Towards a Combined, Integrated, and Adaptable Bioethanol and -Ethylene Process Leveraging Flexible Ratios in Hybrid Production

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Abstract

The production of bioethanol and ethylene offers significant potential as carbon-neutral fuel and raw material *e*.*g*., for polyethylene production, respectively. We present a new approach, where we combined a) the bioethanol production process (pretreatment, hydrolysis, fermentation), b) the ethanol purification under the consideration of trace compounds and their removal to reach solvent-grade ethanol, and c) the coupling of the ethylene process to the ethanol process. The simulation results showed the feasibility of a flexible hybrid production process that fulfills the high-purity grades of both products. In addition, there is a high heat integration potential for all product ratios, thereby offering significant potential for adaptation to different market situations.

**Keywords**: bioethanol and -ethylene, hybrid production, heat integration, simulation

* 1. Introduction

Bioethanol and ethylene offer the potential for sustainable fuel, and carbon-neutral plastics production, respectively. While bioethanol production, especially first-generation concepts, is already established on larger-scale plants, ethylene is still mostly produced from fossil sources in a highly energy-intensive process. In most cases, these processes are still cheaper than the carbon-neutral alternative of bioethanol dehydration (Bayens *et* *al*., 2015). Further, as economic uncertainties increasingly affect the planning of energy-intensive processes, adaptability and flexibility are required for the profitable operation of such processes. As a step towards biobased processes with such desired properties, this work presents an approach that features a hybrid production concept with flexible product ratios that can be adapted in response to price fluctuations of raw materials, products, energy, and heat utility. Further, this approach targets higher-purity products to increase the economic viability as well as to analyze the effects of impurities in raw materials. We present an integrated concept for a standalone plant that fully exploits its heat integration potential. Several aspects of this work have already been analyzed in different works. The effect of trace compounds in the fermentation broth on the bioethanol product was analyzed by Bisgaard *et* *al*. (2017), focusing on ethanol purification performance. Ethanol (Bayens *et al*., 2015, Humbird *et al*., 2011) and ethylene processes (Frosi *et al*., 2021), (Mohsenzadeh *et al*., 2017) have been separately analyzed in many studies, thereby focusing on process configurations, equipment design, and heat integration. However, a combination and optimization of both processes with the target of a hybrid production concept have, to the best of the authors' knowledge, not been performed. In the following, section two provides an overview of both bioethanol purification and the ethylene production processes, and the proposed combined process is presented. This is followed by the used models and methods in section three, and finally, section four presents and discusses the simulation results.

* 1. Process Description
     1. Background scenario

The background scenario considered in this work is the second-generation bioethanol plant-wide simulation model developed by Prunescu *et al*. (2017) for a large-scale plant. The model includes pretreatment, enzymatic hydrolysis, and co-fermentation sections, respectively. The output of the plant-wide simulation model –the fermentation broth coming out of the co-fermentation section –is used as the input for the bioethanol purification model analyzed in this work.

* + 1. Bioethanol Purification

Bioethanol can be produced in fuel-grade purity, which can contain fractions of water, methanol, and other volatiles and higher saturated mono alcohols. Figure 1 illustrates the downstream purification process where the feed is the fermentation broth coming from the second-generation bioethanol plant-wide model. The process configuration is based on Bisgaard *et al*. (2017). In a first step, the beer stripper column separates the solids from the fermentation broth by stripping the product stream with steam.



Figure 1: Model flowsheet of the second-generation bioethanol purification process

The aldehydes column removes acetaldehyde, 1-propanal, 1-butanal, crotonaldehyde, and ethyl acetate. The main function of the third column, the rectification column is to further concentrate ethanol up to a distillate with an azeotropic mixture of ethanol and water. The side draw is implemented to remove benzaldehyde, 1-propanol, 1-butanol, 2-butanol (s-butanol), 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. The top product from the rectification column is sent to a molecular sieve unit to produce anhydrous ethanol. A fourth column, the trace column is required to separate the remaining impurities, which are mainly methanol. Thereby, methanol can be separated with ethanol as the top product. In order to combust the remaining solids, these are separated from the beer column bottoms with a filter press, thereby targeting a low remaining water content. In this work, we target solvent-grade ethanol with a purity of over 99.9 % (*w*/*w*).

* + 1. Bioethylene

Ethanol can be dehydrated to ethylene. Using bioethanol as raw material in this process, carbon-neutral bio-based ethylene can be obtained. The basic process layout of the ethylene process is shown in Figure 2.



Figure 2: Model flowsheet of the ethylene process

In a first step, ethanol is dehydrated to ethylene in a train of adiabatic fixed-bed reactors. Before being fed to the reactor, the ethanol is heated since the dehydration reaction to ethylene is strongly endothermic. As water is produced during the reaction, this is separated in two steps, namely a primary and secondary separation, where the pressure is increased to around 16 bar to further condense the remaining water. Carbon dioxide, a side product of the dehydration reaction, is separated in an absorber column using methyl diethanolamine (MDEA). After that, the remaining humidity is removed using pressure-swing adsorption (PSA) columns followed by a cryogenic olefin separation that removes methane, hydrogen, acetaldehyde, and other impurities to achieve polymer-grade ethylene (high purity, suitable for polymerization).

* + 1. Hybrid process

A flexible, hybrid production of both solvent-grade ethanol and polymer-grade ethylene is considered. Figure 3 shows the configuration of the proposed process: For solvent-grade ethanol production, the previously explained process is used, *i*.*e*. the rectification column features a side-drain to remove components such as benzaldehyde, 1-propanol, and 1-butanol. The distillate with azeotropic composition is dried in a molecular sieve and goes to the trace column, where primarily the methanol is separated to get solvent-grade ethanol (1). Using this configuration, there remain two unused streams with high ethanol content, which are the column side drain (M) and the top product of the trace column (2). In this scenario, these streams are mixed and used as feed for polymer-grade ethylene production. By varying the ratio between the side-drain and distillate outlet flows of the rectification column, the ratio of the products can be adjusted.



Figure 3: Overview of the proposed combined process with hybrid production

* 1. Model and Methods

Mass and enthalpy balances of the second-generation bioethanol plant-wide model developed by Prunescu *et al*. (2017) have been derived to investigate the possibilities of comprehensive heat integration. To further include the potential of the optimized model, the impurities for detailed product grade analysis, and the energy of solids combustion for heat integration, we used a combined feed. Impurities were included using the same component-to-ethanol ratio as given in Bisgaard *et al*. (2017). This inclusion can be justified since their work also addresses second-generation bioethanol with similar raw materials. The inclusion of remaining solids after the fermentation was based on component property data from Wooley and Putsche (1996). Both flowsheets are modeled with AVEVA® Process Simulator (AVEVA, 2023). We use a vapor-liquid equilibrium with activity-coefficient-based UNIQUAC method data for component pairs provided by AVEVA®. The gas phase is modeled as an ideal gas, and the solubility of CO2 is modeled using Henry’s law. Comparing thermodynamic methods, it was found that both NRTL and UNIQUAC only lead to small deviations. For validation of the simulation model, the results of Bisgaard *et al*. (2017) could be replicated with only small deviations. In this work, the initial configuration and equipment specifications were iteratively adapted using a Python-based sensitivity analysis tool that offers an interface to AVEVA®. An adiabatic, fixed-bed plug-flow reactor with three sections was selected for ethanol dehydration, which is standard in the industry (Yakolewa et al, 2016). The reactor was modeled as a first principle model and implemented in MATLAB® utilizing kinetic models from Maia *et* *al*. (2018), and Tripodi *et* *al*. (2019) of which both had plant/experimental data using a Syndol catalyst. After the reactor parameters were optimized, the model was transferred to AVEVA®. In the CO2-stripping section, electrolyte NRTL was used to correctly simulate the interactions between the charged species. The vapor-liquid equilibrium is based on an activity-coefficient model. The solubility of the light components CO, CO2, O2, N2, H2, CH4, ethane, and propylene is modeled using Henry’s law. The reactions taking place in the amine-based CO2 absorption were implemented on all absorber stages, assuming equilibrium.

* 1. Results
     1. Feasibility of the hybrid process

Simulation results showed that a flexible, hybrid production of high-purity chemicals, namely solvent-grade ethanol and polymer-grade ethylene is technically feasible with the given process concept and technologies. Utilizing the remaining solids after fermentation for combustion, the obtained heat can be fully used to cover the heat demands of other units. It was found that the ethylene process is feasible with lower ethanol concentrations as input, while still maintaining a high yield. To exploit this, the rectification column was configured so that the side-drain delivers a stream with a low ethanol concentration of 50-60 mol%, thereby saving energy for further concentration of ethanol. Note that when maximum ethanol production is targeted, there is still a small side-drain flow as well as a significant top product flow in the trace column, which cannot be utilized for solvent-grade ethanol. Therefore, the maximum possible ratio in favor of solvent-grade ethanol is 0.72:0.28 (mole-based). In contrast, when full ethylene production is targeted, the whole ethanol product stream can be used as ethylene process feed by closing the side-drain and reducing the distillate ethanol concentration to 59 mol%, meaning that a 0:1 ratio is possible (results not shown). Expectedly, the obtained rectification column duties reduce significantly with lower required distillate purity.

* + 1. Varying the Product Ratio

The results presented in Table 1 show the obtained values of economically important process parameters for different product ratios. Note that the hot and cold utility targets are significantly lower than the heating and cooling demand of a non-integrated process, meaning that there is a high heat integration potential. The results further indicate that there are several opposing trends regarding specific parameters when changing the ratio of the product. Interestingly, the pinch analysis in Figure 4 shows that there is an optimal point regarding heat recovery potential and minimization of hot and cold utility, respectively.

A graph of a graph showing the temperature of a heat flow

Description automatically generated

Figure 4: Composite Curves of the hybrid process for 0.5 SG Ethanol:0.5 PG Ethylene

This minimum is located around the 0.5:0.5 ratio of both products. In contrast, the sum of electric duty, mainly determined by the compressors in the ethylene process, increases with a higher ethylene product ratio.

Table 1: Results of important process parameters for different product ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Ethanol (SG): Ethylene (PG) | 0.72:0.28 | 0.5:0.5 | 0.25:0.75 | 0:1 |
| Ethanol product, kmol/h | 3.80 | 2.65 | 1.32 | - |
| Ethylene product, kmol/h | 1.48 | 2.65 | 3.98 | 5.30 |
| Ethylene reaction yield in % | 99.0 | 99.3 | 99.3 | 99.2 |
| Sum of electric duty in kW | 7 | 10 | 17 | 23 |
| Heating demand in kW | 2201 | 2055 | 1971 | 2024 |
| Cooling demand in kW | 2447 | 2286 | 2178 | 2230 |
| Hot utility target in kW | 226 | 39 | 67 | 157 |
| Cold utility target in kW | 471 | 269 | 273 | 362 |

Depending on prices for electricity as well as heating and cooling utility, the economically optimal product ratio will differ. A more detailed analysis as well as dynamic behaviour during variation of product ratios will be part of future work.

* 1. Conclusions

The results showed that a flexible, hybrid production is possible that maintains the high-purity grades of both products at all points. Configuration one (only polymer-grade ethylene) showed a reduction of 31 % in hot and 23 % in cold utilities and an increase of 229 % in electric demand compared to configuration two with a product ratio of 72 % solvent-grade ethanol to 28 % polymer-grade (molar-based). For all configurations and product ratios, there is a high heat integration potential as the obtained heat from the combustion of solids after fermentation can be fully used to cover the heat demands of other units. Overall, the hot and cold utility can be drastically reduced. Further, by varying the product ratio, the sensibility of the heat integration towards the solid fraction and its heating value, respectively, can be reduced, thereby ensuring more robust operation. Further, a minimum for utility was found between these extreme points. Therefore, the presented process offers a versatile concept with potential for adaptation to different market situations.

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