EXPERIMENTAL STUDIES OF A CHROMATOGRAPHIC MOVING-BED REACTOR — CATALYTIC OXIDATION OF CARBON MONOXIDE ON ACTIVATED ALUMINA AS A MODEL REACTION —

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The chromatographic moving-bed reactor is a new device which possesses functions of both reactor and adsorptive separator. This paper demonstrates experimentally that reaction and separation occur simultaneously in the device for the oxidation of carbon monoxide over activated alumina with first-order irreversible kinetics.

The observed concentration profiles of the reactant and the product along the longitudinal direction of the bed are compared with the theoretical curves to show that the proposed model is valid. The effect of non-linearity of adsorption isotherms for the product at high surface concentration is also discussed.

Introduction

Industrial reaction processes are almost always followed by separation processes. Most process engineers have been, therefore, oriented toward optimizing possible combinations of known reaction and separation processes. On the other hand, only a few attempts have been made to propose new processes which possess these two functions in one apparatus. Distillation accompanied by homogeneous chemical reaction and parametric pumping with heterogeneous catalytic reaction are examples. In previous papers^{3,4}, the authors proposed a new combined process of adsorptive separation and catalytic reaction, called a chromatographic moving-bed reactor. In the new reactor, the product formed on catalyst surface is continuously separated from the unreacted component utilizing differences between adsorptivities of the reactant and the product. Though simplification and size reduction of the reactor-separator system is the primary significance of this process, its potential applications lie in improving the yield of the desired product in reversible or consecutive reactions such as of reactive distillation.

This process can also be considered for continuous large-scale operation of the chromatographic (pulse) reactor in chemical laboratories where reaction and adsorptive separation take place in unsteady-state fashion. This fixed-bed chromatographic technique has been applied to various reaction schemes such as

$A \rightarrow B$, $A \rightleftharpoons B$, and $A + B \rightleftharpoons C$ as Langer *et al.*¹ pointed out in their comprehensive review.

Similarly, the chromatographic moving-bed reactor can be applied to any reaction scheme mentioned above. It is, however, necessary first to investigate a fundamental case such as first-order irreversible reaction in order to show the validity of such a new process experimentally.

As in the case of reactive distillation, an exhausting section is required to recover the unreacted component adsorbed on catalyst surface as is discussed elsewhere⁵.

Only the rectifying section of the chromatographic moving-bed reactor is discussed in this paper, however, because analysis of the exhausting section differs from that of the rectifying section only in the boundary conditions.

1. Experimental

1.1 Catalyst/adsorbent

Activated alumina KHA-46 from Sumitomo Chemical Co. for catalytic oxidation of carbon monoxide was chosen for the following reasons: (1) it exhibits first-order kinetics with no noticeable decay of catalyst activity during the experiments, (2) the reaction rate is moderate enough to make the assumption of isothermal conditions valid; (3) the difference between adsorptivity of the reactant and that of the product is quite large; and (4) it has good mechanical strength for the use in the moving bed.

Adsorption equilibrium constants, adsorption rate constants and intraparticle diffusivities for carbon

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Fig. 1 Experimental results for fixed bed reactor (conversion vs. contact time)

1. Helium cylinder (99.995%)
2. Cylinder of mixed gas of oxygen (20.1%) and helium
3. Carbon monoxide cylinder (99.5%)
4. Mass-flow valve
5. Sampling valve for inlet gas stream
6. Simultaneous gas sampling device
7. Sampling valve for outlet gas stream
8. Gas chromatograph
9. Catalyst hopper (2000 ml)
10. Preheating section (30 cm)
11. Test section (55 cm)
12. Water-jacketed cooling section (30 cm)
13. Vibratory feeder
14. Solid sampling valve
15. Glass vessel for solid flow rate measurement
16. Catalyst reservoir
17. Soap film flow meter
18. Vacuum pump

Fig. 2 Schematic diagram of experimental apparatus

monoxide and carbon dioxide were reported in the previous paper⁶⁾ along with physical properties of the catalyst.

1.2 Surface reaction rate constant

Gas mixture of CO (0.53%), O₂ (20.1%) and helium (balance) was introduced to a steady-state laboratory fixed-bed reactor (i.d. 4 mm × 10.0 cm) packed with catalyst of 48–70 mesh at 307°C–378°C. Measurements of inlet and outlet concentration of carbon monoxide were made with a gas chromatograph

equipped with a silica gel column (i.d. 3 mm × 100 cm) at 40°C.

Logarithmic plots of fractional non-conversion versus contacting time show straight lines as shown in Fig. 1, indicating first-order kinetics. Surface reaction rate constant k_r was obtained from the slopes of the lines in Fig. 1 and the following relations obtained by Suzuki and Smith²⁾ using a one-dimensional Fibonacci search.

$$1-X=\exp\{-v(q_0-1)Z/(2E_A)\} \quad (1)$$

$$q_0=\{1+4E_A G(0)/v^2\}^{1/2} \quad (2)$$

$$G(0)=\frac{3(1-\alpha)Bi}{\alpha R^2/D_i}\left[1-\frac{Bi}{A_0(0)+Bi}\right] \quad (3)$$

$$A_0(0)=\phi(0)\coth\phi(0)-1 \quad (4)$$

$$\phi(0)=R\left[\frac{\beta}{D_i\{(1/k_{aF})+(1/k_r K_F)\}}\right]^{1/2} \quad (5)$$

Arrhenius-type description of surface reaction rate constant is given by

$$k_r=5.33\times 10^4 \exp(-14700/R_g T) \quad (6)$$

The values of adsorption equilibrium constant and adsorption rate constant for carbon monoxide over activated alumina were adopted from the previous work⁶⁾. Average tortuosity factor for intraparticle diffusion was found to be 2.83. Sherwood number was assumed to be 2. Axial dispersion coefficient was calculated by the correlation of Wen and Fan⁷⁾. The effectiveness factor is greater than 0.99; it is defined by

$$E.F.=3[\phi(0)\coth\phi(0)-1]/[\phi(0)]^2 \quad (7)$$

1.3 Description of the moving-bed reactor and experimental procedure

A schematic diagram of the moving-bed reactor is shown in Fig. 2. The moving bed is made of stainless steel with an inner diameter of 14.0 mm. The rectifying section is 55 cm long, and the locations of gas sampling are 5 cm, 15 cm, 25 cm, 35 cm, and 45 cm above the feed location.

Simultaneous gas sampling at these locations is necessary because sequential sampling procedure inevitably disorders the concentration profiles in the axial direction of a moving-bed reactor of this size. The apparatus was initially filled with a gas mixture of oxygen (20.1%) and helium (balance) and the catalyst surface was saturated with oxygen. During the operation, the apparatus was made airtight except at the gas inlet and outlet. Gas chromatograph with TCD detectors equipped with double columns of silica gel (i.d. 3 mm × 100 cm) and molecular sieves 5A (i.d. 3 mm × 200 cm) was used to analyse CO, CO₂ and O₂ at 40°C. The feed was a mixture of carbon monoxide (5.5%), oxygen (19.0%) and helium (balance). It took 2 to 5 hours for the reactor to reach steady state. The catalyst particles of 40–60 mesh used were regenerated in a fixed bed at 430°C for 48 hours to

Fig. 3 Comparison of experimental concentration profiles at 341°C with theoretical prediction

desorb carbon dioxide from the surface. All experimental runs were carried out at 341°C and under atmospheric pressure. Maximum pressure drop across the test section did not exceed 3 cm Hg. The values for v_g and v_s were so chosen that v_g/v_s was within the separation conditions shown in the previous work³⁾.

1.4 Experimental results

Typical concentration profiles of the reactant and the product in the chromatographic moving-bed reactor are shown in Figs. 3 to 6. Also shown in Fig. 3 is the theoretical concentration profile of the product in a fixed bed reactor operated under the same conditions as the moving-bed reactor except for v_s , which is set at zero. The concentration profile of the product in a fixed bed reactor can be safely predicted from the measured reaction rate constant in Eqs. (1) to (6) and the simple mass balance relation $C_F + C_P = C_0$ for $0 \leq x \leq Z$. The difference between C_{P1} (C_P at $x=Z$) in the fixed bed and C_{P1} in the moving bed shows that reaction and separation are actually occurring simultaneously in this apparatus. Runs 11 and 12 in Fig. 3 are performed for reproducibility checks. The void fraction of the moving bed, α , is assumed to be the same as that of a randomly packed bed of the same geometry, namely, $\alpha=0.40$.

2. Interpretation of the Results Based on Linear Adsorption Isotherms

To formulate a model, the following assumptions are made: (1) isothermal operation, (2) constant linear gas and solid velocities in the reactor, (3) first-order irreversible reaction with respect to surface concentration of the reactant, (4) linear adsorption isotherms, (5) negligible axial dispersion in both fluid and solid phases and (6) continuous steady-state operation of the whole system.

Fig. 4 Comparison of experimental concentration profiles at 341°C with theoretical prediction

Fig. 5 Comparison of experimental concentration profiles at 341°C with theoretical prediction

Fig. 6 Comparison of experimental concentration profiles at 341°C with theoretical prediction

Fig. 7 Outlet concentration of the product C_{P1} vs. v_s when v_g is fixed

Fig. 8 Surface concentration of the product at $x=0$ vs. v_s when v_g is fixed

From these assumptions, the following mathematical model is proposed along with three kinds of parameters, i.e., adsorption equilibrium constants (K_F and K_P), adsorption rate constants (k_{aF} and k_{aP}), and surface reaction rate constant (k_r). This model is named Model III after the number of kinds of parameters. In Model III, there are no concentration gradients in fluid film and pore spacing with respect to the radial direction of the particles. Pointwise adsorption equilibrium between the surface and pore spacing is assumed not to be attained.

Under these conditions, basic equation of the rectifying section for the reactant and the product are given by

$$(v_g - \gamma v_s)(dC_F/dx) + \gamma(k_{aF}C_F - k_{aF}n_F/K_F) = 0 \quad (8)$$

$$v_s(dn_F/dx) + k_{aF}C_F - (k_r + k_{aF}/K_F)n_F = 0 \quad (9)$$

$$(v_g - \gamma v_s)(dC_P/dx) + \gamma(k_{aP}C_P - k_{aP}n_P/K_P) = 0 \quad (10)$$

$$v_s(dn_P/dx) + k_{aP}C_P - (k_r + k_{aP}/K_P)n_P = 0 \quad (11)$$

The velocity terms in Eqs. (8) and (10) are $(v_g - \gamma v_s)$ because of the effect of the pore volume and the relation $C_J = C_{iJ}$.

The boundary conditions are written as follows:

$$C_F = C_0 \quad \text{at } x=0 \quad (12)$$

$$n_F = 0 \quad \text{at } x=Z \quad (13)$$

$$C_P = 0 \quad \text{at } x=0 \quad (14)$$

$$n_P = 0 \quad \text{at } x=Z \quad (15)$$

Table 1 Discontinuities of concentration profiles of reactant and product in Model III ($J=F$ or P)

	C_J	C_{iJ}	n_J
$x=Z^*$	$C_{J1}^* = \left(\frac{v_g - \gamma v_s}{v_g}\right) C_{J1}$	0	0
$x=Z$	C_{J1} setting $x=Z$ in Eqs. (16) and (22)	$C_{iJ1} = C_{J1}$	$n_{J1} \neq K_J C_{iJ}$ Eqs. (17) and (23)

Table 2 Special cases of Model III for reactant

Limiting cases	Effectiveness factor	$\frac{C_{F1}}{C_{F1}} \left(\frac{\text{Model II}}{\text{Model III}} \right)$	$\frac{n_{F0}}{n_{F0}} \left(\frac{\text{Model II}}{\text{Model III}} \right)$
$\Psi \rightarrow 0$	1.0	1.0	1.0
$K_F \rightarrow 0$	$\frac{1}{1+\Psi}$	$\exp\left(\frac{\Psi}{1+\Psi}\right)$	$\frac{1}{1+\Psi}$

The x -coordinate is taken as positive in the direction of fluid flow. The solutions of the basic equations (8) and (9) for the reactant are given by

$$C_F/C_0 = A_1 \exp(\lambda_1 \xi) + A_2 \exp(\lambda_2 \xi) \quad (16)$$

$$n_F/(C_0 K_F) = B_1 \exp(\lambda_1 \xi) + B_2 \exp(\lambda_2 \xi) \quad (17)$$

The constants of integration are given in Appendix 1. Discontinuities of the concentration profiles exist at $x=Z$, because $C_J = C_{iJ}$ for $0 < x < Z$ and $C_{iJ}^* = 0$ at $x=Z^*$, while $C_{iJ} \neq 0$ at $x=Z$. They are summarized in Table 1.

The characteristic equation with two real roots λ_1 and λ_2 is given by

$$K_F \Psi \lambda^2 + \Omega \left\{ \frac{K_F b}{1-b} - (1-\Psi) \right\} \lambda - \Omega^2 \left(\frac{b}{1-b} \right) = 0 \quad (18)$$

where dimensionless constants are given by

$$\Psi = k_r K_F / k_{aF} \quad (19)$$

$$\Omega = k_r K_F Z / v_s \quad (20)$$

$$b = \gamma v_s / v_g \quad (21)$$

The characteristic equation (18) is reduced to a first-order equation for the following special cases. When Ψ approaches zero, λ approaches $\lambda_s = \gamma k_r K_F Z / \{ \gamma v_s (1 + K_F) - v_g \}$, which is the single pole of the simplest model described in the previous paper⁴). This model is a limiting case of the present Model III with k_{aF} , $k_{aP} \rightarrow \infty$; it is proper to call this simple case Model II.

When K_F approaches zero, λ approaches $\lambda_s/(1+\Psi)$. The term $1/(1+\Psi)$ is an effectiveness factor for finite adsorption rate constant as shown by Suzuki and Smith²). These relations are summarized in Table 2. On the other hand, the solutions for the product are given by

$$C_P/C_0 = C_1 e^{\lambda_1 \xi} + C_2 + C_3 e^{\lambda_1 \xi} + C_4 e^{\lambda_2 \xi} \quad (22)$$

$$n_P/(C_0 K_P) = D_1 e^{\lambda_1 \xi} + D_2 + D_3 e^{\lambda_1 \xi} + D_4 e^{\lambda_2 \xi} \quad (23)$$

Constants of integration are shown in Appendix 2. The third pole for the product concentration profiles is given by

$$\kappa = \Phi \left\{ \frac{b(1+K_P) - 1}{b-1} \right\} \quad (24)$$

where

$$\Phi = k_{aP}Z/v_s \quad (25)$$

3. Discussion

As shown in Figs. 3 to 6, the difference between the theoretical (from Model II and III) and the experimental results for the reactant concentration lies within the range of the reactivity deviation of repeatedly-regenerated catalyst from run to run.

Consideration of the accuracy of the results is required with regard to the use of extrapolated values for k_{aP} and K_P obtained below 165°C in the previous investigation⁶). Since C_{P1} (Model III) is close to C_{P1} (Model II) as long as $1/(1+\Psi)$ is sufficiently close to 1, as shown in Table 2 and $\Psi \ll 1$, inaccuracy of k_{aP} associated with extrapolation can be considered insignificant. Furthermore, because the operating conditions are so chosen that v_g is considerably greater than v_s , the error associated with extrapolated K_P in the term of $\{v_g - \gamma v_s(1 + K_P)\}$ is also insignificant.

For the product, the slowest mass transfer stage is found to be the adsorption rate because $\delta_a \gg \delta_D \gg \delta_f$ under the experimental conditions, where the contributions of adsorption rate constant, intraparticle diffusivity and film mass transfer coefficient in second central moment for impulse response in adsorption chromatography (δ_a , δ_D , and δ_f , respectively) are written as²⁾

$$\delta_a = 2\gamma K_P^2/k_{aP} \quad (26)$$

$$\delta_D = 2\gamma(1 + K_P)^2 R^2 \beta / (15D_{iP}) \quad (27)$$

$$\delta_f = 2\gamma(1 + K_P)^2 R \beta / (3k_{fP}) \quad (28)$$

The agreement between the theoretical and experimental profiles for the product in Figs. 3 and 4 are good when v_g/v_s is relatively small.

Model III with finite mass transfer rate for the product can predict the non-zero values for C_{P1} at $x=Z$, while Model II with $k_{aP} \rightarrow \infty$ cannot. Model III is, however, not sufficient for the cases shown in Figs. 5 and 6. This discrepancy will be discussed in the next section.

3. Interpretation of the Results with Nonlinear Adsorption Isotherm

Figure 7 shows the results of outlet concentration of the product versus v_s , when v_g is fixed. Figure 8 shows the experimental values for $n_{P0}/C_0 K_P$ calculated from a simple mass balance equation given by

$$\gamma v_s n_{P0} = C_0(v_g - \gamma v_s)\{1 - \exp(\lambda_s)\} - (v_g - \gamma v_s)C_{P1} \quad (29)$$

They tend to deviate from the theory for the case of linear adsorption isotherm and to level off as v_s decreases. In other words, the experimental $n_{P0}/C_0 K_P$ asymptotically approaches saturation at high surface coverage, which implies nonlinear isotherm such as

the Langmuir type.

To describe the whole concentration profile for the product with nonlinear isotherm, a two-point boundary value problem for a pair of nonlinear differential equations must be solved. Though such a numerical calculation is beyond the scope of this report, the behaviour for C_{P1} can be discussed as follows.

Let adsorption isotherm for the product be assumed as Langmuir type, written as

$$n_P = \theta N = K_P C_P / \{1 + (C_P K_P / N)\} \quad (30)$$

where N is the concentration of adsorption sites and θ is the surface coverage of the product. Since K_P is much smaller than K_P , the surface coverage of the reactant can be neglected.

Maximum surface coverage of the product θ_{max} is given by

$$\theta_{max} = K_P / (K_P + \nu) \quad (31)$$

when

$$C_P = C_0$$

where

$$\nu = N/C_0$$

When θ is close to θ_{max} , the mass balance equation described below holds.

$$\begin{aligned} C_0(v_g - \gamma v_s)\{1 - \exp(\lambda_s)\} &= C_{P1}(v_g - \gamma v_s) + \gamma n_{P0} v_s \\ &= C_{P1}(v_g - \gamma v_s) + \gamma v_s N K_P / (\nu + K_P) \end{aligned} \quad (32)$$

The theoretical curves for C_{P1}/C_0 calculated from Eq. (32) for given ν are also shown in Fig. 7. Since the effect of finite mass transfer rate is neglected, these curves (solid lines) intersect the abscissa instead of approaching it asymptotically as v_s increases, as in the case of Model III. This may be the reason why the experimental data in Fig. 7 do not exactly lie on a certain theoretical curve.

Nevertheless, such a simplified correction of isotherms is helpful in the qualitative explanation of the change of experimental C_{P1}/C_0 with the change of v_s . Namely observed C_{P1}/C_0 decreases at larger v_s than predicted from Model III.

Conclusions

- 1) It was confirmed that reaction and separation were actually taking place in this reactor/separators.
- 2) The concentration profiles for the reactant can be interpreted theoretically based on a linear adsorption isotherm.
- 3) Deviation of the product from the theory with linear isotherm is observed when v_g/v_s is relatively large. This is attributed to nonlinearity of adsorption isotherms.

Appendix 1: Constants of integration for the reactant in Eqs. (16) and (17)

$$A_1 = \left[1 - \left\{ \frac{(1-b)\lambda_1 + \Omega b/\Psi}{(1-b)\lambda_2 + \Omega b/\Psi} \right\} e^{(\lambda_1 - \lambda_2)\xi} \right]^{-1} \quad (A-1)$$

$$A_2 = 1 - A_1 \quad (\text{A-2})$$

$$B_1 = \{1 + (1 - b)\lambda_1 \Psi / (\Omega b)\} A_1 \quad (\text{A-3})$$

$$B_2 = \{1 + (1 - b)\lambda_2 \Psi / (\Omega b)\} A_2 \quad (\text{A-4})$$

Appendix 2: Constants of integration for the product in Eqs. (22) and (23)

$$C_3 = -\frac{B_1}{\kappa} \left(\frac{1}{\lambda_1 - \kappa} - \frac{1}{\lambda_1} \right) \left(\frac{\Omega \Phi b}{1 - b} \right) \frac{1}{K_P} \quad (\text{A-5})$$

$$C_4 = -\frac{B_2}{\kappa} \left(\frac{1}{\lambda_2 - \kappa} - \frac{1}{\lambda_2} \right) \left(\frac{\Omega \Phi b}{1 - b} \right) \frac{1}{K_P} \quad (\text{A-6})$$

$$C_1 = \left[C_3 \left\{ \frac{(1 - b)\lambda_1}{b\Phi} \right\} e^{\lambda_1} + C_4 \left\{ \frac{(1 - b)\lambda_2}{b\Phi} \right\} e^{\lambda_2} \right] \times \left[1 - \left\{ 1 + \frac{(1 - b)\kappa}{b\Phi} \right\} e^{\kappa} \right] \quad (\text{A-7})$$

$$C_2 = -C_1 - C_3 - C_4 \quad (\text{A-8})$$

$$D_1 = C_1 \left\{ \frac{(1 - b)\kappa}{b\Phi} + 1 \right\} \quad (\text{A-9})$$

$$D_2 = C_2 \quad (\text{A-10})$$

$$D_3 = C_3 \left\{ \frac{(1 - b)\lambda_1}{b\Phi} + 1 \right\} \quad (\text{A-11})$$

$$D_4 = C_4 \left\{ \frac{(1 - b)\lambda_2}{b\Phi} + 1 \right\} \quad (\text{A-12})$$

Nomenclature

A_1, A_2	= defined by Eqs. (A-1) and (A-2) in Appendix 1	[—]
$A_0(0)$	= defined by Eq. (4)	[—]
B_1, B_2	= defined by Eqs. (A-3) and (A-4) in Appendix 1	[—]
Bi	= $k_f R / D_i$, Biot number	[—]
b	= defined by Eq. (21)	[—]
C	= concentration in bulk phase	[mol/cm ³]
C_1, C_2, C_3, C_4	= defined by Eqs. (A-5) to (A-8) in Appendix 2	[—]
C_i	= concentration in pore spacing	[mol/cm ³]
C_0	= inlet concentration of reactant	[mol/cm ³]
D_1, D_2, D_3, D_4	= defined by Eqs. (A-9) to (A-12) in Appendix 2	[—]
D_{AB}	= molecular diffusivity	[cm ² /sec]
D_i	= effective intraparticle diffusivity	[cm ² /sec]
E_A	= axial dispersion coefficient	[cm ² /sec]
$E.F.$	= effectiveness factor defined by Eq. (7)	[—]
G_0	= defined by Eq. (3)	[—]
K	= adsorption equilibrium constant based on unit pore volume	[—]
k_a	= adsorption rate constant based on unit pore volume	[1/sec]
k_f	= film mass transfer coefficient	[cm/sec]
k_r	= first-order surface reaction rate constant	[1/sec]
N	= concentration of adsorption sites based on unit pore volume	[mol/cm ³]
n	= surface concentration of adsorbed	

	species based on unit pore volume	[mol/cm ³]
q_0	= defined by Eq. (2)	[—]
R	= average particle radius	[cm]
R_g	= gas constant	[cal/mol-°K]
Sh	= Sherwood number, $2k_f R / D_{AB}$	[—]
v	= interparticle linear gas velocity in fixed bed	[cm/sec]
v_g	= interparticle linear gas velocity in moving bed	[cm/sec]
v_s	= linear solid velocity in moving bed	[cm/sec]
X	= fractional conversion	[—]
x	= axial distance from gas inlet, positive in direction of gas flow	[cm]
Z	= length of test section	[cm]
α	= void fraction of bed	[—]
β	= porosity of catalyst	[—]
γ	= $(1 - \alpha)\beta/\alpha$	[—]
θ	= surface coverage of the product	[—]
κ	= defined by Eq. (24)	[—]
λ_1, λ_2	= roots of Eq. (18)	[—]
λ_s	= $\gamma k_r K_F Z / \{ \gamma v_s (1 + K_F) - v_g \}$, pole of Model II	[—]
μ_2	= second central moment for impulse response in adsorption chromatography	[sec ²]
ν	= N/C_0	[—]
ξ	= dimensionless length along axis of moving bed, x/Z	[—]
Φ	= defined by Eq. (25)	[—]
$\phi(0)$	= Thiele modulus defined by Eq. (5)	[—]
Ψ	= defined by Eq. (19)	[—]
Ω	= defined by Eq. (20)	[—]

<Subscripts>

F	= reactant
J	= arbitrary component
P	= product
0	= at $x=0$
1	= at $x=Z$

<Superscript>

*	= refers to the position just outside the test section
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