NON-ISOTHERMAL EFFECTIVENESS FACTORS IN BIDISPERSED CATALYSTS UNDER CONDITIONS OF EXTERNAL TRANSPORT RESISTANCES

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ABSTRACT

Effectiveness factors in bidispersed catalysts under conditions of internal and external heat and mass transport resistances have been obtained numerically. The parametric dependence of the utilization of such catalysts has been formulated in the form of an equation which predicts the values to within a per cent accuracy.

INTRODUCTION

A large number of studies concerning reaction and diffusion in bidispersed catalysts are reported in chemical engineering and a recent survey by Dogu[1] covers some of the important aspects and conclusions of these studies. Ors and Dogu[2] define a parameter α for bidispersed system to characterize the ratio of diffusion times in the macro and micro particle regions. The approach of Ors and Dogu[2] is convenient and its application to analysis of several nonlinear rate forms such as power law[3,4], Langmuir-Hinshelwood types of rate models[5] and to analysis of bidispersed catalysts under non-isothermal conditions[6] has been subsequently reported. In this note we present the results of reaction-diffusion behaviour of bidispersed catalysts for a first order reaction under non-isothermal conditions where external transport resistances become important.

This particular aspect does not appear to have been studied so far and is relevant when problems such as parametric sensitivity in pellets or in fixed-bed reactors become important. In fact, while a large number of studies dealing with parametric sensitivity have been reported[1] for conventional monodispersed catalysts those in presence of bidispersed catalyst have yet to be studied. This apparently a simple problem is compounded by severe numerical problems and as will be seen in the present work, numerical integration of the governing equations requires substantial amount of central processing unit (CPU) time even when run on fast computers. As a first step towards this more general study, in the present work, we report the values of effectiveness factors for bidispersed catalysts under non-isothermal conditions in the presence of external transport resistances. The study covers substantial variations in the system parameters and final results are correlated in the form 2 of an equation which predicts the effectiveness factors as a function of system parameters with reasonable degree of accuracy.

Problem formulation

Referring to figure 1, which shows a schematic diagram of the spherical geometry of micro-macro particle catalyst system, the governing
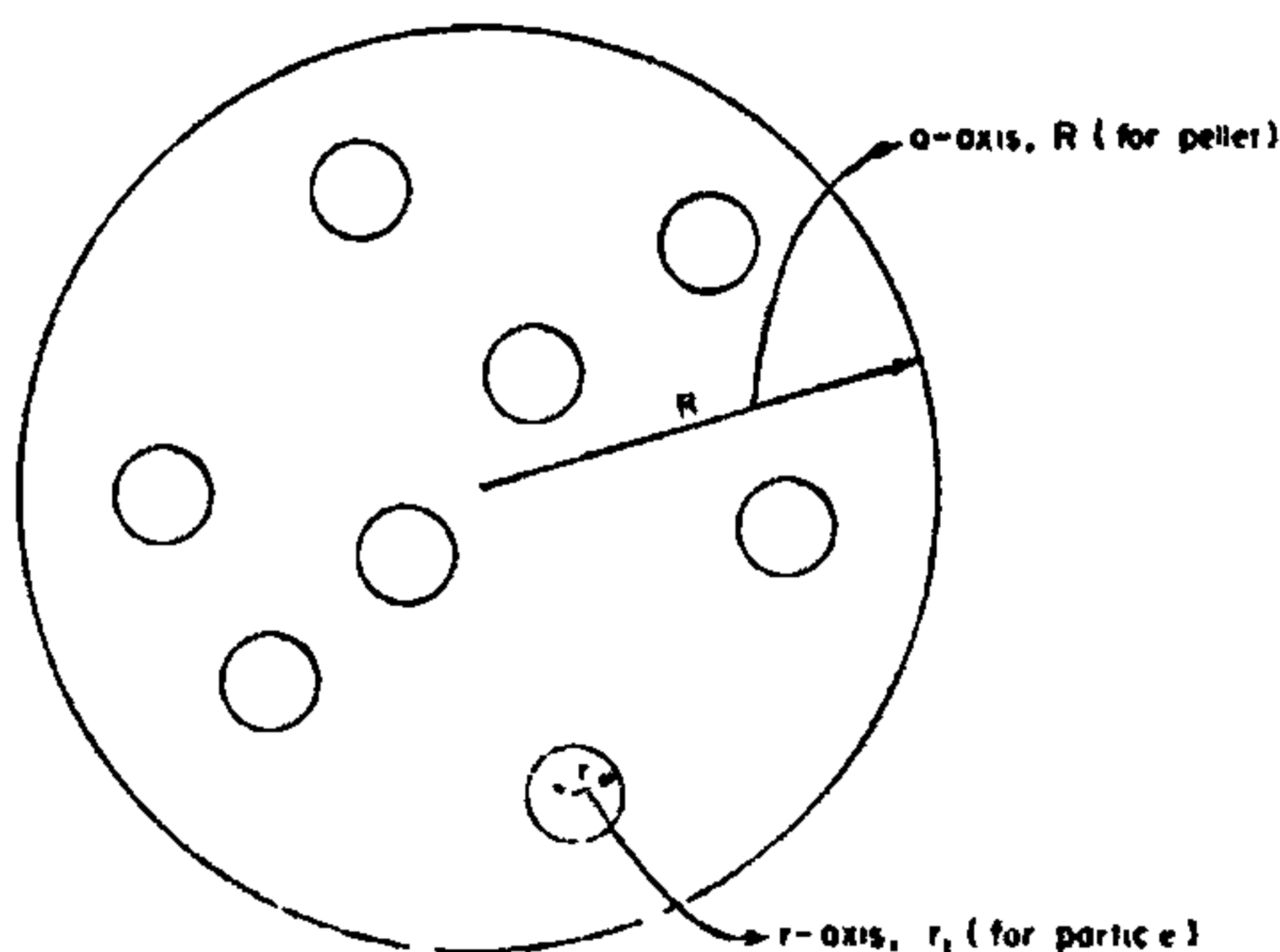

Figure 1. Diagram of macro–micro particles in a pellet.

equations for mass and heat conservation can be written in non-dimensional form as:

Microparticle

$$\nabla_x^2 C_i = \phi^2 \exp\left[\gamma\left(1 - \frac{1}{T_i}\right)\right] C_i$$

with boundary conditions;

$$C_i(x = 1) = C_a, \frac{dC_i}{dx}\bigg|_{x=0} = 0 \tag{1}$$

$$\nabla_x^2 T_i = -\phi^2 \beta \exp\left[\gamma\left(1 - \frac{1}{T_i}\right)\right] C_i$$

with boundary conditions;

$$T_i(x = 1) = T_a, \frac{dT_i}{dx}\bigg|_{x=0} = 0. \tag{2}$$

Macroparticle

$$\nabla_y^2 C_a = \alpha \frac{dC_i}{dx}\bigg|_{x=1}$$

with boundary conditions,

$$\frac{dC_a}{dy}\bigg|_{y=0} = 0; \frac{dC_a}{dy}\bigg|_{y=1} = \mathrm{Sh}(1 - C_{as}) \tag{3}$$

$$\nabla_y^2 T_a = \alpha_T \frac{dT_i}{dx}\bigg|_{x=1}$$

with boundary conditions,

$$\frac{dT_a}{dy}\bigg|_{y=0} = 0; \frac{dT_a}{dy}\bigg|_{y=1} = \mathrm{Nu}(1 - T_s^s), \tag{4}$$

where C_a is defined as dimensionless concentration in the macroparticle normalized with respect to concentration in the bulk and the various parameters appearing in (1), (2), (3) and (4) are defined as follows:

$$\phi = \sqrt{(k/D_i)r_i^2}; \beta = (-\Delta H)\frac{D_i C_{as}}{k_t T_s^s}$$

$$\alpha = 3(1 - \varepsilon)\frac{D_i R^2}{D_a r_i^2}; \alpha_T = 3(1 - \varepsilon)\frac{k_i R^2}{k_p r_i^2}$$

$$\gamma = (E/R_g T_s^s); \mathrm{Sh} = \frac{k_g R}{D_a}; \mathrm{Nu} = \frac{h_f R}{k_p}.$$

T_i and T_a from (1), (2), (3) and (4) can be eliminated appropriately to give governing microparticle mass conservation equation as:

$$\nabla_x^2 C_i = \phi^2 \exp$$

$$\left[\gamma\left(1 - \frac{1}{C + \beta C_a\left(1 + \frac{\alpha_T}{\alpha}\right) - \beta C_i}\right)\right] C_i$$

with boundary conditions;

$$C_i(x = 1) = C_a, \frac{dC_i}{dx}\bigg|_{x=0} = 0. \tag{5}$$

Equations (3) and (5) together describe the behaviour of the system subject to appropriate initial and boundary conditions. Numerical integration of these equations involves considerable trial and error besides the small step size requirements due to stiffness of the equations. It is desirable to avoid trial and error in the numerical computations and hence an alternate scheme, as will be explained shortly, yield the concentration and temperature profiles in the micro and macro particles and the information is used to compute the eventual quantities of interest which are defined as

$$\eta = \left[9\frac{dC_a}{dy}\bigg|_{y=1}\right]\bigg/\alpha\phi^2 \tag{6}$$

$$\frac{dT_a}{dy}\bigg|_{y=1} = \beta\frac{\alpha_T}{\alpha}\left[\frac{dC_a}{dy}\bigg|_{y=1}\right] \tag{7}$$

$$T_s^s = C + \beta\frac{\alpha_T}{\alpha}C_{as} \tag{8}$$

$$\mathrm{Sh} = \left[\frac{dC_a}{dy}\bigg|_{y=1}\right]\bigg/(1 - C_{as}) \tag{9}$$

$$\mathrm{Nu} = \left[\frac{dT_a}{dy}\bigg|_{y=1}\right]\bigg/(T_s^s - 1) \tag{10}$$

The detailed steps involved in solving (3) and (5) are:

(i) Equation (5) represents a boundary value problem and solution of it to obtain the concentration profile in the micropore, for a defined set of parameter values α, α_T, β, γ and ϕ, requires considerable trial and error. It is possible however, to integrate this equation using Weisz and Hicks[7] method as an initial value problem. This however, requires to fix up the concentration at the center of the micropore and for the set of parameters (α, α_T, β, γ) and other variables (C and C_a) defined, the integration gives the value of ϕ.

(ii) For the set of parameter values (α, α_T, β, γ) assumed and for the values of C and C_a fixed, step (i) gives ϕ for assumed values of c_{i0}. These values of C_{i0} and ϕ (for same values of other parameters) when used in (5) gives the value of surface flux at the micropore.

(iii) The value of surface flux $(dc_i/dx)|_{x=1}$ as obtained in step (ii) is then used in macropore (3) which is integrated in y direction to obtain the new value of C_a and dC_a/dy at the next incremental step.

(iv) With this new value of C_a obtained in step (iii) we shall return to step (i) to redefine the boundary condition $C_i|_{x=1} = C_a$. For the other parameters held constant, this change in the value of C_a—for the same value of ϕ— suggests that c_{i0} would now be different. There is no easy way, however, to calculate this changed value of C_{i0}. In fact, since step (i) envisages to regard (5) as an initial value problem we should specify this value of C_{i0} *a priori*.

To circumvent this problem the procedure followed here assumes several values of C_{i0} in the neighbourhood of the value assumed in the earlier stage of step (i) and corresponding to each of these C_{i0} values obtains the values of ϕ-for the value of C_a from step (iii) and all other parameters same as before. The information is intrapolated and used to obtain the precise value of C_{i0} that corresponds to the value of ϕ as has been originally fixed in step (i). With this new set of C_{i0}, C_a and the other

parameters that remain unaltered, step (ii) suggesting integration of (5) gives the surface flux dC_i/dx. We then proceed to step (iii) and the new values of C_a and dC_a/dy.

(v) The entire procedure as suggested in steps (i–iv) is repeated until we reach the macroparticle surface (i.e. $y = 1$) where the values of $C_a|_s$ and $(dC_a/dy)|_s$ are noted.

(vi) Knowing the macroparticle surface concentration and the flux now allows us to determine the extent of external film resistance (Sh) and the value of the effectiveness factors using (6), (7), (8), (9) and (10).

(vii) The entire procedure is repeated for different sets of parameter values (α, α_T, β, γ) and different values of initial conditions such that C_{i0}, C_a, C etc. in step (i). The general results obtained in the form of $\dot{\eta}$ vs Sh or Nu number as a function of ϕ and other parameters can then be plotted using the calculated values.

A substantial range of parameters was investigated although the equations were becoming stiff in certain regions. The step size employed was of the order of 10^{-4}–10^{-5} and in such instances the CPU time consumed by the NEC 1000 supercomputer was in the range of 4–5 h.

RESULTS AND DISCUSSION

The governing equations were solved by the procedure outlined earlier to obtain the values of η, Sh and Nu. The corresponding ϕ values are also listed in the plots.

Figures 2a and 3a show Sh vs η and Nu vs η obtained by varying ϕ. Here η shows a monotonic increase as the value of ϕ is increased. The appropriate value of C_{i0} as calculated using the procedure suggested is also included along with the value of ϕ to provide checks on the numerical calculations. η monotonically increases as the center micropore concentration decreases. The subsequent results will be compared with this case to seek the influence of various parameters.
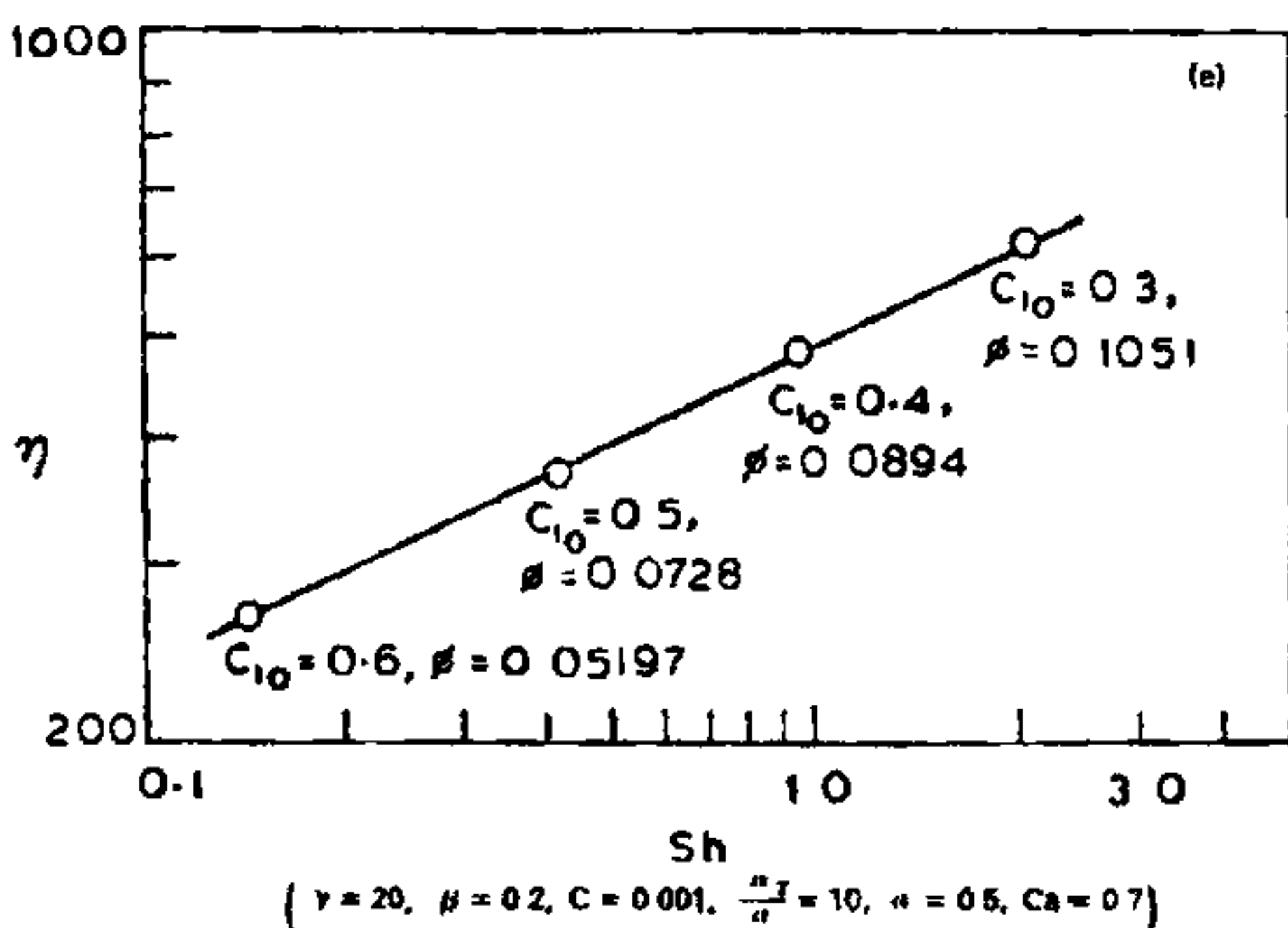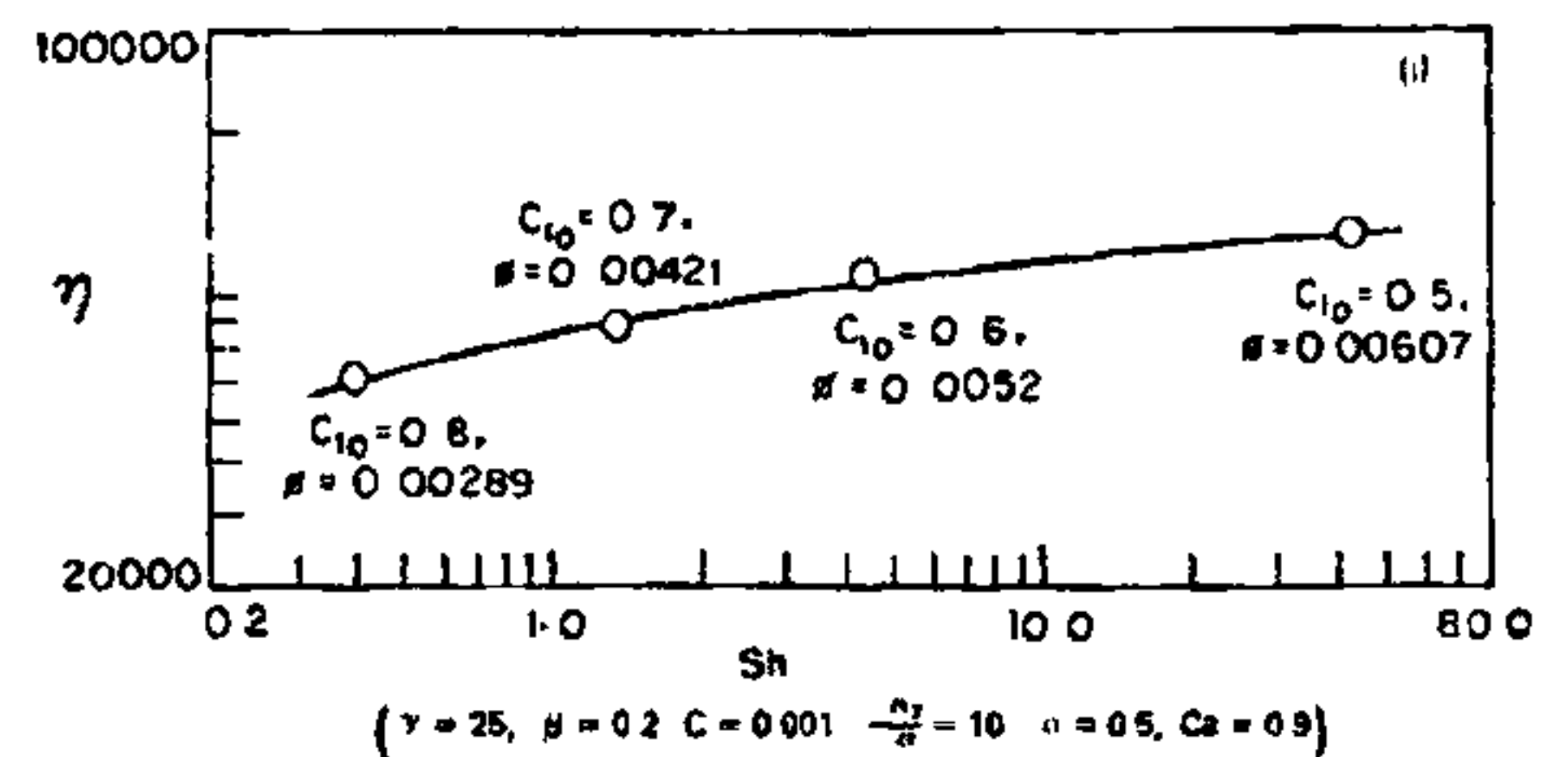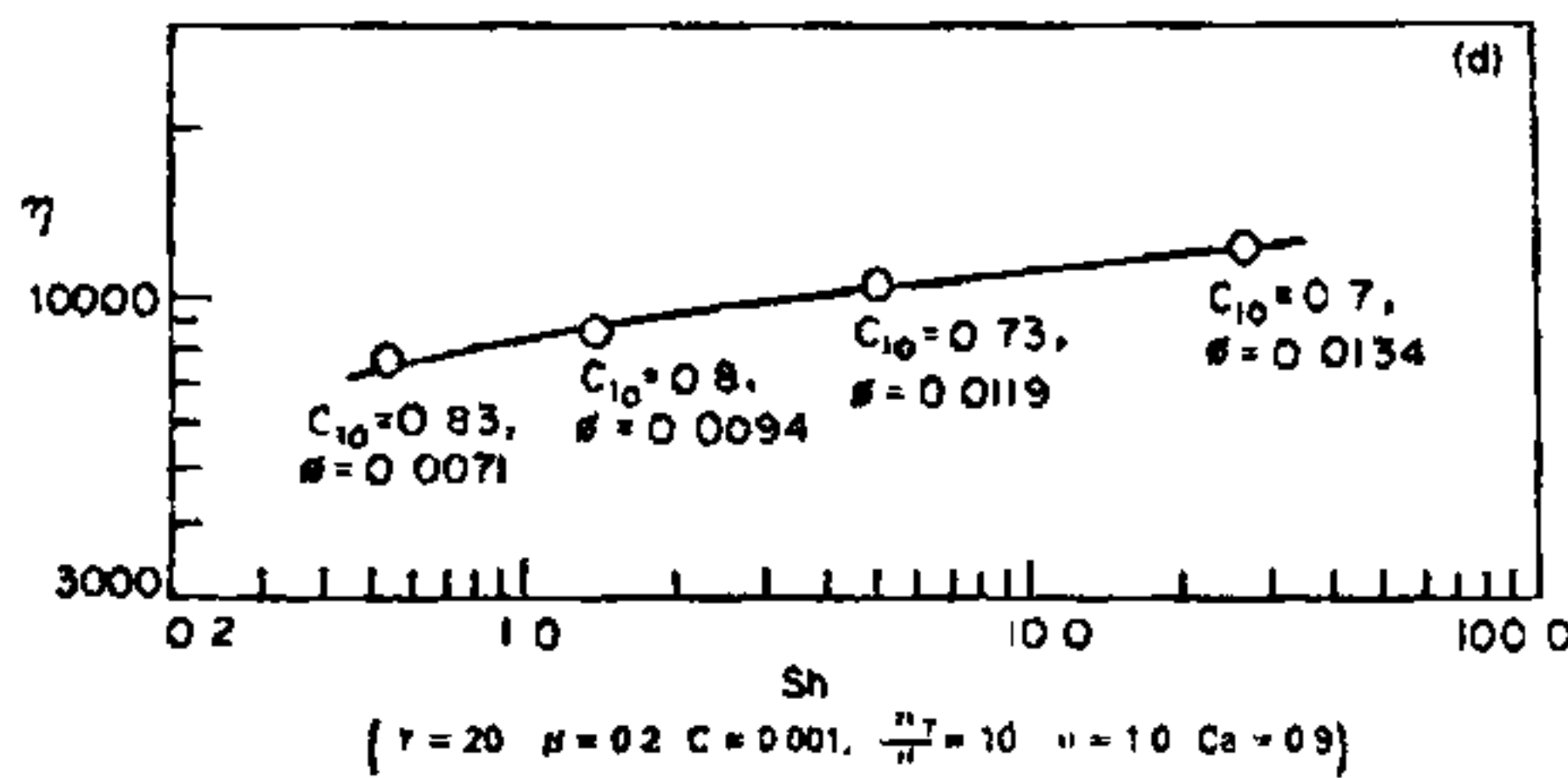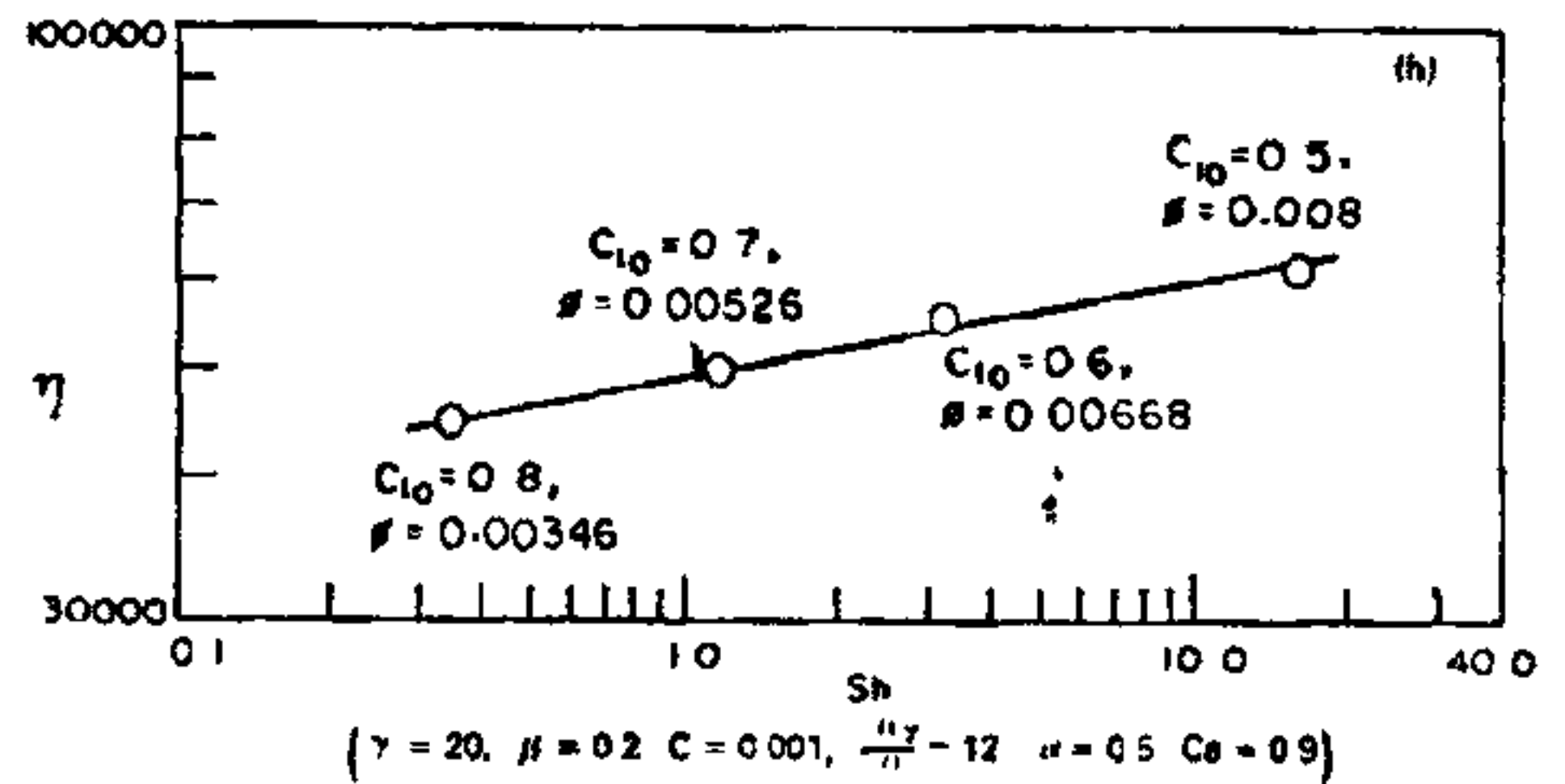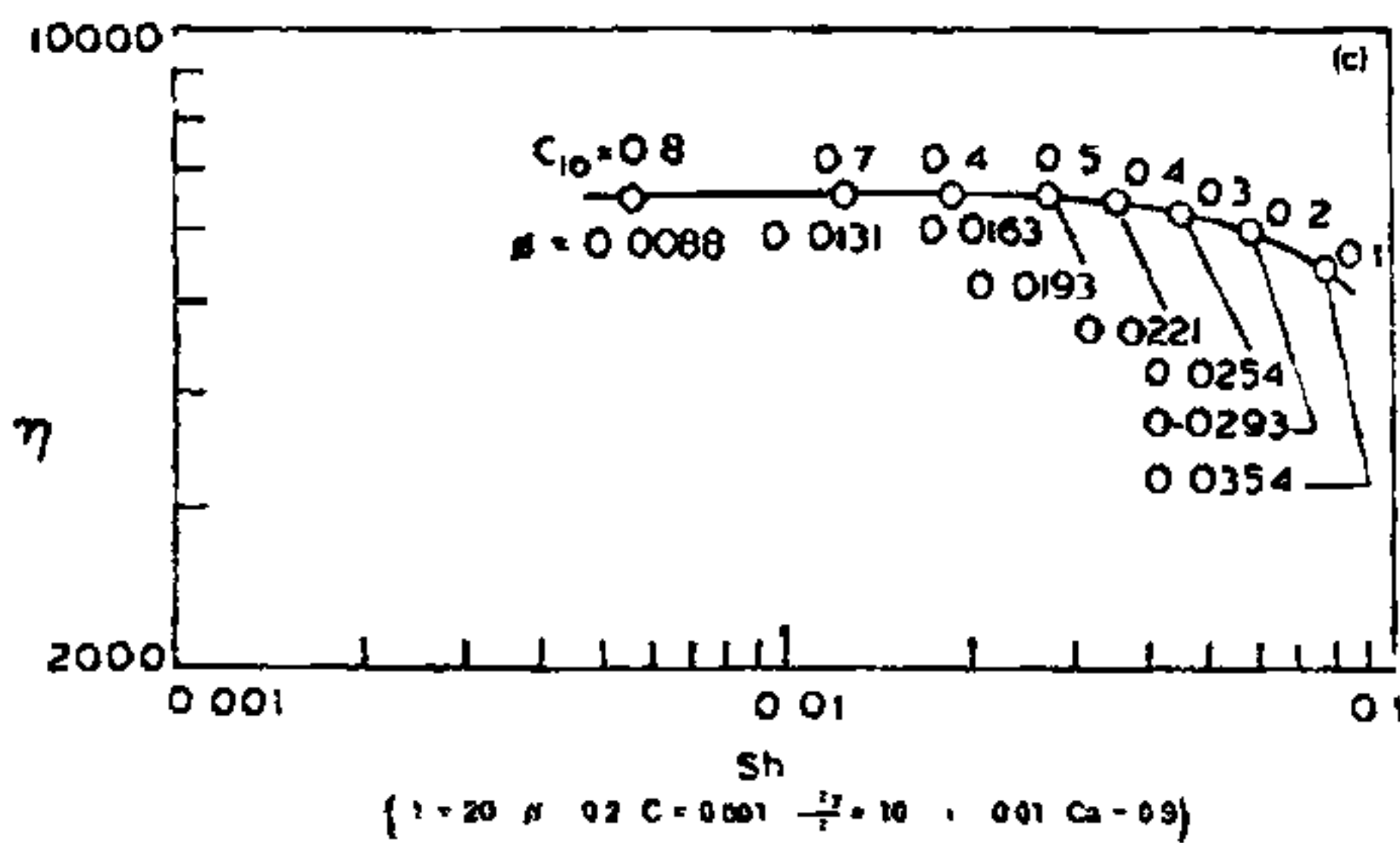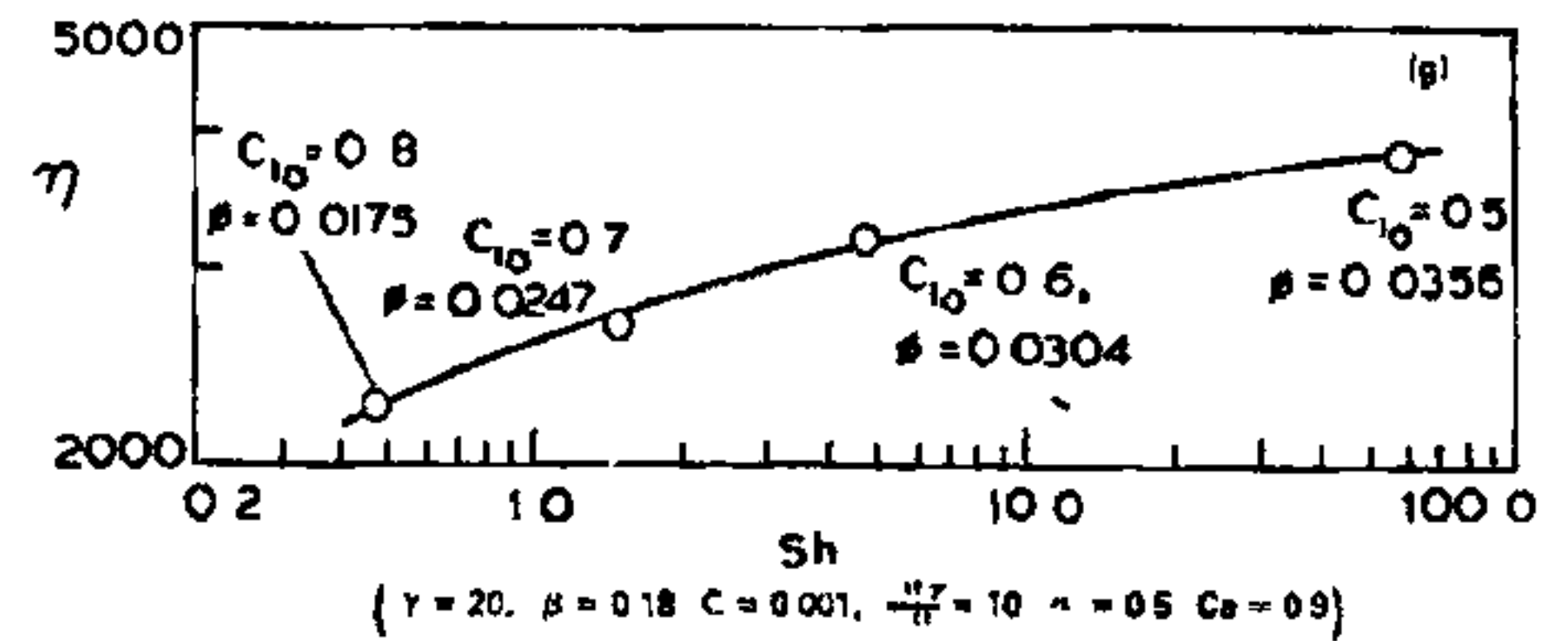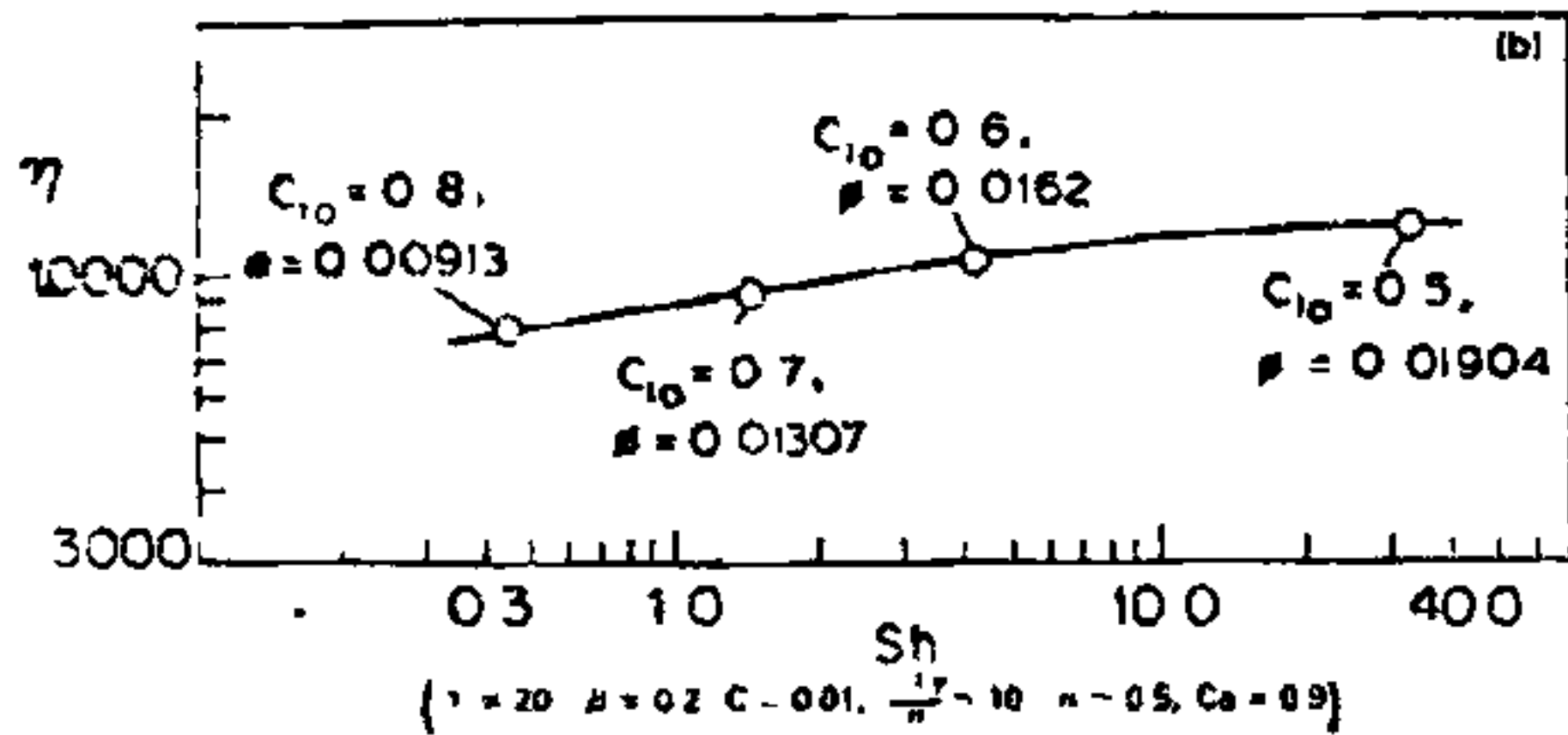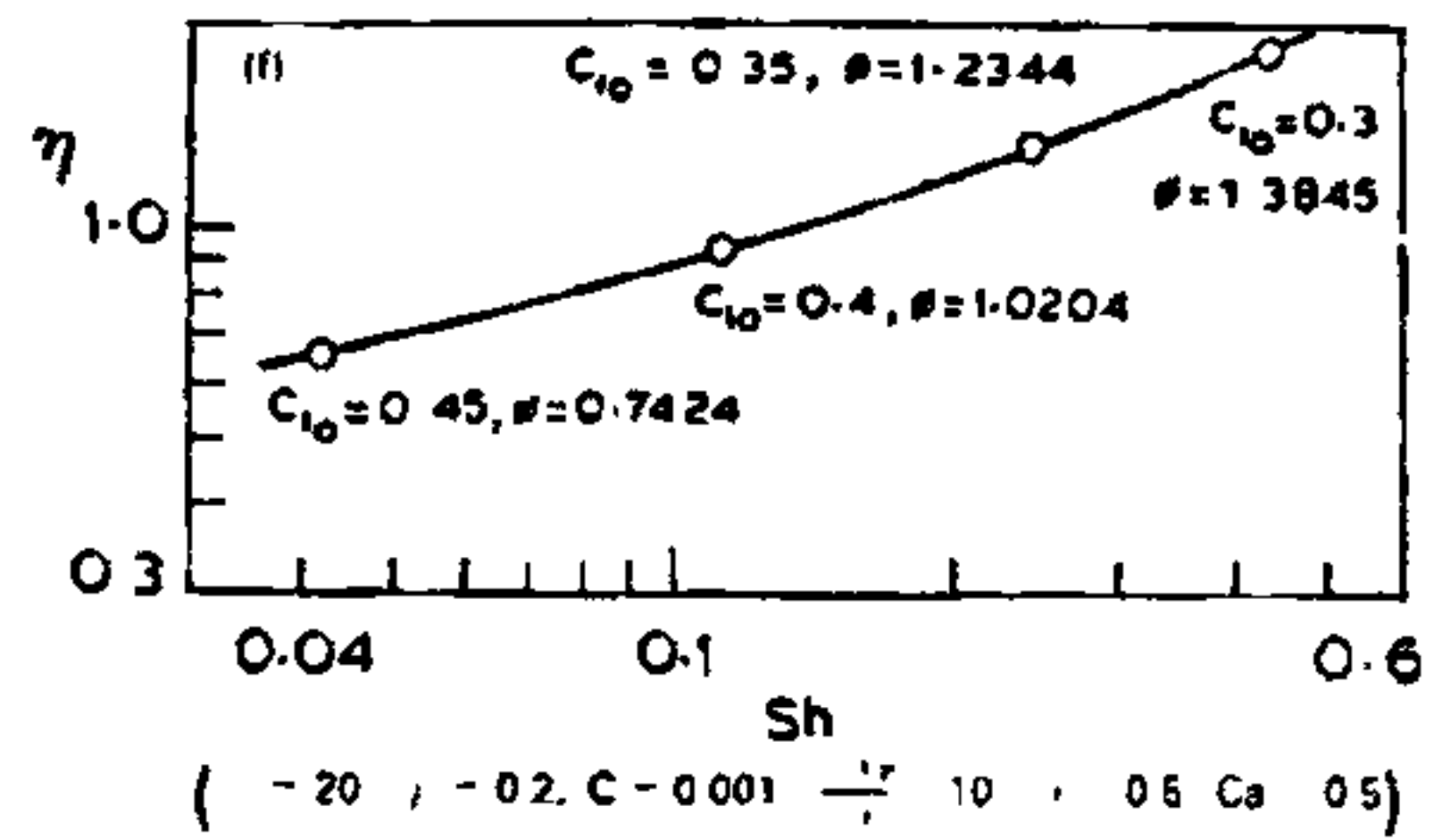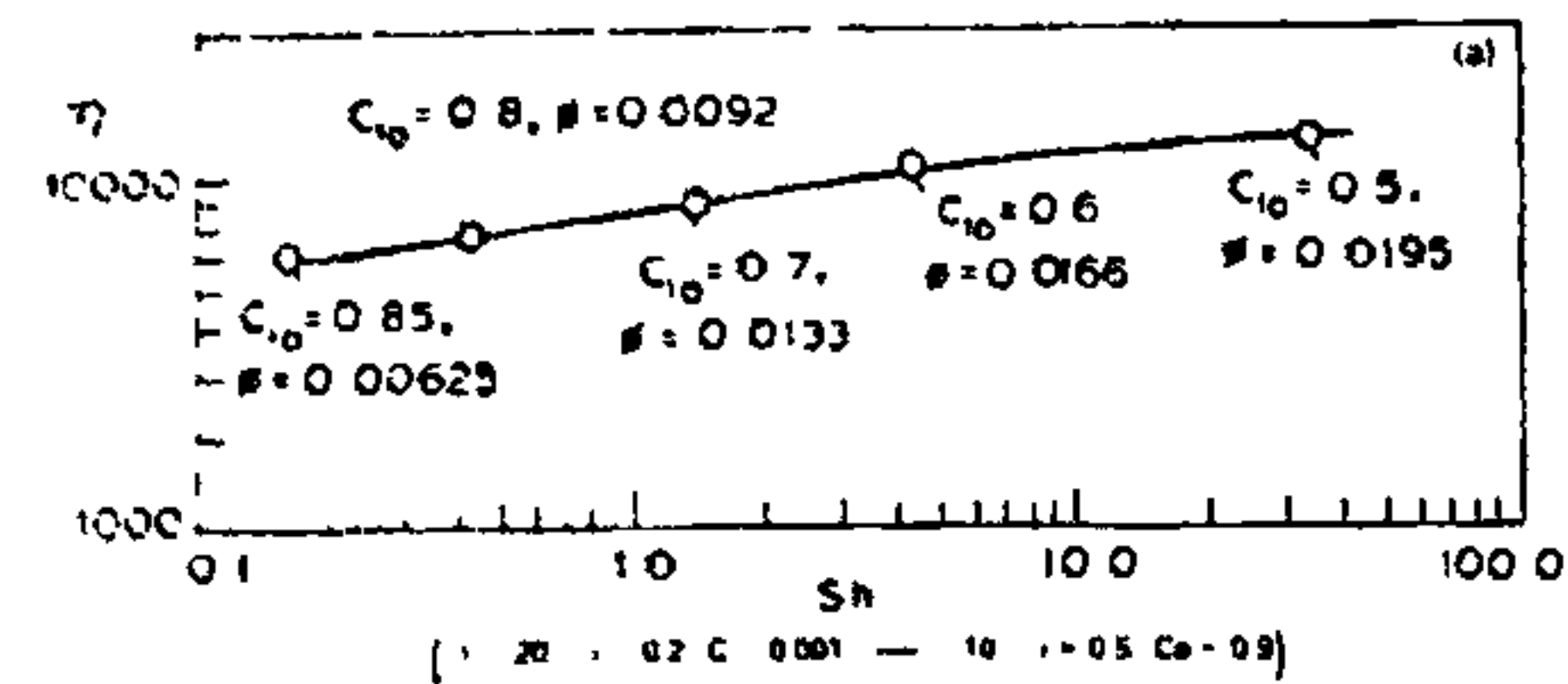
Figure 2a–i. Sherwood number vs effectiveness factor plot.

Figures 2b and 3b indicate the influence of parameter C. It can be easily seen that the nature of these plots does not differ significantly from the previous case except for the actual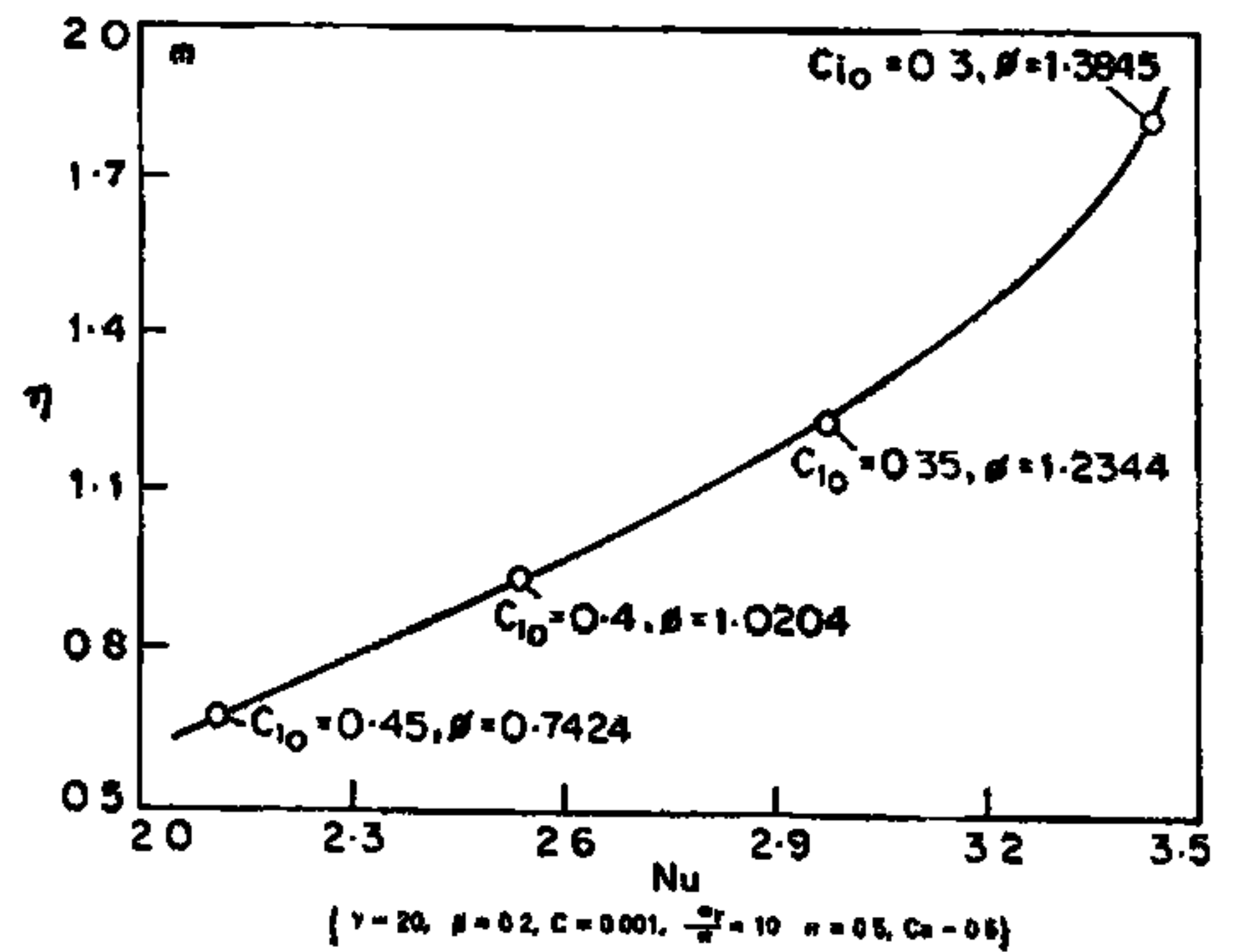 magnitudes of the derived quantities. From the definition of parameter C, it is clear that C can increase either due to the increase in surface temperature or decrease in surface concentration and results in enhancing η and marginal decrease in ϕ values.
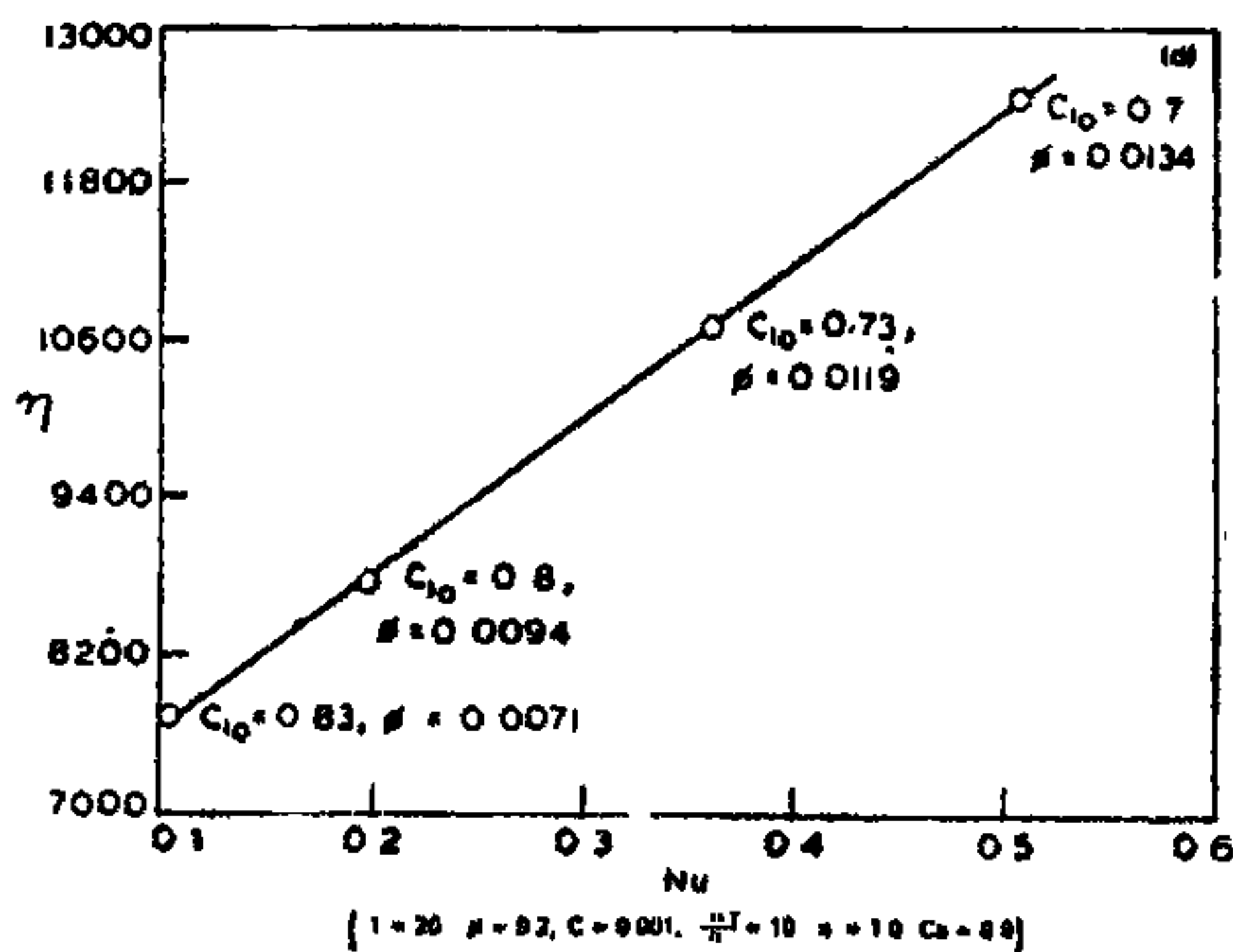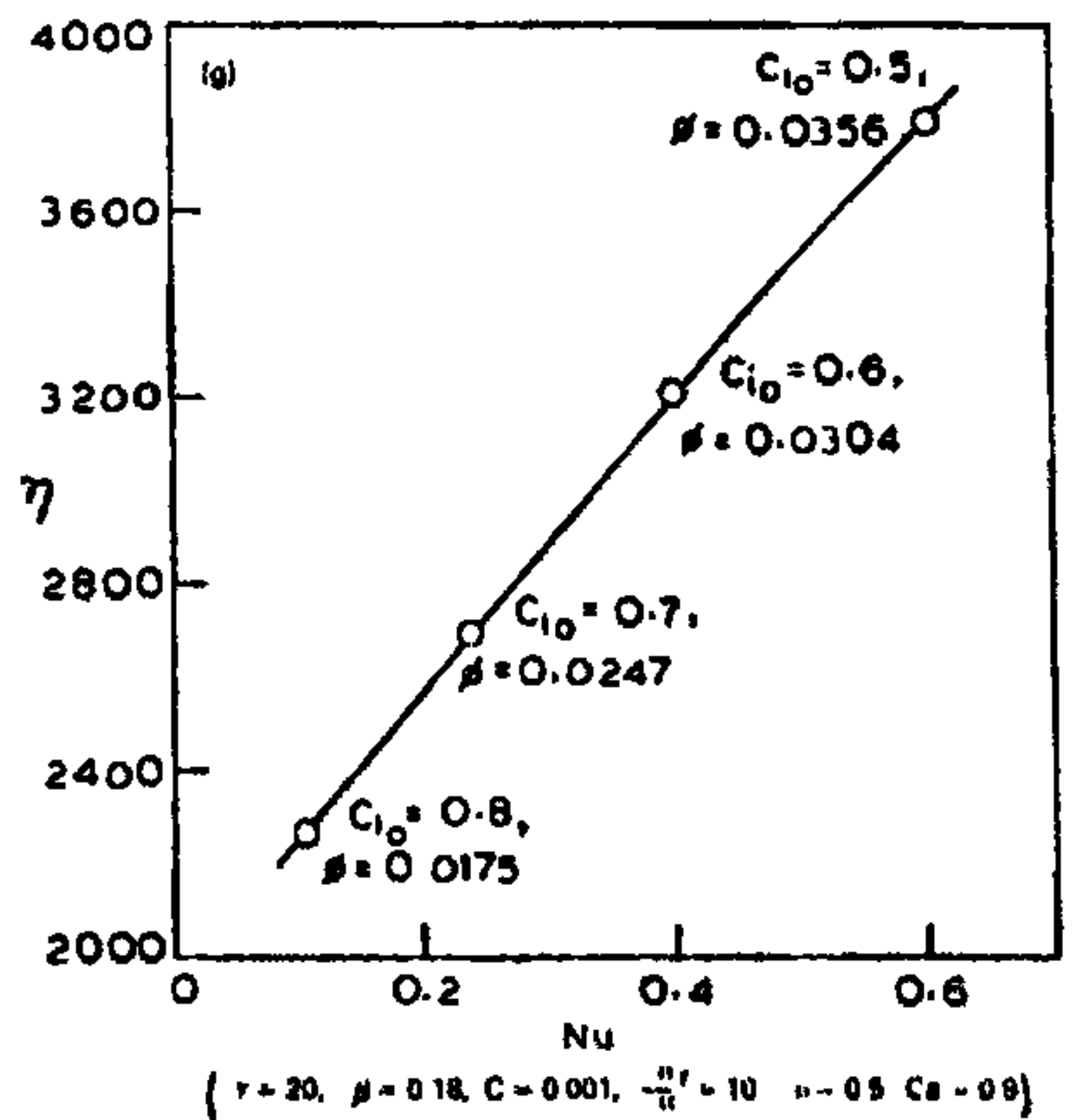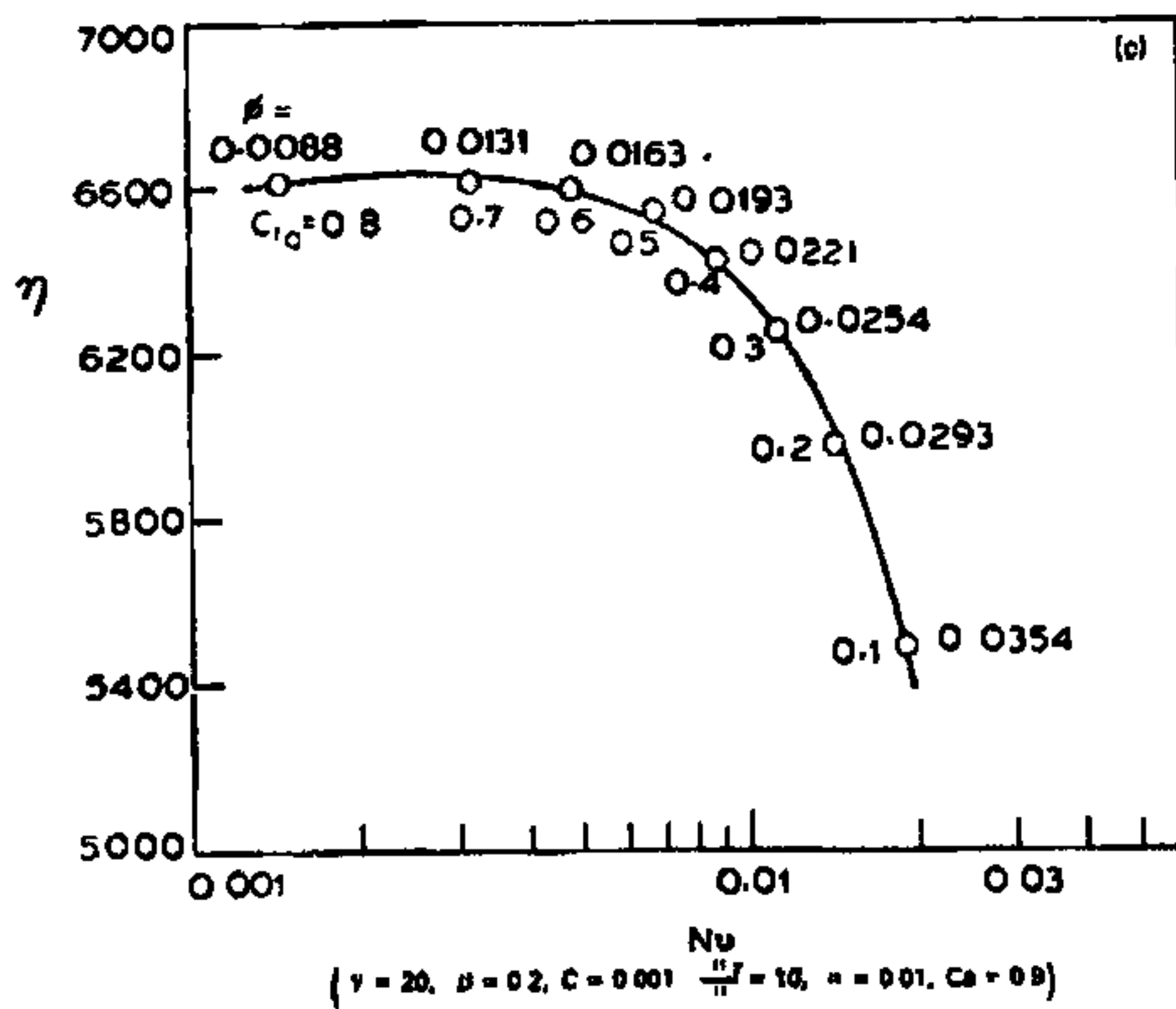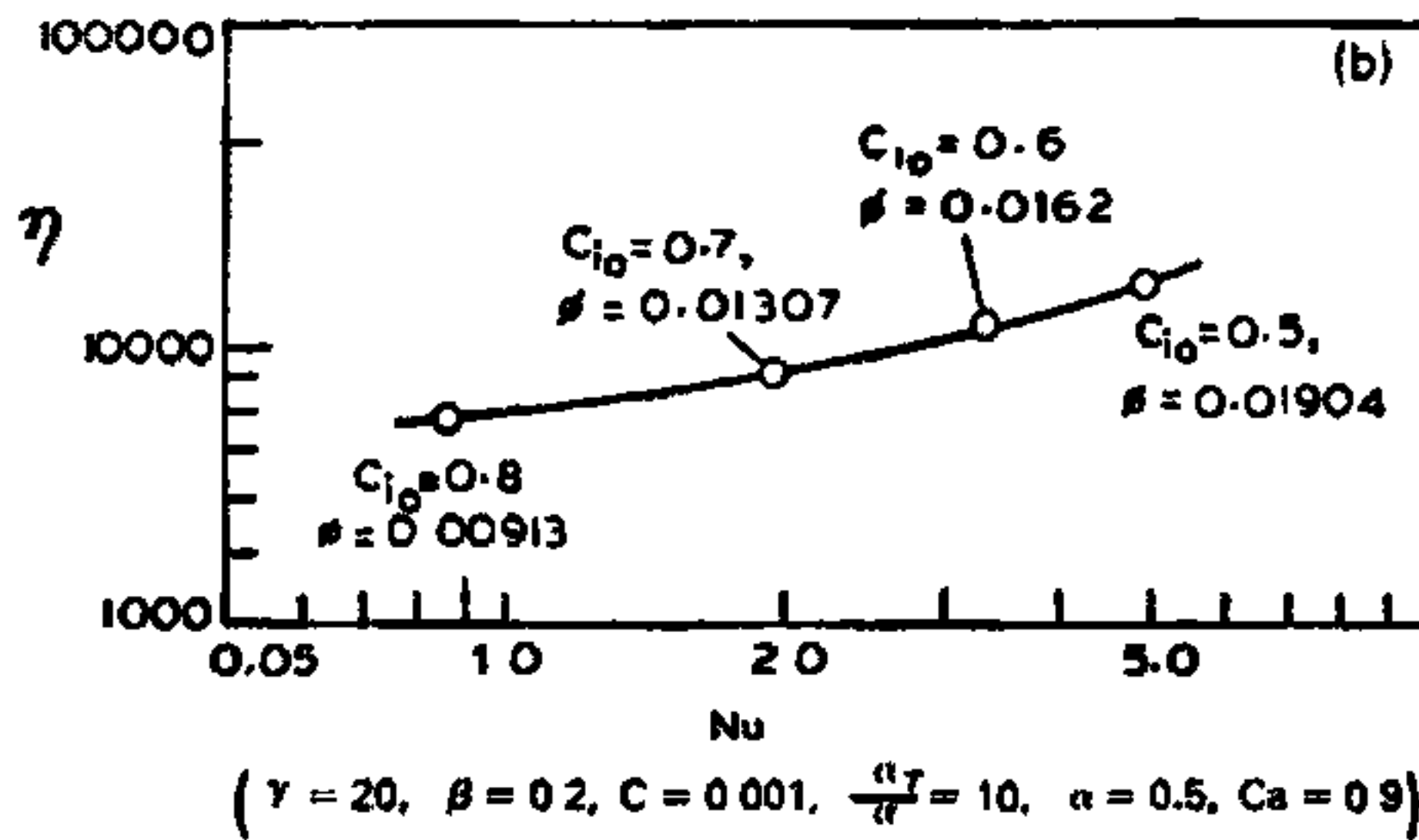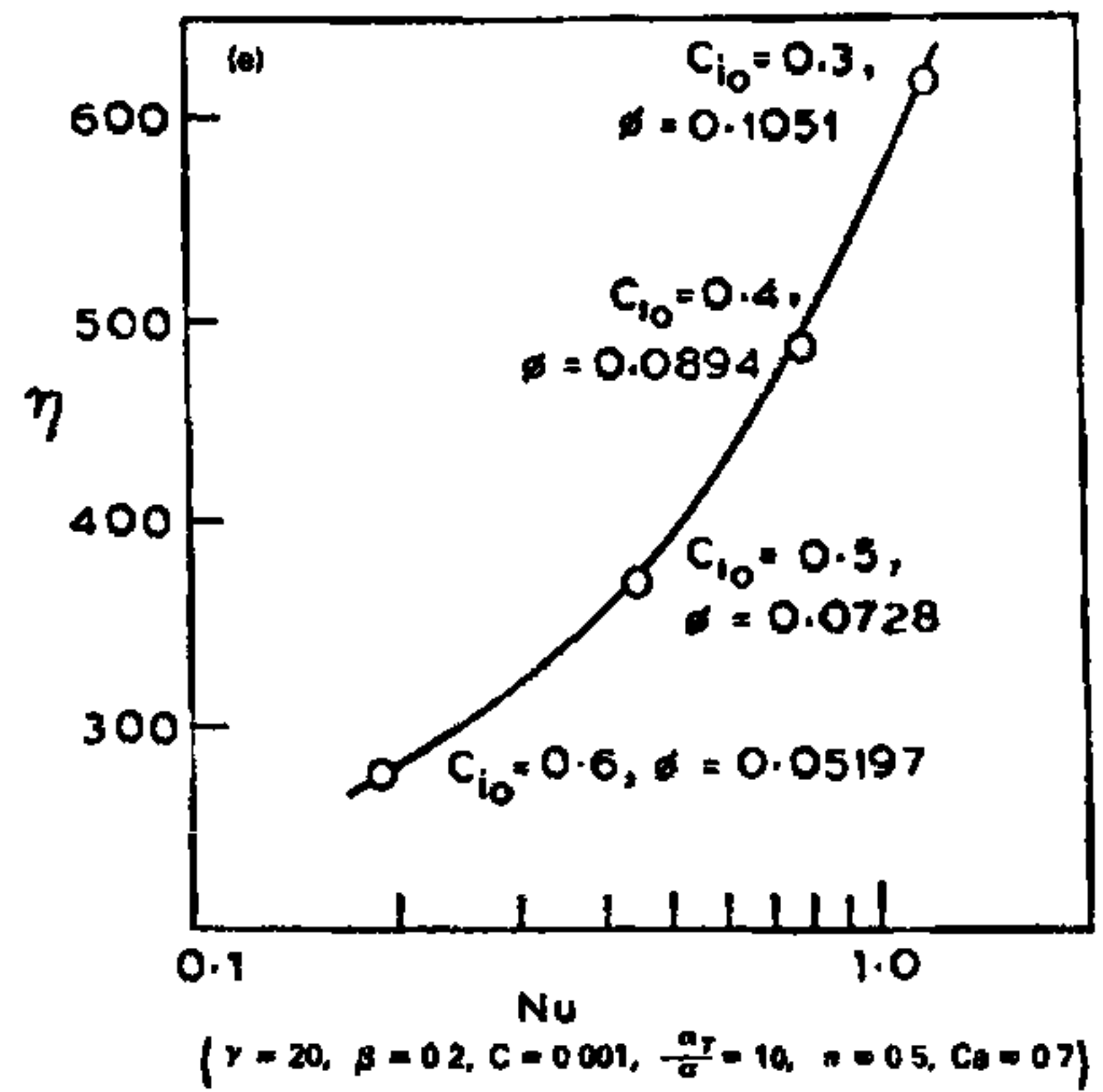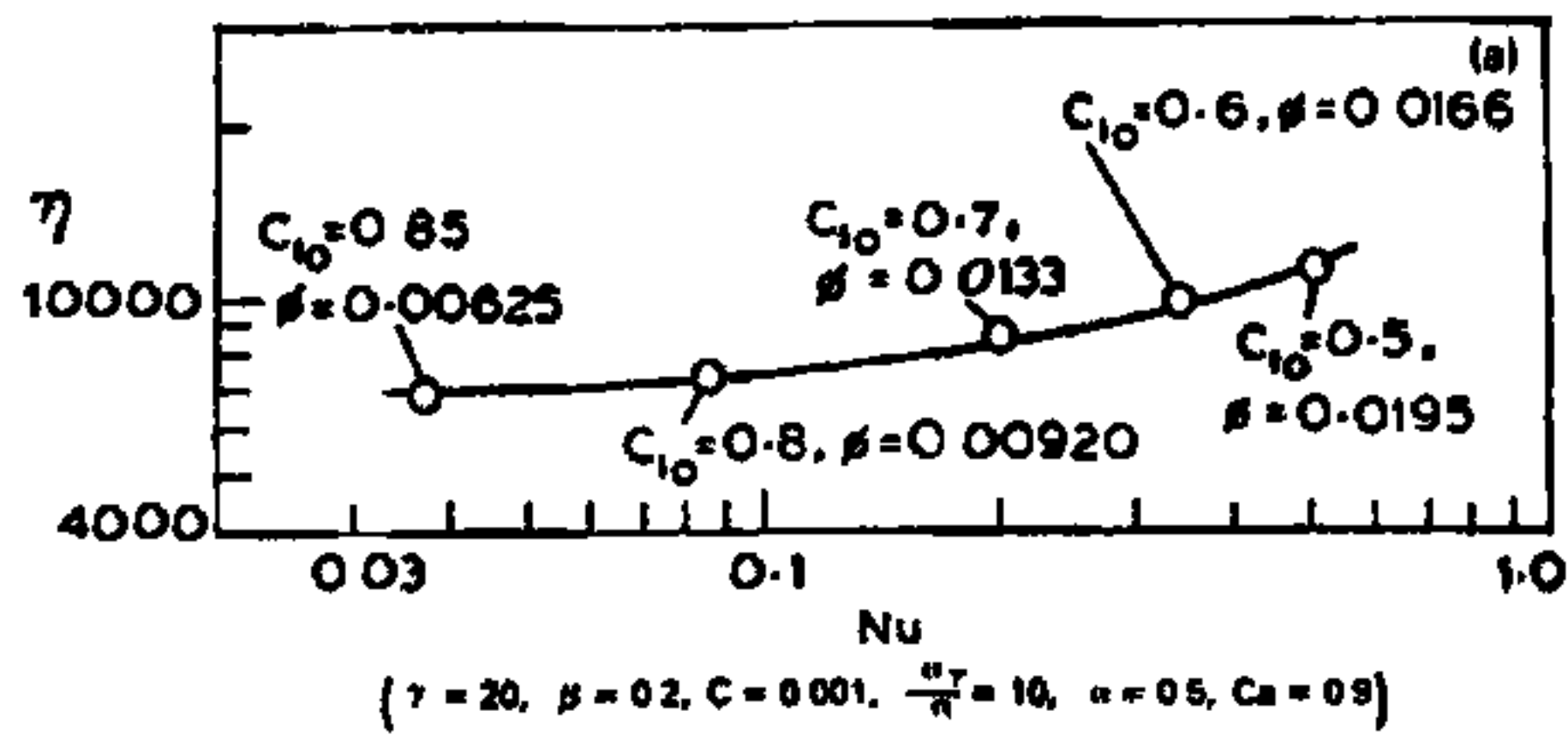
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Figure 3a–i. Nusselt number vs effectiveness factor plot.

The effect of variation in α [and thereby in α_T since (α_T/α) is kept constant] is shown in figures 2c and 2d. The decrease in the α value (from 0.5 to 0.01) results in the decrease i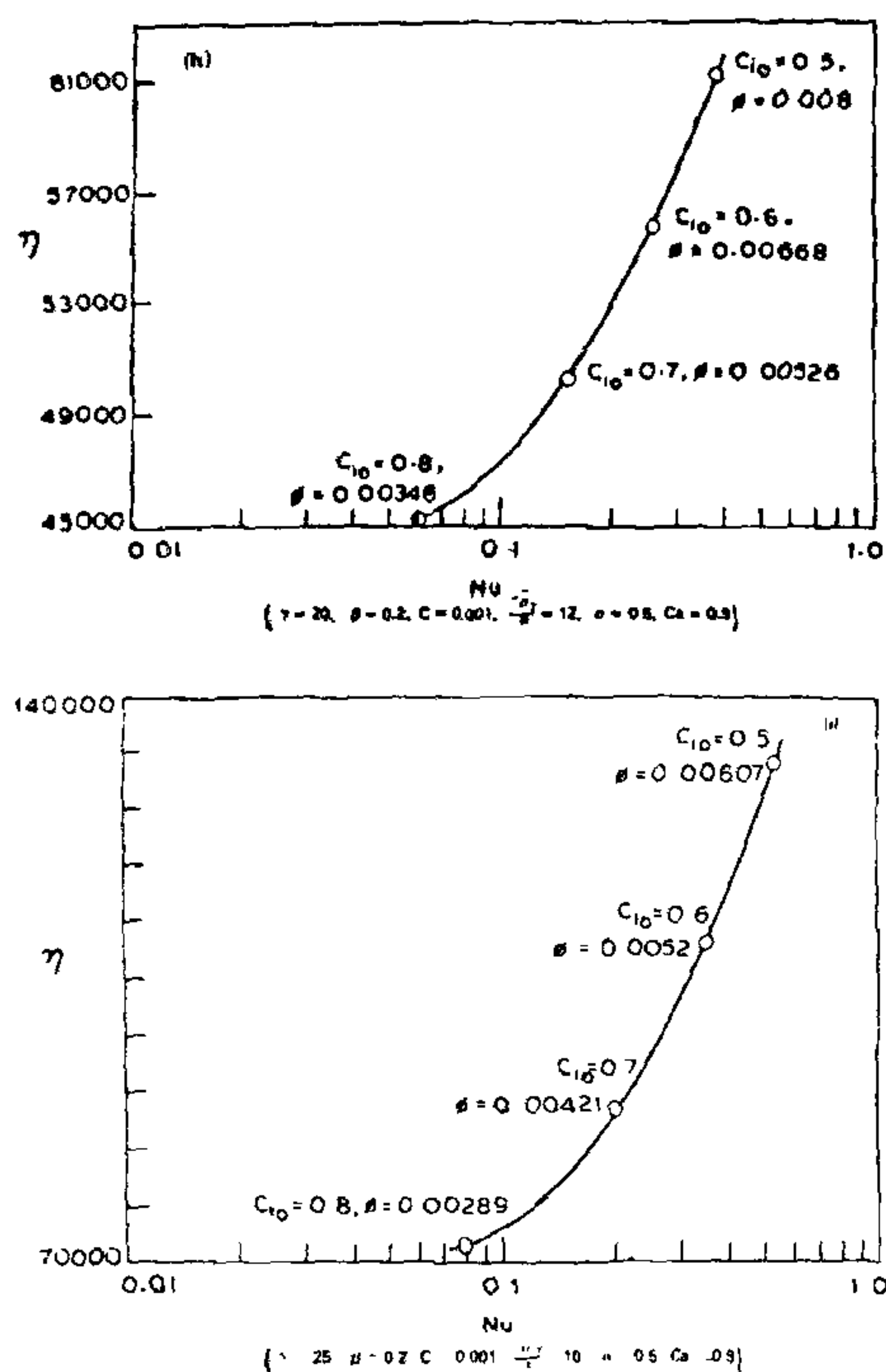n η, Sh, Nu. It can also be noticed after comparison with figures 2a and 3a that decrease in Sh and Nu is substantial while that in η is marginal. Furthermore the plots 2c and 3c go through a maxima and therefore it is possible to have two values of Sh and Nu for the same value of η. The variations in the starting micropore concentration C_{i0} do not result in large changes in the effectiveness factor values as noticed in previous cases.

Increase in the value of α (0.5 to 1) has the effect of enhancing effectiveness factor significantly though ϕ values show marginal increase (in the fourth decimal place) over the ϕ values obtained for $\alpha = 0.5$ [figures 2d and 3d].

The initial macropore concentration C_a was varied (0.7 and 0.5) and the results for each, for different values of C_{i0} are depicted in figures 2e, f and 3e, f. It is observed that lowering of the C_a value results in the substantial reduction in the ϕ value.

The results obtained by changing β value are shown in figures 2g and 3g. The well known feature of reduction in η values with decrease in β is clearly noticed. The Sherwood number rises sharply for the lower C_{i0} values tried.

In figures 2h and 3h the effect of higher α_T is shown. The high η's obtained are obviously due to the increase in the thermal conductivity of macropore effecting higher reaction rates. Increase in the magnitude of parameter γ signifying dimensionless activation energy results in very high values of effectiveness factors (figures 2i and 3i).

In view of the large computer time required for the procedure adopted here, it is more appropriate to summarize these results and present them in the form of an equation. The several data points generated have been fitted in the form of a correlation by using nonlinear optimization routine based on Marquardt's algorithm[8]. As could be noticed the general form of the equation has been chosen in analogy with the form for limiting situation and appropriately modified by inserting arbitrary exponents and coefficients. The form of the equation is thus given by:

$$\eta = \frac{b_1(\text{Sh.Nu})\left[\exp\left(1+\dfrac{1}{\gamma\beta}\right)\right]^{b_2}\left(\dfrac{\alpha_T}{\alpha}\right)^{b_3} b_4^{(0.2-\beta)}}{\alpha\phi^2(\text{Sh}+\text{Nu})},$$

(11)

where the values of the coefficients and the exponents are; $b_1 = 0.642$, $b_2 = 0.8413$, $b_3 = 0.00935$ and $b_4 = 0.00172$. It should be noted that the functional form of (11) is purely empirical and should not mislead one to conclude that the heat and mass transfer resistances are in series.

The equation has been tested for all the results discussed above and for the parameter values lying in between. In each one of these

cases the value of η given by (11) conforms within $< 1\%$ error in comparison with the value obtained numerically.

The expression thus obtained should therefore prove useful in predicting the effectiveness factors and also in related studies on the sensitivity behaviour of pellets or that of fixed bed reactors. While for all other parameter variations reported here (11) yields almost accurate results, the prediction becomes sensitive to the variations in the parameter β beyond the range investigated.

Notation

$b_1, b_2,$	: coefficients and exponents appear-
b_3, b_4	: ing in equation (11)
C	: parameter defined as $T_s - C_{as}\beta(\alpha_T/\alpha)$
C_a	: dimensionless concentration in macroparticle
C_i	: dimensionless concentration in microparticle
C_{as}	: concentration of species at the surface of the catalyst pellet
D_a	: effective diffusitivity in macroparticle
D_i	: effective diffusitivity in microparticle
h_f	: heat transfer coefficient
k_i	: thermal conductivity in microparticle
k_p	: thermal conductivity in macroparticle
k_g	: mass transfer coefficient
Nu	: Nusselt number
r_i	: radius of the microparticle
R	: radius of macroparticle
Sh	: Sherwood number
T_a	: dimensionless temperature in macroparticle

T_i	: dimensionless temperature in microparticle
T_s^i	: temperature at the surface of the catalist pellet
x	: dimensionless distance variable used in microparticle
y	: dimensionless distance variable used in macroparticle
α	: parameter defined as $3(1-\varepsilon)(D_i/D_a)$ (R^2/r_i^2)
α_T	: parameter defined as $3(1-\varepsilon)(k_i/k_p)$ (R^2/r_i^2)
β	: exothermicity factor defined as $(-\Delta H)D_i\, C_{as}/k_i\, T_s^i$
γ	: defined as $E/R_g\, T_s^i$
η	: effectiveness factor
ϕ	: Thiele modulus
ε	: void fraction of the pellet.

1. Dogu, G., In: *Handbook of heat and mass transfer*, Vol. II, (ed.) N. P. Cheremisinoff, Gulf Publ. Co., Houston, Texas, 1986, p. 433.
2. Ors, N. and Dogu, T., *AIChE J.*, 1979, **25**, 723.
3. Jayaraman, V. K., Kulkarni, B. D. and Doraiswamy, L. K., *Chem. Eng. Sci.*, 1981, **36**, 943.
4. Jayaraman, V. K., Kulkarni, B. D. and Doraiswamy, L. K., *AIChE J.*, 1983, **29**, 521.
5. Namjoshi, A. N., Kulkarni, B. D. and Doraiswamy, L. K., *AIChE J.*, 1984, **30**, 915.
6. Datar, A. S., Kulkarni, B. D. and Doraiswamy, L. K., *AIChE J.*, 1986, **32**, 859.
7. Weisz, P. B. and Hicks, J. S., *Chem. Eng. Sci.*, 1962, **17**, 256.
8. Marquardt, D. M., *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.