



# Optimally designed reactive distillation processes for eco-efficient production of ethyl levulinate

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1 **Optimally designed reactive distillation processes for eco-efficient**  
2 **production of ethyl levulinate**

3  
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15  
16 **Abstract**

17 **BACKGROUND:** Ethyl levulinate (EL) is an important chemical that can be used as a bio-based  
18 replacement of fuel additives such as MTBE and TAME. The EL production from lactic acid  
19 and ethanol is a viable option, as both precursors can be obtained from biomass. But the  
20 problem of EL production by esterification is that this reaction is hindered by the chemical  
21 equilibrium limitations and the boiling points ranking which is not the most favorable.

22 **RESULTS:** This study provides novel optimally designed reactive distillation (RD) processes  
23 for the production of EL, taking into account costs, environmental impact and safety. The  
24 thermally coupled RD process is the most appealing, with the lowest energy use (1.667 MJ/kg  
25 EL), minimal investment cost, major energy savings (up to 54.3% lower than other RD  
26 processes), reduced environmental impact (up to 51% lower ECO 99 index value) and similar  
27 safety as other RD processes considered (less than 2% differences in the IR indicator).

28 **CONCLUSION:** The multi-objective optimization approach used here showed its robustness,  
29 practicality and flexibility to provide multiple optimal designs of intensified processes that are  
30 economically attractive, environmentally friendly, and inherently safe.

31  
32 **Keywords:** reactive distillation, sustainable process, optimal design, safety, green chemistry

33

## 1 1. INTRODUCTION

2 Levulinic acid (LA) is a key biobased chemical used among others in the production of eco-  
3 friendly herbicides, flavor and fragrance ingredients, skin creams and degreasers. Production  
4 of LA is hindered by key challenges such as the low concentrations of LA resulting from the  
5 deconstruction of cellulose and recovering the mineral acids used for that task. LA is usually  
6 recovered from the reaction mixture using energy-intensive processes involving distillation,  
7 (reactive) extraction, adsorption, electrodialysis, esterification, and reactive distillation.<sup>1,2</sup>  
8 Promising fuel additives can be obtained from LA, such as 2-methyltetrahydrofuran (MTHF)  
9 and ethyl levulinate (EL). The use of bio-fuels additives grants several advantages, such a  
10 better performance of engines and lower environmental impacts. Particularly, EL can be used  
11 as a biobased replacement of fuel additives, such as MTBE and TAME.<sup>3</sup> The market cost of  
12 MTHF and EL is in the range of \$1.53-5.68 per liter, which is still higher than the price of  
13 petrol or additives in many countries.<sup>4</sup> Therefore, reducing the production cost of the bio-  
14 based additives is a stimulating economic reason to optimize their production from levulinic  
15 acid. The current forecast for the EL production is very promising and the global EL market is  
16 expected to reach USD 11.8 mln by 2022.<sup>5,6</sup> The interest in the development of economically  
17 feasible and sustainable processes for EL has increased due to the potential application of EL  
18 in biodegradable polymers like polyesters, polyurethane, and thermoplastics. EL can be also  
19 used to produce diphenolic acid (used to replace the bisphenol-A that is widely applied in the  
20 production of polycarbonate).<sup>7</sup>  
21 Second generation biorefineries need to focus on sustainable chemical products made using  
22 green chemical technologies with high efficiency as well as improved bioprocesses that could  
23 convert biomass directly into esters.<sup>8</sup> In this respect, further research into the production of  
24 EL is necessary, for example on high efficiency catalysts<sup>9,10</sup> and novel efficient routes that are  
25 economically attractive and ecologically friendly.<sup>11</sup> A mesoporous solid superacidic zirconia  
26 modified catalyst was reported to exhibit high performance for the LA esterification to EL,<sup>12</sup>  
27 while other used acid ionic liquid as catalyst to produce EL.<sup>13</sup> Studies also point out some  
28 challenges to be addressed for competitive EL bioprocesses, such as the hydrolysis of biomass  
29 and the consequent separation operations of products and byproducts.<sup>6</sup> The route that involves  
30 the direct conversion of lignocellulosic material through the hydrolysis reaction to produce  
31 EL presents drawbacks, e.g. energy demanding difficult separations employing techniques  
32 such as vacuum distillation, evaporation, stripping or extraction with harmful toxic solvents.  
33 The downstream processing would clearly benefit from more insights into fluid separations.<sup>14</sup>

1 A more appealing route is the conversion of biomass to LA, followed by esterification with  
2 ethanol to obtain EL,<sup>15</sup> but this route is limited by the equilibrium of the reaction.<sup>16</sup> Reactive  
3 distillation (RD) can be effectively used to overcome the equilibrium limitations. This well  
4 known process intensification technique offers higher conversion, better selectivity and  
5 reduced operational and capital expenditures as compared to classical processes.<sup>17-19</sup> The  
6 advantages of RD are attributed to the continuous removal of the products (thus pulling the  
7 chemical equilibrium instead of pushing it with an excess of reactant). Recent studies have  
8 also highlighted the reductions in energy usage and costs that can be achieved by applying  
9 thermal coupling to RD processes, with energy savings and lower costs in the range of 24-  
10 63% and 8-43%, respectively.<sup>20-23</sup> The major reductions in energy use and associated CO<sub>2</sub>  
11 emissions are due to the thermal coupling that minimizes the remixing phenomena. Hence  
12 thermal coupling helps to further improve the advantages of the RD operation, transforming  
13 this operation into a more sustainable and eco-friendly process.

14 This work is the first to present optimally designed reactive distillation processes (including  
15 thermal coupling) for EL production, taking into account several key aspects for optimization:  
16 total annual cost (TAC), environmental impact (Eco-indicator 99) and process safety  
17 (Individual Risk). To allow a fair comparison, some of the topology of the RD processes is  
18 based on previous work reported recently (but focused on economics only),<sup>24</sup> while others are  
19 new (e.g. based on RD and DWC technology). However, besides considering the economic  
20 aspects, this work uses rigorous process simulations in Aspen Plus and it implements a  
21 rigorous multi-objective optimization algorithm in which the three key factors (economics,  
22 environmental, and safety) are simultaneously evaluated. The meta-heuristic optimization  
23 algorithm used here is based on multi-objective differential evolution and tabu list (MODE-  
24 TL). This multi-objective algorithm allows the comparison of multiple solutions and it was  
25 used to determine multiple designs that meet the desired specifications of the products, at  
26 minimal cost and environmental impact while meeting process safety standards. Obviously,  
27 the assessment of the economic, environmental and safety issues has a strong relevance in the  
28 context of designing green and sustainable processes for a circular economy.<sup>25,26</sup>

29

## 30 **2. PROBLEM STATEMENT**

31 EL production from LA and ethanol is a viable biofuel option, since both precursors can be  
32 obtained from biomass. But the problem of EL production by esterification is that this  
33 reaction is hindered by the chemical equilibrium limitations. RD is a feasible process that  
34 could overcome all these limitations,<sup>27</sup> but the boiling points ranking is not the most favorable

1 as the reactants are the lightest and heaviest components respectively, while the products are  
2 mid-boiling components – so this system belongs to group  $I_r^{28,29}$  with the order of normal  
3 boiling points: ethanol ( $T_{b,A}=78.3\text{ }^\circ\text{C}$ ), water ( $T_{b,C}=100\text{ }^\circ\text{C}$ ), ethyl levulinate ( $T_{b,D}=205.8\text{ }^\circ\text{C}$ )  
4 and levulinic acid ( $T_{b,B}=257.0\text{ }^\circ\text{C}$ ). The consequence is that a single RD column is  
5 insufficient to produce both products on-spec hence at least two columns will be required for  
6 neat operation using stoichiometric reactants ratio (see Figure 1). To solve this problem, this  
7 study proposes several optimally designed RD processes that make use of multiple distillation  
8 columns that are thermally coupled and/or heat integrated for increased eco-efficiency.

9

### 10 **3. APPROACH AND METHODOLOGY**

11 The reactive distillation process configurations considered in this work are shown in Figure 2:  
12 conventional RD process (CRDP), thermally coupled RD (TCRD), RD with heat integration  
13 (RDHI), thermally coupled and heat integrated RD (THRD), and RD with dividing wall  
14 column (PDWC). These RD processes produce 100 kmol/hr EL (equivalent to about 120  
15 ktpy) with a purity of 99.5 mol% (same as for water by-product). This is consistent with the  
16 purity values reported in previous studies about the design of EL processes,<sup>6</sup> and in the  
17 context of using EL as a fuel bio-additive.<sup>30</sup>

18 All processes consist of a reactive distillation column (RDC) and two separation columns  
19 (RC-1 and RC-2). The fresh reagents (LA and ethanol) are fed near the top of the RDC at a  
20 rate of 100 kmol/h each. An excess of LA is used actually due to the recycle of unreacted LA  
21 (in addition to the continuous reflux of LA). Excess operation was proved to perform better  
22 than the neat operation.<sup>24</sup> The first separation column (RC-1) performs the separation of water  
23 by-product as distillate from the main product (EL) and the unreacted LA. The second  
24 separation column (RC-2) performs the separation of EL product as top distillate from the  
25 excess LA that is removed as bottom product and recycled (LA-R) to the RDC unit.

26 The thermally coupling in TCRD is performed between the reboiler of the RC-1 column and  
27 the bottom of RDC unit, whereas the RDHI configuration uses heat integration between the  
28 top vapor leaving the RC-2 column (highest temperature equipment) and the bottom of the  
29 RDC unit. THRD combines thermal coupling (between the reboiler of RC-1 and the bottom  
30 part of the RDC unit) and heat integration (between the top vapor of RC-2 column and a  
31 withdrawal product side-stream of RC-1). PDWC is a novel configuration that includes an RD  
32 and a dividing wall column (DWC), which results of merging the columns RC-1 and RC-2 in  
33 a single shell divided by an internal wall. From a conceptual point of view the length of the  
34 wall is determinate by the number of trays of the sections of columns RC-1.

1

2 **3.1. Chemistry and kinetics**

3 EL is produced by the esterification reaction of LA with ethanol, where the following notation  
4 is used: A = Levulinic acid; B = Ethanol; C= Ethyl levulinate, and D = Water.



6 The reaction rate is given by the following kinetics equation:

$$7 \quad -r_A = k_1 \left( a_A a_B - \frac{a_C a_D}{K_a} \right) \quad (2)$$

8 and the equilibrium constant ( $K_a$ ) can be expressed as the ratio between the kinetics constants  
9 of the forward and reverse reactions:

$$10 \quad K_a = \frac{k_1}{k_2} \quad (3)$$

11 The kinetic constants  $k_1$  and  $k_2$  are expressed as follows:

$$12 \quad k_1 = A_f \exp\left(\frac{-E_{0,f}}{RT}\right) \text{ and } k_2 = A_r \exp\left(\frac{-E_{0,r}}{RT}\right) \quad (4)$$

13 The kinetic parameters of the esterification reaction are the following:<sup>31</sup>

$$14 \quad A_f \left( \frac{\text{mol}}{\text{kg min}} \right) = 0.08 \cdot 10^8 \quad (5)$$

$$15 \quad E_{0,f} \left( \frac{\text{kJ}}{\text{kg min}} \right) = 37.79 \quad (6)$$

$$16 \quad \frac{A_f}{A_r} = 43.33 \quad (7)$$

$$17 \quad \frac{\Delta h_f}{R} (K) = 105.2 \quad (8)$$

18

19 **3.2. Property model**

20 NRTL-HOC (non-random two-liquid model with Hayden-O'Connell correction) model was  
21 selected as adequate thermodynamic model to estimate the vapor-liquid equilibrium (VLE).  
22 This property model handles in a consistent way the phenomena associated with the presence  
23 of polar compounds and carboxylic acids, such as the solvation and the dimerization in the  
24 vapor phase of carboxylic acids.<sup>17,32</sup> The binary interaction parameters of the components  
25 were taken from another reported work,<sup>33</sup> and implemented in Aspen Plus v8.4.

26

### 1 **3.3. Process optimization**

2 This study uses a multi-objective meta-heuristic optimization algorithm based on differential  
3 evolution and tabu list (MODE-TL) - further details on this algorithm can be found  
4 elsewhere.<sup>34</sup> This algorithm allows the comparison of multiple solutions of optimized designs  
5 in the terms of multiple objective functions, described hereafter.

6  
7 **1. Total Annual Cost** (TAC) of each reactive distillation process considered here has been  
8 estimated as follows:

$$9 \quad TAC = OPEX + \frac{CAPEX}{Payback \ period} \quad (9)$$

10 The capital cost of each RD process was calculated by using the modular method.<sup>35</sup> The  
11 capital cost includes the cost of distillation columns, trays, heat exchangers, and compressors.  
12 The parameters and equations to calculate the cost can be found elsewhere.<sup>36</sup> Carbon steel  
13 was the assumed as construction material for all the equipment, and a payback time of 5 years  
14 was considered. The operating cost includes cooling utilities, heating utilities, and 8400 hours  
15 of yearly operation for each configuration. The utilities considered were: oil for heating at \$  
16 6.28/ GJ, low-pressure steam (6 bar, 160 °C) at \$ 7.78/GJ, electric power with a cost of \$  
17 16.8/GJ and cooling water (received at 20 °C and returned at 30 °C) with a unit cost of \$  
18 0.72/GJ.<sup>37,38</sup>

19  
20 **2. Environmental impact** quantified by the Eco-Indicator 99 (ECO99). The Eco-Indicator 99  
21 was used to evaluate the sustainability of the processes, to quantify the environmental impact  
22 and to detect the factors that largely affect in the environmental impact. This approach was  
23 proposed by Goedkoop and Spriensma.<sup>39</sup> Several authors have demonstrated that applying the  
24 Eco-Indicator 99 during the design and synthesis phases of chemical processes can lead to  
25 significant improvements and waste reduction.<sup>40-42</sup> This methodology is consistent with the  
26 philosophy of life cycle analysis (LCA) and sustainability in the design of chemical processes.  
27 The calculation of ECO99 is based on evaluating three major damage categories: human  
28 health, ecosystem quality, and resources depletion. Each category is divided into 11 sub-  
29 categories. In case of distillation columns, the factors that have the strongest influence on  
30 ECO99 are the steam used to supply the heat duty, electricity utilized for pumping of cooling  
31 water, and the steel necessary to build the equipment. The Eco-Indicator 99 is defined as:

$$1 \quad Eco - Indicator \ 99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (10)$$

2 where  $\beta_b$  represents the total amount of chemical  $b$  released per unit of reference flow due to  
 3 direct emissions,  $\alpha_{b,k}$  is the damage caused in category  $k$  per unit of chemical  $b$  released to the  
 4 environment,  $\omega_d$  is a weighting factor for damage in category  $d$ , and  $\delta_d$  is a normalization  
 5 factor for damage of category  $d$ , respectively. According to the importance of three major  
 6 impact categories (human health, ecosystem quality, and resources depletion) the weighting  
 7 for Eco-Indicator 99 was specified as follows: damages to human health and damage to  
 8 ecosystem quality were set equal in importance (i.e. both categories were equally weighted),  
 9 while the damage to the resources was considered to be half of importance for weighting. The  
 10 impact categories and the values of these used in this study were taken from a previously  
 11 reported work<sup>32</sup>. The scale of the values was chosen such that the value of 1 point is  
 12 representative for a 1000th of the yearly environmental load of one average EU inhabitant.

13

14 **3. Process safety** quantified by the individual risk (IR) index. The IR can be defined as the  
 15 risk of injury or decease to a person in the vicinity of a hazard.<sup>43,44</sup> The main objective of this  
 16 index is the estimation of likelihood affectation caused by the specific incident that occurs  
 17 with a certain frequency. The IR does not depend on the number of people exposed. The  
 18 mathematical expression for calculating the individual risk is the following:

$$19 \quad IR = \sum f_i P_{x,y} \quad (11)$$

20 where  $f_i$  is the occurrence frequency of incident  $i$ , whereas  $P_{x,y}$  is the probability of injury or  
 21 decease caused by the incident  $i$ . In this work, an irreversible injury (decease) is used, for  
 22 which more data are recorded. The calculation of IR can be carried out through quantitative  
 23 risk analysis (QRA), which is a methodology used to identify incidents and accidents and  
 24 their consequences. The QRA starts with the identification of possible incidents, for  
 25 distillation columns are identified continuous release and instantaneous releases. A  
 26 continuous release is produced mainly by a rupture in a pipeline or partial rupture on process  
 27 vessel causing a leak. The instantaneous release consists in the total loss of matter from the  
 28 process equipment originated by a catastrophic rupture of the vessel. These incidents were  
 29 determined through hazard and operability study (HAZOP). The frequencies for each incident  
 30 ( $f_i$ ) were taken according to the previously reported values by American Institute of Chemical  
 31 Engineers<sup>43</sup> and using the event tree diagrams obtained with all probabilities of instantaneous  
 32 and continuous incidents, along with their respective frequencies. Accordingly, instantaneous  
 33 incidents are: boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud



1 explosion (UVCE), flash fire and toxic release, whereas the continuous release incidents are:  
 2 jet fire, flash fire and toxic release.

3 Once the incidents have been identified, the probability  $P_{x,y}$  can be calculated through a  
 4 consequence assessment, which consists in determining the physical variables as the thermal  
 5 radiation, the overpressure and the concentration of the leak originated by incidents, and their  
 6 respective damages. The calculation of the physical variables was realized according to the  
 7 equations reported by AIChE<sup>43</sup> and some other authors.<sup>45,46</sup> The worst scenario was  
 8 considered for calculating the dispersion, as well as a wind speed of 1.5 m/s and atmospheric  
 9 stability type F.<sup>43,45,46</sup>

10 The quantification of the damage caused by physical variables of each incident is calculated  
 11 through a vulnerability model commonly known as the probit model. In this work, the damage  
 12 considered is death due to fires, explosions and toxic releases. The probit models associated  
 13 with deceases by thermal radiation (teEr) and overpressure due to explosions ( $p^0$ ) are:

$$Y = -14.9 + 2.56 \ln \left( \frac{t_e E_r^{\frac{4}{3}}}{10^4} \right) \quad (12)$$

$$Y = -77.1 + 6.91 \ln(p^0) \quad (13)$$

16 Due to the lack of reported probit models of toxicity of components considered in this work,  
 17 the calculation of the damage for toxic releases were carried out using the LC50.<sup>43</sup> Finally, the  
 18 probability  $P_{x,y}$  is calculated substituting the probit results into the following equation:

$$P_{x,y} = 0.5 \left[ 1 + \operatorname{erf} \left( \frac{Y - 5}{\sqrt{2}} \right) \right] \quad (14)$$

20 The physical properties for each substance used for the consequence assessment are reported  
 21 in Table 1. These were taken from the National Institute for Occupational Safety and Health.<sup>47</sup>

22

23 **4. Objective function.** The optimal design of RD processes means minimizing the objective  
 24 function that considers TAC, EI99, and IR. These are restricted to satisfy the mass flowrates  
 25 and purity constrains. All the objectives (TAC, EI99, IR) had been considered equally  
 26 important, thus the weights are the same:

27

$$\min [TAC, EI99, IR] = f(NS_i, FS_i, R_i, VF, LF, DC_i, HD_i, k, C_{i,j}) \quad (15)$$

$$\begin{aligned} \text{1 Subject to: } & \vec{y}_m \geq \vec{x}_m \\ & \vec{w}_m \geq \vec{u}_m \end{aligned} \tag{16}$$

2 where  $NS_i$  is the total number of stages,  $F_{S_i}$  are the feed stages,  $R_i$  the reflux ratios,  $VF$  and  $LF$   
 3 the interconnection vapor and liquid flows,  $DC_i$  the distillation columns diameters,  $HD_i$  the  
 4 heat duties of the reboilers, and  $C_{i,j}$  the concentrations of chemicals inside the column. The  
 5 optimization problem is subjected to constraints related to purity and mass flowrates. In this  
 6 work,  $y_m$  and  $w_m$  are the vectors of obtained purity and mass flowrate, while  $u_m$  and  $x_m$  are the  
 7 vectors of required purity and mass flowrate, respectively. The purity constraints for EL and  
 8 water were defined as 99.5 mol%, whereas the molar flow rate was set at least 99.5 kmol/h for  
 9 both EL and water in their respective streams. The decision variables used for optimizing the  
 10 RD processes (see Figure 2) are a combination of discrete and continuous variables, all of  
 11 them conveniently listed in Table 2.

12

13 **5. Multi-objective optimization strategy.** The multi-objective optimization algorithm (MODE-  
 14 TL) used in this work is a powerful stochastic global optimization tool which combines two  
 15 optimization techniques: the Differential Evolution (DE) and Tabu search (TS). The  
 16 combination of the features of these techniques confers to the multi-objective optimization  
 17 algorithm a faster convergence to global optima when compared with a single differential  
 18 evolution method and less computational time and effort. A more extensive description of the  
 19 differential evolution with tabu list (DETL) algorithm is provided by other authors,<sup>34,48</sup> as  
 20 well as in our recent study.<sup>46</sup>

21 The values of the parameters associated with the used MODE-TL algorithm are the following:  
 22 Population size (NP): 200 individuals, Generations Number (GenMax): 500, Tabu List size  
 23 (TLS): 100 individuals, Tabu Radius (TR): 0.01, Crossover fractions (Cr): 0.8, Mutation  
 24 fractions (F): 0.3. The values of NP, GenMax and TLS were determined through a previous  
 25 tuning process on the optimization algorithm, whereas the values of Cr, TR and F were taken  
 26 from the recommended values for these parameters.<sup>34,48</sup> This optimization method had been  
 27 implemented using a hybrid platform that interconnects Aspen Plus and Excel through Visual  
 28 Basic. Rigorous simulations are implemented in Aspen Plus using the RADFRAC model that  
 29 includes all mass and energy balances, equilibrium and reaction (MESHR) equations. The  
 30 recent implementations of this algorithm for the optimization of multiple chemical processes  
 31 can be found in other works that proved its robustness, practicality and flexibility to provide  
 32 the multiple designs of these processes.<sup>49,50</sup>

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**4. RESULTS AND DISCUSSION**

This section provides the simulation results of the optimized RD processes considering the economic, environmental and safety indexes. All processes were rigorously modeled using the process simulator Aspen Plus v8.4 (including the RADFRAC module) that provided the complete set of mass and energy balances along with the phase equilibrium calculations. All the runs to carry out the optimization were performed on an Intel<sup>(R)</sup> Core<sup>TM</sup> i7-4790 CPU @ 3.6 GHz, 12 GB computer.

Pareto charts are used in order to simplify the analysis of the results in a practical way. These Pareto front correspond to the 200 individuals for the generation 500, which is the last generation. By the generation 500 there are no more significant improvements to all objectives functions. The Pareto fronts are studied according to utopic point methodology that is based in the Pareto optimality concept. A Pareto optimal is a set of solutions on the border of the feasible solutions (usually called Pareto front), and the utopic corresponds to the solution were two or more objectives are in equilibrium and these objectives cannot improve anymore.<sup>51</sup>

The solutions in the Pareto chart can help in the decision making process by selecting the best option among all of the configurations to produce EL. The Pareto charts obtained for all of the RD processes at the end of the optimization process are illustrated in Figure 3 (lower left corner is better). Each point in the graphics represents a solution or design that meets the purity requirements with the best values of the three objective functions under evaluation.

The shapes of Paretos fronts for the ECO99 vs TAC are similar for all process configurations. This is explained by the influence of total energy used in each process (e.g. the energy required in the form of steam for heating, the electricity used for pumping of cooling water, the amount of steel required to build the equipment). The results are consistent with the findings reported for other processes involving separation operations.<sup>52</sup> Important reductions in the ECO 99 values for the TCRD process are obtained due to the energy savings of this process with respect to the others. This work also reveals that the PDWC configuration is actually not the best alternative in terms of energy savings and TAC, as one might have expected, since the integration of RC-1 and RC-2 columns in a single shell leads to an increased column diameter and larger amounts of substances present and processed in the column, thus leading to an increase in the energy use and total annual cost.

Concerning the Pareto front of IR vs TAC, it can be noticed that the forms exhibits a trend of opposite objectives. This behavior indicates that the selection of a design with the lowest

1 TAC causes the IR to increase hence the solutions that offer the best trade-offs between the  
2 two objectives are those located in the curve zone of the Pareto chart. Two key factors  
3 determine the value of the IR index in the processes, one of them is the represented by the  
4 physical properties of the substances and the other is the amount of the substances inside the  
5 columns. For instance, it was found here that there is a direct trade-off among the diameter of  
6 the RDC and the diameters of the separation columns. Despite a large value of diameter of  
7 RDC in a process with low values of both diameters of RC-1 and RC-2, the process will be  
8 favored in the IR index, meaning that the process will be safer than a process with larger  
9 diameters in RC-1 and RC-2.

10 The Pareto front of IR vs ECO 99 for all processes exhibits a similar trend as the IR vs TAC  
11 Pareto for these same configurations. In the optimal designs, the larger reflux ratios and  
12 reboiler duties the higher the usage of heating services and electricity for cooling services, and  
13 these larger values have a direct contribution in the increment of the ECO 99 values.

14 According to the behaviour of the Paretos of the objective functions IR vs ECO 99 and IR vs  
15 TAC, it is possible to assert that the best optimal designs of all the processes are found in the  
16 zone of the Pareto that compensates both objectives, this being the curve zone. Therefore, the  
17 selection of a design that compensates the IR index with the TAC, this choice directly  
18 balances the IR index with the ECO 99.

19 The chosen designs were selected according to the utopian point methodology, in which the  
20 utopic point corresponds to a hypothetical and ideal solution on the border of the Pareto front  
21 where two objectives cannot improve anymore and both are in equilibrium. The selected  
22 designs correspond to solutions closer to the utopic point.<sup>51</sup> The practicality of this  
23 methodology has been proved in recent work by other authors.<sup>46,49,50</sup>

24 Table 3 provides the design variables of the selected designs of the Pareto charts for all RD  
25 processes - the points selected for the sequences are the ones located in the curve zone where  
26 the best trade-offs between the two objectives are established. The TCRD process revealed  
27 the lowest energy use (10.8% lower than CRDP, 24.3% lower than THRD, 54.3% lower than  
28 RDHI, and 9.6% lower than PDWC). The energy savings are also reflected in the values of  
29 the TAC for TCRD which is 3.1%, 24.4% , 45.3%, and 12.8% lower as compared to CRDP,  
30 THRD, RDHI, and PDWC respectively. In terms of environmental impact (ECO 99), TCRD  
31 presents a value that is 6.8%, 22.7%,51.0% and 5.7% lower as compared with CRDP, THRD,  
32 RDHI, and PDWC respectively. However, in terms of safety all the processes are rather  
33 similar with small differences of 2% or less in terms of the IR index. Yet, these small  
34 differences in IR are translated in valuable information on the probability of catastrophic

1 events in the process, because of the models utilized in the calculation of the IR index, so  
2 even a difference of 1% in the IR value of a process compared to others implies differences of  
3 ten or even hundreds of meters in the affected region caused by events such as explosions,  
4 fires and instantaneous releases.

5 The results obtained in this work are different than reports of other authors.<sup>24</sup> The contrasts  
6 are explained by the fact that the implementation of a multi-objective optimization algorithm  
7 needs some adjustments to the rigorous process simulation: e.g. for the THRD process, the  
8 withdrawal side stage number and the side molar flow rate in the first separation column are  
9 both variables subject to optimization, while an additional constraint was added for the  
10 minimum temperature difference (driving force of 10 K) as it was found that only a fraction  
11 of the condenser energy of RC-2 was feasible to be utilized. In case of the RDHI sequence, a  
12 liquid stream enters the top of the RC-2 column while a vapor stream leaves the top via a heat  
13 exchanger, the heat duty of which is the heat that is subtracted from the heat duty of the  
14 reboiler of the reactive column. Based on the overall comparison, the TCRD process is the  
15 most appealing to be implemented in the EL production, having the lowest specific energy  
16 requirements (1.667 MJ/kg EL) and an annual cost of utilities of only \$ 30.35 per ton of EL  
17 produced, as well as lowest CO<sub>2</sub> emissions (110.4 kg/ton EL) due to thermal coupling. Figure  
18 4 provides the molar flow rates, temperatures and energy use for the optimal TCRD process.

## 20 5. CONCLUSIONS

21 The simulation results show that the eco-efficient production of ethyl levulinate is possible in  
22 reactive distillation processes with thermal coupling and/or heat integration. The multi-  
23 objective optimization takes into account simultaneously the total annual cost (TAC), eco-  
24 indicator 99 (EI99) and individual risk (IR), these parameters being selected according with  
25 the principles of green sustainable processes and circular economy, as they provide good  
26 detailed metrics to measure the economy, environmental impact, and safety of the process,  
27 which are necessary to create sustainable process.

28 The results of the optimization revealed that the thermally coupled reactive distillation  
29 (TCRD) process has the lowest energy use (1.667 MJ/kg EL) with major energy savings (9.6-  
30 54.3% lower than other RD processes), reduced environmental impact (5.7-51% lower ECO  
31 99 index value) and similar process safety (less than 2% difference as compared to other RD  
32 processes considered). Thus, the TCRD process is suggested as the best process alternative to  
33 produce ethyl levulinate, although there is room for further selection of other feasible RD  
34 processes where other tradeoffs among the indicators may be devised. The multi-objective

1 optimization approach used here showed its robustness, practicality and flexibility to provide  
2 multiple designs of intensified processes that are economically attractive, environmentally  
3 friendly, and inherently safe.

4 A potential way to further improve the EL production could be the use of RD starting from an  
5 aqueous solution of LA (instead of pure LA) that undergoes esterification with alcohols, but  
6 this is a topic for a future research study.

7

## 8 **ACKNOWLEDGMENT**

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12

## 13 **ABBREVIATIONS**

14	CAPEX	Capital expenditures
15	CRDP	Conventional reactive distillation process
16	DE	Differential Evolution
17	EL	Ethyl levulinate
18	LA	Levulinic acid
19	MODE-TL	Multi-objective differential evolution and tabu list
20	MTBE	Methyl tert-butyl ether
21	OPEX	Operating expenditures
22	QRA	Quantitative risk analysis
23	RD	Reactive distillation
24	RDHI	Reactive distillation with heat Integration
25	TAC	Total annual cost
26	TAME	Tert-amyl methyl ether
27	TCRD	Thermally coupled reactive distillation
28	THRD	Thermally coupled and heat integrated reactive distillation
29	TS	Tabu search
30	VLE	Vapor-liquid equilibrium

31

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1 **Tables**

2

3 **Table 1.** Safety related physical properties of the components

Component	Lower flammability limit (LFL)	Upper flammability limit (UFL)	Median lethal concentration (LC50)	Heat of combustion (kJ/mol)
Ethanol	3.3	19	14,000ppm / 1h	2344
Levulinic acid	1.8	9.87	1500 ppm / 1h	726
Ethyl levulinate	1.8	9.89	83 ppm / 1h	876.1

4

1

2 **Table 2.** Discrete and continuous decision variables for the optimized RD processes

Decision Variables	CRDP		TCRD		RDHI		THRD		PDWC	
	Cont.	Disc.	Cont.	Disc.	Disc.	Disc.	Cont.	Disc.	Cont.	Disc.
Number of stages, RDC		X		X	X	X		X		X
Number of reactive stages		X		X	X	X		X		X
Heat duty of RDC, kW	X								X	
Distillate flow, kmol h <sup>-1</sup>	X		X				X		X	
Diameter of RDC, m	X		X				X		X	
Number of stages, RC-1		X		X	X	X		X		X
Feed stage, RC-1		X		X	X	X		X		X
Reflux ratio of RC-1	X		X				X			
Interlinking flow, kmol h <sup>-1</sup>			X				X		X	
Bottom flow of RC-1, kmol h <sup>-1</sup>	X		X				X			
Diameter of RC-1, m	X		X				X		X	
Withdrawal side stage					X	X		X		
Side flow, kmol h <sup>-1</sup>							X			
Number of stages, RC-2		X		X	X	X		X		X
Feed stage, RC-2		X		X	X	X		X		X
Reflux ratio of RC-2							X		X	
Bottom flow, kmol h <sup>-1</sup>	X		X						X	
Heat duty of RC-2, kW	X		X				X		X	
Diameter of RC-2, m	X		X						X	
Total number of variables		15		15		13		17		16

3

1

2 **Table 3.** Design variables of optimal designs of reactive distillation processes

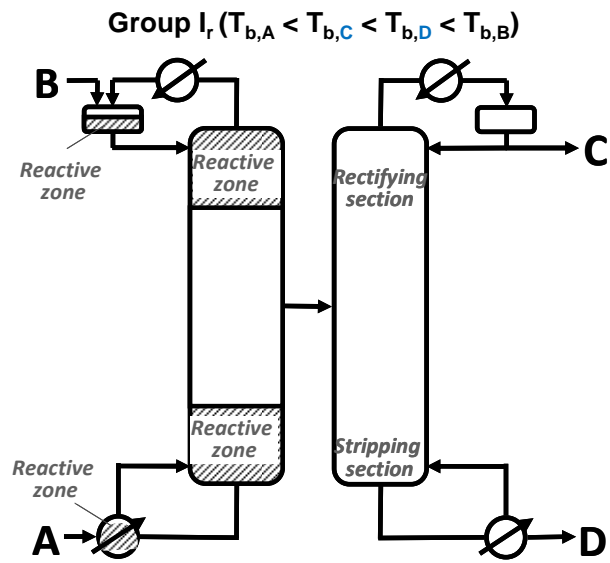
<b>Design Variables</b>	<b>CRDP</b>	<b>TCRD</b>	<b>RDHI</b>	<b>THRD</b>	<b>PDWC</b>
<b><i>Topology of columns</i></b>					
Number of stages, RDC	83	93	48	58	66
Number of reactive stages, RDC	2-45	2-63	2-23	2-37	2-32
Number of stages, RC-1	26	23	32	19	43
Number of stages, RC-2	31	34	16	16	57
Feed stage, RC-1	13	15	21	15	—
Feed stage, RC-2	21	27	1	14	18
Withdrawal side stage, RC-1	—	—	—	14	—
Withdrawal side stage, RC-2	—	—	—	—	22
Diameter of RDC, m	1.009	1.334	1.04	1.17	1.20
Diameter of RC-1, m	1.170	1.036	1.13	1.60	—
Diameter of RC-2, m	1.080	1.090	1.07	1.88	1.56
<b><i>Operating conditions</i></b>					
Top pressure, atm	1	1	1	1	1
Distillate flow, kmol h <sup>-1</sup>	493.73	441.58	532.464	342.606	201.294
Tray holdup, l	44.004	76.951	46.687	59.442	62.259
Reflux ratio of RC-1	0.5371	0.5819	0.9651	1.152	—
Reflux ratio of RC-2	—	—	—	0.7045	2.27
Heat duty of RDC, kW	3019.17	0	10211.3	0	2630.71
Heat duty of RC-1, kW	2738.91	4830.74	3226.57	6750.52	—
Heat duty of RC-2, kW	1698.80	1839.34	1122.45	2052.30	4745.72
Interlinking flow, kmol h <sup>-1</sup>	—	151.446	—	272.922	127.879
Side flow of RC-2, kmol h <sup>-1</sup>	—	—	—	24.7091	100.368
Bottom flow of RC-1, kmol h <sup>-1</sup>	118.687	119.813	117.416	125.435	—
Bottom flow of RC-2, kmol h <sup>-1</sup>	18.7575	19.9172	17.4219	25.6693	34.7812
Temperature bottom, RDC (°C)	118.95	117.70	117.94	117.15	122.72
Temperature bottom, RC-1 (°C)	227.31	232.07	227.47	228.63	—
Temperature bottom, RC-2 (°C)	247.83	267.91	230.42	235.69	278.02
<b><i>Molar flowrates of process streams</i></b>					
Ethyl levulinate stream, kmol h <sup>-1</sup>	99.5081	99.877	99.5036	99.7631	99.9950
Water stream, kmol h <sup>-1</sup>	99.6249	99.990	99.5128	99.9929	99.6316
<b><i>Purity of products (molar fraction)</i></b>					
Ethyl levulinate	0.9964	0.9998	0.9951	0.9999	0.9962
Water	0.9957	0.9981	0.9950	0.9979	0.9999
<b><i>Performance indexes</i></b>					
Energy per ton of product (GJ/ton EL)	1.8712	1.6676	3.6539	2.2033	1.8420
Total CO <sub>2</sub> Emissions (kt/yr)	14.960	13.309	29.707	17.650	14.107
CO <sub>2</sub> Emissions (kg/ton EL)	124.14	110.04	246.53	146.09	116.49
Utilities cost (million \$/yr)	3.8125	3.7141	6.9426	5.0005	4.2692
Equipment cost (million \$)	0.2544	0.2305	0.2767	0.2218	0.2580
TAC (million \$/yr)	4.0670	3.9447	7.2193	5.2224	4.5272
Eco99 (million Eco-points/yr)	1.7803	1.6592	3.3916	2.1465	1.7606
IR (1/yr)*10 <sup>5</sup>	45.994	46.766	46.150	46.962	44.934

3

1 **Figures**

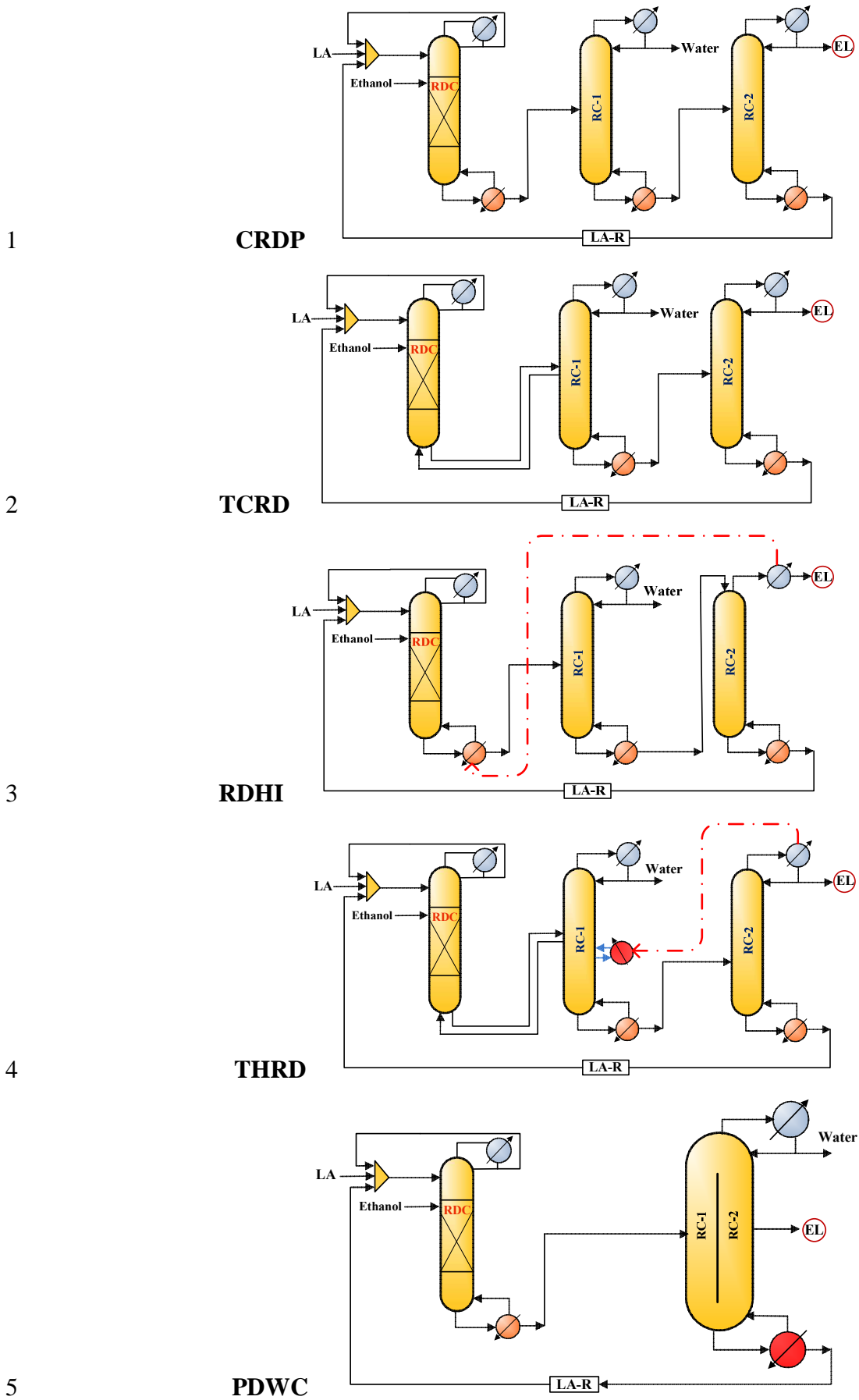
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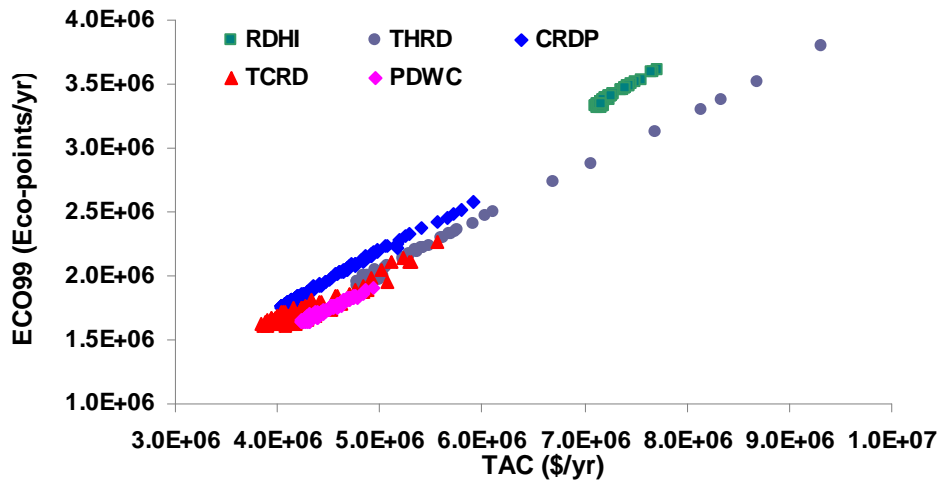
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5 **Figure 1.** Reactive distillation process for quaternary systems (group I<sub>r</sub>)

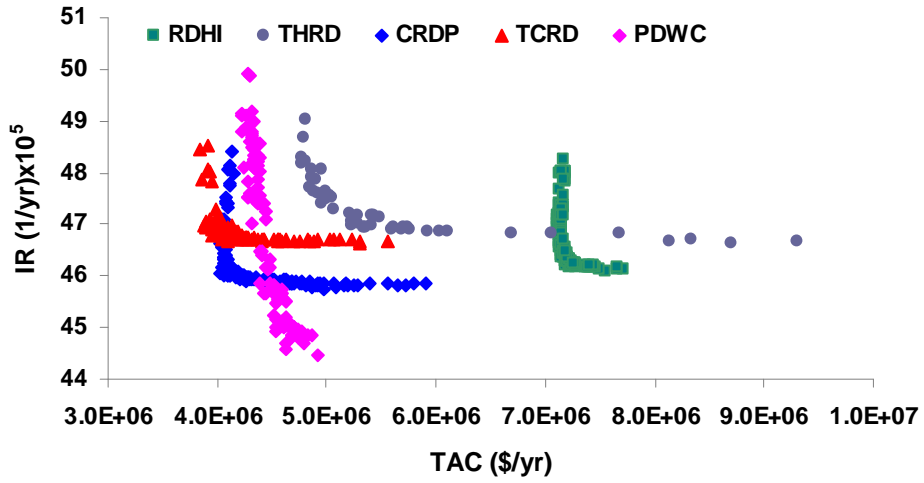


6 **Figure 2.** Reactive distillation based processes to produce ethyl levulinate

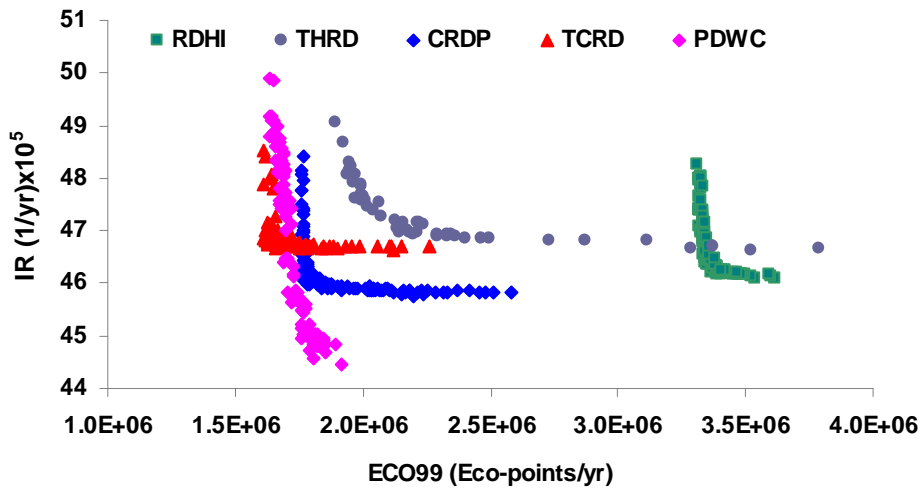
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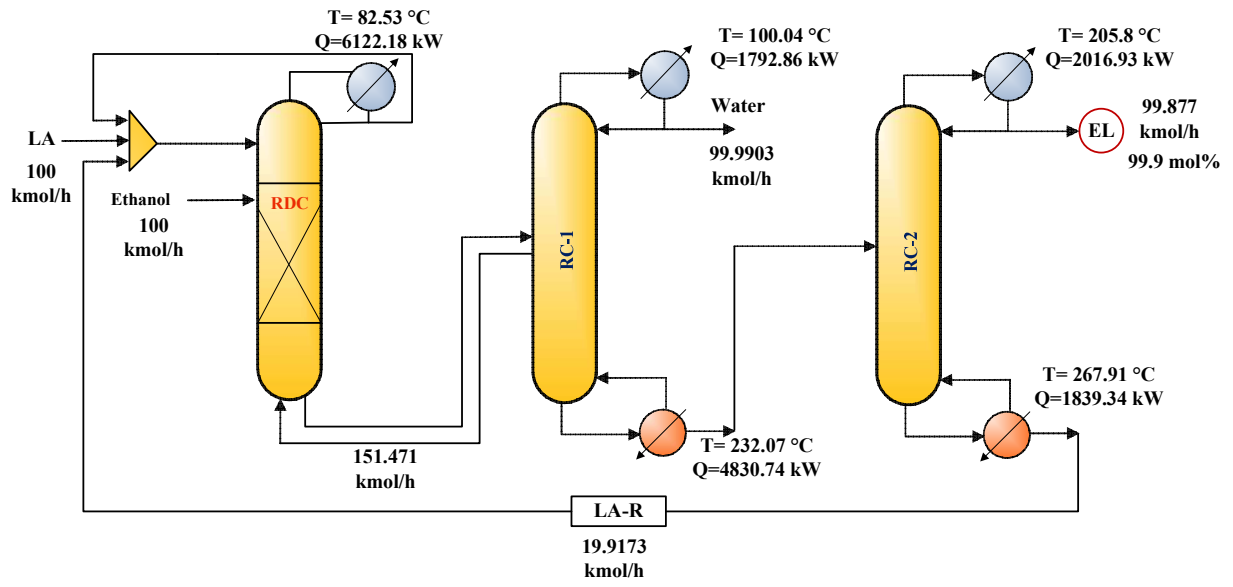


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5 **Figure 3.** Pareto fronts between: TAC vs ECO99, TAC vs IR, and ECO99 vs IR.



1



2

3 **Figure 4.** Molar flows, temperatures and energy requirements for the optimal TCRD process.

4