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Optimal simultaneous production of i-butene and ethanol from switchgrass

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ABSTRACT

In this work, we propose the optimization of a flowsheet for the production of i-butene from switchgrass. A superstructure embedding a number of alternatives is proposed. Two technologies are considered for switchgrass pretreatment, dilute acid and ammonia fiber explosion (AFEX) so that the structure of the grass is broken down. Surface response models are used to predict the yield. Next, enzymatic hydrolysis follows any of the pretreatments to obtain fermentable sugars, mainly xylose and glucose. i-Butene is obtained by fermentation of the sugars. Next it is separated mainly from CO_2 for which PSA or membrane separation are considered. However, xylose cannot be easily converted, and thus we also evaluate the possibility of using it to produce ethanol. The problem is formulated as an MINLP with simultaneous optimization and heat integration. Finally, an economic evaluation is performed. The most promising process involves the use of dilute acid pretreatment and membrane purification of the i-butene. However, the decision related to the production of i-butene alone or the simultaneous production of i-butene and ethanol depends on the prices for ethanol and for switchgrass.

1. Introduction

i-Butene is an important intermediate that is mainly obtained from the cracking of the C4 fraction of crude oil using catalytic or thermal cracking [1]. This chemical is the basis for the production of a common additive to gasoline for a cleaner burning fuel, the methyl-tert-butyl ether (MTBE) as well as a monomer for the polymerization including butyl rubber or direct additive to gasoline. Its importance can be reflected in its price, around 2 $ kg^{-1}. However, the dependency on the crude oil, and the already limited availability due to the large number of applications, has increased the need for new sources of this chemical.

Recently, the company Global Bioenergies has patented their research on the fermentative production of isobutene, showing that bio-based isobutene production is possible [2–4]. Since isobutene is a gaseous compound at fermentative conditions, it can easily be recovered from the bioreactor. Moreover, if this compound is produced at a lower cost, its conversion into biofuel, or any other possible product, might become attractive. Also, i-butene has recently been used for the production of diesel substitutes from glycerol [5–7]. Although the main drawback of its use is its high cost from the energy and water consumption standpoint, its use for the enhanced production of diesel substitutives is competitive with the process that directly sells the glycerol as byproduct. However, the expected decrease in the production cost of glycerol due to the saturation of the market, and the increased

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yield to fuels from oil around 20%, when using the glycerol to obtain further diesel substitutes, have increased the interest of the production of i-butene from renewable sources.

In this paper, we study the production process of ethanol from lignocellulosic raw materials comparing two hydrolytic pretreatments of the lignocellulosic biomass and several purification methods for the i-butene produced using mathematical optimization techniques [8,9]. We propose a limited superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in i-butene production from switchgrass where we consider alternatives for some of the technologies. These units are interconnected to each other through network flows and other utility streams. The goal is to simultaneously optimize and heat integrate the production process of i-butene to assess its competitiveness with current crude based production. The optimization of the system is formulated as a mixed-integer nonlinear programming (MINLP) problem, where the model involves a set of constraints representing mass and energy balances, experimentally based models and rules of thumb for all the units in the system. Finally, an economic evaluation is also performed.

2. Overall process description

Grinding is the first stage to reduce the size of the raw material, and to increase the contact area before pretreatment. There are a number of alternative pretreatments and a few comprehensive review papers have been published recently on the topic [10–13]. Among them, the two most promising ones due to their scale up feasibility are the (1) dilute acid (H_2SO_4) pretreatment [14–17], and (2) ammonia fiber explosion (AFEX) [11,18,19] So far both have been used to release the cellulose and hemicelullose for their hydrolysis.

Once the physical structure of the switchgrass is broken to allow the contact between the polymers and the enzymes, hydrolysis of the polymeric sugar takes place. This process is carried out in stirred tank reactors at 45–50 °C for 3 days where the accessible cellulose and hemicellulose are broken into fermentable sugars [14,15,20–22].

Next, the sugars, mainly glucose and xylose, are fermented. So far only glucose has been proved to generate i-butene using *Saccharomyces cerevisiae* [2–4] Therefore we evaluate three different options. The first one is the production of i-butene from the glucose that can be obtained from the biomass. Second, the possibility that xylose is also converted, which, although regarded as a future possibility, is currently already feasible. Finally, the simultaneous generation of ethanol and i-butene so that the xylose that is not converted into i-butene is fermented into ethanol using *Zymomonas mobilis* such as second generation of ethanol production [15,23]. The gas phase consists of i-butene together with CO_2 and steam. First, we condense the water vapour accompanying the gas phase, and then two options are considered, either PSA or membrane separation of the two cases. For the case where the unconverted xylose is further fermented to ethanol, we use a multieffect distillation column to separate the water – ethanol mixture, and next a molecular sieves system to dehydrate the ethanol as in Martín & Grossmann [23], see Fig. 1.

3. Mathematical modeling

All the operations in the bio-i-butene production process are modeled using short–cut models consisting of mass and energy balances, models based on the design of experiments (DOE) methodology from experimental data in the literature, rules of thumb and design correlations. The mathematical model is written in terms of total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. These are the main variables whose values have to be determined in the optimization. The components in the system include those present in the switchgrass, plus those produced during the process of i-butene production, and belong to the set J = {Water, i-butene, ethanol, H_2SO_4, CaO, Ammonia, Protein, Cellulose, Hemi-Cellulose, Glucose, Xylose, Lignin, Ash, CO_2, O_2, Cells, Glycerol, Succinic acid, Acetic acid, Lactic acid, gypsum}. The different units in the superstructure are modeled as described below, but for the sake of limiting the size of the paper, we refer the reader to previous papers for details [23] of common units.

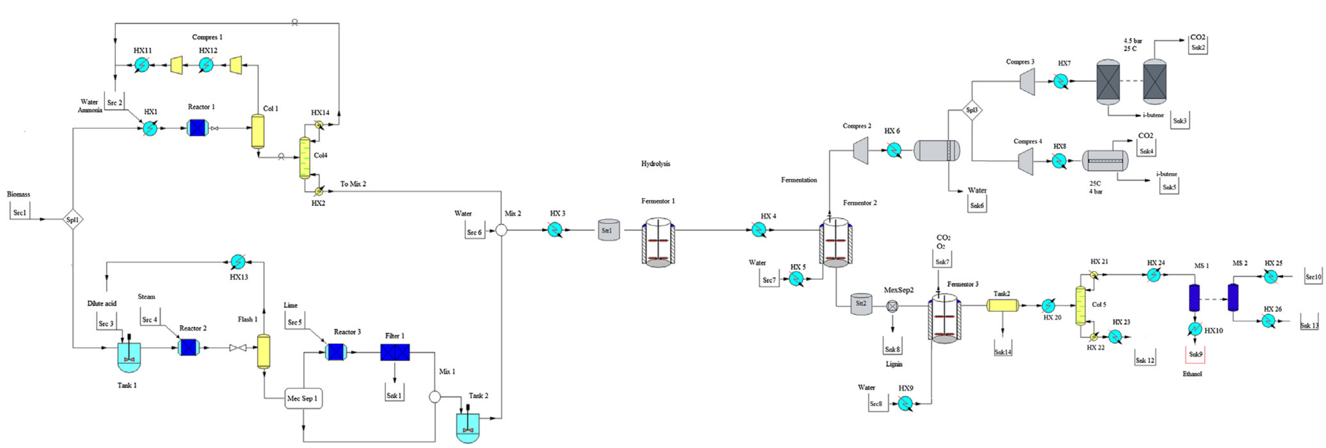

Fig. 1 – Superstructure of for the simultaneous production of ligno – i-butene and lignocellulosic based ethanol.