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DESIGN STUDY OF THE CONTROL OF A REACTIVE THERMALLY COUPLED DISTILLATION SEQUENCE FOR THE ESTERIFICATION OF FATTY ORGANIC ACIDS

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Design Study of the Control of a Reactive Thermally Coupled Distillation Sequence for the Esterification of Fatty Organic Acids

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This article reports the esterification of lauric acid and methanol studied using a thermally coupled distillation sequence with a side rectifier and the Petlyuk distillation column. The product of the esterification can be used as biodiesel. It was found that the thermally coupled distillation sequence with a side rectifier can produce ester with a high purity (around 0.999) and also pure water, and the excess of methanol is recovered in the side rectifier. The results indicate that the energy requirement of the complex distillation sequence with a side rectifier can be reduced significantly by varying operational conditions. These reductions in energy requirements can be interpreted as reductions in carbon dioxide emissions. Moreover, dynamic tests for control of the composition of the ester and control of two temperatures for the thermally coupled distillation sequence with a side rectifier indicate that it is possible to eliminate disturbances in the feed composition, while the composition of the biodiesel remains at the desired value.

Keywords Control; Energy savings; Biodiesel; Reactive distillation

Introduction

Due to increased energy demand and environmental concerns worldwide, important research is currently underway on biofuels and alternative energy sources, e.g., biodiesel, biomass, and bioethanol. In the case of biodiesel, it has been reported that its production can be competitive with fossil diesel when the price of crude oil reaches USD 100 per barrel (Frondel et al., 2007), a price that has been recently reached, although the current price of oil is lower. As a result, important process intensification policies have been taken into account in the design of new processes, due

This article is dedicated to the memory of Rodrigo Sandoval.

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to reduction in oil reserves, and for minimization of carbon dioxide emissions and use of alternative energy sources (Carraretto et al., 2004; Islas et al., 2007; Quintero et al., 2008). Attention has been paid to these important aspects in the process systems engineering area of chemical engineering. For example, in a chemical plant, the energy requirement in a separation process such as distillation can be up to 40% of total consumption. As a result, researchers in the field of distillation are developing new configurations that can be capable of reducing both energy requirements and carbon dioxide emissions (Mascia et al., 2007; Rong and Turunen, 2006; Plesu et al., 2008; Malinen and Tanskanen, 2007).

One alternative that has been explored in detail is the use of thermally coupled distillation sequences (TCDS), which can achieve energy savings between 30 and 50% over conventional distillation sequences for the separation of some multicomponent mixtures. For instance, for the separation of a nonreactive ternary mixture, two conventional distillation sequences (direct and indirect distillation sequences) and three thermally coupled distillation sequences (two using side columns and the Petlyuk distillation column) can be used. According to thermodynamic studies, thermally coupled distillation sequences can be more efficient in energy use because there is no remixing, in contrast to conventional distillation sequences (Triantafyllou and Smith, 1992; Hernández et al., 2006). This is because, in the first column of the conventional distillation sequence, the composition profile of the intermediate component reaches a maximum below the feed stage and then decreases as the bottom part is reached. Similarly, in the first column of the indirect distillation sequence, the composition profile of the intermediate component reaches a maximum above the feed stage and then decreases as the top of the distillation column is reached.

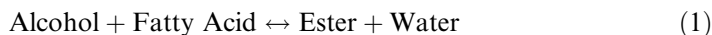
This reduction in the composition profile of the intermediate component is called “remixing” and is associated with a higher energy requirement in the second distillation column. In contrast, the side stream fed to the second column in the thermally coupled distillation sequences with side columns is extracted from the maximum in the composition profile of the intermediate component in the first column. Regarding this important aspect, in the case of the Petlyuk column, the side product is obtained from the maximum in the composition profile of the intermediate component in the main column. As a result, the energy requirement is reduced because there is no remixing effect. This explains the fact that TCDS options can lead to important energy savings and reduction in diameter of distillation columns because low energy requirement implies low reflux rates, i.e., reduction in traffic of liquid and vapor. These energy savings have been predicted using steady-state simulation and mathematical programming, and their theoretical control properties and dynamic behavior have also been determined (Hernández and Jiménez, 1999; Cárdenas et al., 2005; Huang et al., 2006; Wang and Wong, 2007). Based on these studies, practical implementation of thermally coupled distillation sequences has been conducted using dividing wall columns.

Reactive distillation is considered to be the most representative intensification operation because it combines reactions and separation in a single process unit. As a result, TCDS options can be used to carry out reactions of esterification of fatty organic acids, and the produced esters can be used as biodiesel. This leads to important processes to produce biofuels using complex distillation systems that can reduce energy requirements, capital costs, and carbon dioxide emissions. Thus, this paper reports the esterification of fatty organic acids studied using a thermally coupled distillation sequence with a side column and the fully thermally coupled distillation

sequence. We have selected these distillation sequences because, for the separation of ternary mixtures, there are two types of thermally coupled distillation sequences: TCDS with side columns and the fully thermally coupled distillation sequence (Petlyuk distillation sequence).

Esterification of Fatty Organic Acids

The stoichiometric reaction equation for the esterification is



This equilibrium reaction can be favored if the products are removed as the reaction proceeds. An additional problem may present itself, depending on the acid and the alcohol used, as binary or ternary homogeneous azeotropes can be formed in the reactive system. For highly nonideal systems, heterogeneous azeotropes can be formed. These key factors must be considered to select the appropriate thermodynamic model when the system is studied with process simulators. For this class of reactive systems, thermodynamic models such as NRTL, UNIFAC, or UNIQUAC can be used to calculate vapor-liquid or vapor-liquid-liquid equilibria. In this study, the nonrandom two liquid (NRTL) model was used because two liquid phases can be presented in the complex reactive distillation sequences.

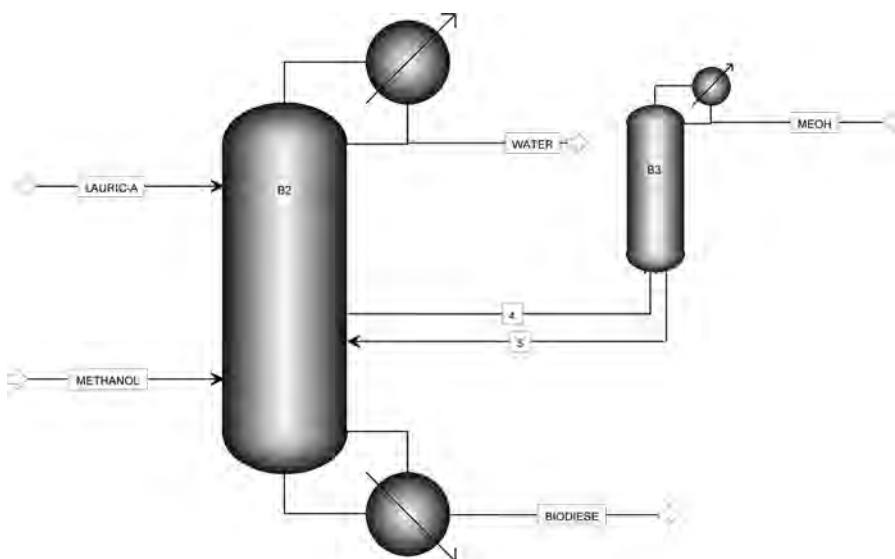
Search for Minimum Energy Requirement of the Reactive Systems

The design and optimization methods of thermally coupled distillation described in Hernández and Jiménez (1996) for nonreactive mixtures can be extended to the reactive case. This methodology requires an initial tray structure that can be obtained from the conventional distillation sequence, and subsequently the recycle stream (VF) is varied until the minimum energy requirement is achieved in the reboiler for the case of reactive thermally coupled distillation involving a side rectifier; however, in the case of the reactive Petlyuk distillation column, two recycle streams must be varied in order to obtain the minimum energy requirement required in the reboiler. It is important to highlight that this equilibrium reaction is usually catalyzed using sulfuric acid or p-toluensulfonic acid introduced directly into the reboiler of the reactive distillation column; therefore, it is expected that most of the conversion of reactants to products occurs in the reboiler, but hydrolysis can be presented at other stages. As a result, the search for the minimum energy requirement considers reactions at all equilibrium stages.

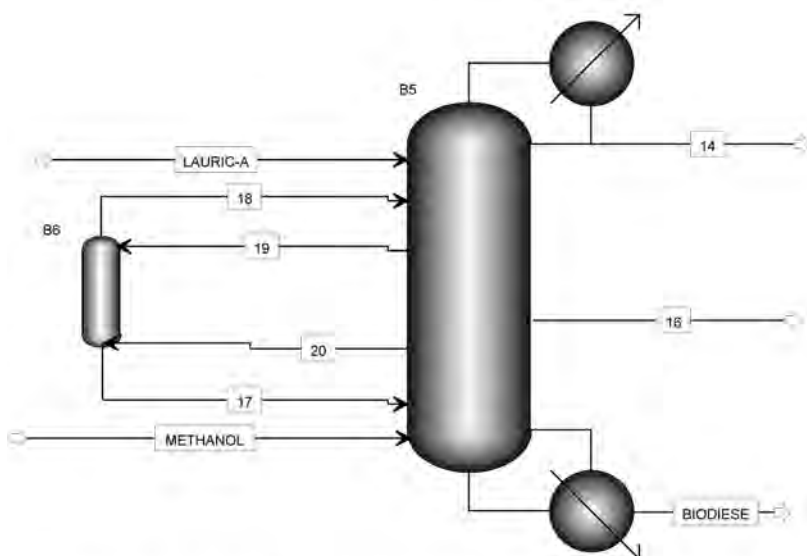
This study considers homogeneous catalysts for the reaction, but important advances have been made using solid acid catalysts; for example, Lotero et al. (2005) have reported that the use of these can avoid corrosion problems associated with the use of strong acids and reduce production costs. In the same context, Kiss et al. (2006a) have studied the esterification of lauric acid with methanol, 2-ethylhexanol, and 1-propanol using several solid acid catalysts, concluding that sulfated zirconia can be a good candidate. Other important studies (Kiss et al., 2006b, 2008; Kiss, 2009) have shown that solid acid catalysts can be used in reactive distillation and reactive absorption as a sustainable technology.

The search for the minimum energy requirement has three design specifications for the composition of the three products that are included as constraints in the

procedure implemented in AspenONE Aspen Plus. The equilibrium chemical reaction was included in all stages and the NRTL model was used for the vapor-liquid equilibrium. All the parameters required in the NRTL model were obtained directly from the process simulator database. Moreover, it is important to note that



(a) Thermally coupled distillation with a side rectifier



(b) Fully thermally coupled distillation sequence (Petlyuk column)

Figure 1. TCDS options implemented in AspenONE Aspen Plus for the production of biodiesel.

steady-state results do not depend on using an equilibrium reaction model or kinetically controlled reaction.

The systems include two feed streams; the first is lauric acid with a flow of 45.4 kmol/h as saturated liquid at 1.5 bar, and the second is methanol with a flow of 54.48 kmol/h as saturated vapor at 1.5 bar. A mass fraction of 0.999 was assumed for the purity of the biodiesel stream. Figure 1 shows the two TCDS options implemented in AspenONE Aspen Plus. The main columns have 30 reactive stages, and the lauric acid stream is introduced into stage 3 while the methanol stream is fed to stage number 19 (numbered from top to bottom). As can be seen in Figure 1, the reactive thermally coupled distillation sequences require an additional distillation column. The side rectifier (Figure 1(a)) and the prefractionator (Figure 1(b)) have 10 nonreactive stages, respectively. The values of the theoretical stages and flows of the reactants were set according to Dimian et al. (2009). It is important to highlight that they used a reactive distillation column using three feeds and two additional conventional distillation columns to recover the esters, methanol, and water, but the approach presented here uses reactive thermally coupled distillation sequences that separate the products and the excess of methanol in the same complex distillation sequence. Furthermore, the practical implementation of thermally coupled distillation columns can be achieved using dividing wall distillation columns. Regarding this technology, it is important to mention that this is the main contribution of the present work, because according to the open literature (Kiss et al., 2009), one of the first reactive dividing wall distillation columns has been implemented recently at Akzo Nobel Chemicals. This novel implementation presents significant savings in both energy and capital costs.

Therefore, the stages are different, because the thermally coupled distillation sequences include the three distillation columns of the flow sheet reported in Dimian et al. (2009). A final comment can be made on the subject of rigorous optimization: since there are some differences in the alcohols used in this study and those used in the work of Dimian et al. (2009), the optimization procedure must take into account the number of stages of the thermally coupled distillation sequence.

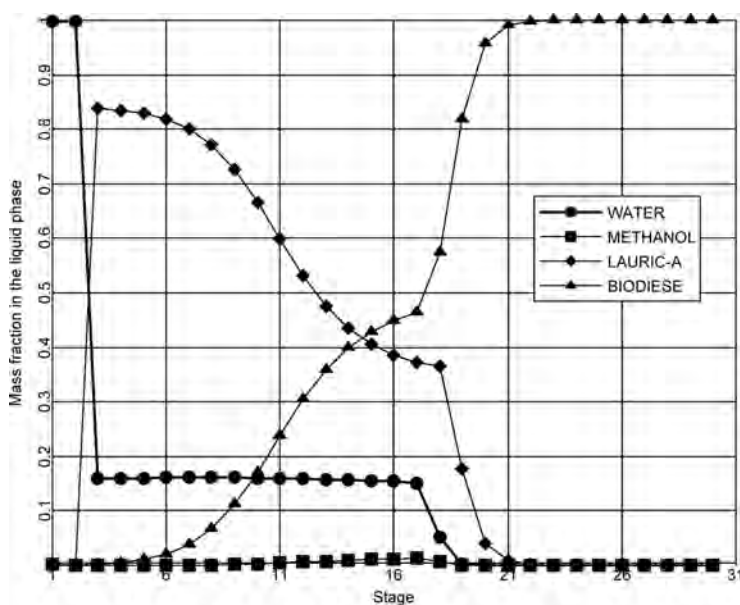
Results

Steady-State Results

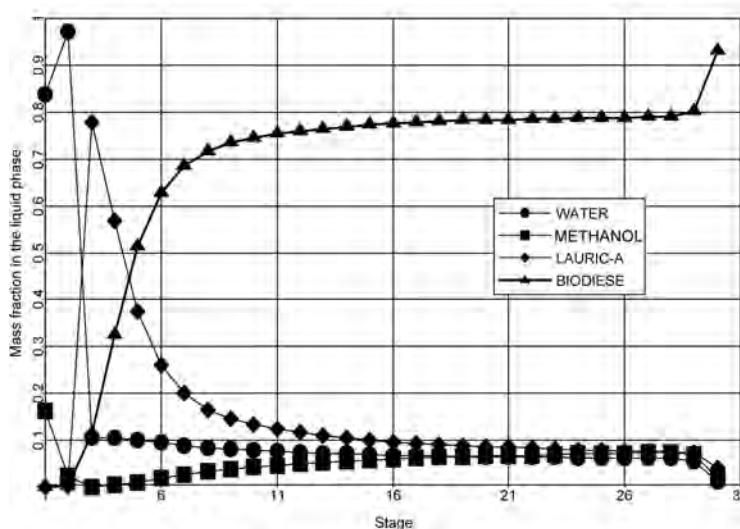
In the first part of the analysis, the composition profiles were analyzed in order to determine biodiesel composition. This is very important because the amount of acid is critical in motor vehicles. Figure 2 presents the composition profiles in the liquid phase.

In the case of the TCDS option with side rectifier (Figure 2(a)), it is observed that it is possible to obtain almost pure biodiesel as the bottom product of the main column (mass fraction equals 0.999). In the distillate product of this column, the water produced in the reaction is removed, and the excess of methanol is recovered in the side rectifier column. This methanol, of course, could be returned to the reactive distillation column in order to obtain a more efficient reactive distillation process.

When the composition profiles for the Petlyuk distillation column are analyzed (Figure 2(b)), it can be seen that mass fraction of the biodiesel is around 0.93, which is very low in comparison to that obtained in the TCDS with a side rectifier. This low



(a) Thermally coupled distillation with side rectifier



(b) Petlyuk distillation column

Figure 2. Composition profiles in the liquid phase of the main columns of the TCDS sequences.

purity is the result of a significant amount of biodiesel obtained in the side product of the Petlyuk distillation column. The fully thermally coupled distillation option requires an additional distillation column to adjust the composition of the biodiesel, since a significant amount of water appears in the bottoms product. Also, biodiesel leaves in the water removed in the side stream. It can be concluded that these

different compositions in products for the base designs will lead to very different dynamic behavior, because the control of a high-purity distillation column is more difficult than that of a low-purity column.

In order to obtain the minimum energy requirement for the TCDS option with side rectifier, different values for the reflux ratio (RR) and interconnecting vapor stream (VF) were investigated to determine the minimum energy requirement of this reactive complex distillation sequence. Figure 3 shows that the energy requirement greatly depends on RR and VF. For this case, a minimum energy requirement of 600 kW is obtained for RR and VF values of 6 and 36.54 kmol/h respectively. These curves for energy requirement are similar to those of a nonreactive thermally coupled distillation sequence. It can be observed that, for higher values of the interconnecting stream, taking the minimum energy requirement as a reference, energy requirement increases slowly; but if the search is conducted for lower values of the interconnecting stream, energy requirement increases dramatically (Figure 3) and convergence problems can easily arise. These curves can be used to infer potential control problems, because sharp curves might imply severe control problems, i.e., small changes in the interconnecting flows will cause significant energy requirement increases. On the other hand, distillation systems with non-sharp curves might have good operational properties. Serra et al. (2003) found that the operation of the dividing wall distillation column can be improved by operating in regions outside minimum energy requirement.

The energy requirement of the reactive Petlyuk distillation column was studied implementing parametric studies in AspenONE Aspen Plus. For instance, Figure 4 shows the mass fraction of the biodiesel in the product stream (bottoms product of the main column) for different values of the side product. It can be seen that the mass fraction of the biodiesel in the product stream increases up to a maximum value of 0.93 and then decreases for higher values of the flow of the side product. This figure also shows that the mass fraction of the biodiesel in the side product

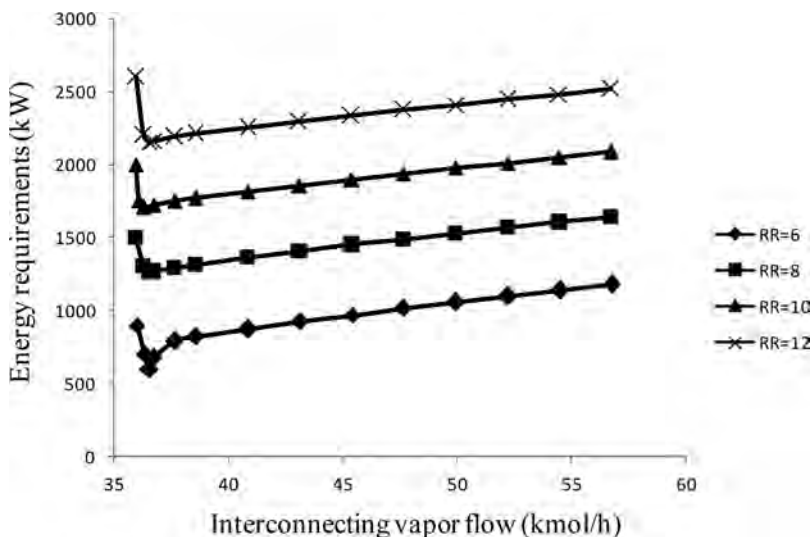


Figure 3. Energy requirements in the reboiler of the thermally coupled distillation sequence with a side rectifier.

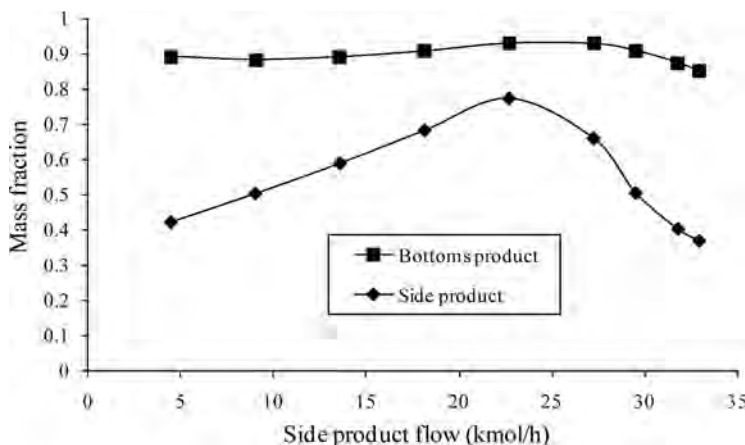


Figure 4. Mass fraction of the biodiesel in the bottoms product and side product of the reactive Petlyuk distillation column.

presents a trend similar to that obtained in the bottoms product of the main distillation column of the Petlyuk column. As a result, it is not possible to obtain a high purity of biodiesel in the bottoms product, since a considerable amount of biodiesel is extracted in the side product. Regarding the energy requirement of the reactive Petlyuk distillation column, it increases dramatically as the value of the side product decreases (Figure 5).

Regarding environmental aspects, Kencse and Mizsey (2007) have reported that, in fact, gas emissions are directly linked to energy requirement since, in the chemical industry, the energy required in distillation is obtained from crude oil. As a result, Figures 3 and 5 can be used to obtain carbon dioxide emissions, and it can be seen that emissions can increase significantly when the distillation sequences are operated at nonoptimal conditions.

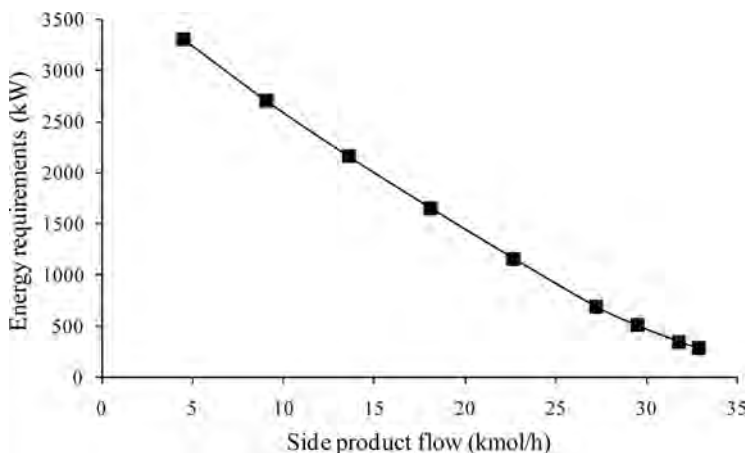


Figure 5. Energy requirements of the reactive Petlyuk column for different values of the side product.

From the steady-state analysis, it can be concluded that the reactive thermally coupled distillation sequence with a side rectifier is the best option to obtain biodiesel, because the composition of the biodiesel obtained can be adjusted to the required purity. In contrast, in the reactive Petlyuk column, the required composition of the biodiesel cannot be obtained. Thus, the dynamic tests presented in the next section correspond only to the reactive thermally coupled distillation sequence using a side rectifier.

Closed-Loop Dynamic Behavior

According to steady-state performance, the TCDS option with side rectifier was the best option in terms of energy requirement and purity of the biodiesel product. As a result, it is important to test the closed-loop dynamic behavior of this reactive complex distillation sequence. The mathematical model used for this stage includes transient total mass balance, transient component mass balances, transient energy balance, equilibrium relationship, summation constraints, and stage hydraulics. Because of the chemical reaction, the complexity of the model is increased, since the mass and energy balances are coupled.

The dynamic study was conducted in AspenONE Aspen Dynamics to test different operational condition scenarios. For closed-loop dynamic study, the kinetic model (Table I) reported in Steinigeweg and Gmehling (2003) was used. Moreover, for proper hydraulic behavior, residence times of 5 min for liquid holdups were assumed as recommended by Luyben (1992). Equation (2) shows the kinetic equation used in the dynamic tests:

$$r = kC_{\text{Alcohol}}C_{\text{Acid}} - k'C_{\text{Ester}}C_{\text{Water}} \quad (2)$$

The dynamic study is important due to the high composition of the biodiesel product; this could lead to control problems because the column is highly nonlinear. A proportional integral controller (PI) was implemented to control the composition of the biodiesel by manipulating the heat duty required in the reboiler. For a PI controller, with gain of 20 and integral time of 1 min, the system was tested for changes in biodiesel composition and disturbances in flows or reactants. Figure 6 presents the dynamic response for a positive set point change of magnitude 0.0004 in biodiesel composition, and, as seen in the figure, it is difficult to achieve the new set point, and the heat duty required is almost doubled; thus, the new composition cannot be reached. This is in agreement with the previous assumption that control could be impeded by the high purity of the biodiesel. When the system was subjected to a negative set point change of magnitude 0.009, the new composition of the biodiesel was achieved in a short period of time (Figure 7). This result is consistent with the

Table I. Kinetic parameters for the pseudohomogeneous kinetic model of the esterification reaction

Reaction	k_i^0 (mol/g s)	$E_{A,i}$ (kJ/mol)
Esterification	9.1164×10^5	68.71
Hydrolysis	1.4998×10^4	64.66

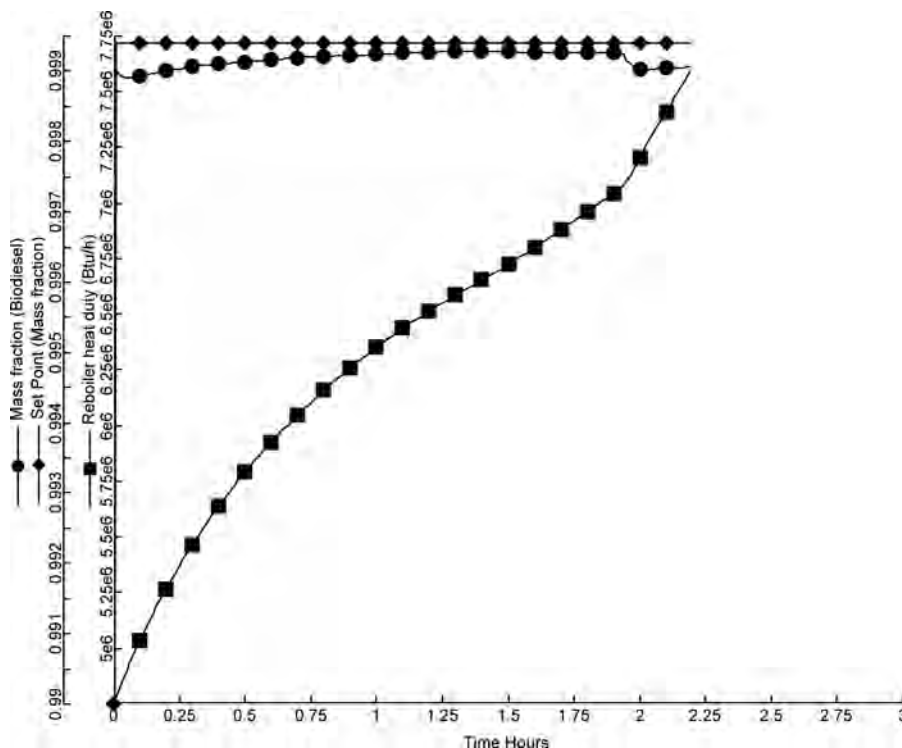


Figure 6. Positive set point change in the composition of the biodiesel mass fraction (0.999 $\rightarrow$ 0.9994).

fact that distillation systems exhibit high nonlinearities when they are operated at high compositions. The study of composition control was complemented for load rejection in the flows of the reactant; for example, Figures 8 and 9 show dynamic responses for disturbances in lauric acid flow. It can be seen that the system can eliminate the effect of the disturbances. In general, the system could eliminate the disturbances in the flows of methanol and lauric acid.

In order to complete the study of the control, two temperature control loops were implemented, since control of composition requires online gas chromatography, which is expensive and presents dead times. It is important to highlight that the control of temperature is more common in industrial practice, because it can be implemented using thermocouples, which are cheaper than gas chromatography. The first step in the implementation of temperature control loops is detecting the most sensitive stages in the temperature profile for changes in the manipulated variables (reflux ratio and reboiler heat duty). Figure 10 presents the temperature gains of the stages of the main distillation column for $\pm 0.5\%$ changes in reflux ratio as recommended by Kaymak and Luyben (2005). In this figure, it can be noted that the temperature of stage 21 is the most sensitive to changes in the reflux ratio, but the temperature of stage 2 also presents a significant gain. When the reboiler heat duty is changed, stage 2 is seen to be the most sensitive. According to these results, the first temperature control loop was established between the temperature of stage 2 and the reboiler duty, and the second one was established between the temperature

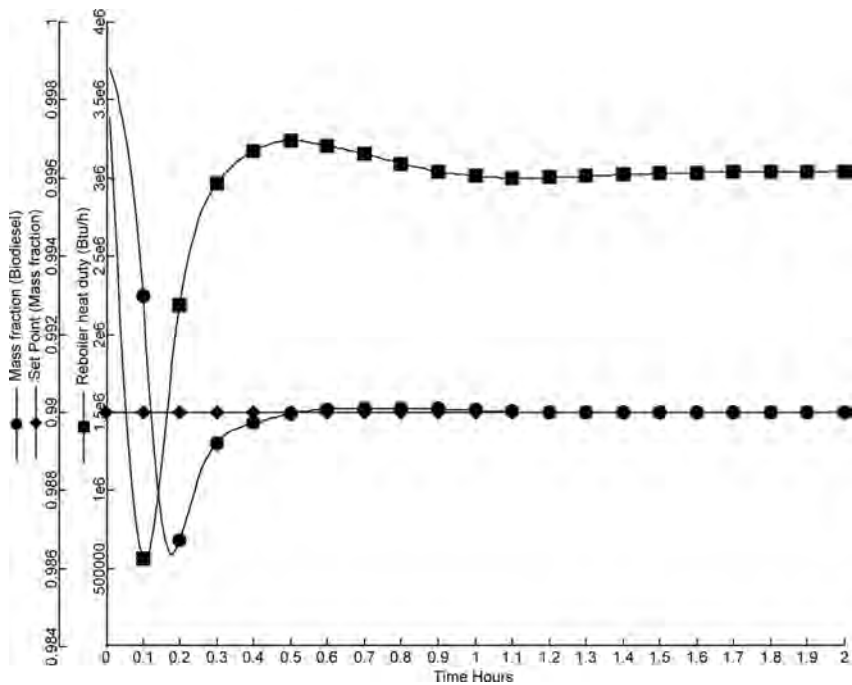


Figure 7. Negative set point change in the composition of the biodiesel mass fraction (0.999 $\rightarrow$ 0.99).

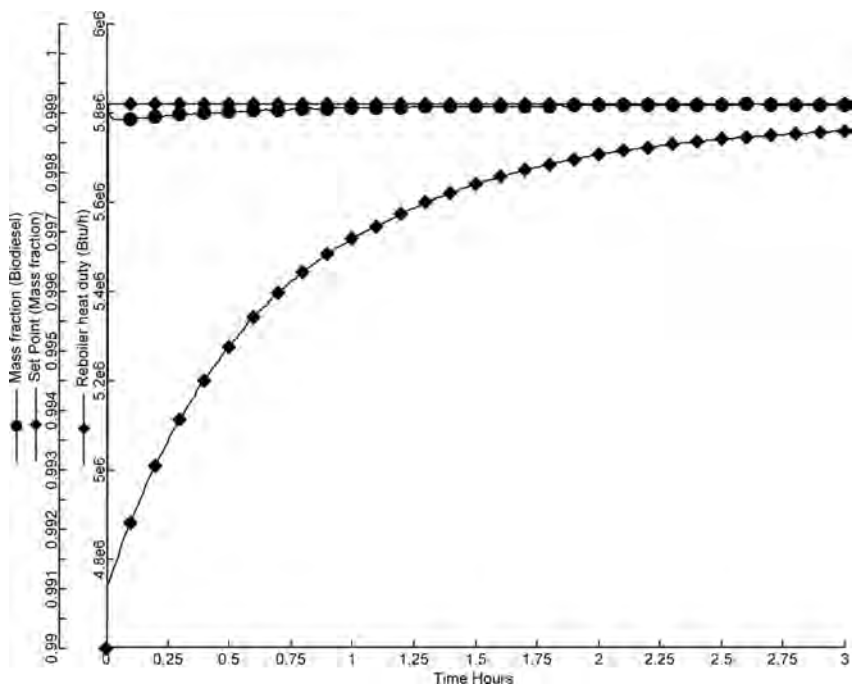


Figure 8. Positive disturbance in acid feed (45.4 $\rightarrow$ 49.94 kmol/h).

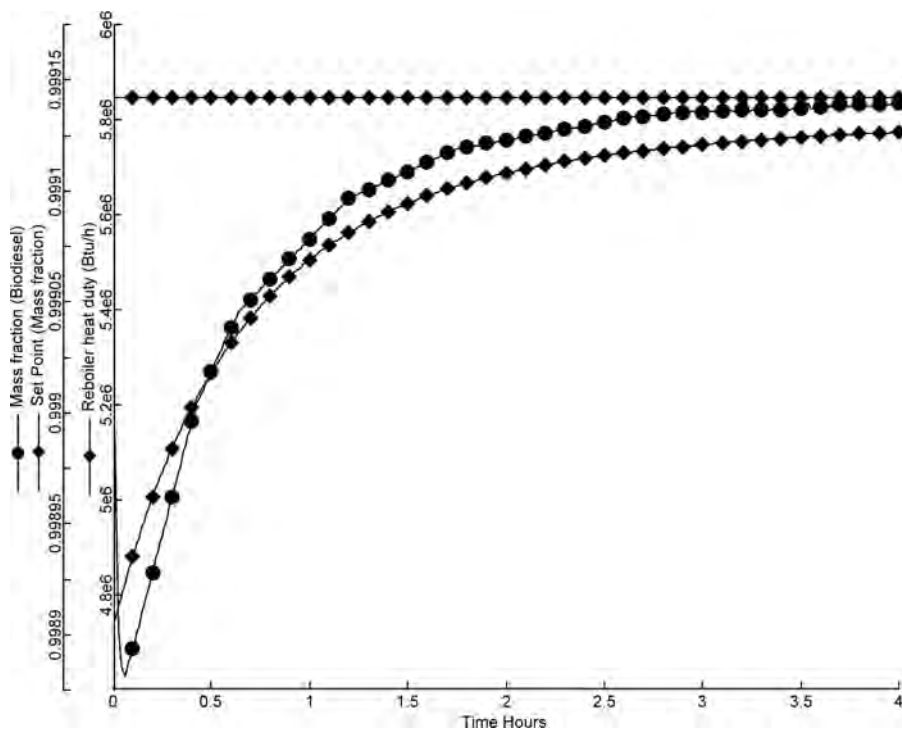


Figure 9. Negative disturbance in acid feed ($45.4 \rightarrow 40.86$ kmol/h).

of stage 21 and the reflux rate. The two implemented temperature control loops are shown in Figure 11; in this figure, the two temperature control loops are labeled PI_1 and PI_2. In addition, proportional controllers for pressure and level are included as default in AspenONE Aspen Dynamics.

The temperature control loops were tuned minimizing the integral of the absolute error. Optimal values of the temperature controllers are indicated in Table II.

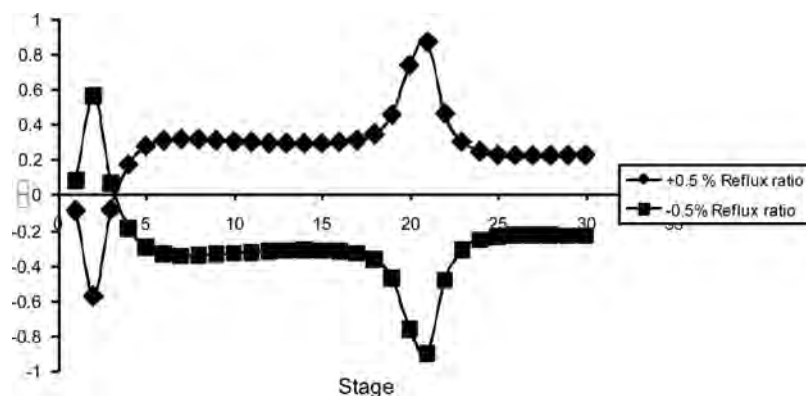


Figure 10. Temperature gains ΔT (K) in the trays of the main distillation column for changes in the reflux ratio.

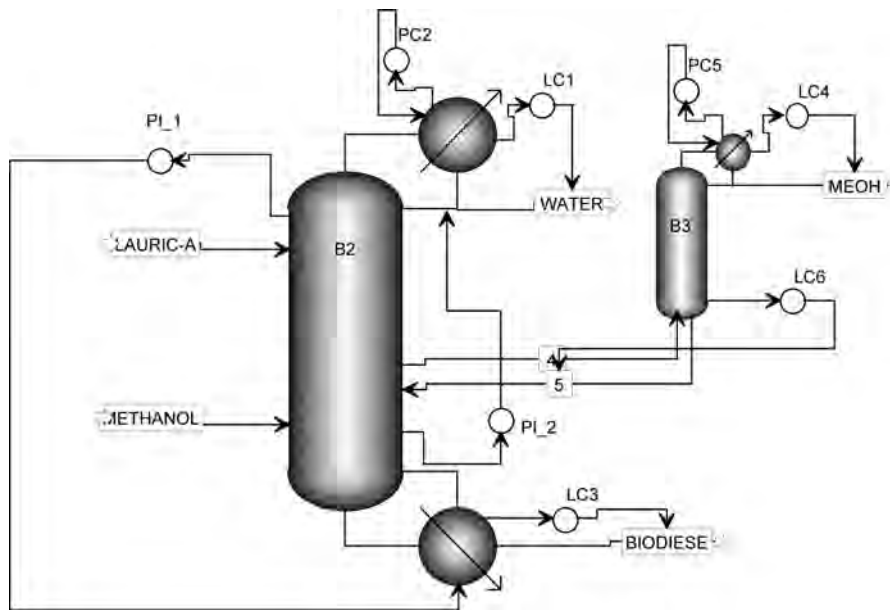


Figure 11. Implemented control loops in the reactive thermally coupled distillation sequence with a side rectifier.

The optimization procedure assumes a controller gain value, and integral time is varied until a local minimum for the integral of the absolute error is identified. This optimization task is repeated for other gain values until the global optimum is determined. Figure 12 presents a typical search for the optimum tuning parameters of the first control loop.

Regarding one temperature control, in general the reactive thermally coupled distillation sequence achieved positive and negative set point changes. Figure 13 presents the dynamic responses for a positive set point change in the temperature of stage 2, manipulating the reboiler duty. It can be observed that the system can achieve the set point in a short time (under 0.5 h). Figure 14 shows that when the system is subjected to a disturbance in the feed composition, the system can eliminate the effect of the disturbance in approximately 0.5 h.

When the reactive thermally coupled distillation was studied considering two closed loops, dynamic responses were more oscillatory and the time to reach the new steady state increased over that for a single closed loop. Figure 15 corresponds to the dynamic response of the second control loop when the set point in the first control loop was kept constant, but under closed-loop operation.

In general, the complex reactive distillation system could achieve set point changes and eliminate the effect of disturbances in the feed composition for one

Table II. Tuning parameters of the controllers

	K_c	τ_i (min)
First control loop	20	1
Second control loop	3	1.5

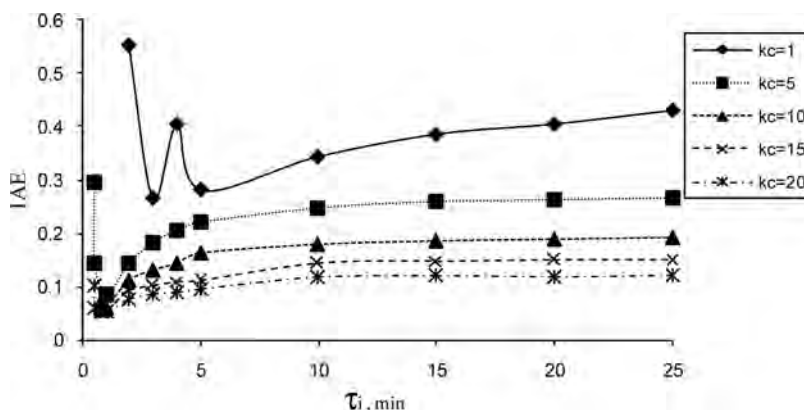


Figure 12. Search for optimum tuning parameters of the controller of the first closed loop (temperature of stage 2 coupled to reboiler duty).

and two closed loops of temperature. It is important to mention that more advanced controllers can be used, for instance, internal model control, but simple PI controllers can be used to control the complex reactive distillation sequence (Hernández et al., 2009).

Regarding recent advances in the use of dividing wall distillation columns, it is possible to propose a single distillation column using a dividing wall and a side

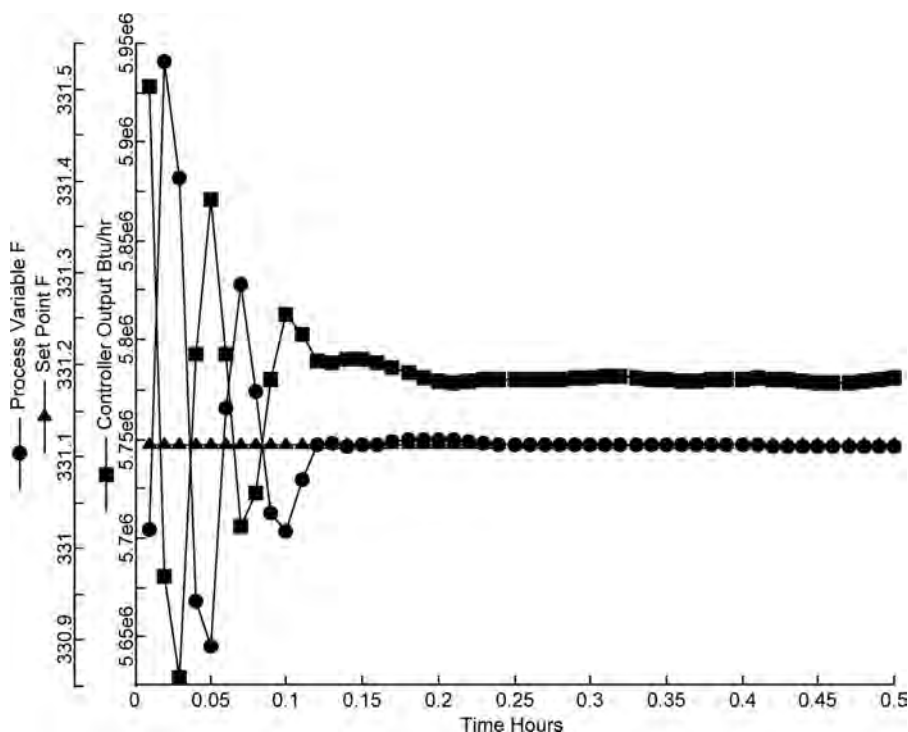


Figure 13. Positive set point change in temperature of stage 2 for one closed loop, using the reboiler duty as manipulated variable.

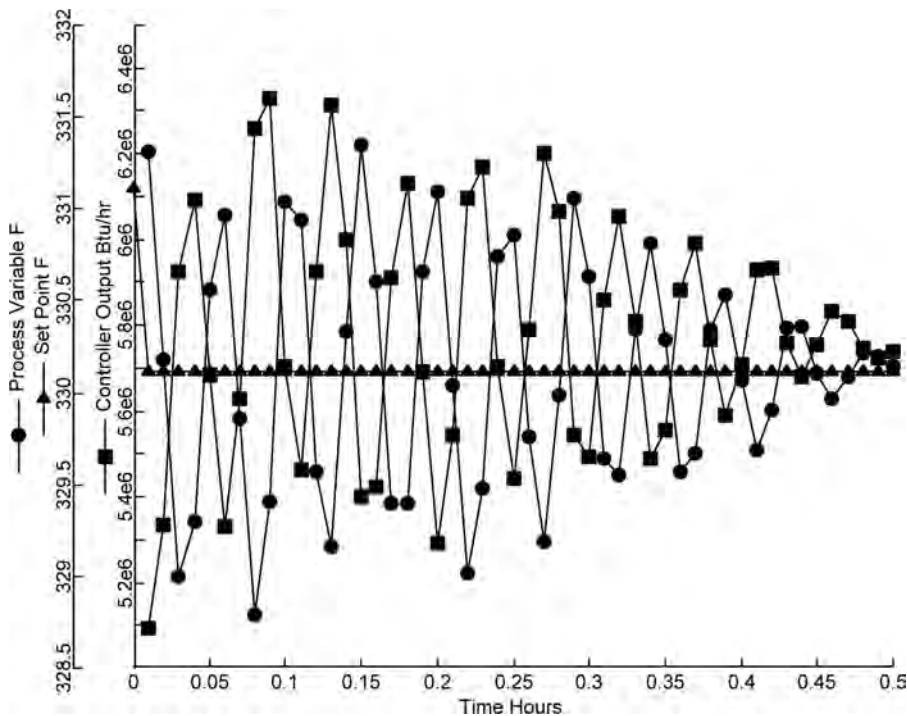


Figure 14. Positive disturbance in ethanol feed ($54.48 \rightarrow 55.388$ kmol/h) for one closed loop, using the reboiler duty as manipulated variable.

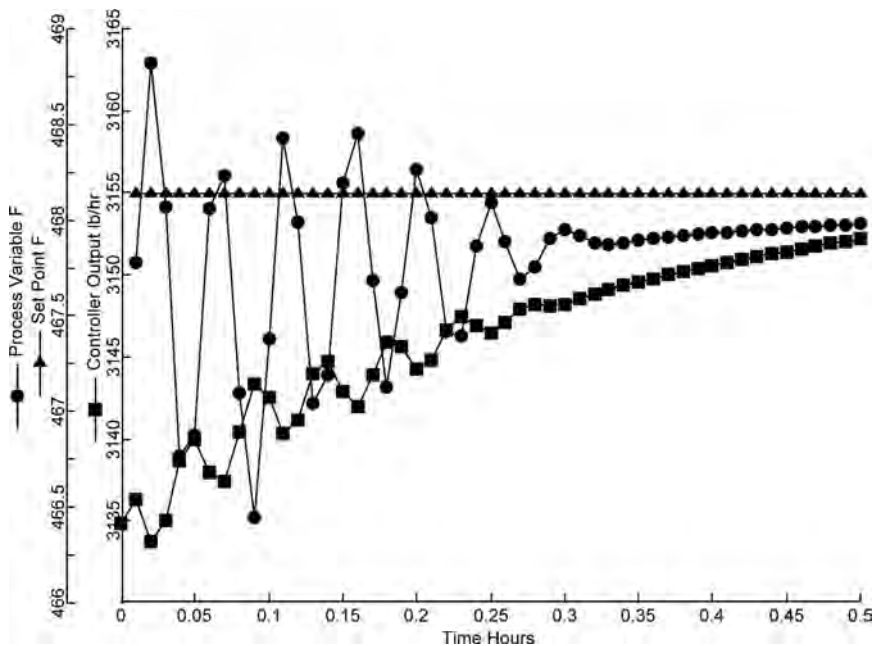


Figure 15. Positive set point change in the temperature of stage 21 for two control loops, using the reflux rate as manipulated variable.

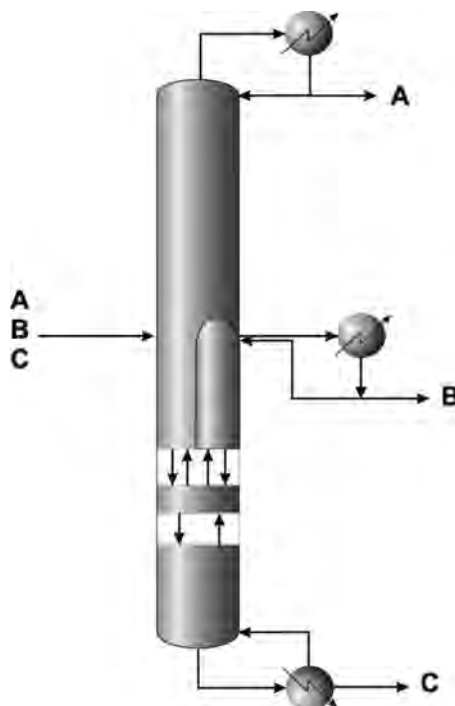


Figure 16. Practical implementation of the thermally coupled distillation sequence with a side rectifier.

condenser. Additionally, this idea leads to reductions in capital costs. The proposed scheme is shown in Figure 16. Details regarding the practical implementation of reactive dividing wall distillation columns can be found in Hernández et al. (2009).

Conclusions

The esterification of methanol and lauric acid was studied in a thermally coupled distillation sequence with a side column and the Petlyuk distillation column. The thermally coupled distillation sequence with a side rectifier was the best option in terms of energy requirement and purity of biodiesel in the product. The results for the reactive complex distillation sequence with a side column showed that energy requirement can be reduced drastically depending on operational conditions, and for conditions different than those of the optimal solution, carbon dioxide emissions can increase significantly. The closed-loop dynamic responses showed that it is possible to operate and eliminate the disturbances in the feed composition of the reactive thermally coupled distillation sequence with a side rectifier.

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