
ANALYSIS OF THE OSCILLATORY BEHAVIOUR OF AN INDUSTRIAL REACTOR FOR THE OXONATION OF PROPENE. EVALUATION OF FLOW MODELS BASED ON THE RESPONSE TO A PULSE SIGNALJosef HORÁK^a, Zdeněk BĚLOHLAV^a and František MADRON^b^a *Department of Organic Technology,**Prague Institute of Chemical Technology, 166 28 Prague 6 and*^b *Research Institute of Inorganic Chemistry, 400 60 Ústí nad Labem*

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The response of an industrial reactor for the oxonation of propene to its spiking with a radioactive tracer was compared with simulated responses obtained for models of various structures, *viz.* a cascade of two perfectly stirred cells of different size, a cascade of two perfectly stirred cells of the same size with recirculation of the reaction mixture, a cascade of two perfectly stirred cells of the same size with inflow into both cells, and a system of two perfectly stirred cells with back-flow involving a plug-flow element. None of the flow models fitted the experiment perfectly; the best fit was obtained for the combination of perfectly stirred cells and back-flow with a plug-flow element.

A simplified layout of the treated oxonation reactor is in Fig. 1. The exothermal reaction, hydroformylation of propene, takes place in a cylindrical reactor, stirred only by the entering gases or by the effect of temperature fields formed in the reaction mixture. Cooling of the system is provided by a set of cooling coils and by the cooling effect of entering propene. Examination of the distribution of the holdup time by means of a radioactive tracer gave evidence that the liquid phase in the reactor is stirred vigorously. Therefore, the causes of temperature oscillations in the reactor were analyzed¹ on a simple flow model, *viz.* a perfectly stirred vessel. The stability analysis, however, showed that an unstable behaviour of the reactor can only be expected at unreasonably high activation energies. More sophisticated flow models, better approaching the actual situation in the reactor, had thus to be used for a detailed investigation into the causes of the oscillatory behaviour. The present work gives the results obtained for various models based on their response to a pulse input signal.

THEORETICAL

Reactor response to an input pulse. The nature of the flow in the industrial equipment was studied by the impulse-and-response approach by spiking the system with a radioactive tracer. The distribution of the holdup time of the liquid in the reactor

was characterized by the time dependence of concentration of the tracer at the system output in relation to the concentration that would be attained if all the tracer were dispersed over the whole reactor volume (henceforth this dependence will be briefly referred to as the *C*-curve). The mean holdup time for the approximately basic technological regime of the reactor was 55 min, the dimensionless variance was 0.66.

Comparison of the treated models. The choice of the models was based on a comparison of the experimental value with the model responses for various values of the adjustable parameters. The simulated responses were obtained by numerical integration of mass balance equations for the input pulse signal.

The assumptions made previously¹ for a simplification of the models were adopted. The equations

$$dc_F/d\tau = (\dot{V}_R/V_F) c_E - [\dot{V} - \dot{V}_S + \dot{V}_R]/V_F c_F \quad (1)$$

with the starting condition $c_F = c_1(\dot{V} - \dot{V}_S)(V_F + V_S)/(\dot{V}V_F)$ at $\tau = 0$, and

$$dc_E/d\tau = [(\dot{V} - \dot{V}_S + \dot{V}_R)/V_S] c_F - (\dot{V}/V_S) c_E - (\dot{V}_R/V_S) c_E \quad (2)$$

with the starting condition $c_E = c_1\dot{V}_S(V_F + V_S)/(\dot{V}V_S)$ at $\tau = 0$ were used for the first and second perfectly stirred cascade cells with recirculation or with a simultaneous inflow into the two cells (Fig. 2, models No. 2–4).

For the model of two perfectly stirred cells with a plug-flow and back-flow (Fig. 2, model No. 5), Eqs (1) and (2) were used with the starting condition $c_F = c_1\dot{V}V/[(\dot{V} + \dot{V}_T)V_F]$ at $\tau = 0$ and the boundary condition $c_F = c'_F + c_1\dot{V}_T^n\dot{V}V/[(\dot{V} + \dot{V}_T)^{n+1}V_F]$ at $\tau = (V_T/\dot{V}_T)n$, where n is a natural number.

The time dependence of the tracer concentration at the model output was determined in the form of the *C*-curve from the relation

$$C = c_E\dot{V}/(c_1V). \quad (3)$$

The differential equations were solved by means of the 4th order Runge–Kutta method. The correctness of the solution was checked by calculation with a step of a one-half length.

Determination of the rate constant. Hydroformylation of propene is a catalytic reaction. The activity of a catalyst in an industrial reactor is variable and its instantaneous value is not known in advance. For this reason, the rate constant value was chosen such that the output degree of propene conversion in the steady state and in the basic technological regime was 0.933 for each model. For verification purposes, the rate constant was also determined from the experimental *C*-curve using the equa-

tion

$$x = \int_0^{\infty} e^{-k\tau} C \, d\tau, \quad (4)$$

based on the assumption that the reaction is 1st order, no changes occur in the density of the reaction mixture, and the model constitutes a closed system.

Flow models. The used models are in Fig. 2; Table I gives a survey of the adjustable parameters and their resulting values leading to the best fit of the simulated response to the experiment.

RESULTS AND DISCUSSION

With regard to the fact that the results of only a single experiment were available for the examination of the liquid flow in the reactor, two approaches to the evaluation of the industrial reactor response were adopted:

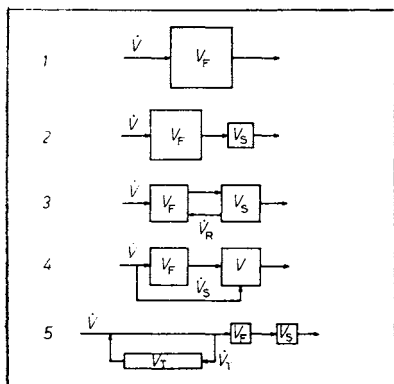


FIG. 1

Simplified layout of oxonation reactor. 1 catalyst solution, 2 synthesis gas, 3 propene, 4 products, 5 cooling water

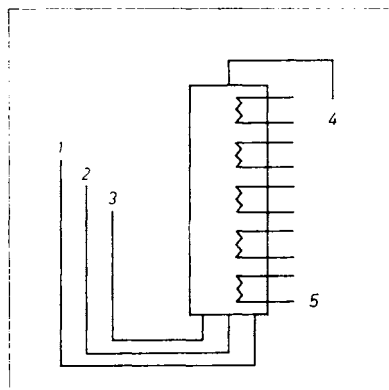


FIG. 2

Survey of models used. 1 perfectly stirred cell, 2 cascade of two perfectly stirred cells of different size, 3 cascade of two perfectly stirred cells of identical size with recirculation of reaction mixture, 4 cascade of two perfectly stirred cells of identical size with inflow into both cells, 5 combined model of two perfectly stirred cells of identical size with back-flow with plug-flow element

a) The "waves" observed on the response were regarded as a manifestation of information noise lacking physical meaning. The aim was to achieve agreement between the simulated course and the smoothed-out experimental response. The plug-flow element then had not to be considered in the models.

b) The "waves" were regarded as a manifestation of the flow of the reaction mixture inside the reactor, and the objective of the treatment was the setup of a simple model that would be able to simulate, to an approximation at least, the actual shape of the experimental response.

1 *A perfectly stirred cell.* The shape of the *C*-curve differs considerably from the experimental curve (Fig. 3). This model thus can only be regarded as a very crude approximation.

2 *Cascade of two perfectly stirred cells of different size.* The dependence of the dimensionless variance on the ratio of the volume of the first cell to the volume of the entire system is shown in Fig. 4. The higher the difference between the cell sizes, the better the model flow approaches a perfectly stirred system. Since the identification of the model is based on a linear phenomenon, the same responses are obtained for the reverse cell size ratios. The characteristics of the holdup time distribution in the reactor is roughly satisfied by the volume ratio $V_F/V_S = V_S/V_F = 4$. The *C*-curve for this case is shown in Fig. 3.

3 *Cascade of two perfectly stirred cells of identical size, with recirculation of the reaction mixture.* Fig. 5 shows that the intensity of stirring of the system increases with increasing back-flow. A response of the model consistent with the characteristics

TABLE I
Adjustable parameters of flow models

No.	Model	Parameter	Value, $k \cdot 10^{-3} \text{ s}^{-1}$	
1	Perfectly stirred cell	—	—	4.1
2	Cascade of two perfectly stirred cells	V_F/V	0.80	2.0
3	Cascade of two perfectly stirred cells with recirculation	\dot{V}_R/\dot{V}	0.50	2.0
4	Cascade of two perfectly stirred cells with inflow into both cells	\dot{V}_S/\dot{V}	0.25	2.6
5	Cascade of two perfectly stirred cells with plug-flow and back-flow	$V_T/(V_F + V_S)$ \dot{V}_T/\dot{V}	0.66 0.50	2.1

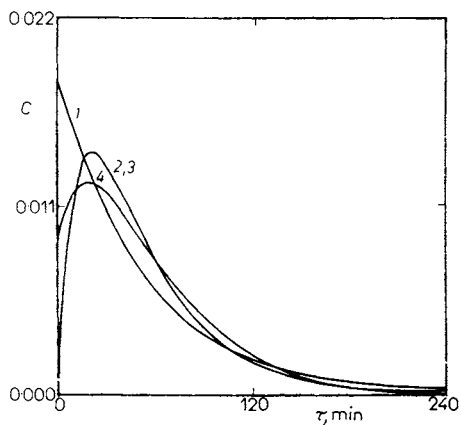


FIG. 3
Model responses to spike pulse. Curve numbering corresponds to model numbering in Fig. 2

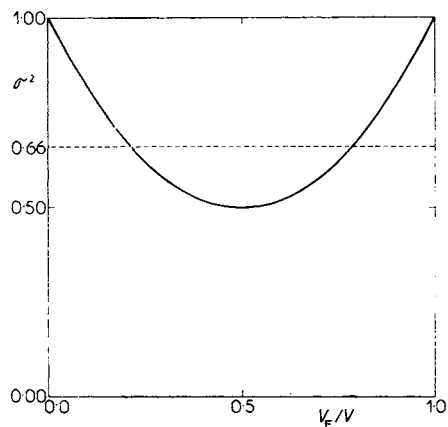


FIG. 4
Dependence of dimensionless variance on the relative size of the first cell in model No. 2

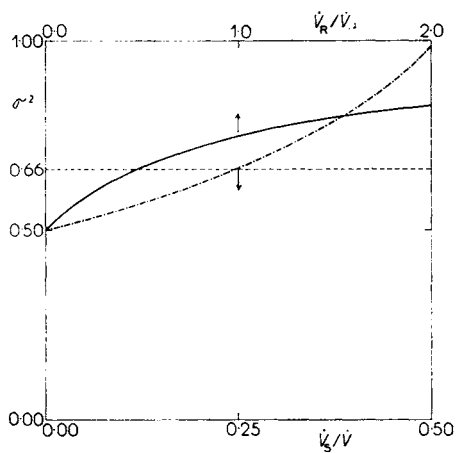


FIG. 5
Dependence of dimensionless variance on the relative value of back-flow in model No. 3 (full line) and on the relative value of inflow into the second cell in model No. 4 (dot-and-dash line)

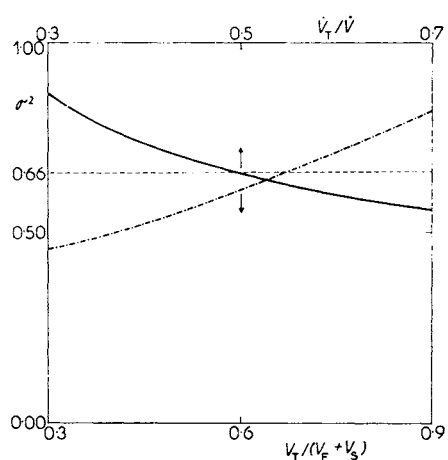


FIG. 6
Dependence of dimensionless variance on the relative value of back-flow (full line) and on the size of the plug-flow element in model No. 5 (dot-and-dash line)

of the experimental C -curve was obtained for a back-flow of $\dot{V}_R = \dot{V}/2$; this response is identical with the responses of the preceding models (Fig. 3).

4 Cascade of two perfectly stirred cells of identical size with inflow into both cells. The dimensionless variance of the C -curves obtained increases with increasing inflow into the second cell of the cascade (Fig. 5). The simulated response was attained at the inflow into the second cell $\dot{V}_S = \dot{V}/4$ (Fig. 3).

5 Combined model of two perfectly stirred cells of identical size with back-flow containing a plug-flow element. In contrast to the preceding models, the combined model of a perfectly stirred, plug and back-flow fits the experimental response fairly well. Fig. 6 shows that the dimensionless variance of the C -curves increases with increasing holdup time in the element with plug-flow. For the model parameters $V_T/(V_F + V_S) = 0.66$ and $\dot{V}_T = \dot{V}/2$, the C -curves of the model and of the actual reactor are compared in Fig. 7.

It is clear from Table I that for the composed models of two cells and for the combined model the rate constant is about two times lower than for a single perfectly stirred cell. Model No. 4 is an exception, where the higher value of the constant is due to the short-circuit effect arising from the direct inflow into the second cell.

It is not possible to unambiguously and exactly characterize the flow of the liquid phase in the oxonation reactor based on a single experimentally determined response of the reactor to a spike pulse. Some uncertainty is thus also transferred into the evaluation of the rate constant. Provided that the "waves" on the experimental C -curve are not a manifestation of information noise, devoid of physical meaning, this dependence is best fitted by the combined model of a cascade of two perfectly stirred cells with back-flow containing a plug-flow element. In the reverse case, the

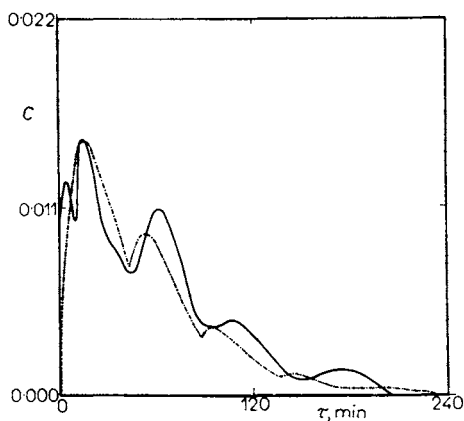


FIG. 7
Experimental response of reactor (full line)
and theoretical response for model No. 5
(dot-and-dash line)

flow of the liquid phase in the reactor can be simulated by various models of pairs of perfectly stirred cells.

LIST OF SYMBOLS

C	distribution of liquid holdup time at the system output, s^{-1}
c_E	concentration of tracer in second cell of cascade, $kg\ m^{-3}$
c_F	concentration of tracer in first cell of cascade, $kg\ m^{-3}$
c'_F	concentration of tracer in first cell of cascade after entering of a next dose of recirculating tracer, $kg\ m^{-3}$
c_I	concentration of tracer corresponding to the dispersion of amount added over the whole volume of system, $kg\ m^{-3}$
k	rate constant of reaction, s^{-1}
V	volume of liquid phase in reactor, m^3
V_F	volume of first cell of cascade, m^3
V_S	volume of second cell of cascade, m^3
V_T	volume of plug-flow element, m^3
\dot{V}	flow rate of reaction mixture, $m^3\ s^{-1}$
\dot{V}_R	back-flow rate in two-cell cascade, $m^3\ s^{-1}$
\dot{V}_S	rate of inflow into second cell of cascade, $m^3\ s^{-1}$
\dot{V}_T	rate of back-flow with plug-flow element, $m^3\ s^{-1}$
x	degree of conversion
σ^2	variance
τ	time, s

REFERENCES

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