

A NEW APPLICATION OF FLUIDIZED BEDS AS THE COOLING MEDIUM FOR EXOTHERMIC CATALYTIC OXIDATION OCCURRING INSIDE A MULTITUBULAR REACTOR

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Introduction

Fluidized Beds with immersed heat-transfer tubes take advantage of the uniformity of bed temperature and of the high rate of heat transfer between immersed tubes and the bed. Particularly, in the case of vertical tubes the rate of heat transfer is the same all around the perimeter. This characteristic increases the range of application of vertical tubes in chemical reactor design such as for the heat carriers of a tubular reactor⁸⁾.

Studies related to heat transfer between vertical tubes and bed have been reviewed by Gelperin and Einshtein²⁾ and by Botterii¹⁾. Afterwards, new evidence has appeared in the literature^{3,4)}. However, there has been little evidence to advance the practical design of vertical-tube reactors.

The present work is concerned with a new application of fluidized beds. Such a bed containing 333 vertical tubes was designed on the basis of our previous work⁶⁾ and was then built as a commercial plant. In this plant, the fluidized bed was used as a cooling device for the exothermic catalytic oxidation of *p*-methoxytoluene (PMT) to *p*-anisaldehyde (AA) occurring inside the tubes.

In this paper, the heat transfer between vertical tubes and bed is discussed, and the erosive wear of this plant with fluidizing solid particles is elucidated.

1. Experimental

1.1 Apparatus and particles

A sketch of the multitubular reactor, made of stainless steel (304), is shown in **Fig. 1**. The fluidized-bed column had a bed height of 1.8 m, an inside diameter of 1.35 m and a column thickness of 6 mm. The number of vertical tubes was 333. The outside diameter of each tube was 34 mm and the wall thickness was 2.8 mm. The tubes were arranged on a rectangular pitch on 60-mm centers. The gas distributor consisted of a layer of 100-mesh wire cloth sandwiched between two perforated plates with 332 holes of 3 mm diameter, with an open

area of 0.21%.

The fluidized bed was filled with granular alumina particles to a fixed depth of 0.9 m. The particle properties are listed in Table 1, where the incipient fluidizing velocity was observed by measuring pressure drops at $T_f = 733$ K.

The charge of active catalyst⁵⁾ was 0.56 kg per tube, and the active catalyst was sandwiched between two inert packing layers.

1.2 Operations

Bed temperatures were measured with thermocouples at four selected positions. The temperatures inside tubes were measured only in three tubes (A,B,C), which were at various distances from the center of the fluidized bed as shown in **Fig. 1**. Each of the three tubes had a stainless pipe of 4 mm outside diameter attached in its vertical center line, in which a narrow thermocouple was inserted to measure the axial temperature profile by motion up and down.

Operations were carried out as follows.

1) The bed was heated with hot air of 743 to 763 K at which $u_o = 0.17$ to 0.24 m/s.

2) When the bed approached a definite temperature (730 to 736 K), air containing *p*-methoxytoluene (PMT) of 0.73 vol% was fed into the tubes at a total flow rate of 0.96 kg/(m²s)⁷⁾.

3) When the bed was raised over the definite temperature by heat generation from the catalytic oxidation shown in **Fig. 2**⁷⁾, cold air of 500 to 620 K was fed into the bed to reduce the temperature.

The bed was kept at the definite temperature with an accuracy of ± 0.5 K by switching hot or cold air according to the ON-OFF temperature controller.

Since there was no change in catalyst activity after 10 days' operation, that is, a steady state was reached⁷⁾, the axial temperature profiles of tubes A, B and C were measured. In addition, the reactant gas was led to two gas chromatographs directly at high temperature, at which PMT and AA (*p*-anisaldehyde) in reactant gas were analyzed using a DC-550 column, while CO₂ (carbon dioxide) was analyzed in an activated carbon column.

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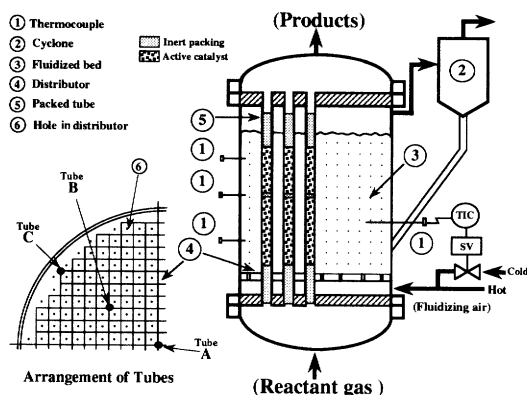


Fig. 1 Sketch of multitubular reactor with vertical tubes

Table 1. Properties of solid particles.

| | |
|--|--|
| Incipient fluidizing velocity | $= 9 \times 10^{-3}$ m/s (at 733 K) |
| Bulk density | $= 800$ kg/m ³ |
| Average diameter | $= 157$ μ m |
| Voidage at incipient fluidizing velocity | $= 0.44$ |

2. Heat and Material Balances

In our previous work⁽⁶⁾ we showed that the radial variations of temperature inside the tube were very small and that a one-dimensional packed-bed model can be used.

Assuming that the heat transfer resistance between the solid particles and air within the bed is ignored, the heat and material balances on reactant gas can be written by Eqs.(1)-(5) at steady state.

a) Heat balance on reactant gas

$$G C_{pg} (dT_g/dZ) = 4U (T_f - T_g) / d - \sum_i r_i \Delta H_i \quad (1)$$

b) Material balance on reactant gas

$$-u_{or} (dy_p/dZ) = (k_1 + k_2 + k_3) y_p \quad (\text{PMT disappearance}) \quad (2)$$

$$u_{or} (dy_A/dZ) = k_1 y_p - k_3 y_A \quad (\text{AA formation}) \quad (3)$$

$$u_{or} (dy_c/dZ) = k_2 y_p + k_3 y_A \quad (\text{CO}_2 \text{ formation}) \quad (4)$$

$$\text{at } Z = 0, y_p = 1.0 \quad y_A = y_c = 0 \quad (5)$$

On the other hand, the heat balance on solid particles in the fluidized bed can be written by Eq.(6) at steady state.

$$UA(\bar{T}_g - T_f) + f C_{pa}(T_{in} - T_f) - H = 0 \quad (6)$$

where

$$\bar{T}_g = (1/L_f) \int_0^{L_f} T_g dZ \quad (7)$$

H is the heat loss from the reactor.

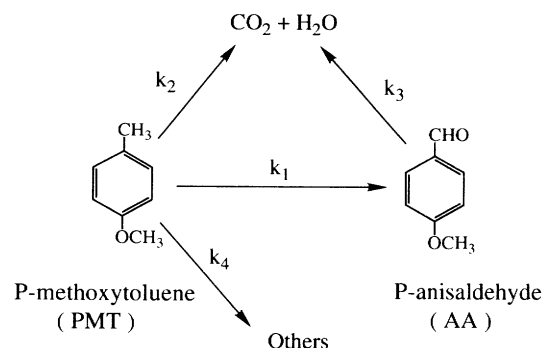


Fig. 2 Reaction scheme for oxidation of PMT to AA

3. Results and Discussion

3.1 Effect of air velocity at fluidizing condition (u_o) on flow regimes

When u_o was changed, three flow regimes --imperfect mixing, perfect mixing and slugging-- were observed. We considered that the bed was in perfect mixing when the four thermocouples inserted in the bed showed the same temperature with an accuracy of ± 1.0 K. Consequently, when u_o was higher than 0.14 m/s and lower than 0.40 m/s at which $T_f = 730$ to 736 K, perfect mixing of solid particles was obtained. When u_o was higher than 0.40 m/s, solid particles were carried out of the bed and slight oscillation of the bed took place. This behavior was the same as that in our small-scale 52-tube reactor⁽⁶⁾.

3.2 Estimation of overall heat transfer coefficient (U)

Whenever we renewed the catalyst, eight times throughout the four-year-operation, we measured the axial temperatures of tubes A, B and C, along with the product distribution at steady state. Finally, we obtained eight sets of axial temperature profiles and their product distribution at the exit of the reactor.

An example of the eight sets is shown in Figs. 3 and 4 where the solid lines show the calculated values obtained from Eqs.(1) to (5). As is obvious from Fig. 3, the observed temperature profiles of tubes A and B deviated from the calculated ones with higher axial distance. Although differences in three axial temperature profiles were also observed in the other seven sets, there was no relationship among these eight sets of temperature profiles. This is due to the slight variation in each pressure drop in the 333 packed tubes because of the difficulty in adjusting each pressure drop to the same value precisely. According to the calculation of Eqs.(1) to (5), the temperature profiles of tubes A and B in Fig. 3 can be explained by a 15 to 20% increase in the flow rate of reactant gas. On the other hand, the observed values of PMT, AA and CO₂ at the reactor exit agreed fairly well with the calculated ones, as shown in Fig. 4.

Furthermore, although we tried to examine the difference in heat transfer in the radial direction of the bed by using three axial temperature profiles of tubes A, B and C, our experimental accuracy was not satisfactory. However, we can at least say that the difference is little if

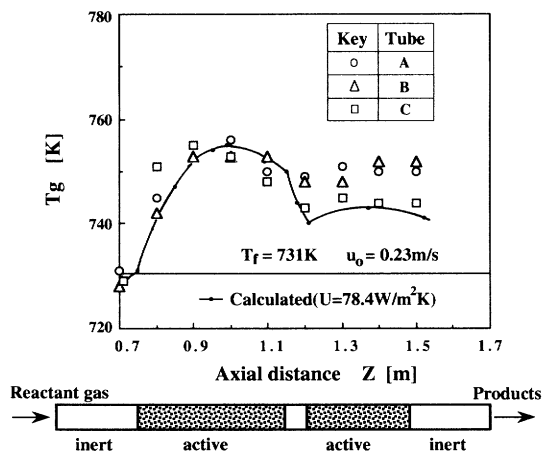


Fig. 3 An example of axial temperature profiles of tubes A, B and C

any.

To evaluate the value of the overall heat transfer coefficient (U), the axial temperature profiles of the eight sets and the many other temperature profiles which were obtained by the change in u_o were analyzed by solving Eqs.(1) to (5) according to a non-linear least-square method. Consequently, the values of U tended to increase gradually with increasing u_o , and the measured value of U was 63-92 W/m²K at values of u_o = 0.17-0.24 m/s.

Furthermore, to evaluate the heat absorbed by the fluidized particles, Eq.(6) was solved in the range from $Z = 0.75$ m to $Z = 1.48$ m as shown in Fig.3, together with Eqs.(1) to (5) with the assumption of heat loss (H) being zero. The first term on the left-hand side of Eq.(6) is the heat absorbed by the solid particles. Its value in the range described above was about 81% of the total reaction heat at the operating condition shown in Fig. 3. This shows that the heat removal by the fluidized bed has high efficiency and that application of the fluidized bed would can be expanded to various chemical reactors with heating or removal.

3.3 Erosive wear

The multitubular reactor was dismantled after operating four years (about 29,500 hrs) and the erosive wear of some parts was studied. In tubes A and C and the fluidized column, no erosive wear was found. In the protective pipes of the thermocouple horizontally inserted in the bed, the bottom of the pipes which directly contacted upward fluidizing particles was slightly polished, though their diameter was the same as that at the time of first installation. It may therefore be considered that the operating life of the multitubular reactor would be almost infinite at u_o = 0.17 to 0.24 m/s, if reactor damage is limited to erosive wear.

Conclusions

A fluidized bed containing 333 vertical tubes was designed for industrial use, in which the fluidized bed

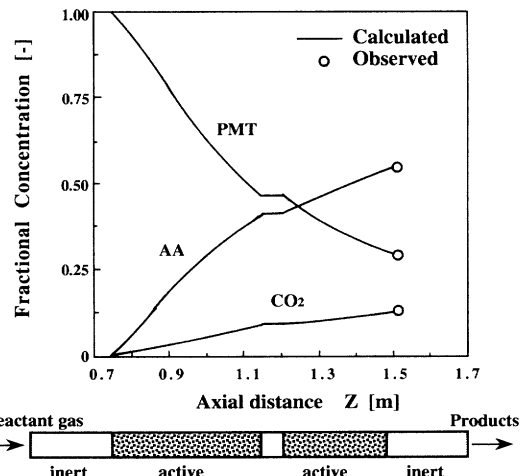


Fig. 4 An example of product distribution

was used as a cooling medium for an exothermic oxidation occurring inside the tubes.

Heat transfer between tubes and bed is influenced by the fluidizing air velocity, and the overall heat transfer coefficient is about 63 to 92 W/m²K, at which the fluidizing air velocity is 0.17 to 0.24 m/s. The heat absorbed by the fluidized bed is about 81% of total reaction heat. Although we tried to examine the difference in heat transfer with radial direction, the accuracy of our data is still not satisfactory. However, we found that the difference would be small or perhaps nonexistent. The erosive wear of stainless steel was negligibly small in four-year operation. The evidence obtained here suggests a wider range of application of fluidized beds to various chemical reactors with heating or removal.

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Nomenclature

| | | |
|--------------|--|--------------------------|
| A | = heat transfer area based on interior | [m ²] |
| C_{pa} | = specific heat capacity of air | [J/(kgK)] |
| C_{pg} | = specific heat capacity of reactant gas | [J/(kgK)] |
| d | = inside diameter of reactor tube | [m] |
| f | = velocity of fluidizing air | [kg/s] |
| G | = total flow rate based on cross-section area of tube | [kg/(m ² s)] |
| ΔH_i | = heat of reaction for reaction i | [J/mol] |
| L_f | = bed height of fluidized bed | [m] |
| r_i | = elementary rate based on catalyst volume | [mol/(m ³ s)] |
| T_f | = temperature of fluidized bed | [K] |
| T_g | = reactant gas temperature inside tube | [K] |
| T_{in} | = temperature of fluidizing air at inlet of fluidized bed | [K] |
| U | = overall heat transfer coefficient between packed tube and fluidized bed at internal tube surface | [W/(m ² K)] |
| u_o | = superficial air velocity at fluidizing condition based on empty bed | [m/s] |
| u_{or} | = superficial velocity of reactant gas based on empty tube | [m/s] |
| y_i | = fractional concentration of component i on a carbon-accounted-for basis | [-] |
| Z | = axial distance from inlet of tube | [m] |

<Subscripts>

A = *p*-anisaldehyde
C = carbon dioxide
P = *p*-methoxytoluene

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