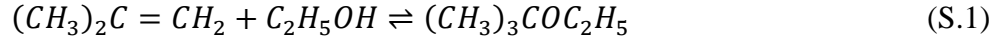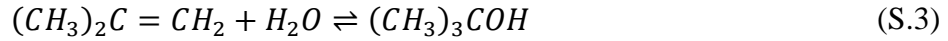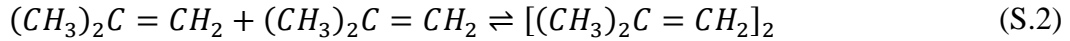**ETBE reaction mathematical model**

The liquid phase reaction for the production of ETBE is carried out over an acid catalyst. It is a reversible and exothermic reaction as shown in Equation S.1.

$$(CH_3)_2C = CH_2 + C_2H_5OH \rightleftharpoons (CH_3)_3COC_2H_5 \tag{S.1}$$

Additional side reactions may occur, like the dimerization of isobutene and the hydration of isobutene to isobutyric acid as seen in Equations S.2 and S.3. It is possible to avoid these side reactions. The hydration of the isobutene is avoided by working in an anhydrous medium, and by using an excess in ethanol higher than 4%. This last condition avoids the dimerization by having the surface of the catalyst covered by ethanol [1].

$$(CH_3)_2C = CH_2 + (CH_3)_2C = CH_2 \rightleftharpoons [(CH_3)_2C = CH_2]_2 \tag{S.2}$$

$$(CH_3)_2C = CH_2 + H_2O \rightleftharpoons (CH_3)_3COH \tag{S.3}$$

The pseudo-homogeneous kinetics is based on the Langmuir, Hinshelwood, Hougen, and Watson (LHHW) model, which considers the kinetic factor, the driving force of the reaction and the adsorption over the catalyst. This mechanism assumes two active adsorption sites for the ethanol and one for the isobutene. Taking into account that the liquid is strongly non-ideal, the reaction rate is expressed in terms of the activity of the components γx instead of the molar composition. The kinetic expression was obtained by Jensen et al. [2] and described below.

$$\mathcal{R} = \frac{\kappa_{rate}(\gamma x)^2_{ETBE}\left((\gamma x)_{IB} - \frac{(\gamma x)_{ETBE}}{\kappa_{Eq}(\gamma x)_{EtOH}}\right)}{(1 + \kappa_A(\gamma x)_{EtOH})^3} \tag{S.4}$$

where the reaction rate constants are given by the following expression.

$$\ln \kappa_{Eq} = 10.387 + \frac{4060.59}{T} - 2.89055 \ln T - 0.01915144(T) + 5.28586 * 10^{-5}(T)^2 \\ - 5.32977 * 10^{-8}(T)^3 \tag{S.5}$$

$$\kappa_{rate} = 2.0606 * \exp\left(\frac{-60.4 * 10^3}{RT}\right) \tag{S.6}$$

$$\ln \kappa_A = -1.0707 + \frac{1323.1}{T} \tag{S.7}$$

where T is the temperature in Kelvins, and R is the ideal gas constant. The computation of this reaction rate has to be made in each reactive stage independently.

The reaction is carried on an Amberlyst 15 (A15) catalyst produced by Rohm and Haas®. This type of catalyst is a copolymer of styrene and divinylbenzene sulfone [1], with the physical characteristics listed in the **¡Error! No se encuentra el origen de la referencia.**.

Table S.1. Physical properties of the A15[1]

Property	Unit	Value
Surface area	$[m^2/g]$	53
Pore average size	$[10^{-10}\ m]$	300
Total pore volume	$[ml/g]$	0.40
Active sites concentration	[equivalents/kg]	4.8
Apparent density	$[kg/m^3]$	770

It should be noted that this catalyst is susceptible to be deactivated, in other words, the specific catalyst area and the number of active sites decrease with time due to the desulfonation [3].

Dynamic response of reaction rate, compressibility factor, and pressure

Since the reflux ratio and the reboiler duty are manipulated over time, there are changes in the flows and not only of the compositions through the column. These changing flow rates have an effect on the variables related to them, such as the stage pressure, the compressibility factor or the reaction rate. The profiles for the sinusoidal disturbance with $\omega = 1$ are shown in Figure S.1.

The three profiles are shown here correspond to the dynamic response of the reaction rate, the compressibility factor, and the stage pressure. It can be noted that the response to the disturbance is considerable for the reaction rate, mild for the compressibility factor and negligible for the pressure. The reaction rate appears to have been controlled indirectly by solving the OCDP and showing a higher rate in the lowest stage with the catalyst.
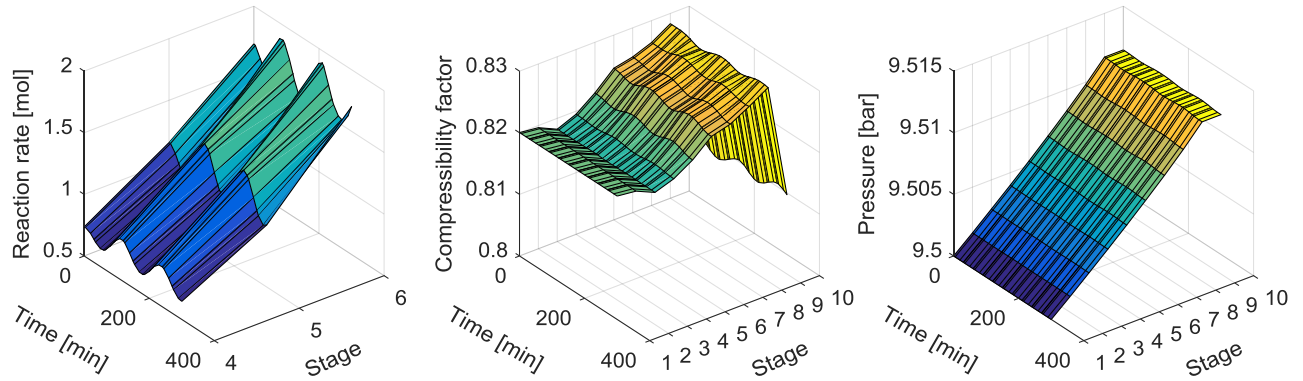
Figure S.1. Dynamic behavior of reaction rate, compressibility factor and stage pressure in the ODCP solution with sinusoidal disturbance and ω=1

The standard deviation σ and relative deviation for all stages has been calculated and are shown in the Table S.2.

Table S.2. Standard and relative deviations for reaction rate, compressibility factor and stage pressure in the OCDP solution with sinusoidal disturbance and ω=1

Stage	Reaction rate		Compressibility factor		Stage pressure	
	$\sigma \left[\dfrac{mol}{kg_{cat}}\right]$	$\dfrac{\sigma}{\mathcal{R}}$ [%]	σ	$\dfrac{\sigma}{Z}$ [%]	σ [bar]	$\dfrac{\sigma}{P}$ [%]
1	-	-	3.21E-06	3.91E-04	0	0
2	-	-	7.55E-06	9.21E-04	3.71E-06	3.71E-06
3	-	-	3.82E-05	4.67E-03	7.91E-06	7.91E-06
4	0.0623	8.5274	1.36E-04	1.66E-02	1.31E-05	1.35E-05
5	0.1201	10.5261	3.23E-04	3.93E-02	1.39E-05	2.09E-05
6	0.1271	7.5800	3.96E-04	4.80E-02	1.96E-05	2.89E-05
7	-	-	3.79E-04	4.59E-02	3.53E-05	3.75E-05
8	-	-	3.20E-04	3.87E-02	5.81E-05	4.50E-05
9	-	-	3.34E-04	4.04E-02	8.78E-05	4.87E-05
10	-	-	7.00E-04	8.64E-02	8.78E-05	4.87E-05
Average	0.1032	8.8812	2.64E-04	3.21E-02	3.24E-06	2.55E-05

It can be noticed again that the compressibility factor and the stages pressures dependence on the time are negligible. Similar results are found for the two other sinusoidal disturbances analyzed in this work, with $\omega=0.5$ and $\omega=1.5$.

For the completeness of this work, a dynamic analysis of the reaction rate, the compressibility factor, and the pressure is analyzed. The profiles are shown in the Figure S.2.
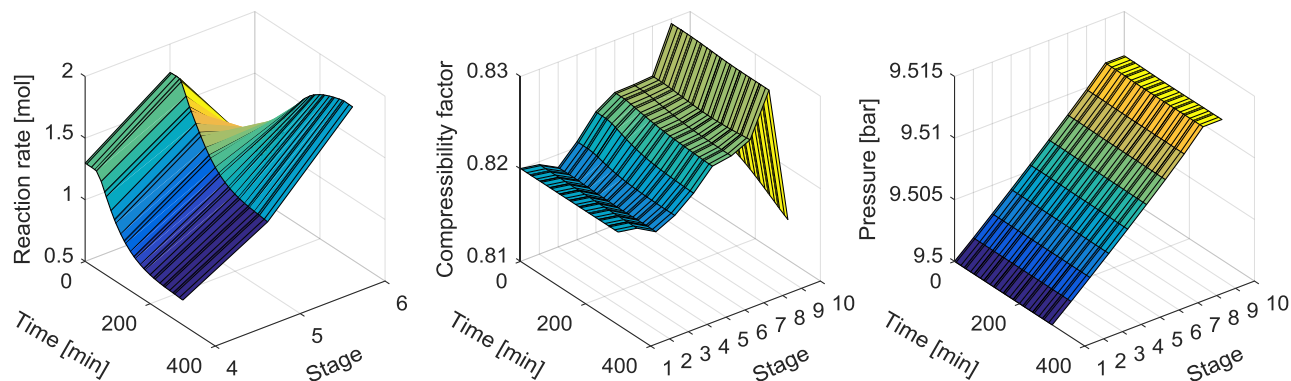

Figure S.2. Dynamic behavior of reaction rate, compressibility factor and stage pressure in the ODCP solution with step disturbance

As in the dynamic simulations and the simultaneous ODCP with a sinusoidal disturbance, the standard deviation of the reaction rate, the compressibility factor, and the stage pressure are determined in the Table S.3.

The obtained results clearly show that the stage pressure is non-sensitive to a disturbance in the feed composition, either a step function or an oscillatory disturbance. The same can be remarked for the compressibility factor, but the reaction rate is strongly dependent on the feed composition. These results were shown because several studies in the literature have considered these variables as constants[4]. It has been shown that such an assumption may be valid for the stage pressure and the compressibility factor, but not for the reaction rate.

Table S.3. Standard and relative deviations for reaction rate, compressibility factor and stage pressure in the OCDP solution with step disturbance

Stage	Reaction rate		Compressibility factor		Stage pressure	
	$\sigma \left[\dfrac{mol}{kg_{cat}}\right]$	$\dfrac{\sigma}{\mathcal{R}}$ [%]	σ	$\dfrac{\sigma}{Z}$ [%]	$\sigma\ [bar]$	$\dfrac{\sigma}{P}$ [%]
1	-	-	3.07E-06	3.74E-04	0	0
2	-	-	8.65E-06	1.06E-03	4.74E-06	4.99E-05
3	-	-	5.21E-05	6.37E-03	8.19E-06	8.62E-05
4	0.2209	24.4073	4.26E-04	5.19E-02	1.55E-05	0.0001635
5	0.2515	19.0442	7.05E-04	8.57E-02	2.39E-05	0.0002516
6	0.3390	24.2345	3.79E-04	4.60E-02	2.88E-05	0.0003029
7	-	-	3.09E-04	3.75E-02	2.89E-05	0.0003041
8	-	-	1.25E-04	1.52E-02	2.38E-05	0.0002507
9	-	-	1.33E-04	1.60E-02	1.52E-05	0.0001596
10	-	-	1.42E-03	1.73E-01	1.52E-05	0.0001596
Average	0.2705	22.5620	3.56E-04	4.34E-02	1.64E-05	1.73E-04

References

(1)   Rohm and Haas Company. *AMBERLYST^{TM} 15WET Industrial Grade Strongly Acidic Catalyst For Catalysis and Separation Technologies*; Philadelphia, 2003.

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(4)   Sneesby, M. G.; Tadé, M. O.; Datta, R.; Smith, T. N. ETBE Synthesis via Reactive Distillation. 2. Dynamic Simulation and Control Aspects. *Ind. Eng. Chem. Res.* **1997**, *36* (5), 1870.