## TITLE：

# Adsorption and Fluid－mixing Characteristics of Packed Bed Catalysts with Blow－by <br> Sections Part I．An Empirical Approach to the Problem of Concentration Distribution 

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# Adsorption and Fluid-mixing Characteristics of Packed Bed Catalysts with Blow-by Sections 

Part I. An Empirical Approach to the Problem of Concentration Distribution

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#### Abstract

Adsorption and fluid-mixing characteristics of packed bed catalysts with blowby sections, those which are effective for rapid catalytic reactions, were measured by means of a pulse technique, and the results obtained by gas chromatography were examined by dynamic analysis. The exit age distribution function, $E(\theta)$, for blow-by packed tubes was divided into two parts: the blow-by section, part $B$, and the residence section, part $R$, according to the normalized residence time, $\theta$, in the range of $\theta<1$ and $\theta>1$, respectively. For the semicircular blow-by packing, $B$ was found to become maximum at a packing ratio of $13 / 16$. For the cylindrical blow-by packing, the tracer concentration extended into the packing layer, maintaining a more uniform distribution than with either the $13 / 16$ semicircular blowby packing or full packing. This suggests that the incorporation of cylindrical blow-by sections in packed tube catalysts can improve both the efficiency and the lifespan of this type of catalyst.


## 1. Introduction

For many important catalytic reactions, for example, elimination of detrimental gaseous components in exhaust gases from automobiles and factories ${ }^{1)}$, oxidation of ammonia to produce nitrogen oxides ${ }^{2)}$, and efficient synthesis of gaseous fuels ${ }^{32}$, high reactant flow rates are necessary to realize rapid catalytic reaction rates. In these cases, the high back-pressures and non-uniform reactant distribution throughout the catalyst bed, because of the rapid reactant flow rates, are believed to be the principal obstacles for maintaining smooth, effective and uniformly distributed reactions. Attempts to overcome these obstacles have included supporting catalysts on a honey-

[^1] adhering catalysts to a metallic net ${ }^{9)}$, and coatong catalysts onto the surface of metallic pipe ${ }^{103}$. However, in each case, the preparation method for the catalyst was largely restricted, due to the difficulty of coating or impregnating the support structures with the active catalytic components. On the other hand, when spherical catalyst pellets were packed into a pipe with an appropriate blow-by section, not only the back pressure was reduced but also the reaction performance in general was remarkably improved when compared to the reaction performance obtained with a fully packed catalyst. The improved catalytic performance obtained with the blowby catalyst was due to improved uniform mass-and heat-transfer over the catalyst bed.

Blow-by phenomena as well as channeling in fluidized beds in flow reactors have thus been considered to be ineffective, since they are believed to decrease the reactor efficiency ${ }^{11-13}$. Therefore, the fluid-mixing characteristics in reactors with blow-by sections have not been extensively studied. Only a few studies in which by-passing phenomena are incorporated into the analyses of fluid-mixing characteristics are found in the literature of this matter. Gilliland and Mason ${ }^{123}$ proposed the I-factor to describe the sequential interaction of the plug and complete mixing flow mechanism in a fluidized bed system. Nagata et al. ${ }^{13,14)}$ proposed a parallel mechanism to describe the fraction of the piston-type flow resulting from the combination of both the plug and complete mixing flow in a liquid phase, a continuous back reactor agitated with multi-stage paddles. Yagi and Miyauchi ${ }^{11}$ analyzed a model catalyst contatining a blow-by section using a residence time analysis. However, in each of these studies, a practical reaction apparatus employing a blow-by section was not the object of the study. Therefore, a quantitative analysis of the exit age distribution function, $E(\theta)$, ranging between $0<\theta<1$, that would determine the proportion of the input gas that exited from the flow tube by way of the blow-by section was not performed. The mean residence time in the flow tube of input gas that exits by way of the blow-by section would be considerably shorter than that for gases that enter and exit from the packed part of the flow tube.

The present paper presents the results from a fundamental study on tublar reactors having blow-by sections with emphasis centered on analyses of the influences of geometric disposition of the blow-by section. Also considered were changes in the volume of the blow-by section with respect to the total flow tube volume on the adsorption and mixing properties of silica packed flow tubes. The analyses were accomplished by injecting a tracer gas into the carrier gas at the gas inlets of the flow tubes, and continuously measuring the exit of the tracer by gas chromatography.

The results obtained as values of $E(\theta)$ as a function of $\theta$ are discussed with
particular emphasis given to the values of $E(\theta)$ for $\theta<1$ which previously have not been given adequate attention.

## 2. Experimental Section

## 2. 1. Apparatus

Simadzu's GC-4BPT type gas chromatograph was used for gas flow measurements. Glass tubes of 50 cm length and 10.7 or 14.4 mm inner diameter were used as packing columns. The packing spaces were 45 and $81 \mathrm{~cm}^{3}$, respectively. As shown in Fig. 1, the fluid pressures were measured by a pressure gauge mounted at the column inlet, and the pressure differences between the inclets and exits of the packed columns were determined by a water manometer.


Fig. 1. Sketch of the tubes with blow-by packing. A, gas inlet; B, pressure gauge; C, tracer injecting cyringe; D, spherical pellets-packed tube; E, water manometer; F, gas outlet; G, semicircular blow-by packing; H , cylindrical blow-by packing.

### 2.2. Packing Methods

Eleven $\sim 81 \mathrm{~cm}^{3}$ portions of the spherical catalyst support made of silica, 3.0 mm diameter, were used. The silica support ${ }^{3}$ ) has a bulk density of $0.72 \mathrm{~g} / \mathrm{cm}^{3}$, a porosity of $0.76 \mathrm{~cm}^{3} / \mathrm{cm}^{3}$, a mean macro-pore diameter of 600 nm , a mean meso-pore diameter of 5 nm , and a BET-surface area of $359 \mathrm{~m}^{2} / \mathrm{g}$. It has been shown that this spherical support with a bimodal meso-macro pore structure has a remarkably larger effective diffusivity and a faster mass-transfer rate compared to silica or alumina supports having only a meso pore structure ${ }^{3}$.

The spherical cataiyst support was uniformly packed into horizontally set glass tubes (Fig. 1 D), leaving space for blow-by sections either in the form of a semicircle at the top or a cylinder through the center of the packed tube, as illustrated by the cross-sectional diagrams in Fig. 1 G and H , respectively. The packed to total tublar volume ratio varied from $1 / 4$ to 1 (full packing). The survey of the

Table 1. Survey of the structural parameters of the semicircular packing tubes.

| packing ratio | bulk volume of <br> packed spheres <br> $\mathrm{cm}^{3}$ | ratio of <br> unpacked space <br> $\%$ | sectional area of <br> the blow-by part <br> $\mathrm{mm}^{2}$ | total void of <br> outer spheres <br> $\%$ |
| :---: | :---: | :---: | :---: | :---: |
| $16 / 16$ | 45.0 | 0 | 0 | 47.7 |
| $15 / 16$ | 42.2 | 6 | 6 | 50.8 |
| $14 / 16$ | 39.4 | 13 | 11 | 54.2 |
| $13 / 16$ | 36.6 | 19 | 17 | 57.6 |
| $12 / 16$ | 33.8 | 25 | 23 | 60.7 |
| $8 / 16$ | 22.5 | 50 | 45 | 73.9 |
| $4 / 16$ | 11.3 | 75 | 67 | 86.8 |

structural parameters for the semicircular blow-by packed tubes are presented in Table 1. The cylindrical blow-by section was made of stainless steel, a 40 mesh screen of 3.5 mm outer diameter. The sectional area of this pass was closed to be identical to the $13 / 16$ packing for the semicircular blow-by section in which the fluid-mixing characteristics were maximum or minimum for the functions (1- $\phi$ ) or q , respectively, as will be discussed below.

### 2.3. Measurements

After the packed support was dried by flowing dry $\mathrm{N}_{2}$ at $150^{\circ} \mathrm{C}$ for 1 h , gas flow measurements were conducted at $18^{\circ} \mathrm{C}$. Hydrogen carrier gas was allowed to flow through the reactors with the flow rates ranging from 20 to $1300 \mathrm{~cm}^{3} / \mathrm{min}$, which correspond to the linear velocities per sectional void area of packed tubes of $0.7 \sim 50 \mathrm{~cm} / \mathrm{sec}$ for tubes of 10.7 mm inner diameter. A volume of $20 \times 10^{-3} \mathrm{~cm}^{3}$ of $\mathrm{N}_{2}$ as a non-adsorptive tracer, or ethylene as an adsorptive tracer, was injected into the carrier gas stream at the inlet of the packed tube within a 0.2 sec time interval, using gas chromatograms of the pulse responses at the outlet of the tube, which were recorded using a chart speed of $80 \mathrm{~mm} / \mathrm{min}$.

## 3. Results and Discussion

## 3. 1. Fluid-mixing Characteristics of the Semicircular Blow-by Packed Tube

### 3.1.1. Pressure Drop of the Fluid in the Packed Tube

Regardless of the packed volume of the 10.7 mm inner-diameter tube, for flow rates, $F$, of $400 \mathrm{~cm}^{3} / \mathrm{min}$ or less the flow-rate dependence of the inlet pressure, $P$, was found to be:

$$
\begin{equation*}
P=C_{1} F^{2.5} \tag{1}
\end{equation*}
$$

where $P=61$ Torr for $F=400 \mathrm{~cm}^{3} / \mathrm{min}$. When $F$ was greater than $400 \mathrm{~cm}^{3} / \mathrm{min}$, the flow rate dependence of $P$ was:

$$
\begin{equation*}
P=C_{2} F^{1.5} \tag{2}
\end{equation*}
$$

The pressure differences between the inlet and outlet of the packed tubes, i.e.
either full or blow-by packing, and the empty tube at the maximum flow rate, 1300 $\mathrm{cm}^{3} / \mathrm{min}$, were 0.1 and 0.04 Torr., respectively. Therefore, the pressure decreases between the inlet and outlet of the packed tubes were negligible. Accordingly, the mean linear velocity, $\bar{U}$, which is adopted for calculation of the height equivalent to a theoretical plate, $H$, was computed by $U_{0} / P$, where $U_{0}$ is the linear velocity per sectional area of void space in the packed bed.
3.1.2. Variation of the Exit Age Distribution Function $E(\theta)$ with Gas-flow Rate Gas chromatograms were obtained at the outlet as pulse responses. The concentration time function, $E(t)$, was calculated in terms of the exit age distribution function, $E(\theta)$, by using dimentionless, reduced time, $\theta . \theta$ was calculated by Ep. (3) :

$$
\begin{equation*}
\theta=\frac{t}{\tau} \tag{3}
\end{equation*}
$$

where $t$ is the elapsed time after tracer injection, and $\tau$ is the mean residence time expressed as Eq. (4):

$$
\begin{equation*}
\tau=\Sigma t_{i} C_{i} / C_{i} \tag{4}
\end{equation*}
$$

where $C_{i}$ is the outlet tracer concentration at time $t_{i}$. A variation of $E(\theta)$ with its gas-flow rate for the semicircular blow-by packed tube of 10.7 mm inner diameter was measured using ethylene as the tracer. The packed volume ratio for this tube was $12 / 16$, where a packed volume ratio of $16 / 16$ indicates a fully packed tube, and $0 / 16$ indicates an empty tube.

As the gas flow rate was increased, the curve for $E(\theta)$ (Fig. $2 \mathrm{~b} \sim \mathrm{e}$ ) deviated


Fig. 2. Variation of $E(\theta)$ curve with carrier-gas flow rates. Packing ratio, $12 / 16$; tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; a, ideal plug flow; f , ideal complete mixing flow; arrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): b, $120 ; \mathrm{c}, 240 ; \mathrm{d}, 480 ; \mathrm{e}, 970$.
more and more from that for the ideal gas flow plug (Fig. 2a). This was seen as flattering effects on the curve or both sides of $\theta=1$, i.e. $\theta<1$ and $\theta>1$. Furthermore, as the flow rate is increased, the curve for $E(\theta)$ approaches that of an ideal complete mixing flow cueve (Fig. 2f).

The earlier eluted tracer, $\theta<1$, clearly represents that portion of the tracer gas that entered the blow-by section of the flow tube. On the other hand, the later eluted tracer, $\theta>1$, represents that portion of the tracer gas that entered the packed portion of the tube. The tracer that entered the packed portion of the tube had a longer residence time and was more effectively mixed with the carrier gas than the tracer which entered the blow-by section of the flow tube.

From this view point, using the ideal plug flow curve, $E(\theta)=\infty$, as standard (Fig.2), that part of $E(\theta)$ for $\theta<1$ is defined as the portion of $E(\theta)$ for $\theta>0, B$, that is contributed by the portion of the tracer gas that passes through the blow-by section of the flow tube. That part of $E(\theta)$ for $\theta>1, R$, is defined as that portion of $E(\theta)$ contributed by the tracer which enters the packed portion of the flow tube. $B$ and $R$ are examined in more detail as follows.

## 3. 1.3. Linearization of $\boldsymbol{E}(\boldsymbol{\theta})$ Curve

First, in order to examine the linearity of the $R$ part of the $E(\theta)$ curve, the logarithm of the internal age distribution function, $R(\theta)=1-\int_{0}^{\infty} E(\theta) \mathrm{d} \theta$, was plotted


Fig. 3. Variation of the relations $\log R(\theta)$ vs. $\theta$ with carrier-gas flow rate. Packing ratio, $12 / 16$; tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; a, ideal plug flow; f, ideal comglete mixing flow; carrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): b, 240; c, 480; d, 760, e, 970.
against $\theta$ which is well known for the ordinary flow apparatus. Consequently, as shown in Fig. 3, a good linearity for $R(\theta)$ with respect to $\theta$ was found for $\theta>1$. Therefore, for $\theta>1 R$ can be expressed by Eq. (5):

$$
\begin{equation*}
R(\theta)=s \exp \{-s(\theta-\phi)\} \tag{5}
\end{equation*}
$$

where $\phi$ is the value of the abscissa where the extraporated line for $R(\theta)$ with respect to $\theta$ crosses the line of $R(\theta)=1$, and $s$ is the slope of the line. For the ideal plug flow, $\phi=1$ and $s=\infty$; and for the ideal complete mixing flow, $\phi=0$ and $s=1$. $\phi$ corresponds to the I-factor proposed by Gilliland and Mason ${ }^{12)}$ for a fluidized bed and to the fraction of the piston-type flow as proposed by Nagata et al. ${ }^{13,14)}$ for batch reactors agitated with multi-stage paddles. However, their data fit well onto a linear plot of $R(\theta)$ versus $\theta$ in the wide range of $\theta<1$, which contrasts with the results of the present study where plots of $R(\theta)$ versus $\theta$ largely deviate from the linear plot in the range of $\theta<1$ (Fig.4). The cause of this deviation is considered to be due to the blow-by packing structure.


Fig. 4. Comparison of $R(\theta)$ vs. $\theta$ curves of the present work with those described in the leteratures. a, data of Gilliland and Mason ${ }^{12}$; b, tada of Nagata et al. ${ }^{13}$; c, data of the present work, obtained from Fig. 3; d, ideal plug flow; e, ideal complete mixing flow.

For the $B$ part of the $E(\theta)$ versus $\theta$ curve, which corresponds to the range of $\theta<1$, some attempts at linearization were made. Consequently, by plotting the logarithm of the residence time distribution function, $F(\theta)$, which is related to $R(\theta)$ according to Eq. (6) against $1 / \theta$,

$$
\begin{equation*}
R(\theta)=1-F(\theta) \tag{6}
\end{equation*}
$$

the B part of $E(\theta)$ versus $\theta$ could be linearized as shown in Fig. 5. This relation is expressed by Fq. (7):

$$
\begin{equation*}
E(\theta)=\left(q / \theta^{2}\right) \exp \{-q(1 / \theta-\eta)\} \tag{7}
\end{equation*}
$$

where $\eta$ is the value of the abscissa where the extraporated line crosses the line of $F(\theta)=1.0$, and $q$ is the slope of the line. $\eta$ and $q$ take the values of $\eta=1$ and $q=$ $\infty$, respectively, for ideal plug flow, and $\eta=0$ and $q \doteqdot 0.46$, respectively, for ideal comlete mixing.

### 3.1.4. Variation of the Blow-by Ratio with Packing Ratio

On the supposition that the elution from the outlet of the packed tube occurs exactly according to that predicted by Eq. (5) for all values of $\theta, \phi$ in Eq. (5) is then identical to $\theta$ when $R(\theta)=1$ which is the point of the initial tracer elution. Therefore, $(1-\phi)$, the fraction of the elution which is eluted faster than that predicted from the ideal plug flow, $\phi=1$, can be regarded as the blow-by ratio. As mentioned above, the data in Fig. 5 deviate from linearity in the range of $\theta<1$, but these discrepancies occur systematically with respect to the variation of the carriergas flow rate. Consequently, it is considered that the blow-by ratios with various packing ratios may be compared using the factor ( $1-\phi$ ). On the other hand, $q$ in Eq. (7) is considered to indicate the degree of the plug flow. The decreasing values for $q$ indicate a more rapid elution for a given mean residence time due to the


Fig. 5. Variation of the relations $\log F(\theta)$ vs. $1 / \theta$ with carrier-gas flow rate. Packing ratio, $12 / 16$; tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; a, ideal plug flow; $f$, ideal complete mixing flow; carrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): $b$, 240 ; c, 480 ; d, 760 ; e, 970.
increased elution via the blow-by section. The larger of $q$ are obtained as the elution approaches that of the ideal plug flow. Therefore, $q$ is termed the ideal plug flow coefficient. Plots of ( $1-\phi$ ) and $q$ versus the packing ratio are shown in Figs. 6 and 7 , respectively. Irrespective of the carrier gas-flow rate, elution via blow-by becomes maximum at a packing ratio of $13 / 16$. This tendency becomes more pro-


Fig. 6. Variation of the blow-by ratios ( $1-\phi$ )'s with packing ratios. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; carrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): a, $250 ; \mathrm{b}, 500 ; \mathrm{c}, 1000$.


Fig. 7. Variation of the plug flow coefficients $q$ 's with packing ratios. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; carrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): a, $250 ; \mathrm{b}, 500 ; \mathrm{c}, 1000$.
nounced as the carrier-gas flow rate is increased (Figs. 6 and 7). Further, first order correlations between $\phi$ and $\eta$ and $q$ and $s$ can be demonstrated as shown in Figs. 8 and 9, respectively. Therefore, when $(1-\eta)$ or $s$ is plotted against the packing ratio, curves similar to those in Figs. 6 and 7 , respectively, are obtained. Furthermore, since the degree of the extension of $E(\theta)$ in the range of $\theta<1$ corresponds to the magnitude of blow-by elution, the second moment, $\sigma^{2}$, of $E(\theta)$ calcu-


Fig. 8. Correlation of the $\eta$ with the $\phi$. All the $\eta$ 's and $\phi$ 's of this study are plotted.


Fig. 9. Correlation of the $s$ with the $q$. All the $s$ 's and $q$ 's of this study are plotted.
latedby Eq. (8):

$$
\begin{equation*}
\sigma^{2}=\int_{0}^{\infty}(\theta-1)^{2} E(\theta) \mathrm{d} \theta / \int_{0}^{\infty} E(\theta) \mathrm{d} \theta \tag{8}
\end{equation*}
$$

can be plotted against the packing ratio. As shown in Fig. 10, the curves obtained from these plots are similar to the curves ( $1-\phi$ ) versus the packing ratio (Fig.6), and relative comparisons of the magnitude of the blow-by elution can be made. The packing ratio that yields a maximum blow-by elution is $13 / 16$ which is simlar to the packing ratio for the maximum blow-by elution suggested from these results, as depicted in Figs. 6 and 7. Results for the tube of 14.4 mm inner diameter were identical in principle with the results mentioned above.


Fig. 10. Variation of the variance with packing ratios. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; carriergas linear velocity ( $\mathrm{cm} / \mathrm{sec}$ ) : a, $5 ; \mathrm{b}, 10 ; \mathrm{c}, 20$.

### 3.1.5. Variation of Mass-transfer and Adsorption-Desorption Coefficients with Packing Ratio

Adsorption of the ethylene tracer onto the silica gel support is greatly affected by the fluid-mixing characteristics of the packed tubes as described above. In order to differentiate between the effects of adsorption and mixing, the pulse response of $\mathrm{N}_{2}$, for which adsorption can be neglected, was then studied. However, when $\mathrm{N}_{2}$ was used as a tracer, the $E(\theta)$ versus $\theta$ curves peaked so sharply that the plots could not be compared due to their inaccuracy. Therefore, the retention volume, $V_{R}$, and the height equivalent to a theoretical plate, $H$, were examined with respect to a packing ratio using $\mathrm{N}_{2}$ as a tracer. $\quad V_{R}$ was calculated as the product of the retention time, $t_{K}$, and the gas-flow rate, $f\left(\mathrm{~cm}^{3} / \mathrm{min}\right)$. $H$ was calculated according to Eq. (9) :

$$
\begin{equation*}
H=L t_{R}{ }^{2} / 16 W^{2} \tag{9}
\end{equation*}
$$

where $W$ is the peak width of the $E(t)$ curve and $L$ is the length of the packed tube. As can be seen in Figs. 11 and 12, maximum blow-by occurred at the 13/16 packing ratio as was observed using the ethylene tracer. This fact indicates that


Fig. 11. Variation of the retention volume with packing ratios. Tracer, $\mathrm{N}_{2}$; carrier-gas flow rate ( $\mathrm{cm}^{3} / \mathrm{min}$ ): a, 250; b, 500; c, 1000.


Fig. 12. Variation of the height equivalent to a theoretical plate $H$ with packing ratios. Tracer, $\mathrm{N}_{2}$; packing ratio: a , vacant; $\mathrm{b}, 4 / 16$; c, $8 / 16$; d, $12 / 16$; e, $13 / 16$; f, $14 / 16$; g, $15 / 16$; h, full packing.
the results obtained with the ethylene tracer mentioned above were not due to the effects of adsorption. To examine this point in more detail, the term $\left(C_{g}+C_{k}\right)$ which is directly proportional to the linear velocity was used in Eq. (10), which is the equation for the height equivalent to a theoretical plate in gas-solid chromatography ${ }^{15)}$ :

$$
\begin{equation*}
H=A+B / \bar{u}+\left(C_{g}+C_{k}\right) u \tag{10}
\end{equation*}
$$

where $C_{g}$ is the coefficient of resistance to mass-transfer, and $C_{k}$ is the rate coeff. cient for resistance to adsorption-desorption. Since $C_{k}$ could be neglected when $N_{2}$ was used as tracer, $C_{g}$ was obtained from the slope of the asymptote of the $H(\bar{u})$ curve in Fig. 12. The $C_{g}$ values plotted against the packing ratio are shown as curve a in Fig. 13. When ethylene was used as the tracer, the peak of the $E(\theta)$ curve was so broad and asymmetric that values for the variables in Eq. (10) were difficult to obtain accurately. Therefore, $C_{g}$ and $C_{k}$ in this case were obtained from the second moment, $\sigma^{2}$, of the $E(\theta)$ curve. The relationship between $\sigma^{2}$ in Eq. (8) and $H$ in Eq. (10) can be expressed as the following equation ${ }^{16)}$ :

$$
\begin{equation*}
H=\sigma^{2} L \tag{11}
\end{equation*}
$$

and therefore,

$$
\begin{equation*}
\sigma^{2}=(1 / L)\left\{A+B / \bar{u}+\left(C_{g}+C_{k}\right) \vec{u}\right\} \tag{12}
\end{equation*}
$$

Hence, $A$ can be neglected ${ }^{177}$ and $\left(C_{g}+C_{k}\right)$ can be determined from the slope of the line obtained by plotting $\sigma^{2} \bar{u}$ against $\bar{U}^{2}$, i.e., $\left(C_{g}+C_{k}\right] / L$. These values are shown as curve $b$ in F!g. 13. Then the $C_{k}$ term for ethylene can be separately de-


Fig. 13. Variation of term $\left(C_{g}+C_{k}\right)$ in $\sigma^{2}$ equations and of the individual terms $C_{g}$ and $C_{k}$ with packing ratios. a, $C_{g}$ for $\mathrm{N}_{2}$ as tracer; b , $\left(C_{9}+C_{k}\right)$ for $\mathrm{C}_{2} \mathrm{H}_{4}$ as tracer; c, calculated $C_{k}$ for $\mathrm{C}_{2} \mathrm{H}_{4}$ as tracer.
termined from curve c in Fig. 13, which was obtained by subtracting a from b . The term $C_{k}$ for ethylene ( Fig .13 c ) attains a maximum plateau in the range of packing ratios from $6 / 16$ to $13 / 16$. The term $C_{g}$ (Fig. 13a) shows a shape peak at the packing ratio of $13 / 16$. Thus, in the semicircular blow-by packed tube, the variables which define the fluid-mixing properties of the packed tubes were uniformly maximum when a $13 / 16$ packed volume to the total volume ratio was used. As the volume of the blow-by section was increased, $C_{g}$ became maximum at a $13 / 16$ packed to the total volume ratio, $C_{k}$ became maximum at a smaller packing ratio than $C_{g}$, and values for both $C_{k}$ and $C_{g}$ were decreased for packing ratios greater than 13/16.

### 3.2. Fluid-mixing Charcteristics for the Cylindrical Blow-by Packing

### 3.2.1. Differences in the $E(\theta)$ Curves for warious Blow-by Packing Structures

A cylindrical blow-by section of $0.17 \mathrm{~cm}^{2}$ sectional area was used. The ratio of the blow-by to the total tube volume (i.e. packed to the total volume ratio) for packed tubes with this size cylindrical blow-by was identical to the $13 / 16$ packed to the total volume ratio that produced the best results for the semicircular blow-by packed tubes. The $E(\theta)$ curve for this cylindrical blow-by packed tube is shown in Fig. 14. Using the $E(\theta)$ curve obtained with a fully packed tube as standard, the change in the $B$ part of the curve, i.e. $\theta<1$, was considerably less for a packed tube with a cylindrical rather than semicircular blow-by section. We can express the symmetry of the $E(\theta)$ curve by $W_{1} / W$, where $W$ is the distance between the intersection with the abscissa of two lines, $W_{1}$ and $W_{2}$, that are tangential to the


Fig. 14. Comparison of $E(\theta)$ curves among various packing tubes. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; carrier-gas flow rate, $960 \mathrm{~cm}^{3} / \mathrm{min}$; a, full packing; b, $13 / 16$ semicircular packing; c, cylindrical blow-by packing.
inflection points of the $E(\theta)$ curve. $W_{1}$ is in the front side of the peak and $W_{2}$ is in the tail side of the peak. $W_{1}$ is the distance between $W_{1}$ and the intersection with the abscissa of a perpendicular line from the tip of the peak. The $W_{1} / W$ values for the cylindrical blow-by packing, the semicircular blow-by packing, and full packing are $0.41,0.09$, and 0.36 , respectively. Thus, we can demonstrate that the symmetry of the $E(\theta)$ curve obtained with the cylindrical blow-by packed tube is better than that for either the semicircular blow-by packed or fully packed tubes.

### 3.2.2. Difference of Blow-by Ratio with Various Packed Structures

As shown in Fig. 15, the blow-by ratios, ( $1-\phi$ ), for the cylindrical blow-by packed tube are smaller than those for the semicircular blow-by packed tube for all ranges of gas flow rate, and nearly the same as those for the fully packed tube. However, at high flow rates the blow-by ratios for the cylindrical blow-by packed tube become larger than those for the full packed tubes. On the other hand, the values for the plug coefficient, $q$, for the cylindrical blow-by packed tube were in between those for the semicircular blow-by packed tube and the fully packed tube (Fig. 16). These results are consistent with the fact that for the cylindrical blow-by packed tube the front part of the $E(\theta)$ curve is increased, but the tail part is not so much different from that for the $E(\theta)$ curve obtained with the fully packed tube. The symmetry of the $E(\theta)$ curve at a high flow rate was better for the cylindrical blow-by packed tube than for the fully packed tube.

### 3.2.3. Difference in $C_{g}$ and $C_{k}$ for Various Packing Structures

As shown in Table 2, the values of $C_{g}$ and $C_{k}$ for the cylindrical blow-by packing


Fig. 15. Comparison of ( $1-\phi$ ) vs. $u$ curves among various packing tubes. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; a, full packing; $\mathrm{b}, 13 / 16$ semicircular packing; c , aylindrical blow-by packing.


Fig. 16. Comparison of $q$ vs. $\bar{u}$ curves among various packing tubes. Tracer, $\mathrm{C}_{2} \mathrm{H}_{4}$; a, full packing; b, $13 / 16$ semicircular packing; c, cylindrical blow-by packing.

Table 2. Comparison of the values of $C_{g}$ and $C_{k}$ for the various packing tubes.

| coefficient | full packing | semicircular <br> $13 / 16$ packing | cylindrical <br> blow-by packing |
| :---: | :---: | :---: | :---: |
| $C_{g}+C_{k}$ sec | 0.14 | 0.91 | 0.28 |
| $C_{g} \mathrm{sec}$ | 0.04 | 0.44 | 0.12 |
| $C_{k} \mathrm{sec}$ | 0.10 | 0.47 | 0.16 |
| $C_{q} / C_{k} \mathrm{sec}$ | 0.40 | 0.94 | 0.75 |

are 3 and 1.6 times their respective values with fully packed tubes, and $1 / 4$ and $1 / 3$ times their respective values with semicircular, i.e. $13 / 16$ packing. The ratio $C_{g} / C_{k}$ is nearly 1 for both blow-by packings which is about 2 times the $C_{g} / C_{k}$ ratio of the fully packed tubes. This indicates that the degree of increase in resistance to masstransfer is greater than the increase in the adsorption-desorption rate for packed tubes incorporating either type of blow-by, i.e. cylindrical or semicircular, compared to fully packed tubes.

In conclusion, the cylindrical blow-by packing will be of more practical usefulness for various rapid reaction systems due to a more uniform distribution of reactants throughout the reactor.

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