

# Modeling and Simulation of Consecutive-Competitive Reactions in a CSTR

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**Abstract**—The rate equations for a three-step consecutive - competitive reaction of the type  $A + B \rightarrow C$ ,  $C + B \rightarrow D$ ,  $D + B \rightarrow E$  has been solved for the special cases of stoichiometric ratios of the reactants A and B. A steady state mathematical model has been presented for consecutive-competitive reactions in a CSTR based material balances, resulting in a set of ordinary differential equations (ODE). MATLAB is used to find solution for the ordinary differential equations. The initial conditions and experimental kinetics parameters for simulation of consecutive-competitive reactions and the computational results have presented concisely. The main conclusions of the study are: in the consecutive-competitive reactions, only the stoichiometric molar ratio of the reactants (3:1) is not enough for complete conversion to the final product whatever be the space time; yield and maximum concentration of desired product (first, second or third) depends on many factors; e.g., rate constants, relative values of the rate constants and molar ratio of the reactants; in a CSTR.

## 1. INTRODUCTION

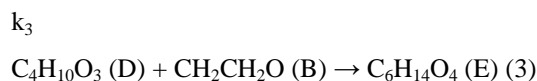
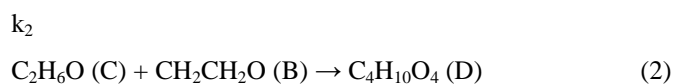
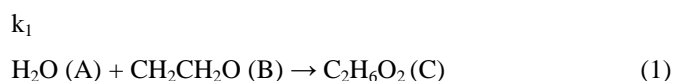
Many industrially important chemical reaction systems possess stoichiometry which may be characterized as consecutive-competitive. The main aspect of this class of reactions is the formation of a spectrum of desired products and byproducts. Studies done in the past concentrated on either determination of kinetic parameter or distribution of products. Consecutive-competitive reactions can be thought as combination of series ( $A \rightarrow R \rightarrow S$ ) and ( $B \rightarrow R$ ,  $B \rightarrow S$ ).

Arthur et al (1952), introduced differential rate equations for the kinetics of the reactions of the type resulting differential equations have been integrated for the special case of stoichiometric amounts of the reactants A and B in the feed. Svrbely and blauer(1963) has been solved, the rate equations for a three-step competitive-consecutive second-order reaction in terms of a variable  $\lambda$  When  $A_0 = 3B_0$ . A similar solution was obtained by Blauer et al. (1963) for four-step competitive-consecutive second-order reaction. Friedman et al (1962) had proposed experimental kinetic data are most conveniently correlated by the integrated form of the differential rate equations which the reactions are presumed to obey.

Renken (1972) found through a numerical simulation of a CSTR that selectivity to an intermediate product C in a homogeneous, consecutive-competitive reaction network can be increased by in-phase concentration cycling of reactants A and B. Others who have looked at consecutive-competitive reaction networks have reached the same conclusion (Lee and Bailey, 1980). Batiha (2004), proposed a brief review on the kinetics of consecutive-parallel reactions using the non-catalytic process of ethylene oxide hydrolysis. Nitin et al (2012) simulated the model equation for series parallel reaction with CSTR. Selvamony (2013) compared the performance of second order consecutive-competitive reaction in fed-batch reactor with that in continuous plug flow reactor.

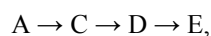
## 2. THE REACTION SYSTEM

The following type of reaction system is a representation of consecutive-competitive reaction, hydration of ethylene oxide for the production of mono-, di and tri- ethylene glycol and also written symbolically in a generalized form as follows.

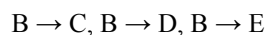


Where  $\text{H}_2\text{O}$  = Water,  $\text{CH}_2\text{CH}_2\text{O}$  = Ethylene oxide,  $\text{C}_2\text{H}_6\text{O}_2$  = Mono-ethylene glycol,  $\text{C}_4\text{H}_{10}\text{O}_4$  = Di- ethylene glycol,  $\text{C}_6\text{H}_{14}\text{O}_4$  = Tri-ethylene glycol.

The above set of reaction is **consecutive** (series) with respect to reactant A (water),



and **competitive** (parallel) with respect to reactant B(ethylene oxide)



### 3. MATHEMATICAL MODEL

The general material balance for the reactions (1-3) is written based on the basic assumption of ideal mixing condition (ideal CSTR), constant volume (density), isothermal process and that all the reaction steps are elementary second-order. For component A (series reactant),

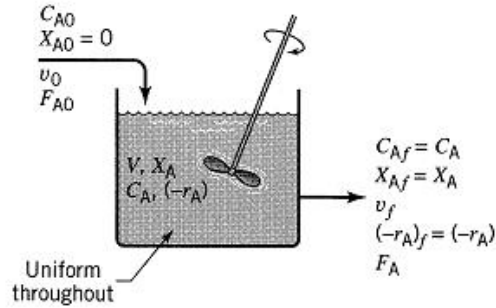


Fig. 1: Notation for an ideal continuous stirred tank reactor (CSTR)

$$\frac{d(C_A)}{d(t)} = \frac{(F_0 C_{A0} - F C_A)}{V} - k_1 C_A C_B \quad (4)$$

Similarly, for the products, components B, C, D, and E, the resulting equations are respectively,

$$\frac{d(C_B)}{d(t)} = \frac{(F_0 C_{B0} - F C_B)}{V} - k_1 C_A C_B - k_2 C_B C_C - k_3 C_B C_D \quad (5)$$

$$\frac{d(C_C)}{d(t)} = \frac{(F_0 C_{C0} - F C_C)}{V} - k_1 C_A C_B - k_2 C_B C_C \quad (6)$$

$$\frac{d(C_D)}{d(t)} = \frac{(F_0 C_{D0} - F C_D)}{V} + k_2 C_B C_C - k_3 C_B C_D \quad (7)$$

$$\frac{d(C_E)}{d(t)} = \frac{(F_0 C_{E0} - F C_E)}{V} + k_3 C_B C_D \quad (8)$$

This set of nonlinear ODE describes behavior of the state variables which are in this case concentrations of components A, B, C, D and E are  $C_A$ ,  $C_B$ ,  $C_C$ ,  $C_D$ , and  $C_E$  in time  $t$  respectively. Assuming inlet flow rate is equal to outlet flow rate.

Reaction mixture concentrations and kinetic parameters in the consecutive-competitive reactions for the production of monoethylene glycol (MEG), di-ethylene glycol (DEG) and tri-ethylene glycol (TEG) are taken from the work of **Altiokka et al (2009)** and these are summarized in Table 1.

Table 1: Parameters for consecutive-competitive reaction in the hydration of ethylene oxide

Sr. No	Parameters	Value of Parameter with unit
1	CA0	34.35 mol/L
2	CB0	6.872 mol/L
3	k1	7.8438 L/mol.min
4	k2	2.7136 L/mol.min
5	k3	2.9197 L/mol.min
6	F	0.001 L/min
7	V	0.150L

Where,  $C_{A0}$  = initial concentration of water,

$C_{B0}$  = initial concentration of ethylene oxide

$k_1$  = reaction rate constant for the production of monoethylene glycol, L/mol.min

$k_2$  = reaction rate constant for the production of di-ethylene glycol, L/mol.min

$k_3$  = reaction rate constant for the production of tri-ethylene glycol, L/mol.min

$V$  = volume of the reactor, L

$F$  = volumetric flow rate, L/min

For complete conversion to the final product TEG, stoichiometrically, three moles of ethylene oxide are required for each mole of water in the initial feed mixture / stream. However, the reactant ratios in the feed mixture are expected to influence the composition of the reaction mixture. In the hydration of ethylene oxide the numerical value of the rate constant for the first reaction is approximately three times of the second reaction, which is approximately of the same order as the third reaction ( $k_1 > k_3 > k_2$ ). The results of computation have been presented graphically as concentration versus time (space time) with different parameters held constant under isothermal operating conditions. These are presented in the follows

#### Case 1 Initial reactant ratio ( $C_{B0}/C_{A0}$ ) about one fifth (ethylene oxide, $C_{B0} = 6.872$ ; water, $C_{A0} = 34.35$ )

The yield of the third product, tri-ethylene glycol (TEG) is almost negligible in comparison to mono-ethylene glycol (MEG) and di-ethylene glycol (DEG).

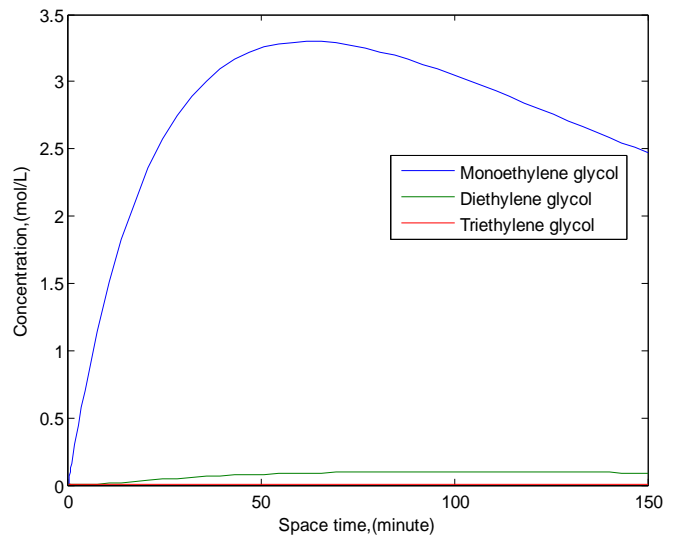
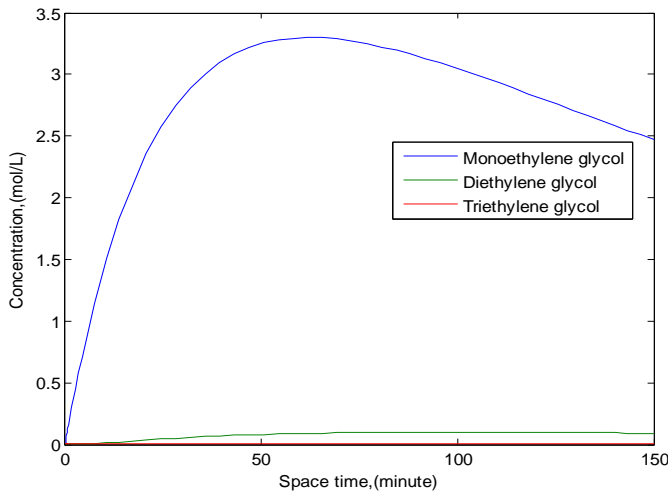
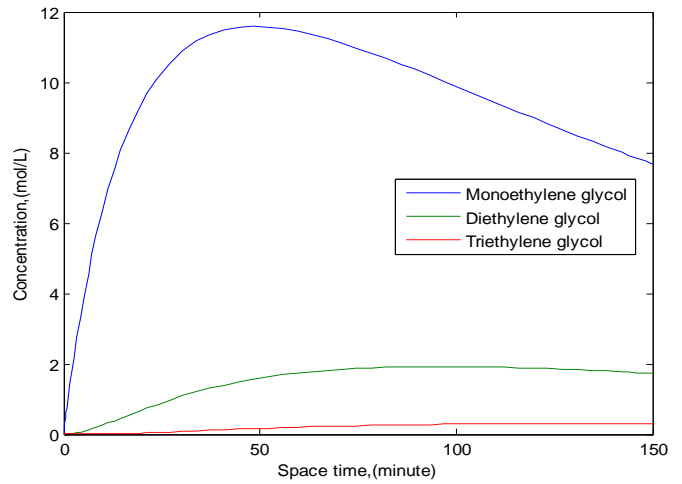


Fig. 2: Concentration profile of the reactants ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 0.2)



**Fig. 3** Concentration profiles of the products, MEG, DEG and TEG ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 0.2)



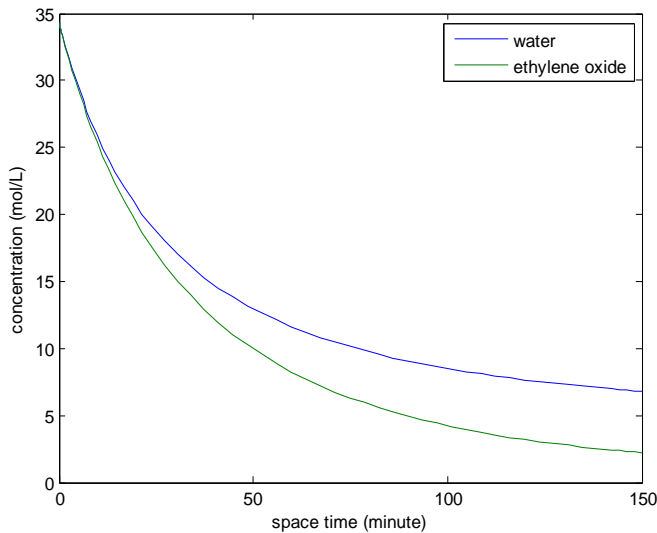
**Fig. 5** Concentration profiles of the products, MEG, DEG and TEG ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 1.0)

**Case 2 Initial reactant ratio ( $C_{B0}/C_{A0}$ ) is one (ethylene oxide,  $C_{B0} = 34.35$ ; water,  $C_{A0} = 34.35$ )**

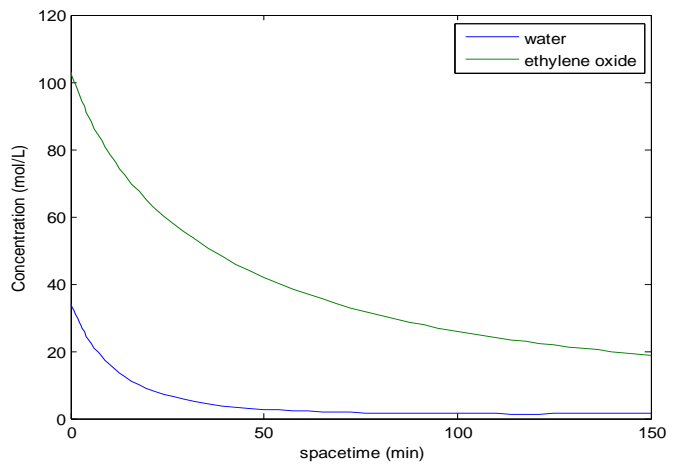
In this case too, when the ratio of reactant concentration,  $C_{B0}/C_{A0}$  in the feed mixture is one,  $C_{B0}$  (Ethylene oxide) is equal to  $C_{A0}$  (water), though the concentration of the product tri-ethylene glycol (TEG) has increased, it is much smaller in comparison to mono-ethylene glycol and di-ethylene glycol.

**Case3 Initial reactant ratio ( $C_{B0}/C_{A0}$ ) is three (EO,  $C_{B0} = 103.05$ ; water,  $C_{A0} = 34.35$ ), same as the stoichiometric ratio**

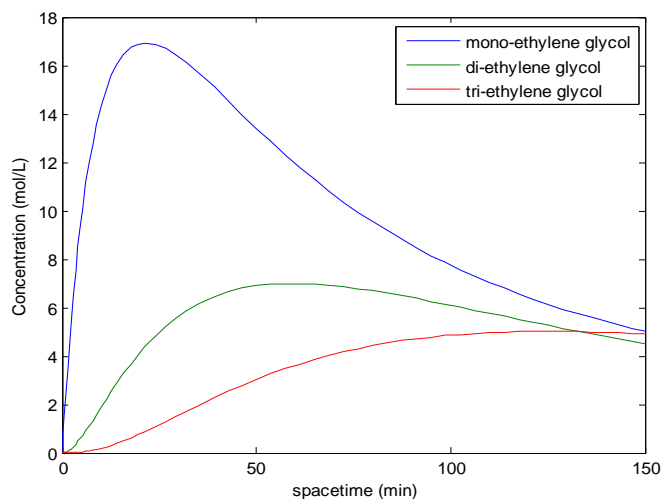
The resulting product composition shows interesting features. The composition of the two intermediate products, MEG (16.95 mol/L at space time 21.38 minutes) and DEG (6.99 mol/L at space time 53.78) reach maximum values, while the concentration / yield of the final product (TEG) goes on increasing and appears to be approaching a constant value. The result is typical of consecutive-competitive reactions presented in literature.



**Fig. 4** Concentration profile of the reactants ( $C_{B0}/C_{A0}$ , ethylene oxide/water=1.0)



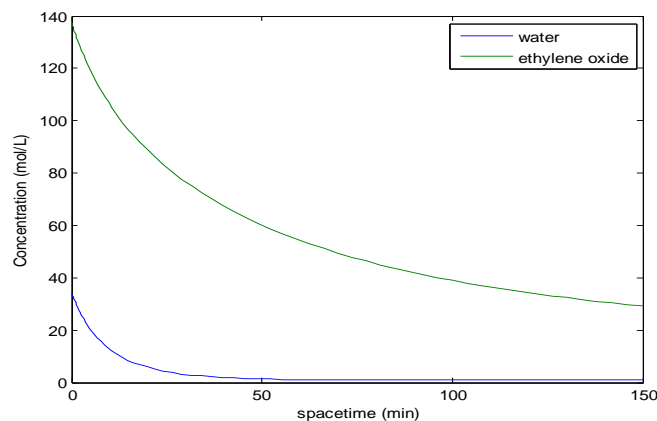
**Fig. 6:** Concentration profile of the reactants ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 3.0)



**Fig. 7: Concentration profiles of the products, MEG, DEG and TEG ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 3.0)**

**Case 4 Initial reactant ratio ( $C_{B0}/C_{A0}$ ) is four (ethylene oxide,  $C_{B0} = 137.35$ ; water,  $C_{A0} = 34.35$ )**

Here, The composition of both the intermediate product, MEG and DEG reaches some maximum values, latter following the former. The concentration of the final product, TEG appears to reach a maximum value (8.259 mol/L) at a space time (103.70 minute) followed by marginal decrease. It is also observed that the rate of formation of DEG is highest when the concentration of the MEG is at its maximum value (17.66 mol/L) at a space time (16.23 minute).

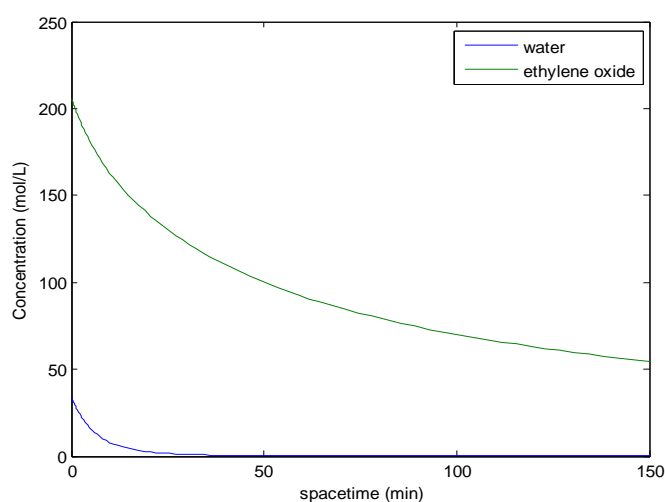


**Fig. 8: Concentration profile of the reactants ( $C_{B0}/C_{A0}$ , ethylene oxide/water =4.0)**

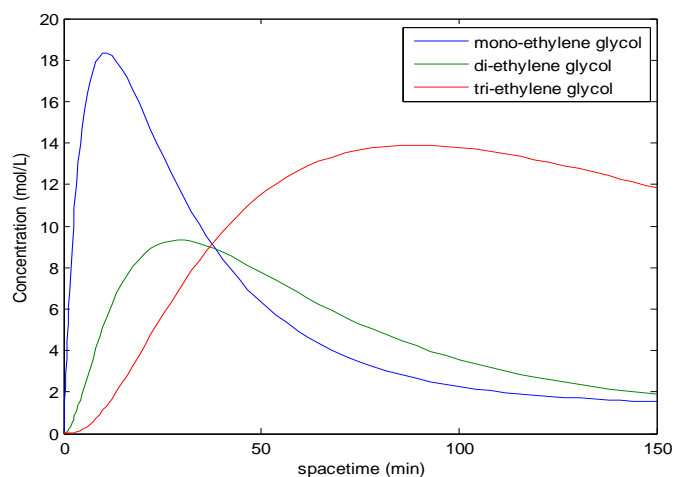
**Fig. 9 Concentration profiles of the products, MEG, DEG and TEG ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 4.0)**

**Case 5 Initial reactant ratio ( $C_{B0}/C_{A0}$ ) is six (ethylene oxide,  $C_{B0} = 206.1$ ; water,  $C_{A0} = 34.35$ )**

Here, the concentration of the first and second intermediate products (MEG and DEG) follows a trend similar to the one observed above. However, the concentration of final product TEG increases further reaching a maximum value (18.34 mol/L) at a space time (10.94 minute) when the concentration of intermediate products (MEG and DEG) both diminishing. These observations are in line with the reported trends for consecutive-competitive reactions in general. These observations are in line with the reported trends for consecutive-competitive reactions in general.



**Fig. 10: Concentration profile of the reactants ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 6.0)**



**Fig. 11: Concentration profiles of the products, MEG, DEG and TEG ( $C_{B0}/C_{A0}$ , ethylene oxide/water = 6.0)**

#### 4. CONCLUSION

This study on the modeling and simulation of consecutive-competitive reactions proposes a comprehensive numerical model for the simultaneous material balance as applied to the CSTR is a system of ordinary differential equations (ODE) which are simulated at the initial state in order to obtain time trajectories of all variables of interest. This model is simulated for consecutive-competitive reactions for the production of mono-ethylene glycol, di-ethylene glycol and tri ethylene glycol under isothermal and results of computation have been presented graphically as concentration-time (space time) with different parameters held constant. The main conclusions of the study are: in the consecutive-competitive reactions, only the stoichiometric molar ratio of the reactants (3:1) is not enough for complete conversion to the final product whatever be the space time; yield and maximum concentration of desired product (first, second or third) depends on many factors; e.g., rate constants, relative values of the rate constants and molar ratio of the reactants; in a CSTR.

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