Experimental Study of Thermal Runaway in Tubular Reactor with Acetic Anhydride Hydrolysis Reaction

Jaynik Vyas¹ Prof. Tejal Patel² Prof. Devesh Vyas³ Dr N S Jayakumar⁴
¹UG Student ²,³ Associate Professor ⁴Ex. Professor
¹,²,³,⁴Department of Chemical Engineering
¹,²,³,⁴Faculty of Technology, D.D. University Nadiad, Gujarat, India

Abstract—Thermal runaway is a major problem found during designing of chemical reactors. A small variation in the system operating conditions can lead to a much larger change in the system thermal behavior. In the present work, the dynamics of tubular reactor is experimentally investigated by carrying out an exothermic liquid phase hydrolysis reaction of acetic anhydride with acetic acid as solvent and sulfuric acid as catalyst. With Residence time distribution (RTD) experiments, Parametric Sensitivity has been studied practically and the experimental transient temperature data are verified with one parameter model of Tanks in series model. The predicted transient temperature data are compared with the experimental data and they are found to be in satisfactory agreement.

Key words: Thermal Runaway, Parametric Sensitivity, Tubular Reactor

I. INTRODUCTION

In chemical industry, one of the major causes of accident during the run of a desired reaction is thermal runaway. Many industrial processes are based on fast and strongly exothermic reactions. In these systems, a small variation in the system operating conditions can lead to a much larger change in the system thermal behavior. As the sake of example, if the efficiency of a reactor cooling system drops (this can happen for many different reasons in a chemical plant), the reactor temperature will rise very quickly. This sharp temperature rise, which characterizes thermal runaway conditions, can lead to serious consequences, from the opening of a relief system to the physical explosion of the reactor.

For these reasons, fast and strongly exothermic reactions have been the object of a large number of studies, aimed at identifying both safe and unsafe operating conditions. Many researches are found for parametric sensitivity using almost continuous reactors, i.e. Plug Flow Reactor (PFR), Continuous Stirred Tank Reactor (CSTR) etc.

II. CONCEPT OF PARAMETRIC SENSITIVITY

The study of dynamic behavior for chemical reactor includes parametric sensitivity, output multiplicity, input multiplicity, limit cycle behavior etc. Parametric sensitivity primarily deals with a small change in one or more of the reactor input variable leads to larger changes in the output variables. This drastic change in system behavior across a threshold value of a parameter is also known as runaway or hotspot region of reactor. When an exothermic reaction is carried out; the reactor is said to operate in the parametric sensitivity region, where for a given small variation of input variable, it causes large variations for output variable.

In other words, when an exothermic reaction occurs within non-adiabatic tubular reactor, the temperature profile at steady state exhibits a maximum, which is usually known as “Hotspot”. In the region of parametric sensitivity the magnitude of the hot spot can undergo very large variation even for a very small variation of one or more of the input parameters.

The more convincing and physically sound definition proposed by Dente and Collina [1], who defined runaway as the occurrence of a positive second order derivative region before the hotspot in the temperature - reactor length plane. This is physically sound since it identifies runaway with “acceleration” in the temperature - reactor axis plane. According to this criterion, regions in the parameter space where runaway occurs can be identified, and the boundaries of these are given by the locus of parameter values where the third derivative of temperature versus reactor axis is zero. Very simple explicit analytical expression for the boundaries of the runaway region was produced by Van Welsenaere and Froment [2]. They had introduced a second criterion, based on the occurrence of a maximum in the locus of the maxima in the temperature – conversion plane. It is substantially equivalent to the previous criterion.

The first a priori runaway criterion was proposed by Barkelew [3] based on the geometry property of temperature trajectories deduced from an empirical analysis of a large number of solutions of the model.

Originally the criterion of parametric sensitivity was derived from the thermal explosion theory by Semenov [4] and later on, it is applied to reaction engineering field. This criterion for ignition or explosion was based on the occurrence of a region with positive second order derivative in the temperature versus time profile.

In nutshell the parametric sensitivity study leads to the knowledge of boundaries between sensitive and non-sensitive region in the reactor parameter space, which becomes an important tool for accurate and safe design of reactor with ease in operation and control too [5].

III. EXPERIMENTAL WORK ON PARAMETRIC SENSITIVITY

In the present work, the dynamics of tubular reactor in terms of parametric sensitivity have been experimentally investigated by employing an exothermic liquid phase hydrolysis reaction of acetic anhydride with acetic acid as solvent and sulfuric acid as catalyst in the S.S. 316 jacketed tubular reactor.

The main aim of the present work is to experimentally investigate the parametric sensitivity in the jacketed tubular reactor by varying the different input parameters like temperature of reactant feed mixture, coolant flow rate and coolant input temperature using acid catalyzed hydrolysis reaction obeying the first order kinetics under non-isothermal conditions.

The experimental work on parametric sensitivity has been planned and carried out in the following manner.
Design of experimental setup
- Residence time distribution studies in tubular reactor
- Reaction experiments for observing dynamics and parametric sensitivity for various parameters.
- Simulation using mathematical model and verification of the same with experimental results.

IV. DESIGN OF EXPERIMENTAL SETUP
A stainless steel 316 jacketed tubular reactor having 570 cubic centimeter volume with the necessary storage tanks, constant overhead tanks, constant temperature water bath and necessary process flow auxiliaries has been designed and fabricated as an experimental setup for carrying out the experimental investigations [6].

V. RESIDENCE TIME DISTRIBUTION STUDIES IN TUBULAR REACTOR
Residence time distribution (RTD) experiments are carried out in the tubular reactor by giving step input of sodium hydroxide solution of known concentration as tracer. For the various flow rate values of tracer, the time versus concentration data are obtained. Using the above data, the exit age distribution, the mean residence and the dimensionless variance are calculated [7]. The numbers of tanks in series, \( N \) is found out using the reciprocal value of calculated dimensionless variance.

VI. REACTION EXPERIMENTS FOR OBSERVING PARAMETRIC SENSITIVITY
The reaction experiments for studying the parametric sensitivity; have been carried out by varying the different input parameters like temperature of reactant feed mixture, coolant flow rate and coolant input temperature in a small variation, when the acid catalyzed exothermic hydrolysis reaction of acetic anhydride is allowed to take place in a jacketed tubular reactor in presence of sulfuric acid as catalyst [8].

For observing the parametric sensitivity, the reaction experiments are carried out using acid catalyzed hydrolysis reaction of acetic anhydride in the tubular reactor. Initially, the tubular reactor is filled with the reactant mixture comprising of acetic acid, water and sulfuric acid as catalyst in a specific volume proportion at some fixed temperature. The two reactants - acetic anhydride and the reactant mixture - are allowed to flow into the tubular reactor at constant flow rate at specific feed temperature after passing them through the two separate stainless steel coil immersed in the constant temperature water bath. The time versus temperature data are obtained by measuring the temperature at four equal distance locations along the axis of the tubular reactor. The reaction system is observed to exhibit the existence of parametric sensitivity for the various input parameters like the feed temperature of reactants mixture, coolant flow rate and coolant feed temperature [9].

From the experimental observations, it is found that when the input parameters like feed temperature of reactant mixture is changed from 74°C to 75°C, the reactor showed the existence of parametric sensitivity with the change in output reactor temperature difference of around 40°C. The reactor is also found to exhibit parametric sensitivity by varying coolant flow rate from 42cm³/min to 43cm³/min. The similar sensitive behavior of the tubular reactor is observed when coolant feed temperature is varied by 1°C at 19°C temperature of coolant water.

VII. MATHEMATICAL MODELING, SIMULATION AND ANALYSIS OF RESULTS
In the present work, the mathematical Tanks in series model have been applied to study the nonlinear behavior of tubular reactor in terms of parametric sensitivity using acid catalyzed hydrolysis reaction of acetic anhydride. The unsteady state mass and energy balance equations for all the tanks under non- isothermal conditions have been written to describe the dynamics of tubular reactor.

From RTD experiments it has been found out that there are seven numbers of tanks in series. Each tank in series model has the same volume and the volume is obtained as equal to 1/7 of the total reactor volume.

\[ V_1 = V_2 = V_3 = V_4 = V_5 = V_6 = V_7 = \frac{V}{7} \]  

Similarly on the jacket side, volume of the coolant medium associated with series model has been found as equal to 1/7 of the total jacket volume.

The unsteady state mass and energy balance equations for all the tanks under non- isothermal conditions can be written as:

For tank 1
\[ \frac{dC_{1a}}{dt} = q(C_{a0} - C_{1a}) - V_1 \frac{dC_{ia}}{dt} \]  

\[ V_1 \frac{dC_{1a}}{dt} = \rho C_p (T_f - T_1) + (\Delta H) \rho K_a(T_c - T_1) + UA(T_r - T_1) \]  

\[ V_{c1} \frac{dT_{c1}}{dt} = \frac{q_{c}C_{pc}}{V_{c1}} (T_{c0m} - T_{c1}) + UA(T_r - T_{c1}) \]

These stiff differential equations have been solved numerically. By solving the nonlinear stiff differential equations, the simulated transient temperature data have been obtained and tabulated for the study of various parameters like feed temperature, effect of coolant flow rate and the effect of coolant temperature [10].

Finally, the simulated data have been compared with the experimental results. By analyzing such records, the transient temperature data measured at specific locations on tubular reactor are found to be in satisfactory agreement with the simulated results. The predicted maximum temperature i.e. hot spot in parametric sensitivity region so called runaway conditions has been found to be observed very near to the entry point of tubular reactor, which is in exact agreement with the experimental observations.

VIII. CONCLUSIONS
In the present work, the various salient conclusions drawn from the experimental research work have summarized as under.
- The acid catalyzed hydrolysis reaction of acetic anhydride in the presence of acetic acid as solvent and sulfuric acid as catalyst is used as a reaction system that is seldom reported in the literature.
- From Residence Time Distribution (RTD) experiments, one parameter mathematical model of Tanks in series is found to be equal to 7.
- The parametric sensitivity behavior exhibited by the present simulation system in the tubular reactor is observed...
Experimental Study of Thermal Runaway in Tubular Reactor with Acetic Anhydride Hydrolysis Reaction

(IJSRD/Vol. 5/Issue 03/2017/093)

for small variance of input parameters like feed temperature of reactant mixture, coolant water flow rate and coolant water feed temperature. The output reactor temperature obtained experimentally showed the large temperature variation with respect to small variation of the input parameters.

- The unsteady state mass and energy balance equations, under non-isothermal condition with counter current flow of coolant, for all the 7 tanks in series are proposed and all these equations are solved numerically. The predicted transient temperature data for all the reaction experiments are found to be in satisfactory agreement with the experimental data.

NOMENCLATURES

- $A$ : Heat transfer area, cm$^2$
- $C_A$ : Concentration of Acetic anhydride gm mole/cc
- $C_p$ : Specific heat of mixture cal/gm °C
- $E$ : Activation energy, cal/gm mole
- $(-\Delta H)$ : Heat of reaction, cal/gm mole
- $K_1$ : First order rate constant, min$^{-1}$
- $K_0$ : Frequency factor
- $N$ : Number of stirred tank reactor
- $q$ : Total flow rate of reactant, cc/min
- $q_c$ : Total flow rate of coolant, cc/min
- $R$ : Universal gas constant, cal/gm mole °K
- $t$ : Time, min
- $T$ : Temperature, °K
- $U$ : Overall heat transfer coefficient, cal/cm$^2$min °K
- $V$ : Volume of reactor, cc
- $\delta$ : Density of reactant mixture, gm/cc

REFERENCES