VISCOUS FLUID RESIDENCE TIME DISTRIBUTION AND CONVERSION IN CONTINUOUS STIRRED REACTOR

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Two single parameter characteristics of residence time distribution functions (RTD) of viscous fluid in a continuous stirred reactor (CSTR) were defined: $\overline{\Delta}$ — the Θ normalized area between the real and ideal $I(\Theta)$ curves and Z^* — the ratio of fractional conversions for a single first order reaction in a real and ideal CSTR. These parameters were evaluated for experimental RTD functions and the highest statistical significance was found for the following correlation of the parameter $\overline{\Delta}$: $(1/\overline{\Delta})\,(1/n\bar{t})^{1/2} = 0{\cdot}0551\ \mathrm{Re}^{0.932}$ which applies to standard baffled cylindrical reactors with Rushton turbine ($D = H$, $D/d = 3$, $h = D/2$, n and $\bar{t}$ denote speed of the impeller and mean residence time, respectively) for $\mathrm{Re} < 20$. It was further shown that nonideal RTD considerably decreases the actual relative degree of conversion especially at low values of Damköhler number $\mathrm{Da} < 1{\cdot}0$. A way of using the results for better prediction of conversions in non-ideal CSTR was suggested.

The influence of the type of continuous reactor or the kind of mixing in the reactor on molecular weight distribution and therefore on the final properties of a polymer product was revealed by Denbigh[1]. There also was experience that the productivity of industrial continuous stirred reactors (CSTR) often differs from the one precalculated on the basis of ideal mixing.

Recently some attention was paid to the ideality of mixing in continuous stirred tank reactors[2]. It was learned from the literature and also from our preliminary experimental work that one could easily maintain ideal mixing conditions with low viscosity fluids. On the contrary, little information was found about the ideality of mixing in viscous fluids, *e.g.* for situations frequently encountered in continuous polymer production.

It was believed that the study of macromixing in a CSTR using the residence time distribution (RTD) technique could be useful for better understanding of behaviour and better prediction of conversions in continuous reactors.

Residence time distribution concept. Using the terminology of "macromixing" and "micromixing" introduced by Danckwerts[3] it is necessary to point out that by the measuring RTD only macromixing phenomena can be studied. In an ideal CSTR perfect mixing is assumed, the consequence of which is that a differential volume of material just entering the reactor can appear at the next moment anywhere in the system. Therefore, also each element has finite probabilities

of exiting from the reactor and of staying inside for longer periods of time. To evaluate the above mentioned probabilities is one method of calculating an age distribution function. A simple solution of the problem for ideal CSTR is found elsewhere[4].

It is easy to understand that when some of the functions $I(t)$, $I(\Theta)$, $F(\Theta)$, $E(\Theta)$ are measured for a real system and compared with appropriate ideal ones, it is possible to decide whether the system deviates from an ideal one and to modify the design in such a way that the deviation diminishes. This approach has actually been realized in case of fluidized beds[5].

Some typical features of distribution curves can be with confidence qualitatively interpreted in a specific way only if basic physical characteristics of the system are known. There exist characteristic shapes of $I(\Theta)$ curves indicating *e.g.* plug flow or stagnant regions[6] and it has also been pointed out that one type of distribution function may appear more sensitive in disclosing deviations of some kind, *e.g.* the intensity function was shown to have a typical shape for the system with stagnant zones and bypass[7,8].

Characterization of RTD *curves.* For situations far from plug-flow two different approaches should be mentioned: characterization by a mixed model and characterization by a single parameter.

Mixed models have been given considerable attention recently[5,9] and computational techniques for their application to an experimental RTD curve have been described[10,11]. Any practical situation can be handled that way and the point is to find out a well fitting, simple and realistic model of the system.

Single parameter characterization of RTD curve is in a way an inefficient utilization of the effort expeded in obtaining RTD curve. On the other hand single parameter characteristics have often been used because of their simplicity and namely when it has been aimed at correlating the overall pattern of nonideal behaviour of CSTR with mixing parameters.

In this work two new single parameter characteristics of RTD were defined:

intergral mean deviation $\bar{\Delta}$

$$\bar{\Delta} = (1/\Theta_{max}) \int_0^{\Theta_{max}} \left| (I(\Theta) - I_{id}(\Theta)) \right| \mathrm{d}\Theta \,, \tag{1}$$

which represents the Θ_{max} normalized area enclosed by real $(I(\Theta))$ and ideal CSTR $(I_{id}(\Theta))$ age distributions and chosen limits;

conversion index Z^*

$$Z^* = \zeta_A/\zeta_{A,id} = \frac{\int_{F=0}^{F_{max}} (1 - \exp(-\mathrm{Da}\,\Theta))\,\mathrm{d}F(\Theta)}{\int_{F=0}^{F_{max}} (1 - \exp(-\mathrm{Da}\,\Theta))\,\mathrm{d}F_{id}(\Theta)} \,, \tag{2}$$

which represents the ratio of fractional conversions in real and ideal CSTR as calculated for single first order reaction at a specified Damköhler Group[12] from corresponding age distributions.

Both parameters $\bar{\Delta}$ and Z^* are dimensionless and dimensional analysis suggests that each of them should be correlated in geometrically similar vessels by the correlation

$$\bar{\Delta}\,(\text{or } Z^*) = b_0(1/\text{Re})^{b_1}\,(n\bar{t})^{b_2}\,. \qquad (3)$$

Reactor purging experiments believed to simulate well the ideal step method for RTD measurement[9] were performed and the concentration of the tracer at the reactor exit was measured.

Experiments were carried out in cylindrical vessels with flat bottom fitted with four vertical baffles. Rushton turbines (disc style of construction[13], $w/d \approx 1/5$, $h = D/2$) were used and it was complied with standard tank geometry ($D/d = 3$, $H = D$). The apparatus was described in detail previously[2].

RESULTS AND DISCUSSION

Principal data for the above mentioned experiments are summarized in Table I and an example of age distribution curves measured is shown in Fig. 1. (Numerical $I(\Theta)$ values for all experiments for $\Theta = (0{\cdot}0 \div 0{\cdot}5)$ and $(0{\cdot}5 \div 3{\cdot}0)$ in steps of 0·025 and 0·1 respectively, are available[14]).

Mixed model of our system consisting of one back-mixed region and a plug flow

TABLE I

The Summary of Experimental Conditions

Exp. No	D cm	H cm	d cm	μ kg/ms	n RPM	$\bar{t}$ min	Re	$n\bar{t}$	$\bar{\Delta}$
1	10·80	10·80	3·60	0·740	505·0	8·5	19·89	4 292·5	0·0143
2	10·80	10·80	3·60	1·066	505·0	24·5	13·81	12 372·5	0·0175
3	10·80	10·80	3·60	0·954	250·0	4·3	7·64	1 089·9	0·1048
5	10·80	10·80	3·60	0·820	250·0	11·9	8·89	2·974·9	0·0491
10	10·80	10·80	3·60	0·575	85·0	8·3	4·31	709·7	0·1298
13	10·80	10·80	3·60	0·650	82·0	50·5	3·67	4 141·0	0·0665
14	10·80	10·80	3·60	7·160	500·0	48·3	2·06	24 149·9	0·0720
16	10·80	10·80	3·60	7·550	1 000·0	37·3	3·91	37 299·9	0·0333
18	10·80	10·80	3·60	8·220	1 280·0	18·7	4·60	23 935·9	0·0233
19	10·80	10·80	3·60	7·000	1 280·0	38·5	5·41	49 280·0	0·0159
26	19·10	19·90	6·26	0·570	88·0	5·6	13·61	497·1	0·0600
27	19·10	19·10	6·26	0·510	88·0	14·8	15·21	1 306·7	0·0432
37	19·10	19·90	6·26	5·590	800·0	35·9	12·80	28 759·9	0·0139

TABLE II
Conversion Index Z^* for Various Da (ζ_{id}) Values

Exp. No	0·111 0·100	0·334 0·250	1·000 0·500	2·335 0·700	9·000 0·900	19·00 0·95	99·00 0·99	$\bar{\Delta}$
1	0·94337	0·94609	0·95218	0·95967	0·97566	0·98404	0·99565	0·0143
2	0·92404	0·92547	0·93144	0·94323	0·96730	0·97588	0·98318	0·0175
3	0·53382	0·55682	0·61704	0·70245	0·85069	0·91186	0·96026	0·1048
5	0·92929	0·93988	0·96493	0·99406	1·03178	1·04194	1·03690	0·0491
10	0·46935	0·50010	0·58257	0·70558	0·93332	0·99285	0·98469	0·1298
13	0·67147	0·67983	0·70605	0·75379	0·87062	0·92009	0·94309	0·0665
14	0·65280	0·67296	0·72117	0·78247	0·89441	0·94362	0·97456	0·0720
16	0·83494	0·85158	0·89024	0·93560	0·99435	1·00347	0·98674	0·0333
18	0·90265	0·91654	0·94692	0·97388	1·01501	1·01843	0·99843	0·0233
19	0·89137	0·89693	0·90966	0·92493	0·95126	0·96117	0·96923	0·0159
26	0·78978	0·79512	0·81972	0·87464	0·98959	1·00285	0·97091	0·0600
27	0·81721	0·82297	0·84374	0·88443	0·96918	0·98717	0·97085	0·0432
37	0·94408	0·95318	0·97353	0·99525	1·01499	1·01401	0·99901	0·0139

region in series with a common stagnant region parallel to it was proposed and relative sizes of "backmixed" and "stagnant" regions were correlated with dimensionless Reynolds (Re < 20) and ($n\bar{t}$) numbers[2], *e.g.* for the "stagnant" region the correlation was:

$$V_d/V = 0{\cdot}771(\mathrm{Re})^{-0.651}(n\bar{t})^{-0.289}. \qquad (4)$$

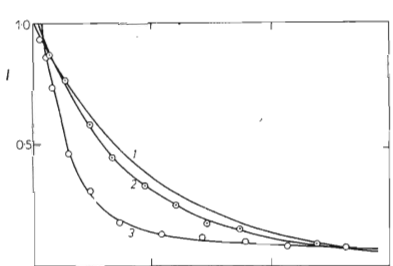

FIG. 1
Experimental Age Distribution Functions
1 Ideal CSTR, *2* exp.16, *3* exp.10.

Because it is impractical to measure the $I(\Theta)$ curve up to $\Theta = \infty$, some cutoff point Θ_{max} must be chosen for any model evaluation. One realizes that Θ_{max} also defines what is considered a stagnant zone, namely, any region of a reactor where the fluid stays longer than Θ_{max}. These zones are ignored in age distribution analysis and thus – if conversion in a reactor is calculated using age distribution information – they do not contribute to it. If a real reactor is then compared with an ideal one we feel it fair to apply the same concept of stagnancy to both of them. Ideal CSTR should then be considered as the one having a stagnant region of 13·53% or 4·97% of its volume V depending whether Θ_{max} was chosen 2·0 or 3·0, respectively.

The values of Z^* calculated for each age distribution at different values of Damköhler group for first order kinetics can be found in Table II. Actually our numerical calculating procedure followed the graphical method[15] of the first order reaction conversion calculation using the $F(t)$ curve (significant details are given in the Appendix).

A remarkable observation is that $Z^* = f(\zeta_{id})$ decreases rather sharply with decreasing fractional conversion (see Table II, *e.g.* No 10 and 14), so that at lower fractional conversions ($\zeta_{id} < 0{\cdot}5$) the values of Z^* go down to $(0{\cdot}7 \div 0{\cdot}5)$. But Z^* values are significantly different from 1·0 even for experiments with rather small $\bar{\Delta}$ (*e.g.* No 16). This suggests that one should be quite concerned about age distribution and perfectness of mixing in reactors, particularly those low fractional conversion (*e.g.* in a cascade of CSTR).

Parameters Z^* were also correlated at one arbitrarily chosen conversion, *e.g.* for $\zeta_{id} = 0{\cdot}5$ the result was

$$\log (Z^*_{0.5}) = -0{\cdot}563 + 0{\cdot}189 \log (\mathrm{Re}) + 0{\cdot}0843 \log (n\bar{\imath}) \pm 0{\cdot}0407 \qquad (5)$$

with $K = 0{\cdot}863$ and $f = 16{\cdot}1$ (ref.[16,17]).

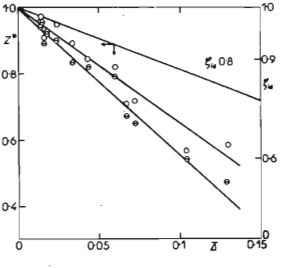

FIG. 2

Conversion Index Z^* Against Integral Mean Deviation $\bar{\Delta}$.

The scale for $\xi_{id} = \text{const.}$ line intercepts is based on data from Table II. Typical experimental data scatter is shown for ξ_{id} equal ○ — 0·5 and ⊖ — 0·1.

The second single parameter characteristics – compared to the others – is quite intuitive and can easily be applied to an age distribution curve. In addition to that it yields a remarkably significant correlation with Re and $n\bar{t}$ ($\Theta_{max} = 3{\cdot}0$ was chosen):

$$\log(\bar{\Delta}) = 0{\cdot}972 + 0{\cdot}877 \log(1/\mathrm{Re}) - 0{\cdot}436 \log(n\bar{t}) \pm 0{\cdot}0941 ;$$
$$(K = 0{\cdot}964,\ f = 73{\cdot}1) . \qquad (6)$$

It was realized that correlations with Re as an independent variable were favoured in mixing and therefore one was attempted. Because the exponent of $(n\bar{t})$ in Eq. (6) was not far from 0·5, the complex parameter $(1/\bar{\Delta}) . (1/n\bar{t})^{1/2}$ was correlated with Re with the result:

$$\log((1/\bar{\Delta}) . (1/n\bar{t})^{1/2}) = -1{\cdot}259 + 0{\cdot}932 \log(\mathrm{Re}) \pm 0{\cdot}0998 ;$$
$$(K = 0{\cdot}945,\ f = 100{\cdot}7) . \qquad (7)$$

Let us keep in mind that an important objective in reactor design is conversion prediction. To predict conversion for a single first order reaction (Da, Re and $n\bar{t}$ numbers must be known) using present work results one can use an equation analogous to Eq. (5) or to do the job in two steps: *1*) to calculate $\bar{\Delta}$ using Eq. (6) or (7); *2*) to calculate Z^* using that $\bar{\Delta}$ value and a correlation of $Z^* = f(\bar{\Delta})$ at the appropriate value of ζ_{id} (or Da) which can be obtained from data in Table II (*e.g.* for the dimensionless conversion $\zeta_{id} = 0{\cdot}5$ the correlation would be: $\log(Z^*_{0.5}) = -0{\cdot}365 - 0{\cdot}198 \log(\bar{\Delta}) \pm 0{\cdot}0374$; $(K = 0{\cdot}875,\ f = 39{\cdot}2)$); it is also conveniently possible to interpolate the needed value of Z^* for ζ_{id} as a parameter and $\bar{\Delta}$ in Fig. 2.

It is finally emphasized that the suggested way of conversion prediction theoretically applies only for first order kinetics. Using a model of the system can not be avoided, if conversion is to be predicted for reaction orders different from one. Nevertheless it is believed that the correlations of our model parameters mentioned earlier can be helpful in handling such a situation, even if the calculations are lengthier and the result probably less reliable than in the case of first order kinetics.

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APPENDIX

Calculation of Conversion in a CSTR when F(Θ) Curve is Known (1st Order Kinetics)

The average degree of conversion in the exit stream ξ_A is obtained by integrating along the F coordinate:

$$\xi_A = \int_0^{F=1} \xi_A(t)\, \mathrm{d}F(t) .$$

After substituting the appropriate equation for the plug flow reactor and introducing dimensionless time Θ, one obtains for the relative degree of conversion ζ_A:

$$\zeta_A = t \int_0^{F_{max}} (1 - \exp(-k t \Theta))\, \mathrm{d}F(\Theta) ,$$

where F_{max} is determined by Θ_{max} chosen. The latter formula was used for the definition of Z^*.

The conversion index Z^* was evaluated by a simple computer program[14] that calculated for the given $I(\Theta)$ and Damköhler group both the numerator and the denominator of Eq. (2) by the approximation:

$$\zeta_A/\bar{t} = \sum_{i=2}^{i=j} ((F(\Theta))_i - (F(\Theta))_{i-1}) . (1 - \exp(-k\bar{t}(\Theta_i + \Theta_{i-1})/2 \cdot 0)) ,$$

where $\Theta_1 = 0$; $\Theta_j = \Theta_{max} = 3 \cdot 0$ and $F(\Theta) = 1 - I(\Theta)$.

LIST OF SYMBOLS

C_A, C_{AO}	concentration and initial concentration of the reactant expressed by their mass fractions
d	impeller diameter (m)
D	reactor diameter (m)
E	exit age distribution function
f	the value calculated for F-test of significance of multiple regression
F	distribution function
h	clearance of impeller of vessel bottom (m)
H	liquid depth (m)
I	internal age distribution function
k	1^{st} order reaction velocity constant (s^{-1})
$k' = V_b/V_p$	ccefficient
K	multiple correlation coefficient
n	impeller rotational speed (s^{-1})
q	volumetric flow rate ($m^3\ s^{-1}$)
t	real time (age) (s)
$\bar{t}$	mean residence time (s)
V	total volume of the vessel (m^3)
V_d	volume of stagnant region (m^3)
w	width of impeller blade (m)

Z^*	conversion index
$\mathrm{Da} = k\bar{t}$	Damköhler group (1st order reaction)
$\mathrm{Re} = nd^2\varrho/\mu$	Reynolds number
$\overline{\Delta}$	integral mean deviation
ζ	relative degree of conversion
Θ	dimensionless time
ξ	degree of conversion
μ	dynamic viscosity ($\mathrm{kgm^{-1}\,s^{-1}}$)
ϱ	density ($\mathrm{kgm^{-3}}$)

REFERENCES

1. Denbigh K. G.: J. Appl. Chem. *1*, 227 (1951).
2. Žaloudík P.: Brit. Chem. Eng. *14*, 657 (1969).
3. Danckwerts P. V.: Chem. Eng. Sci. *2*, 1 (1953).
4. Levenspiel O.: *Chemical Reaction Engineering*. Wiley, New York 1961.
5. Glaser M. B., Lichtenstein I.: A.I.Ch.E.J. *9*, 30 (1963).
6. Levenspiel O.: Can. J. Chem. Eng. *40*, 135 (1962).
7. Naor P., Shinnar R.: A.I.CH.E.J. *2*, 278 (1963).
8. Bischoff K. B., McCracken E. A.: Ind. Eng. Chem. *58*, 18 (1966).
9. Cholette A., Cloutier L.: Can. J. Chem. Eng. *37*, 105 (1959).
10. Van de Vusse J. G.: Chem. Eng. Sci. *17*, 507 (1962).
11. Sinclair C. G.: A.I.CH.E.J. *7*, *709* (1961).
12. Catchpole J. P., Fulford G.: Ind. Eng. Chem. *58*, 46 (1966).
13. Uhl V. W., Gray J. B.: *Mixing, Theory and Practice*. Academic Press, New York 1966.
14. Žaloudík P.: Engineering Science Research Report CH-1-67, Faculty of Engineering Science, University of Western Ontario, London, Canada.
15. Schoenemann K.: Dechema Monogr. *21*, 203 (1952).
16. Neville A. M., Kennedy J. B.: *Basic Statistical Methods for Engineers and Scientists*. International Textbook Co., Penna 1964.
17. I.B.M., 1130 Scientific Subroutine Package (1130-CM-02X), Programmers'Manual.