

2.1.1. *Anaerobic digestion*

Brown algae (i.e., Phaeophyceae), the single largest seaweed resource, are considered one of the most likely candidates for energy processing with a yearly production of 9.72 million tons dry weight in 2004 (Roesijadi et al., 2010). Macroalgae generally consist of 85–90% moisture with a high ash content of up to 5% of the wet mass (Roesijadi et al., 2008, 2010). In this study, drying of brown algae to achieve 20% moisture content prior to reaching the plant gates is assumed. The remaining mass consists mainly of proteins, carbohydrates, and lipids. Typical brown algae have a carbohydrate content of greater than 40% with a lipid composition of less than 5% (Reith et al., 2005). The primary carbohydrates in brown algae are as follows: (1) mannitol (a sugar alcohol), (2) laminaran (a β-1,3-linked glucan that also contains mannitol), (3) alginic acid (composed of mannuronic and guluronic acids), and (4) fucoidan (a sulfated fucan that mainly consists of sulfated L-fucose). Generally, the chemical composition of brown algae varies considerably between species and habitats throughout the year (Adams et al., 2011). Brown algae subject to seasonal variation usually accumulate mannitol and laminaran in the light season (i.e., spring to autumn) and consume these stored carbohydrates in the dark season. The availability of polysaccharides and sugar alcohols makes brown algae a good candidate for conversion to biofuels. Additionally, the low lignin content makes these algae suitable for downstream processing via anaerobic digestion or the fermentation process (Horn, 2000). Table 1 lists the composition, elemental analysis, minerals, and heating values for the brown algae Laminaria species (Reith et al., 2005).

Anaerobic digestion of biomass involves four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. During hydrolysis, the polymeric structures of carbohydrates,