THERMAL RUNAWAY PREVENTION IN CATALYTIC PACKED BED REACTOR BY SOLID TEMPERATURE MEASUREMENT AND CONTROL

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Abstract — Magnetic crystallite thermometry has been used to measure the average nickel crystallite temperature in packed bed reactors during ethane hydrogenolysis, an exothermic reaction. The technique is based on the temperature dependence of the magnetic moment of dispersed nickel catalysts. Measurement of the average catalyst temperature is very useful for reactor control because of its shorter time constant compared with exit fluid temperature. Bed temperature control based on the exit fluid temperature, which has often been used as a control variable, is too slow to protect thermal runaway of the bed. The advantage of short time constant by measuring the average catalyst temperature has been incorporated with enhanced feedback control system to control the bed temperature and prevent the thermal runaway of the catalyst bed. An enhanced feedback control structure with supervisory action performed better than the classical proportional-integral control in runaway prevention when the two control schemes were compared with each other on the basis of the trip-point (incipient thermal runaway).

INTRODUCTION

A common control practice for exothermic reaction in industrial catalytic packed bed reactor systems is to adjust the manipulated variable based on the exit fluid temperature rather than the solid phase temperature within the reactor [1]. This approach however may have a problem associated with time delay. The chemical reaction mostly takes place within the micropores of the catalyst, and thus the temperature at the reaction site is often significantly higher than that of the fluid [2, 3]. In an exothermic reaction, the fluid temperature changes with the solid temperature, and the heat transfer rate from the reaction site to the bulk fluid may be much slower than the local heat generation rate in the solid phase, which may result in a significant time delay in detecting the solid temperature change [5]. Therefore, the thermal runaway occurring in the catalyst may not be controlled instantly by measuring exit fluid temperature only [1, 4, 5]. It may well be too slow to protect against thermal runaway. In several industrial reactors, such solid temperature is sometimes high enough to deactivate the

catalyst and/or cause structural damage to the reactor [1, 6, 7]. Therefore, to protect against those thermal runaway problems, conservative and suboptimal control strategies are currently used [2, 8, 9], and one may adopt an operation within some safe temperature range. However, the important thing to be borne in chemical engineer's mind is to operate the catalytic packed bed reactor at as high a production rate as possible, while ensuring that thermal runaway does not occur.

Reactor control based on solid temperature measurement can provide advantages over that based on exit fluid temperature. The bed temperature behavior can be detected early by measuring the solid temperature, provided that a thermometric method is available. This early detection of the bed temperature behavior may prevent the thermal runaway of the packed bed reactor [5]. The measurement technique for the determination of the solid phase temperature has been demonstrated by Cale [10] in his exothermic ethane hydrogenolysis reaction system over Ni/SiO$_2$ catalysts. The purpose of this paper is to demonstrate the usefulness of the solid temperature measurement in a thermal runaway protection for a packed bed reactor. Though the presence of sensor drift in the solid temperature measurement brings about some trou-

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bles, the solid temperature measurement which is used in an enhanced feedback control scheme with supervisory action accounts well for the sensor drift at steady state. The benefit of knowing solid temperature is shown by comparing the enhanced feedback control scheme to a single-input single-output proportional integral (SISO PI) control scheme. The results are applicable to any method for measuring solid temperature.

THEORETICAL BACKGROUND

When an exothermic reaction, e.g., ethane hydrogenolysis, occurs in a catalytic packed bed reactor, the axial temperature profiles of solid phase and fluid phase at steady state are often characterized by a peak temperature [2, 4, 12]. For certain operating conditions, the peak temperature may become very sensitive to the inlet conditions, e.g., flow rates, concentrations, temperature, etc. [6, 7], or to the changes in the heat generation or transfer rates in the reactor [4, 13]. If it is not controlled properly, the bed temperature may rise in an uncontrolled way. Such a phenomenon is called thermal runaway [14]. The thermal runaway may result in the catalyst deactivation or low productivity, in the ruptures of reactor tubes, and in the release of toxic spills and explosive vapors [6, 7, 12, 13]. Nevertheless, the packed bed reactor is often operated near a parametric sensitive region due to an economic benefit. Therfore, it is very important to provide a method for preventing the thermal runaway.

Several methods have been used to prevent the thermal runaway: (1) Theoretical approaches have been developed on the basis of reactor models to find the runaway criteria or diagrams [4, 6, 7]. (2) The runaway criteria from the theoretical approaches have been experimentally identified to examine their reliability [12]. (3) Potential runaway risk can be assessed by runaway scenario and risk evaluations [13]. (4) The runaway can be handled by stoppage of manipulated variables [1] or feeding a fraction of the reactants at an intermediate point along the reactor [9]. The purpose of methods (1), (2), and (3) is to operate the reactor at a stable region by avoiding the runaway conditions determined from the runaway criteria or diagrams. Whereas, method (4) is the conservative approach often used in industry.

A catalytic packed bed reactor can have thermal runaway state in solid phase only even though the fluid temperature is not in the runaway state. This phenomenon is called local runaway, in comparison with the global runaway which occurs in whole heterogeneous reactor [4, 7]. The local runaway is caused by the time delay in heat transfer between the two-phase temperatures [4]. Therefore, the control of fluid temperature alone may not prevent thermal runaway of the solid phase [1, 5]. The solid phase temperature is an important variable to be controlled in heterogeneous reactors because it governs the reaction rate and selectivity as well as any change in catalyst activity [4]. However, no proper method for measuring the solid temperature has been available until Cale [10] used a magnetic crystallite thermometry.

The magnetic thermometry based on the temperature dependence of the superparamagnetic properties of dispersed nickel crystallites has been used to determine the average crystallite temperature of supported nickel catalysts during ethane hydrogenolysis [10]. Cale [10] used an ac permeameter (ACP) to determine the low field sample moment (M_s) which is a function of temperature (T_{ca}). He showed that the net output voltage of the ACP varies linearly with the sample magnetic moment within it.

$$E_s = E_t - E_o = c \ M_s(T_{ca}) \tag{1}$$

Eq. (1) leads to the relation of the output voltage of the ACP to the average sample temperature. Instead of measuring total sample moment, only the change in sample moment is measured to minimize the background subtraction. From the change in sample moment, the crystallite temperature change is determined by a temperature calibration which provides a sensitivity ($\mu V/K$) for the sample. Thus, the average solid phase temperature is determined from changes in ACP voltage. The thermometric method is described in detail in the literature [10, 11]. The method is also used to prevent the thermal runaway within the solid phase by measuring and controlling the average soid phase temperature [5].

EXPERIMENTAL

ACP is composed of a primary coil surrounding two secondary coils [10]. The coils are placed in an oven which is operated at ca. 510 K. A schematic of the ACP is shown in Figure 1. The ACP and the peripheral devices for the ACP have been discussed in the literature [10, 11, 15]. All the experiments are performed at a poor adiabatic condition. The poor adiabatic condition means a possible allowance of the heat transfer from the catalyst bed to the ACP. This is due to a poor vaccum shield between the ACP and the catalyst bed.
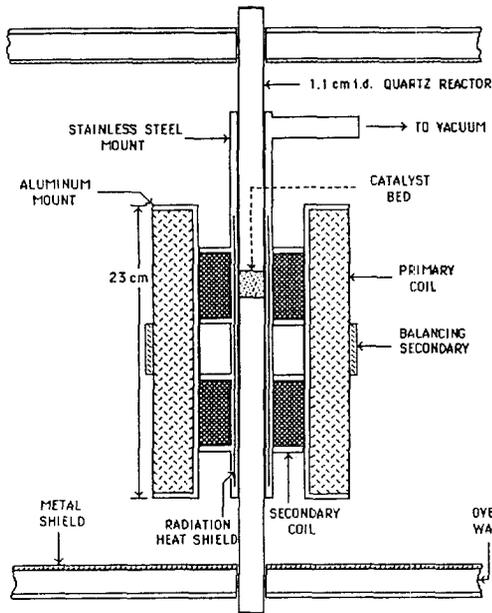
Fig. 1. AC permeameter.

As shown in Figure 2, the reactants, ethane and hydrogen, and the diluent, helium, enter the quartz reactor after being purified. Reactor is packed with a supported nickel catalyst for ethane hydrogenolysis. A personal computer (PC) controls and communicates with peripheral devices. The peripherals are directly connected to the several measuring sensors. The exit fluid temperature is measured by the thermocouple at the exit of the packed bed. One may realize the difficulty of installing a measuring device in the mid-point of the short length of bed. It might be effective if the mid-point temperature could be measured. The solid phase temperature is determined by measuring the output voltage of ACP via a lock-in amplifier. The ethane flow rate during control run is measured by a Tylan mass flow controller. A control program handles all the data logging and control implementation. Details of control program and process PC interfacing are provided by Cho [5].

Figure 3 shows a block diagram of enhanced feedback control (EFC) for the packed bed reactor used in this study [5]. The diagram shows two feedback
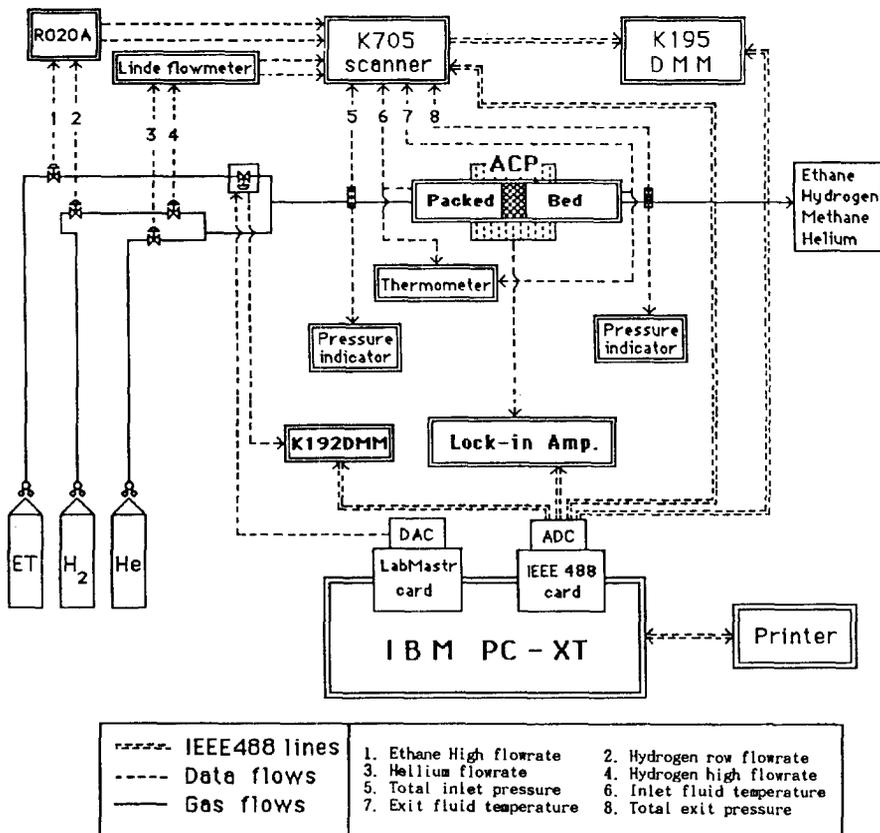

Fig. 2. Schematic of packed bed reactor and control elements.

PERSONAL COMPUTER
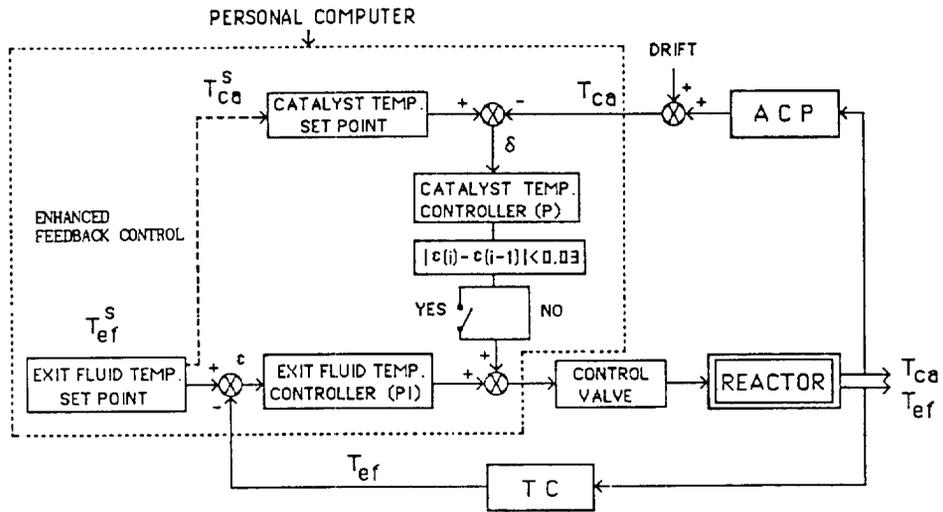
Fig. 3. A block diagram of enhanced feedback control for packed bed reactor.

control loops. One loop which is composed of a PI controller and a thermocouple sensor controls the bed temperature based only on the exit fluid temperature (T_e). The other loop which is composed of a P controller and the ACP sensor controls the bed temperature based on the average solid temperature (T_{ca}). The above two loops are used for an EFC scheme, whereas the loop with a PI controller is used as a reference for comparing purpose with the EFC. Comparison is performed on the basis of the trip-point (incipient thermal runaway) when the SISO PI and EFC schemes are used for runaway protection. The velocity form of a PI control algorithm [16] for this study is

$$C_1(k) = C_1(k-1) + K_c[\varepsilon(k) - \varepsilon(k-1) + (T_s/\tau_i)\ \varepsilon(k)] \quad (2)$$

and the velocity form of a P control algorithm is

$$C_2(k) = C_2(k-1) + K_{rp}[\delta(k) - \delta(k-1)] \quad (3)$$

$C_1(k)$ in Eq. (2) represents a control command for the SISO PI control, but adding Eq. (2) and (3) gives an enhanced feedback control command

$$C(k) = C_1(k) + C_2(k) \quad (4)$$

These control algorithms are used for the SISO PI and EFC controls. The manipulated variable for both control cases is ethane flowrate. A limiter on the ethane flowrate is installed in the control program to prevent the quartz reactor from being ruptured by thermal runaway.

Process dynamics are identified by performing an open-loop step response test with a first-order plus dead time (FOPDT) model. The step response test
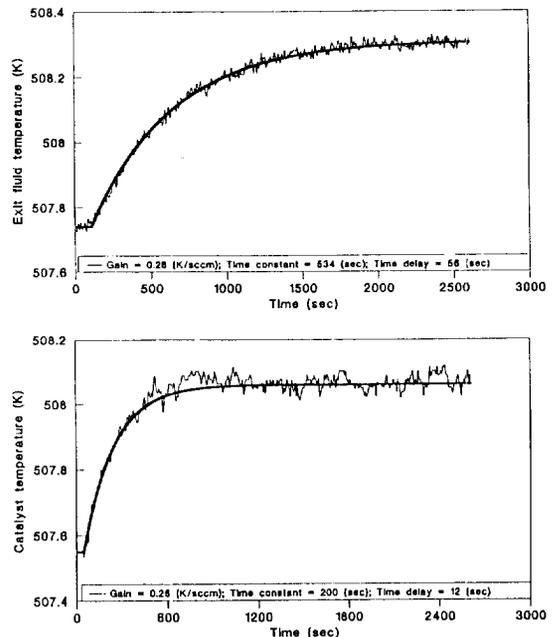
Fig. 4. First order plus delay time model fit to open-loop step response data.

is to obtain the response curves of the bed temperatures to a step change in ethane flow rate. Response curves of both exit fluid temperature and solid temperature and solid temperature are shown in Figure 4. Process model parameters are estimated by fitting the model to the response data, and are represented in the legend of Figure 4. The parameters of the SISO

PI controller are set with the process model parameters and with the integral of the time-weighted absolute error (ITAE) tuning relation for set-point change. The parameters of the PI and the P controllers in the EFC are tuned by comparing the simulation and experimental results [5]. These two controllers are designed to have sufficient safety margins at an early step of initiation. Procedures for the identification of process dynamics and controller design are described in detail in the literature [5].

The ACP output voltage has a drift component, which may be originated from the resistance change of ACP secondary coils due to the heat transfer from the bed to the ACP during exothermic reaction. Since the drift is low frequency noise, it cannot be separated from voltage signal. Also, the drift changes reluctantly with time and operating conditions. So, it is hard to predict the behavior exactly. Therefore, it is calibrated using a slope of the ACP output voltage vs. time in the process dynamics identification experiments. The effect of the ACP drift on the controlled output is removed using the EFC accounting for the ACP drift at the steady state (EFCAD). The EFCAD is accomplished by making the control command from the P control loop zero when the error difference $[\varepsilon(k) - \varepsilon(k-1)]$ in Eq. (3) is less than a specified value. When the value is 0.03, the effect of the drift removal was excellent for this experimental system [5].

Thermal runaway tests are performed as follows: Initially the packed bed reactor is under a steady state operating condition, where the exit fluid temperature of the reactor is controlled at 508 K. The exit fluid temperature is increased step by step by increasing the set-point of the exit fluid temperature. The step size is 1 K. The set-point is changed every 2000 second except the first 1000 second until a thermal runaway occurs.

RESULTS AND DISCUSSION

Figure 5 shows typical transient curves of average solid (catalyst) and exit fluid temperatures during a thermal runaway. The response time of the bed average solid temperature is much shorter than that of the exist fluid temperature. This is due to the shorter time constant and delay time of the solid temperature than those of the exit fluid temperature. As shown in Figure 4, the time constant of the exit fluid temperature is 534 second while that of the solid temperature is 200 second. The shorter response time means that the thermal behavior of the bed during the runaway can be detected early and controlled faster. The
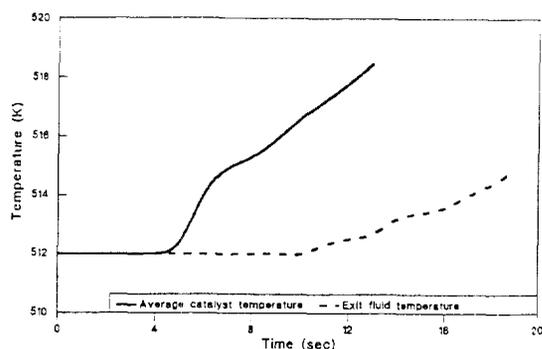

Fig. 5. Typical transient curves of average solid and exit fluid temperatures during thermal runaway.
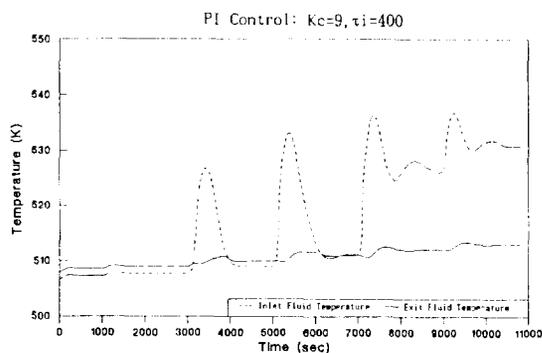

Fig. 6. Thermal runaway protection by PI control; dotted and solid lines show inlet fluid and outlet fluid temperatures respectively.

higher peak which appears at the beginning of the transient state and often leads to the thermal runaway could be reduced using the enhanced feedback controller. This can be accomplished by instantly detecting the control error at the transient state with the ACP and then reducing the error by the P action of the enhanced feedback controller.

The results of the thermal runaway experiments are represented in Figures 6 and 7 for a PI controller and the EFCAD, respectively. As shown in Figure 6, the first thermal runaway occurs at 3000 second, when the set-point of the exit fluid temperature is changed from 509 to 510 K. Meanwhile, using the EFCAD shown in Figure 7, the first thermal runaway occurs at 7000 second, where the set-point change is from 511 to 512 K. The appearance of sequential runaway peaks is due to the installation of a limiter.

As these figures show, though the exit fluid temperature is being controlled at a given set-point, the inlet fluid temperature indicates the reactor under thermal
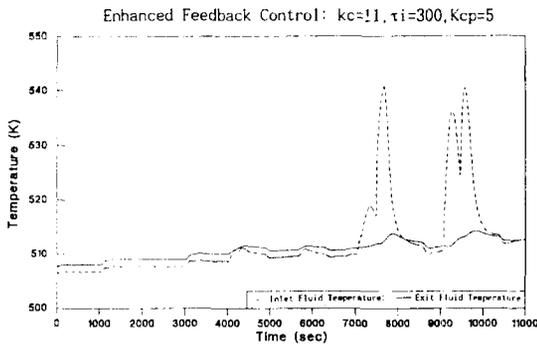
Fig. 7. Thermal runaway protection by enhanced feedback
control; dotted and solid lines show inlet fluid and
outlet fluid temperatures respectively.

Fig. 8. Typical cross-sectional average temperature pro-
files of average solid and fluid temperatures by sim-
ulation.

runaway. It is easily understood that for this type of catalytic reactors, most reaction occurs in the front part of the bed. Composition analysis of the exit fluid showed complete (100%) conversion. At the rear part of the bed, almost no reaction occurs and the exit fluid temperature can actually be reduced at the threshold of the local runaway. This phenomenon may be due to the followings: (1) When the process is in the parameter sensitive state (catalyst temperature vs. ethane flow rate), a positive change of set-point drives the ethane flow rate to increase and thus increases catalyst temperature in the front part of the bed, where the reaction heat is produced. (2) A large percentage of the sensible heat generated by reaction at the bed inlet is lost through the reactor wall when the reactor is not being run in adiabatic condition. (3) No reaction occurs at the rear part of the bed because the reactant, ethane, is completely consumed in the front part of the bed. Therefore, the fluid temperature as well as solid phase temperature is relatively low at the rear part of the bed because the heat in the rear part of the bed is mainly transferred from the front part of the bed through fluid flow.

Figure 8 shows the simulation results of the typical axial profiles of cross-sectional average solid temperature rise and fluid temperature rise when ethane is completely converted in the front part of the bed. The condition for the runaway simulation is not exactly same as the experimental conditions, but in this paper it would be enough to show the system has the same feature of profiles [17]. In Figure 8, the cross-sectional average solid temperature is significantly higher than the fluid temperature at the front part of the bed. Both the experimental data and simulation results show that the catalyst temperature at the front part of the bed is certainly in a runaway state when
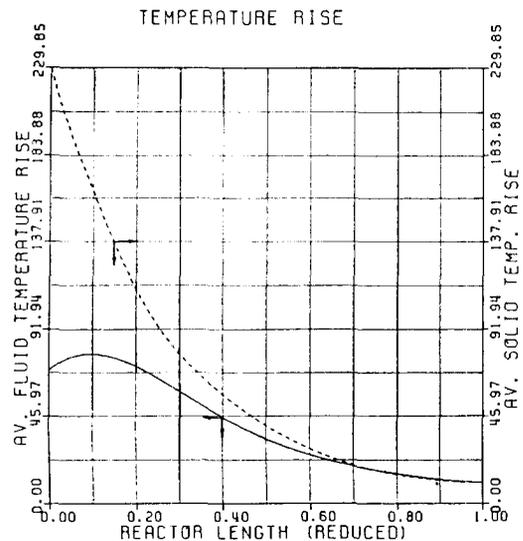
we experience thermal runaway in fluid temperature.

Although both fluid and solid temperatures at the front part of the bed increase with reaction, the temperatures in the rear part of the bed do not rise so much because no reaction occurs in the rear bed and the fluid loses heat to the solid part and surroundings as it flows to the rear part of the bed. Thus, the bed average solid temperature or the temperature in the middle position of the bed does not increase proportionately with the bed temperature even in thermal runaway state. This is the reason why the inlet fluid temperature is used for the comparison of runaway control scheme tests instead of the average solid temperature or exit fluid temperature. Runaway in the front part of the bed increases ethane flow rate by the action of a PI controller because the PI control is based on the exit fluid temperature. Therefore, any decrease in exit fluid temperature may accelerate the thermal runaway until the exit fluid temperature starts to increase.

Heat produced in the front part of the bed transfers to the rear part of the bed via the fluid flow. Thus, the exit fluid temperature changes by axial heat flow. As the exit fluid temperature rises above set-point, the ethane flow rate is reduced by the action of the controllers. Furthermore, the catalyst and inlet fluid temperatures decrease, as shown in Figures 6 and 7. At this time the reaction may occur over the whole bed, but the conversion decreases. The temperature returns to set-point condition.

Figure 7 represents the same situation as Figure 6 except that the incipient thermal runaway occurs at 7000 second. The trip-point (incipient thermal runaway) determined from these figures is 2 K apart from the initial steady state when the PI controller is used and 4 K apart from the initial steady state when the EFCAD is used. From the above comparison, the EFCAD using ACP is better than the SISO PI control in preventing thermal runaway. Even the enhanced feedback control however could not prevent the runaway completely. It only extended the trip-point by 2 K when compared with a PI control. This means that the EFCAD also has a limitation because though its response time is shorter than the conventional PI controller but still longer than that of the ideal response controller which has no time lag.

The enhanced feedback control technique with an ACP sensor can be potentially applied for controlling the hot spot temperature of long packed bed reactors and also for the temperature control of automobile catalytic converter and porous radiant burner [5]. As a construction material for the above reactors, stainless steels or aluminum can be used because it is scarcely magnetized in magnetic field.

CONCLUSION

A magnetic crystallite thermometry based on the temperature dependence of magnetic moment of the supported nickel catalysts has been successfully implemented in helping prevent the thermal runaway occurring within the catalysts by measuring the average solid temperature in a packed bed reactor. The bed temperature control scheme with average solid temperature provides advantages over the scheme with exit fluid temperature only because the former can detect early the thermal behavior of the bed and prevent effectively thermal runaway. It is proved that the enhanced feedback control using average solid temperature is better than the classical PI control using exit fluid temperature only when the two control schemes are compared with each other on the basis of incipient thermal runaway.

ACKNOWLEDGEMENT

NOMENCLATURE

c : empirical calibration constant $[mV/Oe \cdot cm^3]$
$C(k)$: output vector of enhanced feedback controller
$C_1(k)$: output vector of PI controller
$C_2(k)$: output vector of P controller
E_t : total output voltage of ACP $[mV]$
E_s : ACP output voltage due to the sample $[mV]$
E_o : ACP output voltage without sample $[mV]$
K : proportional gain of PI controller
K_p : proportional gain of P controller
M_s : low field magnetic sample moment $[Oe]$
T_s : sample time $[sec]$
T_f : exit fluid temperature $[K]$
T_{ss} : average solid temperature $[K]$

Greek Letters

$\varepsilon(k)$: control error; set point value of T_f-measured value of T_f $[K]$
$\delta(k)$: control error; set point value of T_{ss}-measured value of T_{ss} $[K]$
τ_i : integral time constant of PI controller $[sec]$

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