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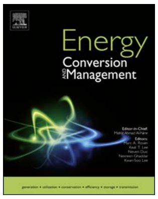

Techno-economic comparison of Acetone-Butanol-Ethanol fermentation using various extractants

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ABSTRACT

This work compares various chemicals for use as extractants in second-generation Acetone-Butanol-Ethanol fermentation on economic and environmental bases. Both non-toxic and toxic extractants are considered in this study. The combinative extractive-distillation separation process was modelled using a combination of Microsoft Excel 2013, MATLAB 2015 and Aspen Plus v8.8. Separation trains were designed and optimized for each extractant to best take advantage of extractant properties. Upstream units considered in this analysis include: biomass (switchgrass) solids processing, biomass pre-treatment and saccharification, and fermentation. Downstream processes considered include utility generation and wastewater treatment. The cost of CO_2 equivalent emissions avoided (CCA) was used as the metric to compare the environmental impact of each process as compared to conventional petroleum-based gasoline. The economic and environmental best extractant is shown to be 2-ethyl-hexanol with a minimum butanol selling price of \$1.58/L and a CCA of \$471.57/tonne CO_2 equivalent emissions avoided.

1. Introduction

The rapid depletion of fossil fuels, combined with increased concern surrounding greenhouse gas emissions and global warming has made the quest for alternative fuels a high priority. In Canada, the transportation sector accounted for 23% of greenhouse gas emissions in 2014, second in emissions to only the oil and gas sector [1]. These large contributions precipitate a motivation for alternative transportation fuels that should ideally be carbon–neutral, with minimal net addition of greenhouse gases into the atmosphere throughout their life cycle. Along these lines, agricultural based alternative fuels (biofuels) are being championed by policy makers as a key strategy for greenhouse gas emission reduction. The 2012 biofuel market in Canada was estimated to have an aggregate positive impact of 2 billion CAD on the economy annually [2].

Biobutanol is a candidate biofuel that has the potential to reduce the life-cycle emissions of the transportation and fuels industries. The interest in biobutanol stems from its potential to act as a substitute for both gasoline and diesel, though it is more commonly used as a gasoline substitute [3,4]. Moreover, biobutanol has a higher energy content and lower affinity for water when compared to the more studied bioethanol. In addition, biobutanol is more compatible with current automobile engines and gasoline pipelines than ethanol [3].

Biobutanol can be produced biochemically from various forms of *Clostridia* bacteria in a process known as Acetone-Butanol-Ethanol (ABE) fermentation. During ABE fermentation, acetone-butanol and ethanol are produced in an approximate 3:6:1 ratio with total product yields typically peaking at around 20 g/L [5]. Product yields are limited to this concentration because butanol is toxic to the bacteria causing them to die off as butanol accumulates in the fermentation broth [3].

ABE fermentation has historically been a first-generation biofuel process. First-generation biofuel feedstocks consist primarily of food crops such as cereals, oil seeds and sugar crops such as corn or sugarcane. The choice of feedstock (and consequently feedstock price) have been shown to be important factors to influence the cost of biobutanol. In particular, first-generation feedstocks, which generally have high prices, make the production of butanol economically unfavourable [5–7].

An alternative to the above substrates are the so-called second-generation substrates. Second-generation biofuels seek to address the limitations of first generation biofuels by using non-food-competitive biomass such as lignocellulosic biomass. These crops are either food by-products or can be produced on land that cannot be effectively used for food production, such as corn stover or dedicated energy feedstocks such as grasses. With proper biomass pre-treatment, ABE fermentation has been shown to be compatible with barley straw [8], corn stover [9], distillers' dry grains and solubles (DDGS) [10], switch grass [9], and wheat straw [11].

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1.1. Product removal in downstream processing

Due to low product yields, product recovery from the dilute fermentation broth also hinders industrial production of bio-butanol. Product recovery, typically accomplished using pure distillation, is quite energy intensive, requiring 13–25 tonnes of steam per tonne of butanol produced [6]. To bring down the cost of separation, many alternative separation methods have been proposed including: gas stripping [12,13], pervaporation [14], adsorption [15], and liquid-liquid extraction [16–18]. Qureshi et al., suggested that adsorption or extraction are the most energy-efficient product removal alternatives [15]. Vane 2008 also noted that the energy requirement of liquid-liquid extraction for butanol fermentation is attractive when compared to a pure-distillation approach [19]. Liu et al., generated a superstructure for downstream ABE processing that compared conventional distillation, gas stripping and extraction. The optimal configuration they identified considered liquid-liquid extraction combined with distillation [20]. It is for these reasons that this work further explores the use of liquid-liquid extraction to reduce the cost of biochemical biobutanol production.

1.2. Liquid-liquid extraction

Candidate extractants for butanol liquid-liquid extraction can be defined by three major properties: their distribution coefficient for each of the products (especially butanol), selectivity and toxicity. The distribution coefficient defines the affinity of the product for the extractant over the affinity of the product for the fermentation broth (mass fraction of butanol in the extractant phase over mass fraction of butanol in the aqueous phase). Selectivity is the ratio of water taken up by the extractant relative the quantity of butanol (distribution coefficient of butanol over the distribution coefficient of water). The toxicity of an extractant falls into two sub-categories: non-toxic extractants are harmless to the bacteria and thus can be used directly in the fermentation broth to improve yields by removing toxic compounds from the fermentation broth (*in-situ* applications) [21,22]. The downside to non-toxic solvents is that they have inferior extraction properties compared to their toxic counterparts, which in contrast to non-toxic options cannot be used *in-situ* [3].

Many extractants have been extensively studied at the lab scale; Groot et al. examined the properties of 36 different chemicals including both toxic and non-toxic compounds. In general they found that extractants with higher butanol distribution coefficients (this study considers a range of products with butanol distribution coefficients between 0.3 and 12) had lower selectivities (from 160 to 4300) and vice versa [16]. Other popular extractants include oleyl alcohol and 2-ethyl-1-hexanol. Both of these compounds are non-toxic and have moderately high distribution coefficients of 3.8 for oleyl alcohol and 6.9 for 2-ethyl-hexanol [23]. It is also possible to blend toxic solvents with non-toxic solvents to produce a non-toxic mixture with better extractive properties than the non-toxic extractant could achieve on its own, while still remaining non-toxic. An example of this type of extractant is 20 wt% decanol (toxic) mixed with oleyl alcohol (non-toxic) [24]. Kraemer et al. used computer-aided molecular design to screen thousands of chemicals for their potential use as ABE extractants. The best chemical they identified was mesitylene. Mesitylene is toxic to butanol-producing bacteria, however it boasts excellent mechanical properties and a distribution coefficient of 2.2 and a selectivity of 1970 [17]. The use of ionic liquids for extraction has also been proposed. The proposed extractants are biocompatible, however they report low selectivities (2.6–132.4) and butanol distribution coefficients (0.8–2.3) [18].

Systems-level comparisons of alternate product recovery techniques can also be found in literature. Liu et al. generated a superstructure for downstream ABE processing that compared conventional distillation, gas stripping and liquid-liquid extraction using 2-ethyl-1-hexanol. Processes were modelled using short-cut distillation methods. The optimal solution, which minimized the annualized cost of the separation over a three year timespan, identified extraction as the optimal solution. In fact, each of the top ten configurations involved extraction [20]. As previously mentioned, Kraemer et al. studied the use of the extractant mesitylene. They compared the energy requirements of product separation using pure-distillation, oleyl alcohol, and mesitylene for continuous ABE fermentation. Assuming ideal vapour-liquid equilibrium (VLE) they determined that mesitylene had the lowest energy demand per kilogram of butanol produced (4.8 MJ/kg) followed by oleyl alcohol (18.5 MJ/kg) and lastly the traditional distillation method (25.6 MJ/kg) [17]. van der Merwe et al. compared the energy requirements of several separation trains. Once again, liquid-liquid extraction (coupled with gas stripping) featured in the best scenario with an energy input of 1.72 MJ/kg of butanol. The extractant in this case was 2-ethyl-1-hexanol. The simulations in this study are thermodynamically robust, however the authors note uncertainty in liquid-liquid equilibrium predictions and remarked that “improved physical property methods should be used for more accurate simulation of the complicated system.” [25].

For biobutanol to be a viable diesel or gasoline substitute, the economics of ABE fermentation need to be assessed. Recent economic analyses include that by Qureshi et al., who investigated the economics of second-generation ABE fermentation using wheat straw as the fermentation substrate. Their work used a combination of pervaporation, distillation and membrane separation to recover the products. The final minimum butanol selling price (MBSP; butanol selling price which results in an NPV of zero over the plant lifetime) in this study was $1.05/kg for a production rate of 150,000 tonnes per year [26]. Kumar et al. compared the economics of ABE fermentation using various substrates including: corn, corn stover, bagasse, wheat straw and switchgrass. The plant was designed to produce 10,000 tonnes of butanol per year with an assumed mass yield of 39% total ABE products per unit of sugars and an assumed recovery of 99%. They determined that the cheapest option was corn stover or bagasse with a butanol sales price of $0.59/kg followed by switchgrass ($0.6294/kg), wheat straw ($0.6856/kg) and corn ($1.2953/kg) [27]. However, this study did not perform rigorous simulations of the plant (especially the separation section in particular), did not account for the significant cost of wastewater treatment, and did not consider alternative technologies (such as liquid-liquid extraction) for product separation. Therefore, the estimates presented in that work have a high uncertainty.

This study seeks to compare various proposed ABE extraction chemicals at a plant-wide level on both environmental and economic bases. Products are recovered to their ASTM standard specifications [28–30]. The novelty of this paper stems from three major aspects of this work: this is the first work to compare different extractants taking full advantage of their properties, this work performs the most detailed separation modeling by explicitly considering the heteroazeotropic butanol-water vapour-liquid-liquid equilibrium and by considering experimentally validated properties for the extractants, and this is the first work to consider wastewater treatment in ABE plant economics. Some questions that are addressed by this work are: (1) which extractant results in the lowest MBSP when the full VLLE for the butanol-water system is considered? (2) Which extractant has the lowest cost of CO_2 equivalent emissions when compared to conventional gasoline? (3) How does downstream broth wastewater treatment affect the MBSP?

2. Methods

The design for this process was inspired by a design proposed by the National Renewable Energy Laboratory (NREL) for a biochemical biomass-to-ethanol process [31], with major modifications made to the fermentation and separation sections of the plant to account for production of biobutanol. Fig. 1 displays a block flow diagram of the major sections of the plant for the conversion of switchgrass to biobutanol. The fermentation was modelled in MATLAB 2015, while product