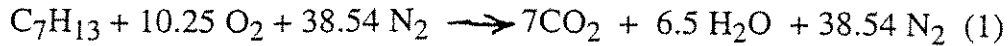
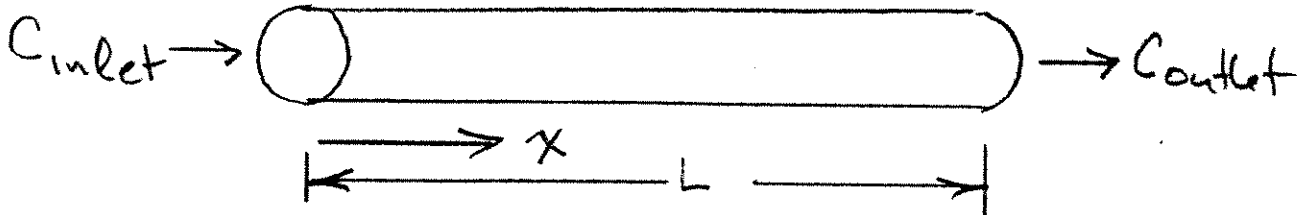


## Oxidation of HC in HoneyComb Catalytic Converter by M. Pilat (10/19/00)

Given: Principal Chemical Reaction - oxidation of assumed gasoline as  $C_7H_{13}$



Cylindrical tube of Catalyst of Diameter  $D$  and Length  $L$  inside a honeycomb matrix



The  $C_7H_{13}$  and  $O_2$  diffuses to the inside surface of the cylindrical tube catalyst and is assumed to react quickly (i.e. reaction rate constant  $k_r$  equal or greater than gas film mass transfer coefficient  $k_m$ ). In the easiest first case, it can be assumed that the reaction rate is so fast (i.e.  $k_r =$  very large compared to  $k_m$ ) that the reaction of the  $C_7H_{13}$  with the  $O_2$  is limited by the rate of mass transfer (diffusion) to the catalyst surface. The pressure drop from the tube inlet to outlet is small (less than 10"  $H_2O$ ) and hence the gas velocity is assumed to be constant in the  $x$  or  $L$  direction. The ratio of the catalytic converter outlet to inlet HC concentrations is given by the equation:

$$\frac{C_{outlet}}{C_{inlet}} = \exp\left(-\frac{a K_o x}{v}\right)$$

The nomenclature is as follows:

$C$	=	concentration of the $C_7H_{13}$ in the air	gms $C_7H_{13}$ /cm <sup>3</sup>
$a$	=	surface area of catalyst / unit volume of reactor	cm <sup>2</sup> /cm <sup>3</sup>
$D$	=	effective diameter of the tube of channel	cm
$K_o$	=	overall mass transfer coefficient	cm/sec
$k_m$	=	mass transfer coefficient	cm/sec.
$k_r$	=	reaction rate constant of $C_7H_{13}$ with $O_2$	cm/sec
$L$	=	Length of the catalyst reactor channel	cm
$L_m$	=	Length of one mass transfer unit	cm
$N$	=	Number of mass transfer units	
$v$	=	velocity of the gas in the catalyst tube	cm/sec
$\delta$	=	diffusion coefficient of $C_7H_{13}$ in air	cm <sup>2</sup> /sec

The change in the  $C_7H_{13}$  concentration down the tube caused by the diffusion of  $C_7H_{13}$  to the catalytic converter tube wall and catalytic oxidation to  $CO_2$  and  $H_2O$  is given by the equation

$$\frac{dC, \frac{\text{gm } C_7H_{13}}{\text{cm}^3}}{dx, \text{cm}} = - \frac{\left( \frac{a \cdot \text{cm}^2 \text{ surface area}}{\text{cm}^3 \text{ volume}} \right) \left( K_o \frac{\text{cm}}{\text{sec}} \right) \left( C \frac{\text{gm } C_7H_{13}}{\text{cm}^3} \right)}{(v, \text{cm} / \text{sec})} \quad (2)$$

Rearranging equation 2

$$\frac{dC}{C} = - \frac{(a) (K_o) dx}{v} \quad (3)$$

and integrating from the catalyst tube inlet ( $x = 0$  and  $C = C_{inlet}$ ) to some distance  $x$  (where  $x =$   $x$  and the  $C_7H_{13}$  conc. is  $C$ )

$$\int \frac{dC}{C} = - \int \frac{(a)(K_o)}{v} dx \quad (4)$$

The results of the integration are

$$\ln C - \ln C_{inlet} = \ln \frac{C}{C_{inlet}} = - \frac{(a)(K_o)(x)}{v} \quad (5)$$

$$\frac{C}{C_{inlet}} = \exp\left(-\frac{a K_o x}{v}\right) \quad (6)$$

With no vapor pressure of  $C_7H_{13}$  over the catalyst surface, number of mass transfer units is given by

$$\text{Number of mass transfer units} = N = \ln\left(\frac{C_{inlet}}{C_{outlet}}\right) \quad (7)$$

$$\text{For one mass transfer unit, } N = 1 = \ln [ C_{inlet} / C ] \quad (8)$$

Taking the anti log of both sides of equation 8:

$$e^1 = (C_{inlet} / C) \quad e^{-1} = (C / C_{inlet}) \quad (9)$$

Equating equations 6 and 9

$$\frac{C}{C_{inlet}} = \exp\left(-\frac{a K_o x}{v}\right) = e^{-1} \quad (10)$$

Taking the ln of eq. 10 and solving for x for one mass transfer unit,  $N = 1$ , gives  $L_m$

$$\frac{a K_o x}{v} = 1 \quad \text{Solving for x for 1 mass transfer unit: } x = \frac{v}{a K_o} = L_m \quad (11)$$

Equation 11 provides the distance  $L_m$  the gas must travel in the catalyst tube to oxidize the  $C_7H_{13}$  concentration by one mass transfer unit ( 63.21 % oxidation of  $C_7H_{13}$  ).

For catalyst with small tubes, the gas flow is in laminar flow (i.e. Reynolds number  $Re < 2100$  and  $Re = D v \rho / \mu$  where  $\rho$  = gas density and  $\mu$  = gas viscosity). In laminar flow, the gas film mass transfer coefficient  $k_m$  is related to the Sherwood Number (which has the magnitude of 4.4 for cylindrical channels) by:

$$Sh = \frac{\text{Total mass transfer}}{\text{molecular mass transfer}} = \frac{k_m D}{\vartheta} \quad (12)$$

$$\text{Solving for the gas film mass transfer coefficient } k_m \quad k_m = \frac{4.4 \vartheta}{D} \quad (13)$$

The surface area  $a$  ( $\text{cm}^2/\text{cm}^3$  or  $\text{ft}^2/\text{ft}^3$ ) inside the tube of the honeycomb catalyst is given by

$$a = \frac{L \pi D}{L \pi (D^2 / 4)} = \frac{4}{D} = \frac{\text{surface area of catalyst}}{\text{volume of catalyst}} \quad (14)$$

$$\text{Solving for the tube diameter } D = 4 / a \quad (15)$$

Some example data ( where  $k_r$  is very large so that  $K_O = k_m$  is assumed ) is shown below:

	Holes/sq. inch of catalyst support		
	200	300	400
Open Area (%)	72	65	77
Effective Hole Diameter ( inches )	.059	.046	.044
Gas Vel. in holes (ft/sec)	27.7	30.8	26.0
Reynolds Numbers	153	133	107
Length of 1 Mass Transfer Unit ( inches )	0.80	0.54	0.42
Gas Pressure Drop (" H <sub>2</sub> O )	1.8	2.0	1.5

**Effect of Reaction Kinetics** The oxidation reaction shown in equation 1 is not actually "instantaneous" and hence the effect of the reaction kinetics on the  $\text{C}_7\text{H}_{13}$  oxidation should be included. The overall mass transfer coefficient  $K_O$  can be given by:

$$\frac{1}{K_O} = \frac{1}{k_m} + \frac{1}{k_r} \quad (16)$$

where  $k_r$  is the reaction rate constant. In reality, there are a number of reaction rate constants (for each of the gaseous hydrocarbon compounds or VOCs), however, for this example they will be combined into the one reaction rate constant,  $k_r$ . One then can calculate the overall mass transfer coef.  $K_O$  and then use the equation 6 to obtain the concentration ratio  $C/C_{\text{inlet}}$

How would you measure the magnitude of this reaction rate coefficient  $k_r$  from experimental data?

### Gas Pressure Drop Across the Catalyst

The gas pressure drop across the catalyst can be calculated by 
$$\Delta p = \frac{2 f L v^2 \rho}{g_c D}$$

The Fanning friction factor  $f$  is  $16/\text{Re}$  for circular tubes and  $14/\text{Re}$  for square channels.

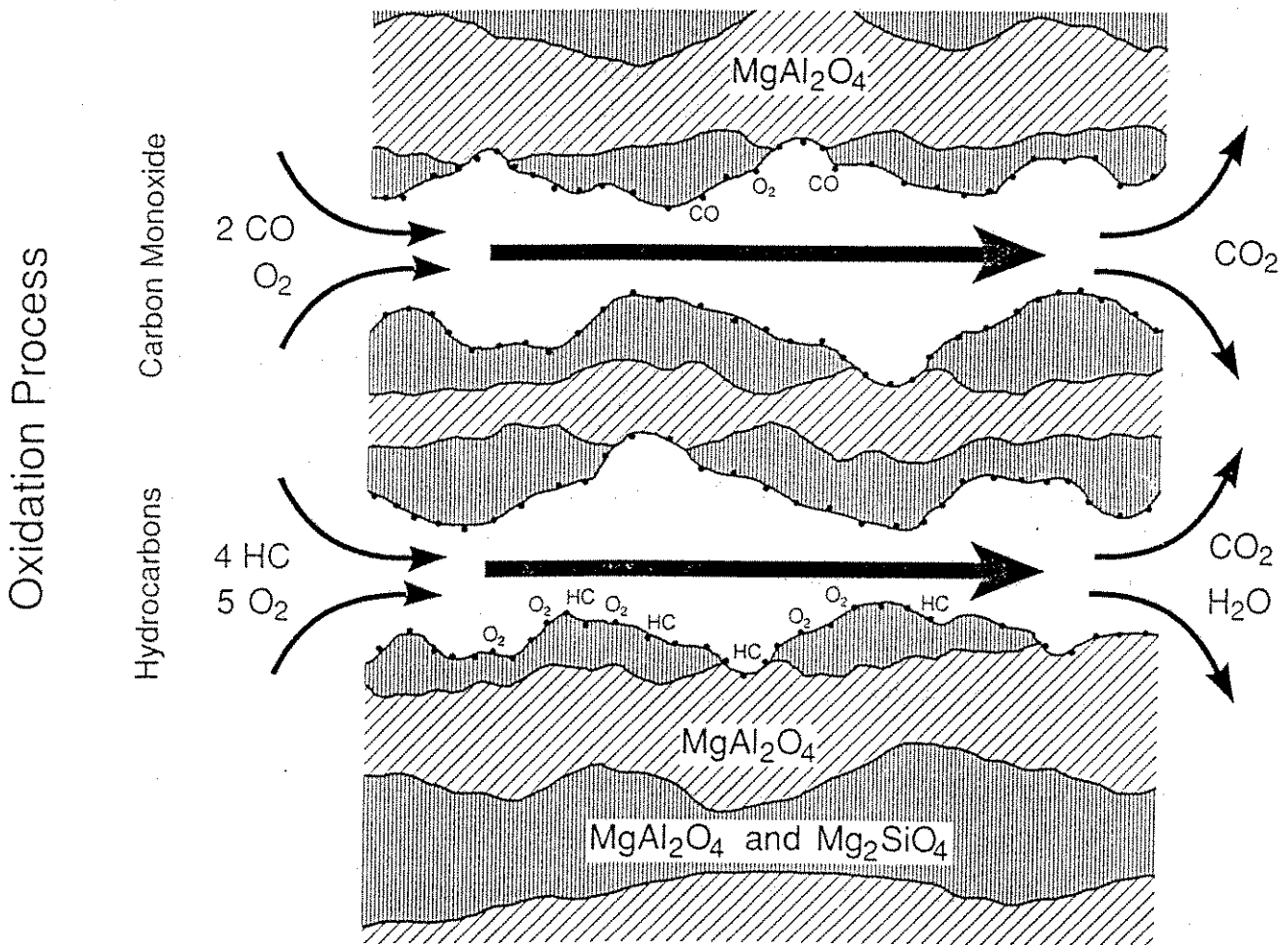
Reynolds Number for gas flowing in catalytic converter tube = 
$$\text{Re} = \frac{D v \rho}{\mu}$$

The other variables are  $L$  = total length of catalyst tube,  $v$  the gas velocity,  $\rho$  the fluid gas density,  $g_c$  the gravitational constant, and  $D$  the effective diameter of the channel or tube.

Platinum-based catalyst systems require virtually lead-free fuels. However, platinum has proven effectiveness regarding low threshold activation temperatures, low light-off temperature, fast warm-up, its ability to withstand thermal stress, and sustain a 50,000 mile service life. Since about 1988, palladium (Pd) has been more commonly used as it is less expensive than Platinum (Pt).

**Note:** As the loading of platinum is reduced below 0.1% [ (Pt/Al<sub>2</sub>O<sub>3</sub>) /total of 100 in<sup>3</sup>/820 grams ] severe activity loss occurs. Typical loading range is from 1.086g to 3.588g.

**Note:** Pt/Pd loaded catalysts have also been shown to be very effective in the reduction of NO<sub>x</sub> emissions.



## Design of Mass-Transfer Limited Catalytic Units

$$\frac{[\text{Voc}]_{\text{outlet}}}{[\text{Voc}]_{\text{inlet}}} = e^{-L_{\text{outlet}}/L_m}$$

$L_{\text{outlet}}$  = length of catalyst

$L_m$  = length of one mass transfer unit

For laminar flow

$$L_m = \frac{u d^2}{17.6D}$$

$u$  = gas velocity (cm/sec)

$d$  = effective diameter of holes in catalyst (cm)

$D$  = diffusivity of VOC (cm<sup>2</sup>/sec)

Based on the kinetic theory of gases (consider the gas a mixture of hard spheres without intermolecular forces of attraction and repulsion), the diffusivity of a molecule can be estimated using the molecular weights and a known diffusivity. Consideration should be given to using the known diffusivity of similar type molecule (non-polar, polar, halogenated, etc.).

$$\frac{D_A}{D_B} = \left[ \frac{M_B}{M_A} \right]^{0.5} \quad \text{where } M = \text{molecular weight}$$

To determine the diffusivity (or diffusion coefficient) at a temperature other than the temperature listed for the diffusivity,

$$\frac{D_{T_2}}{D_{T_1}} = \left[ \frac{T_2}{T_1} \right]^{1.5}$$

Properties of some substances

Compound	Formula	Mol. Wt.	Diff. (cm <sup>2</sup> /sec)	Melt T. (°C)	Boil. p. (°C)
1. Acetic acid	CH <sub>3</sub> COOH	60.05	0.1065	16.7	118.1
2. Benzene	C <sub>6</sub> H <sub>6</sub>	78.11	.0751	5.4	80.1
3. Bromopropane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	123.0	.095	-109.9	70.8
4. n-butanol			.0703	-79.9	117
5. benzyl chloride	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	126.58	.066	-39	179.4
6. ethyl benzene	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	106.16	.0658	-94.4	136.2
7. dichloromethane (methylene dichloride)	CH <sub>2</sub> Cl <sub>2</sub>	84.93		-96.7	40.1
8. ethyl alcohol	CH <sub>3</sub> CH <sub>2</sub> OH		.102	-112	78.4
9. isopropanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	60.10		-85.8	82.5
10. toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92.14		-95.0	110.8
11. Freon 113 (trichlorotrifluoroethane)	CCl <sub>2</sub> FCClF <sub>2</sub>			-35	47.57
12. Trichloroethane (methyl chloroform)	CH <sub>3</sub> CCl <sub>3</sub>	133.41		-36.7	113.5
13. Carbon tetrachloride	CCl <sub>4</sub>	153.84		-22.6	76.8

- ref: 1. Controlling Volatile Emissions at Hazardous Waste Sites, by Ehrenfeld, Ong, et al, Noyes Publ. 1986, pp. 236-237.
2. Handbook of Air Pollution by Sheehy, Achinger, & Simon, Air Pollution Training Program, US Dept. HEW

# Design of transfer-limited catalytic incinerators

When mass transfer of reactants is the limiting step in a catalytic-combustion reaction, the design procedure is simplified to a number-of-transfer-units method.

*William B. Retallick, Consultant*

□ The reaction of two fluids over a solid catalyst takes place in two steps: transport of reactants to the catalyst surface, and reaction at the surface. At steady state, of course, the rate of mass transfer and the rate of reaction are the same. Yet the rate may be limited by either of the two steps.

Fig. 1 shows two possible concentration profiles for a reactant over a catalyst surface. When reaction is the rate-limiting step, the surface concentration is nearly equal to the bulk concentration. When mass transfer limits the rate, the surface concentration is nearly zero. In the latter case, we can estimate the reaction rate by estimating the mass-transfer rate.

For a channel in a catalytic reactor, as shown in Fig. 2, we can express the mass-transfer rate of reactant  $A$  as a function of  $x$ :

$$\frac{d[A]}{dx} = -\frac{ak_m[A]}{v}$$

where the driving force is equal to the bulk concentration because the concentration at the surface is approximately zero. Integrating from 0 to  $x$  yields:

$$[A]_x = [A]_0 e^{-ak_mx/v}$$

When  $x = v/k_ma$ ,  $[A]_x = [A]_0 e^{-1}$ . We can call  $v/k_ma$  the length of a mass-transfer unit:

$$L_m = \frac{v}{k_ma}$$

For a given reactor of length  $L$ , we can calculate the number of transfer units and  $[A]$  at the reactor outlet:

$$N = L/L_m \quad [A] = [A]_0 e^{-N}$$

## Turbulent flow

When the Reynolds number for flow in the reactor channels is greater than 2,000, the flow is considered turbulent. We can use the Reynolds analogy, which as-

sumes that all transfer is caused by turbulent eddies, for a first estimate of the mass-transfer rate. In this case:

$$\frac{\text{rate of mass transfer}}{\text{mass driving force}} = \frac{\text{rate of momentum transfer}}{\text{momentum driving force}}$$

$$\frac{d[A]}{[A]} = \frac{-2g_c dP}{\rho v^2}$$

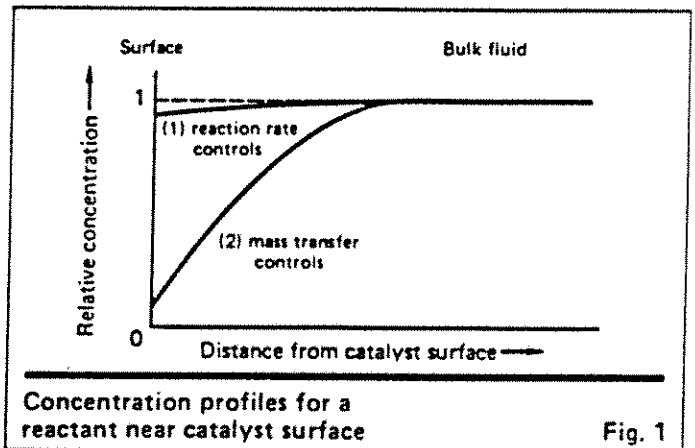


Fig. 1

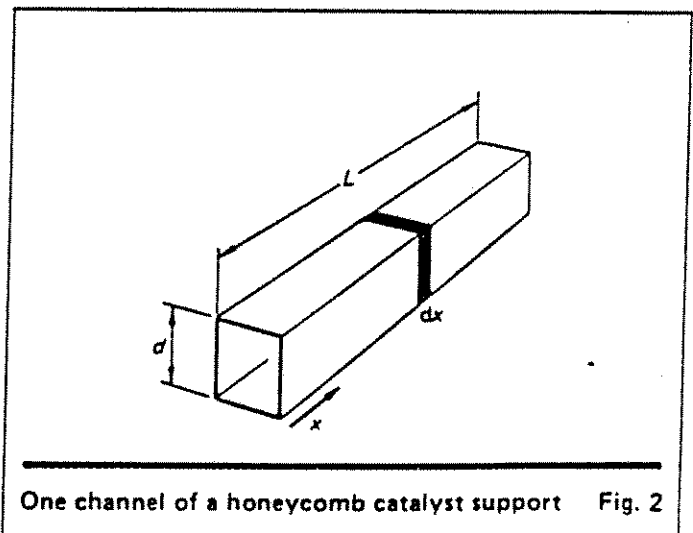


Fig. 2

Introducing the mass-transfer coefficient and the friction factor converts this expression to:

$$\frac{v}{k_m a} = \frac{2}{f a} \quad L_m = \frac{2}{f a}$$

Thus, the Fanning friction factor yields  $L_m$  directly when the Reynolds analogy holds.

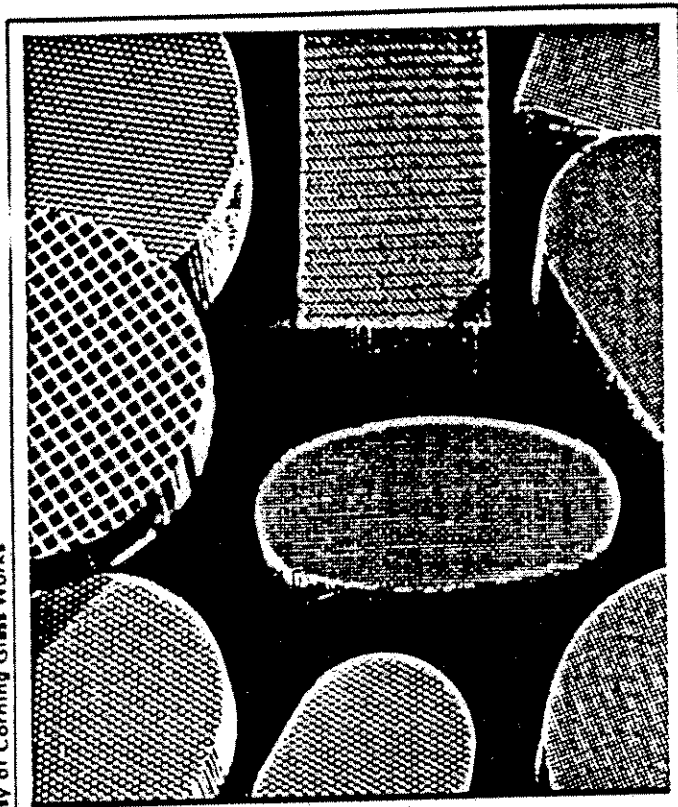
In the usual case, when diffusional transfer is not completely negligible, Colburn's analogy corrects for diffusional effects:

$$\frac{v}{k_m a} (Sc)^{-2/3} = \frac{2}{f a} \quad L_m = \frac{2}{f a} (Sc)^{2/3}$$

### Catalytic combustion

Catalysts are used to speed up the reactions between oxygen and organic compounds for a variety of purposes. The most common example of catalytic combustion is the oxidation of unburned hydrocarbons to water vapor and carbon dioxide in an automobile's catalytic converter. By speeding up the oxidation reaction, the precious-metal catalyst ignites the hydrocarbons below their normal ignition temperature. Catalytic incinerators that are used for fume abatement perform a similar function. For example, they can be used to control emissions of industrial solvents that cannot be vented. In the food industry, exhausts from frying and roasting operations can be incinerated to destroy objectionable odors. Table I shows several other examples of catalytic incineration. Fig. 3 shows several types of extruded catalyst supports. Though smaller holes provide greater surface area, larger holes are used when entrained particles could cause plugging.

Catalytic combustors that burn fuel upstream from gas turbines are currently being developed. Here, the advantages of catalytic combustion are threefold: less  $NO_x$  production because the combustion temperature is lower; less emission of unburned hydrocarbons and carbon monoxide; greater heat release per unit volume. A recent development that improves heat release is the graded-cell support, in which hole size decreases in the direction of flow.



Courtesy of Corning Glass Works

Samples of honeycomb-type catalyst supports Fig. 3

Examples of industrial applications for catalytic incineration [7]

Table I

Industry	Flue-gas components	Incinerator inlet temperature ( F )	Gas concentration (ppm)	
			Inlet	Outlet
Rhotogravure printing	Butyl acetate	500-800	300-1,000	7-10
	Ethyl acetate			
	Isopropanol			
	n-Hexane			
	Toluene			
Magnetic printing	MEK	500-800	1,200-2,500	8-10
	MIBK			
	Toluene			
Metal printing	Butanol	500-800	500-1,500	7-10
	MIBK			
	Toluene			
	Xylene			
Synthetic resins	Acetone	400-600	1,200-1,500	1-20
	Formalin			
	Methanol			
	Phenol			
	Toluene			

Example data and results

Table II

	Holes/in <sup>2</sup> in catalyst support		
	200	300	400
Open area, %	72	65	77
Effective hole dia., in. ( <i>d</i> )	0.059	0.046	0.044
Velocity through holes, ft/s ( <i>v</i> = 20/open area)	27.7	30.8	26.0
Reynolds number ( <i>Re</i> )	153	133	107
Length of transfer unit, in. ( $L_m = vd^2/17.6D$ )	0.80	0.54	0.42
Length of reactor for 99% conversion, in. ( $L = 4.6L_m$ )	3.7	2.5	1.9
Pressure drop, in. of water	1.8	2.0	1.5

Thus,  $L_m$  for turbulent flow depends only on the friction factor—which is easy to measure—and on the Schmidt number.

### Laminar flow

When the flow is laminar, all of the transfer is diffusional, and not coupled to the friction factor. We can derive the mass-transfer coefficient directly from the Nusselt number and the diffusion coefficient [2]:  $k_m = Nu_m D/d$ . For laminar flow,  $Nu_m$  depends only on the shape of the channel: 4.4 for circular channels, 4.1 for parallel plates, and between those two values for other shapes. In a circular channel:

$$L_m = \frac{v}{k_m a} = \frac{vd^2}{4Nu_m D} = \frac{vd^2}{17.6D}$$

Because the diffusion coefficient does not depend on the flow parameters, this relationship is very easy to use.

### Example

Exhaust air from a baking oven in an enamel-coating process contains 1,000 ppm methyl ethyl ketone (MEK). The exhaust velocity is 20 ft/s, temperature is 1,000°F, and the diffusion coefficient of MEK in air is 0.00055 ft<sup>2</sup>/s at this temperature. We have a choice of three square-holed catalyst supports—200, 300 and 400 holes/in<sup>2</sup>—coated with a catalyst that reduces the ignition temperature of MEK to 750°F. If local air-quality ordinances demand a maximum of 10 ppm MEK in the exhaust, what length of each type do we need to reduce MEK emissions to the permissible level?

Because the exhaust temperature is above the catalytic ignition temperature, we can assume that the reaction is mass-transfer-controlled. The 10-ppm outlet concentration is 1% of the inlet concentration. Thus:

$$e^{-N} = 0.01 \quad N = 4.6$$

Using the manufacturer's data on hole size and open area, we can calculate  $v$  and  $Re$  for flow through the holes in each type of support, as shown in Table 2. Because all of the  $Re$  values are well below 2,000, we know that the flow is laminar. We can thus use the laminar-flow equations to calculate  $L_m$  and the required reactor length ( $L = NL_m$ ) for each type of support. If pressure

## Nomenclature

$a$	Surface area per unit volume of reactor, (length) <sup>-1</sup>
$d$	Effective diameter of a channel ( $d = 4/a$ ), (length)
$D$	Diffusion coefficient, (length) <sup>2</sup> /(time)
$f$	Fanning friction factor
$g_c$	Gravitational constant, (mass)(length)/(force)(time) <sup>2</sup>
$k_m$	Mass-transfer coefficient, (length)/(time)
$L$	Length of reactor channel
$L_m$	Length of a mass-transfer unit
$N$	Number of transfer units
$v$	Bulk velocity of fluid, (length)/(time)
$\rho$	Density of fluid, (mass)/(length) <sup>3</sup>
$\mu$	Viscosity of fluid, (mass)/(length)(time)
$Nu_m$	Nusselt number for mass transfer ( $Nu_m = k_m d/D$ )
$Re$	Reynolds number ( $Re = vd\rho/\mu$ )
$Sc$	Schmidt number ( $Sc = \mu/\rho D$ )

drop is important, we can use  $Re$  to estimate the friction factor for laminar flow:  $f = 14/Re$  for square channels (16/ $Re$  in circular channels). By definition:

$$\Delta P = \frac{2fLv^2\rho}{g_c d}$$

Table 2 shows calculated reactor lengths and pressure drops for each type of support.

In this example, we did not need  $f$  to calculate  $L_m$ . If the flow had been turbulent, we could have measured pressure drops in samples of the three supports at  $Re$  values near the design values, and derived  $f$  directly from these data.

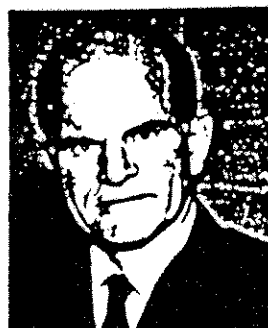
In practice, the calculated length should be considered a minimum effective length for achieving the desired conversion. Doubling the calculated length will provide an adequate safety factor in most cases; but a greater safety factor may be needed if the exhaust gases contain dust or poisons that could blind the catalyst.

Mark A. Lipowicz, Editor

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2. Holman, J. P., "Heat Transfer," 4th ed., McGraw-Hill, New York, 1976.

## The author



William B. Retallick is a consulting chemical engineer with an office at 1432 Johnny's Way, West Chester, PA 19380. He took his M.S. and Ph.D. in chemical engineering at the University of Illinois, after completing his B.S. at the University of Michigan. At Air Products and Chemicals, his work in catalysis led to several patents and a chapter in the "Kirk-Othmer Encyclopedia of Chemical Technology." (Wiley, New York). He joined Oxy Catalyst in 1974 as vice-president for research. Since January 1980, he has been a consultant in the fields of catalyst development, catalytic combustion, and synthetic fuels.