

The theoretical and experimental investigation of a catalyst-controlled semi-continuous process. An alternative approach

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Abstract

In catalyst-controlled reactions, an alternative reaction procedure is possible, namely adding the catalyst to the educt solution. This is demonstrated by investigating the reaction of phenol with formaldehyde, catalysed by sodium hydroxide. The reaction enthalpy was found to be -35 kJ mol^{-1} and the activation energy was 80 kJ mol^{-1} , in good agreement with the literature values. The reaction procedure of adding the catalyst can be described by a simple set of differential equations, and was simulated with a computer to investigate the influence of different parameters on the course of the reaction. The relation between runaway conditions for the primary reaction and the secondary reaction is discussed.

LIST OF SYMBOLS

B	thermal reaction characteristic parameter
$c_p / \text{J g}^{-1} \text{K}^{-1}$	specific heat
D_a	Damköhler number
$E_a / \text{kJ mol}^{-1}$	activation energy
F / m^2	heat exchange surface area
Fo	formaldehyde
$H_r / \text{kJ mol}^{-1}$	heat of reaction
$k_2 / \text{l mol}^{-1} \text{s}^{-1}$	second-order rate constant
$k_w / \text{W m}^{-2} \text{K}^{-1}$	heat transfer coefficient
K_0	pre-exponential factor
M_r / g	reaction mass
Ph	phenol
Q_r / W	heat production rate
R	ideal gas constant
St	Stanton number
t	time

t_{add}	time of addition
T/K	temperature
$\Delta T_{\text{adia}}/\text{K}$	adiabatic temperature increase
T_0/K	initial temperature
T_k/K	cooling temperature
V_r	reaction volume
x	normalized concentration

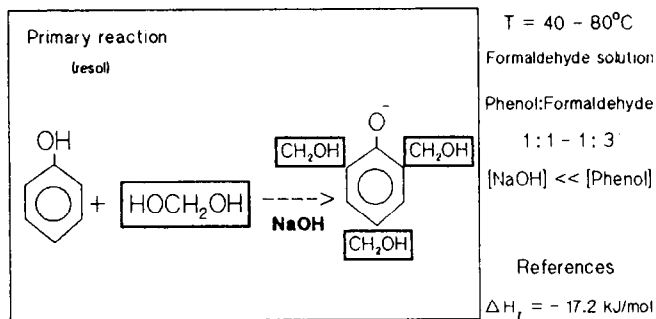
Greek letters

Φ	normalized temperature = $(T - T_0)/\Delta T_{\text{adia}}$
Θ	normalized time = t/t_{add}
μ	normalized cooling efficiency = $(T_0 - T_k)/\Delta T_{\text{adia}}$
$\phi/\text{kg l}^{-1}$	density

1. INTRODUCTION

A semi-continuous process has a distinct advantage over an ordinary batch process: the accumulation of unreacted educts can be easily controlled by the rate of addition. In case of a cooling failure, the adiabatic temperature increase due to the accumulation of unreacted material can be kept low so as to avoid temperatures at which secondary decomposition reactions can be initiated. If the reaction rate is proportional to the concentration of a catalyst, the reaction can be performed in an alternative way: instead of adding an educt, the catalyst can be added to the reaction mixture. From the perspective of the process design, the only major difference is that the added volume is much smaller than that of the starting material. Therefore the convective heat term of the added catalyst has no influence on the heat balance and the heat exchange area does not vary significantly during the phase of addition. From the safety perspective there is of course a marked difference with respect to an ordinary semi-continuous process: at any stage during the time of addition the reaction will continue to equilibrium even when the addition has been stopped. Nevertheless, this reaction procedure can have some advantages over a simple batch process and, hence, this alternative reaction process has been investigated and reported here.

As a model reaction we have investigated the well-studied resol formation of formaldehyde with phenol, catalysed by sodium hydroxide (Fig. 1). Although a number of fundamental papers [1–5] have been



Kinetik : Freeman (1953) / Zavitsas (1968) / Jones (1946)

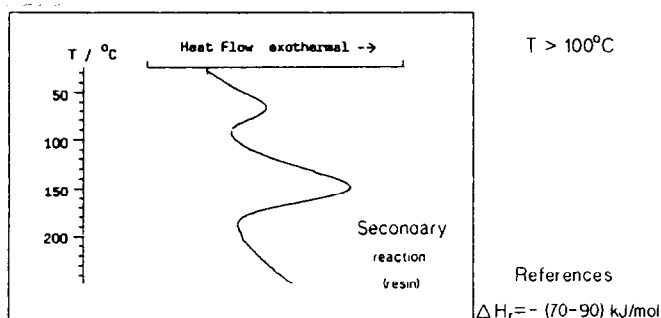
Fig. 1. The formation of resol by the reaction of phenol and formaldehyde, catalysed by sodium hydroxide.

published about this reaction system, there is little information about the reaction enthalpy of the formation of the resol, which is $-17.2 \text{ kJ mol}^{-1}$ [3].

Although the kinetics is complicated due to different equilibria which affect the active formaldehyde monohydrate concentration, it is convenient to assume a simple pseudo-first-order rate law to describe the course of the reaction

$$\frac{d[\text{HCHO}]}{dt} = -k_2[\text{HCHO}][\text{C}_6\text{H}_5\text{O}^-]$$

with $[\text{C}_6\text{H}_5\text{O}^-] = [\text{NaOH}]$. The unwanted secondary reaction to be avoided is the formation of resins. Figure 2 shows a DSC trace (Mettler TA3000, 3 K min^{-1}) of a phenol/formaldehyde mixture. The first peak starting at 30°C is due to the formation of resol while the second peak starting at around 100°C is caused by the unwanted resin formation. The heats of



Addition Condensation
DSC: -34 kJ/mol -92 kJ/mol Formaldehyde

Fig. 2. DSC curve of a phenol/formaldehyde mixture.

reaction were found to be -34 kJ mol^{-1} (resol) and -98 kJ mol^{-1} (resin). The first value is a factor of 2 larger than the literature value [3]. The overlap of the two peaks clearly demonstrates the hazardous potential of this reaction system.

2. EXPERIMENTAL

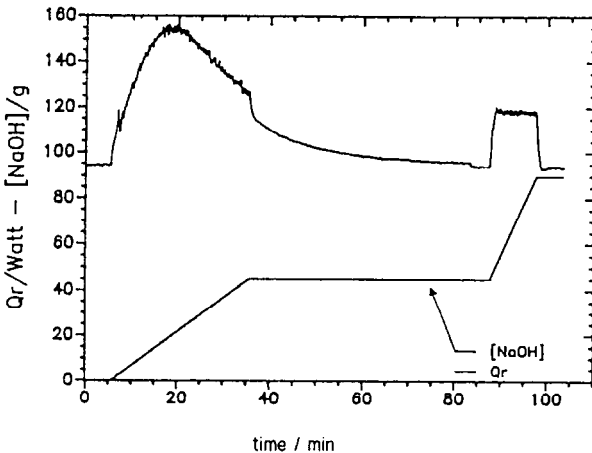
A RC1 (Mettler) heat flow reaction calorimeter was used for studying the thermokinetics of the resol formation. Experiments were carried out in the temperature range $60\text{--}80^\circ\text{C}$ under nearly isothermal conditions. All the experiments employed formaldehyde in an aqueous solution (37%), the catalyst in a 33% aqueous solution and pure phenol. In all cases, the catalyst was added to the reaction mixture at a constant rate. Figure 3 shows an experimental profile. After the start of the addition, the heat production rate increases linearly confirming the assumption that the rate is first-order with respect to the catalyst concentration. With increasing reaction time, the accelerating effect is compensated for by the decreasing formaldehyde

Phenol : Formaldehyde : NaOH = 1 : 0.25 : 0.04 (mol)

T = 60°C

Starting material : 1058 g - addition : 45 g NaOH (32%)

Time of addition : 30 min



Reaction : Addition Neutralisation

Enthalpy : -35 kJ/mol Formaldehyde -41 kJ/mol NaOH

$\Delta H_r = -88 \text{ J/gK}$ / $c_p = 2.45 \text{ J/gK}$ $\rightarrow \Delta T_{ad} = 36 \text{ K}$

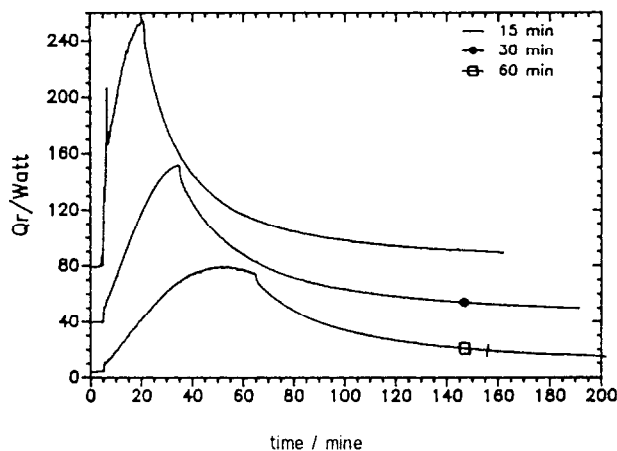
Fig. 3. The rate of heat production plotted against time for the reaction of phenol and formaldehyde, catalysed by sodium hydroxide added at a constant rate.

Parameter : Time of addition (15/30/60) min

Phenol : Formaldehyde : NaOH = 1 : 1 : 0.04 (mol)

Temperature : 60°C

Starting material : 1742 g - addition : 45 g NaOH (32%)



$k(60^\circ\text{C})$: $0.97 \cdot 10^{-3} \text{ l/mol s}$

Zavitsas (1968) : $1.0 \cdot 10^{-3} \text{ l/mol s}$

---> Heat production rate

Fig. 4. The rate of heat production plotted against time for different rates of catalyst addition.

concentration. This leads to a maximum in the heat production rate and the subsequent decay. Both at the beginning and end of the addition, there is a sharp increase and then a decrease in the heat production rate; this is due to the rapid formation of the active phenate ion ($\text{C}_6\text{H}_5\text{O}^-$). The heat of neutralization was determined only at the end of the reaction. The reaction enthalpy was determined to be -35 kJ per mol formaldehyde, while the heat of neutralization was -41 kJ per mol sodium hydroxide. Experiments at different temperatures enable one to determine an overall activation energy. With increasing temperature, the maximum of the heat production rate is increased and is shifted towards the beginning of the addition. The same effect is caused by increasing the rate of addition (Fig. 4). By increasing the rate by a factor of 4, the maximum value of the heat production rate is increased by a factor of 2.4. The value of 84 kJ mol^{-1} for the activation energy is in good agreement with literature values [1, 6].

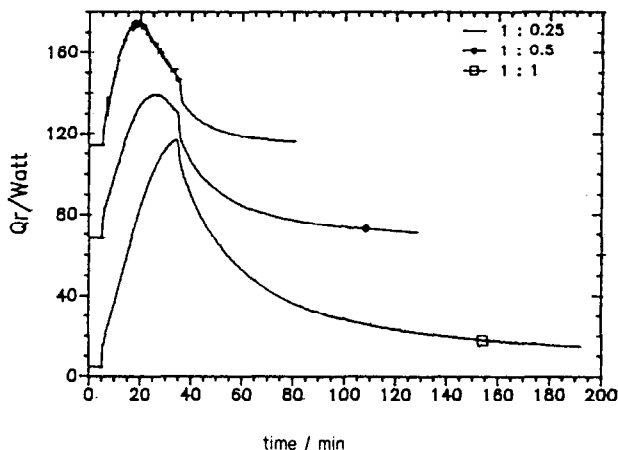
According to Zavitsas and co-workers [1, 2], the rate constant is strongly influenced by the solvent medium. Although the phenol seems to be active only through the low amount of the phenate ion [$\text{C}_6\text{H}_5\text{O}^-$] which is

Parameter : Phenol/Formaldehyde = 1 : (0.25/0.5/1) mol

Temperature : 60°C

Starting material : Phenol/Formaldehyde – addition : NaOH (33%)

Time of addition : 30 min



Phenol:Formaldehyde : (mol:mol)	1 : 0.25	1 : 0.5	1 : 1
k_3 (60°C) : [10 ⁻³ l/mol*s]	6.9	2.1	0.97

Fig. 5. The rate of heat production plotted against time for different ratios of phenol formaldehyde.

determined by the catalyst concentration, the ratio $[\text{HCHO}]:[\text{C}_6\text{H}_5\text{OH}]$ has a considerable effect on the rate constants. This is demonstrated in Fig. 5 which presents the heat production rate profile for different ratios of formaldehyde/phenol. With increasing dilution of the formaldehyde the reaction is accelerated, which can be observed by the maximum of the heat production rate being shifted towards the beginning of the reaction. The rate constant k_3 at $T = 60^\circ\text{C}$ as a function of the ratio $[\text{HCHO}]:[\text{C}_6\text{H}_5\text{OH}]$ was 0.97, 2.1 and 6.9 ($\text{l mol}^{-1} \text{s}^{-1}$) $\times 10^{-3}$ for phenol:formaldehyde ratios of, respectively, 1:1, 1:0.5 and 1:0.25 (mol:mol).

3. MODELLING

The rate of reaction as a function of temperature in conjunction with the reaction enthalpy gives the heat production rate, which is the most important parameter for controlling a chemical reaction. The use of a model offers the opportunity to investigate the influence of several parameters, such as, for instances, the cooling capacity, the rate of addition

and the starting temperature, on the course of the reaction. To characterize the thermodynamic and kinetic potential of a reaction it is convenient [7, 8] to use dimensionless parameters, such: the Damköhler number, $Da = k_2[\text{NaOH}]t_{\text{add}}$; the Stanton number, $St = k_w Ft_{\text{ad}} V_r^{-1} \phi^{-1} c_p^{-1}$; and the thermal reaction parameter, $B = E_A \Delta T_{\text{adia}} R^{-1} T_0^{-2}$.

The following assumptions were made to simplify the calculation as far as possible, without major restrictions to the application: $T_0 = T_k$; $V_r = \text{constant}$; and $\Delta H(\text{neutralization}) = \Delta H(\text{convective}) = 0$.

The first assumption is really a strong limitation to the procedure for the sake of simplicity. The next two are certainly true for a lot of reactions considering the small amount of catalyst usually involved in chemical reactions. The following differential equations describe the course of the concentration and temperature:

$$\frac{dx}{d\theta} = -Da(\theta x)$$

$$\frac{d\phi}{d\theta} = Da(\theta x) - St(\phi)$$

where $\Theta (< 1)$, x and Φ are the normalized time, concentration and temperature, which refers to the adiabatic temperature increase.

Figure 6 shows the satisfactory agreement between the calculated heat production profiles and the experimental values.

Further calculations were made to study the course of temperature as the most important parameter as a function of the cooling capacity (Stanton)

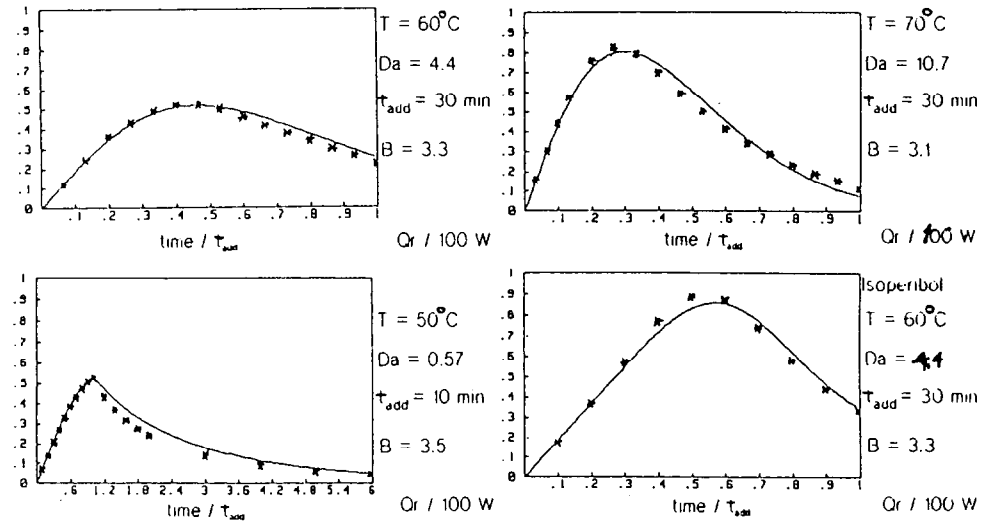
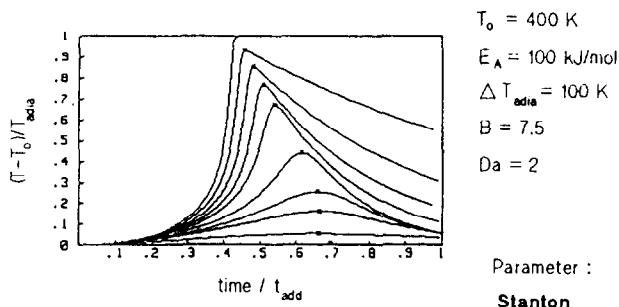


Fig. 6. Experimental heat production profiles (*) and profiles calculated with the model (—), with different values of the parameters.



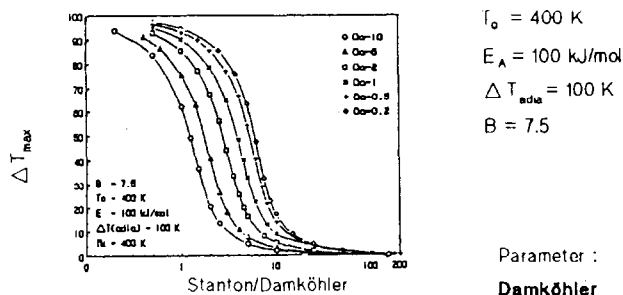
Temperature increase = $f(\text{time})$

$$B = E_A \Delta T_{\text{adia}} / R T^2$$

Fig. 7. The temperature profiles with time, with constant Damköhler number.

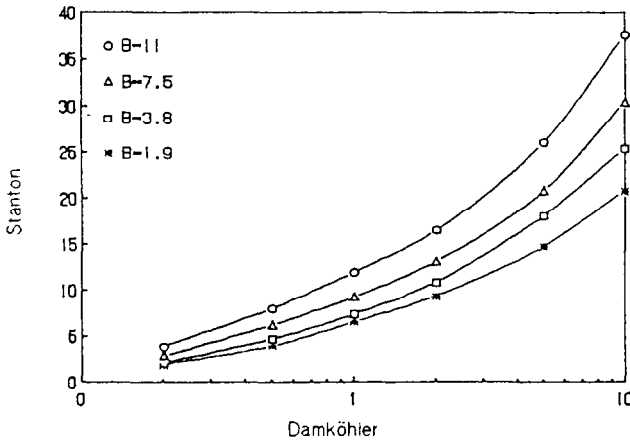
and the kinetic parameters (Damköhler). Figure 7 shows the temperature profile (normalized to the adiabatic temperature increase) versus the time (normalized to the time of addition). With fixed values for the Damköhler number, the parameter is the cooling capacity. With decreasing cooling capacity, the course of the reaction changes from a nearly isothermal profile to an adiabatic one: neither extremum is of interest. The last one is due to a high temperature increase, while the first is accompanied by only a low conversion over the time of addition which is equivalent to an ordinary batch process. The medium range is more interesting, with only moderate temperature increase and a sufficient conversion during the phase of addition.

The maximum temperature as a function of the cooling capacity for different Damköhler numbers is presented in Fig. 8. The highest sensitivity of these curves is around 40% of the adiabatic temperature increase. To define a borderline between a safe and hazardous course of reaction, a



Maximum temperature increase = $f(\text{Stanton})$

Fig. 8. The maximum temperature plotted as a function of the coding capacity, for different Damköhler numbers.



$$St = f(Da)$$

Criteria :

$$\Delta T(\max) = 0.1 \Delta T_{\text{adia}}$$

Example : cooling capacity = 1 / 20 min
 time of addition = 3 h
Stantonzahl = 9

B	Da	Conv./%
11	0.61	44
7.5	0.93	55
3.8	1.45	62
1.9	1.84	66

Fig. 9. Plots of Stanton versus Damköhler numbers for different values of the characteristic thermal reaction parameter *B*.

maximum temperature increase of 10% was chosen. In Fig. 9, the Stanton and Damköhler numbers which lead to a 10% temperature increase are plotted for different values of the characteristic value *B*. From these curves, it can clearly be seen that this reaction procedure can only be realized with relatively slow reactions ($Da < 2-5$). Performing faster reactions, one needs high Stanton numbers to control the reaction which can only be achieved by an extensive time of addition.

The knowledge of the thermokinetic parameters enables one to design the process in a way that can be safely handled under normal conditions. In addition, it is important to know the course of the reaction in case of deviations, for instance loss of the cooling medium. In Fig. 10, this scenario is calculated for a given set of parameters. The upper curves show the temperature profiles for the normal and the adiabatic case. The lower curves were calculated under the following assumptions: at different times the cooling capacity was drastically reduced and (as a consequence) the addition of the catalyst was stopped at once. So there is a sharp transition from a controlled course of reaction to a runaway reaction characterized by the adiabatic induction time. With increasing time ($t < 0.2$) of detecting the cooling failure, the adiabatic induction time is significantly reduced, while the final temperature is nearly equal to the maximum adiabatic temperature increase due to the low conversion at the beginning of the reaction. At later times ($t < 0.5$), the adiabatic temperature increase is reduced due to the increased conversion up to the time at which the failure is detected.

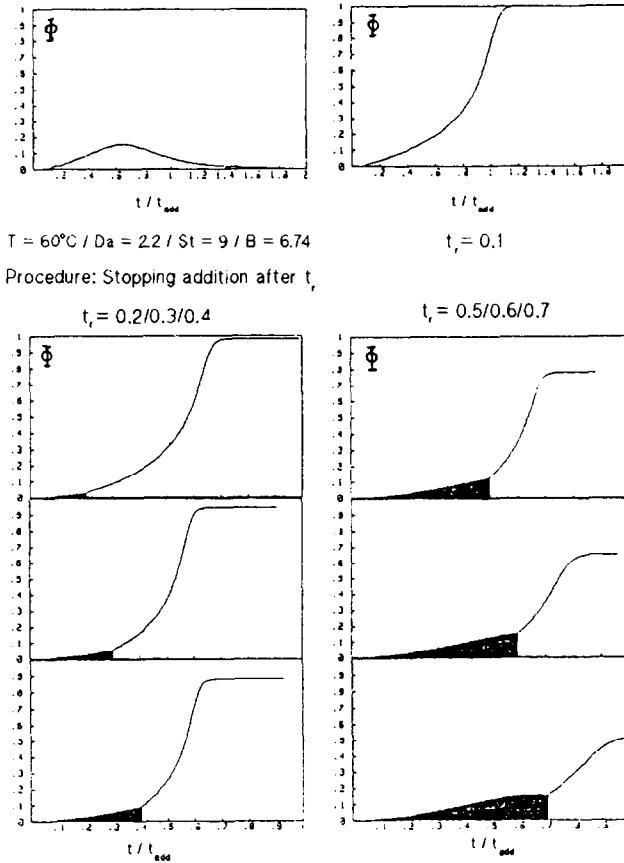


Fig. 10. Temperature profiles for a runaway reaction caused by loss of cooling medium, calculated for a given set of parameters.

From the safety perspective, it is important to know how much time remains to rectify this kind of deviation in order to prevent initiation of the secondary reactions. For this, one needs the thermal stability data of the reaction product of the primary reaction (resol). The adiabatic induction time as a function of temperature for a resol mixture is presented in Fig. 11. In Fig. 12 the adiabatic induction time for the resol formation and the adiabatic temperature increase are plotted as a function of the reaction time. The reaction temperature is 60°C ; the time of addition was set to 90 min.

If the deviation (loss of cooling medium) is registered during the first 15 min, the adiabatic induction time is long enough (>50 min) to respond and to remove the cause of failure or to dump the contents of the vessel. At later times (>120 min), the adiabatic temperature increase is small enough (<30 K) to reach a temperature level at which the adiabatic induction time of the resin formation is big enough (>25 min) to react in the same way. In

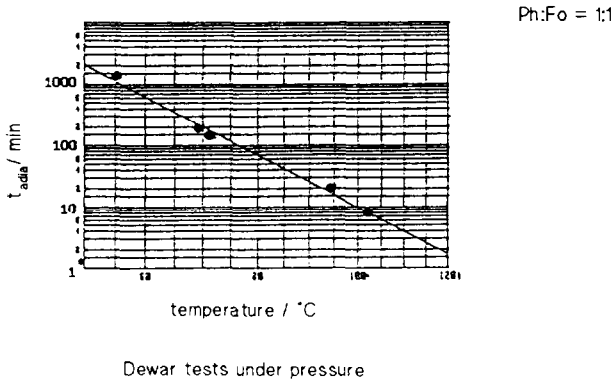


Fig. 11. The adiabatic induction time for a resol mixture, plotted as a function of temperature.

Adiabatic induction time and maximum temperature

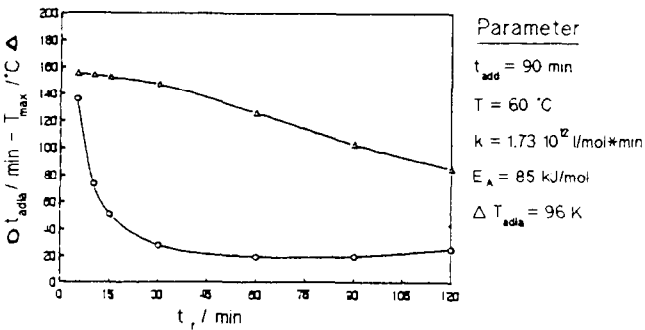


Fig. 12. The adiabatic induction time and the adiabatic temperature increase for the resol formation, plotted as a function of reaction time.

between, there is a range in which both parameters (adiabatic induction time and increase) are critical with respect to any preventative actions.

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