

# DYNAMIC BEHAVIOR OF COUPLING EXOTHERMIC AND ENDOTHERMIC REACTIONS IN A CONTINUOUS STIRRED TANK REACTOR FOR CONTROL APPLICATIONS

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**ABSTRACT**-The unsteady state behaviour of coupling exothermic and endothermic reactions in a continuous stirred tank reactor is analysed. Material Balance, as well as Energy Balance are mathematically modelled and simulated using MATLAB. The different operational behaviours obtained are modelled using ode45 non-stiff integrator. The reactor behaviour is carried out for the first – order reaction with equal activation energies. The conditions when the reactor behaves in an endothermic fashion and when in an exothermic fashion are concluded.

**KEYWORDS**-Coupling exothermic and endothermic reactions, CSTR, MATLAB

## I. INTRODUCTION

With the advancement of technology, reduction in operation cost and, increase in process efficiency and output becomes one of the major goals of industries. Many process optimization methods are followed to have better results. Amongst those, coupling reactions provides significant results in the best utilization of the entropy of systems.

In the impact of making a process more compact and efficient and reduction in manufacturing cost, multifunctional reactors are used. Multifunctional reactor – single piece of equipment, not only carries out the reaction but also helps to perform heat, mass and momentum transfer operations and even reactions [1]. In the use for coupling of the exothermic and the endothermic reactions in the multifunctional reactors, the exothermic reaction provides considerable source of energy to carry out the endothermic reaction.

Categorically, the reaction coupling process can be grouped into three: Direct coupling, Regenerative coupling, and Recuperative coupling [2]. Direct coupling refers to the coupling of exothermic reactions with endothermic one, oxidation with reduction, dehydrogenation with hydrogenation, hydration with dehydration and series of tandem reactions. It involves one or more reactions proceeding simultaneously in the same reactor zone. Here both the energy and materials are interchanged directly in the reaction mixture [8-9]. In the regenerative coupling two or more reactions are conducted in the same reaction zone alternatively. There is only one reaction occurring at one time. The interchange of energy and materials happens via storing and discharge cycles. It provides direct heat supply and the efficient heat recovery. Here in the first half of the cycle the exothermic reaction takes place and in the next half of the cycle the flow pattern is reversed. The endothermic reaction occurs by using the stored energy in the bed during the previous exothermic cycle [10]. In recuperative coupling, the two reactions occur simultaneously separated by a membrane or separation wall. Heat transfer occurs through the membrane/wall, whereas the material transfer takes place only via the permeation through membrane [11-12].

Coupling of the exothermic and endothermic reactions requires fulfillment of various conditions. They are as follows:

- The temperature of exothermic reactions should be more than endothermic ones.
- The pressure of endothermic reaction should be more than exothermic ones.
- The rate of reactions should be definite.

Though, thermal coupling have been studied earlier, the impact and usefulness were more significantly recognized and many works have been carried out after the year 1994 [3]. Coupling reactions integrates more than one chemical process and physical operations.

This integration gives rise to synergetic effects, which may enhance the performance of chemical reaction or/and physical effects. General benefits include: higher productivity, higher selectivity, reduced capital investment and energy consumption, improved operational safety, improved ecological harmlessness [10, 13-14]. Industrially, many oxidative and reductive processes are enhanced via coupling mode of operation [15-17]. Methane Steam reforming [14, 18-19], styrene synthesis [20], conversion of ethyl benzene [21] are prominent areas where coupling reactions are studied and applied greatly.

All the above studies focused on various reactors such as shell and tube heat exchangers [4-6], fixed-bed reactors [7] and fluidized-bed reactors. However, behaviour exhibited by continuous stirred tank reactor (CSTR) is not available in the literature. Hence, in this work, we investigate the dynamic behaviour of CSTR using a suitable mathematical model. This paper is arranged as follows. The mathematical models used and the solution procedure are presented first (Section II). Then the results for dynamic behaviour are discussed (Section III). Conclusions are provided at the end (Section IV).

## II. SYSTEM MODEL AND SOLUTION PROCEDURE

A CSTR is used wherein two independent parallel reactions, one endothermic (A-C) and the other exothermic (B-D) take place. The system behaves with the following assumptions.

- Density ( $\rho$ ) remains constant.
- Specific heat capacity is taken constant.
- Two first order irreversible reactions.
- The reacting mixture is assumed to be well mixed.
- The heat losses from the process to the atmosphere are negligible.
- The overall heat transfer coefficient is assumed constant.
- The resistance across the gas-solid film for heat and mass transfer is assumed to be negligible.
- Physical properties of fluid and heat of reaction are assumed to be independent of the temperature and the total pressure of the system is constant.
- Constant inlet and outlet flow rates.
- Equilibrium is instantaneous.
- Elutriation of solids is neglected at the top of the bed.
- Spherical and constant mean particle size.

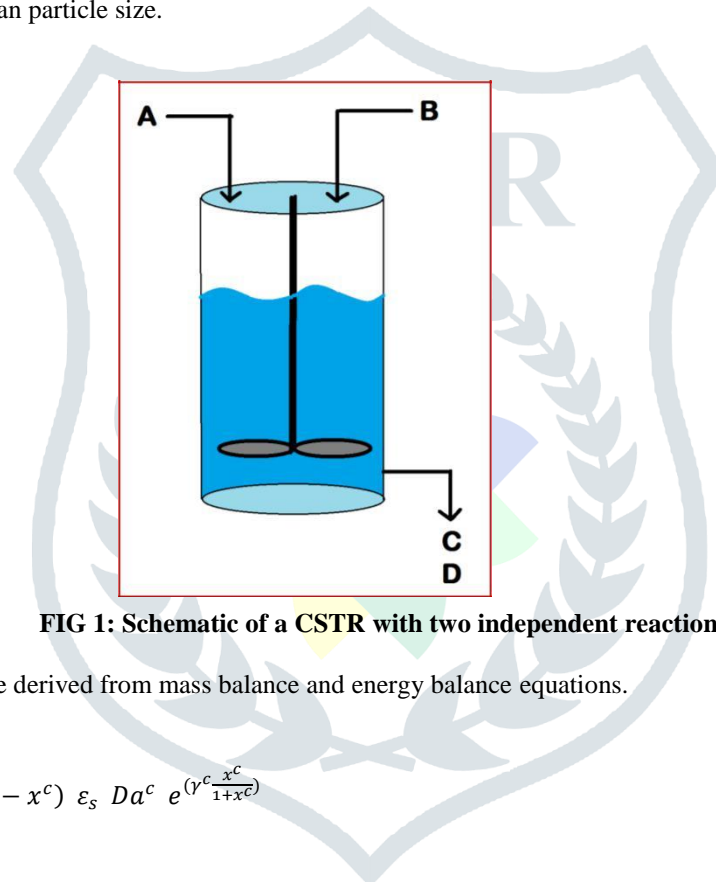


FIG 1: Schematic of a CSTR with two independent reactions

The following equations are derived from mass balance and energy balance equations.

Mass balance:

$$\frac{dx^c}{dt} = (1 - x^c) \varepsilon_s Da^c e^{(\gamma^c \frac{x^c}{1+x^c})} \quad (1)$$

$$\frac{dx^h}{dt} = (1 - x^h) \varepsilon_s Da^h e^{(\gamma^h \frac{x^h}{1+x^h})} \quad (2)$$

:

Energy Balance:

$$\frac{d\theta}{dt} = \varepsilon_s \left( \beta^c (1 - x^c) Da^c e^{(\gamma^c \frac{\theta}{1+\theta})} + \beta^h (1 - x^h) Da^h e^{(\gamma^h \frac{\theta}{1+\theta})} \right) \quad (3)$$

The dimensionless parameters used in the equations are given below with  $j = c, h$  to designate the endothermic or the exothermic reaction parameters respectively.

$$Da^j = \frac{k^j V_r}{Q}, \quad \beta^j = \frac{(-\Delta H^j) C_0}{\rho_g C_{pg} T_{ref}}, \quad x_g^j = \frac{C_0^j - C^j}{C_0^j}, \quad \gamma^j = \frac{E^j}{R_g T_{ref}}, \quad \theta_g^j = \frac{T^j - T_{ref}}{T_{ref}}$$

The solution to the above differential equations is obtained by using the MATLAB ode solver –‘ode45’. The initial values for the endothermic conversion, exothermic conversion and temperature are taken to be zero. For all the operation, the activation energies for both the endothermic and the exothermic reaction are assumed to be equal and constant.

**III. RESULTS AND DISCUSSIONS:**

The simulated conversion and temperature profiles for different possible cases with parameters are presented in below Figures-2-13. The parameters used for different cases are displayed in the Table-1.

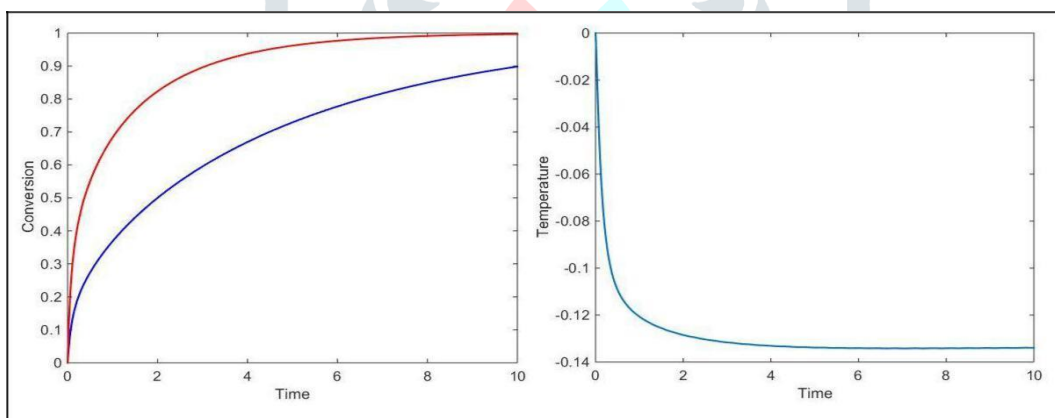
**Table-1: The parameters used for different cases.**

Cases	Parameters
1	$Da^h = 10, Da^c=4, \beta^h=0.4, \beta^c = -0.4$
2	$Da^h = 2, Da^c =2, \beta^h=0.5, \beta^c = -0.1$
3	$Da^h = 4, Da^c =10, \beta^h =0.6, \beta^c = -0.4$
4	$Da^h = 2, Da^c =2, \beta^h =0.1, \beta^c = -0.5$
5	$Da^h = 4, Da^c =6, \beta^h =0.6, \beta^c = -0.4$
6	$Da^h = 6, Da^c =4, \beta^h =0.4, \beta^c = -0.6$
7	$Da^c = Da^h,  \beta^c  >  \beta^h $
8	$Da^c = Da^h,  \beta^c  <  \beta^h $
9	$ \beta^h  =  \beta^c , Da^c < Da^h$
10	$ \beta^h  =  \beta^c , Da^c > Da^h$
11	$ \beta^h  * Da^h >  \beta^c  * Da^c$
12	$ \beta^h  * Da^h <  \beta^c  * Da^c$
13	$ \beta^h  * Da^h =  \beta^c  * Da^c$

**A) Conversion and Temperature Profiles**

In all the figures of cases 1-10, the left side plot shows the conversion profile and the right side plot shows the temperature profile. The red and blue solid lines in every conversion profile represent exothermic and endothermic conversion respectively.

Case: 1

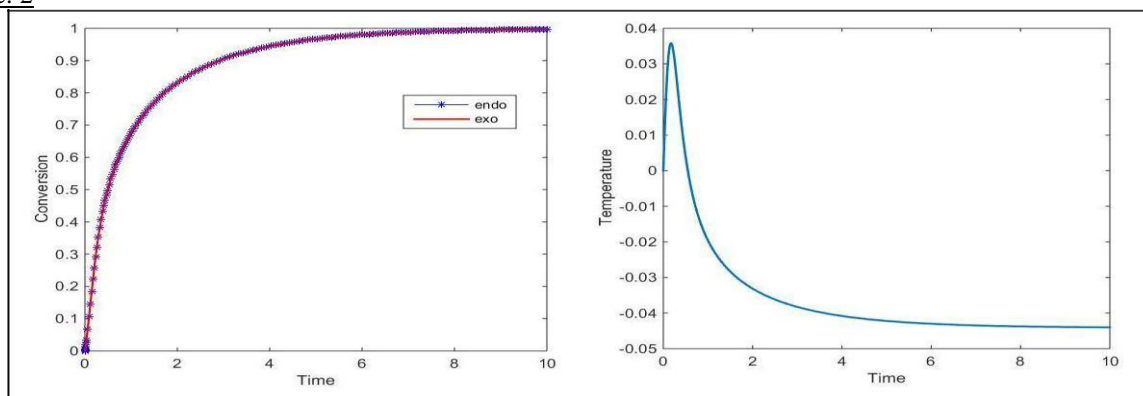


**Fig-2 Conversion and temperature profiles with  $Da^h = 10, Da^c=4, \beta^h=0.4, \beta^c = -0.4$ .**

**Observation:**

- The exothermic reaction conversion is reached faster as the  $Da^h > Da^c$ . Therefore the exothermic conversion is more than of the endothermic conversion.
- The temperature values are negative due to the absorption of heat by the endothermic reaction.

Case: 2



**Fig-3 Conversion and temperature profiles with  $Da^h = 2, Da^c =2, \beta^h =0.5, \beta^c = -0.1$**

Observation:

- Both the exothermic and endothermic conversion coincides as the rate of reaction remains same.
- The temperature profile attains a small peak initially before collapsing down to remain constant later.
- The temperature peak is attained due to  $|\beta^h| > |\beta^c|$ . The quenching effect of endothermic reaction brings the downfall in the temperature profile.

Case: 3

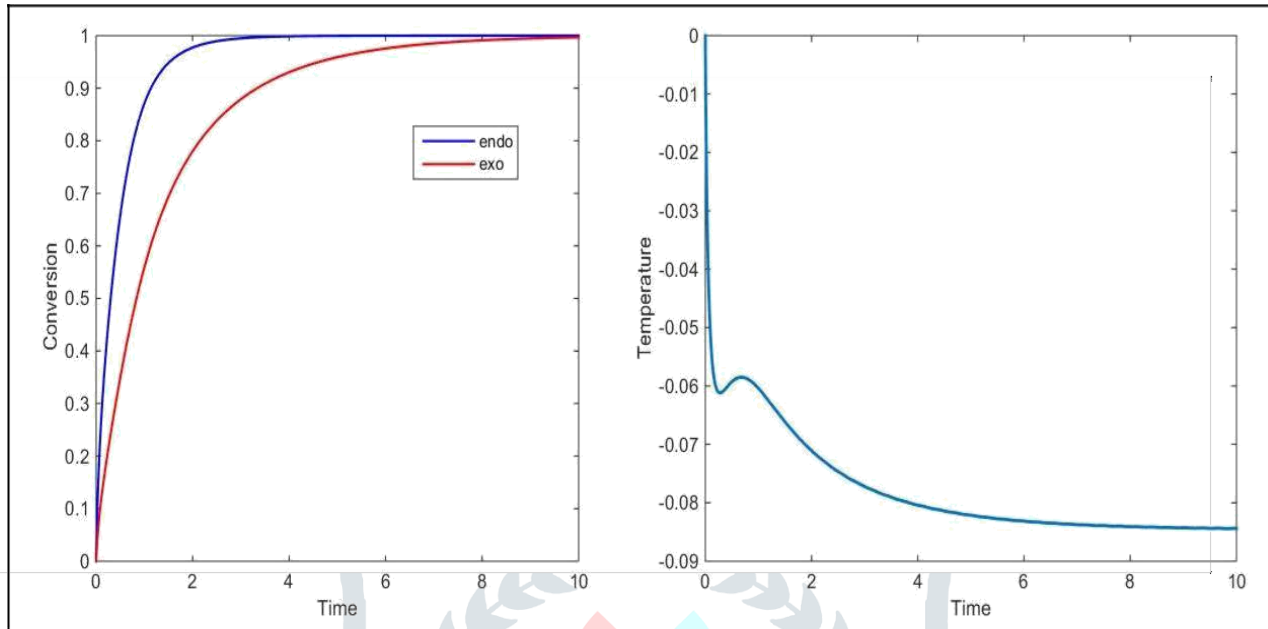


Fig-4 Conversion and temperature profiles with  $Da^h = 4, Da^c = 10, \beta^h = 0.6, \beta^c = -0.4$

Observation:

- Here as  $Da^c > Da^h$ , the endothermic conversion profile is reached faster.
- Due to the higher enthalpy change for exothermic reaction than that of endothermic reaction, there is slight deviation in the start of the temperature profile. The temperature profile becomes near to steady due to the quenching effect from the endothermic reaction.

Case: 4

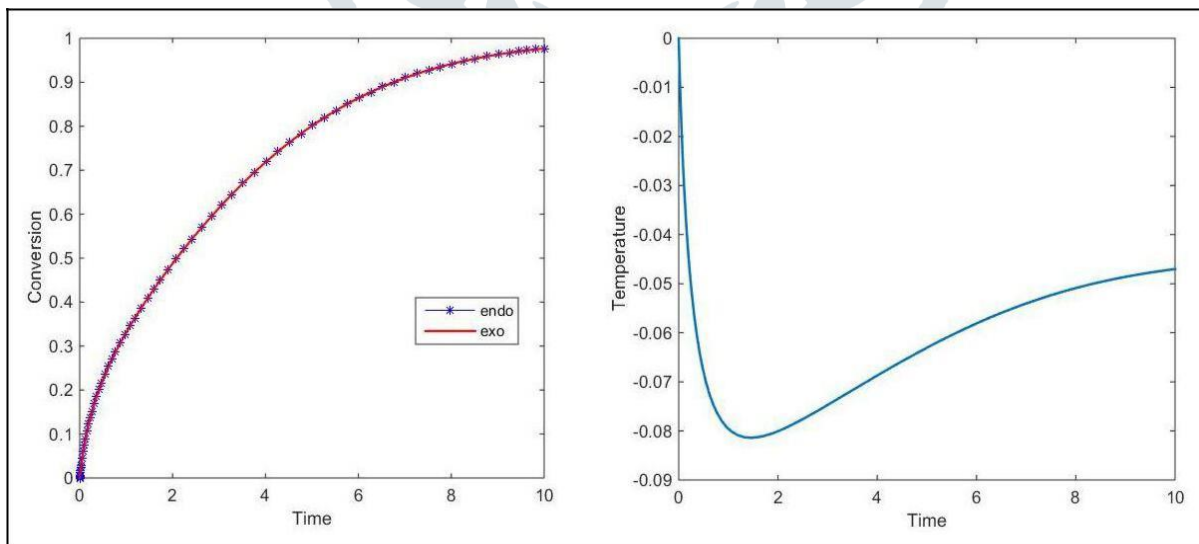


Fig-5 Conversion and temperature profiles with  $Da^h = 2, Da^c = 2, \beta^h = 0.1, \beta^c = -0.5$

Observation:

- Again, the conversion profile coincides due to equal Damkohler number for both the exothermic and endothermic reactions.

Case: 5

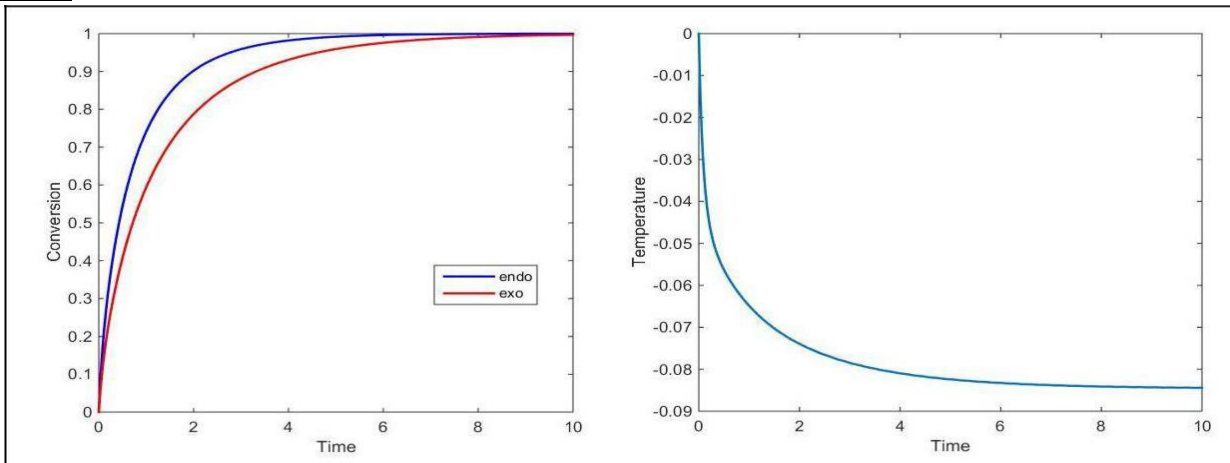


Fig-6 Conversion and temperature profiles with  $Da^h = 4, Da^c = 6, \beta^h = 0.6, \beta^c = -0.4$

Case: 6

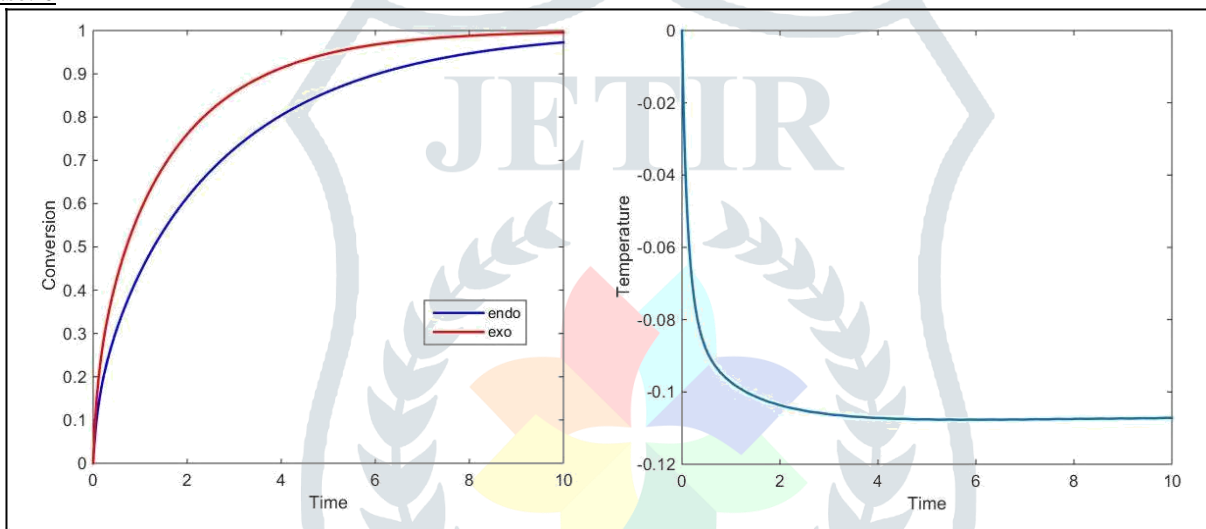


Fig-7 Conversion and temperature profiles with  $Da^h = 6, Da^c = 4, \beta^h = 0.4, \beta^c = -0.6$

Observation:

- The amount of heat generation and heat consumption is equal in both the endothermic and exothermic reaction, but since the  $Da$  number of the endothermic reaction is higher in case 5, the conversion of it is achieved faster. The  $Da$  number is higher of the exothermic reaction in in case 6, so the exothermic conversion is reached faster in it.

**B. Conversion and Temperature profiles with equal Damkohler number**

Case: 7

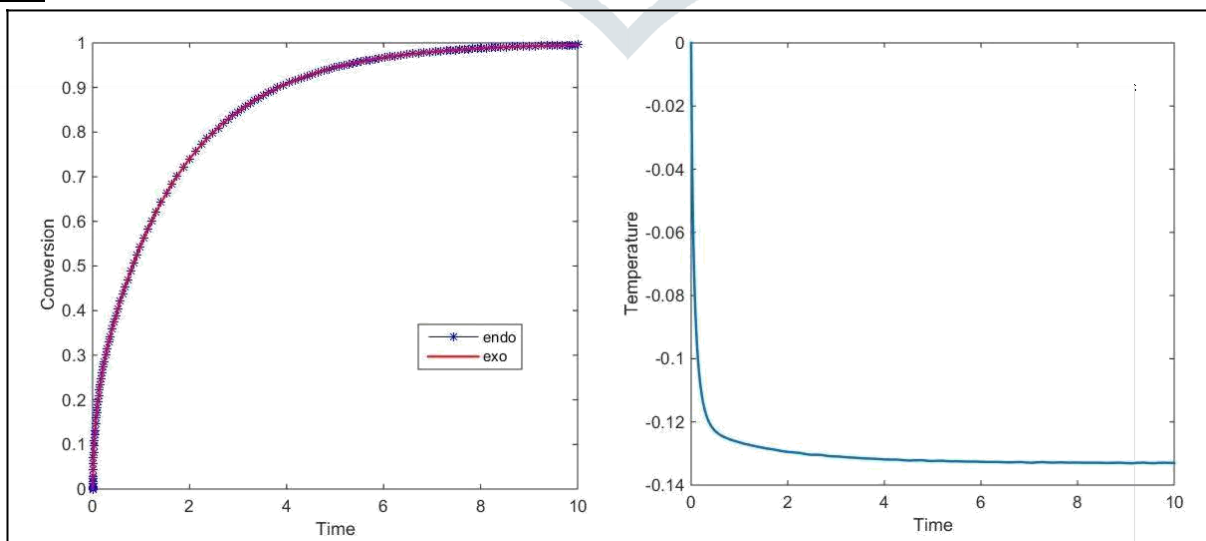


Fig-8 Conversion and temperature profiles with  $|\beta^c| > |\beta^h|$

Observation:

- The temperature is less than the inlet temperature and the reactor is operated in endothermic fashion.

Case: 8

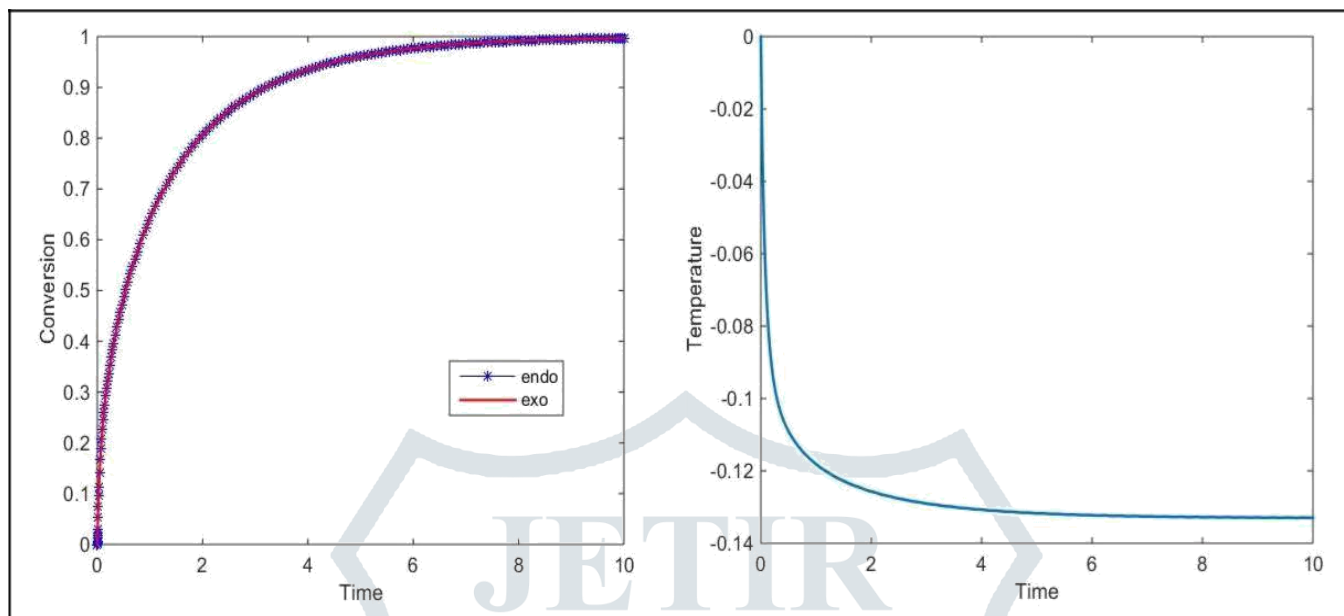


Fig-9 Conversion and temperature profiles with  $|\beta^c| < |\beta^h|$

C. Conversion and Temperature profiles with equal heat of reaction ( $|\beta^h| = |\beta^c|$ )

Case: 9

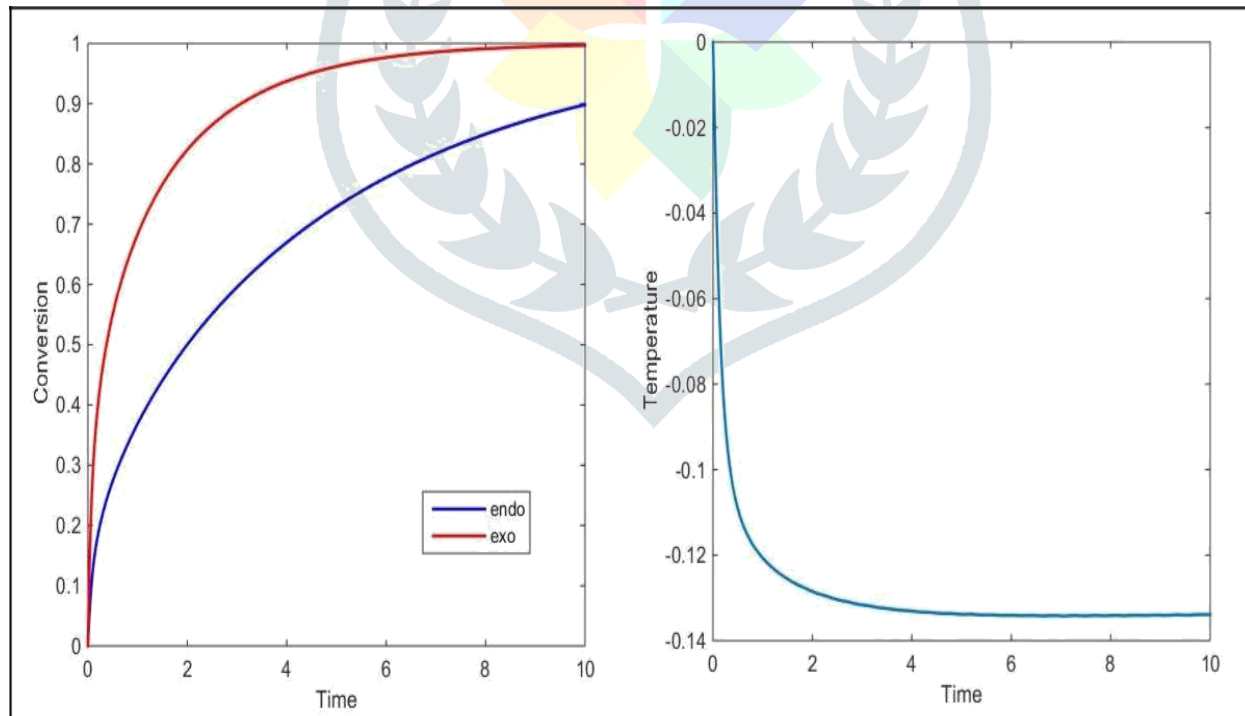


Fig-10 Conversion and temperature profiles with  $Da^c < Da^h$

Observation:

Due to lesser Damkohler number, it is found that exothermic conversion is achieved faster.

Case: 10

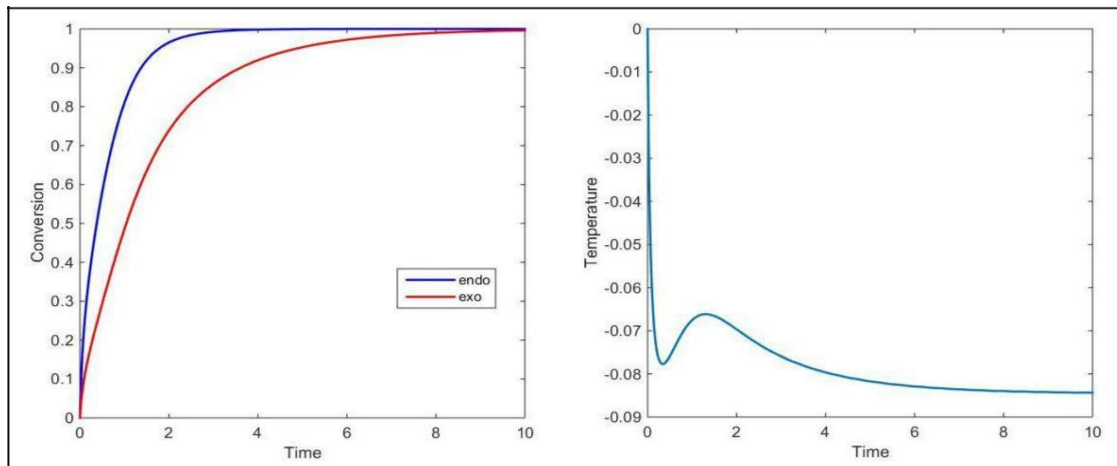


Fig-11 Conversion and temperature profiles with  $Da^c > Da^h$

Observation:

Due to higher Damkohler number, it is found that endothermic conversion is achieved faster

**D. Comparison of temperature profiles:**

Case: 11:(Case:1vs case 2)

Case: 12:(Case:3vs case 4)

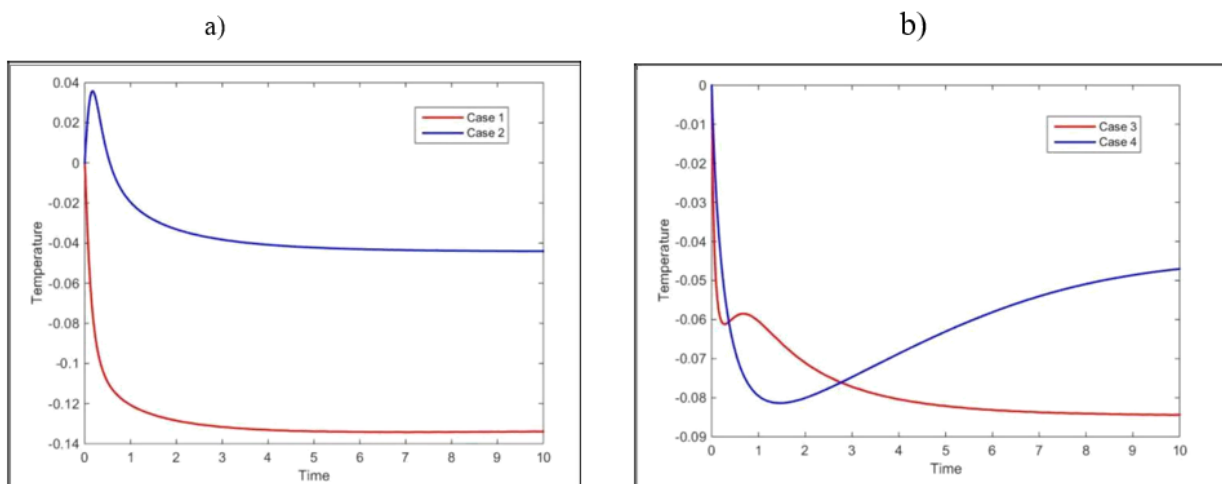


Fig-12 Temperature profiles a)  $[ |\beta^h| * Da^h > |\beta^c| * Da^c ]$ , b)  $[ |\beta^h| * Da^h < |\beta^c| * Da^c ]$

Case: 13:(Case:5vs case 6)

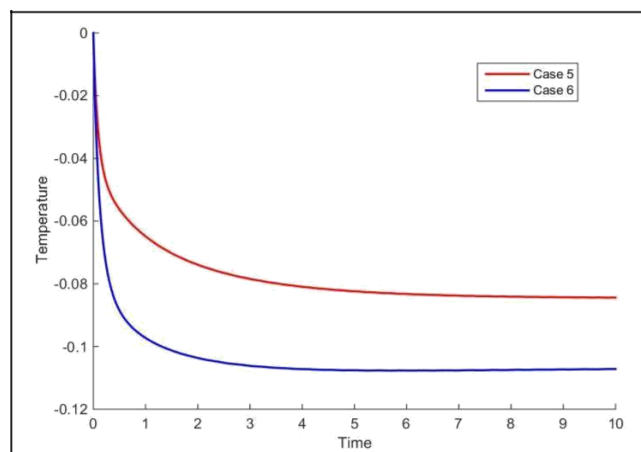


Fig-13 Temperature profiles with  $[ |\beta^h| * Da^h = |\beta^c| * Da^c ]$

The results as presented here are limited to the cases where both the endothermic reactions and the exothermic reactions have first order kinetics and equal activation energies. The simulation plots of model equations reveal the behaviour of the reactor. Higher Damkohler number dominates the conversion profile, as seen from the observations of the plots.

#### IV. CONCLUSIONS

The reactor system, CSTR is one of the widely used means to convert reactants into valuable products in chemical industries. The low operating costs and consistent product quality (due to reproducible process control) drive us to test simulation for coupling of endothermic reaction and exothermic reactions in the reactor. This work probed into different experimental parameters of exothermic and endothermic reactions. Simulations were carried out for two independent parallel reactions- one endothermic and the other exothermic. All the equations were modeled and solved using MATLAB with non-stiff integrator- 'ode45'.

The reactor was observed to behave as endothermically or exothermically under various operating conditions. It was seen that when the heat generation is higher than that of heat consumption ( $|\beta^h| * Da^h > |\beta^c| * Da^c$ ) the reactor behaved exothermically while it behaved endothermically on vice-versa parameters ( $|\beta^h| * Da^h < |\beta^c| * Da^c$ ).

With the effect of thermal coupling coming into the industrial scale, much of the operational cost is reduced and the process output efficiency has been increased. The integration of the endothermic and exothermic reactions has proved to reduce the size of the reactor and has been utilizing the entropy to the best optimal way. Though much of the work has been carried out in adiabatic reactors or directly coupled reactors, therefore there opens much scope to have a research in the studying coupling in continuous stirred tank reactors.

#### NOTATIONS:

C	-	Concentration of the reactant
C <sub>0</sub>	-	Inlet concentration of the reactant
k	-	Rate constant of the reaction
k <sub>0</sub>	-	Frequency factor
E	-	Activation energy
R	-	Universal gas constant
r	-	Rate of reaction
T <sub>ref</sub>	-	Reference temperature
T	-	Gas phase temperature
V <sub>r</sub>	-	Volume of the reactor
ε <sub>s</sub>	-	Solid holdup
Da	-	Damkohler number
L	-	Reactor length
t	-	Time
x	-	Dimensionless concentration
Q	-	Volumetric flow rate
C <sub>pg</sub>	-	Specific heat capacity of the gas mixture
Da	-	Damkohler Number

E- Activation energy  
 ΔH-Heat of the reaction

#### *Greek letters*

β - Dimensionless heat of reaction  
 Θ - Dimensionless temperature  
 γ - Dimensionless activation energy  
 ε<sub>b</sub>- Void fraction  
 ρ - Density

#### *Subscripts/superscripts*

c - Endothermic reaction  
 g - Gas phase  
 h - Exothermic reaction  
 j - c, h  
 s - solid phase



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