

THEMAL STABILITY OF CHEMICAL REACTORS

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Received: October 18, 1973.

The occurrence of thermal instability of large chemical reactors is a well known fact. Experience has shown that during the start and shut down periods, the instability can be considerable and even dangerous. On more than one occasion it was observed that a relatively small change of the feed rate (B), the concentration (c_0) or the temperature of the feed (T_0) caused a rapid drop of the temperature and conversion of a working reactor, characterized by high temperature and high degree of conversion. There are apparent contradictions in the observations of reactors running at low temperature and with a small degree of conversion, that an insignificant alteration of the previously mentioned parameters resulted in a sudden increase of temperature and conversion. In practice, this latter phenomenon was called "ignition", independently from the fact whether burning or an increase of the catalyst temperature only took place. A different type of instability could be observed and also reproduced at certain critical parameter values, when the working condition of a reactor changed suddenly between the mentioned limits, and regarding the thermal phenomena, an oscillation came into existence.

Summing up the experiences, it can be stated that there are narrow unstable domains in the working conditions of a reactor which cannot be described merely by the heat balance of the system.

WAGNER [1] first elucidated the causes of this phenomenon in his theoretically well grounded work. Due to the Second World War his article was not widely available, and van HEERDEN [2] again

elaborated the conditions of the stability in 1953. BILOUS and AMUNDSON's article [3] published in 1955; examined this thermal stability, and for this the linearisation of their mathematical model was used. As a result, numerous researchers have dealt with the problem. VOLTERRA and SALNIKOV summarized the published statements in their book [4].

In the present work it will be shown that in the thermal sense both the extreme types of reactors, i.e. the adiabatic and isotherm reactors can be discussed, utilizing the same theory. The following discussion is based on the well mixed reactors.

Starting with the well known equation (e.g. [5]), which describes the rate of heat generation:

$$\dot{Q}_R = v_i r \Delta H V_R \quad (1)$$

It is known that the expression of the reaction rate ($v_i r$) can be divided into the product of two functions, one of these depends on temperature, the other one is only the function of the concentration:

$$(v_i r) = k(T) f(c)$$

In the following, the thermal stability will be examined only, so the substitution of $f(c) \equiv c$ is introduced, i.e. the derived equations refer to the reactions of first order, but the thermal considerations are also valid for reactions of any kind of order.

The ARRHENIUS' equation is commonly accepted and valid for the description of the $k(T)$ function:

$$k(T) = A e^{-\frac{E}{RT}} \quad (2)$$

In the case of tank reactors it is known [6] that the actual concentration c or the degree of conversion x , is the function of the initial concentration (c_0) and the mean residence time (\bar{t}); substituting Eq. (2) into this relation:

$$c = c_o(1 - x) = c_o \frac{1}{1 + k\bar{t}} = c_o \frac{1}{1 + A e^{-\frac{E}{RT}} \bar{t}} \quad (3)$$

i.e. the generated heat given by Eq. (1) is as follows:

$$\Delta Q_R = v_i \Delta H v_R c_o \frac{A e^{-\frac{E}{RT}}}{1 + A e^{-\frac{E}{RT}} \bar{t}}$$

Using simple transformations, the following equation of suitable form can be written:

$$\Delta \dot{Q}_R = v_i \Delta H v_R c_o \frac{1}{\bar{t}} \frac{A \bar{t} e^{-\frac{E}{RT}}}{1 + A \bar{t} e^{-\frac{E}{RT}}} \quad (5)$$

If in Equation (5) all the quantities - with the exception of the temperature - are constants, then the heat generated in an adiabatic reactor will be proportional with the following function:

$$Y = \frac{e^{-\frac{1}{T}}}{1 + e^{-\frac{1}{T}}} \quad (6)$$

For isotherm reactors, this seems to be less of a problem because the substitution $T = \text{constant}$ theoretically holds. However, this is valid only in principle, chemical engineers are aware that isotherm reactors work in a similar manner to heat exchangers, and there exists a certain inner temperature (T) which differs from the temperature of the wall (T_1); this forms the boundaries of their working conditions and determines their dimensions. Therefore, in the practice either the amounts of heat generated at the mentioned temperatures or the quotient of these heat quantities have to be taken into account. Regarding Equation (4) at temperatures (T) and (T_1), and taking their quotient:

$$\Delta\dot{Q}_R^* = \frac{\Delta\dot{Q}_R}{\Delta\dot{Q}_{Rf}} = \frac{1 + \frac{1}{A\bar{t}} e^{\frac{E}{RT_1}}}{1 + \frac{1}{A\bar{t}} e^{\frac{E}{RT}}} \quad (7)$$

If in this case A , \bar{t} , E and R are constants, then a relation can be obtained which is similar to Equation (6):

$$y^* = \frac{1 + e^{\frac{1}{T_1}}}{1 + e^{\frac{1}{T}}} \quad (8)$$

Plotting $\Delta\dot{Q}_R$ or $\Delta\dot{Q}_R^*$ vs. T , the result is a sigmoid heat generation curve, known from literature. As an example, HODOSSY's work [7] can be mentioned. Here the author examined the hydrogenation of furfural to furfuryl alcohol and plotted the measured values. The results were the mentioned sigmoid curves.

In addition, for setting up a relation with Equation (6) valid for adiabatic reactors, the numerator and denominator of Equation (8) is multiplied by $[\exp(-1/T)]$ and transforming the result we obtain:

$$y^* = \frac{e^{-\frac{1}{T}}}{1 + e^{-\frac{1}{T}}} + \frac{e^{\frac{1}{T_1} - \frac{1}{T}}}{1 + e^{-\frac{1}{T}}} \quad (9)$$

It is now evident that although the conditions are equal, why the degree of conversion in isotherm reactors is higher compared to the same one of adiabatic reactors. The first term of Equation (9) is identical with Equation (6) valid for adiabatic reactors, and to this a second term is added. If the latter is marked with Y_1 , thus:

$$y^* = Y + Y_1 \quad (10)$$

The above relation is shown in Fig. 1. Introducing the designation

$$e^{\frac{1}{T_1}} = D$$

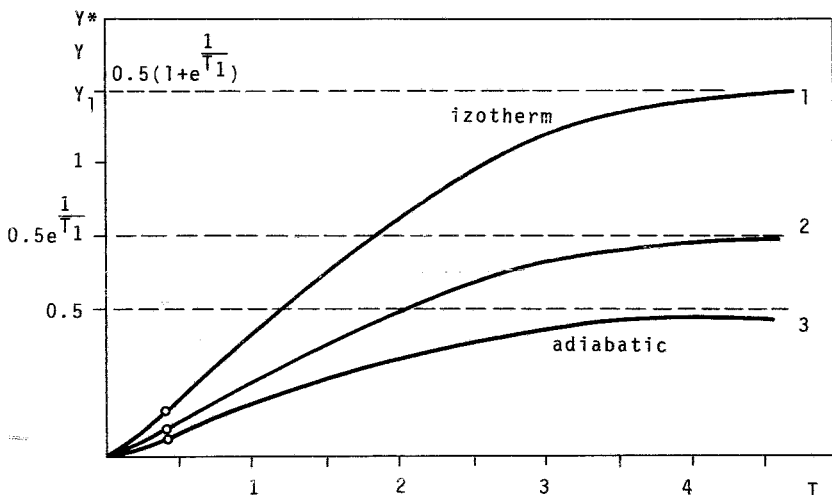


Fig. 1. 1 - $Y^* = Y + Y_1 = (1 + e^{1/T_1}) \frac{e^{-1/T}}{1 + e^{-1/T}}$

2 - $Y_1 = e^{1/T} \frac{e^{-1/T}}{1 + e^{-1/T}} (T = 2.5)$; 3 - $Y = \frac{e^{-1/T}}{1 + e^{-1/T}}$

so the result is basically the same, but it is expressed differently as it is shown below:

$$Y^* = Y + \frac{D e^{-1/T}}{1 + e^{-1/T}} \quad (11)$$

or

$$Y^* = (1 + D) \frac{e^{-1/T}}{1 + e^{-1/T}} = (1 + D) Y \quad (12)$$

Although there are significant differences between the working conditions and characteristics of adiabatic and isotherm reactors, the conclusion can be drawn that they can be treated theoretically on the basis of the same principle.

This result provided encouragement to proceed further, transgressing the theory and methods usually applied in chemical engineering science, and to introduce the methods used in process control for the examination of the thermal stability of chemical reactors.

At first it was assumed that a chemical reactor as a whole is a dynamic system which can exist in different steady states. The response of the system was examined: if it is disturbed whether it returns to the previous steady state or does not. LJAPUNOV's first method was used in the examination of small disturbances, but if the disturbances were major, the non-linear model was solved and the plotted phase-plane provided the answer to the question.

The steady states of the system can be determined by the help of the

1. main isoclinics,
2. heat generation and removal curves,
3. bifurcating diagrams.

The last two methods can be applied well in practice and with their assistance the optimum working parameters of a reactor can be determined. The methods used and the experiments will be discussed in the following paper.

Acknowledgement

The authors are indebted to Mrs. M. Varga for her assistance in the mathematical analysis.

SYMBOLS

- A pre-exponential factor (1/sec)
- B feed rate (cu. metre/second)
- c concentration (kg moles/cu. metre)
- c_0 concentration of the feed (kg moles/cu. metre)
- E activation energy (kilocalories/kg mol)
- ΔH heat of reaction (kilocalories/kg mol)
- k reaction rate constant (1/second)
- $\Delta \dot{Q}_R$ heat generation rate (kilocalories/second)
- $\Delta \dot{Q}_{RF}$ heat generation rate at the temperature of the wall
(kilocalories/second)
- $\Delta \dot{Q}_R^* = \Delta \dot{Q}_R / \Delta \dot{Q}_{RF}$ (dimensionless)
- r reaction rate (kg moles/cu. metre)
- R gas constant (kilocalories/kg mol $^{\circ}K$)
- \bar{t} mean residence time (second)
- T temperature ($^{\circ}K$)
- T_0 feed temperature ($^{\circ}K$)
- T_1 wall temperature ($^{\circ}K$)
- V_R reactor volume (cu. metre)
- x degree of conversion (dimensionless)
- v_i stoichiometric coefficient of the i-th component
(dimensionless)

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РЕЗЮМЕ

Неустойчивое поведение непостоянного типа больших химических реакторов является хорошо известным явлением. Как показывает практика, неустойчивость может быть довольно значительной и даже опасной, особенно в случае пуска или останова реактора. Часто замечали что у реакторов, работающих в режимах с высокой температурой и высокой степенью превращения, изменение скорости подачи вещества (V) концентрации (c_0) или температуры (T_0) приводило к неожиданному снижению температуры и конверсии. Наблюдается противоречивым тот факт, что незначительное изменение указанных параметров приводит к скачкообразному увеличению температуры и степени превращения. В практике об этом последнем явлении говорят, что реактор "загорелся", независимо от того действительно ли происходит горение или только неожиданный разогрев катализатора. В отличие от вышеописанного, авторы наблюдали и неоднократно воспроизвели при определенных критических параметрах такую неустойчивость, когда поведение реактора в определенных границах неожиданно изменялось, реактор осциллировал.

Обобщив результаты можно сказать, что существуют такие узкие неустойчивые условия работы реактора, которые нельзя описать уравнением теплового баланса системы.