Development and theoretical analysis of mathematical expressions for change of entropy for exothermic reactions in different reacting environments and conditions for minimization of energy losses in the process

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Abstract—This paper introduces a novel technique and algorithm for theoretical study of entropy changes for exothermic reactions by mechanistic modelling and dynamic simulation; considering factors such as kinetics, reaction environment and flow patterns with an ultimate objective of minimization of energy loss and entropy generation in the system. It mainly focuses on exothermic reactors cooled by means of a constant inlet temperature utility fluid which flows along the external surface of the reactor vessel. Using basic concepts of heat and mass balances and definitions in thermodynamics, variation of related system variables with time is modelled and by simulation in MS-Excel, a polynomial fit is generated for sample problems in order to make the illustrations handier. Usages of the developed expressions for energy optimization are also commented upon.

I. INTRODUCTION

In almost all process plants involving exothermic reactions and/or heat exchange, formation of energy cascades is gaining prominence owing to the increasing costs of energy and in order to minimize energy expenditures of the plant. Exergy available for a process can be most effectively used by selection of correct parameters for energy cascading. The values of thermodynamic variables also need to be chosen so as to optimize the performance of the cascade.

Quality of energy is often associated with amount of entropy generation associated with utilization of that energy. More the generation of entropy, lower is the grade of the energy for practical purposes [1]. Frequently it is observed in engineering systems that with time exergy degradation takes place leading to rise in entropy making some part of energy unavailable for practical use.

For chemical reactors incorporating exothermic reactions, the reactor is often jacketed and another fluid is made to flow through the jacket. The fluid gains heat from the outer surface of reactor and flows out. The heat gained by the utility fluid is used to heat other systems installed in the plant that require heating. The temperatures of the process fluid and the utility fluid are expected to have effect on the rate of degradation of available exergy. A reactor may be continuously operated or batch operated. The mode of operation may also affect the trends of availability of energy at a certain instant of time.

This paper aims at analysis of exergy degradation (i.e.) entropy generation as a function of time for different systems encountered in process plant design that make a certain amount of heat available to the external surface of the system by means of heat conduction. Further the focus is upon ideal utilization of the available energy for the different systems considered. Certain assumptions are made prior to the analysis which rarely poses a problem to practical feasibility of the generated expressions as far as chemical reactors are considered. They are:

1) Assume heat transfer by conduction to be the most dominant mode of heat transfer as compared to other modes and hence the other modes can be neglected.
2) Assume that entropy generation due to factors like turbulence, friction (internal factors) is negligible.
3) The insulation over the jacket of an exothermic reactor is a perfect insulator and isolates the system thermally from rest of the universe.
4) The reaction takes place in unit volume.

II. DEVELOPMENT OF MODELS FOR ENTROPY GENERATION

A. Development of expressions for entropy data for pure conduction heat transfer from heated surface:

Let us assume a hypothetical isolated system separated into two compartments by a conducting surface of mean surface area A, thickness x and thermal conductivity k. The left hand side of the surface is at a higher temperature (T_1) than the right hand side of the surface which is at temperature (T_2). Let us also assume that temperature is uniformly distributed at every thickness value x in the surface. Accordingly, multidimensional temperature gradients are eliminated.

Fourier's law for heat conduction is given as [2]:

$$\dot{Q} = -kA\frac{\Delta T}{\Delta x}$$

For an infinitesimal time interval, the equation can be written as:

For heat donating part of system,

$$\frac{dQ}{dt} = -kA\frac{dT}{dx} \tag{2.1}$$

As dQ =TdS [3]

$$\frac{T_1 dS_{donor}}{dt} = -kA\frac{dT}{dx} \tag{2.2}$$

Similarly, for heat gaining part of system

$$\frac{T_2 dS_{acceptor}}{dt} = kA\frac{dT}{dx} \tag{2.3}$$

Differentiating equation 2.2 with respect to time,

$$T_1\frac{d^2S_{donor}}{dt^2} + \frac{dS}{dt}\cdot\frac{dT_1}{dt} = -kA\frac{d^2T}{dx\cdot dt}$$

Similarly, differentiating equation 2.3 with respect to time,

$$T_2\frac{d^2S_{acceptor}}{dt^2}+\frac{dS}{dt}\cdot\frac{dT_2}{dt}=kA\frac{d^2T}{dx\cdot dt}$$
$$T_1\frac{d^2S_{donor}}{dt^2}=-kA\frac{d^2T}{dx\cdot dt}$$
$$T_2\frac{d^2S_{acceptor}}{dt^2}=kA\frac{d^2T}{dx\cdot dt}$$

Assuming $\frac{dS}{dt}\cdot\frac{dT}{dt}\ll T\frac{d^2S}{dt^2}$

$$\therefore \frac{d^2S_{donor}}{dt^2}+\frac{d^2S_{acceptor}}{dt^2}=\frac{d^2T}{dx\cdot dt}\left(\frac{kA}{T_2}-\frac{kA}{T_1}\right) \quad (2.4)$$

Usually, for conduction heat transfer, temperature varies almost linearly with thickness.

Let $\frac{dT}{dx}=\frac{T_1-T_2}{x}$ (2.5)

Substituting equation (2.5) in equation (2.4),

$$\frac{d^2S_{total}}{dt^2}=kA\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{d}{dt}\left(\frac{\Delta T}{x}\right)$$
$$\frac{d^2S_{total}}{dt^2}=kA\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{d}{dt}\left(\frac{T_1-T_2}{x}\right)$$
$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{d}{dt}(T_1-T_2)$$
$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_1}{dt}-\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_2}{dt} \quad (2.6)$$
$$\frac{dS}{dt}=\frac{dS_{donor}}{dt}+\frac{dS_{acceptor}}{dt}=-\frac{kA}{T_1}\frac{dT}{dx}+\frac{kA}{T_2}\frac{dT}{dx}$$
$$\frac{dS}{dt}=\frac{dT}{dx}\left(\frac{kA}{T_2}-\frac{kA}{T_1}\right) \quad (2.7)$$

For local minimization of entropy [4],

$$\frac{dS}{dt}=0,\frac{d^2S}{dt^2}>0$$

More positive is the value of d^2S/dt^2, less is the entropy generated. This will be practically feasible when terms on RHS give the most positive value. However T_1 is subject to decrease with time for no heat generation after t=0. Accordingly,

$$\frac{dT_1}{dt}\leq 0$$

On the other hand,

$$\frac{dT_2}{dt}\geq 0$$

For more positive value of d^2S/dt^2, both $\frac{dT_1}{dt}$ and $\frac{dT_2}{dt}$ should be as small as possible. This suggests constant temperature for utility stream.

B. Development of expressions for entropy data for constant T_2, decreasing T_1, and no heat generation in the system after t=0:

For varying T_1 and constant T_2, the modelled equation becomes:

$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_1}{dt}-\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\cancel{\frac{dT_2}{dt}}$$
$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_1}{dt} \quad (2.8)$$
$$\frac{dS}{dt}=k\cdot A\frac{(T_1-T_2)}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad (2.9)$$

For such a case, heat must be getting transferred from a high temperature 'body' to a low temperature 'reservoir'[4]. If m and c_p represent mass and specific heat capacity of the 'body', by first law of thermodynamics [5],

Heat lost by body = heat conducted by the wall

$$m\cdot c_p\cdot\frac{dT}{dt}=-kA\frac{\Delta T}{\Delta x}=kA\frac{T_1-T_2}{x}$$
$$T_{1(new)}=T_1-\frac{kA(T_1-T_2)}{m\cdot c_p\cdot x} \quad (2.10)$$

Where T_1 is initial temperature and T_{1new} is new temperature of the inner surface due to loss of heat to the surroundings by conduction in one iteration.

C. Development of expressions for entropy data; for constant T_2, decreasing T_1, for heat generation in the system after t=0:

This case is observed when rate of conduction of heat is greater than the rate of generation of heat. For exothermic reactors, generation of heat occurs by means of a chemical reaction. Hence few terms will get added to the original equation; due to generation of heat. Let r = rate of exothermic reaction taking place in the system (moles of reactant consumed/time)

Rate of generation of heat [6] =

$$\frac{dQ}{dt}=\dot{Q}_{gen}=r\times H_r$$

Rate of generation of entropy:

$$\frac{dS_{gen}}{dt}=\frac{r\times H_r}{T_1}$$

Assume first order reaction [7]

$$\frac{T_1d^2S_{gen}}{dt^2}\approx\frac{d}{dt}(H_r\times k_0)e^{-\frac{E}{RT_1}}C_A$$
$$\frac{d^2S_{gen}}{dt^2}=\frac{(H_r\cdot k_0)}{T_1}\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}C_A\right)$$
$$\frac{d^2S_{gen}}{dt^2}=\frac{(H_r\cdot k_0)}{T_1}\left[e^{-\frac{E}{RT_1}}\frac{dC_A}{dt}+C_A\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}\right)\right]$$

Rate of heat generation = Rate of enthalpy rise + Rate of heat conduction

$$r\times H_r=mc_p\frac{dT_1}{dt}+kA\frac{T_{1(lr)}-T_2}{x}$$

For a first order reaction,

$$(H_r\times k_0)e^{-\frac{E}{RT_{lr}}}C_A=mc_p\frac{dT_1}{dt}+kA\frac{T_{1(lr)}-T_2}{x}$$
$$\frac{dT_1}{dt}=\frac{(H_r\times k_0)e^{-\frac{E}{RT_{lr}}}C_A-kA\frac{T_{1(lr)}-T_2}{x}}{mc_p} \quad (2.11)$$
$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_1}{dt}+\frac{(H_r\cdot k_0)}{T_1}\left[e^{-\frac{E}{RT_1}}\frac{dC_A}{dt}+C_A\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}\right)\right] \quad (2.12)$$

From equation (2.11) and (2.12)

$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{(H_r\times k_0)e^{-\frac{E}{RT_{lr}}}C_A-kA\frac{T_{1(lr)}-T_2}{x}}{mc_p}+\frac{(H_r\cdot k_0)}{T_1}\left[e^{-\frac{E}{RT_1}}\frac{dC_A}{dt}+C_A\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}\right)\right] \quad (2.13)$$

Also,

$$\frac{dS}{dt}=k\cdot A\frac{(T_1-T_2)}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)+\frac{r\times H_r}{T_1} \quad (2.14)$$
$$(T_{1new})=\frac{(H_r\times k_0)e^{-\frac{E}{RT_1}}C_A-kA\frac{T_1-T_2}{x}}{mc_p}+T_1 \quad (2.15)$$

D. Development of expressions for entropy data; for constant T_1 and T_2, with heat generation in the system after t=0:

For this case, the equation,

$$\frac{d^2S_{total}}{dt^2}=\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_1}{dt}-\frac{kA}{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\frac{dT_2}{dt}$$

Reduces to

$$\left(\frac{T_1T_2}{T_1-T_2}\right)\cdot\frac{x}{kA}\frac{d^2S}{dt^2}=0 \quad (2.16)$$

For no heat generated in the system. This is possible only at thermal equilibrium, or when the two bodies exchanging heat are heat reservoirs [8]

Although above both possibilities exist; in chemical reactors, it is more probable that generation of heat takes place in the process fluid section and if rate of heat generated = rate of heat removed by conduction, a steady state non-changing temperature T_1 is obtained at the process fluid section. On the other hand, the heat is rejected to constant inlet temperature utility. In this case, the equation reduces as:

$$\frac{d^2S_{total}}{dt^2} = \frac{kA}{x}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\cancel{\frac{dT_1}{dt}} + \frac{(H_r \cdot k_0)}{T_1}\left[e^{-\frac{E}{RT_1}}\frac{dC_A}{dt} + C_A\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}\right)\right]$$

$$\frac{d^2S_{total}}{dt^2} = \frac{(H_r \cdot k_0)}{T_1}\left[e^{-\frac{E}{RT_1}}\frac{dC_A}{dt} + C_A\frac{d}{dt}\left(e^{-\frac{E}{RT_1}}\right)\right] \qquad (2.17)$$

On analyzing a process that could yield constant T_1, and T_2, considering same surface as that considered in previous sections, it is observed that if total amount of heat generated in the system is flown out of the system by conduction, T_1 remains constant. For T_2 to remain constant, continuous circulation of utility fluid is necessary.

Hence,

$$\dot{Q}_{conduction} = \dot{Q}_{generation}$$

$$(H_r \times k_0)e^{-\frac{E}{RT_{lr}}}C_A = mc_p\frac{dT_1}{dt} + kA\frac{T_1 - T_2}{x}$$

For $dT_1/dt = 0$

$$(H_r \times k_0)\, e^{-\frac{E}{RT_{lr}}}C_A = kA\frac{T_1 - T_2}{x}$$

Take natural logarithm on both sides,

$$\ln(H_r \times k_0C_A) - \frac{E}{R}\cdot\frac{1}{T_1} = \ln(kA/x) + \ln(T_1 - T_2)$$

$$\ln(T_1 - T_2) + \frac{E}{R}\cdot\frac{1}{T_1} = \ln(H_r \times k_0C_A) - \ln\left(\frac{kA}{x}\right) \qquad (2.18)$$

k, A, x, H_r, k_o , E, R being constants, we have to decide either of the variables (i.e.) T_1 or T_2

III. OBSERVATIONS FOR SAMPLE SYSTEMS

A. Analysis of expressions developed for entropy data for constant T_2, decreasing T_1, and no heat generation in the system after t=0:

Let us consider following sample problem [9]. (system) for effective production of the results of the theoretical experiments presented in previous section

"The inner and outer surfaces of a closed brick well of surface area 30m^2 and thickness 30 cm are maintained at temperatures of 20 ^{0}C and 5 ^{0}C respectively. For variable T_1 and constant T_2, we make following assumptions. Inner surface of wall gets heat from 100 kg of a process fluid of temperature independent specific heat capacity 1070 J/kg.^{0}C. Initial temperature at inner surface, as stated in the problem is 20 ^{0}C. Whereas the outer surface of the wall is exposed to a thermal reservoir at constant temperature 5 ^{0}C.There is no generation of heat in the process fluid compartment."

For this problem,

Heat lost by process fluid = Heat conducted by the wall

For the above problem,

$$T_{1(new)} = T_1 - \frac{0.69\times 30\times(T_1 - T_2)}{100\times 1060\times 0.3}$$

After 10000 such iterations, following type of profiles were obtained for dS/dt and d^2S/dt^2. Here each iteration can be considered to be equivalent to time as the iterations are done for processes that occur immediately one after the other in series.

Also, by substituting above obtained values for d/dt(dT/dx), we can easily obtain the value for d^2S/dt^2

The profiles obtained are as follows:

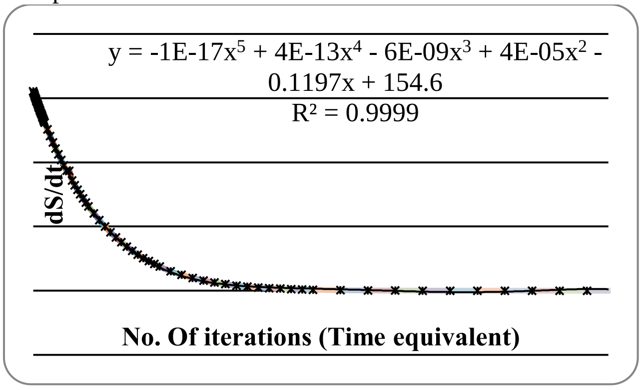

Fig. 1: Variation of dS/dt with time equivalent for (III-A)

The data plot fits the fourth order polynomial equation

$dS/dt = 4E\text{-}13t^4 - 6E\text{-}09t^3 + 4E\text{-}05t^2 - 0.119t + 154.6$

Which on integrating gives

$$\int_{S_{t=0}}^{S_{t=t}} dS = 8\times 10^{-14}t^5 - 1.5\times 10^{-9}t^4 + 1.33\times 10^{-5}t^3 + 0.0995t^2 + 154.6t$$

$$\Delta S = 8\times 10^{-14}t^5 - 1.5\times 10^{-9}t^4 + 1.33\times 10^{-5}t^3 + 0.0995t^2 + 154.6t$$

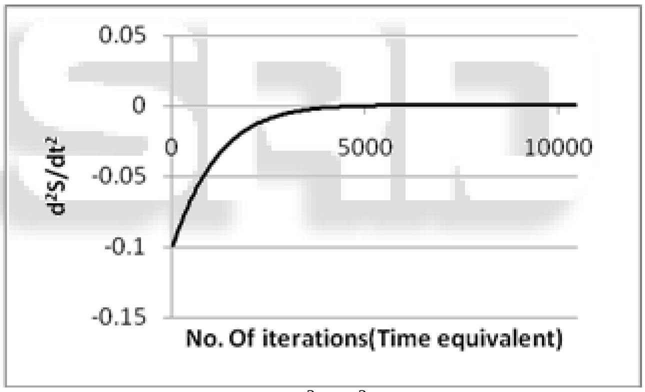

Fig. 2: A Variation in d^2S/dt^2 w.r.t. time for (III-A)

The graph below shows that the data fits a polynomial equation of order three

$$\frac{d^2S}{dt^2} = 6E\text{-}12t^3 - 3E\text{-}08t^2 + 8E\text{-}05t - 0.099$$

B. Analysis of expressions developed for entropy data for constant T_2, decreasing T_1 with heat generation in the system after t=0:

Let us assume the same problem that we have analyzed (in section II, A) with only one difference (i.e.) unlike in previous section, here we consider an exothermic reaction with slow rate going on in the brick well at the time of analysis. Let the reaction be decomposition [10] of N_2O to N_2 and O_2.

$$N_2O \longrightarrow N_2 + \frac{1}{2}O_2$$

If the reaction is assumed to be of first order, the rate of reaction can be written as:

$$r = 0.24813 \cdot \exp\left(-\frac{6893.74}{T}\right)\cdot C_{N_2O}$$

The system needs to be analyzed separately for high and low initial values of (T_1-T_2).

Case-1: $C_A \approx$ Constant, Low initial temperature differences

For a very low rate of reaction, C_A may be assumed to be unit concentration; constant for a definite interval of time.
Let T_1 = 300 K and T_2 = 270 K,
If the transient behaviour of the system is simulated using MS-Excel, following profiles are obtained

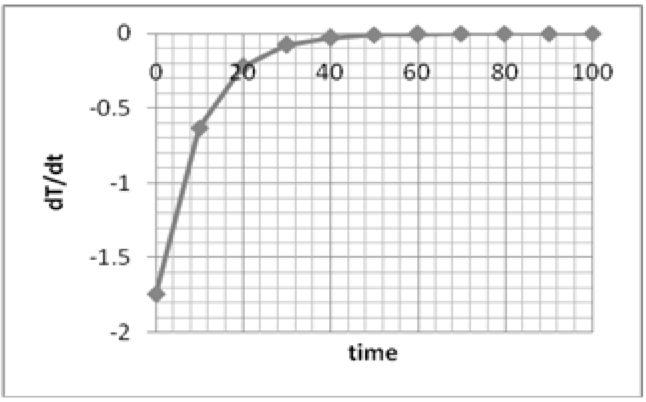

Fig. 3: Change in dT/dt with time equivalent for (III-B)

This data also fits a polynomial equation of order 5.

$\frac{dT}{dt}$= -3E-09t^5 + 8E-07t^4 - 1E-04t^3 + 0.005t^2 - 0.154t + 1.736

Graph for second order differential of entropy with respect to time can also be generated as shown below

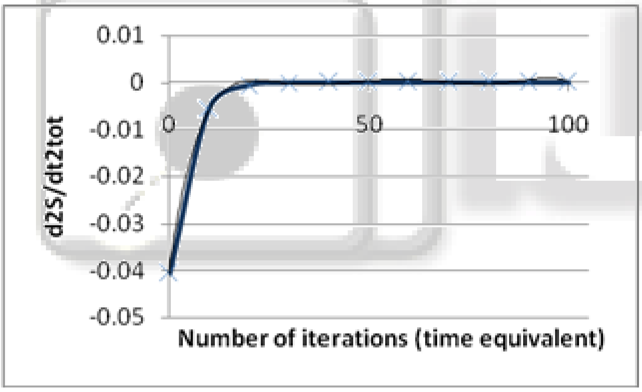

Fig. 4: Variation in d^2S/dt^2 w.r.t. time for (III-B, Case 1)

The analysis of data fits a polynomial equation of degree 6

$\frac{d^2S}{dt^2}$ = -3E-12t^6 + 1E-09t^5 - 1E-07t^4 + 1E-05t^3 - 0.000t^2 + 0.006t - 0.040

The rate of entropy generation can also be plotted as:

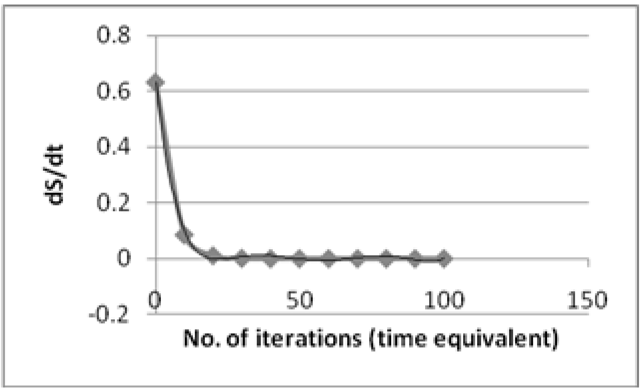

Fig. 5: Variation of dS/dt w.r.t. time equivalent, for (III-B, Case-1)

The polynomial equation that fits the observations is:
dS/dt = 5E-11t^6 - 2E-08t^5 + 2E-06t^4 - 0.000t^3 + 0.005t^2 - 0.094t + 0.630
Integrating gives,

$\Delta S = 7.143 \cdot 10^{-12}t^7 - 3.33 \cdot 10^{-9}t^6 + 10^{-5}t^5 + 1.667 \cdot 10^{-3}t^3 - 0.047t^2 + 0.63t$

The rate of generation of entropy as function of time equivalent (t) can be plotted from above equation.

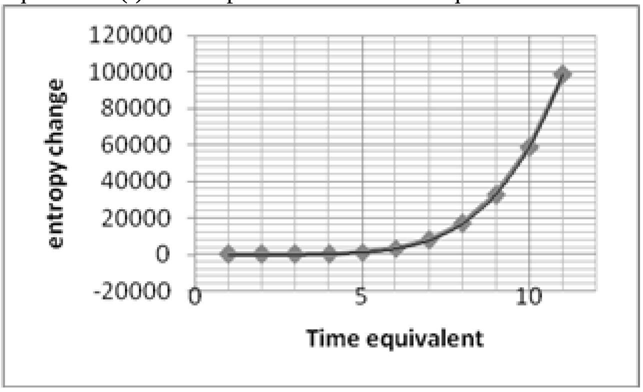

Fig. 6: Change in entropy with time equivalent, for (III-B, Case-1)

The data better fits a 4th order polynomial equation perfectly:

ΔS= 24.03t^4 - 302.1t^3 + 1491.t^2 - 3054.t + 1954

Case 2: $C_A \approx$ constant, Large initial (T_1-T_2)
Keeping all other parameters same, if the initial temperature of the system is maintained at 2000 K, following type of profile is obtained for the reaction:

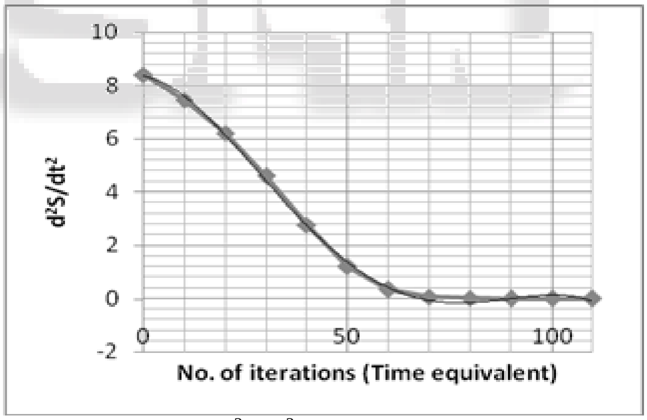

Fig. 7: Variation of d^2S/dt^2 w.r.t. time equivalent, for (III-B, Case-2)

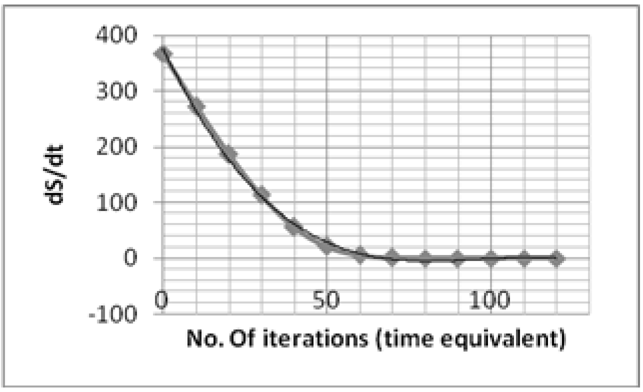

Fig. 8: Variation of dS/dt w.r.t. time equivalent, for (III-B, Case-2)

The polynomial equation that fits the observations is:

$$dS/dt = 0.130t^2 - 12.33t + 375.8$$

Integrating above expression gives

$$\Delta S = 0.0433t^3 - 6.615t^2 + 375.8t$$

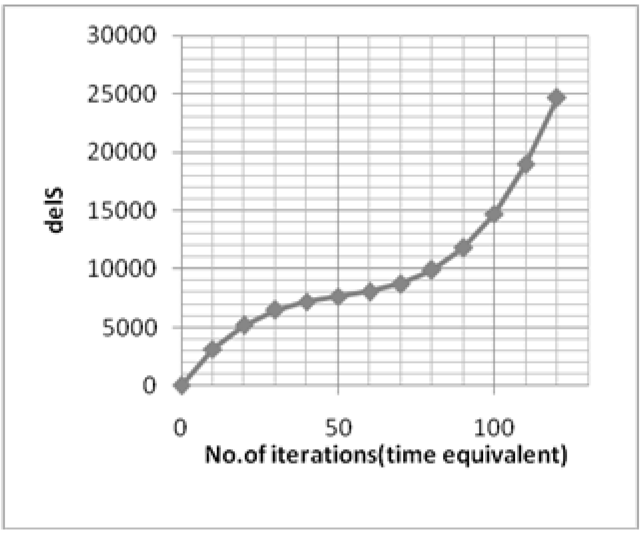

Fig. 9: Change in entropy with time equivalent, for (III-B, Case-2)

This gives plot of entropy generation as function of time equivalent (t).

C. Analysis of expressions for entropy data; for constant T_1 and T_2, with heat generation in the system after t=0:

Let us assume the same problem that we have analyzed (in section II-A) with only one difference (i.e.) unlike in that section, here we consider an exothermic reaction with slow rate going on in the brick well at the time of analysis. Let the reaction be decomposition of N_2O to N_2 and O_2. [11]

$$N_2O \longrightarrow N_2 + \frac{1}{2}O_2$$

If the reaction is assumed to be of first order, the rate of reaction can be written as:

$$r = 0.24813 \cdot \exp\left(-\frac{6893.74}{T}\right) \cdot C_{N_2O}$$

The variation of values of T_2 with values of T_1 for having constant values of T_1 and T_2 considering the problem of 'decomposition of N2O' is as follows:

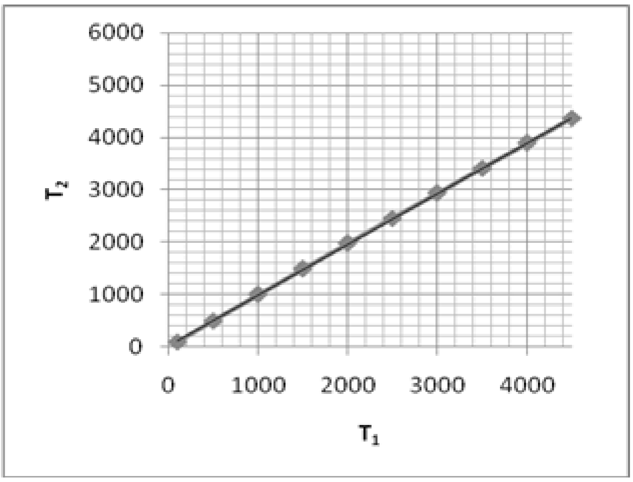

Fig. 10: Values of T_2 corresponding to values of T_1 for (III-C)

The plot follows a linear equation:

$$T_2 = 0.967T_1 + 28.02$$

Corresponding entropy change rates for universe and the surroundings are respectively plotted as function of T_1 as follow:

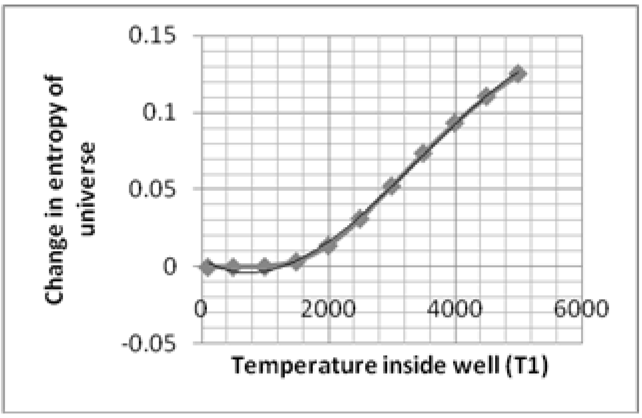

Fig. 11: Change in entropy of universe with T_1 for (III-C)

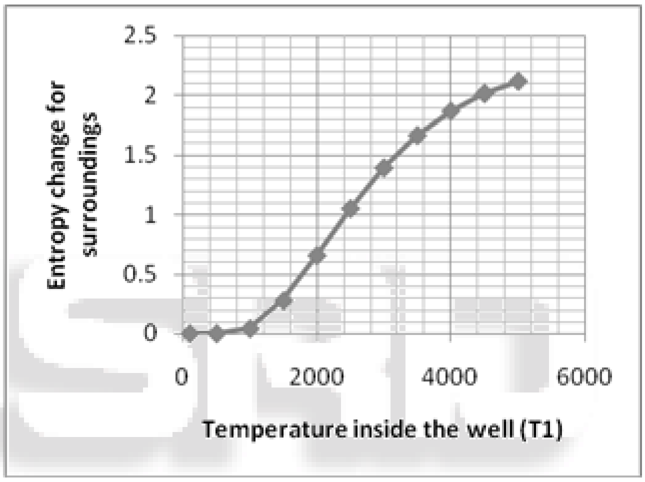

Fig. 12: Change in entropy of universe with T_1 for (III-C)

Note that we have not considered / analyzed any case where temperature of the process fluid side undergoing exothermic chemical reaction increases with time. Such process may take place if not all of the heat generated by exothermic reaction is removed by conduction. As rate of any general exothermic reaction decreases with increase in temperature [10], accumulation of heat in process fluid section may lead to decrease in rate of entropy generation in some cases, but at the cost of reduction in rate of reaction, which is not practically acceptable. Hence, the case needs to be discarded in material selection for conducting surface itself.

IV. RESULTS AND DISCUSSIONS

A. Development of an algorithm for entropy analysis of exothermic reactors:

In order to obtain the transient entropy changes in a system and accordingly to manipulate the variables in order to minimize the energy losses according to the technique used in section II, III, IV, hereby an algorithm can be proposed that suggests sequence of steps for how any system is to be analyzed for entropy change.

Step. 1 : Using energy balances and definitions in classical thermodynamics develop expressions for first and second order differentials of entropy with respect to time.

Step. 2 : Using heat balances, develop an expression for change in temperature of the system under observation with time.
Step. 3 : Feeding the initial conditions and process parameters to the expression developed in STEP 2, obtain new value for temperature attained by the system (For one iteration)
Step. 4 : At the new temperature attained, calculate values for entropy differentials from expressions developed in STEP 1.
Step. 5 : If no temperature gradient is left between system and surroundings, stop the calculation and go to next step. Else go to STEP 4.
Step. 6 : Plot entropy differentials with respect to time and obtain a polynomial fit for them. Integrating the first differential of entropy would produce data for actual entropy changes in the universe.
Step. 7 : Repeat the procedure for different values of variable parameters and obtain the most optimum set by trial and error method.

B. Proposing a suitable mechanism:

From the mathematical analysis of entropy for pure conductive heat transfer, in order to minimize entropy rise, we considered a constant temperature utility. However, this is possible if a huge amount of utility is used. In such case, a negligible rise in the utility temperature after heat transfer may cause the energy absorbed by utility to be significantly lost. Accordingly, a mechanism as follows can be suggested:

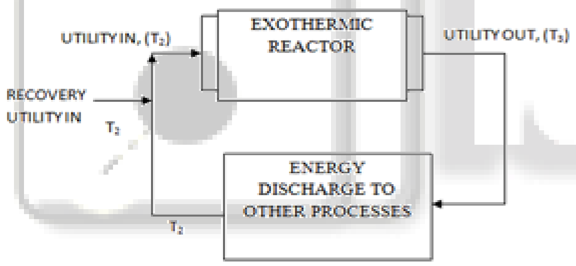

Fig. 13: Suitable mechanism for less energy losses from the process

The utility stream is made to enter the jacket of the reactor at say temperature T_2. The utility fluid gets heated due to heat of reaction and attains temperature T_3. The heated utility is circulated through rest of the plant for heat exchange (as heating fluid) in such a way that it again reaches the original temperature T_2. In such a way the temperature of contacting of the reactor surface and the utility fluid remains can be kept constant and accordingly, entropy losses can be minimized. The decision parameters that need to be optimally fixed in this case are- temperature of utility and flow rate of utility. However evaluation of these parameters is out of the scope of this paper.

C. Significance of the expressions developed for various cases:

The modelled expressions in section (II-B) are developed for constant T_2, decreasing T_1, assuming no heat generation in the system after t=0. In practical life, this situation is observed in case of instantaneous reactions and especially in case of exothermic batch reactors wherein conversion is rapid while removal of heat is gradual.

The modelled expressions in section (II-C) are developed for constant T_2, decreasing T_1 with continuous heat generation in the reactor system. This depicts moderate or low rate reactions taking place in the exothermic batch reactors with gradual heat removal arrangement.

Finally, expressions derived in section (II-D) represent reactions taking place in continuous reactors as, due to continuous flow of reactants and utility at definite inlet temperature, both $T_1$and T_2 remain constant. The choice is offered in temperatures $T_1$and T_2 case and no transient variation of entropy is plotted in this case owing to the constant entropy change with respect to time

D. Usage of the equations:

As mentioned before, this technique of entropy analysis is totally trial and error based. Accordingly, one can change the values of system variables (e.g. k, $T_{1(initial)}$,T_2, mass flow rates, etc.) and obtain different trends of entropy change with respect to time. Finally, the set of values that offer lower entropy change without altering the performance of the reactor in successfully carrying out the process reactions much, can be selected. Again the energy lost from reactor to the surrounding fluid can be calculated[3] by formula $Q = T_1 \Delta S$. The point at which Q starts falling to a negligible value, the circulation of utility can be stopped and the control of heating can be shifted to another utility section. For non-continuous processes (variable $T_1$and T_2), it should be suggested that two separate parallel utility systems should be used as far as possible (one-exothermic heat based and other operating with other source of sufficient exergy), and a control system should be adopted, sensitive to the heat output changes of the exothermic reaction such that only extra amount of heat needed be drawn from the external utility, the main source being the constant temperature utility used to cool the exothermic reactor.

LIST OF IMPORTANT SYMBOLS USED

TABLE-I

SYMBOL	UNITS	DESCRIPTION
T_1	K	Temperature of higher temperature section/process fluid
T_2	K	Temperature of lower temperature section/utility fluid
k	$J/m.^0K$	Thermal conductivity of the conducting surface
x	m	Thickness of conducting surface
A	m^2	Surface area of conducting surface
t	-	Time equivalent (No. of iterations)
Q	J	Amount of heat transferred
S	J/K	Amount of entropy
delS	J/K	Change in entropy
H_r	J/mol	Heat of exothermic reaction
m	kg	Mass of process fluid
c_p	J/kgK	Specific heat of process fluid
C_A	mol	Concentration of reactant in pure terms

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