

## Hydrolysis of Micron Alkylketene Dimert Particles Under Alkaline Conditions

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The hydrolysis of alkylketene dimer (AKD) in a diluted dispersion was studied under alkaline conditions. The dispersion consisted of particles with 1  $\mu\text{m}$  in diameter with the reaction product forming a porous insoluble layer on the particle surface. The shrinking core model (SCM) for particles of unchanging size is proposed for describing the overall rate of hydrolysis reaction. The model assumes a process controlled by a surface reaction on the boundary between unreacted AKD core and outer ketone layer, with no significant transport phenomena due to the small particle dimensions and porous structure of the reaction product layer on the particle surface. Under conditions studied (at pH 10.3), where the concentration of  $\text{OH}^-$  ions is in excess compared to the AKD concentration and in the temperature range between 40 and 60  $^{\circ}\text{C}$ , the proposed model is in good agreement with experimental data. A temperature dependence of reaction rate was tested and the apparent activation energy was calculated as well. Compared to the activation energy for reaction between AKD and cellulose, AKD hydrolysis can represent an important competitive process that significantly influences the sizing efficiency.

*Key words:*

Alkylketene dimer, hydrolysis, unreacted-core model, shrinking core model, reaction kinetics, sizing, papermaking

### Introduction

Alkylketene dimers (AKD) represent one of the most widely used type of sizes in modern papermaking. Although they were discovered as early as in the 1950's, their use was spread over the last thirty years, when the use of calcium carbonate in field of fillers increased and consequently many paper mills changed their papermaking system from acid to neutral or alkaline. The main role of AKD in finished paper is to provide a certain level of hydrophobicity to paper in order to control the penetration of liquid into paper structure.

AKD belongs to a group of so-called reactive sizes because of the mechanism of its interaction with cellulose fibres. Although much debated, it is generally accepted nowadays that a part of AKD reacts with cellulose molecules. The reaction takes place during the drying process after the majority of water is removed from the paper web and with reactive sites on cellulose presumably being hydroxyl groups. It is also believed that the effect of temperature is very important because it can have a significant impact on the sizing efficiency. Higher temperatures and longer reaction (drying) times should

promote the reaction of AKD with cellulose.<sup>1-4</sup> The amount of AKD that reacts with cellulose varies from less than 10 % to a maximum around 50 % of total amount retained in a paper sheet, depending on the conditions of reaction.<sup>1,5</sup> Regardless of the extent of reaction, it seems that hydrophobicity can be obtained only by means of AKD that is chemically bound to cellulose.

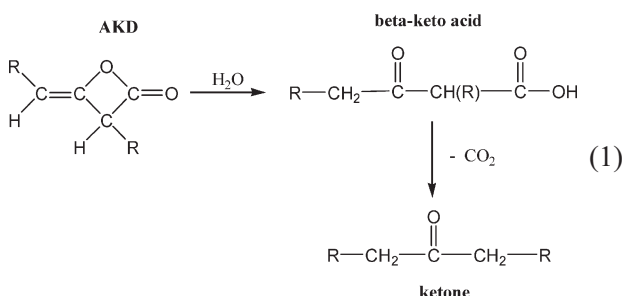
However, this is not the only reaction of AKD that occurs in the papermaking system. The second one is the reaction with water, namely a hydrolysis reaction that produces a ketone with no sizing features. The importance of hydrolysis reaction lies in the fact that it represents a competitive reaction to the AKD reaction with cellulose and thus potentially diminishes the efficiency of sizing. Secondly, the AKD remaining in process water (because it was not retained within the paper web) is subject to hydrolysis producing the ketone which can either be retained in paper (without any sizing effect) or form deposits together with other constituents of process water that were not retained in paper. With improved knowledge of hydrolysis kinetics, the effect of time on the activity of AKD remaining in process water that is being recycled on the paper machine can be estimated.

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The aim of presented work was to describe the hydrolysis process in AKD dispersion under alkaline conditions, with excess of  $\text{OH}^-$  compared to the amount of AKD, and in the temperature range between 40 and 60 °C by means of a shrinking core model.

## Theory

Although the exact mechanism of the hydrolysis reaction between AKD and water is not precisely known, it is most probably a two-step reaction mechanism.<sup>6,7</sup> The first step is the opening of lactone ring with  $\beta$ -keto acid as the reaction product.  $\beta$ -keto acid is thermodynamically unstable and easily eliminates a  $\text{CO}_2$  molecule to form a relatively stable ketone (equation 1).



For the description of the relation between conversion and time, a (pseudo) first order reaction kinetics was proposed.<sup>8,9</sup> Higher temperature and pH were shown to accelerate the hydrolysis.<sup>9,10</sup> It was also shown that some wet end additives and fillers can enhance the extent of hydrolysis in the wet end as well as in finished paper.<sup>10,11</sup> By means of an analogy with the mechanism proposed for the hydrolysis of alkenyl succinic anhydride (ASA),<sup>7</sup> it can be assumed that the reaction proceeds from the surface to the centre of AKD particles. However, in contrast to ASA, both AKD and the resulting ketone are insoluble in water. Thus, it can be expected that the ketone remains on the surface of AKD particles as an adsorbed layer after hydrolysis. The measured reaction rate would depend on the extent of active surface on the AKD particles rather than on the bulk AKD concentration in the dispersion.

In a dispersed system, each single particle can be represented as a small sphere. If a chemical reaction between the liquid surrounding the particle and the solid occurs, such a sphere is comprised of the unreacted core and the surface film of a reaction product and/or emulsifier. In the case of water-based AKD dispersions, unreacted AKD forms particles with diameter of about 1  $\mu\text{m}$ , which are surrounded by a starch layer necessary for the stabilization of their formation during the sizing agent

preparation process. After the hydrolysis reaction, a layer of water insoluble solid ketone surrounds the core comprised of unreacted AKD as well. In terms of process kinetics, starch and ketone layers could represent resistance to material transfer as they reduce the overall rate of the process (Fig. 1).

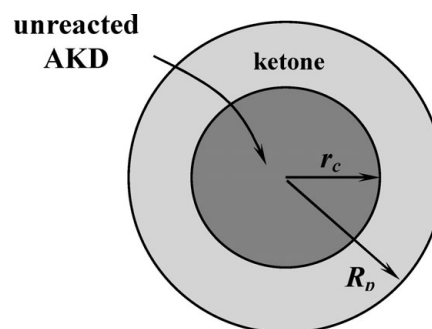


Fig. 1 – Schematic representation of AKD particle composition

Considering probable small thickness of starch layer and the fact that starch easily swells in water, it can be assumed that there is no resistance to the transport of water or  $\text{OH}^-$  ions (in this case representing one of the reagents) to the solid surface. After the reaction start the outer layer of the particle consists of a solid ketone which is neither soluble in water nor reacts with it but nevertheless seems to form a layer that doesn't hinder the transport of liquid reactant to the surface of an unreacted AKD core.

The penetration of  $\text{OH}^-$  ions through the hydrolysed AKD wax can be indirectly proved with Fig. 2. Here the hydrolysis was performed at 60°C

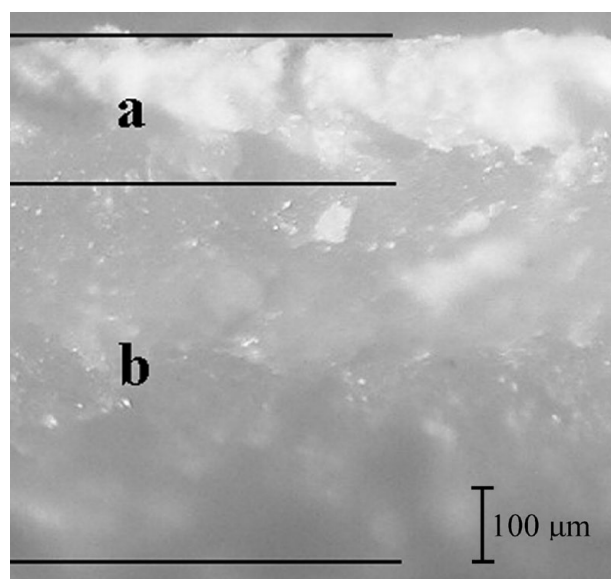


Fig. 2 – Profile of solid AKD wax, a – ketone layer, b – unreacted AKD layer

on 1 mm a plate of AKD wax that was submerged into NaOH solution with pH 12. While after 4 h AKD wax was still in solid state, two layers formed under these conditions as they could be observed under microscope.

The analysis by gas chromatography revealed that the outer layer of about 200  $\mu\text{m}$  thickness consisted mostly of ketones (over 80 %), while their presence in the inner layer was very low. The outer ketone layer seemed to have more “porous” structure than the AKD layer. Possible explanation of this observation is crystallisation of hydrolysed AKD with simultaneous emission of gaseous  $\text{CO}_2$  formed as a reaction product during hydrolysis. Similar structure is expected for AKD particles in the dispersion although with much smaller dimensions. With particle diameter being about 1  $\mu\text{m}$  the thickness of the ketone layer can be 0.5  $\mu\text{m}$  at the most (completely hydrolysed particle). Under conditions where the concentration of  $\text{OH}^-$  ions is in excess, it is reasonable to believe that the mass transport does not limit the overall rate, due to the small distance between particle surface and unreacted core surface.

Thus, with particles of so small dimensions under the conditions described above, the major rate-controlling step is the rate of chemical reaction on the surface of unreacted AKD core. For the description of such situation in terms of process kinetics the unreacted-core model can be used,<sup>12</sup> analogous to the model proposed for the hydrolysis kinetics of ASA.<sup>7</sup> Since the quantity of material reaction is proportional to the available surface of unreacted core, for the reaction stoichiometry in equation 1, the rate of reaction (based on unit surface of unreacted core with radius  $r_c$ ) is expressed as following:

$$-\frac{1}{4\pi r_c^2} \frac{dn_{\text{AKD}}}{dt} = k_s c_{\text{OH}^-} \quad (2)$$

With  $dn_{\text{AKD}}$  moles of AKD disappearing during the reaction, the reduction of unreacted core in volume is given by

$$-dn_{\text{AKD}} = -\rho_{\text{AKD}} dV = -4\pi r_c^2 \cdot \rho_{\text{AKD}} \cdot dr \quad (3)$$

where  $\rho_{\text{AKD}}$  represents moles of AKD per volume of solid particle. By combining eq. (2) and (3), we obtain

$$-\frac{1}{4\pi r_c^2} \cdot 4\pi r_c^2 \cdot \rho_{\text{AKD}} \frac{dr_c}{dt} = -\rho_{\text{AKD}} \frac{dr_c}{dt} = k_s c_{\text{OH}^-} \quad (4)$$

On integration for particle radius between  $R_p$  (outer particle radius) and  $r_c$  and within time between 0 and  $t$  equation 4 becomes

$$-\rho_{\text{AKD}} \int_{R_p}^{r_c} dr_c = k_s c_{\text{OH}^-} \int_0^t dt \quad (5)$$

With concentration of  $\text{OH}^-$  ions on the particle surface being in excess compared to the AKD concentration and by assuming that the particle density remains constant the term  $k_s c_{\text{OH}^-} / \rho_{\text{AKD}}$  can be substituted by a constant  $k$ . The equation 5 now rearranges to

$$t = \frac{1}{k} (R_p - r_c) \quad (6)$$

When the conversion is complete,  $r_c$  is equal to zero and the time needed for a complete conversion ( $\tau$ ) can be determined:

$$\tau = \frac{1}{k} R_p \quad (7)$$

where  $1/k$  equals  $\rho_{\text{AKD}} / k_s c_{\text{OH}^-}$ . Increase in fractional conversion or decrease in radius of an (unreacted) particle, for a reaction of pseudo-first order with respect to concentration of  $\text{OH}^-$  ions, can be calculated by combining equations 6 and 7:

$$\frac{t}{\tau} = 1 - \frac{r_c}{R_p} = 1 - (1 - X_{\text{AKD}})^{1/3} \quad (8)$$

Eq. 8, rearranged to the fractional conversion, can be used for calculation of time dependence of AKD conversion:

$$X_{\text{AKD}} = 1 - \left(1 - \frac{t}{\tau}\right)^3 \quad (9)$$

## Materials and methods

Commercial sizing agent dispersion and AKD wax were used in hydrolysis experiments. Samples were kindly provided by a sizing agent manufacturer. AKD wax consisted of 90 % stearyldiketene (as reported by manufacturer) while the sizing agent contained  $\gamma = 182 \text{ g l}^{-1}$  of dry matter consisting of starch and AKD. A minor part of AKD in the dispersion was already present in a hydrolysed form (as a ketone).

The hydrolysis reaction was studied by the following procedure. A commercial sizing agent dispersion was diluted to an AKD mass concentration of about  $\gamma = 25 \text{ mg l}^{-1}$  and pH was set to a desired value. The dispersion was divided into five 50 ml flasks that were put into water bath and thermostated at constant (desired) temperature. Each flask was taken from the bath after a desired time interval and instantly cooled to about 10 °C. After cooling,

three 5 ml aliquots of dispersion were taken from the flask and each aliquot was extracted three times with 2 ml of organic solvent (methyl t-butyl ether). The organic phase from each aliquot was collected into a test tube and evaporated. The same procedure was used also for the diluted dispersion prepared at the beginning of the experiment.

A spectrophotometric method<sup>13,14</sup> that was used to determine AKD in samples is based on the reaction of AKD with 4-dimethyl aminopyridine (DMAP) in dichloromethane giving a yellow coloured product, which absorbs light in UV and visible region of spectrum. The spectrum shows two absorbance maximums (at 338 nm and 450 nm) with a 338 nm peak being sharper and therefore more suitable for quantitative determinations. Due to DMAP being supposed to react with the lactone ring in AKD molecule, the reaction does not take place with the hydrolysed form (ketone). For the spectrophotometrical analysis, 5 ml of DMAP/dichloromethane solution (mass concentration  $\gamma = 5 \text{ g l}^{-1}$ ) was added to evaporated samples in test tubes. The tubes were then sealed and heated at 80 °C for two hours. When the samples were cooled, the AKD content was determined by means of spectrophotometry (at 338 nm wavelength) on a Varian Cary50 UV-VIS spectrophotometer. A dispersion without AKD was prepared and analysed by the same procedure in order to find out if there is some other constituent of the sizing dispersion that possibly reacts with DMAP. The resulting signal was taken as a blank for the determination.

The original AKD wax applied in dispersion production was used for the preparation of a calibration curve in the spectrophotometrical method as well. The wax was first recrystallised to remove any impurities. Then, standard solutions for the calibration curve ranging from 1 to 100 mg l<sup>-1</sup> of AKD were prepared. From the calibration curve, the relation between absorbance ( $A$ ) and AKD concentration ( $c$ ) in the form  $A = 0.00847 c + 0.07667$  was deduced. This relation was used for calculation of AKD concentrations in individual samples.

For additional analyses of AKD wax composition a analytical method based on gas chromatography was employed.<sup>15</sup>

## Results and discussion

Three sets of experimental data were obtained, each at a different temperature level (40, 50 and 60 °C), and all at the same pH value of 10.3. The measured time dependence of AKD conversion for each temperature is represented in Fig. 3. Compared to the predictions of a shrinking core model a good

agreement between modelled and experimental data can be concluded.

If the rate-controlling step is the surface reaction of AKD with OH<sup>-</sup>, the relation between AKD conversion and time should follow equation 9 providing that the bulk concentration of OH<sup>-</sup> ions remains fairly constant during the reaction. The latter is true with initial bulk mass concentration of AKD of about  $\gamma = 25 \text{ mg l}^{-1}$  under experimental conditions described above. For each temperature level, the most satisfactory correspondence of equation 9 to the experimental data was determined by the method of least squares, providing values for the time needed for the complete conversion ( $\tau$ ). Fig. 3 indicates that the theoretical curves are in accordance with the experimental data.

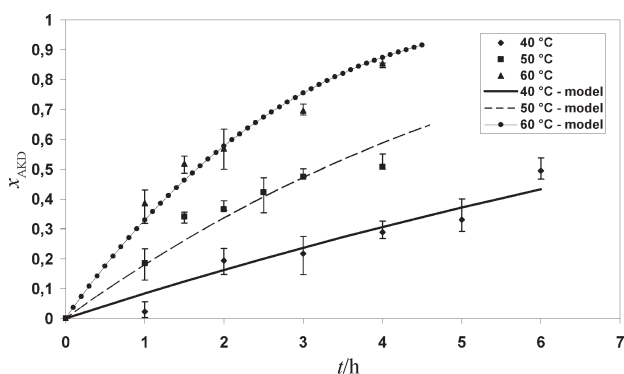


Fig. 3 – Experimental and calculated data for the dependence of AKD conversion on reaction time

On the basis of  $\tau$  values,  $k$  values were calculated for each temperature level by using equation 7. In the calculation, the molar density of solid AKD particles was  $\rho_{\text{AKD}} = 1.518 \text{ mol l}^{-1}$ , the concentration of OH<sup>-</sup> ions at pH 10.3 was  $c_{\text{OH}^-} = 1.995 \cdot 10^{-4} \text{ mol l}^{-1}$  and the average particle diameter was  $d = 1 \mu\text{m}$  (as measured by the sizing agent manufacturer). On the basis of equation 8, the time needed for a 0.5 conversion ( $t_{1/2}$ ) can be calculated for each temperature level as well (Table 1).

The results for  $t_{1/2}$  are in accordance with data provided by Jiang and Deng.<sup>10</sup> At pH 10.4 and at 50 °C, they measured the time needed for a 0.5 conversion. The results ranged between 3.5 and 4 h.

Table 1 – Calculated values of  $1/\tau$ ,  $k$  and  $t_{1/2}$  for each temperature level

$T / \text{°C}$	$1/\tau / \text{h}^{-1}$	$k / \text{m s}^{-1}$	$t_{1/2} / \text{h}$
40	0.02868	$7.97 \times 10^{-12}$	7.19
50	0.06387	$1.77 \times 10^{-11}$	3.23
60	0.1246	$3.46 \times 10^{-11}$	1.66

The values for  $k$  in Table 1 can also be used for the estimation of activation energy for the surface reaction. The estimation is based on the Arrhenius equation:

$$k = k_0 \exp(-E_a/RT) \quad (10)$$

where  $k_0$  is the rate constant,  $E_a$  is the activation energy,  $R$  is the gas constant and  $T$  is temperature. By plotting the  $\ln k$  versus  $1/T$ , a linear plot is obtained where the slope and intercept are equal to  $-E_a/R$  and  $\ln k_0$  respectively.

In Fig. 4, such a plot is presented for the hydrolysis of AKD particles. The value for  $E_a$  calculated on the basis of this plot is  $63.8 \text{ kJ mol}^{-1}$  (within confidence limit of  $R^2 = 0.997$ ).

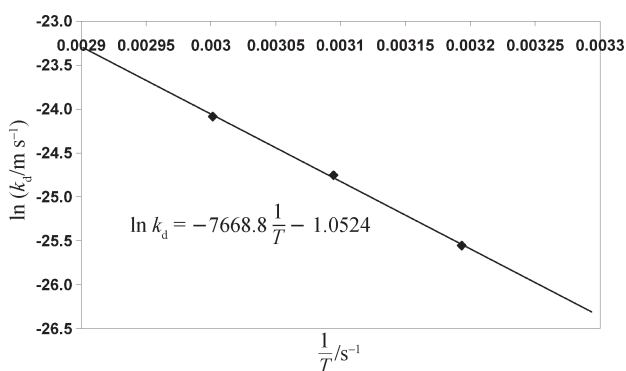


Fig. 4 – The plot of  $\ln k$  versus  $1/T$  for the hydrolysis reaction

In comparison to the values of apparent activation energy of hydrolysis reported by *Marton*<sup>8,9</sup> ( $\sim 105 \text{ kJ mol}^{-1}$ ), the value determined here is reasonably lower, which is most probably caused by the different conditions used in those studies that were conducted at AKD concentrations five to ten times higher than in our study. Under such conditions, the mole ratio of  $\text{OH}^-$  to AKD either approximates  $\gamma_{\text{OH/AKD}} = 1 : 1$  or AKD is in surplus, and it is very likely that the concentration of  $\text{OH}^-$  ions reduces with time. For this reason the latter also becomes a limiting factor that influences the reaction rate.

Similar reaction conditions were achieved in our experiments by reducing the pH value. Two series of experiments at  $50 \text{ }^\circ\text{C}$  and different pH values (8.5 and 10.3) were performed. The results are shown in Fig. 5. In comparison to above mentioned experiments performed by *Marton*<sup>8,9</sup> at pH 8.5 with similar  $\text{OH}^-$  to AKD ratio the available surface of AKD is lower due to lower bulk AKD concentration (and consequently particle concentration). As expected the measured conversion at pH 8.5 was lower indicating that the reaction mechanism has changed. Possible reason is the time dependent decrease of  $\text{OH}^-$  ions concentration which now becomes the limiting factor for the chemical reaction. Another possi-

ble reason for decrease in reaction rate is also the rate of transport of  $\text{OH}^-$  ions from the bulk liquid that surrounds AKD particles to their surface.

Following the unreacted-core model under the conditions of pH 8.5 the transport phenomena may become important. Due to this relatively low concentration of  $\text{OH}^-$  ions in the bulk liquid, the transport to the active surface of the particle becomes the limiting factor of the process. With the bulk concentration of  $\text{OH}^-$  being equal to  $c_{\text{OH}^-}$  the rate of mass transfer (based on unit of outer particle surface with radius  $R_p$ ) can be written as:<sup>12</sup>

$$-\frac{1}{4\pi R_p^2} \frac{dn_{\text{AKD}}}{dt} = k_d c_{\text{OH}^-} \quad (11)$$

The  $k_d$  is the mass transfer coefficient describing the resistances to mass between bulk fluid and unreacted core surface. Writing  $dn_{\text{AKD}}$  in terms of reduction in volume of unreacted core again gives:

$$-dn_{\text{AKD}} = -\rho_{\text{AKD}} dV = -4\pi r^2 \cdot \rho_{\text{AKD}} dr_c \quad (12)$$

By combining equations 11 and 12 we obtain:

$$-\frac{\rho_{\text{AKD}}}{R_p^2} \frac{dr_c}{dt} = k_d c_{\text{OH}^-} \quad (13)$$

Rearranging and integration equation 13 gives:

$$-\frac{\rho_{\text{AKD}}}{R_p^2} \int_R^{r_c} r_c^2 dr_c = k_d c_{\text{OH}^-} \int_0^t dt \quad (14)$$

After integrating and by substituting the term  $3k_d c_{\text{OH}^-} / \rho_{\text{AKD}}$  by a coefficient  $k$  we obtain:

$$t = \frac{R_p}{k} \left[ 1 - \left( \frac{r_c}{R_p} \right)^3 \right] \quad (15)$$

When the conversion is complete  $r_c$  is equal to zero and the time needed for a complete conversion ( $\tau$ ) again can be determined:

$$\tau = \frac{1}{k} R_p \quad (16)$$

Combining equations 15 and 16 we obtain the expression for the time dependence of AKD conversion:

$$\frac{t}{\tau} = 1 - \left( \frac{r_c}{R_p} \right)^3 = X_{\text{AKD}} \quad (17)$$

By finding the most satisfactory correspondence of equation 17 with experimental data in Fig. 5 the overall rate coefficient ( $k$ ) for the process of AKD hydrolysis at pH 8.3 can be obtained.

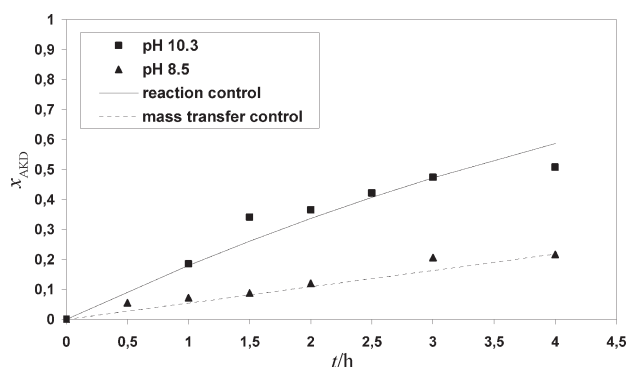


Fig. 5 – Comparison of measured data and model predictions for reaction control regime and for mass transfer control regime

The value for  $1/\tau$  determined in this way from Fig. 5 equals  $0.0544 \text{ h}^{-1}$ . By taking  $1.518 \text{ mol l}^{-1}$  for the molar density of solid AKD particles,  $3.162 \cdot 10^{-6} \text{ mol l}^{-1}$  for the concentration of  $\text{OH}^-$  ions at pH 8.5 and  $1 \mu\text{m}$  for average particle diameter, the overall mass transfer coefficient (for diffusion through liquid boundary layer and starch layer surrounding the AKD particle) was estimated to  $1,51 \cdot 10^{-11} \text{ m s}^{-1}$ .

Although in reality a combination of both influences can be expected it seems that under the conditions with lower pH value (8.5) the influence of mass transfer phenomena prevails over the influence of rate of chemical reaction.

As mentioned above, the molar ratios at pH 10.3 are in favour of the  $\text{OH}^-$  concentration in the system. Under such conditions, the main limiting factor for the process is the rate of chemical reaction, whereas the effect of transport phenomena seems to be more or less excluded. In comparison with the rates of reaction calculated by Marton,<sup>8,9</sup> the rate constants presented here reflect the actual changes in the rate of chemical reaction due to the changes in temperature. The calculated apparent activation energy is in the same order of magnitude as the activation energy reported for the reaction between AKD and cellulose ( $\sim 50 \text{ kJ mol}^{-1}$ ).<sup>1</sup> From this point of view, the hydrolysis of AKD under sufficiently alkaline conditions represents an important competitive reaction to its reaction with cellulose.

Another aspect regarding the temperature should also be noted. The melting point of AKD wax used is slightly above  $60 \text{ }^\circ\text{C}$  so it is very likely that the mechanism of the process will change again. Above the melting point and due to the fact that AKD and ketone are insoluble in water the reaction will probably take place on liquid-liquid phase border in contrast to the presumed reaction on the solid surface taking place below the melting point. With the particle melted it is possible that

there is an internal transport of unreacted AKD from the bulk of the droplet to its surface. Considering the small dimensions of the droplet this internal transport does not limit the rate of the process and the surface chemical reaction still remains main limiting factor. Confirmation of this hypothesis was to some extent done by an experiment at pH level 10.3 and temperature  $70 \text{ }^\circ\text{C}$ . At this temperature the measured AKD conversion is substantially faster than below the melting point (Fig. 6).

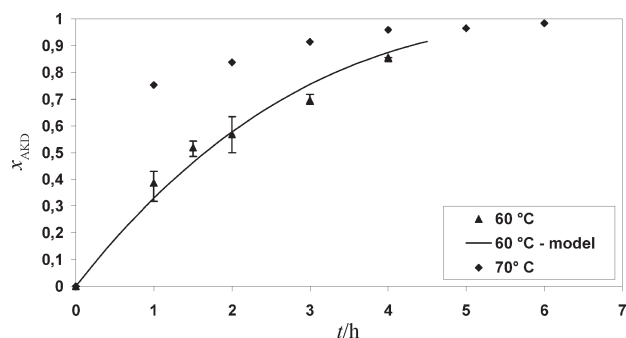


Fig. 6 – Comparison of conversion measured at  $70 \text{ }^\circ\text{C}$  with conversion measured and predicted by the model at  $60 \text{ }^\circ\text{C}$

Both situations – at low and high ratios of  $\text{OH}^-$  to AKD concentrations – have practical importance. For a sizing agent manufacturer, the first situation (low ratio) is applicable. It is known that AKD concentrations in commercial sizing agents amount up to 20 % and at the same time the pH lies in the acidic range. Under such conditions, the rate of hydrolysis reaction is low as confirmed by long storage stability of commercial AKD dispersions.

On the other hand, the situation with high  $\text{OH}^-$  to AKD ratio can be expected in a papermaking system where the amount of sizing agent added is very low by itself, with common doses ranging from 0.5 to 1 % of commercial product per mass of fibres at fibre mass concentrations of  $10 \text{ g l}^{-1}$  (0.05 – 0.2 % of AKD per mass of fibres). A papermaking system where AKD is used contains calcium carbonate as a filler as well. The latter buffers the system to a constant alkaline pH, and with a reported 50 % retention of AKD in paper,<sup>16</sup> it is reasonable to expect conditions where the concentration of  $\text{OH}^-$  ions in process water is a few times higher than the AKD concentration.

The importance of the influence of temperature on chemical reactions has increased in modern papermaking systems. In relation to the facts that process water temperatures around  $50 \text{ }^\circ\text{C}$  are nowadays quite common, and that the majority of process water containing unretained AKD is recycled in the system, it is important to understand how temperature affects the rate of hydrolysis because

such information provides useful data about AKD behaviour in the system. Nevertheless it should be noted, that studies of hydrolysis rate at higher temperatures (70 °C) currently have no practical importance in papermaking. Based on a model for hydrolysis reaction rate the time needed before the AKD remaining in the process water transforms to the ketone can be predicted. In combination with the knowledge of AKD and ketone retention in paper, such predictions can be useful for determining the overall mass balance of these components in the papermaking system. The impact that the AKD hydrolysis can have on the final product can be better understood if we know that the ketone retained in paper causes slipperiness problems as described by different reports.<sup>9,17–19</sup>

## Conclusions

With the studies of hydrolysis in diluted AKD dispersions under alkaline conditions it was established that, for the description of reaction rate under conditions where the molar ratio of OH<sup>-</sup> to AKD is high, the shrinking core model for particles of unchanging size can be used. The reaction takes place on the surface of shrinking unreacted core, while the outer particle layer transforms to water insoluble ketone. With regard to small particle diameter (~ 1 μm) and the porous structure of ketone layer the transport phenomena can be neglected compared to the rate of chemical reaction. Under experimental conditions at pH 10.3 and within the temperature range between 40 and 60 °C the model is in good agreement with experimental data confirming that under these conditions the chemical reaction is the rate controlling process. On the other hand under pH 8.5 another form (mass transfer control) of the unreacted core model is needed. The apparent activation energy of 63.8 kJ mol<sup>-1</sup> calculated on this basis is comparable to the activation energy of the reaction between AKD and cellulose (55 kJ mol<sup>-1</sup>) reported by others,<sup>8,9</sup> which makes the hydrolysis an important competitive process.

Depending on the conditions in the reaction system, the mechanism of the AKD reaction with surrounding media changes. While at high molar ratios of OH<sup>-</sup> to AKD the process is controlled by the rate of surface chemical reaction, at low molar ratio the limiting factor is also the concentration of OH<sup>-</sup> ions. Due to this change in reaction mechanism the model proposed here is not sufficient anymore to describe the reaction rate.

The model described here combined with retention data is useful for predicting the mass balance and behaviour of AKD in the real papermaking system.

## ACKNOWLEDGEMENT

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## List of symbols

$A$	– absorbance
$c_{\text{OH}^-}$	– concentration of OH <sup>-</sup> ions, mol l <sup>-1</sup>
$d_p$	– particle diameter, μm
$E_a$	– activation energy, kJ mol <sup>-1</sup>
$k$	– rate coefficient, mol <sup>-1</sup> l h <sup>-1</sup>
$k_0$	– rate constant, mol <sup>-1</sup> l h <sup>-1</sup>
$k_d$	– mass transfer coefficient, m s <sup>-1</sup>
$k_s$	– rate constant for surface chemical reaction, m s <sup>-1</sup>
$n$	– amount of substance, mol
$R$	– gas constant, J mol <sup>-1</sup> K <sup>-1</sup>
$R_p$	– outer particle radius, μm
$\gamma$	– mole ratio
$r_c$	– core radius, μm
$T$	– temperature, K, °C
$t$	– time, s, h
$X$	– conversion, l
$\gamma$	– mass concentration, mg l <sup>-1</sup> , g l <sup>-1</sup>
$\rho_{\text{AKD}}$	– molar density of AKD, mol l <sup>-1</sup>
$\rho_{\text{ketone}}$	– molar density of ketone, mol l <sup>-1</sup>
$\tau$	– time of complete conversion, h

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