

---

ATTI ACCADEMIA NAZIONALE DEI LINCEI  
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI  
**RENDICONTI**

---

GIANFRANCO LIBERTI, NICOLA PERNICONE, SERGIO  
SOATTINI

**Non-equilibrium phenomena in pulse reactor  
technique**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,  
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 49 (1970), n.1-2, p.  
124-128.*

Accademia Nazionale dei Lincei

<[http://www.bdim.eu/item?id=RLINA\\_1970\\_8\\_49\\_1-2\\_124\\_0](http://www.bdim.eu/item?id=RLINA_1970_8_49_1-2_124_0)>

L'utilizzo e la stampa di questo documento digitale è consentito liberamente per motivi di ricerca e studio. Non è consentito l'utilizzo dello stesso per motivi commerciali. Tutte le copie di questo documento devono riportare questo avvertimento.

---

*Articolo digitalizzato nel quadro del programma  
bdim (Biblioteca Digitale Italiana di Matematica)  
SIMAI & UMI*

<http://www.bdim.eu/>

**Chimica.** — *Non-equilibrium phenomena in pulse reactor technique*<sup>(\*)</sup>.

Nota <sup>(\*\*)</sup> di GIANFRANCO LIBERTI, NICOLA PERNICONE e SERGIO SOATTINI, presentata dal Socio G. B. BONINO.

**RIASSUNTO.** — Il presente lavoro costituisce un tentativo di interpretazione teorica del funzionamento di un microreattore a impulsi, utilizzando come modello la reazione di ossidazione di metanolo a formaldeide, su catalizzatore a base di molibdato di ferro-triosido di molibdeno, per mezzo dell'ossigeno della fase solida. Il calcolo è stato effettuato introducendo le seguenti ipotesi: 1) la velocità di desorbimento del reagente è trascurabile; 2) la velocità di adsorbimento del reagente può essere espressa mediante la formula di Elovich; 3) il ricoprimento della superficie può essere espresso senza tener conto del desorbimento dei prodotti.

L'accordo fra dati calcolati e dati sperimentali è soddisfacente; inoltre le precedenti ipotesi permettono una più approfondita comprensione dei fenomeni di non equilibrio comunemente riscontrati in reattori a impulso.

**INTRODUCTION**

The pulse reactor technique was firstly proposed by Emmett and coll. [1] as an experimental tool to test catalytic activity of solids using very small amounts of gaseous reactants. Nowadays, the importance of pulse reactors is mainly due to the possibility of obtaining kinetic information comparable and often complementary to those obtained from conventional flow reactors [2, 3]. Bassett and Habgood [4] firstly pointed out the relationship between pulse reactor and gas-chromatographic column, namely the possible separation of pulse components along the catalytic bed. On this basis, Gaziev, Filinovskii and Yanovskii [5] solved a gas-chromatographic material balance equation for a pulse reactor, including the rate of reaction as rate of reactant disappearance. Two assumptions were made by these Authors: 1) a power expression was used for the reaction rate; 2) the adsorption of reactant was considered to be in equilibrium, and the surface concentration of the adsorbed reactant was supposed to depend on the reactant concentration in the gaseous phase through a linear adsorption isotherm. Further theoretical analyses of this subject [6, 7, 8] were carried out through the numerical solution of equations similar to the Gaziev equation, using both power and Langmuir-Hinshelwood expressions of the reaction rate.

The present work is a theoretical analysis, with subsequent comparison with the experimental results, of the behaviour of a pulse microreactor in the oxidation of methanol to formaldehyde on  $\text{MoO}_3\text{—Fe}_2(\text{MoO}_4)_3$  catalyst by solid phase oxygen. The main novelty of our approach is the assumption

(\*) Lavoro eseguito nell'Istituto di Ricerche «G. Donegani» della Montecatini Edison S.p.A. — Novara.

(\*\*) Pervenuta all'Accademia il 15 luglio 1970.

of non-equilibrium for reactant adsorption, so that the reaction rate is equal to the adsorption rate, when measured as reactant disappearance. This assumption has led to a deeper understanding of a typical behaviour of pulse reactors, i.e. defective material balance, and also to a satisfactory fit between experimental and theoretical data.

### THEORETICAL

Let our overall reaction be subdivided into reactant adsorption, surface reaction and products desorption.

When reactant adsorption and products desorption are in equilibrium, the amount of reactant disappeared should be equal to the amount of product formed. Nevertheless, a number of cases were reported [9, 10, 11] in which the material balance was found defective, that is, in pulse reactors, often there is accumulation of matter in the adsorbed phase. For example, Bett and Hall [11] showed that, for zero order reactions, the adsorption of both reactant and products is generally not in equilibrium. Indeed, every step of the reaction may be not in equilibrium, because of the small contact time between the pulse and the catalytic bed, usually less than one second.

Our theoretical treatment is based on the following assumptions, which will be shown later to be reasonable in our experimental system:

- 1) the reactant desorption rate is so small that it can be neglected;
- 2) the rate of reactant adsorption follows the Elovich equation;
- 3) the surface coverage can be expressed by the total amount of reactant disappeared in the time interval  $0-t$  in each section of the reactor, without taking into account products desorption.

The material balance of the reactant, neglecting axial dispersion, reads:

$$(1) \quad \frac{\partial C_R}{\partial t} + v \frac{\partial C_R}{\partial x} = -(r_{ads})_R$$

where  $C_R$  is the gas phase concentration of reactant (mgr/cc),  $t$  is the time (sec),  $x$  the axial coordinate of the reactor (cm),  $v$  the linear flow rate (cm/sec) and  $(r_{ads})_R$  is the adsorption rate of the reactant (mgr/cc/sec).

The elimination of the adsorbed phase concentration derivative with respect to time from the equation used by Gaziev is a consequence of our first assumption (no gas-chromatographic retention of the reactant in the catalytic bed, but only disappearance of it by reaction with the solid phase).

Putting  $y = \frac{\sqrt{2}}{2} \left( t - \frac{x}{v} \right)$  and  $z = \frac{\sqrt{2}}{2} \left( t + \frac{x}{v} \right)$  by an axes rotation of  $45^\circ$ , eq (1) becomes:

$$(2) \quad \frac{\partial C_R}{\partial z} = - \frac{1}{2\sqrt{2}} (r_{ads})_R.$$

Owing to our second assumption we may write:

$$(3) \quad (r_{ads})_R = \beta \cdot \sqrt{T} \cdot C_R \exp \left\{ - \frac{\alpha}{T} \right\}$$

where  $T$  is the temperature ( $^{\circ}\text{K}$ ) and  $\vartheta = \vartheta(x, t) = \vartheta(y, z)$  is the surface coverage.

To express  $\vartheta$  as a function of  $C_R$ , the third assumption may be used. Therefore, taking (2) into account:

$$(4) \quad \vartheta(z, y) = -\frac{Q}{K} \frac{1}{v} \int_0^t \left( \frac{\partial C_R}{\partial z} \right)_y dt$$

where  $Q$  is the volumetric flow rate (cc/sec) and  $K/2\sqrt{2}$  is the amount of adsorbed reactant needed for a monolayer per unit length of catalytic bed (mgr/cm). Combining equations (2), (3) and (4) an expression containing only two constants is obtained, which has been numerically solved by the Runge-Kutta method. Conversions were calculated by the formula:

$$(5) \quad \% \text{ conv.} = \left\{ 1 - \int_0^{\infty} C_R(l, t) dt \left/ \int_0^{\infty} C_R(0, t) dt \right. \right\} \cdot 100$$

where  $l$  is the total length of the catalytic bed. The boundary conditions are  $C_R(x, 0) = 0$  and  $C_R(0, t) = \varphi(t)$ , where  $\varphi(t)$ , i.e. the initial shape of the pulse, has been given point by point and supposed almost rectangular

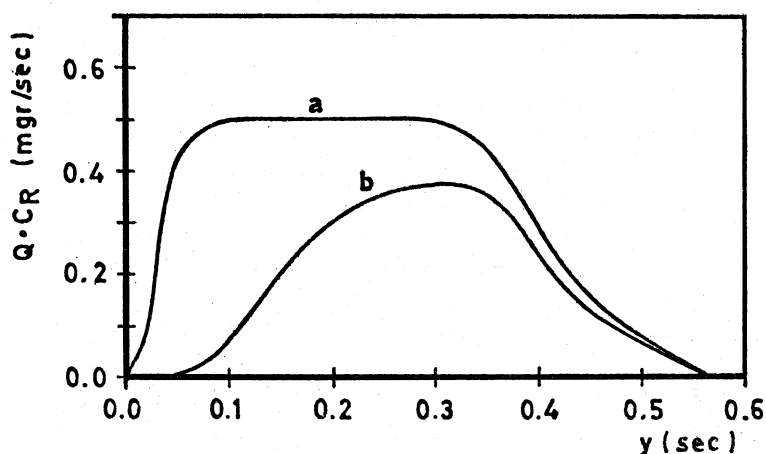


Fig. 1. - Concentration profile of the pulse at the inlet (a) and at the exit (b) of the catalytic bed. The profile b was calculated for the following values:

$$Q = 2 \text{ cc/sec}, \quad T = 483^{\circ} \text{ K}, \quad \alpha = 1.6 \cdot 10^5, \quad \beta = 8.5.$$

(fig. 1 a), owing to our feeding system. While the pulse passes through the catalytic bed, its calculated concentration profile asymmetrically falls (fig. 1 b), which agrees with the expectation that the front of the pulse, always finding fresh catalyst, would react quicker than the tail.

The parameters  $\alpha$  and  $\beta$  were calculated by the least squares method. The calculations were carried out on a «Univac 1108» computer.

## EXPERIMENTAL RESULTS

The experimental part of our work concerns the oxidation of methanol to formaldehyde by means of solid phase oxygen on a mixed  $\text{Fe}_2(\text{MoO}_4)_3\text{--MoO}_3$  catalyst. The length of the catalytic bed,  $l$ , was about 3 mm, the section  $0,67\text{ cm}^2$  and the void fraction  $0,4$ . The flow rate was in the range  $1\text{--}10\text{ cc/sec}$ . Full description of the experimental apparatus will be reported elsewhere.

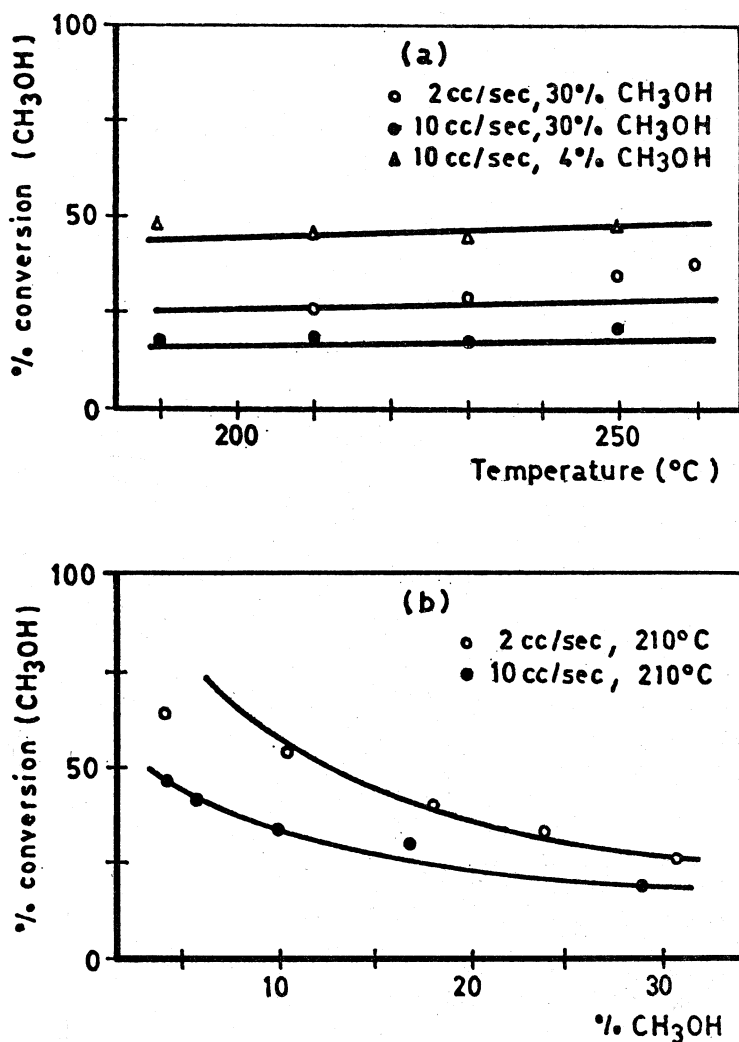


Fig. 2. — Experimental (points) and calculated (solid lines) conversions, referred to methanol disappearance, vs. temperature (a) and vs. methanol concentration (b). Solid lines are calculated from eq. (5), with  $\alpha = 1.6 \cdot 10^5$  and  $\beta = 8.5$ .

As the contact time of the pulse in a section of the catalyst is always less than one second, the hypothesis that methanol adsorption is an irreversible process seems to be quite reasonable in our experimental conditions,

indeed in such a short time adsorption should take place only on the strongest sites. A highly defective material balance always occurred and the conversion referred to products was less than ten per cent except for low flow rates and high temperatures; therefore also the third hypothesis seems to be reasonable. No experimental results, on the contrary, are available to support the use of the Elovich equation (second assumption), instead of which other kinetic equations could be used.

In fig. 2 *a, b* the experimental conversion, calculated from methanol disappearance, is reported versus temperature and methanol concentration for different values of the flow rate.

The reported values are affected by an experimental error of  $\pm 10\%$  with a probability level of 90 %. The continuous lines reported in fig. 2 *a, b* were calculated with equation (2). As may be seen, the theoretical lines satisfactorily fit the experimental points. This result seems to be rather significant, because the experimental dependence of methanol conversion on three independent variables was theoretically obtained by optimizing, by the least squares method, only two parameters. However, at low flow rates and high temperatures there is some disagreement between experimental and calculated conversion (fig. 2 *a*). For in these conditions a marked desorption of products occurs, the third assumption is no longer valid, namely the actual coverages are lower and the corresponding experimental conversions are higher than the calculated ones. Another disagreement is observed for low flow rates and small methanol concentrations (fig. 2 *b*). This may be due to the inadequacy of the Elovich equation: indeed the adsorption activation energy could not vary linearly with the  $s$  parameter of the adsorbent surface [12], but could have a more complex behaviour.

Gli A.A. ringraziano il prof. G. B. Bonino per l'interesse prestato al presente lavoro e il dr. A. Angelini per le costruttive discussioni sulla parte matematica.

#### REFERENCES

- [1] R. J. KOKES, H. TOBIN e P. H. EMMETT, « J. Am. Chem. Soc. », 77, 5860 (1955).
- [2] G. M. SCHWAB e A. M. WATSON, « J. Catalysis », 4, 570 (1965).
- [3] K. KEIZER, A. PH. BATIST e G. C. A. SCHUIT, « J. Catalysis », 15, 256 (1969).
- [4] D. W. BASSETT e H. W. HABGOOD, « J. Phys. Chem. », 64, 769 (1960).
- [5] G. A. GAZIEV, V. Y. FILINOVSKII e M. I. YANOVSKII, « Kinetika i Kataliz », 4, 668 (1963).
- [6] W. A. BLANTON JR., C. H. BYERS e R. P. MERRILL, « Ind. Eng. Chem. Fund. », 7, 611 (1968).
- [7] T. HATTORI e Y. MURAKAMI, « J. Catalysis », 10, 144 (1968).
- [8] T. HATTORI e Y. MURAKAMI, « J. Catalysis », 12, 166 (1968).
- [9] K. C. STEIN, I. J. FEENAN, L. J. E. HOFER e R. B. ANDERSON, U.S. Dept. Interior, Bureau of Mines, Bull. 608, 1962.
- [10] V. M. BELOUSOV e A. V. GERSHINGORINA, Fourth Intern. Congr. Catalysis, Moscow 1968, Preprint 23.
- [11] J. S. BETT e W. K. HALL, « J. Catalysis », 10, 105 (1968).
- [12] D. O. HAYWARD e B. M. W. TRAPNELL, « Chemisorption », p. 94, Butterworths, London 1964.