

EXPERIMENTAL VERIFICATION OF ZOU, UESAKA AND GURNAGUL FORMALISM, BASED ON KINETIC DATA OBTAINED FOR VARIOUS KINDS OF PAPER

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1. Introduction

Application of Arrhenius equation in predicting paper and pulp permanence, where a multiple-reaction system with different activation energies should be taken into account, has been seriously questioned by many authors. However, Zou and co-workers¹ achieved a better understanding of the apparent activation energy even in the case of multiple parallel reactions, and justified the extrapolation based on Arrhenius plot. Their approach was a very promising one, but, unfortunately, this publication was not widely recognized among the researchers working in the fields of papermaking and preservation science. Strong experimental evidence of validity or falsity of this approach is still lacking.

The equation used in paper¹ is based on a well known and widely used Ekenstam equation² and has the following form:

$$\frac{1}{DP} - \frac{1}{DP_0} = t \cdot A_a \exp\left(-\frac{E_a}{RT}\right)$$

where

$$A_a = A_{a0} + A_{a2}[\text{H}_2\text{O}] + A_{a5}[\text{H}^+][\text{H}_2\text{O}].$$

Symbol $[\text{H}_2\text{O}]$ denotes the moisture content in paper. As the concentration of hydrogen ions in paper cannot be measured, the value of $[\text{H}^+]$ was recalculated from the experimentally determined pH value of paper. The parameters A_{a0} , A_{a2} , and A_{a5} , as well as the activation energy E_a , should be empirically determined for the investigated kind of paper. However, they are not independent, and if one wants to use the equation for a different kind of paper, it is necessary to find the suitable values simultaneously. One can try, however, to find at least an approximate prediction of the investigated paper ageing behaviour using the original set of values published in the second part of the cited publication³. This is exactly what we did. We tried to use the parameters of Zou and co-workers equation to the papers differing from the material used in the original experiments described in the literature.^{1,3}

2. Types of papers used

We decided to check the applicability of Zou, Uesaka and Gurnagul formalism, taking our kinetic data obtained for the model P1 paper (containing more than

95% of cellulose from coniferous trees and 0.45% of ash) at temperature 90 °C and at various relative humidities (from 10 to 75%)⁴. Samples of paper P1 have been obtained from TNO, Delft.⁵ It should be stressed here that two different reams of P1 paper, differing slightly in the original value of polymerization degree, have been obtained from this source.

Another set of well documented kinetic data can be taken from the report of Kaminska, Bégin *et al.*⁶. The authors used in their experiments two other kinds of paper – BNSWK softwood ISR paper #1 (Bleached Northern Softwood Kraft fibre, rosin sized) and SW-BCTMP softwood ISR paper #3 (Bleached ChemiThermoMechanical Pulp fibre, unsized). The temperature range used by Kaminska and Bégin was 65–90 °C, and the relative humidity range was 65–72%.

For comparison, one of the kinetic runs obtained by Zou, Uesaka and Gurnagul has been chosen in order to check applicability of the same equation parameters (averaged over temperatures and humidities) to a single curve. The samples used in the experiments of Zou were those of softwood bisulfite pulp (BBSP) originating from various Canadian paper mills and formed into standard handsheets (60 g/m²).

3. Results and Discussion

The most important data concerning the kinetic results are presented in Table 1. Typical curves have been shown in Fig. 1.

The reader should be aware that the residual standard deviation (RSTD) values given in Table 1, though obtained as a result of linear regression analysis, have been recalculated so as to show differences between experimental data and theoretical curves in the natural system of coordinates: DP versus time.

The worst results of fitting the discussed model to the experimental data have been obtained for Kaminska and Bégin paper SW-BCTMP. The remaining results were quite promising. Most of the investigated kinetic curves were quite satisfactorily predicted by the model, though in almost all cases the experimental points were situated below the calculated curve, this meaning that real degradation rate was somewhat higher than the calculated one. Experimental degradation progressing faster than that predicted by the discussed model could be explained by the fact that the model assumes a

Table 1: Selected experimental details of kinetic results obtained for various kinds of paper. The Kraków data have been obtained for P1 paper originating from different paper reams.

Source of data	Zou et al. [1]	Kaminska, Bégin [6]	Kaminska, Bégin [6]	Kraków [4]	Kraków [4]
Paper type	BBSP	BNSWK	SW-BCTMP	P1	P1
Temperature range	90 °C	65–90 °C	65–90 °C	90 °C	90 °C
RH range	75%	65–72	65–72	10–45	23–75
DP ₀ value	1369	2475	1858	921	997
Number of kinetic curves	1	4	4	2	2
Mean value of Residual Standard Deviation (RSTD) in DP units	72	122	188	69	35

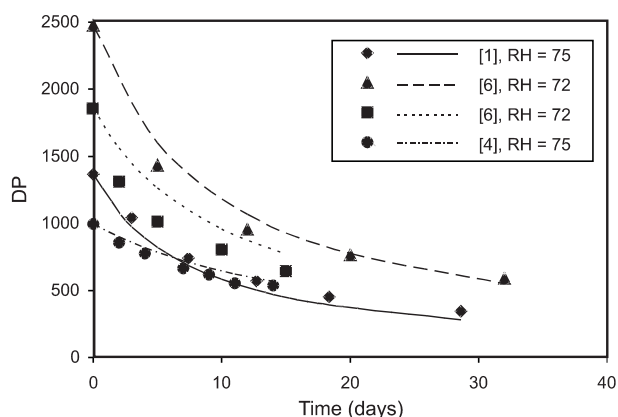


Figure 1: Kinetic curves calculated according to Zou, Uesaka and Gurnagul model (lines), as fitted to the experimental data (points) obtained in various laboratories at temperature 90 °C and relative humidity close to 75%.

constant concentration of hydrogen ions during the degradation process, whereas our own experimental results⁷ clearly show that pH is lowered during the artificial ageing tests, thus resulting in the acceleration of acid hydrolysis process.

4. Conclusion

The results presented here, though not conclusive enough, speak strongly in favor of Zou, Uesaka and Gurnagul formalism. It seems possible to apply the values of parameters experimentally obtained by these

authors for the rough estimation of kinetic behaviour of papers originating from different sources. Of course, better results will be, most probably, obtained if a set of equation parameters is experimentally determined for the specific kind of paper being investigated. Another improvement in the original model could be achieved by taking into account variation of the hydrogen ion concentration in the course of accelerated ageing tests.

5. References

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