

## Safety assessment for polyetherol production using reaction kinetic data

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### Abstract

The exact knowledge of the thermodynamic and the kinetic properties of a chemical reaction allows the prediction of the safe and dangerous states of this reaction under technical conditions.

Reaction calorimetric measurements of the polymerisation reaction of propylene oxide on polyfunctional alcohols showed that this reaction can be described by a modified first-order kinetic equation and that it releases a reaction energy of  $1358 \pm 99$  kJ per kg propylene oxide.

With fixed thermodynamic and kinetic data, technical and operational failures were simulated. This led to a concept for the safe handling of the polymerisation. The concept establishes a limit curve in temperature and pressure. During the dosing of the propylene oxide, the measured temperature and pressure values have to be below this limit, otherwise the design pressure of the production reactor will be exceeded resulting in an adiabatic runaway reaction.

### 1. INTRODUCTION

Polyetherols are produced by acidic- or alkaline-catalysed polymerisation of alkene oxides on polyfunctional alcohols. The reaction under investigation is an alkaline-catalysed semi-batch polymerisation of propylene oxide (PO). After inertisation of the reactor with nitrogen, the alcohol and the catalyst are added and heated up to reaction temperature. During the subsequent dosing of the PO there is normally a small amount of unreacted PO inside the reactor. Different failures in the operation conditions, e.g. a lowered temperature or a higher feeding rate, can lead to undesired high concentrations of unreacted PO. If loss of cooling occurs, a nearly adiabatic runaway reaction will take place with perhaps a dramatic rise in temperature and pressure.

With the help of some simulations of possible operation and failure conditions, the amount of accumulated PO can be quantified and the

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characteristics of the runaway reactions can be calculated. The simulations were performed with a computer code called REAKTOR, which is similar to the commercially available code SAFIRE [1].

## 2. THE REAKTOR SIMULATION PROGRAM

The code REAKTOR calculates pressure, temperature and concentrations as a function of time by integrating the coupled balances for mass, energy and species for a multi-component system. Furthermore, in the case of reactor venting, the mass and enthalpy flow are calculated for different hypotheses concerning the foaming up of the contents of the reactor. Figure 1 gives the simulation program of REAKTOR.

In addition to the data specific to the reactor, e.g. reactor volume, batch-size, heat transfer coefficient and vent area, thermodynamic data for each educt have to be specified. A satisfactory description of the solubility of PO in the polyetherol was obtained with the model of Flory and Huggins [2]. To describe the time behaviour of the reaction, suitable kinetic data for different operating conditions, e.g. various PO concentrations or temperatures, are needed. These were obtained from isothermal measurements in a reaction calorimeter.

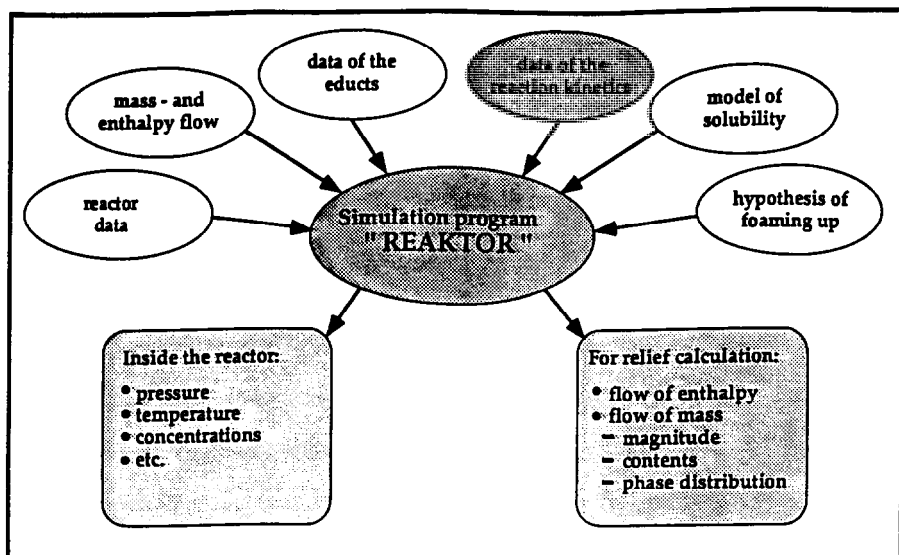


Fig. 1. REAKTOR simulation program.

## 3. MEASURING KINETIC DATA BY REACTION CALORIMETRY

### 3.1. *Experimental set-up*

In a 50-bar pressure reactor of a Mettler RC-1 reaction calorimeter, 14 experiments in a temperature region between 80 and 160°C were carried

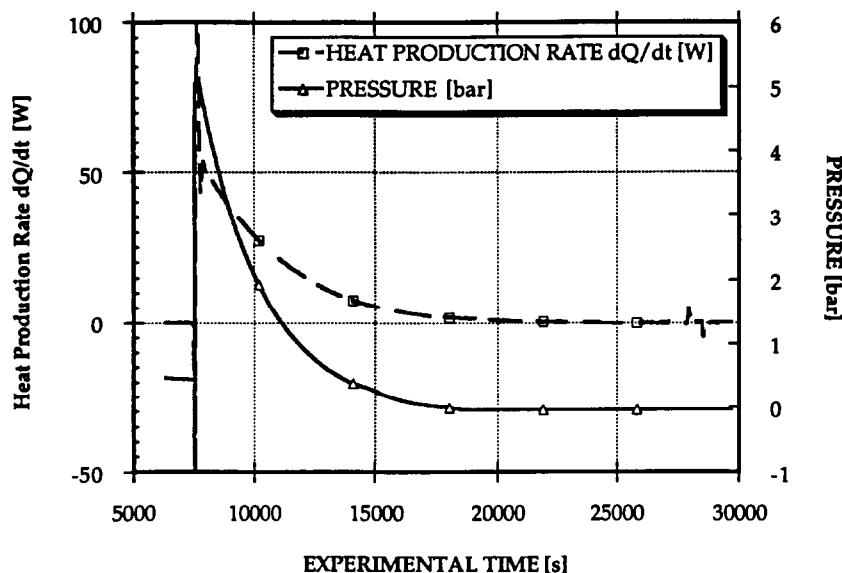


Fig. 2. Results from a typical experiment.

out, in which 800 g of polyetherol with a concentration of about 0.15% alkali hydroxide as catalyst, were added to the reactor and heated up to the reaction temperature. Using nitrogen pressure, 160 g of PO were fed into the reactor as quickly as possible. Figure 2 shows the result of a typical experiment. A short time after adding the PO, the pressure and the heat production reach their maximum and then decrease during the rest of the experiment.

### 3.2. Calculation of the reaction energy

Data for the reaction energy are processed by the evaluation software of the RC1 system. This software takes into account the fact that the PO was stored at ambient temperature and heated inside the reactor to reaction temperature. Because the temperature dependence of the heat capacity of the PO is neglected by the RC1 software, the reaction energy data has to be corrected. The correction was performed with a linear fit for the temperature dependence of the heat capacity:  $c_p = (1944 + 11.64T)$   $\text{J kg}^{-1} \text{K}^{-1}$  ( $T$  in  $^{\circ}\text{C}$ ).

From the 14 experiments, a mean reaction energy results:  $\Delta U_r = 1359 \pm 99$  kJ per kg propylene oxide. This is in good agreement with data from other measurements by BASF and estimations according to Benson [3]. No temperature dependence could be found for the reaction energy; this confirms the assumption that conversion was complete and that the reaction did not run into an equilibrium.

### 3.3. Calculation of kinetic data

The reaction scheme for the chain-propagation reaction of propylene oxide is presented schematically in Fig. 3. As well as the chain-propagation reaction, chain-transfer reactions have to be taken into account. The transfer reaction involves hydrogen abstraction from the  $-\text{CH}_3$  group followed by very rapid ring cleavage to form an allyl ether anion [4]. The allyl ether anion can start a new polymerisation chain leading to high molecular-weight products. The vapour pressure of the allyl ether is neglected in the subsequent considerations; with respect to a safety technical assessment, only the consumption of the monomer is considered:

$$-\frac{d[\text{PO}]}{dt} = (k_p + k_{tr})[\text{PO}][\text{XOH}]$$

Because every hydroxyl group reacting with PO produces a new hydroxyl group, the concentration of  $-\text{OH}$  is constant provided volumetric effects are neglected. The catalyst concentration was not changed for the experiments. therefore, the term that reflects this concentration remained constant and was multiplied by the reaction rate constant, resulting in a modified constant:

$$k = (k_p + k_{tr})[\text{XOH}]$$

Thus, the reaction rate depends only on the PO concentration.

Assuming that the kinetic model is first-order in the PO concentration, the heat production is given by

$$\ln(dQ/dt) = \ln(\Delta U_R M V_R [\text{PO}]_0 k) - kt$$

where  $M$  is molecular weight and  $V_R$  is reaction volume. Hence, a logarithmic plot of the heat production rate over time should result in a straight line. This is confirmed in Fig. 4.

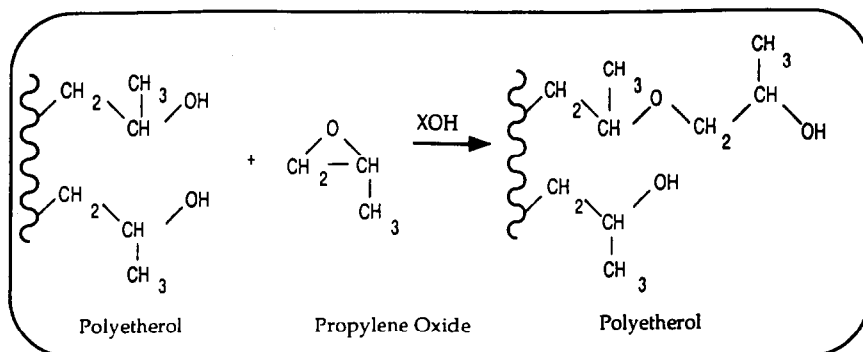


Fig. 3. Alkaline-catalysed propylene oxide polymerisation.

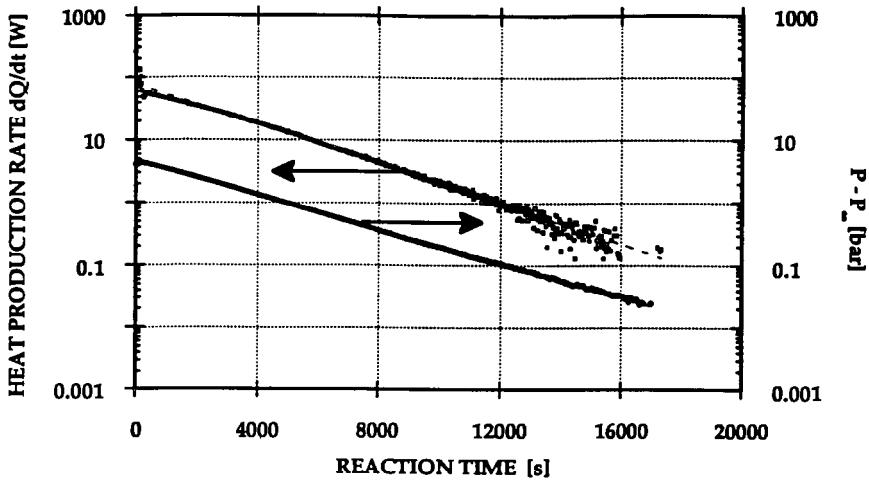


Fig. 4. Pressure and heat production over time for a typical experimental run at 120°C.

For every experiment, the reaction rate constant  $k$  is given by the slope of the linear fit or can be determined from the ordinate intersection of the logarithmic plots of heat production over time. The constant  $k$  is also given by the slope of a logarithmic plot of the propylene oxide partial pressure over time (see Fig. 4). As the polyetherol partial pressure can be neglected, the PO partial pressure is given by the difference between the total pressure  $p$  and the nitrogen pressure  $p_x$  which remains after total conversion. The determined reaction rate constants are presented in the Arrhenius plot of Fig. 5.

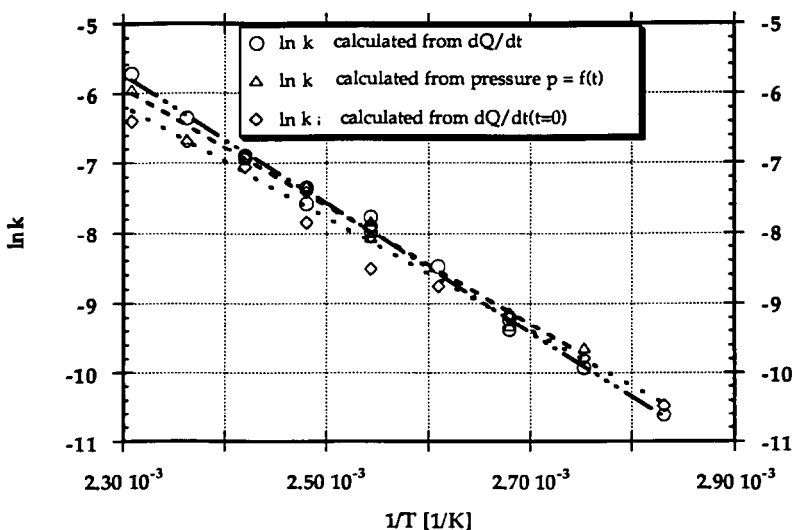


Fig. 5. Arrhenius plot for the polymerisation of propylene oxide.

Because the data obtained from the heat production over time are based on the largest number of measurements, they have the greatest confidence. Therefore, the Arrhenius parameters from these data are used subsequently. Nevertheless, within the limits of the calorimetric method, all three estimations yield the same results.

Because the temperature interval covered by the experiment is rather narrow (80°C), small deviations in the single points of the Arrhenius plot may result in quite large differences in the Arrhenius parameters, especially in the pre-exponential factor. Therefore care has to be taken, if the data are extrapolated to higher temperatures, for example if a runaway reaction is to be described.

#### 4. ADIABATIC RUNAWAY REACTION

In order to test the suitability of the data estimated above for the simulation of a runaway reaction, an adiabatic calorimetric test was performed in a set-up that is a modification of the VSP calorimeter described in refs. 5 and 6, see Fig. 6. A 65-ml glass bulb or a 115-ml stainless steel can (with magnetic stirrer) was placed in an electrically heated 740-ml

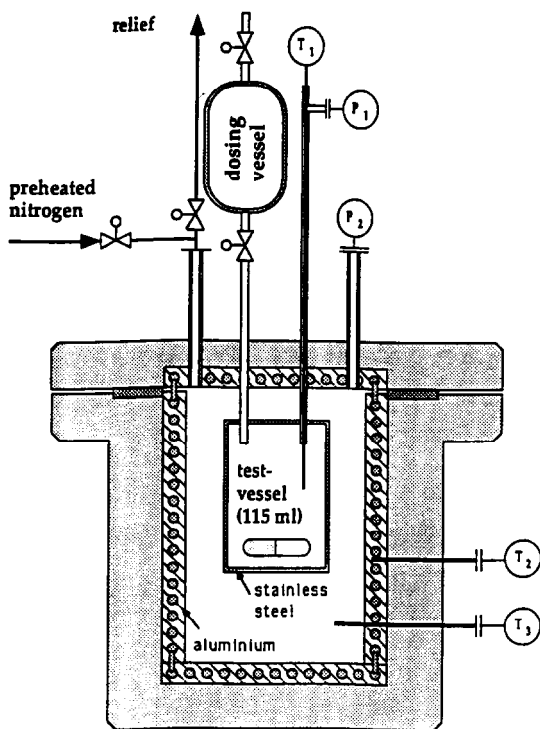


Fig. 6. Device for adiabatic runaway test.

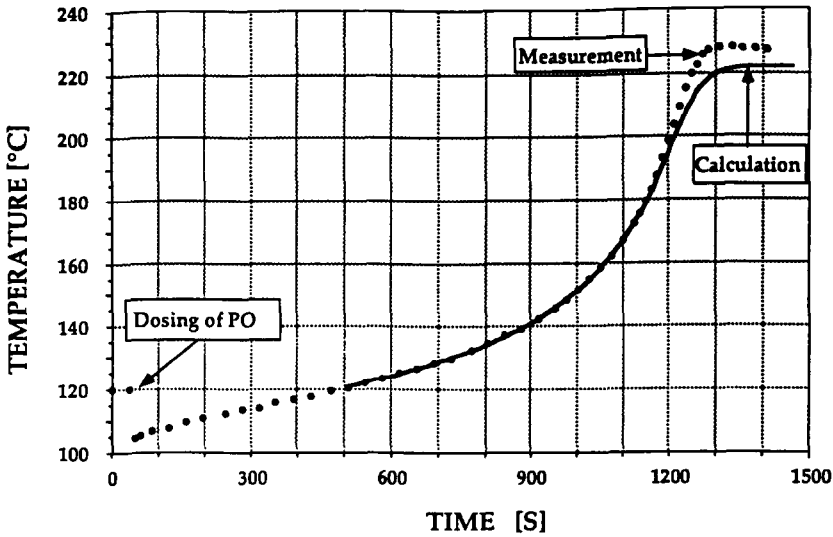


Fig. 7. Comparison of measured and predicted temperature curves for an adiabatic runaway experiment with a starting concentration of 20% PO.

autoclave. The educts were fed through different lines by air or nitrogen pressure. The wall heater of the autoclave was controlled by the bulk temperature of the reactor in order to assure nearly adiabatic conditions. Bursting of the thin-wall reactor during the course of vapour or gas production is avoided by pressurising the autoclave with preheated nitrogen to the pressure level inside the reactor.

Figure 7 shows the measured temperature curve for an experiment with a starting concentration of 20% PO. The polyetherol and the catalyst were heated up to 120°C and cold PO was added as quickly as possible. A mixing temperature of 105°C resulted. After an adiabatic induction time of about 1300 s, a maximum temperature of nearly 230°C was reached.

This experiment was simulated with the *REAKTOR* program on the basis of the above-estimated kinetic data. A comparison of the predicted and the measured temperature curve (see Fig. 7) shows an excellent agreement up to about 210°C. The predicted adiabatic maximum temperature is slightly lower than the measured one. This may be explained by a small error in the temperature dependence of the heat capacity of the polyetherol at higher temperatures, for example.

Calculating the adiabatic induction time (with the very conservative assumption of a reaction of zeroth-order and ideal adiabatic behaviour):

$$\tau = \frac{c_p RT_0^2}{\Delta U A_0 E_a} \exp\left(\frac{E_a}{RT_0}\right)$$

where  $A_0$  is the Arrhenius pre-exponential factor,  $E_a$  the activation energy

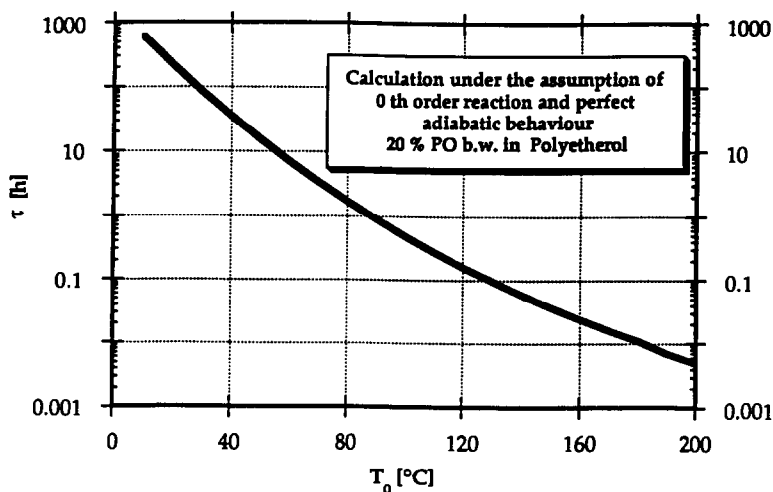


Fig. 8. Adiabatic induction time as a function of the start temperature.

and  $T_0$  the start temperature in kelvin, yields, for a start temperature of 105°C, an induction time of about 1300 s (see Fig. 8). This is in accordance with the above-mentioned measured value.

## 5. SIMULATION OF TWO TYPICAL OPERATIONAL FAILURES

With fixed thermodynamic and kinetic data, technical and operational failures can be simulated in order to determine the amount of unreacted PO which can be allowed to accumulate without being the cause of a potential hazard. These simulations were made with the REAKTOR code. For the first example, a failure in the reaction temperature is examined. Figure 9 shows the mass fraction of accumulated PO for two isothermal conditions. In the case of the normal reaction temperature of 120°C, only 7% PO will accumulate in the reactor. Under isothermal conditions the consumption of this PO at the end of the feeding period will take nearly 2 h. As a typical consequence of a failure in the temperature measurement or a wrongly set temperature, the reactor temperature could be lowered, for example, to 100°C. Then the mass fraction would rise to 20% and the post-reaction period would increase to more than 5 h.

If the loss of cooling takes place the reactor content will react nearly adiabatically from the starting conditions of 120°C, 7% PO or 100°C, 20% PO. For these two cases, the calculated pressure curves are presented in Fig. 10. The total pressure consists of the partial pressures of the PO and the nitrogen (there is a nitrogen contribution of about 0.6 bar from the inertisation of the reactor).

During the adiabatic reaction, the temperature and the vapour pressure



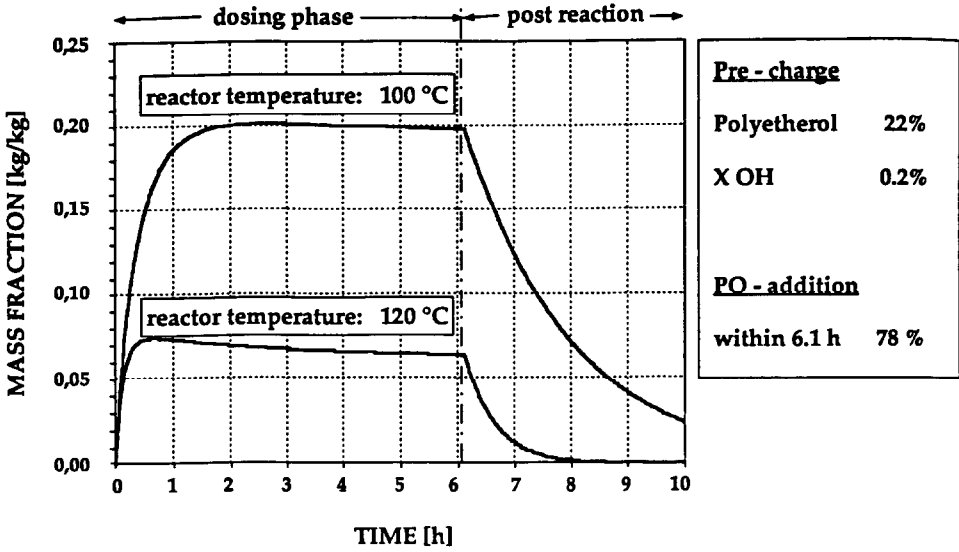


Fig. 9. Accumulation of PO during the dosing phase for two isothermal conditions.

of the PO increase while the mole fraction decreases. For the runaway-reaction starting during normal operation mode, i.e. at 120°C, the total pressure decreases monotonously due to the consumption of the PO. For the reaction starting at 100°C, the total pressure rises up to a maximum of 5.7 bar<sub>abs</sub>. Then the pressure decreases until the nitrogen pressure is reached.

If in addition to the lowered temperature (100°C), the PO is charged into the reactor with a false feeding rate, a higher amount of PO may

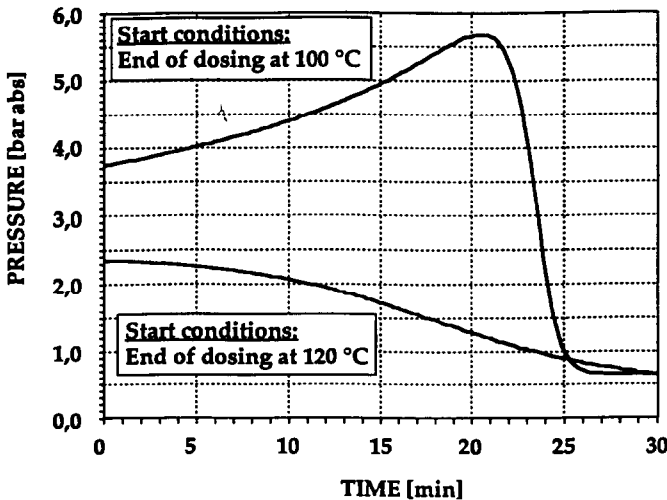


Fig. 10. Pressure evolution during two adiabatic runaway reactions.

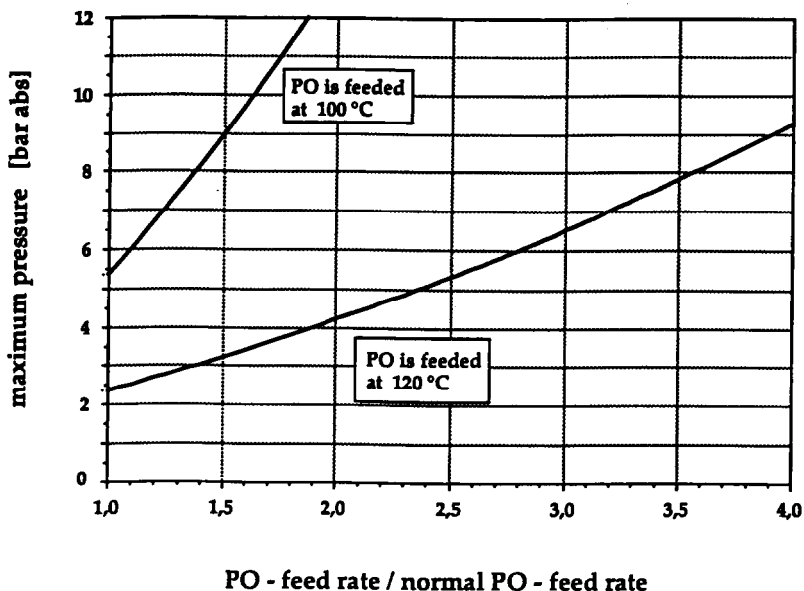


Fig. 11. Maximum pressure for different feeding rates.

accumulate, e.g. 26% PO for a feeding rate multiplied by 1.5, or 33% PO for a doubled feeding rate. The maxima of the pressure curves for the runaway reactions starting at 100 and 120°C are shown in Fig. 11.

## 6. PRESSURE AND TEMPERATURE LIMITS FOR SAFE OPERATION

From the above considerations the question arises, which PO concentrations can be allowed during the PO dosing if the pressure is not to exceed a certain value, e.g. the design pressure of the reactor or the set pressure of a safety valve. From runaway simulations with various start temperatures and PO concentrations, a limit between allowable concentrations and concentrations that must be avoided can be found. Neglecting the partial pressure of the nitrogen, every temperature–concentration data set is represented by a temperature–pressure pair, and a limit in the pressure–temperature plane can be formulated. For a maximum allowable pressure of 10 bar<sub>abs</sub>, this limit is presented in Fig. 12. The limiting curve corresponds to the pressure–temperature curve of the runaway reaction that starts, for example, at 80°C and reaches just 10 bar<sub>abs</sub>.

If, during the dosing of the PO, the measured pressure–temperature pairs approach the limit of the “safe region”, automatic safety functions must stop the PO feed immediately in case the allowable pressure limits of the reactor are exceeded or else the reactor must be vented if loss of cooling occurs.

It should be mentioned that simulations to determine the “safe region”

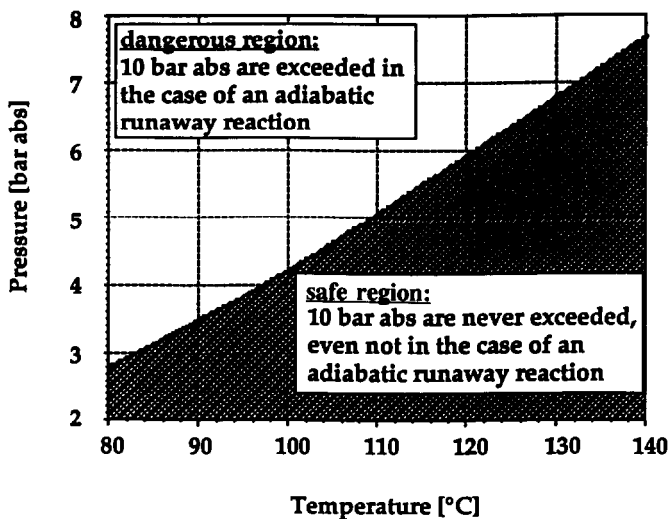


Fig. 12. “Safe region” and “dangerous region” for an allowable maximum pressure of 10 bar<sub>abs</sub>.

are possible even if no kinetic data are available; instead of over time, the calculations can be performed over consumption. In addition, the kinetic-based simulations give informations about the time behaviour of the runaway reactions. Starting from the limiting curve of Fig. 12, the maximum pressure of 10 bar<sub>abs</sub> is reached within 2 min for a start temperature of 140°C, whereas it takes nearly 15 min for a start temperature of 100°C.

#### REFERENCES

- 1 Fauske and Associates, Inc., SAFIRE Computer Program and Documentation, System Analysis for Integrated Relief Evaluation (SAFIRE) User's Manual, AIChE/DIERS, 1986.
- 2 P.J. Flory, Principles of Polymerisation Chemistry, Cornell University Press, Ithaca, New York, 1953.
- 3 S.W. Benson, Thermochemical Kinetics, Wiley, New York, 2nd edn., 1976.
- 4 G. Odian, Principles of Polymerisation, Wiley, New York, 2nd edn., 1981.
- 5 H.K. Fauske and J.C. Leung, New experimental technique for characterizing runaway chemical reactions, CEP, 81 (1985) 39–46.
- 6 J.C. Leung, H.K. Fauske and H.G. Fischer, Thermal runaway reactions in a low thermal inertia apparatus, Thermochim. Acta, 104 (1986) 13–29.