

## Modeling, simulation and optimization of ethanol extractive distillation using glycerol

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### Abstract

The extractive distillation process of ethanol (using glycerol as extractor) was modeled, simulated, analyzed and finally optimized. The model was implemented in EMSO and involves equipment such as distillation columns (with condensers and reboilers), splitter, mixers, pressure modifiers elements (valve and pump) and a heat exchanger. The process modeling was developed in steady state. The optimization problem focused in finding optimal value for three operational variables (extraction column reflux ratio, makeup glycerol flow and regenerated glycerol purity) in order to maximize a profit objective function. For solving it, surrogate model strategy was adopted; getting elude typical convergence failure on solving non-linear algebraic system of equation. For building the surrogate model, a data set of objective function values for different combinations of decision variables was obtained; by using the EMSO Case Study tool, which carries out a global sensitivity analysis. Surrogate model parameters were estimated using this data set. Only two cycles of optimization task were needed: a first surrogate model to reduce the feasible region and a second one (with updated model parameters) for increasing the accuracy. Using the surrogate model, optimal values for decision variables were found by applying the interior point optimization algorithm built in EMSO. The optimal point was fed into the rigorous model for verifying it really corresponds to a maximum of the objective function in the rigorous model. Sensitivity analysis was performed with rigorous model for testing the sensitivity of objective function to deviation from the optimum values; demonstrating the iterative optimization procedure using adaptive surrogate model was successful.

**Keywords:** ethanol; extractive distillation; optimization; surrogate model.

## 1 Introduction

The researches of new energy sources for replacing fossil fuels have promoted the development of biorefineries for production of biodiesel or bioethanol. Efficient design and operation of distillation systems are critical for success of bioethanol; since this process of separation and purification to obtain fuel grade ethanol has high energy consumption.

There are several papers and articles about the subject. Use of commercial simulation software such as ASPEN, HYSYS or MATLAB for modeling and simulating the systems is common. In this work modeling, simulation and optimization were implemented and executed in EMSO (Environment for Modeling, Simulation and Optimization) [1] instead of any commercial software.

There are some papers approaching both operational and design variables optimization [2]; or comparing cases using different design configurations or extractors [3]. In this work, design characteristics of distillation system were considered fixed for optimization purpose.

Regarding the optimization method employed, mostly papers use stochastic or deterministic algorithm, and a few use a combination of both. Kiss and Ignat [4] use Sequential Quadratic Programming (SQP) optimization method and sensitivity analysis tools from Aspen Plus. In the other hand, García-Herreros and Gómez [2] implemented in MatLab stochastic algorithm for discrete variables and nonlinear programming (NLP) for continuous variables. Finally, Dias [5] apply Pinch Analysis concepts to determine the optimal conditions from an Aspen Plus simulation. In this work, surrogate model strategy was adopted for solving the optimization problem. Surrogate models have been successfully applied in many complex and nonlinear optimization problems [6] and [7].

## 2 Process description

Extractive distillation is a separation process by distillation in presence of an additional miscible substance; which is able to modify relative volatility of components present in the original mixture to be separated. The addition of this new substance modifies the grade of components purity separation feasible by distillation [8].

The studied extractive distillation system has two distillation columns: the first one where extraction process is executed and the second one for extractor regeneration process. Both, the extractor and the mixture to be separated are fed into the first column in different trays. This column operates at atmospheric pressure and highly concentrated ethanol (over 99.5% [9]) is obtained as distillate stream. Bottom liquid stream of first column (mostly glycerol and water) is supplied into the second one. This column operates at vacuum pressure (0.2 atm.) in order to avoid thermal decomposition of glycerol; and produces regenerated glycerol as liquid bottom stream. Regenerated glycerol is mixed with make-up glycerol and return to the extraction column. There are also a valve and a pump for handling operating pressure differences between columns; and a heat exchanger for fixing the temperature of glycerol entering into extraction column. The process diagram is shown in Fig. 1.

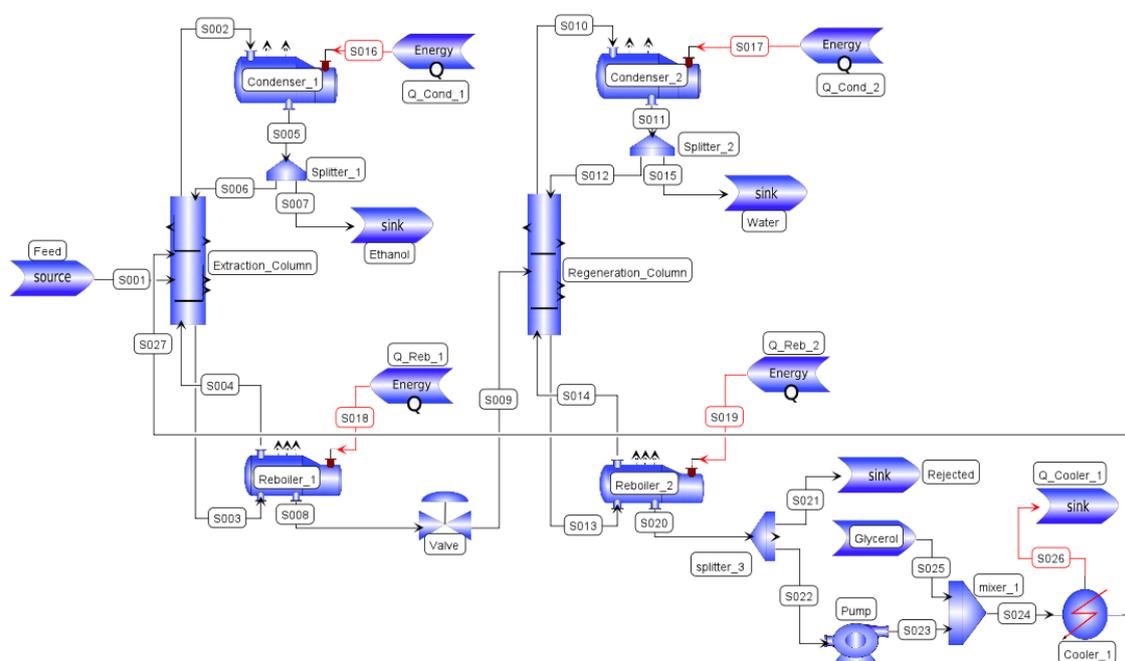


Figure 1: Extractive distillation process diagram in EMSO

## 3 Methods

### 3.1 Process modeling and simulation

Distillation column was modeled as several separation stages in series; where each tray is consider a separation stage. The equilibrium stage model approach [10], consist on the solution of MESH equation (M: Material balance, E: Equilibrium relations, S: Summation constraints of compositions and H: Head balance) was adopted. Material and heat balances for each tray, in steady state and without consider side draw-off or heat addition were made according to [11].

$$0 = F_j z_j + V_{j+1} \bar{y}_{j+1} + L_{j-1} x_{j-1} - V_j \bar{y}_j - L_j x_j \quad (1)$$

$$0 = F_j h_j^F + V_{j+1} h_{j+1}^V + L_{j-1} h_{j-1}^L - V_j h_j^V - L_j h_j^L \quad (2)$$

where  $F$ ,  $V$  and  $L$  are the molar flow of feed, vapor and liquid respectively for one tray.  $z$ ,  $y$  and  $x$ , are the molar compositions of feed, vapor and liquid respectively. The different notation for the vapor composition is due to this valor is already rectified by the tray efficiency. In the heat balance,  $h^F$ ,  $h^V$  e  $h^L$  are the molar enthalpy of feed, vapor and liquid respectively for one tray.

The effect of incomplete mass transference was considered by applying the Murphree efficiency equation. In Eq. (3)  $E_j$  is the Murphree efficiency related with the vapor phase for each component in the tray  $j$ ,  $\bar{y}$  is the media molar composition of the vapor phase corrected and  $y$  is the media molar composition of the vapor phase in thermodynamic equilibrium with the liquid phase leaving the tray.

$$E_j = \frac{\bar{y}_j - \bar{y}_{j+1}}{y_j - \bar{y}_{j+1}} \quad (3)$$

Compositions of vapor and liquid phases leaving each tray are correlated for the thermodynamic equilibrium condition [12]. In Eq. (4)  $y$  and  $x$  are the molar composition of vapor and liquid phases in equilibrium respectively, and  $K$  is the vapor-liquid equilibrium ratio. This equation is used to calculate the ideal molar composition of vapor phase according to thermodynamic equilibrium. Otherwise, Eq. (3) allows obtain the real molar composition of vapor phase leaving a tray; which is use in the material balance equations.

$$y_j = K_j x_j \quad (4)$$

There are also constraints for the summation of molar compositions that should be equal to 1.

$$\sum_{i=1}^{NC} \bar{y}_i = 1 \quad (5)$$

$$\sum_{i=1}^{NC} x_i = 1 \quad (6)$$

In steady state simulation, pressure profile of the column should be specified. Despite of in the process studied pressure profile were not considered, the developed model is able to deal with different pressures on top and bottom. Condenser was modeling as total condenser, assuming that outlet liquid is saturated and consider pressure drop. Reboiler was modeling as flash with heat supplied and considering pressure drop. Liquid and vapor stream leaving the reboiler were considered in thermodynamic equilibrium [13]. Others equipment such as pressure modifier, heat exchanger, mixer and splitter were also modeled. The Plugin VRTherm of EMSO was used for evaluating physical and thermodynamic properties of components. The vapor phase was considered as ideal gas due to the low operating pressure. Otherwise, the UNIFAC thermodynamic model was used for representing the nonideality of the liquid phases.

Systems involving two distillation columns and recycle are highly nonlinear; so it is difficult to solve the algebraic system of equation if there aren't good initial estimates for unknown variables. For this reason, a modular strategy to get convergence of isolated equipment was adopted. Latter these equipment were interconnected each other until complete the whole system. The main design information and variables specifications used for simulation of the base case are shown in Table 1 and Table 2 respectively.

Table 1: Columns design specifications

Description	Extraction Column	Regeneration Column
Numbers of trays	18	6
Feed tray	2 (Glycerol) / 11 (Feed)	2
Top pressure (atm)	1	0.2
Bottom pressure (atm)	1	0.2
Murphree efficiency (%)	100	100

Table 2: Operational specifications

Description	Azeotropic Mixture	Make-up Glycerol
Flow (kmol/h)	100	73
Temperature (K)	350	300
Pressure (atm)	1	1
Composition (Ethanol, Water, Glycerol)	(85, 15, 0)	(0, 0, 100)
Description	Extraction Column	Regeneration Column
Reflux ratio	0.10	0.04
Ethanol purity / glycerol purity	99.5	99.97
Description	Valve / Pump	Heat Exchanger
Pressure drop / increase (atm)	0.8	-
Outlet Temperature (K)	-	350

### 3.2 Formulation of optimization problem

The mathematical formulation of optimization problem involves only continuous variables; due to potential discrete variables such as design variables are fixed. It includes an objective function, equality constraints concerning to the physical modeling of the process (material and heat balances, equilibrium equations, etc.) and inequality constraints related to operational and quality specifications. The objective function depends on optimization variables. In spite of the objective function is linear, the equality constraints are not; therefore it's expected that the response of the objective function to changes in the optimization variables will be nonlinear. The general form of a nonlinear programming optimization problem for maximizing the economic profit is represented below.

Maximize:  $S(\bar{x})$  (The Objective Function)

Subject to:

$h_i(\bar{x}) = 0 \quad i = 1, \dots, \text{Number of Equality Constraints (NEC)}.$

$g_j(\bar{x}) \leq 0 \quad j = 1, \dots, \text{Number of Inequality Constraints (NIC)}.$

The optimization variables chosen were:

1. Reflux ratio in extraction column ( $R_R$ ).
2. Make-up glycerol flow ( $F_{Gly}$ ).
3. Regenerated glycerol purity ( $X_{Gly}$ ).

The equality constraints (model constraints) are the equations involved on the physical model of the process and the inequality constraints (operational constraints) are maximum values for: operating temperature ( $g_1(\bar{x})$ ), reflux ratio in extraction column ( $g_2(\bar{x})$ ) and regenerated glycerol purity ( $g_3(\bar{x})$ ).

$$\begin{cases} g_1(\bar{x}) = T_{max.} - 555K & \leq 0 \\ g_2(\bar{x}) = R_R - 5 & \leq 0 \\ g_3(\bar{x}) = x_{glycerol} - 0.9999 & \leq 0 \end{cases} \quad (7)$$

The objective function involves the maximization of the annual profit for the production of fuel grade ethanol.

Annual profit (\$/year):

$$S(\bar{x}) = T_S(\bar{x}) - T_C(\bar{x}) \quad (8)$$

Total sales (\$/year):

$$T_S(\bar{x}) = F_{ethanol} P_{ethanol} t_{op}. \quad (9)$$

Total cost (\$/ano):

$$T_C(\bar{x}) = (C_{am} + C_{gly} + C_{en}) t_{op} \quad (10)$$

$$\begin{cases} C_{am} &= F_{am}P_{am} \\ C_{gly} &= F_{gly}P_{gly} \\ C_{en} &= D_{rebs}P_{en} \end{cases} \quad (11)$$

The nomenclature used in the above equations is:  $S(\bar{x})$  is the profit,  $T_S(\bar{x})$  are the total sales and  $T_C(\bar{x})$  are the total cost.  $F_{ethanol}$  is the fuel grade ethanol yield in (kmol/h),  $P_{ethanol}$  is the fuel grade ethanol sale price in (\$/kmol) and  $t_{op}$  is the annual operating time in (h/year).  $C_{am}$ ,  $C_{gly}$  and  $C_{en}$  are the feed azeotropic mixture cost, make-up glycerol cost and reboilers energy costs respectively in (\$/h).  $F_{am}$  and  $F_{gly}$  are the azeotropic mixture and make-up glycerol flow in (kmol/h).  $P_{am}$  and  $P_{gly}$  are the raw material price in (\$/kmol). While,  $D_{rebs}$  is the total reboilers duty in (kJ/h) and  $P_{en}$  is the reboiler energy price in (\$/kJ).

### 3.3 Optimization method

Considering the complexity and nonlinearity of the equality constraints equations involving in the physical model, and the convergence trouble of the numerical methods for this kind of systems; a surrogated model strategy was adopted in order to solve the optimization problem. The methodology employed was similar to described in [6].

It was necessary to implement in EMSO a new model with the economic aspects and the objective function, in order to obtain directly the response of the objective function for different combinations of optimization variables values.

For generating the data set from the rigorous model, could be advisable to use any strategy of design of experiments (like Latin Hypercube Design (LHD) [14]) with the objective of decreasing the computational cost. Considering that the number of independent variables is three and the simulation is in steady state, the computational cost is not high, therefore it was not necessary to apply a computational design of experiments.

According to the results of the sensitivity analysis in the base case, the surrogate model for the objective function was built using reflux ratio in the extraction column and make-up glycerol flow as independent variables. For this reason, regenerated glycerol purity was fixed as an active constraint. There are many examples of using surrogate models on engineering (based on artificial neural network or kriging models) in order to substitute complex model [7]. In this work was used a surrogate model involving only the left member of a kriging model. It means, a polynomial surrogate model of second order with interaction as describe in Eq. (12).

$$S(\bar{x}) = k_{00} + k_{11}R_R + k_{12}R_R^2 + k_{21}F_{Gly} + k_{22}F_{Gly}^2 + k_{33}R_R F_{Gly} \quad (12)$$

where  $S(\bar{x})$  is the profit in (\$/h),  $R_R$  is the reflux ratio in the extraction column and  $F_{Gly}$  is the make-up glycerol flow in (kmol/h).  $k_{ij}$  are the parameters of the surrogate model to be calculated. Notice that it was convenient to work with the objective function in (\$/h) instead of (\$/year) in order to make similar the magnitude orders of the variables involve on the model construction.

## 4 Results and discussion

### 4.1 Base case simulation

The initial model implemented in EMSO has 997 variables, 977 equations and 20 specifications for the simulation of the base case. It is a previous step that facilitates influence and sensitivity analysis of the process variables; as well as the future optimization. With a base case simulation running, sensitivity analysis were realized; focusing on describe the behavior of some of the most relevant variables such as: ethanol yield and reboiler duties; due to they are very involve within process economy. It wasn't analyzed ethanol purity because it's a specification in the model; consequently this requirement will be always satisfied.

Make-up glycerol flow was changed from 50 to 90, within 2 kmol/h steps. When make-up glycerol flow increases, reboiler 1 duty (from extraction column) increases as well, but reboiler 2 duty (from regeneration column) decreases. Nevertheless, net result is total reboilers duty increase with make-up glycerol flow increase, as shown in Fig. 2a. Regarding ethanol yield, it increases when make-up glycerol flow increases, as shown in Fig. 2b. In this case there is a compromise between the benefit of obtaining more ethanol yield by increasing make-up glycerol flow and the disadvantage of bigger total reboilers duty.

Reflux ratio in extraction column was increased from 0.02 to 0.6 within 0.02 steps. The Fig. 2c shows there is a range of reflux ratio values where the total reboilers duty is lower. Concerning the ethanol yield, its variation isn't too significant. Nevertheless, there is also a range of reflux ratio values where ethanol yield is bigger, as shown in Fig. 2d. When reflux ratio is bigger than 0.30, the performance of response variables is not favorable at all; because total reboilers duty increases and ethanol yield decreases.

Regenerated glycerol purity was changed from 0.9989 to 0.9999 within 0.0001 steps. It has also very influence in reboilers duties as shown in Fig. 2e. It's necessary to increase reboiler 2 duty in order to increase regenerated glycerol purity; but on the other hand, it causes a bigger reduction of reboiler 1 duty, and consequently the net total reboiler duty is lower. The Fig. 2f shows the response of ethanol yield and total reboilers duty as function of regenerated glycerol purity. It's notable that they both have a satisfactory behavior when regenerated glycerol purity increases, since ethanol yield increases and total reboilers duty decreases. For this reason it's convenient to operate within high values of regenerated glycerol purity.

## 4.2 Surrogate model construction and optimization

Once added the objective function and others economic aspects, the final model has 1010 variables, 982 equations and 28 specifications. It was executed a Case Study changing the values of optimization variables and obtaining the response of the objective function. The values of inequality constraints were also observed in order to check if they were not violated. A data set reflecting the objective function value for each combination of independent variables and additional information regarding inequality constraints was obtained. These data were examined to check if any inequality constraint isn't satisfied and then exclude this combination of data from the feasible region.

The study of the data set allow conclude that when regenerated glycerol purity is lower than 0.9997, the objective function change to negative values. These results were considered out of the feasible region; consequently these data weren't considered for estimation of surrogate model parameters. It was also observed that regenerated glycerol purity has a direct and proportional influence in the objective function, so as regenerated glycerol purity increases, the objective function increases as well. Consequently, in the optimal point, this variable will have the biggest allowed value, getting the limit of the correspondent inequality constraints. This conclusion was very important because made possible to reduce one dimension in optimization problem, going from three to two degree of freedom (reflux ratio and make-up glycerol flow).

For surrogate model parameters calculation was used the EMSO Parameter Estimation tool. The parameters of the first surrogate model were estimated with an adequate adjust of  $R^2=0.971084$  and are shown in Table 3. Although global adjust between first surrogate and rigorous model is good, it isn't so good precisely for high  $S(\bar{x})$  values, as shown in Fig. 3a and Fig. 4a. For this reason, it was hoped optimal values found using this surrogate model don't meet the optimal for the rigorous one. An approximate optimal solution was obtained by optimizing the first surrogate model, using the EMSO Optimization tool. The independent variables were constraints to the range of values used for the parameters estimation of surrogate model. The operational inequality constraints are fulfilled because for surrogate model calculation was used only a data set from the feasible region.

The results obtained by this first surrogate model (shown in Table 4) don't meet the rigorous model precisely. Besides, by small perturbation on optimization variables and watch over the objective function values, was confirmed this solutions wasn't an optimum for rigorous model. However, these approximate optimal values were used for reducing the search region and update the surrogate model parameters.

In the second Case Study the optimization variables were changed between an interval near to

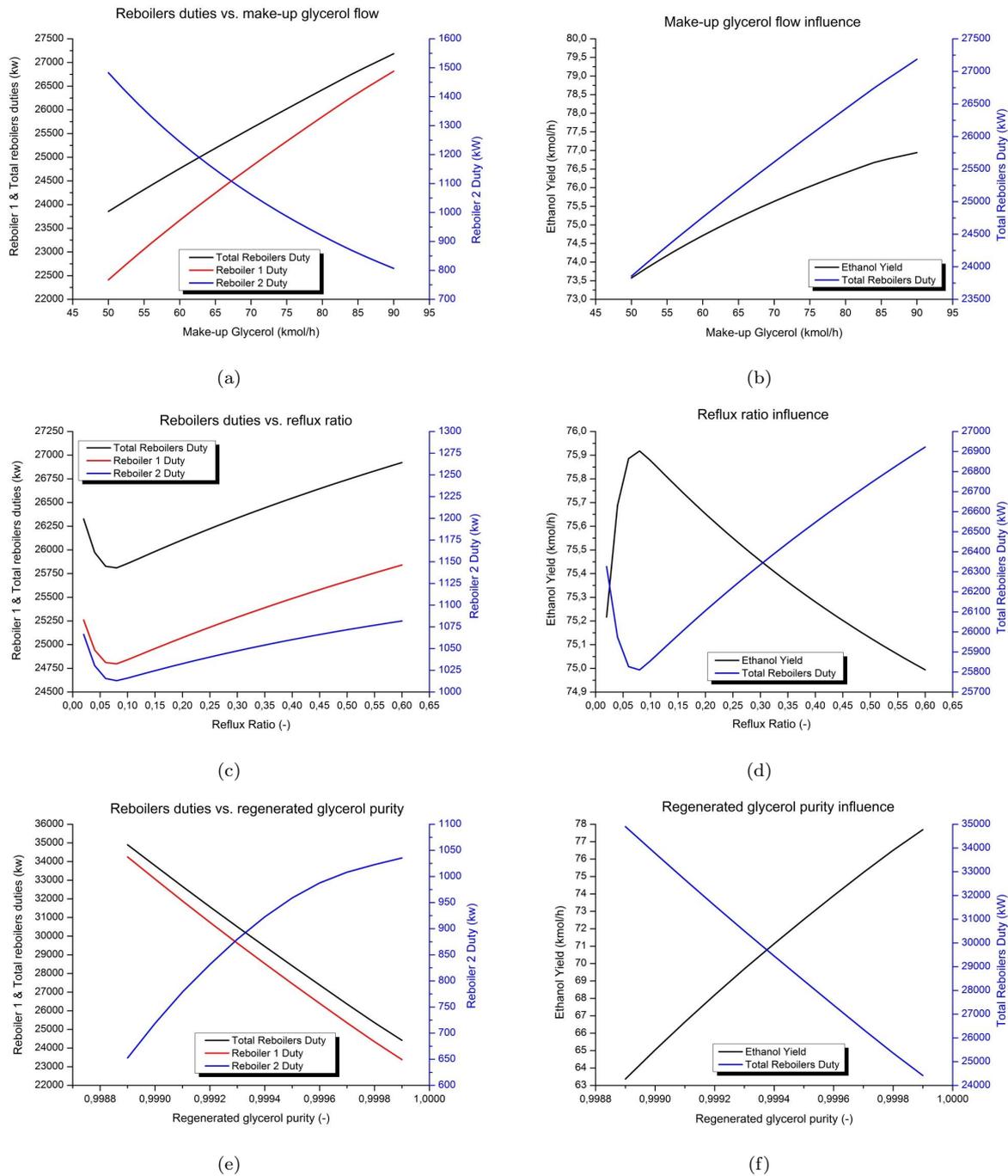


Figure 2: Influence of different operational variables in ethanol yield and energy consumption.

approximated optimal point obtained above. A data set of  $S(\bar{x})$  response surface with a promissory region for a maximum of the objective function was obtained. The parameters of surrogate model were update with a very good fitting of  $R^2=0.999047$  (see Fig. 3b) using the new data set of the promissory region. The estimated parameters for the second surrogate model are shown in Table 3.

Fig. 4b shows the comparison between  $S(\bar{x})$  response surface using the second surrogate model and the rigorous model respectively. Notice that there is a good fitting between the second surrogate model

Table 3: Estimated parameters for the surrogate models.

Surrogate model	$K_{00}$ (\$/h)	$K_{11}$ (\$/h)	$K_{12}$ (\$/h)	$K_{21}$ (\$/kmol)	$K_{22}$ ( $\$/\text{kmol}^2$ )	$K_{33}$ (\$/kmol)
First	288.865	-151.41	26.0665	6.97471	-0.0559346	-0.0278739
Second	218.108	2207.35	-14742.2	6.45417	-0.0520906	-0.503687

and the rigorous one. It's hope now the results obtained by optimizing the surrogate model meet the rigorous model, considering a permissible error.

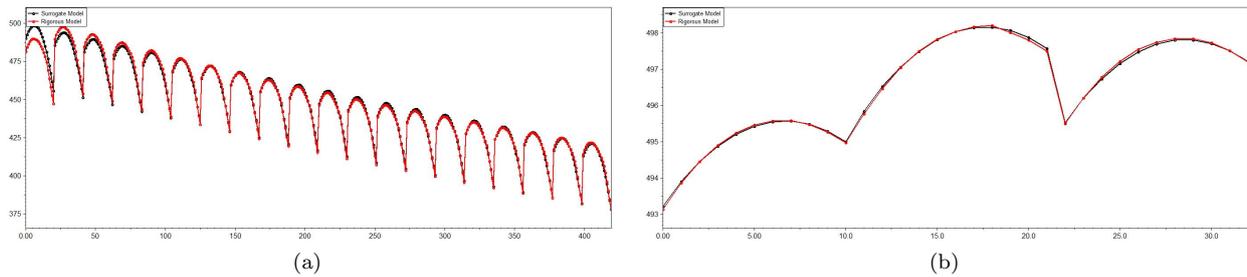


Figure 3: Graphic report for parameter estimation in EMSO, comparing  $S(\bar{x})$  values calculated from rigorous and surrogate models. (a) Using first surrogate model. (b) Using second surrogate model.

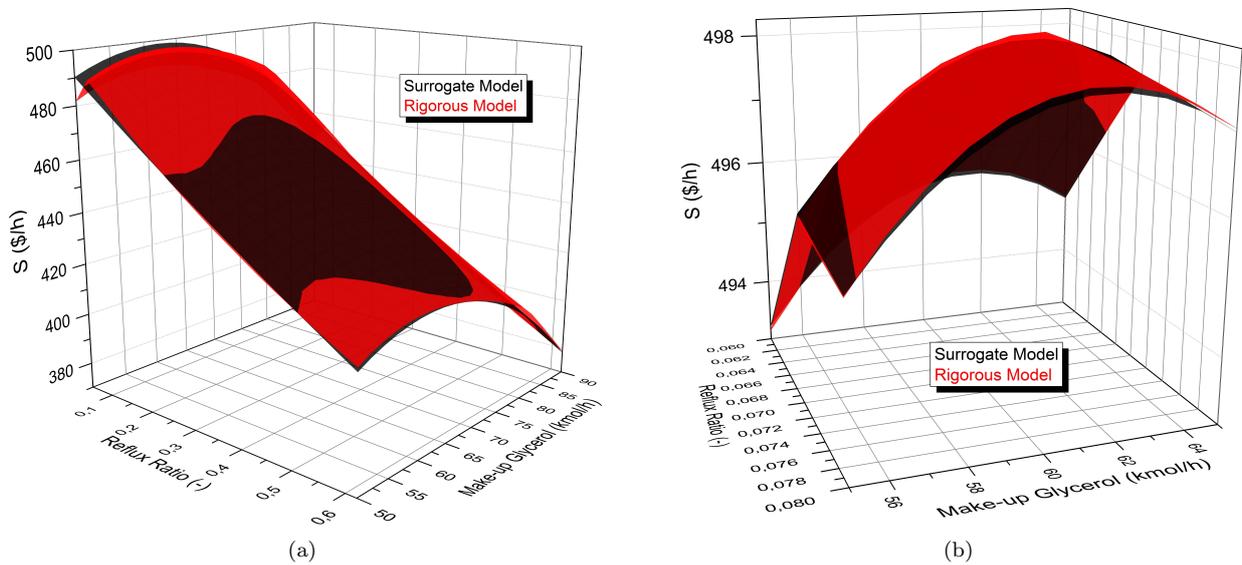


Figure 4: Comparison between response surface from rigorous and surrogate models. (a) Using first surrogate model. (b) Using second surrogate model.

Optimization of the second surrogate model was carried out in EMSO. The optimization variables are constraints to the range of values valid for the estimation of the second surrogate model. The results of optimization are shown in Table 4.

Regarding inequality constrains of operational variables, all of them were accomplished. Regenerated glycerol purity was the only active constrain, while reflux ratio and make-up glycerol flow kept as inactive constrains.

Table 4: Optimization results.

Variable	U/M	Base Case	First surrogate model optimization	Second surrogate model optimization
Reflux ratio ( $R_R$ )	-	0.10	0.05	0.074
Make-up glycerol flow ( $F_{Gly}$ )	kmol/h	73.00	62.33	61.59
Regenerated glycerol purity ( $X_{Gly}$ )	-	0.9997	0.999	0.999
Profit by surrogate model ( $S'(\bar{x})$ )	\$/h	-	513.84	498.34
Profit by rigorous model ( $S(\bar{x})$ )	\$/h	258.33	490.04	498.30

$$\begin{cases} g_1(\bar{x}) = 512K - 555K = -43 \\ g_2(\bar{x}) = 0.074 - 5 = -4.926 \\ g_3(\bar{x}) = 0.9999 - 0.9999 = 0 \end{cases} \quad (13)$$

### 4.3 Sensibility analysis

A sensibility analysis was performed using the rigorous model for verifying if this solution was exactly an optimum. Each optimization variable was changed individually in a range close to its optimal value. The objective function at optimal point is not very sensitive to changes on reflux ratio or make-up glycerol flow, as shown in Fig. 5a. On the contrary, Fig. 5b shown that small changes on regenerated glycerol purity will affect drastically the objective function. For this reason, this variable must be controlled more accurately. Results of the sensibility analysis confirm that optimal point calculated by the surrogate model is also an optimum of the rigorous model and correspond to a maximum of the objective function; due to any change on optimization variables cause a decrease on the objective function.

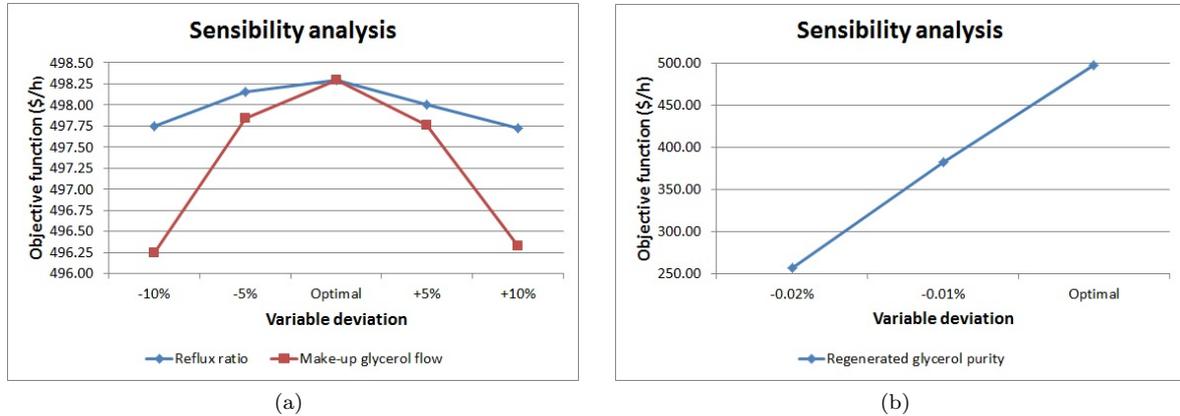


Figure 5: Sensibility analysis for deviation of optimization variables from the optimal point. (a) For reflux ratio and make-up glycerol flow. (b) For regenerated glycerol purity (active constraint).

## 5 Conclusions

The process modeling and simulation allow analyses the influence of different operational variables on the general behavior of the process. The iterative procedure, using adaptive surrogate model, demonstrated to be a successful methodology for solving the optimization problem. Optimal values of operational variables analyzed were calculated for the studied system, and the premises used for it. The optimal point is especially sensitive to variation in the regenerated glycerol purity.

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