

# Experimental Observation of Chaotic Behavior in CO Oxidation in Lumped and Distributed Catalytic Systems

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Measurements of the catalyst temperature and outlet conversion in differential, integral and honeycomb systems give evidence that the catalytic CO oxidation may proceed chaotically in time over a range of inlet CO concentrations and temperatures. Development of aperiodic oscillations from periodic oscillations was experimentally investigated. In distributed systems chaotic behavior may exist only in a narrow range of inlet temperatures.

## 1. Introduction

In the last two decades a great number of theoretical and experimental papers were published on the subject of hysteresis and periodic activity in chemically reacting systems [1–3]. Recently it has been shown that nonlinear deterministic continuous oscillators with more than two variables are in many cases capable of producing effects of considerable dynamic complexity such as multipeak periodic states and complicated oscillations known under the name “chaos” [4, 5]. The most recent interest in this subject apparently was catalyzed by the publication of several theoretical papers dealing with the dynamics of populations whose developments were described by virtue of a single nonlinear difference equation [6]. Rössler [7–9] and May and Leonard [10] recently reported examples of ordinary differential equations which may exhibit similar dynamic behavior. To our knowledge there have been only a few reports of experimental observations of complex dynamics in chemically reacting systems. For the Zhabotinsky reaction the chaotic or chaotic-like behavior was observed by Schmitz [11], Wegmann and Rössler [12], and Marek [13, 14], for an enzymatic reaction, chaos was described by Olsen and Degn [15], in catalytic systems chaotic behavior was reported by Schmitz [5, 16, 17], Luss [18, 19] and Rathouský and Hlaváček [20].

So far there is apparently only one paper which gave evidence of chaotic behavior in distributed chemically reacting systems [14].

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The goal of the present paper is i) to report on complex dynamic behavior in lumped parameter systems and ii) to present information on complex dynamic behavior in distributed systems. The system under study is catalytic oxidation of CO on a porous catalyst and indicates that complex dynamic behavior may be also observed for systems with a porous catalyst.

## 2. Experimental

### Reaction and Materials

The catalytic CO oxidation by pure oxygen was selected as a model reaction. In packed bed arrangements Pt/alumina catalyst in the form of 3.4 mm spherical pellets was used. For the honeycomb experiments, an aluminum honeycomb matrix was adapted. At the surface of the metal a thin layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was created, which was impregnated with Pd.

The CO used in this study was obtained by thermal decomposition of formic acid in hot sulphuric acid. The gas was purified by chromsulphuric acid, NaOH and active charcoal and dried before use.

### Equipment

Three different experimental systems were used:

i) A laboratory recycle reactor packed by spherical Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (catalyst amount 10 g, bed depth  $L=8$  cm, diameter of the bed  $d_t=1.8$  cm) [21]. In this arrangement the recirculation ratio was 1 : 100, i. e. the reactor behaves as an almost isothermal equipment. The temperature of the bed as well as of the gas in the fore and aft sections were measured.

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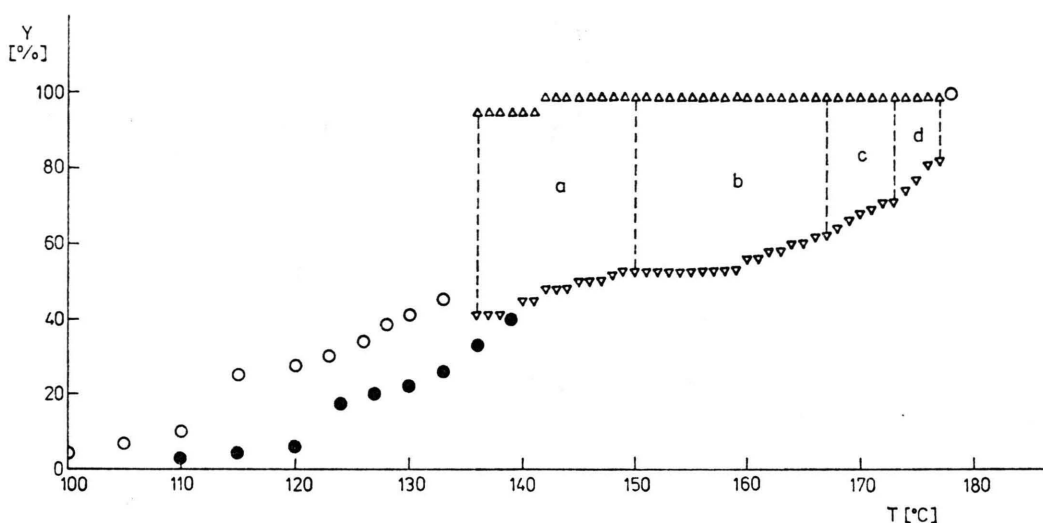


Fig. 1. Observed reactor states (recycle reactor, 5% CO in O<sub>2</sub>). ○ stable state after increasing reactor temperature; ● stable state after decreasing reactor temperature; △ oscillatory state.

Regions: a) asymmetrical periodic oscillations; b) symmetrical periodic oscillations; c) periodic oscillations slightly perturbed by a new oscillation regime; d) aperiodic oscillations.

ii) A tubular nonisothermal nonadiabatic packed bed reactor [22].

This reactor was constructed of three coaxial glass tubes. Through the outer jacket silicon oil was pumped and air flow through the inner jacket as a cooling medium. The catalyst was placed in the central part of the tube ( $d_t = 23$  mm,  $L = 60$  cm). The axial temperature profiles were measured by a thermocouple moving axially in a thermowell.

iii) A honeycomb matrix catalyst (length 5.5 mm, diameter of the matrix 45 mm, diameter of a single channel 0.9 mm, number of channels 300, [22]). The catalyst matrix was suspended on two rods in a Pyrex-glass tube. The temperatures of the catalyst surface as well as of the gas in the fore and aft sections were recorded.

Gas analysis were performed by an infrared analyzer IRGA 10 or by a thermal conductivity cell.

### 3. Results

#### i) Chaotic Behavior in a Recycle Reactor

In these experiments the dependence of exit conversion on the inlet temperature as well as the temporal temperature profiles were measured. A detailed description of the results of these experiments will be presented elsewhere [22]. Here only the facts associated with chaotic oscillations will be given.

In Figs. 1 – 8 the development of different situations (steady state, periodic oscillations, aperiodic oscillations) is shown. From Fig. 1 it may be inferred that multiple states may exist. For low inlet temperatures (110–136 °C) only steady states

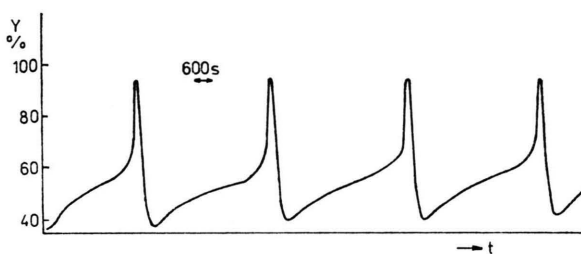


Fig. 2. Recording of asymmetric oscillations ( $T_0 = 137$  °C, approached from the lower stable steady state).

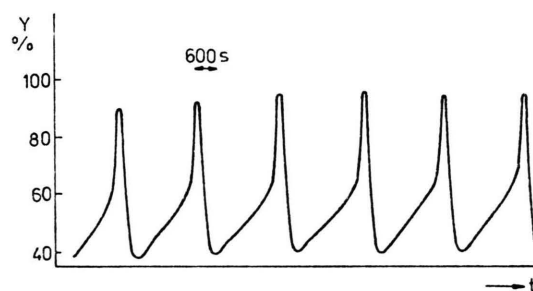


Fig. 3. Recording of asymmetric oscillations ( $T_0 = 139$  °C, approached from the lower stable steady state).

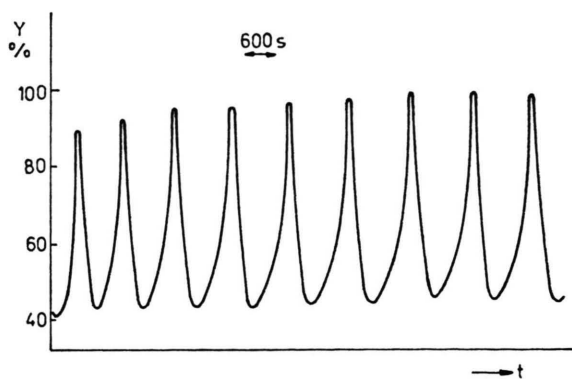


Fig. 4. Recording of asymmetric oscillations ( $T_0 = 143^\circ\text{C}$ , approached from the lower stable steady state).

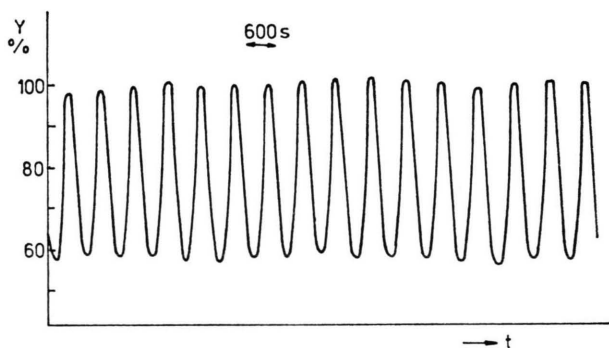


Fig. 5. Recording of symmetric oscillations ( $T_0 = 162^\circ\text{C}$  approached from the lower stable steady state).

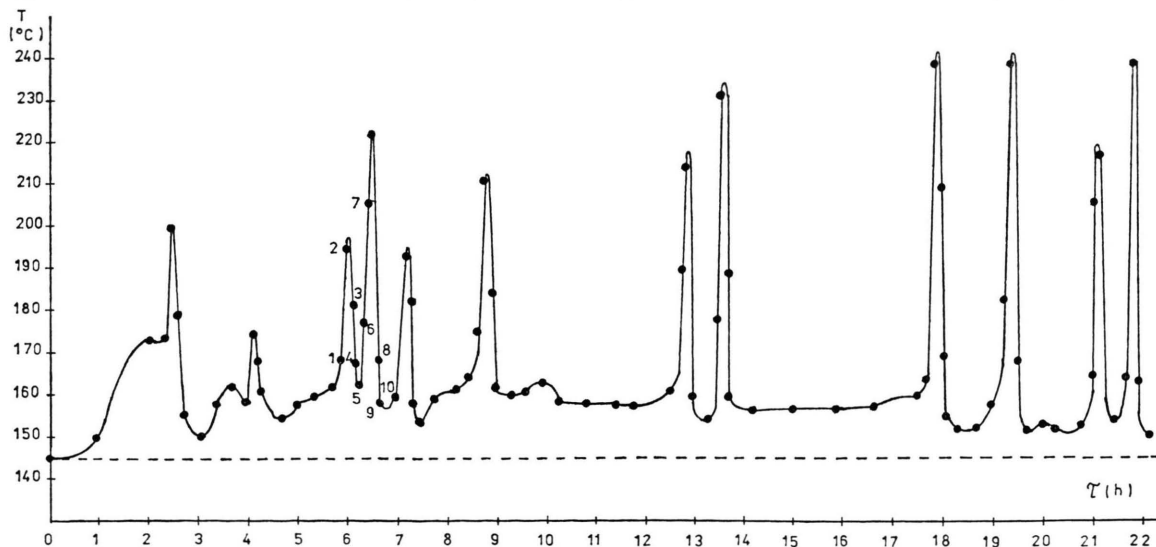


Fig. 9. Recording of oscillations of local temperature ( $T_0 = 145^\circ\text{C}$ , 1% CO,  $G = 1.852 \cdot 10^{-1} \text{ kgm}^{-2} \text{ s}^{-1}$ , position of the thermocouple  $l = 0.2 \text{ m}$ ).

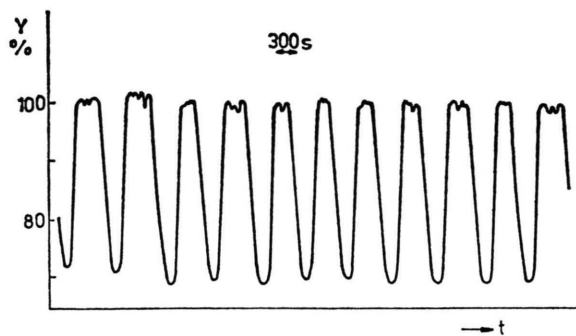


Fig. 6. Recording of perturbed symmetric oscillations ( $T_0 = 171^\circ\text{C}$ , approached from the lower stable steady state).

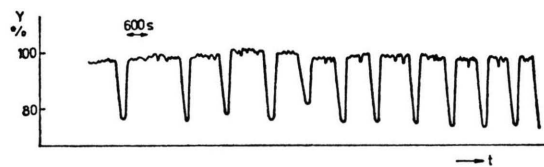


Fig. 7. Recording of chaotic-like oscillations ( $T_0 = 175^\circ\text{C}$  approached from the lower stable steady state).

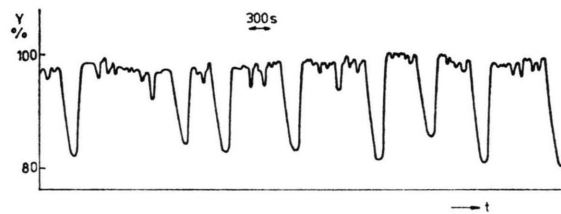


Fig. 8. Recording of chaotic behavior ( $T_0 = 177^\circ\text{C}$ , approached from the lower stable steady state).

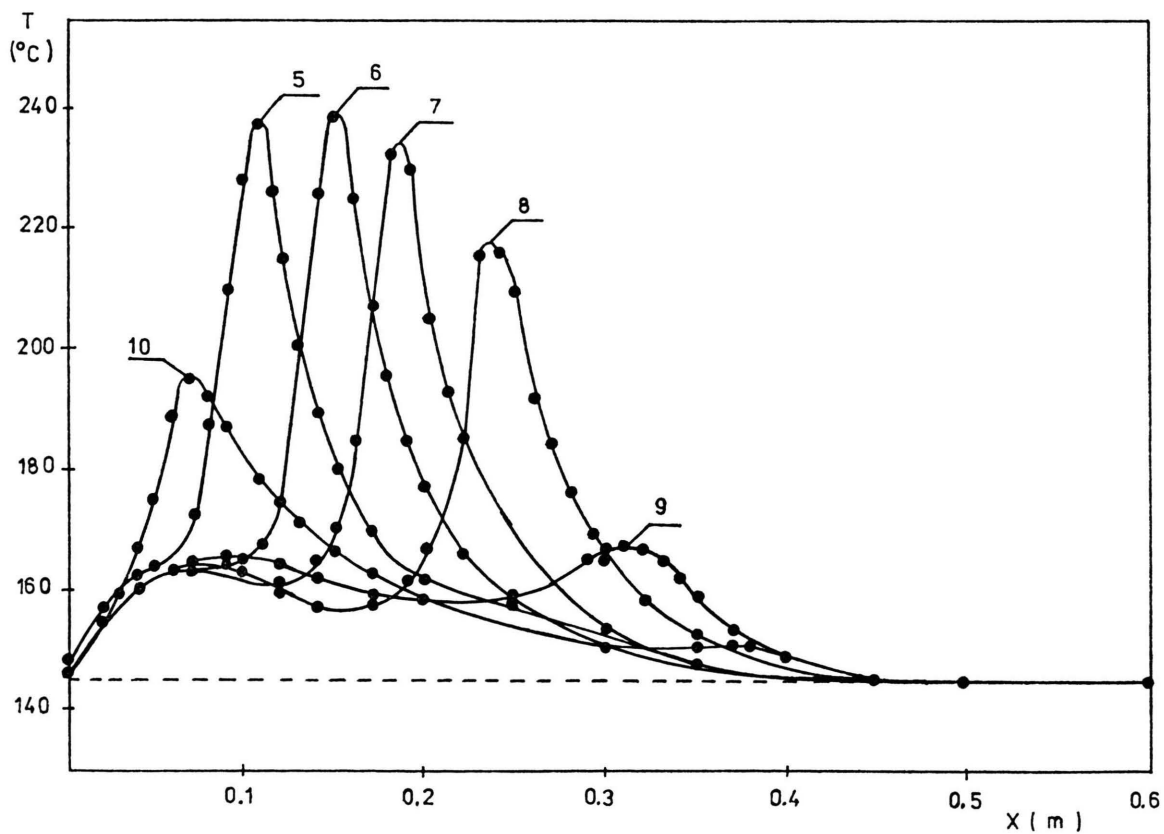
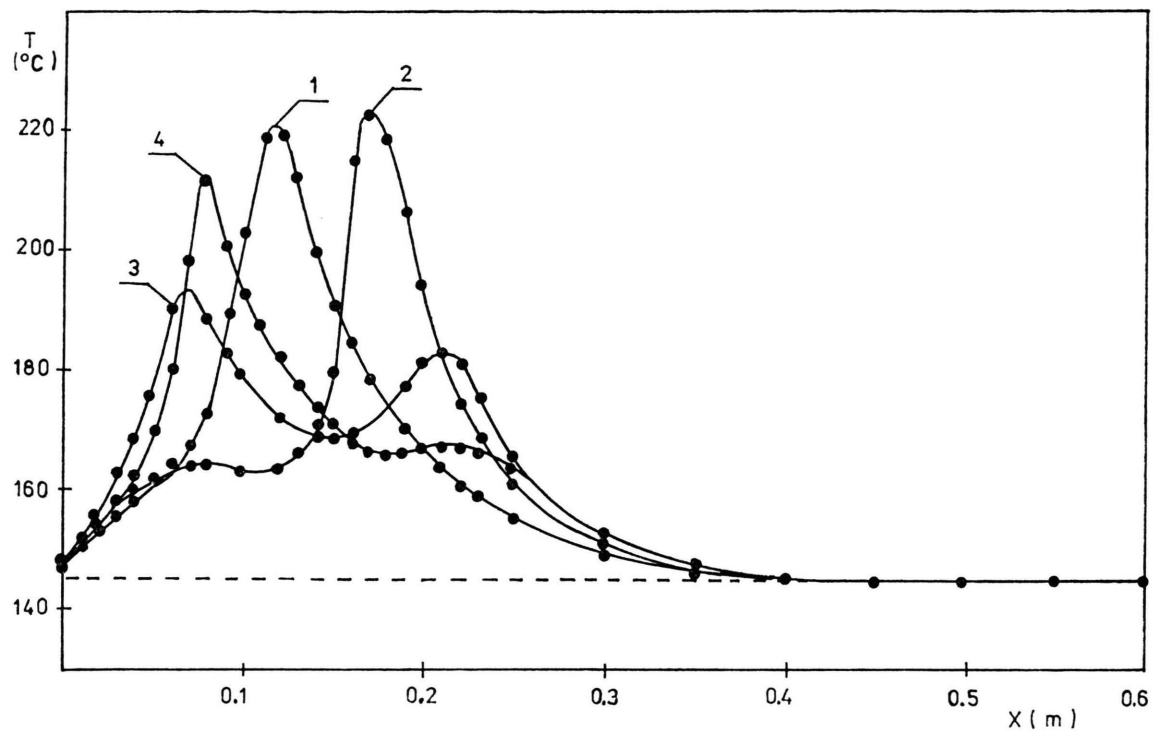


Fig. 10a and 10b. Development of axial temperature profiles.

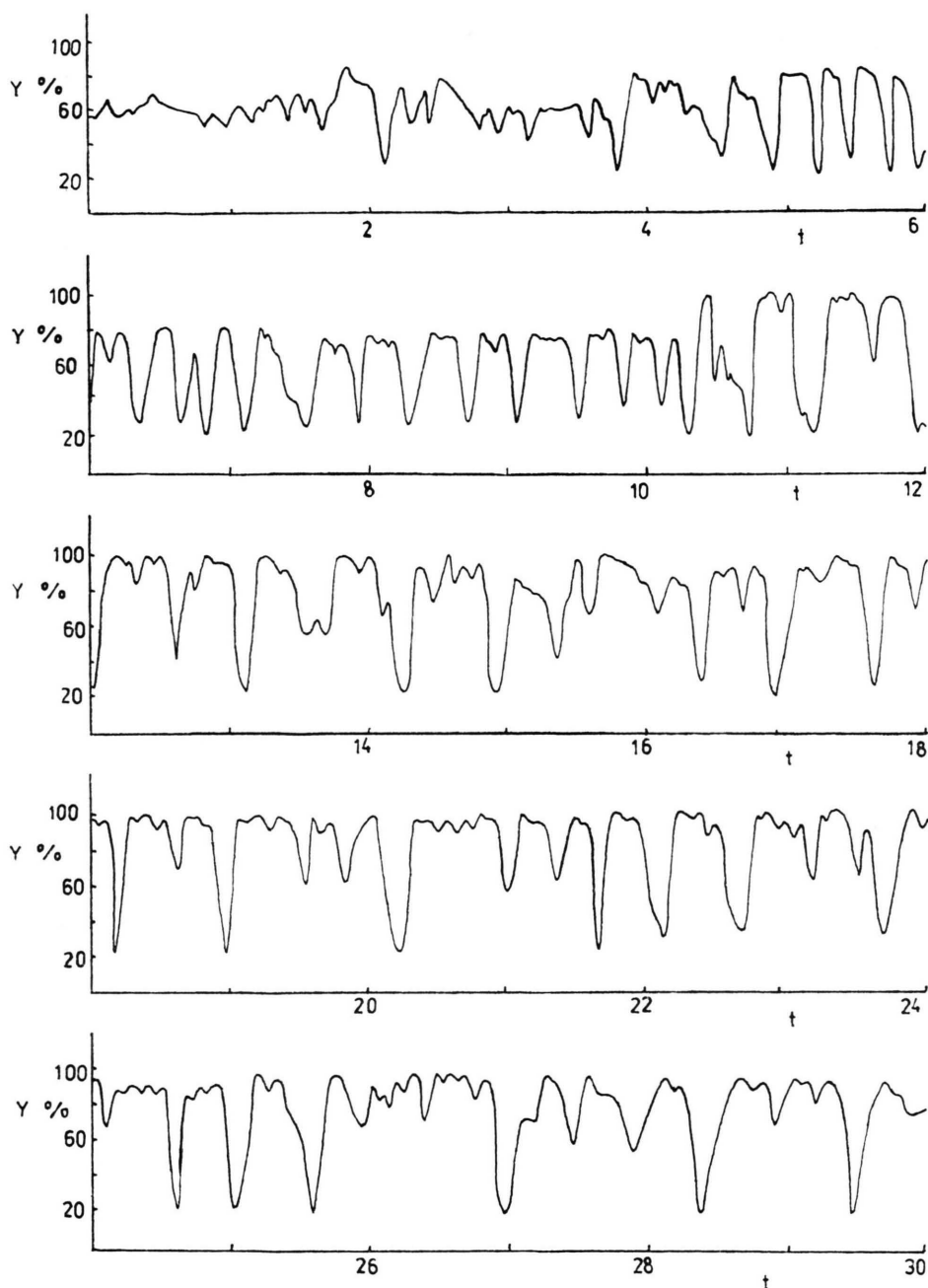


Fig. 11. Recording of oscillations. Honeycomb catalyst ( $T_0 = 143^\circ\text{C}$ , 1% CO).

occur. Asymmetrical periodic oscillations were observed in the region  $136 - 150^\circ\text{C}$  (see Figs. 2 and 3). For higher values of inlet temperature ( $153 - 167^\circ\text{C}$ ) these oscillations become symmetrical, cf. Figs. 4 and 5. For the inlet temperature  $T_0 = 162^\circ\text{C}$  a long time experiment including 70 periods was

performed. In this experiment no important changes of the period, amplitude and character of oscillations were observed. For higher inlet temperature ( $168 - 173^\circ\text{C}$ ) the symmetrical oscillations become complicated. Here during the dynamic regime a new oscillatory process occurs (Figure 6). This effect

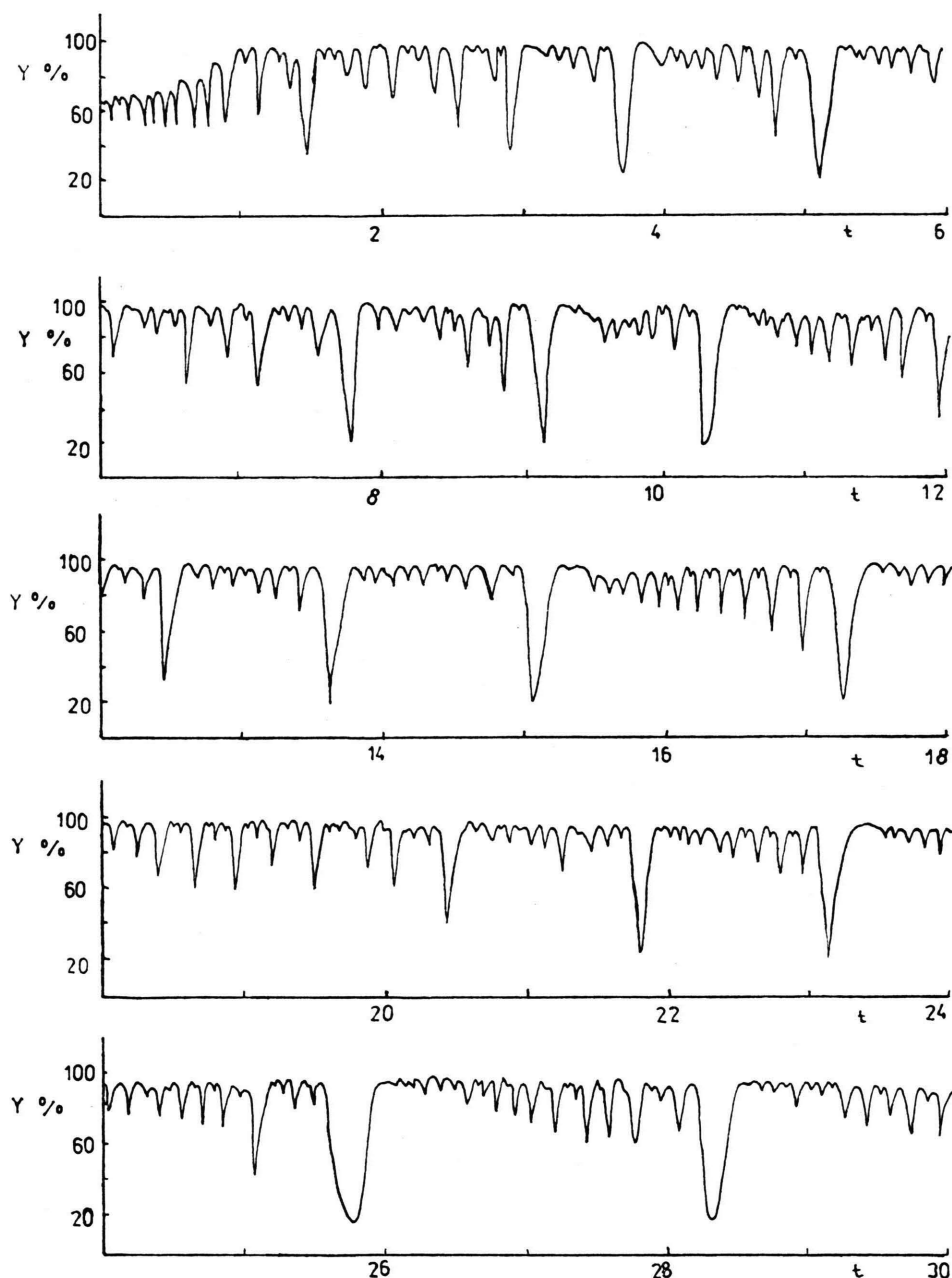


Fig. 12. Recording of oscillations. Honeycomb catalyst ( $T_0 = 194^\circ\text{C}$ , 5% CO).

results only in a slight perturbation of the conversion near 100%. For  $T_0 = 171^\circ\text{C}$  the frequency of the basic oscillations is not strongly influenced. However, after increasing the inlet temperature the interaction with the second oscillatory process becomes strong and the periodic behavior of the oscillations disappears, see Figures 7 and 8.

#### ii) Chaotic Behavior of Temperature Fields in a Tubular Nonadiabatic Reactor

A detailed experimental study of axial temperature profiles in a nonadiabatic tubular fixed bed reactor revealed that for certain operating conditions oscillatory aperiodic behavior of temperature



profiles in the reactor can be observed. For this study both the local thermocouple temperature reading and the measurement of axial temperature profiles were performed. These results were obtained for the inlet temperature  $T_0 = 145^\circ\text{C}$  and the feed concentration 1% CO, cf. Figures 9 and 10 a, 10 b. The temperature wave arose in the inlet part of the reactor, moved downstream and in the middle part disappeared. A number of axial profiles is shown in Figures 10 a and 10 b. Here the numbers correspond to those in Figure 9. These experiments reveal that very complicated dynamic effect may be expected in distributed systems.

### iii) Chaotic Behavior of Honeycomb Structures

Similar to packed bed systems we have observed periodic activity behavior also for a honeycomb structure. Since the honeycomb matrix is relatively short and because of the high thermal conductivity of the supporting material we can reasonably approximate the honeycomb structure by a metal net. As a result we can consider the honeycomb catalyst matrix as a lumped parameter system. A detailed information on the dynamics will be presented elsewhere [21]. Here only two examples associated with chaotic behavior of the process will be presented.

In Fig. 11 temperature recordings showing the development of chaotic oscillations for 1% CO and  $T_0 = 143^\circ\text{C}$  are drawn. Characteristic multippeak oscillations exhibiting chaotic behavior are shown in Fig. 12 ( $T_0 = 194^\circ\text{C}$ , 5% CO).

## 4. Discussion and Conclusions

Several models have been proposed in the literature to describe the kinetic behavior of the CO oxidation [21, 23]. Recent detailed bifurcation analysis of these equations has revealed that these models are capable of predicting multiple steady states and periodic activity. We have however, not been able to model the chaotic behavior [21]. Evidently, further development of theoretical models, which imply a better understanding of the detailed reaction steps on the surface, is necessary. Despite the shortcomings embodied in our experimental systems, the observations reported here suggest a variety of interesting and important effects occurring in porous catalytic systems. Both carefully designed and planned experimental studies and construction of sophisticated mathematical models might be useful in exploring such systems and improving our knowledge and understanding of basic laws governing catalytic reactions.

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