Study of unsteady state process operation

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Abstract

Unsteady state process operation has been studied for three common cases: (i) varying inputs (compositions and flow rate); (ii) processes themselves generating oscillations and (iii) combination of (i) and (ii) to see the combined effect. It is observed that sometimes operation at unsteady state, i.e. dynamic operation, gives higher productivity than the operation at steady state. The various parametric studies have been performed to study the effect of input fluctuations. Unsymmetrical fluctuations in process output have been observed with symmetric sinusoidal disturbances in process inputs. Chemical oscillatory behavior is found very sensitive to disturbance. The reactant concentration and temperature of the process output are found strongly dependent on each other. The variation in input composition is found to be prominent effect on the process output. The variation in temperature and overall heat transfer coefficient has significant effect in chemical oscillatory system, studied herein.
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1. Introduction

Most of chemical plants are designed to operate at steady state. The design and control strategy of a process are based on steady state. The steady state design is based on average values of fluctuating input components. In general, the mean value of the process output of a process operating at unsteady state will not be the same as that of a steady state process output at the mean values of operating variables. Though the process is maintained at steady state, some of the input components like composition, flow rate, etc., vary continuously with time and thus, plants do not operate at steady state [1]. Due to fluctuations in input components or due to generation of instability in the process itself, which is not desirable, leads to fluctuations in process outputs. Attempts have been made to eliminate both of those sources of variation by modifying the design of the process to ensure its stability, by adding a control system or a surge tank [2–4]. The performance may improve or deteriorate as a result of unsteady state operation. Theoretical and experimental studies [5–9] have shown that sometimes working at unsteady state gives higher productivity, conversion, selectivity and efficiency, provides better product distribution and enhances catalytic activity. Though researchers have attempted to understand the unsteady state behavior of a process, still it is not fully understood and needs more attention.

Shen and Ray [10] have forced the process to operate at unsteady state for improving overall reactor performance. They have obtained that with the help of proper choice of parameters and by coupling force and free oscillations, one can generate self-sustained natural oscillations. In this way, no external energy is required to improve the performance. Numerical continuation methods have been used for analysis of unsteady state chemical reactors [11]. An algorithm is presented for the continuation of periodic solutions of large systems, based on numerical bifurcation and continuation method. Albert [12] has studied the unsteady state operation of continuous reactors. He showed that the dynamic behavior of individual steps of the overall reaction and of the reactor

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Nomenclature

a_1	amplitude of fluctuation in feed concentration
a_2	amplitude of fluctuation in feed flow rate
a_3	amplitude of fluctuation in coolant flow rate
A	concentration of reactant
C	specific heat
E	activation energy
$-\Delta H$	heat of reaction
J	Jacobian matrix
k	rate constant
K	defined by Eq. (7)
q, q_c	volumetric flow rate through reactor and coolant flow rate, respectively
Q	heat required to obtained steady state with complete conversion
R	gas constant
t	time
T	reactor temperature
U_a	overall heat-transfer coefficient
V	reactor volume
w_1	frequency of fluctuation in feed concentration
w_2	frequency of fluctuation in feed flow rate
w_3	frequency of fluctuation in coolant flow rate
Y	perturbation from A_s
Y_1	obtained value for dimensionless composition for chemical oscillator with input variations –obtained values for dimensionless composition for chemical oscillator without input fluctuation
Y_2	obtained value for dimensionless temperature for chemical oscillator with input variations –obtained values for dimensionless temperature for chemical oscillator without input fluctuation
Z_1, Z_2, Z_f, Z_c	defined in Eq. (7)

Greek symbols

ρ	density
ω	angular frequency of perturbation

Subscripts

c	coolant
f	feed
s	steady state
i	component index

could be exploited to obtain performance, which cannot be accomplished in the traditional way on steady state operation under comparable conditions and selectivities. Eigenfunction method to a kinetic model via unsteady state operation is used by Dia et al. [13]. The proposed method has been validated by studying dehydration of butane. Mathematical modeling of unsteady state operation on adsorption and chemisorp-
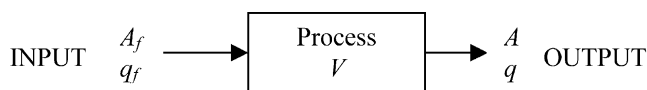
tions processes on a catalyst pellet has been studied by Vernikovskaya et al. [14]. They have used mathematical modeling to study intraparticles limitations under alternating adsorption and oxidation steps. Unsteady state operation of bubble reactors has been studied by Shenderov and Dilman [15]. De and Luus [16] have attempted to optimize the non-steady state operation of reactors. They have used dynamic programming, which gives optimal policy with respect to the periodic cycle-split and amplitude. Farhadpour and Gibilaro [17] have suggested that the optimal mode of operation for two pulse reactions independent of each other is bang–bang but shows also that the two reactants should be pulsed independently of each other. The optimal mode of operations [18] has been developed for a continuous stirred tank reactor (CSTR) in which consecutive competitive-competition reactions take place. Though some processes, such as pulse extraction, unsteady state operation is operated to improve performance. Kouris et al. [19] have presented the unsteady state operation of catalytic particles with constant and periodic changing of external wetting. Yang et al. [20] have investigated on unsteady state performance of *n*-butane selectivity oxidation. They have shown that the unsteady state operation offers new means of controlling total oxidation by segregating the hydrocarbon feedstock from oxygen. Gupalo et al. [21] have studied the unsteady state operation condition of a chemical reactor with nonhomogenous fluidized bed. Taylor and Geiseler [22] have studied the periodic operation of stirred flow reactor with limit cycle oscillations. Vansling [23] has presented the improvement in chemical process by using periodic operation. Silveston et al. [24,25] have reviewed the periodic operation in catalytic reactors. Silveston [26,27] have studied automotive exhaust catalysis under operation. Turco et al. [28] have investigated periodic operation of a trickle bed reactor. Adesina et al. [29] have reviewed Fischer–Tropsch synthesis under periodic operation. Amariglio et al. [30] have showed a two-step procedure using metal catalysts under nonoxidative conditions allows the thermodynamic limitations to be circumvented though homologation of methane is thermodynamically disfavored. They have considered methane homologation on metal. Gulari et al. [31] have presented the past research and present challenges in the catalytic oxidation of carbon monoxide under periodic and transient operation.

Each unit of a chemical plant is connected to other units. The study of unsteady behavior of a process, taking various input fluctuation sources together, is important for clear understanding of a dynamic system. It has been presented in detail in this study. Unsteady state operation has been studied for three common cases: (i) variations in process input; (ii) a CSTR as chemical oscillator; (iii) combination of (i) and (ii). In Section 2.4, the unsteady state operation of oxo reactor, a reactor that converts olefins and syngas to aldehydes and alcohols, has been discussed to present an industrial application of the unsteady state operation. Moreover, the detailed parametric study has been performed to show the effect of input fluctuations.

2. Theory

2.1. Variation in process inputs

The analysis of process operability at preliminary stage is required [32]. When an input composition, the desired product rate, the cost of raw materials and the depreciation costs associated with the reactor have been specified, one can calculate the cost for determining the optimum steady state design [33]. Usually, in a chemical plant, reactants of one unit are the outputs of another unit. It is likely to vary flow rate and composition of reactants together with time. For this purpose and to get a comparative study of both variations on the process output, variations in feed flow rate and composition have been combined. One can get effect of a particular disturbance by putting zeros for another disturbance amplitude. A set of equations for a continuous stirred tank reactor has been formulated to observe the effect in process outputs; though based on this principle, equations for plug flow and batch reactors can also be obtained. Sinusoidal fluctuation variations and second order reaction have been considered.

INPUT $\quad \begin{matrix} A_f \\ q_f \end{matrix} \longrightarrow \boxed{\begin{matrix} \text{Process} \\ V \end{matrix}} \longrightarrow \begin{matrix} A \\ q \end{matrix}$ OUTPUT

Input composition variation can be given as

$$A_f = A_{fs} + a_1 \sin w_1 t \tag{1}$$

Input flow rate variation can be given as

$$q_f = q_{fs} + a_2 \sin w_2 t \tag{2}$$

Material balance across a process gives

$$V \frac{dA}{dt} = q_f A_f - qA - kVA^2 \tag{3}$$

y is taken as a fluctuation in the output compared to its steady state value, i.e. $A = A_s + y$. Density variation in the stream across the process is assumed to be negligible, i.e. $q = q_{fs} + a_2 \sin w_2 t$. Values of A_f and q_f from Eqs. (1) and (2) have been put in Eq. (3), respectively. Eq. (3) can be written as

$$\frac{dy}{dt} + ky^2 + \left(2kA_s + \frac{q_{fs}}{V} + \frac{a_2 \sin w_2 t}{V} \right) y$$
$$= \frac{1}{V}(q_{fs}a_1 \sin w_1 t + a_1 a_2 \sin w_1 t \sin w_2 t$$
$$+ (A_{fs} - A_s)a_2 \sin w_2 t) \tag{4}$$

The values of parameters of above equations used for isothermal continuous stirred tank reactor are as follows [6]:

$$V = 100, \qquad k = 1.2, \qquad q_{fs} = 10, \qquad A_s = 0.25$$

The initial condition is taken as at $t = 0$, $y = -0.01$. Eq. (4) is solved using an iterative procedure. Runga–Kutta fourth-order integration routine is used. Inputs are the previously mentioned steady state values and initial condition. The integration step sizes are progressively reduced from 1.0×10^{-2} until the values of the dependent variables evaluated become independent of the step size. The integration is performed with a step size of 1.0×10^{-3}.

2.2. Chemical oscillator

Chemical oscillator [6,34,35] generates limit cycles when the inputs are held constant. Outputs from such a process vary periodically even if there is no disturbance in input streams. It generates similar oscillation in process outputs as generated due to input variations. In such cases, average values of outputs from a periodic process are not equal to the predicted steady state values. Depending on the system under investigation and the values of the system parameters, the average value can be either higher or lower than the steady state value.

A set of equations obtained [6] for the first order irreversible exothermic reaction in a non-isothermal continuous stirred tank reactor has been studied after solving them numerically. The governing equations are as follows:

$$\frac{dZ_1}{dt} = \frac{q}{V}(1 - Z_1) - kZ_1 \tag{5}$$

$$\frac{dZ_2}{dt} = \frac{q}{V}(Z_f - Z_2) - \frac{U_a K q_c (Z_2 - Z_c)}{VC\rho(1 + Kq_c)} + kZ_1 \tag{6}$$

where

$$Z_1 = \frac{A}{A_f} = x_1, \qquad Z_2 = \frac{TC\rho}{(-\Delta H)A_f},$$
$$Z_c = \frac{T_c C\rho}{(-\Delta H)A_f}, \qquad Z_f = \frac{T_f C\rho}{(-\Delta H)A_f} \tag{7}$$

The initial condition is taken as at $t = 0$, $Z_1 = 0.52$ and $Z_2 = 2.53$. The coupled Eqs. (5) and (6) are solved using an iterative procedure. Runga–Kutta fourth-order integration routine is used. Inputs are the previously mentioned steady state values and initial condition. The integration step sizes are progressively reduced from 1.0×10^{-2} until the values of the dependent variables evaluated become independent of the step size. The integration is performed with a step size of 5×10^{-4}.

The steady state values are obtained by solving two algebraic equations corresponding to Eqs. (5) and (6), taking parameters values from Table 1 using Newton–Rapson algo-

Table 1
Parameters for chemical oscillator

Parameter	Values	Parameters	Values
V	1000	A_f	0.0065
T_f	350	T_c	408.6
E	28000	R	1.987
$-\Delta H$	27000	ρ	1
C	1	U_a	50
K	0.3	q_c	20
q	10	K_0	$e^{29.6298}$

rithm. Initial guesses are taken as $Z_1 = 0.2$ and $Z_2 = 2$. The norm of residual vector has been set less than 10^{-5} to obtain the solution. The quadratic convergence is obtained, which is consistent with Newton–Rapson algorithm. The steady state values are found as $Z_1 = 0.3543$ and $Z_2 = 2.3871$. The Jacobian matrix at steady state is given as follows:

$$\underline{\underline{J}}\,|_{Z_{\text{ss}}} = \begin{bmatrix} -0.02191 & -0.09089 \\ 0.018191 & 0.038033 \end{bmatrix} \tag{8}$$

The eigenvalues of the Jacobian matrix at steady state are found to be $(0.0049 + 0.0236i)$ and $(0.0049 - 0.0236i)$. The eigenvalues are complex so the process itself will generate oscillation, i.e. fluctuation in the process output without any variation in process inputs. Moreover, the real part of eigenvalues is positive, this leads to instability in the process.

2.3. Combination of variation in process inputs and chemical oscillator

In a chemical plant, each unit is connected to other units. The output of one unit is the input of other units; and this leads to the variation in process input composition and flow rate. On the other hand, some processes can themselves be oscillatory in nature, as explained in chemical oscillator section. Hence, the study of combined effects of fluctuations in process inputs and chemical oscillator is important to investigate. In this section, input variation and chemical oscillation have been combined. A set of equations has been developed. In this formulation, the variation in temperature is not considered since the effect of feed and coolant water temperature variations is very slow compared to the effect due to other variations considered herein. The combined equations for variations in process inputs and chemical oscillator are as follows:

$$\frac{\mathrm{d}Z_1}{\mathrm{d}t} = \frac{q_{\text{s}} + a_2 \sin w_2 t}{V}\left(1 + \frac{a_1 \sin w_1 t}{A_{\text{fs}}} - Z_1\right) - kZ_1 \tag{9}$$

$$\frac{\mathrm{d}Z_2}{\mathrm{d}t} = \frac{q_{\text{s}} + a_2 \sin w_2 t}{V}(Z_{\text{f}} - Z_2)$$
$$- \frac{U_{\text{a}}K(q_{\text{cs}} + a_3 \sin w_3 t)(Z_2 - Z_{\text{c}})}{VC\rho(1 + K(q_{\text{cs}} + a_3 \sin w_3 t))} + kZ_1 \tag{10}$$

The parameters used herein are defined in the similar way as they have been defined in Eq. (7). For defining Z_1, Z_2, Z_3 and Z_4, A_{fs} and q_{s} have been used instead of A_{f} and q, respectively. The values of parameters are taken from Table 1. The initial condition is taken as at $t = 0.0$, $Z_1 = 0.52$ and $Z_2 = 2.35$. The coupled Eqs. (9) and (10) are solved using an iterative procedure. Runga–Kutta fourth-order integration routine is used. Inputs are the previously mentioned steady state values and initial condition. The integration step sizes are progressively reduced from 1.0×10^{-2} until the values of the dependent variables evaluated become independent of the step size. The integration is performed with a step size of 0.5×10^{-4}.

Stability analysis of this system will remain same as that for the chemical oscillator, discussed in the last section, since steady state parameter values and steady state equations will remain the same.

2.4. Limit cycle in oxo reactor

The oxo reaction converts olefins and synthesis gas (Co and H_2) to aldehydes and alcohols. The following scheme has been considered for oxonation of mixed olefin isomers:

$$A_i \rightarrow B \rightarrow C$$
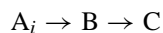
Components A_i represents olefin isomers. Each of which has a different rate, B represents aldehyde, the main product, which partially converts to oxo alcohol, componet C. At a fixed concentration of catalyst and synthesis gas, all reactions are apparent first order and irreversible. In the neighborhood of steady operating state, the overall oxo reaction can be written as

$$A \rightarrow B$$

where A is a pseudo-component olefin and B represents all products both parallel and sequential to the intermediate aldehyde, which is responsible to generate the heat of reaction. The values of rate of constant, reaction enthalpy and activation energy have been obtained from independent experiment. Over the narrow operating conditions, the first-order model is thought to be an adequate representation of the actual process.

This system has been studied by taking two CSTRs in series [37]. It has been shown that volume of first reactor less than $1.72\,\text{m}^3$ limit cycles do not exist, whereas for volumes of the reactor greater than $2.25\,\text{m}^3$ the conversion obtained when limit cycles exist is greater than the steady state conversion. It has been shown that up to 11.6% increase in conversion can be achieved for this system. Developed Eqs. (9) and (10), i.e. chemical oscillator with input variations, have been solved for the oxo reactor system. The parameters and operating variables used for the numerical calculations in this case is representative of the industrial oxo reactors given in Vleeschhouwer and Garton [36]. The parameters used are as follows.

The steady state values are obtained by solving two algebraic equations corresponding to Eqs. (5) and (6), taking parameters values from Table 2 using Newton–Rapson algo-

Table 2
Parameters for oxo reactor

Parameter	Values	Parameters	Values
V	$3.0\,\text{m}^3$	A_{f}	$5076.5\,\text{mol/m}^3$
T_{f}	303 K	T_{c}	445 K
E	91454 J/mol	R	8.314 J/K mol
$-\Delta H$	159000 J/mol	ρ	$650\,\text{Kg/m}^3$
C	2700 J/kg K	U_{a}	75000 W/K
C_{c}	2400 J/kg K	q_{c}	$0.01\,\text{m}^3/\text{s}$
q	$0.004923\,\text{m}^3/\text{s}$	K_0	$61.1 \times 10^7\,\text{s}^{-1}$

rithm. Initial guesses are taken as $Z_1 = 0.1$ and $Z_2 = 2.0$. The norm of residual vector has been set less than 10^{-5} to obtain the solution. The quadratic convergence is obtained, which is consistent with Newton–Rapson algorithm. The steady state values are found as $Z_1 = 0.0737$ and $Z_2 = 1.0950$. The Jacobian matrix at steady state is given as follows:

$$\underline{\underline{J}} \,|Z_{ss} = \begin{bmatrix} -0.0216 & -0.0293 \\ 0.0199 & 0.0221 \end{bmatrix} \tag{11}$$

The eigenvalues of the Jacobian matrix at steady state are found to be $(0.0003 + 0.0104i)$ and $(0.0003 - 0.0104i)$. The eigenvalues are complex so the process itself will generate oscillation, i.e. fluctuation in process output without any variation in process inputs. The real part of eigenvalue is positive, which provides instability in the process.

The initial condition is taken as at $t = 0.0$, $Z_1 = 0.52$ and $Z_2 = 2.35$. The coupled Eqs. (9) and (10) are solved using an iterative procedure. Runga–Kutta fourth-order integration routine is used. Inputs are steady state values and initial condition. The integration step sizes are progressively reduced from 1.0×10^{-2} until the values of the dependent variables evaluated become independent of the step size. The integration is performed with a step size of 0.5×10^{-4}.

3. Results and discussion

Three examples that generate fluctuation in process output have been studied. The examples are (i) variation in inputs, (ii) chemical oscillator and (iii) combination of (i) and (ii). To obtain the steady state values, Newton–Raphson algorithm has been used and to generate the transient plots Runga–Kutta fourth-order algorithm has been used. The solutions presented herein are independent of step size. Various parametric studies for the variation inputs variations have

been done by varying amplitude and frequency. Numerals 1–4 have been used to denote different fluctuation/operating conditions.

Fig. 1 presents the effect of the frequency of disturbance in input composition and flow rate on process output fluctuation, separately. The average value of output fluctuation is negative (-1.8×10^{-4} and -1.65×10^{-4} for numerals 1 and 2 in Fig. 1, respectively), i.e. the higher conversions are obtained when the input is allowed to fluctuate than when it is controlled to give steady state operation because in negative domain of output disturbance the magnitude of its rate of change is more than that in positive domain. It has been obtained that with a decrease in frequency, an increase in productivity is more since with decrease in frequency, the disturbance remains positive or negative for longer period and so it has more effect on process output fluctuations. With an increase in the amplitude of input fluctuations, an increase in productivity grows. It has also been observed that the effect of composition variation is more than with the variation in flow rate.

Fig. 2 presents the effect of the frequency, taking both disturbances in input together, on the process output fluctuation. It is observed that all processes output fluctuations are not symmetric with x-axis, i.e. zero fluctuation level. The average value of process output may be positive or negative and depend on the difference between frequencies of both disturbances. In general, it can be said that if the phase lag is between 90° and 270°, an increase in productivity is observed. The frequency set (0.2 and 0.5 Hz) output fluctuation does not even have repeatable peaks in positive domain since frequencies of both disturbances are not integral multiple. Its average is negative. It is observed that the effect of input variations on output is independent of initial conditions because the different initial conditions result in the same periodic solution, as long as they are in the basin of the periodic limit cycle, which is the case herein.
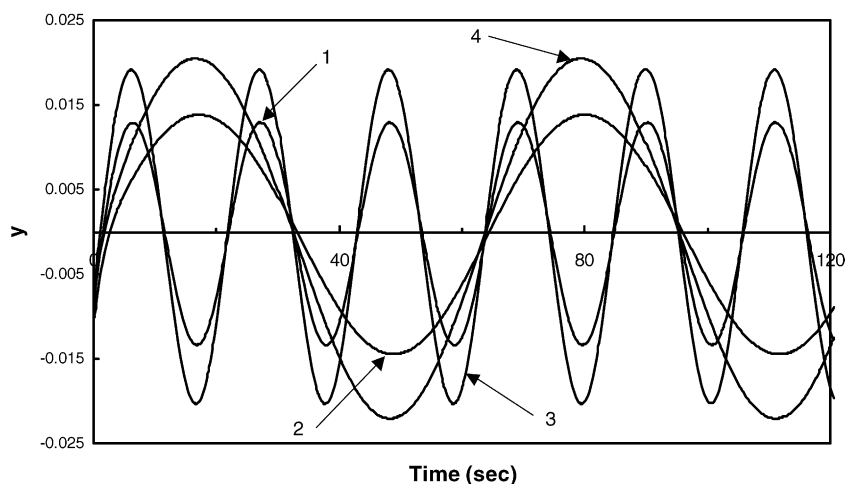

Fig. 1. Effect of frequency of both fluctuations on the process output fluctuation, separately: (1) amplitude and frequency of composition disturbance are 0.10 unit and 0.3 Hz, respectively; (2) amplitude and frequency of composition disturbance are 0.10 unit and 0.1 Hz, respectively; (3) amplitude and frequency of flow rate disturbance are 0.20 unit and 0.3 Hz, respectively; (4) amplitude and frequency of flow rate disturbance are 0.20 unit and 0.1 Hz, respectively.
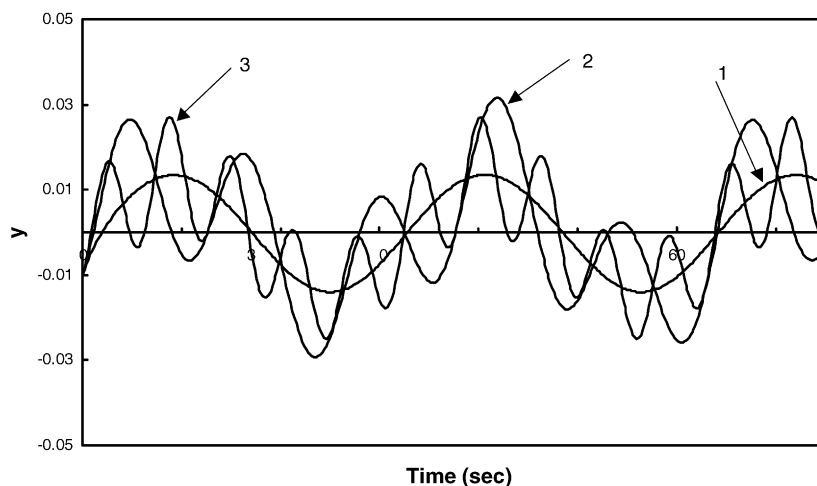
Fig. 2. Combined effect of frequency of both fluctuations on the process output fluctuation. Amplitude is 0.10 unit for each variations: (1) frequencies of composition and flow rate disturbances are 0.2 and 0.0 Hz, respectively; (2) frequencies of composition and flow rate disturbances are 0.2 and 0.5 Hz, respectively; (3) frequencies of composition and flow rate disturbances are 0.2 and 1.0 Hz, respectively.

Fig. 3 presents the effect of the amplitude of input fluctuations, taking both disturbances together, on the output fluctuation. With an increase in amplitude of disturbance, the amplitude of process output fluctuation increases. It is also observed that composition variation has more prominent than flow rate variation. It can be proven by visualizing on output fluctuation responses 2 and 3 in Fig. 3.

Chemical oscillator generates limit cycles when the inputs are held constant. The steady state Jacobian matrix has non-zero imaginary part and positive real part for Table 1 data. The nonzero imaginary part gives oscillation and the positive real part gives instability in the process. In Fig. 4, three common different parameter variations of chemical oscillatory system

have been presented. In two cases, the cooling water temperature is varied, cooler or hotter then Table 1 cooling water temperature. In third case, the overall heat transfer coefficient, U_a has been changed from 50 to 70. It is seen that the effect of each variation on Z_1 (concentration) and Z_2 (temperature) are very large. For Table 1 data, $Z_{1av} = 0.343$ compared with the steady state $Z_{1s} = 0.355$ thus showing a 1.2% increase in conversion. When the cooling water temperature is at 388 °F, initially Z_1 keeps increasing and Z_2 keeps decreasing. Later, the process starts running at steady state with low conversion at low temperature. The decrease in conversion is because of a decrease in the reaction rate constant. Whereas, if the cooling water temperature is at 428 °F, initially Z_1 keeps de-
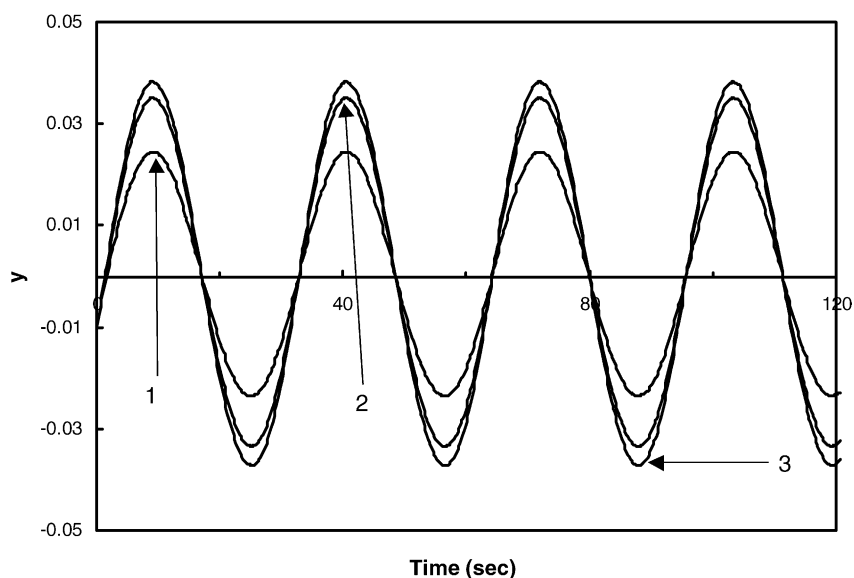

Fig. 3. Combined effect of amplitude of both fluctuations on the process output fluctuation. Frequency is 0.2 Hz for each disturbance: (1) amplitudes of composition and flow rate disturbances are 0.10 unit each; (2) amplitudes of composition and flow rate disturbances are 0.10 and 0.20 unit, respectively; (3) amplitudes of composition and flow rate disturbances are 0.20 and 0.10 unit, respectively.
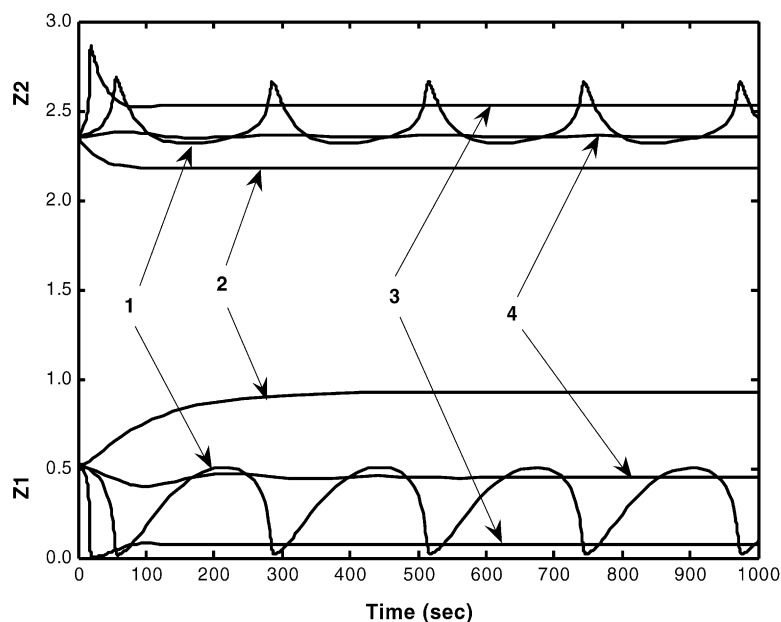
Fig. 4. Z_1 and Z_2 vs. time for Table 1: (1) with cooling water temperature = 408.6 °F and U_a = 50; (2) with cooling water temperature = 388 °F and U_a = 50; (3) with cooling water temperature = 428 °F and U_a = 50; (4) cooling water temperature = 408.6 °F and U_a = 70.

creasing and Z_2 keeps increasing. Both, Z_1 and Z_2 responses are leading to the responses with cooling water at 408.6 °F. Later, the process starts running at steady state with high conversion at high temperature. The increase in conversion is because of an increase in the reaction rate constant. When U_a varies from 50 to 70, the heat transfer increases. Therefore, the temperature peak becomes less prominent and this leads to a decrease in conversion. In Fig. 4, it is seen that the peaks for Z_1 and Z_2 are at the same place and in opposite direction. Z_1 is opposite to the conversion and so it can be said that the peak for conversion and temperature are in the same direction. This is because, with an increase in temperature, the reaction rate increases and this leads to an increase in conversion. It can be said that the dependent of reaction rate constant on temperature makes Z_1 and Z_2 strongly dependent on each other.

In Fig. 5, the variation (=obtained value for dimensionless composition chemical oscillator with input variations − obtained values for dimensionless composition chemical oscillator without input fluctuation) in dimensionless composition of the process output is presented with time. Here, the variations in input composition and flow rate, and cooling water flow rate along with chemical oscillatory system have been considered. It is obtained that, the average values of variations in the process output composition are -0.0017, -3.8899 and 1.4269×10^{-5} with all three variations, only composition variation and both flow rates variations, respectively. The variation in composition is found to be beneficial whereas the variations in only flow rates are not beneficial. The effect of three variations, i.e. input composition and flow rate, and cooling water flow rate, is interactive in nature. The effect of composition variation is found to be prominent and complex. The effect of varia-

tions in only flow rate of input and cooling water is found negligible.

In Fig. 6, the variation (=obtained value for dimensionless temperature chemical oscillator with input variations − obtained values for dimensionless temperature chemical oscillator without input fluctuation) in dimensionless temperature of the process output is presented with time.
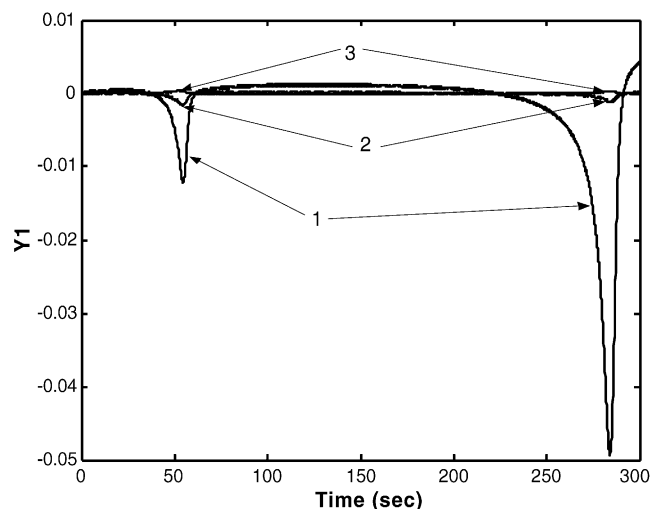

Fig. 5. Fluctuation in output composition due to input fluctuations with time for three cases for Table 1. (1) All three fluctuations into consideration with amplitude and frequency of composition fluctuation are 0.00065 unit and 10 Hz, respectively and amplitude and frequency of other two fluctuations are 0.5 unit and 10 Hz, respectively for each. (2) Only composition fluctuation into consideration with amplitude and frequency of fluctuation is 0.00065 unit and 10 Hz, respectively. (3) Fluctuations in q and q_c are taken into consideration with amplitude and frequency of fluctuations are 0.5 unit and 10 Hz, respectively, for each case.
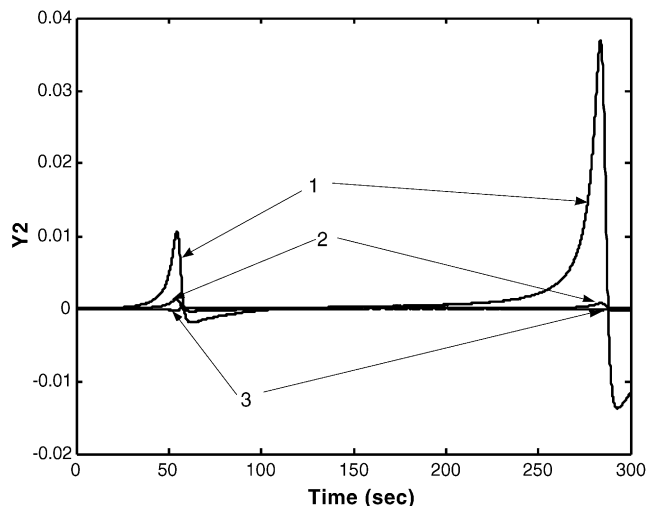
Fig. 6. Fluctuation in output temperature due to input fluctuations with time for three cases for Table 1. (1) All three fluctuations into consideration with amplitude and frequency of composition fluctuation are 0.00065 unit and 10 Hz, respectively and amplitude and frequency of other two fluctuations are 0.5 unit and 10 Hz, respectively for each. (2) Only composition fluctuation into consideration with amplitude and frequency of fluctuation is 0.00065 unit and 10 Hz, respectively. (3) Fluctuations in q and q_c are taken into consideration with amplitude and frequency of fluctuations are 0.5 unit and 10 Hz, respectively, for each case.
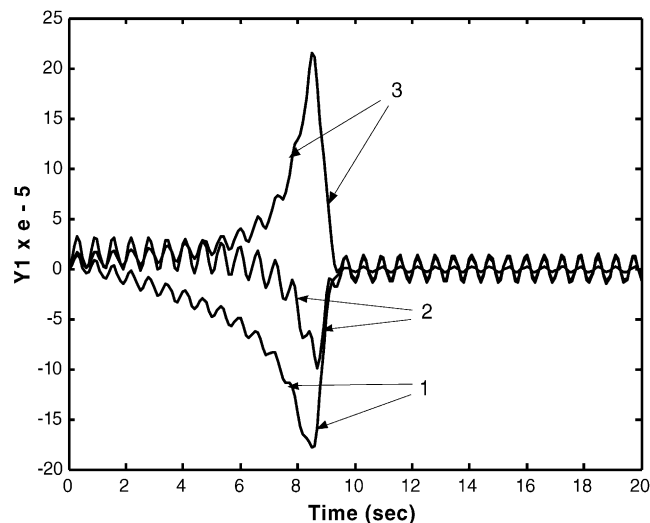

Fig. 7. Fluctuation in output composition due to input fluctuations with time for three cases for Table 2. (1) All three fluctuations into consideration with amplitude and frequency of composition fluctuation are 507.65 unit and 10 Hz, respectively and amplitude and frequency of other two fluctuations are 0.0004 unit and 10 Hz, respectively for each. (2) Only composition fluctuation into consideration with amplitude and frequency of fluctuation is 507.65 unit and 10 Hz, respectively. (3) Fluctuations in q and q_c are taken into consideration with amplitude and frequency of fluctuations are 0.0004 unit and 10 Hz, respectively, for each case.

Here, the variations in input composition and flow rate and in cooling water flow rate along with chemical oscillatory system have been considered. From Fig. 6, it is clear that the effect is interactive in nature. The effect of composition variation is found to be prominent and complex. The effect of variations in flow rates of input and cooling water is found negligible. From Figs. 5 and 6, it is seen that the peaks for Z_1 and Z_2 are at the same place and in opposite direction. Z_1 is opposite to the conversion and so it can be said that the peaks for conversion and temperature are in the same direction. This is because of increase in the reaction rate constant with temperature.

In Fig. 7, the variation (=obtained value for dimensionless composition chemical oscillator with input variations − obtained values for dimensionless composition chemical oscillator without input fluctuation) in dimensionless composition of the process output of oxo reactor is presented with time. Here, the variations in input composition and flow rate and cooling fluid flow rate along with chemical oscillatory system have been considered. It is obtained that, the average values of variations in the process output composition are −4.4813, −1.88 and 3.64 × 10⁻⁶ with all three variations, only composition variation and both flow rates variations, respectively. Therefore, it can be said that the unsteady process operation of an industrial process could be a viable option to improve the productivity. It is more likely to be used in biological systems, which are penchant for periodicity [38]. However, little effort has been made to use natural oscillation to improve the performance of biological reactors.

In Figs. 5–7, unusual observations are obtained because the process runs at unstable focus. The steady state Jacobian matrix has positive real eigenvalue and non-zero imaginary part. The stability analysis of chemical oscillatory system along with all fluctuations is the same, as that of chemical oscillatory since the steady state equations remains the same. Most of combinations discussed for inputs variation give negative values for the average output fluctuation, i.e. higher productivity. This result implies that the commonly accepted assumption that a chemical plant should always be operated on a steady state basis might not give the maximum productivity. But, the complex output variation may effect the product specification, and operation at unsteady state may lead to a complex control strategy and so the safety, etc.

4. Conclusion

The study herein shows that the performance of a chemical reactor is sometimes improved when it is operated dynamically. The dynamic nature of chemical process is due to variations in input composition and flow rate, and process generating fluctuating output due to limit cycle behavior. The reactant concentration and temperature of the process are found strongly dependent on each other. The effect of temperature and overall heat transfer coefficient are found significant on the chemical oscillator system. Sometimes these effects even make the process to operate at steady state. To nullify these effects a very sensitive control system should be used. When the variations in process inputs are

coupled with chemical oscillatory system, the effect of input composition variation is found to be prominent and complex.

The controversial question of whether a dynamic operation of a chemical reactor is economically beneficial or not over the steady state result is not answered in this paper. However, emphasis has been made that the oscillations have been reported for system in all areas of non-linear dynamics, and our system is by no means an exception. Therefore, as a researcher and as an engineer, one should be prepared to utilize these situations for economic benefits, or at least should know how to avoid them in practice.

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