

Optimization of High Temperature Reactive Distillation for Production of Ethyl Levulinate

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Biodiesel has limitations regarding its performance in cold weather. Therefore, the fuel industry requires the production of biodiesel additives from renewable, non-edible sources, at a viable price, and ethyl levulinate is a promising candidate. In this investigation, a reactive distillation column is proposed and optimized to operate at high temperature to promote the uncatalyzed esterification of levulinic acid to ethyl levulinate. A central composite design was applied to determine the optimized operating conditions, and the results were analyzed based on response surfaces. The results showed that optimized reactive distillation column provides a production cost of \$0.247 per kg of ethyl levulinate, including ethanol, capital and operational expenditures, a value 2.3% lower than that of an equivalent process comprised of a reactor followed by conventional distillation.

1. Introduction

The use of biomass in biorefineries can be done via two routes: biochemical and thermochemical. The use of the biochemical route for production of cellulosic ethanol has been a great promise in the last years. However, during fractionation of biomass into fermentable sugars, part of these sugars decomposes, producing furans. Furans have a large impact on fermentation performance, depleting the cells of reduction power (Ask et al., 2013). Therefore, one wise option to be explored for biorefineries is to focus on the production of furans and their derivatives instead of production of fermentable sugars (Yan et al., 2014).

In biomass decomposition, cellulose is hydrolyzed into glucose, which under appropriate conditions is dehydrated into 5-hydroxymethylfurfural (HMF). When available in aqueous acidic medium, HMF easily decomposes into formic acid and levulinic acid (LA) (Lopes et al., 2017). LA is a promising green chemical building block. This 5-carbon molecule presents two chemical functions: a carboxylic acid and a ketone. Among the derivatives of LA, LA esters have a promising future in the biofuels market, especially in the heavy fuels market. One of these esters which has received special attention is ethyl levulinate (EL) (Leal Silva et al., 2018). EL is the product of the esterification of LA with ethanol. EL was demonstrated to ameliorate cold flow properties of diesel and biodiesel, improve combustion and reduce soot emissions, thus proving to be a great option of fuel additive of renewable origin (Wang et al. 2012). The replacement of fossil fuels by their renewable counterparts depends heavily on the production of high performance fuel blends and, in some cases, the use of fuel additives becomes very important (Varatharajan and Pushparani, 2018). Although there is a growing interest over electric vehicles, the liquid fuels market is likely to continue being the main source of power for vehicles around the world up to 2050 (Dale and Smith, 2016). Therefore, EL has a promising future.

Successful large-scale production of EL depends heavily on low production costs of LA (Leal Silva et al., 2018). Production of LA and EL are not well established in the industry and are still extensively investigated (Puccini et al., 2016). Besides reaction technology, there are several process sections with cost reduction potential, being esterification of LA one of them. Process intensification has demonstrated successful endeavors in the esterification of other carboxylic acids using reactive distillation columns (RDC) (Lee et al., 2017). Since ethanol and water are much more volatile than LA and EL, such RDC system requires special design to secure contact of reactants in the liquid phase to increase production. However, and the same time, this design can rely on the high temperature required for separation to provide an attractive reaction rate without using catalyst.

This work presents the process simulation and techno-economic assessment of a uncatalyzed RDC for EL production. The process was simulated in Aspen Plus 8.6 (Aspen Technology, Inc., 2014), and the results of were then used to determine optimized operating conditions to improve economic indicators. The resulting design was then analyzed in terms of technical feasibility and compared to a conventional esterification process.

2. Methodology

The Hayden-O'Connell equation of state was used to model the behavior of the vapor phase due to the presence of carboxylic acids in the system; as for the liquid phase, the NRTL (non-random, two-liquid) model was used. For four components, there are six binary interaction parameters. Interaction parameters of ethanol-water were obtained from the Aspen Plus 8.6 built-in database, whereas data for the other pairs were obtained from the literature (Resk et al., 2014). To simplify the process simulation, LA was supposed to be available at 70 °C and 5 bar, at a purity of 99.5 wt% - the rest is water. Ethanol was supposed to be available at 70 °C and 5 bar, with a purity of 99.6 wt% - again, the rest is water.

2.1 Process description

LA is fed to the top tray of the RDC, simulated with a *RadFrac* block, which considers rigorous mass and energy balances for each stage. The ethanol to LA ratio is adjusted according to each particular process specification, and then the vaporized ethanol (150 °C, 1.5 bar) is fed at the bottom stage of the column. For every column stage, the esterification reaction between LA and ethanol is set to occur, with kinetics described by Eq(1):

$$r = k_0 \exp\left(\frac{-E_A}{RT}\right) \left(C_{LA} C_{EtOH} - \frac{C_{EL} C_W}{K_{eq}} \right) \quad (1)$$

where k_0 is the pre-exponential factor (100 m³/kmol.s), E_A is the activation energy (49 kJ/mol), R is the universal gas constant, T is the reaction temperature, C_{LA} is the concentration of LA, C_{EtOH} is the concentration of ethanol, C_{EL} is the concentration of EL, C_W is the concentration of water – all in molar basis, and K_{eq} is the equilibrium constant at any specific temperature. Kinetic parameters were obtained from Bankole and Aurand (2014).

Bottoms flow rate and reflux ratio of the RDC were varied to recover 99.9% of a mixture of LA and EL as bottom product with 0.1 wt% of impurity. The RDC distillate contains water and unreacted ethanol. Ethanol is dehydrated via molecular sieves, with process conditions and capital investment based on the literature (Kang et al., 2014). Ethanol is recycled to the RDC and fed at the bottom tray. The bottom stream of the RDC is fed to another column to separate EL and LA, being the latter recycled to the RDC. This last column is designed for each single case using rules of thumb and shortcut methods (Seader et al., 2011). EL is obtained at a purity of 99.5 wt%.

2.2 Analysis and optimization

Process conditions for proper operation of the RDC were considered in the optimization: reboiler temperature (RT), number of stages (NST), ethanol to LA ratio (ELA), and weir height (WH). Other parameters were imposed as constraints: LA was fed at the top tray; reflux was varied so that the bottom product contains 99.8 wt% of EL and LA; EL was obtained as top product from a second column at a purity of 99.5 wt%, being the rest composed mostly of ethanol and water; temperature was not allowed to surpass 200 °C (corrosion limitations); and tray spacing of 0.6 m. The system was designed to operate 8000 h/y at a production capacity of 100 kt/y of EL. Column diameter was calculated considering an approach to flooding of 0.2 to achieve higher diameters and allow higher residence times for the liquid phase. Column diameter combined with WH, one of the optimization variables, acts upon the residence time of the liquid phase, in which the reaction occurs. For reboiler and condenser drums, the residence times were 20 and 5 min, respectively.

A central composite design with face centered star points was employed to determine a quadratic surrogate model, which was used as an objective function in the optimization, carried out using the gradient-based method of Solver in Microsoft Excel 2016. Considering that there are four factors and that the process was simulated - replicates to calculate error do not make sense - the design included 25 runs. In the surrogate model shown in Eq(2), the objective function was the upgrading cost of LA (UC):

$$UC = C_0 + \sum_{i=1}^n C_i x_i + \sum_{i=1}^n C_{ii} x_i^2 + \sum_{i=1}^n \sum_{j \geq i}^n C_{ij} x_i x_j \quad (2)$$

where UC is defined as the sum of operating and capital expenses on a yearly basis divided by the annual production of ethyl levulinate, x represents each coded variable, and C represents the coefficients of the surrogate model. Capital cost was calculated using the Economic Analysis module of Aspen Plus, with data updated to June 2017 using the Chemical Engineering Plant Cost Index (CEPCI), and included in the UC after a discount rate of 10% on an equipment life span of 10 years (for corrosion reasons). Material of construction

for the RDC and the other column to separate LA and EL was SS316. Due to recycle, all LA is converted to EL; therefore, there is no need to account for losses of LA in the UC. The lower and upper bounds exploited in the central composite design were defined according to Table 1. Intervals were chosen based on experience and simulations of distillation columns using the *DSTWU* block of Aspen Plus for a reaction feed in the conversion range of 10% to 100%. Another aspect considered is that a RDC with slow reaction rate, as in this case, generally operate at the bubbly flow regime using bubble cap trays with large liquid holdups to provide enough residence time (Górak and Olujic, 2014). The statistical analysis was completed using the software Statistica 12 (StatSoft Inc., 2014). Utilities cost was estimated according to Ulrich and Vasudevan (2006), and ethanol price was calculated as the average of the price from July 2012 to June 2017 (CEPEA, 2017).

Table 1: Variables used in the process optimization and their respective lower and upper levels.

Variable/level	-1	0	+1
RT (°C)	160	180	200
NST	20	40	60
ELA (mol/mol)	1	3	5
WH (mm)	100	150	200

3. Results and Discussion

3.1 Process Design

Firstly, a sensitivity analysis was used to understand the impact of temperature in equilibrium conversion and conversion in a short residence time in the esterification of LA. As observed in Figure 1, temperature has little effect on the maximum attainable conversion, in contrast to the ratio of ethanol to LA. As for the temperature, for a short residence time, interesting conversions for the uncatalyzed reaction are attained at high temperature and high ratio of ethanol to LA. This scenario is expected in the bottom stages of the RDC, where the remaining LA is contacted with all the ethanol fed to column and, therefore, improved conversion may be attained in relatively short residence times. This first analysis helped to determine the levels of the variables in Table 1.

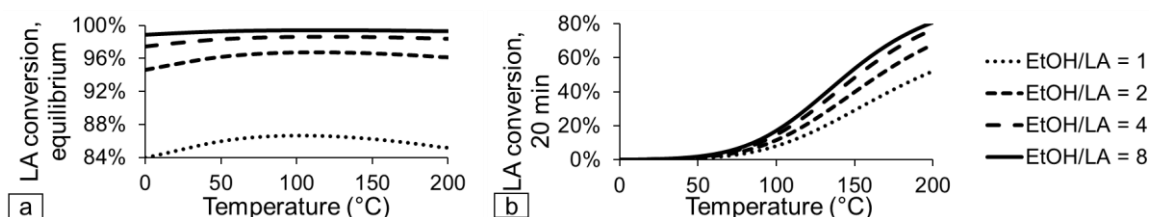


Figure 1: a) LA conversion at equilibrium conditions and b) LA conversion after 20 min of uncatalyzed reaction as a function of temperature, both for different molar ratios of ethanol to LA.

3.2 Simulations and surrogate model

The cases produced by the design of experiment are presented in Table 2, along with the response variable, UC, for each case. Note that these values of UC correspond to the total cost, including capital and operational expenditures, to produce 1 kg of EL, excluding the cost of LA. Ethanol is by far the highest contributor to the UC, accounting for 82% in average. The data was analyzed in Statistica's DOE module with a confidence interval of 95%. The F-test demonstrated that the obtained model presents overall significance, and the R^2 was 0.985. Using the obtained model, the minimum was determined considering the levels of Table 1 as boundaries, and the optimized conditions for this case are presented as case 26 of Table 2. The predicted UC for this point using the model was \$0.2463/kg EL, and the observed value was \$0.2467/kg EL, corresponding to an error of 0.22%. This result demonstrates that the surrogate model safely predicts the results of a simulated rigorous model. Response surfaces were plotted to understand better the impact of each variable on the response variable, UC. Figures 2a, 2b, and 2c show that increases in WH decreases the UC (*n.b.*: for some variables in Figure 2, the axis direction was inverted to provide a better visualization of the response surfaces). Although there is an increase in capital cost with construction material for a column to withstand the weight of its trays filled with more liquid, the increase in residence time provided by the increase in the weir height demonstrated to be more attractive from an economical point of view, showing the importance of a high conversion per tray. An increase in NST contributes to lower UC, as observed in Figures 2d and 2f. However, it can be observed from these two response surfaces that this decrease in UC levels off around 50 stages, and Figure 2b shows

clearly that there is a minimum. Similar behavior occurs for RT, which can be observed in Figures 2c, 2e, and 2f. In this case, the response levels off around 190-200 °C. High temperatures increase substantially conversion rate but at the same time, they demand more corrosion allowance from equipment. This demand for more construction material increases capital cost and, therefore, increases UC.

Table 2: UC for each simulated scenario generated by the design of experiment (cases 1-25) and the resulting optimized scenario with minimum value for UC.

Case	RT (°C)	NST	ELA (mol/mol)	WH (mm)	UC (\$/kg EL)	Case	RT (°C)	NST	ELA (mol/mol)	WH (mm)	UC (\$/kg EL)
1	160	20	1	100	0.279	14	200	20	5	200	0.269
2	200	20	1	100	0.258	15	160	60	5	200	0.280
3	160	60	1	100	0.265	16	200	60	5	200	0.265
4	200	60	1	100	0.251	17	180	40	3	100	0.259
5	160	20	5	100	0.298	18	180	40	3	200	0.257
6	200	20	5	100	0.270	19	180	40	1	150	0.251
7	160	60	5	100	0.284	20	180	40	5	150	0.265
8	200	60	5	100	0.264	21	180	20	3	150	0.264
9	160	20	1	200	0.267	22	180	60	3	150	0.257
10	200	20	1	200	0.253	23	160	40	3	150	0.269
11	160	60	1	200	0.259	24	200	40	3	150	0.256
12	200	60	1	200	0.248	25	180	40	3	150	0.257
13	160	20	5	200	0.279	26	189	47	1	197	0.247

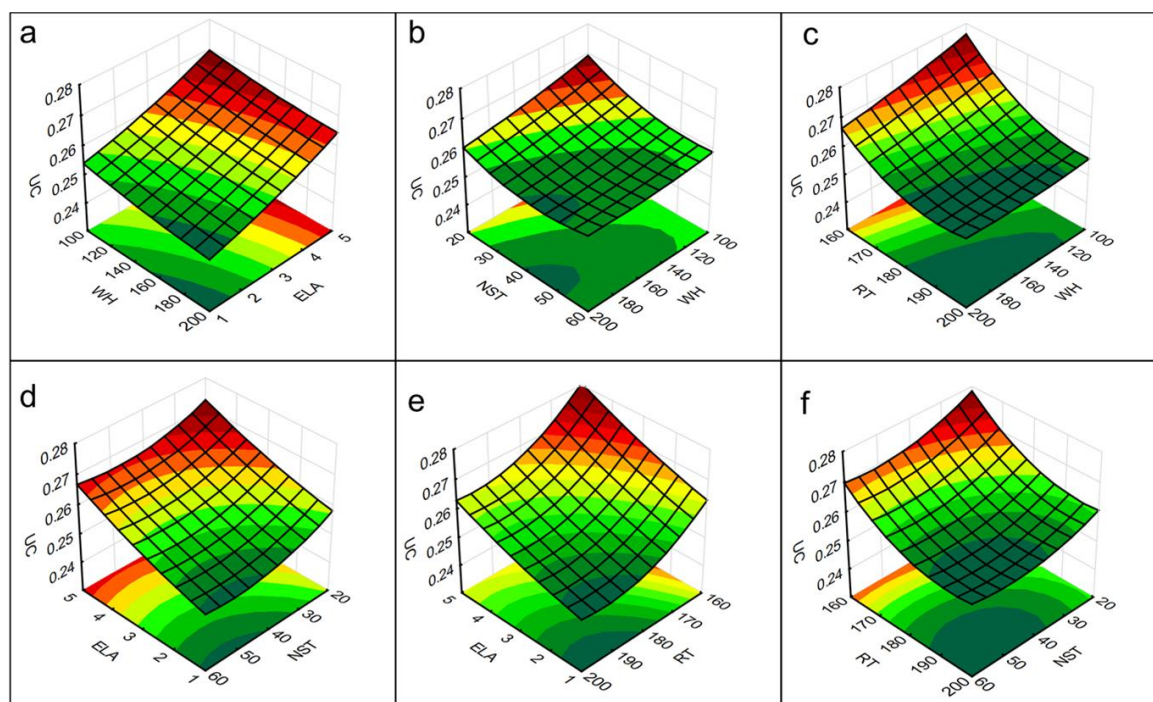


Figure 2: Response surfaces for a) WH vs. ELA, b) WH vs. NST, c) WH vs. RT, d) ELA vs. NST, e) ELA vs. RT, and f) NST vs. RT. In each case, values of the other variables were fixed at their central points.

As for the ELA, analysis of Figures 2a, 2d, and 2e demonstrated that the presence of more ethanol inside the RDC increases UC. Ethanol is the least volatile component among reactants and products, and high flow rates of ethanol increase the size of the column (due to its high concentration in vapor phase) without significantly contributing to the concentration of this reactant in the liquid phase. Therefore, lower ELA is preferable.

3.3 Optimized RDC and comparisons

The optimized RDC is further examined in this section. Temperature (Figure 3a) was almost constant in a long

section of the column. This was a consequence of the decrease in LA concentration towards the bottom of the column (Figure 3b). Fractionation occurred due to the change of volatility of the mixture, which decreased as LA was being converted into EL. Therefore, although pressure increases towards the bottom, the temperature profile remains flat. Furthermore, there is a high difference in volatility between top and bottom products, which also produces an almost flat temperature profile in distillation columns. Similar behavior is observed in the other investigation (Novita et al., 2017). Only stages 46 and 47 presented temperatures higher than 110 °C. The occurrence of high temperature at the bottom of the column helps to improve conversion as the reaction slows down because of the high concentration of EL. Moreover, this result indicates that the trays of the upper stages may have a lower corrosion allowance since they do not operate close to 200 °C, thus decreasing capital cost.

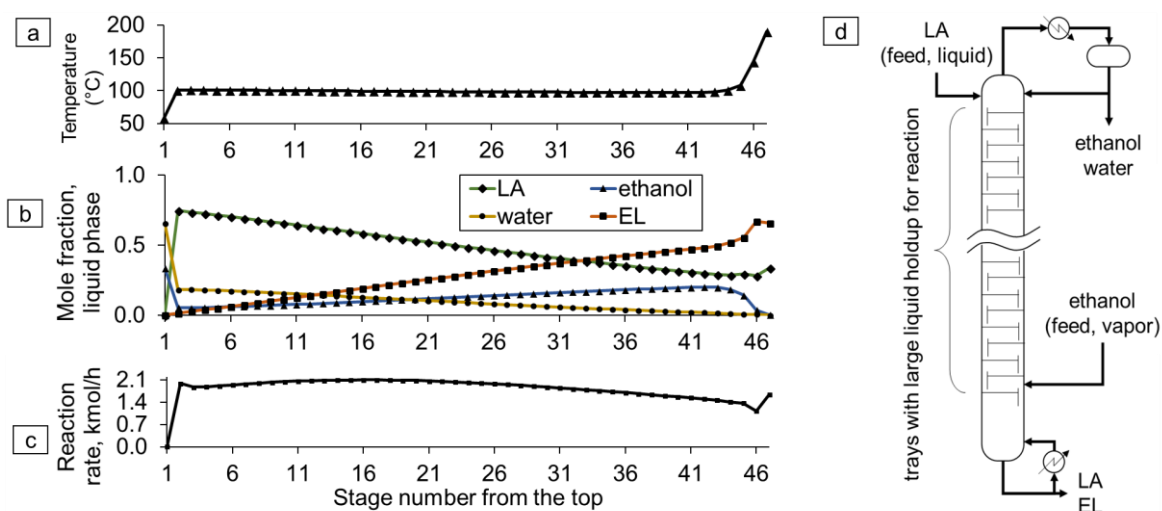


Figure 3: The optimized RDC: profiles of a) temperature, b) liquid phase mole fraction, and c) reaction rate, and d) an illustration of the RDC design.

The main reaction drivers are concentration of LA and temperature. The use of higher flow rates of ethanol was not effective to increase reaction rate because most of the ethanol remained in the vapor phase (high difference in volatility). Indeed, the molar flow rate of ethanol in the vapor phase was five times larger than in the liquid phase of the optimized case. Figure 3c shows that the rate in which EL is produced is low and almost constant, leading to nearly straight lines in the mole fraction profile (Figure 3b). Towards the bottom (stages 26-45), reaction rate decreases, and the slope in which the mole fraction profiles change decreases as well. Simulation results showed that the molar ratio of vapor and liquid flow rates were constant along the column, which was expected since the feeds are located at the top and bottom of the column (Figure 3d) and reaction is equimolar. Lastly, a conventional esterification system was designed to be compared with the RDC system. The conventional system consisted of a CSTR for esterification operating at 200 °C followed by fractionating columns with optimized column sequencing and ELA (Leal Silva et al., 2018). These simulation results were analyzed in the same way as the previous data, and the resulting UC using a CSTR combined with conventional distillation was \$ 0.253/kg EL, 2.3% higher than the UC of the optimized RDC system (both uncatalyzed options). According to Seader et al. (2011), the use of RDC is suitable when: i) reaction occurs in the liquid phase; ii) feasible pressure and temperature for distillation and reaction are the same; and iii) order of volatility is the same that would drive the equilibrium reaction towards completion. This last criterion is not satisfied, as the products of the reaction (EL and water) are neither the least nor the most volatile components.

However, the proposed design demonstrates that indeed a RDC is more attractive than the usual setup. This could encourage more investigation to improve this RDC design with different catalysts, and since the focus is the production of a commodity chemical, the gains become substantial at large scale. A catalyzed esterification of LA in a RDC using Amberlyst 39 is reported in the literature (Novita et al., 2017), and the UC excluding ethanol and LA is estimated to be \$0.020/kg EL. Excluding the ethanol cost from the UC, the optimized RDC developed in this study has a cost of \$0.031/kg EL. Therefore, the Amberlyst catalyzed process outperforms by far the uncatalyzed process assessed in this paper and demonstrates the importance of a high reaction rate.

4. Conclusions

This work assessed the use of a process intensification technology, reactive distillation, in the production of

ethyl levulinate via esterification. Optimized operating conditions were determined using a central composite design. Overall, the optimized reactive distillation column demonstrated to be an interesting equipment, as it carries water, one of the products of the equilibrium-limited esterification reaction, to the upper stages, diminishing the rate of the reverse reaction. Although water is less volatile than ethanol, one of the reactants, this design is still interesting because an upper stage always has a higher concentration of LA than any lower stage, and still drives the reaction forward. The upgrading cost was compared to that of using a CSTR combined with simple distillation for the same uncatalyzed reaction, and the cost reduction when using the reactive distillation column was 2.3%. However, the employment of a catalyst in a reactive distillation column can deliver even lower upgrading costs and contribute to a better economic performance for the whole process.

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References

- Ask M., Bettiga M., Duraiswamy V.R., Olsson L., 2013. Pulsed addition of HMF and furfural to batch-grown xylose-utilizing *Saccharomyces cerevisiae* results in different physiological responses in glucose and xylose consumption phase. *Biotechnology for Biofuels*, 6, 181.
- Bankole K.S., Aurand G.A., 2014. Kinetic and Thermodynamic Parameters for Uncatalyzed Esterification of Carboxylic Acid, *Research Journal of Applied Sciences, Engineering and Technology*, 7, 22, 4671–84.
- CEPEA, 2017, Ethanol - Center for Advanced Studies on Applied Economics, CEPEA/ESALQ <www.cepea.esalq.usp.br/en/indicator/ethanol.aspx> accessed 16.10.2017.
- Dale S., Smith T.D., 2016, Back to the Future: Electric Vehicles and Oil Demand BP Group Chief Economist BP Global Oil Market Economist, London <www.bp.com/content/dam/bp/pdf/speeches/2016/back-to-the-future-electric-vehicles-and-oil-demand.pdf> accessed 24.12.2017.
- Górak A., Olujic Z., 2014, *Distillation: Equipment and Processes*, Academic Press, Oxford, UK.
- Kang Q., Huybrechts J., Van der Bruggen B., Baeyens J., Tan T., Dewil R., 2014, Hydrophilic Membranes to Replace Molecular Sieves in Dewatering the Bio-Ethanol/water Azeotropic Mixture, *Separation and Purification Technology*, 136, 144–49.
- Leal Silva J.F., Grekin R., Mariano A.P., Maciel Filho R., 2018, Making Levulinic Acid and Ethyl Levulinate Economically Viable: A Worldwide Technoeconomic and Environmental Assessment of Possible Routes, *Energy Technology*, 6, 613-39.
- Lee H.Y., Hsiao T.L., 2017, Design and Simulation of Reactive Distillation Processes, Chapter in: Foo D.C.Y., *Chemical Engineering Process Simulation*, Elsevier, Oxford, UK, 311–353
- Lopes E.S., Dominices K.M.C., Lopes M.S., Tovar L.P., Maciel Filho R., 2017, A Green Chemical Production: Obtaining Levulinic Acid from Pretreated Sugarcane Bagasse, *Chemical Engineering Transactions*, 57, 145–50.
- Novita F.J., Lee H.Y., Lee M., 2017, Energy-Efficient Design of an Ethyl Levulinate Reactive Distillation Process via a Thermally Coupled Distillation with External Heat Integration Arrangement, *Industrial & Engineering Chemistry Research*, 56, 24, 7037–48.
- Puccini, M., Licursi D., Stefanelli E., Vitolo S., Maria A., Galletti R., Heeres J., 2016, Levulinic Acid from Orange Peel Waste by Hydrothermal Carbonization (HTC), *Chemical Engineering Transactions*, 50, 223-228
- Resk, A.J., Peereboom L., Kolah A.P., Miller D.J., Lira C.T., 2014, Phase Equilibria in Systems with Levulinic Acid and Ethyl Levulinate, *Journal of Chemical & Engineering Data*, 59, 4, 1062–68.
- Seader J.D., Henley E.J., Roper D.K., 2011, *Separation Process Principles: Chemical and Biochemical Operations*. John Wiley Inc.
- Ulrich G.D., Vasudevan, P.T., 2006. How to Estimate Utility Costs. *Chemical Engineering*, April, 66–69.
- Varatharajan, K., Pushparani D.S., 2018, Screening of Antioxidant Additives for Biodiesel Fuels, *Renewable and Sustainable Energy Reviews*, 82, 2017–28.
- Wang Z.W., Lei T.Z., Liu L., Zhu J.L., He X.F., Li Z.F., 2012, Performance Investigation of a Diesel Engine Using Ethyl Levulinate-Diesel Blends, *BioResources*, 7, 4, 5972–82.
- Yan K., Wu G., Lafleur T., Jarvis C., 2014. Production, Properties and Catalytic Hydrogenation of Furfural to Fuel Additives and Value-Added Chemicals, *Renewable and Sustainable Energy Reviews*, 38, 663–76.