culate the heat transfer ratio. The result as shown in Figure 6 was 4.3, which corresponds to a bubble of 0.052 in., assuming the linear variation of heat flux increase with calculated force. This is a reasonable bubble size for the conditions under discussion.

ACKNOWLEDGMENT

The authors would like to acknowledge the aid of the U. S. Atomic Energy Commission (sponsors of the work) and cognizant engineer, Mr. Ronald M. Scroggins.

NOTATION

a = radius for a bubble, in.
A = heat transfer area, sq. ft.
A_t = area over which electrical force acts, sq. in.
A_w = portion of heat transfer area wetted by the coolant during boiling, sq. ft.
$\overline{E}$ = electric field strength, v./in.
$\overline{F}$ = force vector, lb.
F_r = force acting radially, lb.
K_1 = dielectric constant, liquid
K_2 = dielectric constant, vapor
Q = average heat transfer rate from surface, B.t.u./hr.
r = radius $r_1 < r < r_2$, in.
r_1 = radius of inner cylinder, in.
r_2 = radius of outer cylinder, in.
ΔT_o = overall temperature difference (steam temperature-water boiling point), °F.
V = voltage impressed on boiling liquid, v.

Greek Letters

ϵ = permittivity of the dielectric medium, lb./sq. v.
ϵ_o = permittivity of free space, lb./sq. v.

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Manuscript received September 30, 1964; revision received March 9, 1965; paper accepted March 11, 1965. Paper presented at A.I.Ch.E. Boston meeting.

Model Simulation of Stirred Tank Reactors

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Stirred tank reactor yields are successfully described by the following model. The impeller is considered to act as a local micro-mixer that perfectly mixes the recirculating stream down to the molecular level. All other portions of the vessel act as a large volume macro-mixer, throughout which the impeller discharge stream remains completely segregated. Changes in overall conversion due to variations in mean residence time, impeller size, and rev./min. as predicted by this micro- and macro-mixer model agree with Worrell's data for a relatively slow, second-order, irreversible reaction.

Accurate prediction of reactor yield, selectivity, and product purity is, of course, the ultimate goal of the design engineer. Any successful description of a continuous flow, stirred tank reactor must be based on close physical reality. Unfortunately, a complete theoretical analysis requires the simultaneous solution of the nonlinear, three-dimensional, partial differential equations of nonsteady state, turbulent, multicomponent mass, heat, and momentum transport; hence it is prohibitively difficult. Stirred tank reactor behavior is, therefore, often described with the help of models of varying degrees of physical reality and mathematical complexity.

PREVIOUS MODELS

The earliest and simplest isothermal, continuous flow stirred tank reactor model assumes perfect mixing or micro-mixing (5), that is, the impeller mixes the fluid down to the molecular level. No concentration gradients or fluctuations exist within the tank, hence overall yields may be computed readily from the material balance. At steady state conditions

$$\text{Input} - \text{Output} = \text{Amount reacted}$$
$$F\,c_F - F\,c_o = V_T\,r \tag{1}$$

For a second-order reaction of type 2A → products, $r = k\,c_o^2$ and Equation (1) yields

$$\frac{c_{\mathrm{micro}}}{c_F} = \frac{-1 + \sqrt{1 + 4\,c_F k\,\tau}}{2\,c_F\,k\,\tau} \tag{2}$$

The outlet concentration c_o is called c_{micro} to emphasize that tank contents are completely mixed on the molecular level. In spite of the obvious oversimplification of this model, it has proved surprisingly successful in predicting overall tank yields, especially for relatively slow reactions, low fluid viscosity, and high rev./min. However, recent data (*4, 14*) indicate that this model fails at low rev./min.

In 1958 Danckwerts (2) suggested a macro-mix model. Now individual fluid molecules are pictured as remaining grouped together in small aggregates or lumps. These segregated lumps are assumed to be very small compared to vessel dimensions, but they are also assumed to contain a large number of molecules, for example, about 10^{12}. Reaction now occurs separately within each lump; that is, each aggregate behaves as a small, perfectly mixed, batch reactor. If the age of every lump in the exit stream is known, or, alternatively, if the residence time distribution of fluid in the vessel may be computed, then the overall vessel yield may be calculated. Stimulus-response investi-

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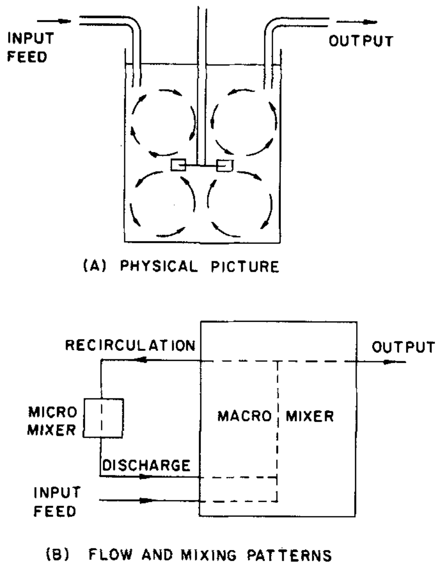

Fig. 1. Macro-mixed feed model.

gations using tracers indicate that agitated vessels may exhibit the perfectly mixed residence time distribution (RTD) even at low impeller speeds. This corresponds to a random rearrangement of the segregated lumps by the impeller and not to any molecular mixing between lumps. For the previously described second-order reaction the concentration of any lump, c_i, is given by (2)

$$\frac{d\,c_i}{dt} = -k\,c_i^2 \tag{3}$$

Integrating between c_F at zero time and c_i at time, t

$$\frac{c_i}{c_F} = \frac{1}{1 + c_F\,k\,t} \tag{4}$$

The mean outlet stream concentration, c_{macro} is given by

$$\frac{c_{macro}}{c_F} = \frac{1}{\tau}\int_0^\infty \frac{1}{(1 + c_F\,k\,t)}\,e^{-t/\tau}\,dt \tag{5}$$

This integral may be rearranged to yield (2) and (5)

$$\frac{c_{micro}}{c_F} = \alpha\,e^{\alpha}\,(ei(\alpha)) \tag{6}$$

where $\alpha = F/k\,c_F\,V_T$.

Danckwerts' complete segregation model assumes that all mixing occurs as late as possible, that is at the reactor outlet. In 1959 Zweitering (*15*) suggested the extreme opposite case, which is called the *maximum mixedness* model. Now, the extent of mixing within the vessel, as indicated by the exit stream's residence time distribution function, is assumed to occur as early as is possible. For a second-order reaction, Zweitering's model predicts greater conversions than Danckwerts' model for identical residence time distributions.

At moderate rev./min. continuous flow stirred tank reactor (CFSTR) behavior lies between the micro- and macromixing predictions based on perfectly fixed RTD (*4, 15*). These intermediate yields may be explained by changes in the vessel RTD or by postulating that the stirred vessel behaves as a series and/or parallel combination of plug flow, perfectly micro-mixed, and completely segregated reactors. Feed bypass and reactor deadspace have also been included (*1*). The division of the stirred vessel into its postulated reactors often lacks physical reality, even though actual vessel performance can be correlated closely after the relatively large number of individual reactor parameters have been obtained experimentally. Recently, two-parameter models involving circulating flows have been reported by van de Vusse (*10*) and by Voncken et al. (*11*). Marr and Johnson (*7*) have measured recirculating flow patterns, while Gutoff (*3*) and Sinclair (*9*) have examined the effectiveness of mixing vessels in smoothing cyclic fluctuations.

COMBINED MICRO- AND MACRO-MIXER MODEL

Experimental data by Manning and Wilhelm (*6*) and by Rice, Toor, and Manning (*8*) prove that turbine impellers can completely mix two different streams in the time they take to pass through the physical confines of the impeller, that is within a fraction of a second. However, outside the impeller the mixing is by no means so intense. This large variation in mixing intensity suggests that the vessel be now divided into two zones: (1) a small region engulfing and surrounding the impeller, which is characterized by violent agitation; and (2) the remaining tank volume where the mixing is comparatively mild. The mixing in zone 1 is assumed to be perfect even down to the micro-level, while macro-scale mixing but no micro-scale mixing occurs in zone 2. Therefore, the fluid emanating from the impeller undergoes no micro-mixing during its recirculation throughout the vessel; that is, it behaves as if it were divided into completely segregated elements. However, all elements lose their identity whenever they pass through the impeller. In summary, this physical model divides the vessel into two zones: (1) a small micro-mixer surrounding the impeller; and (2) a large macro-mixer, which occupies the remaining tank volume. The volume of the micro-mixer is negligibly small.

If quantitative predictions are desired, vessel operating conditions must be known; these include tank size, feed rate and inlet composition, reaction rate constant, impeller discharge rate or impeller pumping capacity, and residence time distribution. Fluid temperature is assumed constant throughout the vessel and the value must be given. Obviously, stirred vessel behavior depends on the physical location of the inlet and outlet ports, for example, if they are close to each other considerable bypassing of the feed stream may occur (*5, 12*). Vessel behavior also depends on the proximity of the feed port to the impeller. Two extremes exist: First, the feed port is so far distant from the impeller that the feed stream is completely mixed on the macro-level with the recirculating

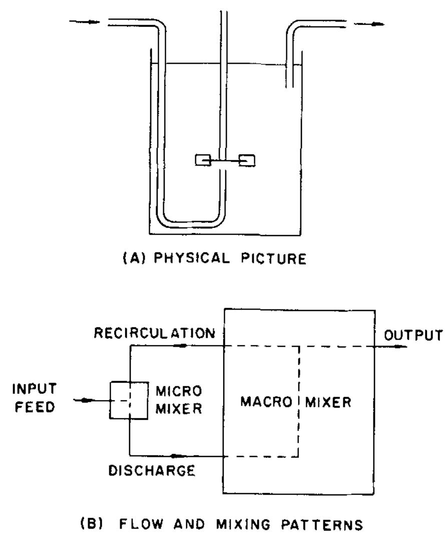

Fig. 2. Micro-mixed feed model.

TABLE 1. SCOPE OF OPERATING VARIABLES FOR MICRO- AND MACRO-MIXER MODEL

Variable	Range
Q/F	1-200
$k\, c_F\, \tau$	1-100
η	0.5-2.0

stream before both reach the impeller; and second, the feed stream is injected directly into the impeller. Hence it is micro-mixed very rapidly with the recirculating stream. These two variations of the combined micro- and macro-mixer model are now treated in detail for the case where all fluid in the macro-mixer is perfectly mixed on the macro-scale.

Macro-Mixed Feed Model

Figure 1*A* shows a typical stirred, baffled vessel in which the feed is assumed to be completely macro-mixed with the vessel contents before it is micro-mixed at the impeller. Figure 1*B* presents the model flow and mixing patterns.

The overall vessel yield is defined from the overall, steady state material balance as given in Equation (1). However, Figure 1*B* shows that the output stream is considered to be a volume average of its segregated component streams, namely, the feed and impeller discharge streams. Mathematically

$$c_o = \left(\frac{1}{Q+F}\right)(Q\, c_q + F\, c_f) \tag{7}$$

Since the feed and impeller discharge streams remain completely segregated, their exit concentrations may be computed from their initial values and the flow rates in and out of the macro-mixer

$$\frac{c_f}{c_F} = \int_o^\infty \frac{1}{c_F}\,(c_f(t)_{\text{batch}})\, E\,(t)\, dt \tag{8}$$

$$\frac{c_q}{c_F} = \int_o^\infty \frac{1}{c_Q}\,(c_q(t)_{\text{batch}})\, E\,(t)\, dt \tag{9}$$

For this case of complete macro mixing, the macro-mixer exhibits the perfectly mixed RTD. Hence

$$E(t) = \frac{1}{\tau_{mm}}\, e^{-t/\tau_{mm}} \tag{10}$$

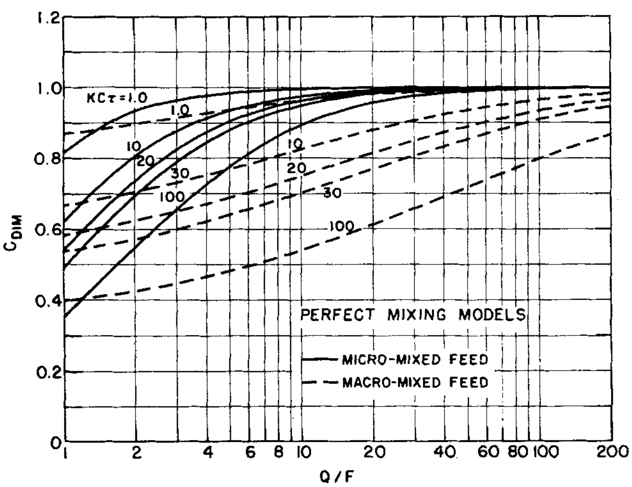

Fig. 3. Model predictions for perfectly mixed RTD.

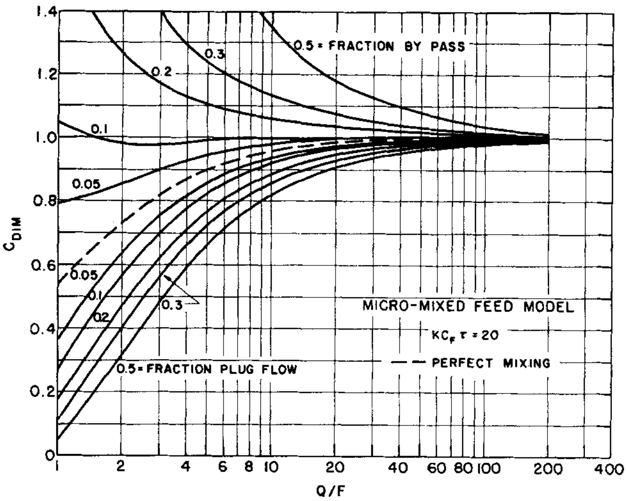

Fig. 4. Micro-mixed feed model predictions when $kc_{F}\tau = 20$.

where $\tau_{mm} = V_T/(Q + F)$ = mean residence time in macro-mixer.

The macro-mixer RTD should not be confused with that for the entire CFSTR. Consideration of the mean residence times will clarify this. For the CFSTR the only inlet stream is the fresh feed, F, and the only exit stream is the vessel output. Hence $\tau_{mt} = V_T/F$. The macro-mixer mean residence time, unlike τ_{mt}, depends on the agitator recirculation rate.

Concentration variation with time in a perfectly micro-mixed batch reactor, $(c_q(t))_{\text{batch}}$ or $(c_f(t))_{\text{batch}}$, depends on the reaction rate order and stoichiometry. Second-order, irreversible reactions of the type $aA + bB \rightarrow$ products with stoichiometric feed ratios were used. Nonstoichiometric feed cases can also be handled. Figure 1*B* shows that the recycle stream concentration, the discharge stream, and the vessel exit stream concentrations are all equal, and hence Equations (7), (8), and (9) may be solved simultaneously for the unknown concentrations c_o, c_f, and c_q if vessel operating conditions are known.

Micro-Mixed Feed Model

Figure 2*A* shows a typical stirred, baffled vessel in which the feed is assumed to be completely micro-mixed with the recirculating stream at the impeller before it reacts. Figure 2*B* presents the model flow and mixing patterns.

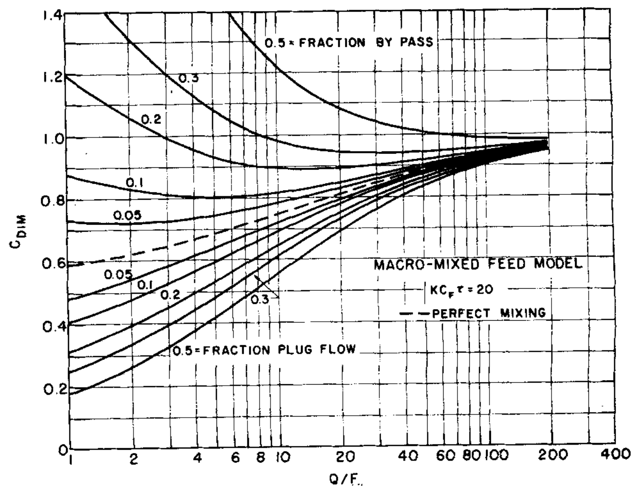

Fig. 5. Macro-mixed model predictions when $kc_{F}\tau = 20$.

Since the impeller discharge stream again remains completely segregated, the output stream concentration is related to the impeller discharge stream concentration by

$$\frac{c_o}{c_Q} = \int_o^\infty \frac{1}{c_Q} \left(c_q(t)_{\text{batch}}\right) E(t)\, dt \qquad (11)$$

The macro-mixer RTD, $E(t)$, is again given by Equation (10), but now Figure 2*B* shows that $\tau_{mm} = V_T/Q$.

Figure 2*B* also indicates that the recirculation stream and the vessel exit stream concentrations are equal. Hence a material balance on the micro-mixer yields

$$c_Q = ((Q - F)\, c_o + F\, c_F)/Q \qquad (12)$$

MODEL PREDICTIONS

Output stream concentrations and hence overall vessel yields were computed for the wide range of operating variables listed in Table 1. All predictions apply to second-order, irreversible reactions. For convenience in subsequent comparison with experimental data, theoretical predictions are presented in terms of the following dimensionless concentration parameter.

$$c_{DIM} = \frac{c_o - c_{\text{plug}}}{c_{\text{micro}} - c_{\text{plug}}}$$

where c_o = computed concentration of stirred vessel outlet concentration.

$c_{\text{plug}} = \dfrac{c_F}{1 + k\, c_F \tau}$ outlet concentration of a plug flow reactor with identical mean holdup time, τ.

c_{micro} = outlet concentration of a perfectly micro-mixed, CFSTR having identical mean holdup time [Equation (2)].

Figure 3 predicts the dependence of c_{DIM} with Q/F when the stirred tank exhibits a perfectly mixed RTD. Both micro-mixed feed and macro-mixed feed models are included and results are shown for a range of $k\, c_{F}\tau$ from 1 to 100.

These macro- and micro-mixed feed models are now extended to cases where the macro-mixer no longer exhibits the perfect RTD. Now the macro-mixer no longer consists of completely macro-mixed fluid and the deviations can be characterized by partial bypass and partial plug flow of its inlet streams.

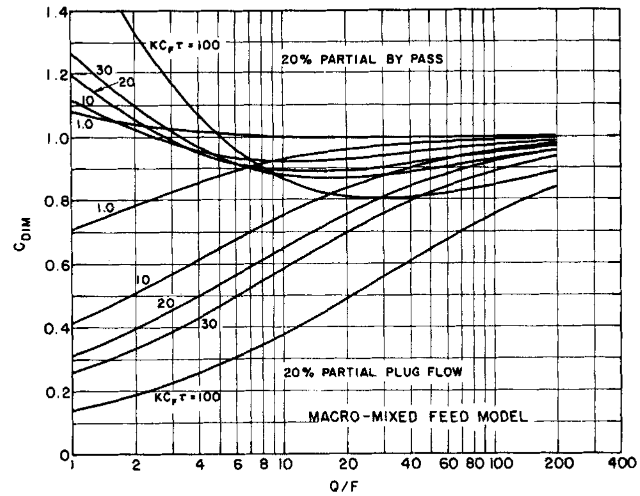

Fig. 7. Effect of $kc_{F}\tau$ on macro-mixed feed model.

The RTD for the portion of the macro-mixer that remains perfectly macro-mixed is represented by

$$E(t) = \eta/\tau_{mm}\, e^{-\frac{\eta t}{\tau_{mm}}} \qquad (13)$$

If $\eta = 1$ the entire macro-mixer is completely mixed on the macro-scale and no bypass or plug flow is present.

$\eta > 1$ plug flow is present and η corrects for the decrease in fluid volume, which is perfectly macro-mixed.

$\eta < 1$ bypass is present and η corrects for the decrease in the feed to that portion of the macro-mixer, which is perfectly macro-mixed.

Mathematically (*13*)

for plug flow: $\eta = 1/(1 - p)$

bypass: $\eta = 1 - f$

For the cases where $\eta \neq 1$, the bypass or plug flows must be considered in determining the overall material balance around the macro-mixer.

Figures 4 and 5 present the effects of variation in RTD due to bypass and plug flow for micro-mixed feed and macro-mixed feed models, respectively, when $k\, c_{F}\tau = 20$. RTD variation is expressed in terms of fraction of feed being bypassed or undergoing plug flow.

Figures 6 and 7 show the results of varying $k\, c_F\, \tau$ from 1 to 100 for the micro-mixed feed and macro-mixed feed

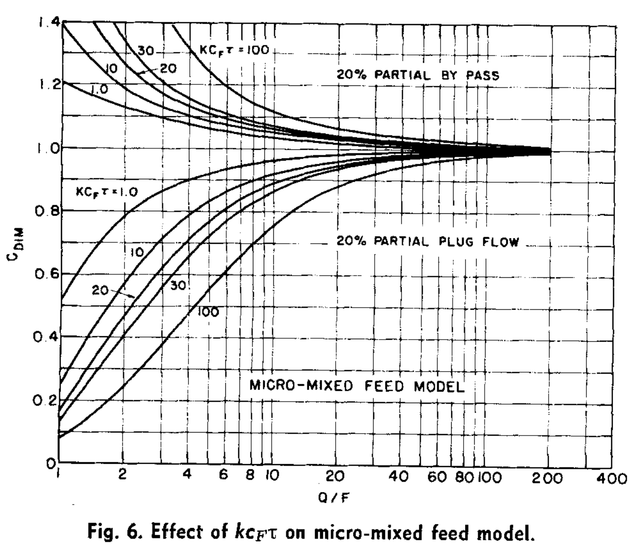

Fig. 6. Effect of $kc_{F}\tau$ on micro-mixed feed model.

TABLE 2. EXPERIMENTAL OPERATING CONDITIONS FOR WORRELL'S DATA (*11*)

Tank volume	2,460 ml.
Impeller characteristics	flat bladed turbine impeller, six blades impeller diameter, D = 2 in. blade width, d = 0.4 in.
Propeller characteristics	standard marine propeller, three blades propeller diameter, D = 2 in. blade width, d = 0.67 in.
Feed rate composition	13.1 ml./sec. 0.200 g.-moles sodium thiosulfate/liter 0.402 g.-moles hydrogen peroxide/liter

Wolf's correlation for pumping capacities (*9*)

Pumping capacity, Q	$2.3\, N D^2 d$	for impeller
	$0.54\, N D^3$	for propeller

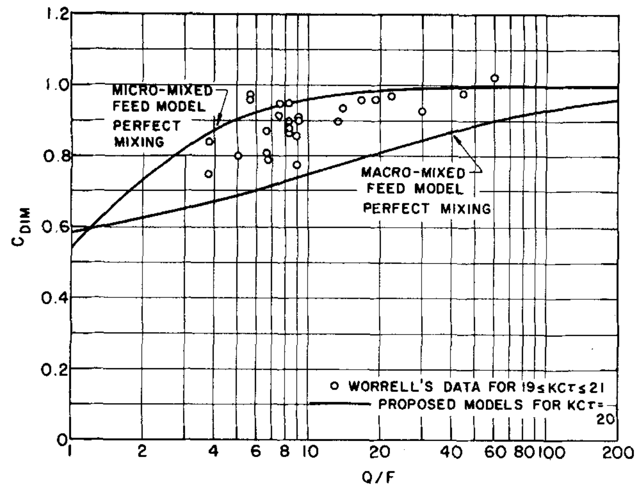

Fig. 8. Comparison of Worrell's data with model predictions.

models, respectively. For each model, the variation of c_{DIM} with Q/F is given for the cases of 20% bypass and 20% plug flow.

COMPARISON OF MODELS WITH DATA

Suitable experimental data of sufficient accuracy to test these models are scarce however, Worrell's data *(14)* on the irreversible second-order reaction between aqueous solutions of sodium thiosulfate and hydrogen peroxide is available. Table 2 presents details of Worrell's experimental operating conditions. Wolf's correlations *(12)* of impeller and propeller discharge rates in terms of impeller type, size, and rev./min. permitted estimation of pumping capacities (Table 2) were used. Figure 8 presents Worrell's data for which $19 < k\,c_F\,\tau < 21$ in the form of c_{DIM} vs. Q/F. For comparison the predictions of both macro-mixed feed and micro-mixed feed models are included for a perfectly mixed RTD and $k\,c_F\,\tau = 20$. These model predictions bracket Worrell's data. At very low rev./min. internal flows are not established completely by the impeller, for example the inlet and outlet stream flows exert appreciable effects, and hence the basic model assumptions become questionable.

CONCLUSIONS

In spite of the preliminary nature of the presently proposed models and the limited comparison with data, several conclusions may be drawn.

(1) While previous data *(1, 4, 5, 14)* have established that the rate of conversion of a second-order reaction in a CFSTR varies with rev./min., the present models permit quantitative estimation of this variation from a minimum of operating conditions: tank volume, feed rate and concentration, reaction rate constant, and impeller type, size, and rev./min.

(2) Model predictions may be refined if experimental RTD data are available, because then feed bypass and plug flow effects may be included. However, since RTD information is seldom available, the perfectly mixed RTD models are more useful for design purposes.

(3) The present model predictions agree generally with the limited data available. At high rotational speeds the assumption of complete macro-mixing of the feed before it enters the impeller is implausible. In this range Worrell's data agree quite closely with the alternative micro-mixed feed assumption. At lower rev-/min. Worrell's data approach the macro-mixed feed model prediction.

NOTATION

c = concentration
$c(t)_{batch}$ = concentration variation with time in a completely micro-mixed, constant volume, batch reactor
c_F = feed concentration when it enters vessel
c_f = concentration of segregated feed stream in output
c_l = concentration of any segregated lump
c_{macro} = output stream concentration when tank is segregated
c_{micro} = output stream concentration when tank is perfectly mixed
c_o = output stream concentration
c_{plug} = output stream concentration from a plug flow reactor
c_Q = impeller discharge concentration when it leaves impeller
c_q = impeller discharge concentration when it leaves vessel
$E(t)$ = residence time distribution function
ei = exponential integral
F = feed rate
f = fraction of feed stream that bypasses vessel without reacting
k = reaction rate constant
p = fraction of feed stream which undergoes plug flow
Q = impeller discharge rate or impeller pumping capacity
R.T.D. = residence time distribution
r = reaction rate per unit volume
t = time
V_T = volume of stirred tank

Greek Letters

α = F/kc_FV_T = dimensionless parameter, Equation (6)
τ = mean holdup time in vessel
τ_{mm} = mean holdup time in macro-mixer
τ_{mt} = mean holdup time in stirred tank
η = vessel mixing efficiency as defined by Equation (13)

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Manuscript received May 1, 1964; revision received March 29, 1965; paper accepted March 30, 1965.