

ANALYSIS OF THE OSCILLATORY BEHAVIOUR OF AN INDUSTRIAL REACTOR FOR OXONATION OF PROPENE: THE CSTR MODEL

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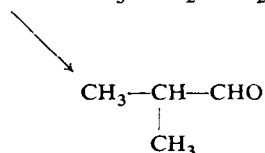
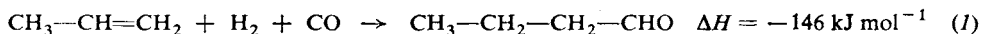
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The paper analyses the oscillatory states of an industrial reactor observed in the process aimed at enhancing its productivity. The model of a perfectly stirred continuous reactor was used for the analysis. Both the stable and the oscillatory states were found to have the same character while their stability depended on the ratio of the heat and mass capacities of the system. The model of the perfectly stirred reactor did not help us explain the observed instability unless a high value of the activation energy was used.

Experimental investigation of oxonation in the laboratory¹⁻⁵ and, at the same time, an industrial unit was monitored by a data logger with the aim of enhancing its productivity. An integral part of the research were also measurements of the residence time distribution in the reactors using a radioactive tracer. During one of the experimental measurements at increased loads spontaneous oscillations of temperature were observed in the first reactor. This paper presents analysis of the behaviour of the reactor with the aid of the simplest model, *i.e.* the model of a perfectly stirred continuous reactor with stabilized inputs. The aim of the analysis was to elucidate the cause for the oscillatory behaviour.

Information regarding the process. Oxonation of propene obeys the following stoichiometric equation.



Two reactors were used in the production unit, operating, from the view point of the synthesis gas (a mixture of CO and H₂), in series, from the view point of propene, in parallel. The reaction heat is removed by cooling coils inside the reactor. The overall heat liberated in the second reactor amounts to about one half of the heat

liberated in the first reactor. Consequently, the presented analysis concerns only the first reactor, where, in fact the oscillations were observed. The reactors were equipped with no mechanical stirres; the mixture was mixed only by the fed gas, or, eventually, by the effect of thermal fields induced by the cooling system. The mixing therefore was not perfect. The measurements of the residence time lead to the conclusion that the response to an inlet impulse corresponds to a system somewhere between a signal perfectly mixed reactor and two perfectly mixed reactors in series. The reactor is schematically shown in Fig. 1. The list of symbols and the data regarding the parameters of individual streams are given in Table I.

Data on the reaction. Parallel experimental research showed the reaction to obey the following equation

$$r = c_k k_0 \exp(-E/RT), \quad (2)$$

where

$$c_k = c_{k2} \dot{V}_2 / \dot{V}_4.$$

The concentration of carbon monoxide and hydrogen was not considered in the calculation for the syntheses gas is supplied to the reactor in surplus. Accordingly, the reaction mixture is saturated by the synthesis gas and the pressure in the reactor remains constant.

The calculations of the reaction rate carries an uncertainty in that we are dealing with a catalytic reaction and the activity of the catalyst may change. For this reason the value of the reaction rate constant, k_0 , was being evaluated from the parameters of the standard (non-oscillatory) regime with the mean degree of conversion 93.3%.

The uncertainty exists also in the value of the activation energy. Experimental research² gave the value $E = 66 \text{ kJ mol}^{-1}$. In older papers, however, one can find values of E as high as 109 kJ mol^{-1} .

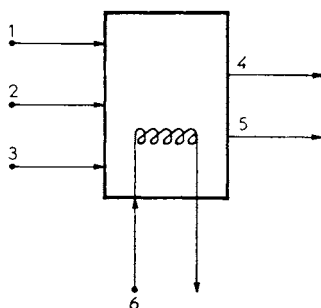


FIG. 1
Scheme of the reactor
1 propylene; 2 solution of catalyst; 3 synthesis gas; 4 product; 5 synthesis gas; 6 cooling water

TABLE I

Symbols and values of parameters of the basic technological regime

A	heat transfer area: 195 m^2
c	propylene concentration in reactor: 320 mol m^{-3}
c_0	inlet propylene concentration: $4\,750 \text{ mol m}^{-3}$
c_1	propylene concentration in stream no 1: $12\,740 \text{ mol m}^{-3}$
c_4	propylene concentration in stream no 4: 320 mol m^{-3}
c_k	catalyst concentration in reactor: $1.34 \cdot 10^{-2} \text{ mol m}^{-3}$
c_{k2}	catalyst concentration in stream no 2: $3 \cdot 10^{-2} \text{ mol m}^{-3}$
c_p	specific heat capacity of liquid in reactor: $3\,200 \text{ J kg}^{-1} \text{ K}^{-1}$
c_{p1}	specific heat capacity of propylene: $3\,800 \text{ J kg}^{-1} \text{ K}^{-1}$
c_{p4}	specific heat capacity of stream no 4: $3\,200 \text{ J kg}^{-1} \text{ K}^{-1}$
c_{p5}	specific heat capacity of synthes gas: $33 \text{ J mol}^{-1} \text{ K}^{-1}$
c_{p6}	specific heat capacity of cooling water: $4\,240 \text{ J kg}^{-1} \text{ K}^{-1}$
E	activation energy: 66 and 109 kJ mol^{-1}
ΔH	reaction enthalpy: 146 kJ mol^{-1}
K	heat transfer coefficient: $500 \text{ W m}^{-2} \text{ K}^{-1}$
k_0	constant: $7.91 \cdot 10^7$ and $2.33 \cdot 10^{13} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$
k_1	constant: 1.35
k_2	constant: 1.11
M	molecular weight of propylene: $42.08 \cdot 10^{-3} \text{ kg mol}^{-1}$
\dot{n}_5	molar flow rate of stream no 5: 9.7 mol s^{-1}
\dot{Q}_c	heat removed by cooling: $1\,800 \text{ kW}$
r	reaction rate: $1.37 \text{ mol m}^{-3} \text{ s}^{-1}$
R	versatile gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
T	temperature of reaction mixture: 410.65 K
T_0	reference temperature: 410.65 K
T_1	temperature of stream no 1: 283.15 K
T_2	temperature of stream no 2: 410.65 K
T_3	temperature of stream no 3: 410.65 K
T_6	inlet coolant temperature: 384.15 K
V	volume of liquid in reactor: 10.6 m^3
\dot{V}_1^a	volume flow rate of stream no 1: 1
\dot{V}_2^a	volume flow rate of stream no 2: 0.83
\dot{V}_4^a	volume flow rate of stream no 4: 2.68
\dot{V}_6	volume flow rate of stream no 6: $3.17 \cdot 10^{-2} \text{ m}^3 \text{ s}^{-1}$
x	degree of conversion: 0.933
ρ	density of reaction mixture: 723 kg m^{-3}
ρ_1	density of propylene: 536 kg m^{-3}
ρ_4	density of stream no 4: 723 kg m^{-3}
ρ_6	density of sooling water: 947 kg m^{-3}
τ	time: s

^a Relative value.

The Model of the Reactor

Following assumptions were adopted for the sake of simplification of the mathematical model:

- Ideal mixing of the reaction mixture
- The presence of propylene in streams number 1 and 4 only. This neglects the propylene in the outlet reacted stream of the synthesis gas (owing to the low vapour pressure of propylene this amount is small).
- The volume of the reactor is constant; for this volume we take that part of the reactor volume occupied by the liquid phase. Since the gas phase occupies only a minor part of the reactor and the concentration of propylene here is substantially lower than in the liquid phase its content was neglected in the balance equations.
- The concentration of carbon monoxide and hydrogen in the liquid phase is constant owing to the surplus of the synthesis gas in the reactor.
- Inlet concentrations of all species are constant.

The mass balance of propene

$$\dot{V}_1 c_1 - Vr = \dot{V}_4 c_4 + \frac{d(Vc)}{d\tau}. \quad (3)$$

The first term on the left hand side of the equation represents molar flow rate of propene in the stream number 1, the second term represents the disappearance of propene due to the chemical reaction. The first and the second term on the right hand side express the molar flow rate of propylene in the stream number 4 and the accumulation of propylene in the reaction mixture.

Molar concentration of propylene in the reactor was expressed as a function of the degree of conversion, x , as follows:

$$c = c_0 (1 - x), \quad (4)$$

where c_0 is the concentration of propylene at the reactor inlet, related to the combined inlet streams number 1 and 2 that part of the stream number 3, which participates in the addition reaction. For the concentration c_0 we may write

$$c_0 = c_1 \dot{V}_1 / \dot{V}_4. \quad (5)$$

After substituting the degree of conversion the mass balance takes the following form:

$$c_1 \frac{\dot{V}_1}{\dot{V}_4} \frac{dx}{d\tau} = r - \left(\frac{\dot{V}_1 c_1}{V} \right) x. \quad (6)$$

For the calculation of the volume flow rate of the exit stream number 4 the following relationship was used

$$\dot{V}_4 = k_1 \dot{V}_1 + k_2 \dot{V}_2, \quad (7)$$

where the empirical constant k_1 incorporates conversion of the volume flow rate of propylene to the volume flow rate of the reaction mixture, while k_2 accounts for the effect of the difference between the conditions of measurement of the flow rate of the inlet stream of catalyst and the conditions at the reactor outlet.

Molar concentration of propylene in the stream number 1 was expressed by

$$c_1 = \varrho_1/M, \quad (8)$$

the enthalpy balance

$$\begin{aligned} \dot{V}_1 \varrho_1 c_{p1} (T_1 - T_0) - \dot{V}_4 \varrho_4 c_{p4} (T - T_0) - \dot{n}_5 c_{p5} (T - T_0) + \\ + Vr(-\Delta H) - \dot{Q}_c = V \varrho c_p \frac{dT}{d\tau}. \end{aligned} \quad (9)$$

The first term on the right hand side of this equation represents the rate of consumption of heat necessary to heat propylene to the reference temperature. The second and the third term represent the heats of the streams leaving the reactor, while the fourth term represents the liberated reaction heat. The term on the right hand side of the last equation expresses the rate of accumulation of the heat in the reaction mixture. The streams number 2 and 3 do not appear in the heat balance as they are heated to the reference temperature T_0 prior to entering the reactor.

Upon assuming that the heat transfer coefficient remains constant throughout the area of the heat exchanger, the quantity \dot{Q}_c was expressed by the following equation:

$$\dot{Q}_c = \dot{V}_6 \varrho_6 c_{p6} \left[1 - \exp \left(\frac{-KA}{\dot{V}_6 \varrho_6 c_{p6}} \right) \right] (T - T_6). \quad (10)$$

In the third term of Eq. (9) (the stream number 5) the volume flow rate of the synthesis gas \dot{V}_5 was replaced by a more appropriate molar flow rate \dot{n}_5 .

RESULTS AND DISCUSSION

Classification of the Steady States

For the purpose of determination of the character of the stationary states the method based on observation of the course of the curves (trajectories) of the pseudosta-

tionary states in the phase plane r, x was used. The reaction rate was used as a state variable instead of the reaction temperature. This is permissible as the reaction rate is a monotonous function of the reaction temperature. The curves of the pseudostationary states were determined numerically from Eqs (6) and (9) by substituting the following conditions:

$$\frac{dx}{d\tau} = 0 \quad \text{and} \quad \frac{dT}{d\tau} = 0.$$

The curve of the pseudostationary states of the degree of conversion determines the orientation of the driving force in the phase plane. At constant temperature the degree of conversion moves along the isotherm, which, for a first order reaction, is a straight line passing through the point $x = 1; r = 0$. The orientation of the driving force of the degree of conversion is always stable, *i.e.* the driving force tends to shift the degree of conversion toward the curve of the pseudostationary states (Fig. 2). The curve of the pseudostationary states of the temperature determines the orientation of the motion in the vertical direction of the phase plane. The driving force for the changes of the temperature tends toward the stable pseudostationary states. For instable pseudostationary states its orientation is such that the systems moves away from them (Fig. 3).

The stationary states of the reactor are determined by the intersections of the curves of the pseudostationary states. Depending on mutual position and character of the pseudostationary curves one can divide possible stationary states into three categories⁶ (Fig. 4).

The states with unconditional stability are such that the driving force for both the degree of conversion and temperature possess stable orientation of the driving force.

The states with unconditional instability are such that the driving force of the degree of conversion as well as temperature possess both instable orientation.

States with conditional stability possess stable orientation of the driving force of the degree of conversion and instable orientation of the driving force of the temperature changes. Their stability depends on the ratio of thermal capacity of the system to the ability to accumulate the reacting species. The states are stable if the system exhibits large thermal capacity; at low thermal capacity they are on the contrary instable. For the assessment of stability of the system it is necessary in this case to analyse the behaviour of the dynamic model.

The Effect of Selected Parameters on the Character of the Stationary States

The Effect of the Load

The cause of the temperature oscillations during experimental observation of the effect of the load on the behaviour of the industrial reactor was an increase of the load of the system. For this reason we determined the course of the curves of the

pseudostationary states for several loads. For the analysis we used two values of the activation energy: 66 and 109 kJ mol⁻¹ (Figs 5 and 6). The shown results prove that the stationary states possess the same character for all loads – the character of the states with conditional stability. The same character displays also normal non-oscillatory regime in which the reactor is operated. The transition to the oscillatory behaviour thus occurs not due to the qualitative but quantitative change of the operating regime.

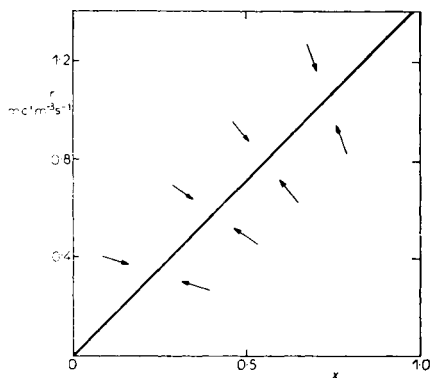


FIG. 2

Trajectories of pseudostationary states of the degree of conversion and orientation of the driving forces for the changes of conversion for $\dot{V}_1 = 1$

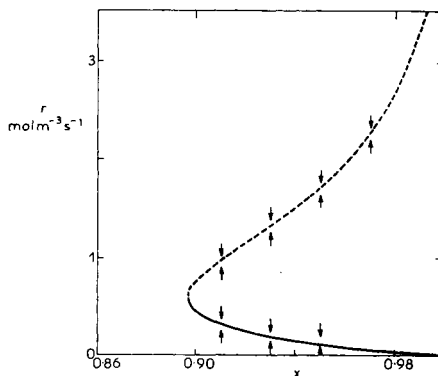
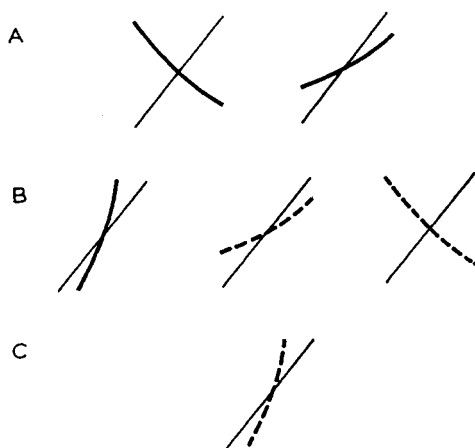


FIG. 3

Trajectories of pseudostationary states of temperature and orientation of the driving forces for the changes of the temperature for $E = 109 \text{ kJ mol}^{-1}$ and $\dot{V}_1 = 1$

FIG. 4

Character of the stationary states; — trajectories of pseudostationary states of conversion, — trajectories of pseudostationary temperature with stable orientation of driving forces, - - - - trajectories of pseudostationary temperature with instable orientation of driving forces; A — states with unconditional stability, B — states with unconditional instability, C — states with conditional stability



The Temperature of the Coolant

In industrial equipment one has to reckon with fluctuations of the inlet parameters. Accordingly, the effect was examined of the inlet temperature of the coolant on the character of the stationary state. The results are depicted in Figs 7 and 8. These figures prove that the changes of the temperature of the coolant cannot affect the character of the operating point.

The Temperature of the Feed Propene

According to the original project propene was preheated to the reaction temperature. Later on a modification was proposed to the effect that propene was fed into the reactor cold. The feed of cold propene facilitates of the reaction heat. As this, however, increases the magnitude of the driving force for cooling, it increases, at the same time, the aptitude of the system to instabilities. Nevertheless, the results of the investigation of the effect of the feed temperature of propene indicate that the absence of preheating of propene had no substantial effect (Fig. 9). It turns out further that current fluctuations of the inlet temperature cannot alter the character of the stationary state.

The Activation Energy

The uncertainty in the determination of the activation energy propted us to examine its effect on the character of the operating point. An example is shown in Fig. 10.

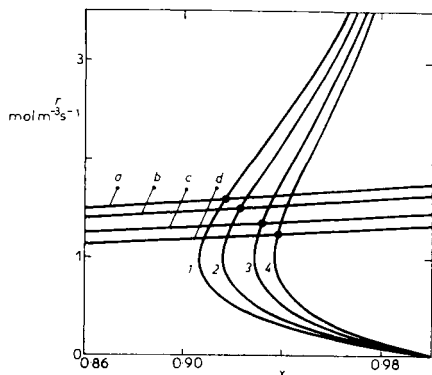


FIG. 5

The effect of the load on the position of the stationary state for $E = 66 \text{ kJ mol}^{-1}$; 1, $a \dot{V}_1 = 1.205$; 2, $b \dot{V}_1 = 1.125$; 3, $c \dot{V}_1 = 1.000$; 4, $d \dot{V}_1 = 0.909$

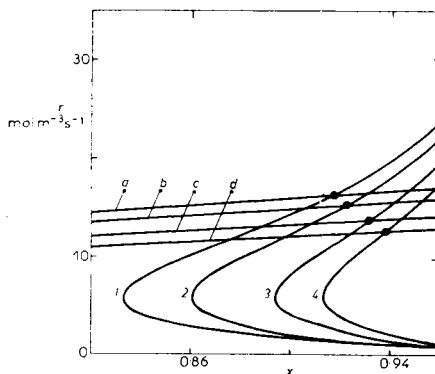


FIG. 6

The effect of the load on the position of the stationary state for $E = 109 \text{ kJ mol}^{-1}$; 1, $a \dot{V}_1 = 1.205$; 2, $b \dot{V}_1 = 1.125$; 3, $c \dot{V}_1 = 1.000$; 4, $d \dot{V}_1 = 0.909$

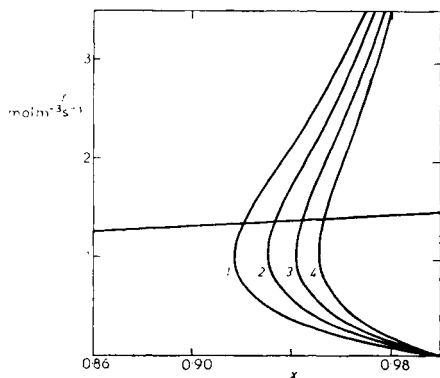


FIG. 7

The effect of the temperature of the coolant T_6 on the position of the stationary state for $E = 66 \text{ kJ mol}^{-1}$ and $\dot{V}_1 = 1$; 1 $T_6 = 380.15 \text{ K}$, 2 $T_6 = 384.15 \text{ K}$, 3 $T_6 = 388.15 \text{ K}$, 4 $T_6 = 392.15 \text{ K}$

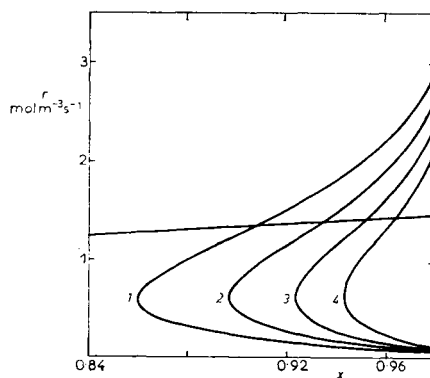


FIG. 8

The effect of the temperature of the coolant T_6 on the position of the stationary state for $E = 109 \text{ kJ mol}^{-1}$ and $\dot{V}_1 = 1$; 1 $T_6 = 380.15 \text{ K}$, 2 $T_6 = 384.15 \text{ K}$, 3 $T_6 = 388.15 \text{ K}$, 4 $T_6 = 392.15 \text{ K}$

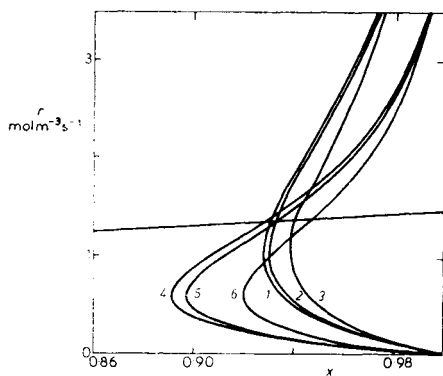


FIG. 9

The effect of the feed temperature of propylene on the position of the stationary state for $\dot{V}_1 = 1$; $T_1 = 273.15 \text{ K}$: 1 $E = 66 \text{ kJ mol}^{-1}$, 2 $E = 66 \text{ kJ mol}^{-1}$, 3 $E = 66 \text{ kJ mol}^{-1}$, 4 $E = 109 \text{ kJ mol}^{-1}$, $T_1 = 293.15 \text{ K}$: 5 $E = 109 \text{ kJ mol}^{-1}$, $T_1 = 384.15 \text{ K}$: 6 $E = 109 \text{ kJ mol}^{-1}$

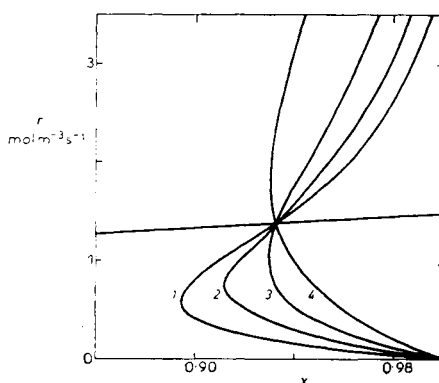


FIG. 10

The effect of the activation energy E on the shape of the trajectories of pseudostationary temperature for $\dot{V}_1 = 1$; 1 $E = 109 \text{ kJ mol}^{-1}$, 2 $E = 88 \text{ kJ mol}^{-1}$, 3 $E = 66 \text{ kJ mol}^{-1}$, 4 $E = 40 \text{ kJ mol}^{-1}$

It is seen that the character of the operating point would not change unless an unrealistic low value of 40 kJ mol^{-1} is used. Only then would the state become unconditionally stable.

The Stability Analysis

For the assessment of stability of the states with conditional stability one has to resort to methods of dynamic analysis. For such analysis we used simulation utilizing a mathematical model. The set of Equations (3) and (9) was solved numerically with the initial condition close to the stationary state. It was found that the oscillatory behaviour at increased loads can be proven only at high value of the activation energy of 109 kJ mol^{-1} . This value originated from an older work and was not confirmed by experimental research².

CONCLUSIONS

From the results of our analysis it follows that the oscillatory behaviour of the reactor cannot be accounted for by the change of the character of the stationary state. Since we are dealing with a quantitative problem it is well possible that even minor details in the flow regime within the reactor may exercise a significant effect on the stability of the operating regime. The model of a perfectly stirred reactor appears too rough for a precise description and predicts oscillatory behaviour only for unrealistically high value of the activation energy. For this reason further research shall be devoted to more detailed descriptions of the flow of the reaction mixture in the reactor.

REFERENCES

1. Kolena J.: Chem. Prům. 34, 213 (1984).
2. Kolena J.: Chem. Prům. 34, 527 (1984).
3. Kolena J.: Chem. Prům. 35, 76 (1985).
4. Kolena J., Šafář J., Trška P., Hájek M.: Chem. Prům. 35, 195 (1985).
5. Kolena J.: Chem. Prům. 35, 300 (1985).
6. Horák J., Jiráček F.: *A Study of the Dynamic Behaviour of Catalytic Flow Reactors*. Proceedings of the Fifth European Second International Symposium on Chemical Reaction Engineering, Amsterdam 1972.

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