J. King Saud Univ., Vol. 13, *Eng. Sci.* (1), pp. 73-83 (A.H. 1421/2001)

Modeling, Simulation and Bifurcation Analysis of a Mutating Autocatalytic Reaction

K. I. Alhumaizi and A. E. Abasaeed*

Chemical Engineering Department, King Saud University,
PO Box 800, Riyadh 11421, Saudi Arabia

(Received on 21April 1999, accepted for publication on 13 February 2000)

Abstract. In this paper, we present a conceptual model for autocatalytic reactions in which the autocatalyst undergoes a mutation process in a continuous stirred tank reactor. Three cases with different mutation coefficient (α) have been considered. The analysis of these cases shows the importance of this parameter and the qualitative and quantitative differences in the resulting bifurcation diagrams. Generally speaking, selectivity towards main product increases with decreasing substrate conversion. Co-existence of a mushroom and an isola has been determined for one of the cases. The isola portion is a low main product yield solution and is to be avoided.

Keywords: Autocatalytic reactions, mutation, bifurcation, selectivity.

Notations

C_A	substrate concentration
C_{af}	feed substrate concentration
C_B	desired product concentration
C_{Bf}	desired product concentration in feed
C_C	mutant concentration
C_{Cf}	mutant concentration in feed
k_1 ,k_2	rate constants
X	substrate conversion
Y	dimensionless desired product concentration
Y_f	dimensionless desired product concentration in feed
Z	dimensionless mutant concentration
Z_f	dimensionless mutant concentration in feed
V	reactor volume
E, F	decomposition product concentrations

* Corresponding author, (Fax: ++966-1-467-8770; Email: abasaeed@ksu.edu.sa)

Greeks

α	mutation coefficient
β	mutation efficiency
θ	residence time in reactor

Introduction

Complex dynamic behavior (multiplicity, stability and chaos) of chemically reactive systems has been a subject of research in recent years [1-6]. Most of the previous work, aiming at showing these exotic behaviors, was focused on non-linearities induced by the exponential dependence of the rate constant on temperature. The simplest reactor in the chemical engineering field is the Continuous Stirred Tank Reactor (CSTR) in which the reactants are continuously fed and product withdrawn from it. Vigorous mixing in the reactor provides the uniformity of its content.

Autocatalytic reactions taking place in an isothermal CSTR provide one of the simplest systems for bifurcation studies. The autocatalyst provides the system with the feedback necessary for multiplicity of steady states, sustained oscillations and possibly chaos. The Gray and Scott two-reaction model (cubic autocatalysis, $A+2B \rightarrow 3B$ and catalyst decay, $B \rightarrow C$) provided a base for a number of studies that followed [6-11].

In this preliminary investigation, a model for an autocatalytic reaction is developed. The autocatalyst is assumed to undergo mutation to another competing form. The model was originally developed as an over-simplification of the formation of cancerous cells from healthy, reproducing cells. This should by no means be taken as a "close" description of the formation and reproduction of cancerous cells and their competition with healthy cells. It is merely an attempt to explore the tip of the iceberg of the mutation process. The bifurcation behavior for a mutant-free feed will be discussed together with effect of substrate conversion on main product selectivity.

The Model

The conceptual autocatalytic reaction with mutation which is assumed to take place in an isothermal CSTR is depicted as follows:

$$A + 2B \xrightarrow{k_1} 3B \qquad : \text{(B replication)}$$

$$B \xrightarrow{k_2} E \qquad : \text{(B decay)}$$

$$A + 2B \xrightarrow{\alpha . k_1} 2C + B \qquad : \text{(B mutation to C)}$$

$$A + 2C \xrightarrow{\beta . k_1} 3C \qquad : \text{(C replication)}$$

$$C \xrightarrow{k_2/\beta} F \qquad : \text{(C decay)}$$

The mass balance equations are derived for the substrate (A), desired product (B) and the mutant (C).

The substrate (A)

$$V\frac{dC_A}{dt} = q(C_{Af} - C_A) - Vk_1C_AC_B^2 - V\alpha.k_1C_AC_B^2 - V\beta.k_1C_AC_c^2 \tag{1}$$

The desired product (B)

$$V\frac{dC_B}{dt} = q(C_{Bf} - C_B) + Vk_1C_AC_B^2 - V\alpha.k_1C_AC_B^2 - Vk_2C_B \tag{2}$$

The mutant (C)

$$V\frac{dC_c}{dt} = q(C_{Cf} - C_C) + V\beta.k_1C_AC_C^2 + 2V\alpha.k_1C_AC_B^2 - V\frac{k_2}{\beta}C_C \tag{3}$$

Equations (1-3) can be transformed to Equations (4-6) respectively by defining the following quantities:

$$X = \frac{(C_{Af} - C_A)}{C_{Af}}; \quad Y = \frac{C_B}{C_{Af}}; \quad Z = \frac{C_C}{C_{Af}}; \quad \gamma_1 = k_1C_{Af}^2; \text{ and } \gamma_2 = k_2$$

$$\frac{dX}{dt} = -\frac{X}{\theta} + (1+\alpha)\gamma_1(1-X)Y^2 + \beta.\gamma_1(1-X)Z^2 \tag{4}$$

$$\frac{dY}{dt} = \frac{(Y_f - Y)}{\theta} + (1-\alpha)\gamma_1(1-X)Y^2 - \gamma_2 Y \tag{5}$$

$$\frac{dZ}{dt} = \frac{(Z_f - Z)}{\theta} + \beta.\gamma_1(1-X)Z^2 + 2\alpha.\gamma_1(1-X)Y^2 - \frac{\gamma_2}{\beta}Z \tag{6}$$

Results and Discussion

It is clear that the model equations include 7 parameters, namely: γ_1, γ_2, Y_f, Z_f, α, β and θ. For mutant-free feed, Z_f=0 and the values of the other parameters are fixed at γ_1=450, γ_2=11.25, β=1 and Y_f=0.067 respectively. The parameter α is varied to provide the cases under investigation. The parameter θ (space time) is used as the main bifurcation parameter. The bifurcation diagrams are constructed using the efficient continuation software developed by Doedel and Kernevez [13]. To ensure accuracy of the simulation results, the bound on the allowable error was maintained at 10^{-12}, with automatic step size integration routines. In regions where multiplicity of steady states occurs, the set of initial conditions dictates the attractor to which the system tends to go.

3.1 Case 1: (α=1.2)

Figure 1 shows the bifurcation diagram with θ being the bifurcation parameter for α=1.2 (high mutation coefficient). The following observations can be drawn from the Fig. 1. From θ=0 to θ=0.01066 there exists a unique stable branch. Due to low residence

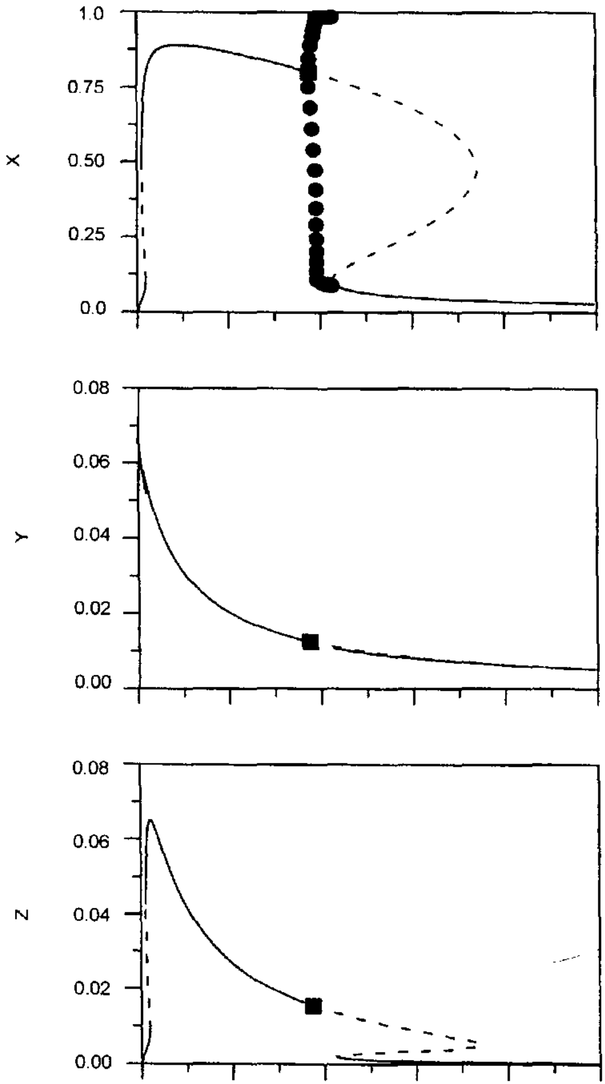

Fig. 1. Bifurcation diagram of *X*, *Y* and *Z* against θ for case 1, α=1.2 [——— = stable static, ----- = unstable static, ■ = Hopf bifurcation point, • = stable periodic].

time (θ) values, the conversion of the substrate on this branch is low together with the yields of both the main product (Y) and the mutant (Z) (2). As the value of θ is increased from 0.01066 to 0.018566, three steady state branches co-exist in this region. Two of these branches are stable fixed attractors whereas the third is unstable. The results of the dynamic simulation at θ=0.015 shown in Fig. 2a confirms the bistability (3). The region extending from θ=0.018566 to θ=0.37513 (corresponding to a Hopf bifurcation point) has a unique stable static attactor whereas the region from θ=0.37513 to θ=0.42557 (corresponding to homoclinic termination of the periodic attractor emanating from θ=0.37513 as it collides with middle unstable saddle-node branch) is characterized by the presence of a stable periodic attractor (see Fig. 2b for dynamic simulation, time trace, at θ=0.4) (4). As θ is increased from 0.42557 to 0.74108, tristability of steady states is experienced, however only one attractor is stable. This attractor is a low substrate conversion attractor (5). The last region (θ>0.74108) has a unique, low conversion stable attractor.

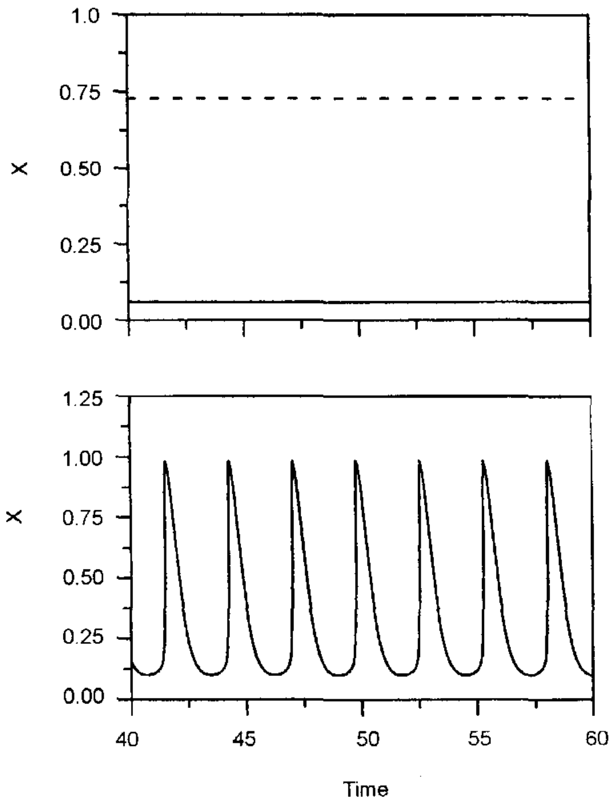

Fig. 2. Case 1: Dynamic simulations (a) θ =0.015 showing bistability, (b)θ=0.4 for periodic attractor.

Figure 3 shows the variation of ratio of main product yield to mutant yield (*Y/Z*) with substrate conversion. For extremely low values of conversion, this ratio approaches 1400, however for conversions as low as 0.1, less main product is formed compared to the mutant (i.e., Y/Z<1). The lowest selectivity (*Y/Z*=0.088) is obtained at the highest conversion (0.889). Some portions of this figure are unstable, however these portions can be stabilized through proper control.

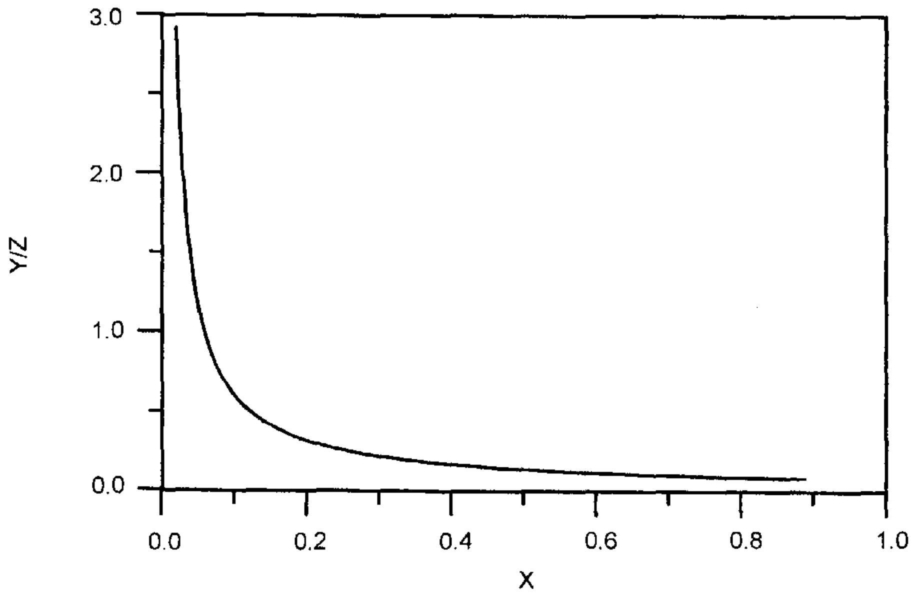

Fig. 3. Case 1: Selectivity (*Y/Z*) against substrate conversion (*X*).

3.2 Case 2: (α=0.2)

Figure 4 shows the bifurcation diagram for X against θ (the Y and Z bifurcation diagrams are omitted for brevity). Figure 4 is obtained for α=0.2 (which indicates lower mutation coefficient compared to case 1). Generally speaking, many of the main features of this bifurcation diagram are quite similar to the first case (i.e., it is mainly a mushroom-type bifurcation). However, in this case three Hopf bifurcation points (HBP) are present compared to only one HBP for the first case. As the bifurcation parameter is increased, the system goes through single static attractor, to tristability of static attractors (2 are stable), back to unique static attractor followed by a one stable periodic attractor and finally one stable fixed attractor.

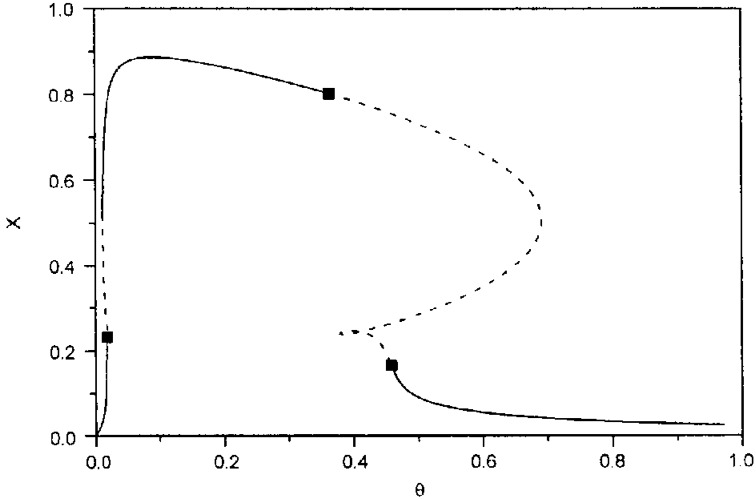

Fig. 4. Bifurcation diagram of X against θ for case 2, α=0.2 [—— = stable static, ----- = unstable static, ■ = Hopf bifurcation point].

The variation of the selectivity (Y/Z) with substrate conversion (X) is shown in Fig. 5. At very low values of conversion, the selectivity approaches 8000. Compared to the previous case, the yield of the main product is higher than the mutant yield (Y/Z>1) at high conversions (X about 0.245). The highest conversion (0.887) which occurs at θ=0.0887 results in the lowest selectivity (Y/Z=0.0807).

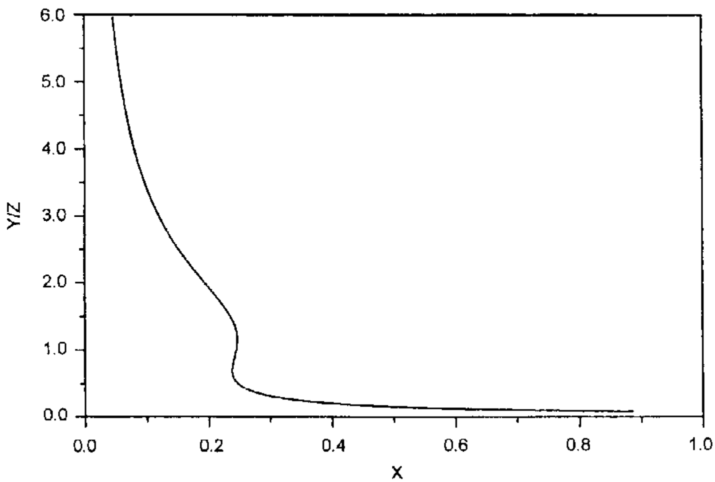

Fig. 5. Case 2: Selectivity (Y/Z) against substrate conversion (X).

3.3 Case 3: (α=0.1)

The bifurcation diagram of substrate conversion (X) against residence time (θ) is shown in Fig. 6. The figure reveals that, there is a sub-region ($0.01154 \leq \theta \leq 0.6846$) in which a bistability between a mushroom and an isola occurs. Therefore, the discussion below is for both the isola and the mushroom.

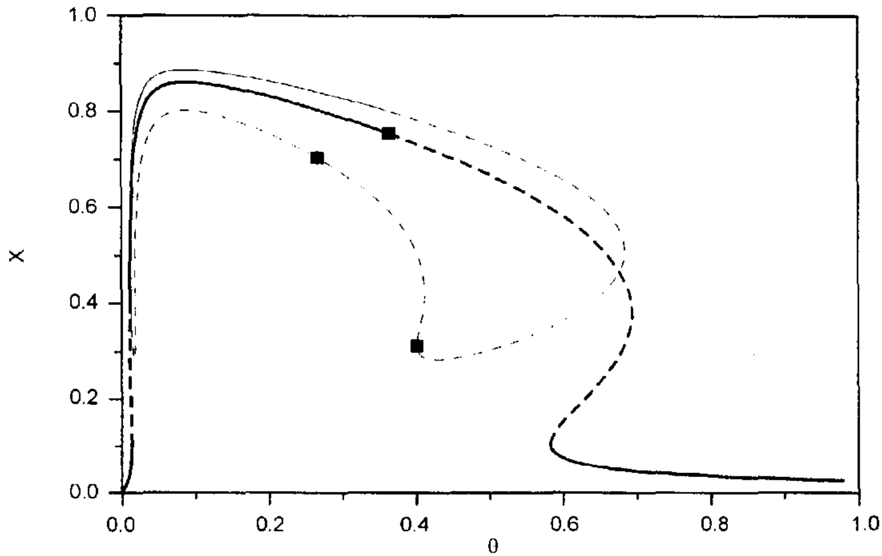

Fig. 6. Bifurcation diagram of X against θ for case 3, α = 0.1 showing coexisting mushroom (thick lines) and isola (thin lines).

As the value of the bifurcation parameter (θ) is increased from θ=0 to θ=0.01139 (corresponding to a limit point on the mushroom) a unique stable static attractor exists and all initial conditions tends to go to the mushroom.. Between θ=0.01139 and θ=0.0115 (corresponding to a limit point on the isola), three steady states static branches (two stable branches and a middle unstable branch) exist on the mushroom. Between θ=0.0115 and θ=0.01355 (corresponding to a limit point on the mushroom), five steady state branches exist (3 branches on the mushroom and 2 on the isola). Two of the mushroom branches are stable fixed attractor while one stable fixed branch is located on the isola. Increasing θ further to θ=0.01916 (corresponding to a limit point on the isola), three steady state branches exist (one stable branch on the mushroom and two branches - one of the two branches is stable- on the isola). The system then alternates between 5 and 3 co-existing steady states branches (some of these branches are periodic attractors) until the vanishing of the isola at θ=0.68466. Finally a unique stable fixed attractor on the mushroom prevails for θ>0.6939.

Figure 7 shows the variation of ratio of main product yield to mutant yield (*Y/Z*) with substrate conversion for both the mushroom and isola. Unlike the previous cases, the lowest value of selectivity (*Y/Z*) that can be obtained when operating on the mushroom is 3.55. This lowest yield occurs at a conversion of 0.861 at a residence time of 0.0896. On the other hand, the highest selectivity obtained on the isola is 1.266 and it occurs at a substrate conversion of 0.803. Therefore, it is quite evident from the aforementioned discussion that if the system is operated to obtain higher main product selectivity, operation on the mushroom is more desirable and operation on the isola is to be avoided.

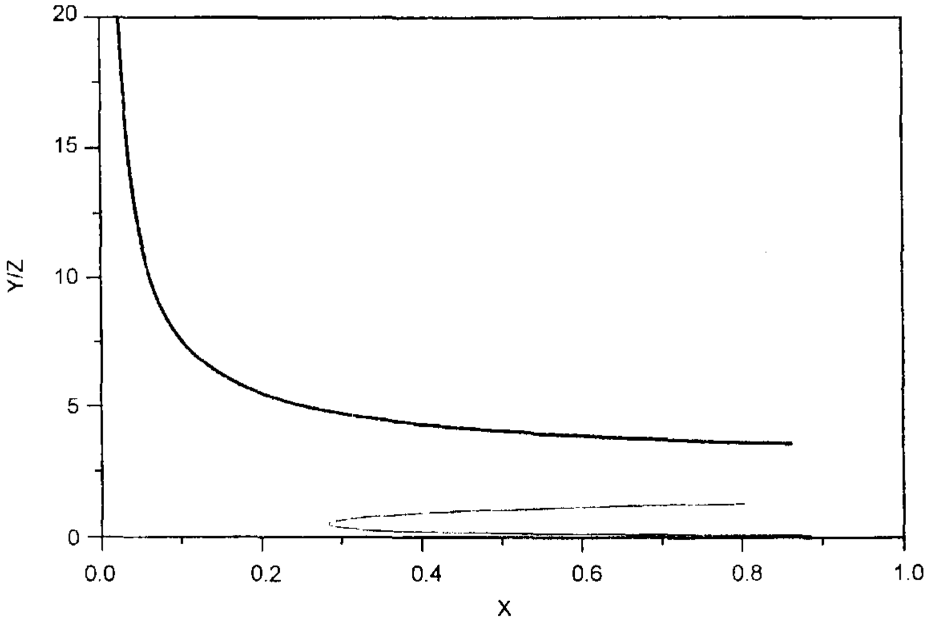

Fig. 7. Case 3: Selectivity (Y/Z) against substrate conversion (X).

Conclusion

A simplified model for autocatalytic reactions taking place in a CSTR has been developed. The autocatalyst is assumed to undergo mutation, with the mutant competing with the original autocatalyst for the limiting substrate necessary for their replication. Both autocatalysts undergo a decay process. The bifurcation diagrams are constructed and analyzed for three representative values of α. Generally speaking, the selectivity of the main product for the three cases increases with the decrease substrate conversion. One case gave an isola and a mushroom type solution; the isola portion gives low main product yield.

References

[1] Balakotaiah, V. and Luss, D. "Multiplicity Criteria for Multiple-Reaction Network." *A.I.Ch.E.J*, 29 (1983), 552-560.

[2] Balakotaiah, V. and Luss, D. "Analysis of Multiplicity Patterns of a CSTR." *Chem. Engng. Commun.*, 13 (1982), 111-124.

[3] Abasaeed, A.E. and Elnashaie, S.S.E.H. "On the Chaotic Behavior of Externally Forced Industrial Fluid Catalytic Cracking Units." *Chaos, Solitons & Fractals*, 9 (1998), 455-470.

[4] Elnashaie, S.S.E.H., Abasaeed, E.A. and Elshishini, S.S. "Digital Simulation of Industrial Fluid Catalytic Cracking Units: V. Static and Dynamic Bifurcation Behaviour." *Chem. Eng. Sci.*, 50 (1995), 1635-1644.

[5] Uppal, A., Ray, W.H. and Poore, A.B. "On the Dynamic Behaviour of Continuous Stirred Tank Reactors." *Chem. Eng. Sci.*, 29 (1974), 967-985.

[6] Alhumaizi, K. and Aris, R. "Chaos in a Simple Two-phase Reactor." *Chaos, Solitons & Fractals*, 4 (1994), 1985-2014.

[7] Gray, P. and Scott, S.K. "Autocatalytic Reactions in the Isothermal, Continuous Stirred Tank Reactor. Isola and Other Forms of Multiplicity." *Chem. Eng. Sci.*, 38 (1983), 29-43.

[8] Gray, P. and Scott, S.K. "Autocatalytic Reactions in the Isothermal, Continuous Stirred Tank Reactor. Oscillations and Instabilities in the System." *Chem. Eng. Sci.*, 39 (1984), 1087-1097.

[9] Peng, B., Scott, S.K. and Showalter, K. "Period-doubling and Chaos in a Three-variable Autocatalator." *J. Phys. Chem.*, 94 (1990), 5243-5246.

[10] Lynch, D.T. "Chaotic Behavior of Reaction Systems: Parallel Cubic Autocatalator." *Chem. Eng. Sci.*, 47 (1992), 347-355.

[11] Lynch, D.T. "Chaotic Behavior of Reaction Systems: Mixed Cubic and Quadratic Autocatalysis." *Chem. Eng. Sci.*, 47 (1992), 4435-4444.

[12] Leach, J.A., Merkin, J.H. and Scott, S.K. "An Analysis of a Two-cell Coupled Nonlinear Chemical Oscillator." *Dynamics and Stability of Systems*, 6 (1991), 341-365.

[13] Doedel, E.J. and Kernevez, J.P. *Auto: Software for Continuation and Bifurcation Problems in Ordinary Differential Equations*. CA, USA: California Institute of Technology, 1986.

نمذجة التشعبية للتفاعلات ذاتية الحفز ذات الطفرة، تمثيلها وتحليلها

خالد. أ. الحميزى و أحمد. ا. أباسعيد

قسم الهندسة الكيميائية ، كلية الهندسة ، جامعة الملك سعود ، ص.ب.٨٠٠ ،
الرياض ١١٤٢١ ، المملكة العربية السعودية

(قدم للنشر في ٢١/٠٤/١٩٩٩ ، و قبل للنشر في ١٣/٠٢/٢٠٠٠)

ملخص البحث. في هذه الورقة ، نقدم نموذج فرضي للتفاعلات ذاتية الحفز و التي يكون المحفز فيها طفرة في المفاعل المستمر المخلوط جيدا. أخذ في الاعتبار ، ثلاث حالات تغير فيها معامل الطفرة. أظهر تحليل هذه الحالات أهمية هذا المتغير وأيضا التغيرات النوعية و الكمية على رسومات التشعبية الناتجة. بصورة عامة ، تزيد الانتقائية بنقصان درجة تفاعل المغذي. تم تحديد الوجود المشترك لايسولا (جزء منعزل) و مشروم في إحدى هذه الحالات. جزء الايسولا يعطي إنتاجية قليلة للمنتج الرئيس و من الأفضل تجنبه.