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Design of thermally coupled reactive distillation schemes for triethyl citrate production using economic and controllability criteria

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HIGHLIGHTS

- Conceptual design of a triethyl citrate process was carried out.
- Reactive residue curve maps used for conceptual design of a multi-reaction system.
- Reactive dividing wall column used as intensification alternative.
- Optimization including controllability at early stages if conceptual design.
- Large energy savings using dividing wall columns with acceptable controllability.

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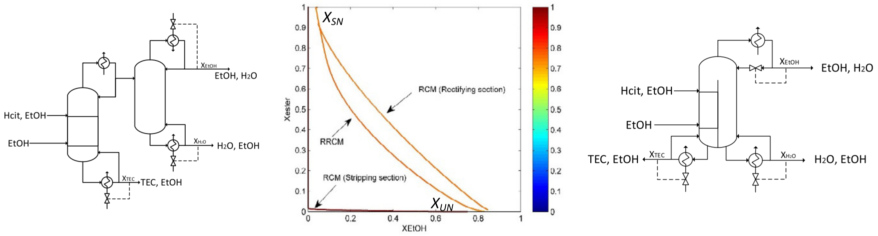
GRAPHICAL ABSTRACT



ABSTRACT

This work describes a systematic process design for triethyl citrate production by direct esterification of citric acid with ethanol via simultaneous reaction-separation technologies. The design methodology includes simultaneous optimization of controllability and profitability criteria. With a novel approach, the conceptual feasibility analysis of the intensified processes was carried out by extending the reactive residue curve maps (RRCM) to mixtures with six components by implementing a substitution degree parameter. The RRCM have been also extended to the conceptual design of dividing wall columns. The configuration of both, traditional and dividing wall reactive distillation columns, were obtained from the conceptual analysis. The processes were simulated using experimentally validated models, and further optimized using a nature inspired multi-objective algorithm. A triethyl citrate production capacity of 10 kTon/yr was used as process specification. Final designs evidenced citric acid conversions above 99.9%, energy consumption from 3-5 MJ/kg, and a TEC production costs of c.a 1.5 USD/kg. Controllability assessment was performed by evaluating the condition number of the proposed operating schemes. Pareto diagrams indicate that the minimization of total annual costs and controllability are conflicting goals in both production schemes. Nevertheless, both alternatives withstand large perturbations over the main process variables. The reactive dividing wall column scheme results in large energy and cost savings over a traditional reactive distillation process.

1. Introduction

Over the last decade, bioderived molecules have increased their market share in the plasticizers sector due to the increasing concerns on the toxicity, biodegradability and sustainability of traditional petroleum based plasticizers [1]. Despite the fact that

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Nomenclature

List of Symbols and Abbreviations

a_i	activity of component *i* in the liquid phase
B_f	molar flow of bottoms product
CA	citric acid
CN	condition number
COF	controllability objective function
D_f	molar flow of distillate
DEC	diethyl citrate
DEE	diethyl ether
D_e	equivalent diameter for RDWC
D_{prefac}	prefactionator column diameter
D_{main}	main column diameter
E_A	activation energy, kJ/kmol
EtOH	ethanol
H	molar holdup of residual liquid, mol
$K_{cat,n}$	kinetic constant for catalytic reaction n, $kg_{sol}/kg_{cat}\ s^{-1}$
$K^0_{cat,n}$	pre-exponetial factor for catalytic reaction n, $kg_{sol}/kg_{cat}\ s^{-1}$
$K_{self,n}$	kinetic constant for autocatalytic reaction n, $kg_{sol}/kg_{cat}\ s^{-1}$
$K^0_{self,n}$	pre-exponetial factor for autocatalytic reaction n, $kg_{sol}/kg_{cat}\ s^{-1}$
K_n	equilibrium constant of reaction n
M_f	molar holdup of stage f
MEC	monoethyl citrate
MNG	maximum number of generations
MODE	multi-objective differential evolution
NP	population size
Pc	crossover probability
Pm	mutation probability
r_j	rate of reaction *j*, s^{-1}
RCM	non-reactive residue curve trajectorie
RD	reactive distillation
RDWC	reactive dividing wall column
RRCM	reactive residue curve map
SD	substitution degree
SDV	singular value decomposition
t	time, s
T	temperature
TAC	total annual cost, \$/yr
TEC	triethyl citrate
V	vapor molar flow, mol/s
w_{cat}	catalyst loading, kg_{cat}/kg_{sol}
x_{ester}	total mole fraction of citric esters in the liquid mixture
X_{EtOH}	reduced concentration of ethanol in the liquid mixture
x_i	liquid mole fraction of component i
X_{SN}	stable node of a residue curve map
X_{UN}	unstable node of a residue curve map
y_i	vapor mole fraction of component i
Y_{ester}	reduced concentration of citric esters in the liquid mixture

Greek Letters

ΔS_i	supply imbalance of component i due to a given disturbance
ξ	forward dimensionless integration variable
σ	backward dimensionless integration variable
k_{pq}	gain of controlled variable p when manipulated variable q is disturbed
$v_{i,j}$	stoichiometric coefficient of component *i* in reaction *j*
$v_{T,j}$	sum of the stoichiometric coefficients in reaction j.
τ	residence time
τ_q	characteristic time

petroleum-based phthalate plasticizers still dominate the current global market (above 80% of world production), it is expected that biobased substitutes will represent nearly 30% of the total market in coming years [2–5]. In some niche applications such as the fabrication of medical devices, toys, food/feed packing, pharmaceuticals and cosmetics; non-phthalate alternatives are preferred for polymers plasticization. Nevertheless, not all bioderived plasticizers have shown better technical performance than the widely used phthalic acid esters. Among various environmentally friendly alternatives, triethyl citrate (TEC) (with or without acetylation) is a well-known phthalate substitute in different applications. In addition to its good plasticizing properties, TEC is generally recognized as safe (GRAS) [6] which make it suitable for sensitive products.

In spite of the TEC benefits from a social and environmental standpoint, its sustainability as a phthalate substitute is still questioned due to the high costs [7]. Factors increasing TEC production costs include: the use of batch instead of continuous processing; the higher prices of the biobased feedstocks (compared with petroleum derived); the need for alcohol excess to dissolve citric acid and to overcome chemical equilibrium limitations; and the large energy consumption in the separation operations. In this direction, there is need for developing enhanced TEC production processes, and to screen them at the early stages of the design to stablish their technical and economic feasibility before up-scaling [8]. Some attempts to reduce TEC production costs through process intensification have been recently reported [9–14]. To reduce the excess of ethanol (EtOH), continual displacement of the esterification equilibrium has been achieved via reactive distillation (RD) [10]. Further improvements by using a RD column with side reactors have also been considered [15]. Additionally, energy saving technologies such as heat integration and thermal coupling have been proposed for TEC RD processes [16].

In recent years, the use of side rectifiers, side strippers, Petlyuk columns, and reactive dividing wall columns (RDWC), as thermally integrated sequences, have shown benefits in terms of capital cost reduction and energy savings in different reactive systems [15–17]. However, a high degree of integration makes process design and optimization a non-trivial task due to the increase in the number of degrees of freedom, and the complex behavior of the intensified units [18]. Although better control characteristics have been observed in some thermally coupled configurations over the traditional ones [19], such verifications are seldom performed due to the complexity of the resulting dynamic mathematical model. Therefore, annual costs and energy consumption are often selected as objective functions during process synthesis and optimization, while controllability is evaluated at a later stage.

To include controllability within the preliminary stages of the design process, recent reports described how the dynamic behavior of distillation columns for multicomponent mixtures can be approximately quantified through the evaluation of steady state simulations assuming first order responses [20]. The methodology consists on performing small perturbations in the manipulated variables of an open loop steady-state simulation, and extracting the gain matrix from the differences observed in the controlled variables. As a result, the time constant from the observed changes in molar holdup and molar flow rate of a key component are