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Comparison of different reactive distillation schemes for ethyl acetate production using sustainability indicators

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ABSTRACT

An assessment of different intensified processes for ethyl acetate production by direct esterification was performed. After the selection and validation of the adequate thermodynamic and kinetic models, a comparison among different reported processing technologies (i.e., conventional, reactive distillation, reactive distillation with pressure swing, dividing wall column with reactive reboiler), and a novel proposed configuration using a reactive dividing wall column was carried out. Specifications of raw materials and products used as constrains during simulations were defined according with market requirements. To perform a fair assessment among different alternatives, each process was optimized using a mixed strategy of sensitivity analysis coupled with sequential quadratic programming algorithm. Total annual cost was selected as the optimization variable. Conversion, productivity, mass intensity, mass productivity, Sheldon's Factor (E-Factor), water-free Sheldon's factor (E_W-Factor), and energy intensity were used as sustainability indicators. According with results, the novel reactive dividing wall column configuration proposed in this work ends up being the more energy efficient and cost effective (46% energy and 26% cost savings compared with the traditional process) and also it is characterized by the best sustainability indicators.

1. Introduction

Over the last decades, there has been an increasing interest in products and processes that meet sustainable development criteria. After the broad definition of sustainability accounting for the triple bottom line dimensions (environmental, social and economic), different attempts have been done to transform such a concept into basic green engineering principles, and furthermore into sustainability indicators to measure how green processes or products can be. Despite the sustainability indicators can be used to evaluate existing processes, its major value can be encountered when applied in the analysis of new processes that need to be more cost-effective and environmentally friendly than existing ones; for example, when developing processes that switch from fossil to bio-based feedstock. Due to the increase use of biomass as a feedstock, and taking into account its higher costs compared with fossil feedstock, it is necessary to develop more efficient technologies to reach cleaner, safer, and more cost-effective production of bio-based derivatives [1].

Among the different types of chemicals currently produced from non-renewable feedstock that can be replaced by bio-based alternatives, solvents stand out because their intensive consumption in a large variety of processes and products. In addition to the fossil resources depletion, the environmental impacts of using traditional solvents are evident, for instance in the contamination of surface and underground waters and also in the air pollution near urban areas. From the variety of traditional solvents, ethyl acetate (EtAc) distinguishes as a major industrial commodity, which is mainly used as solvent for paints, coatings, resins, inks, and in decaffeination. It is also a main ingredient in different fragrances and flavors for consumer products.

There are several chemical routes for EtAc production implemented at the industrial scale, using both fossil-based and bio-based raw materials (Table 1). EtAc is mainly produced by esterification of acetic acid and ethanol in liquid or vapor phase (1), by acetylation of ethylene (2), and by ethanol dehydrogenation (3). The safety indicators [2] and atom economies of these routes are also presented in Table 1.

The presence of ethylene in the olefin acetylation (route 2), the production of hydrogen in the Tishchenko pathway (route 3) together with the extreme conditions of both processes affect negatively their safety indicators. This reduces the benign-ness of

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Nomenclature

BRD	Batch reactive distillation
C	Concentration (mol/L)
E_a	Activation energy (J/mol)
EtAc	Ethyl acetate (–)
EtOH	Ethanol (–)
H_2O	Water (–)
H_2SO_4	Sulfuric acid (–)
HAc	Acetic acid (–)
k	Kinetic constant (mol/s)
K_c	Equilibrium constant
P_S	Pressure swing
RD	Reactive distillation (–)
RDWC	Reactive dividing wall column (–)
W_{cat}	Catalyst mass fraction ($kg_{catalyst}/kg_{solution}$)
x	Mole fraction liquid phase (–)
y	Mole fraction vapor phase (–)
TAC	Total annual cost (million Usd/year)

these routes despite the fact both have high atom economy and that hydrogen co-produced in the second route could be of interest. Comparatively, direct esterification (route 1) has the lowest atom economy from all three reactions; however it has the lower value of the safety indicator being the most benign chemical route according with metrics described by Srinivasan et al. [2]. Additionally, in a recent study it was found that among the chemical routes of Table 1, direct esterification of bio-based acetic acid and ethanol appears to be the more cost-effective alternative as well as the one with the lower global warming potential [3].

Despite Fisher esterification to EtAc is a classic example used in the academia to introduce basic concepts on chemical reaction engineering and thermochemistry, this system is still under active investigation. In recent years, different processing technologies applied to EtAc production have been reported, most of which focus on a process intensification (PI) approach. Notwithstanding the proposed technologies have claimed to be cost-effective and environmentally friendly, no sustainability assessment of such technologies has been carried out. Furthermore, as there is room for future processes development by introducing more complexity during PI (for instance by implementing heat-integrated reactive separations), there is need for including also the sustainability evaluation in the early stages of the process synthesis.

Benefits of PI are associated with the enhanced safety, space and waste reductions, energy savings, higher efficiency and productivity, and consequently better economic and environmental performance. As an effort to classify most PI attempts reported in the literature, Van Gerven and Stankiewick [4] described four approaches commonly used according with the studied domain: thermodynamic, functional, spatial, and temporal.

From a general point of view, the thermodynamic approach for PI consists of energy integration of streams, stages or operations, to replace the required amount of heating and/or cooling provided with utilities. The use of preheating exchangers, pump-arounds, vapor recompression, and dividing wall columns are examples of such energy integrations. The functional domain deals with the integration of two or more operations or technologies within a single unit. This is the case of hybrid and reactive separations such as reactive distillation (RD), catalytic distillation, reactive adsorption, membrane distillation, and membrane reactors among others.

Considering all the above, this work studies and develops a novel processing technology for EtAc production by using a reactive dividing wall column. Although RD and dividing wall column with reactive reboiler has already been proposed separately [5,6], the proposed configuration of using a reactive dividing wall column (RDWC) is innovative for EtAc production, and has not been reported in the open literature. The performance of the proposed technology was compared with other intensified processes by considering quantitative economic and sustainability indicators.

Because most reports on EtAc production by intensified processes have been developed using different modeling basis (thermodynamics, kinetics, models, etc.), specifications (raw materials and product purities, catalysts, etc.), and assumptions; a direct comparison among them is difficult and anyhow subjective. In this sense, it was necessary to carry out such comparison under equivalent conditions with the optimized processes. To the knowledge of the authors, this comparison of current intensified technologies (including economic and sustainability indicators) has not been previously accomplished.

2. Methodology

In order to objectively compare the different intensified processing alternatives reported in the literature, a complete revision of the fundamentals, constrains, and specifications of the process was necessary. To begin with, a proper thermodynamic model that adequately describes phase equilibria of the reactive systems was selected. Regarding reaction kinetics, there was the need to select a specific catalyst and to explore and validate the corresponding kinetic model. Afterwards, a review of the reported intensified processes for EtAc production was performed, paying special attention to reactive distillation sequences. Detailed described processing alternatives were selected for simulations, and further sustainability analysis was performed. Simulation of the different schemes was performed by mean of steady-state equilibrium-stage simulations using Aspen plus 7.3®. Raw materials and product specifications used during simulations were the same for all intensified processes under study. In this sense, specifications were established according with commercial technical datasheets. In some cases, some adjustments over the original reported processes were necessary to achieve the specifications of the commercial product. The design pressure for all columns was selected to be 1 bar, except for the pressured column in the pressure swing process. Temperature in the condensers and decanters was verified to guarantee the use of water from cooling towers, which was assumed to be at 25 °C.

After all simulations met the design criteria, the total annual costs (TAC) were computed for each configuration. To do so, a 3-year period for return on investment was used. Since world's

Table 1
Industrial chemical routes for ethyl acetate production and some sustainability indicators.

Chemical route	Reaction	Atom economy (%)	Safety indicator[a]
1	$CH_3CH_2OH + CH_3COOH \leftrightarrow CH_3COOCH_2CH_3 + H_2O$	83,0	1.7
2	$CH_2 = CH_2 + CH_3COOH \rightarrow CH_3COOCH_2CH_3$	100	2.6
3	$2CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + 2H_2$	95,6	2.2

[a] Calculated as a cumulative index of the four chemical safety parameters (Toxicity, Reactivity, Explosiveness and flammability) as mentioned in [2].