

DEGRADATION PHENOMENOLOGY AND LIFE MODELLING OF PAPER – A REVIEW

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ABSTRACT

This document reviews degradation phenomenology and life modelling of paper, illustrates different approaches, showing their advantages and applicability limits and raises problems relevant to practical applications of degradation indicators and degradation rate models and evaluation of paper permanence and durability. It deals with the fundamentals of paper degradation rate theory and life modelling, seeks to develop the degradation rate equations of paper that will closely track real degradation experimental results over extended period under practical service conditions, shows a collection of degradation rate and life data of different paper and paper insulation materials under a varied of in-service environmental conditions, develops continuous distribution kinetics theory of cellulose and paper degradation to form a united basis in deriving the traditional Ekenstam degradation rate equation and the alternative percentage DP (and TS) loss rate equations recently proposed by the present author and his co-worker, and presents effective methodology for combining time-temperature superposition method and paper degradation investigation towards a more reliable prediction of rate and life of paper degradation over a long time period under real in-service conditions.

OUTLINE

INTRODUCTION

AN OVERVIEW OF PAPER DEGRADATION

Phenomenological paper degradation theory

On the mechanisms of paper degradation

On the indicators of paper degradation

On the rate of paper degradation

Survey of accelerated degradation experimental results

On the end-of-life criteria

Summary

PERCENTAGE DP (DEGREE OF POLYMERIZATION) LOSS RATE MODEL

PERCENTAGE TS (TENSILE STRENGTH) LOSS RATE MODEL

CONTINUOUS DISTRIBUTION KINETICS THEORY OF PAPER DEGRADATION

Continuous distribution kinetics

Application of continuous distribution kinetics to degradation of cellulose

Derivation of reciprocal DP rate equation

Derivation of percentage DP rate equation

TIME-TEMPERATURE SUPERPOSITION METHOD OF PREDICTING THE PERMANENCE AND LIFE OF PAPER BY EXTRAPOLATING ACCELERATED AGEING DATA TO AMBIENT CONDITIONS

The time-temperature superposition principle

TTS to determine the activation energy of paper degradation

Towards a more reliable paper life prediction method

Comparison of natural ageing degradation results with predictions

CONCLUSIONS

ACKNOWLEDGEMENTS

REFERENCES

INTRODUCTION

An old Chinese proverb says, “Men grow old, pearls grow yellow, there is no cure for it”. It does not matter if you would agree with that one-hundred percent, in all of nature this is true, and it is true of paper too. Degradation of paper is a complex but well-documented phenomenon as old books, textiles, and paper insulation in oil-filled power equipments can undergo brittle failure after years, decades, or even centuries of in-service.

The driving force behind the effort to understand the degradation phenomenology of paper has been the vital need to know whether the paper and paper insulation will continue to function for a length of time expected, as required by the papermaker as well as the user of paper and paper insulation. Librarians and archivists are concerned about the life of paper in old books and documents as a consequence of ageing degradation. Utility asset managers and engineers are concerned the life and reliability of paper insulation in ageing power transformers, because the traditional view has been the life of paper insulation being the life of the transformer. In all these cases methods of characterizing paper degradation and determining the rate of paper degradation are important, they not only govern the long-term performance but also ultimately determine the useful life of the paper products such as books, documents, power cables and transformers.

In studying the degradation phenomena of paper, last hundred years have been replete with many milestones increasing the understanding of the causes and mechanisms of paper degradation. A number of good reviews exist on the effects of degradation on the permanence and durability of paper as well as the mechanisms and kinetics of cellulose and paper degradation [1–12]. From time to time however it is necessary to update our knowledge, particularly when requirements change. This is certainly the case with ageing power transformer fleet in substations around the world. There has been an increasing requirement to develop “age-aware” paper model for use in programmes that predict the life of the overall system.

The concepts of rate and life of paper degradation embody the parameter of “time” and provide the challenge, the problems and new perspectives of which are the subjects of this review. This document will focus not only on fundamental achievements and inherent problems relevant to determination of rates and life expectancies of paper degradation, but also seek to develop alternative modelling approach and methodology that will closely track real experimental results and be able to offer a more reliable prediction of rate and life of paper degradation over a long time period under real in-service conditions.

AN OVERVIEW OF PAPER DEGRADATION

Phenomenological paper degradation theory

Numerous experiments have demonstrated that paper degradation is a gradual change of structures and properties that usually leads to a degree of damage [5, 13]. The primal degradation process in almost all cases is that the cellulose chain are repeatedly broken and reformed into new configurations. Degradation of paper is chemical kinetics [14–16]. Without loss of generality, degradation of paper can therefore be described as occurrence of irreversible changes in its material microstructure, which affect its ability to satisfy request performance. Changes affect chemical composition at molecular level and various paper properties on macroscopic scale. Diagnosis and evaluation of degradation of paper can therefore be realized by resorting to observations of appropriately selected properties, which are sensitive to deterioration.

These concepts of paper degradation can then be translated into mathematical language as follows. Referring to applied influence factors (various stresses) F_1, F_2, \dots, F_N as the primary causes of degradation, the dependence of degradation, D , on the property p selected to evaluate the degree of degradation can be written as

$$D = F(p) \quad (1)$$

Where $p \equiv (P_0 - P)/P_0$ is the observed property in relative expressions, P and P_0 are the property of the degraded and the virgin papers respectively. The rate of paper degradation R is given by

$$R = \frac{dD}{dt} \quad (2)$$

The integral of equation (2) gives

$$D = \int_0^t R(F_1, F_2, \dots, F_N) dt \quad (3)$$

When p reduces to reach a limited value of p_L below which the paper is unable to maintain serviceability, failure occurs and the time of degradation becomes lifetime L and equation (3) gives

$$D_L = F(p_L) = \int_0^L R(F_1, F_2, \dots, F_N) dt \quad (4)$$

Where D_L represents the endurance limit of paper which is a dimensionless

characteristic quantity for a paper. Equation (3) can then be called the general rate equation of paper degradation, and equation (4) the general life equation.

Ideally, if the rate of paper degradation depends only on the primary causes but the time, both equation (3) and equation (4) can be further simplified as

$$D = R(F_1, F_2, \dots F_N)t \quad (5)$$

$$L = \frac{D_L}{R(F_1, F_2, \dots F_N)} = \frac{F(p_L)}{R(F_1, F_2, \dots F_N)} \quad (6)$$

Combining equation (5) and equation (6) gives

$$D = D_L \frac{t}{L} \quad (7)$$

Equation (7) shows that whatever the trend of the select property, the cumulative or total degradation D always increases from initial value $D_0(t = 0)$ to the maximum value $D_L(t = L)$. For the same fraction (t/L) of consumed life, D is lower for paper having low D_L , which means that the definition of degradation permits a comparison of papers to be done. Equation (7) also reveals that the physical meaning of the degradation parameter is the extent of progression towards the final failure. The process of degradation of paper could be looked on either as an accumulation of damage toward an endurance limit (i.e. maximum tolerable damage value), or as an exhaustion of the lifetime inherent in the paper. The nature of the paper degradation is that damage accumulates gradually in the course of degradation time and failure occurs when this reaches a limit level.

The picture described above is simplified. In real world, however, variable environmental conditions and therefore different mechanisms of degradation can occur in paper, leading to complicate time variation of the paper properties [3–6, 13]. Several factors of influence may be present at the same time, able to accelerate the rate of paper degradation significantly for a given combination of factors such as temperature, relative humidity, oxygen, acidity, etc. The complexity will increase when accelerated ageing tests try to reproduce the real/natural service conditions [7, 11, 17]. In this case, time-varying temperature cycles and various factors of influence, as well as actual environmental conditions, may have to be considered. Moreover, failure itself is a phenomenon with a stochastic nature. So, to this end, it is important to recognize that a purely phenomenological and/or deterministic approach for the rate of paper degradation would not be very efficient. However, the

concepts as well as the methodology described above are useful to give a general picture of the degradation process of paper and to point out the role of the various quantities involved, as well as to introduce criteria for paper degradation and life investigation.

On the mechanisms of paper degradation

Causes of paper degradation are its environmental conditions which induce chemical and/or physical processes in paper at the molecular level. These processes are the degradation mechanisms of paper. It is the chemical composition and structure of paper which provide clues to understand the degradation mechanisms and characteristics of paper. Paper is a composite material made from cellulose fibre. The condition and strength of the cellulose fibers themselves and the intermolecular hydrogen bonds between the cellulose chains are the most significant control factors that influence the strength of a dried sheet of paper [13]. In 1985, Shroff and Stannett [3] reported a comprehensive study of paper ageing degradation done *in vitro* under oil in atmospheres of nitrogen and air with controlled water contents. The ageing temperatures were in the range 110–140°C with ageing periods up to 1.5 years. This experimental study has confirmed that paper degradation is highly dependent on temperature and the presence of water and oxygen.

It is generally accepted today that hydrolytic, oxidative and thermal degradation are the major ageing degradation mechanisms of paper and paper insulation [6, 12, 18–40].

Hydrolytic degradation This refers to the cleavage at the glucosidic linkage in the cellulose chain. Cellulose is susceptible to hydrolysis by acids. Acids attack the acetal linkages and result in the breakage of the 1-4-glycosidic bonds, which will decrease the value of degree of polymerization by a depolymerisation process. Presence of water will further increase the rate of cellulose and paper degradation.

Oxidative degradation Cellulose is susceptible to oxidation and oxygen will also accelerate the degradation reaction. The hydroxyl groups in cellulose molecule are the weak parts where carbonyl and carboxyl groups are formed and eventually cause secondary reactions giving chain scission. Strong oxidizing agents and/or vigorous reaction conditions can convert cellulose into CO, CO₂ and H₂O by the breakup of the ring structure.

Thermal degradation A number of different thermal degradation reactions are known to occur with cellulose and paper at different temperatures. In summary, these thermal degradation reactions can be grouped into three basic classifications: the first group occurs at lower temperatures (<200°C)

and is similar to the aging reactions. Products are water, CO, CO₂ and a carbonaceous char. At higher temperatures (>200°C), another reaction begins to take over which results in depolymerisation of the cellulose chain and formation of anhydroglucose derivatives, volatile organic materials and tars. At still higher temperatures (>250°C), several competing pyrolytic reactions begin to take over, more-or-less random bond cleavage of cellulose and intermediate decomposition products results in formation of a variety of low molecular weight compounds like furfurals.

On the indicators of paper degradation

As paper degradation results in the formation of by-products, loss in mechanical integrity and change in chemical structure, the progress of degradation in paper can be determined either from the change in material properties (direct measurement) or from the formation of degradation by-products (indirect measurement), as briefly summarized in Figure 1.

Results from accelerated ageing of Kraft paper in sealed glass vessels in an atmosphere of initially dry nitrogen gas, carried out by Lawson, Simmons and Gale in 1977 [21], have indicated that the various mechanical and physico-chemical parameters have different sensitivities to thermal degradation. As shown in Figure 2, almost all mechanical properties deteriorate in a like fashion, but tensile strength is the most sensitive to ageing degradation if 50% retention of characteristic is used as an end point criterion.

Results from accelerated ageing of Kraft paper in sealed stainless steel containers containing Kraft paper, transformer oil, core steel, copper plate and aluminium pipe, carried out by Yoshida *et al.* [22] in 1978, have indicated that there is a close correlation between the formation of gaseous products (mainly CO and CO₂) and the loss in paper permanence. As shown in Figure 3, the decrease in DP and the increase in (CO + CO₂) gas

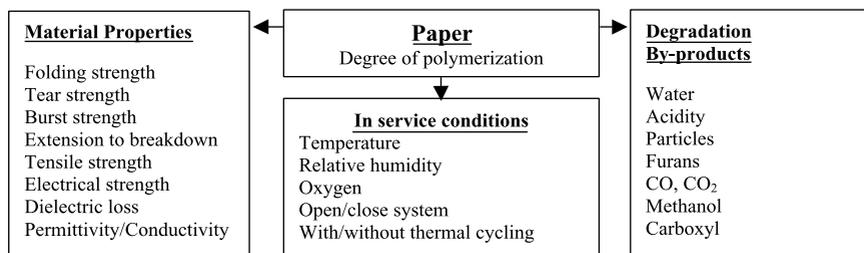


Figure 1. Characteristics of paper degradation.

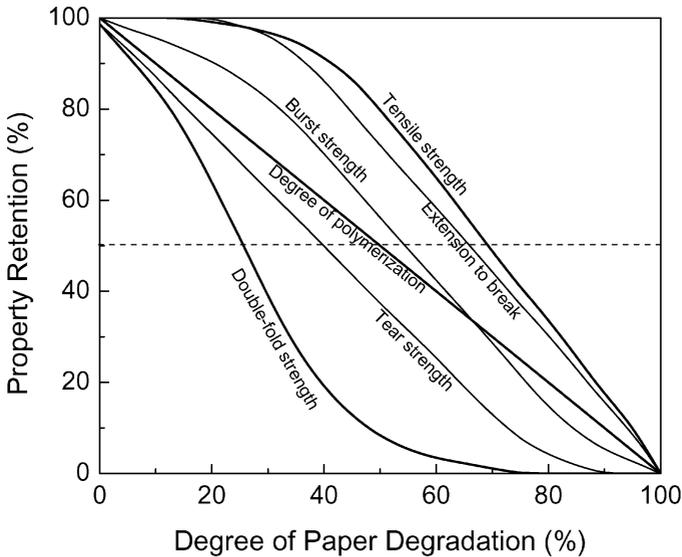


Figure 2. Degree of paper degradation and percentage property retention of Kraft paper [21].

content can be considered in close correlation in nearly all the samples in the ageing degradation temperature range 100 ~ 140°C. Note the use of the same time-temperature shift factor a_T values found for good superposition of the data about loss in DP also results in good superposition of the data about increase in $(CO + CO_2)$. Generally, one confirms the other when establishing the rate of paper degradation and the use of all serves as a safety measure.

During the late 1970s, Burton *et al.* [41] first uncovered the presence of 2-furfuraldehyde and related compounds in transformer oil analysis when they identified excessive paper insulation degradation as a major factor in causing the failure of two 400/22kV generator transformers at a UK power station. Result from various accelerated ageing degradation investigation carried out by different researchers worldwide have confirmed that high concentrations of 2-furfural [2FAL] are a clear indication of paper degradation, as this is the only type of material inside transformers that yields this by-product. An investigation carried out by Heywood [42] in 1997, as shown in Figure 4, has further confirmed that the concentration of [2FAL] increases quicker at lower DP's as the inter fibre bonding begins to collapse.

In literature there are various empirical correlations between the measured

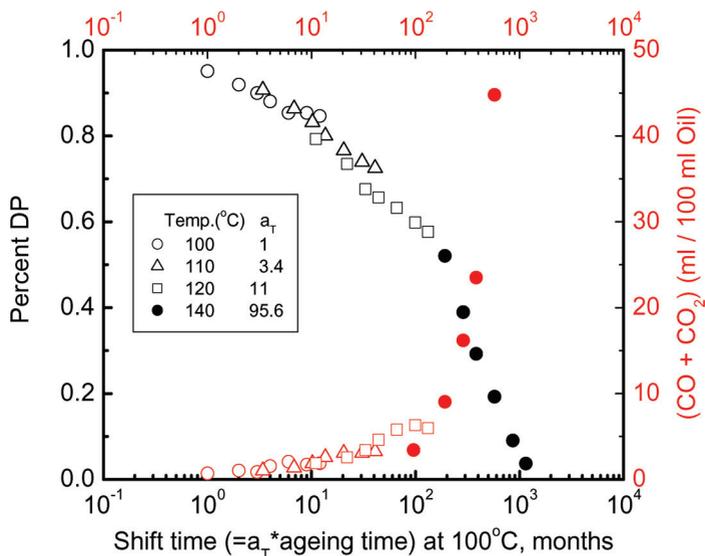


Figure 3. Correlation between increase in CO + CO₂ gas content in oil and decrease in percent DP in an accelerated ageing degradation test of oil-Kraft paper system [22].

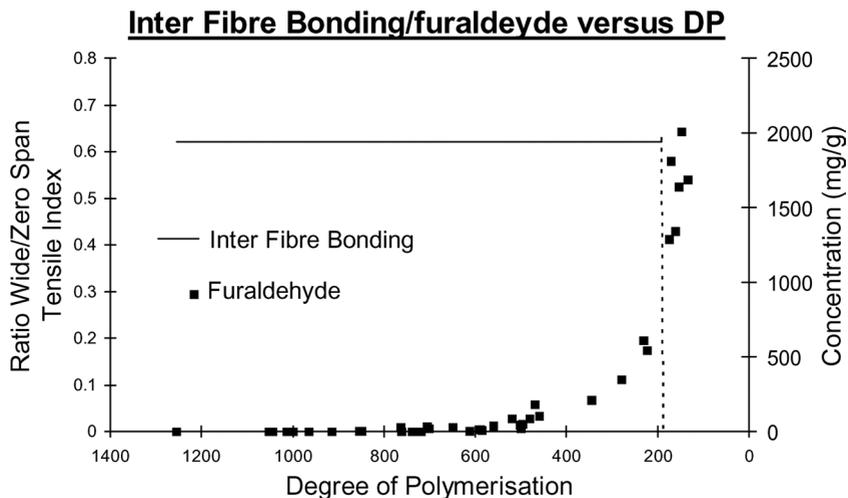


Figure 4. Correlation between the formation of [2FAL] and loss of DP [42].

furfural concentration and the suspected DP of paper insulation. The most often quoted relationship is in the form of equation (8)

$$\text{Log}_{10}[2FAL] = A - B * [DP] \tag{8}$$

Where [2FAL] is the concentration of 2-furfuraldehyde in PPM, both A and B are correlation constants. According to Xue Chendong [43], A = 1.51, B = 0.0035, which predicts a [2FAL] concentration of 6.5 ppm corresponding to a DP of 200. However, it should be noted here that challenges remain in the real world to quantitatively correlate the measured furfural level with the real degradation degree of paper as indicated by its DP. A number of reasons contribute to this uncertainty. There are obvious differences in the equilibrium of furanic compounds between the transformer oil and the paper insulation owing to variation with temperature and oil condition. Both temperature and oil change can affect on measurable furan concentration [12, 44]. Figure 5 illustrates the Doble PowerTest experience [45] which plots the maximum furfural level from UK power transformers removed from service against the lowest DP together with a comparison with the predicted

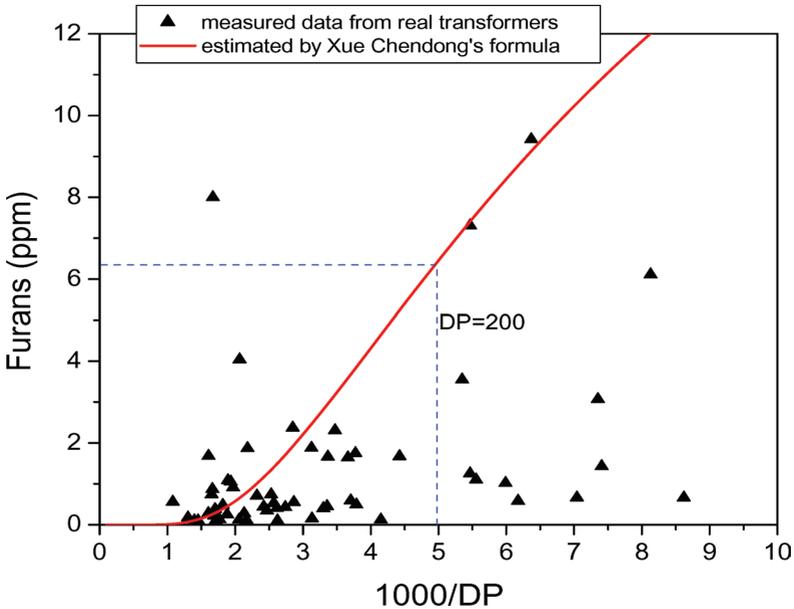


Figure 5. Correlation between DP of winding paper and maximum furfural concentration in oil from scrapped UK power transformers.

correlation in terms of the empirical equation (8). It can be seen that the empirical correlation does not provide a good fit to the results from real transformers, and using the empirical correlation to estimate DP from measured furan concentrations would seriously either underestimate or overestimate the actual paper ageing state.

Jalbert *et al.* [46] have recently reported a linear relationship between one of the oil-soluble degradation by-products, i.e. methanol (CH_3OH), and the number of rupture of 1,4- β -glycosidic bonds of cellulose, regardless of the type of paper (ordinary Kraft or thermally-upgraded (TU) Kraft paper). According to the authors' description, stability tests showed that the methanol content in oil is stable under the oxygen and temperature conditions of open-breathing transformers; the presence of methanol was further detected in 94% of oil samples collected from over than 900 in-service pieces of oil-filled equipment. This finding may introduce the possibility of using methanol as a potential ageing indicator together with furfurals, CO and CO_2 for assessing the paper insulation condition in power transformers.

On the rate of paper degradation

Degradation rates of paper and paper insulation under in-service environmental conditions are among the most important parameter for determining paper permanence and durability and predicting paper life expectancy. There has been a substantial body of knowledge which contributes to our understanding of the rate of paper degradation in terms of its dependence either on tensile strength (TS) or degree of polymerization (DP) of paper.

While many have wrestled with the problem of paper degradation rate, and have contributed to an improved understanding, few pioneering research works, conducted and published in 1930s and 1940s, have become milestones on the road towards the ability to quantitatively evaluate the rate of paper degradation and the life performance of paper.

In the field of transformer insulation, for at least 75 years it has been recognized that thermal degradation of transformer paper insulation results in the reduction of its mechanical properties, and the rate of degradation depends on the rate of tensile strength loss. In a 1930 paper, V. M. Montsinger [47] first described a systematic thermal degradation study in transformer oil as well as in air over a period of 9 years on the tensile strength of yellow varnished cambric, the paper insulation used in transformers in that era. The accelerated thermal degradation data showed a gradual loss of tensile strength over time at temperature, with an accelerated rate of reduction as temperature increased. Similar data for linen paper was also reported by F. M. Clark [48] in 1935 which showed not only the same gradual reduction

of tensile strength but also the like fashion of other mechanical properties like burst strength, tear strength and stretch. Montsinger's pioneering work resulted in an empirical formula

$$t_f = A_0 \exp(-mT) \quad (9)$$

Where t_f is the time to failure, T is the temperature in Celsius, and A_0 and m are empirical constants. A milestone product of this classic study was the well-known 10°C rule in electricity industry, which states that the thermal life of paper is halved for each increase of 10°C or conversely doubled for each decrease of 10°C. It is interesting to note that the original experimental observation, made by Montsinger, is that the doubling factor was not a constant at all degradation temperature ranges. In the vicinity of 100 ~ 110°C, the rate of degradation to double for each 6°C increase in temperature, and at 120°C and higher a temperature increase of 8°C was required to double the degradation rate. However, people tend to remember it as a constant factor of 10°C. The rate of paper tensile strength loss had been formulated empirically by researchers at Weidmann® transformers [32] as follows:

$$TS = TS_0 e^{-C_{TS}t} \quad (10)$$

Where TS_0 and TS are the tensile strength values before and after an ageing degradation time respectively, C_{TS} is the coefficient of ageing degradation rate by 1/days and t is the duration of ageing by days. This rate equation has the advantage of requiring fewer data points, but can only be applied to long-term ageing of paper.

A more significant advance in improving the predictability of paper degradation rate was made by Dakin [16]. In 1948, he published a classical article "Electrical Insulation Deterioration Treated as a Chemical Rate Phenomena" which proposed a chemical rate theory interpretation of thermal ageing and paper degradation. This is probably the first time that the observed physical changes during the thermal degradation were found to be a reflection of internal chemical change. Since the ageing degradation processes are chemical in nature, the rate of change of any measured physical property might therefore be expressed in the form of a reaction rate constant,

$$k_0 = A \exp(B/(T+273)) \quad (11)$$

Where A and B are constants determined by the activation energy and reaction rate of the particular degradation reaction, and T is temperature. This form of degradation rate relationship is frequently referred to as an

Arrhenius chemical reaction rate equation in literature, and has become the backbone of the existing knowledge of thermal degradation and has been in use ever since.

Apart from the use of tensile strength as most sensitive physical parameter of paper to degradation, historically, people have been using DP as most sensitive chemical parameter of paper to measure and characterize the extent of degradation of paper too. The traditional view on the subject of the kinetics of paper degradation has been to assume that the rate of degradation of paper can be described by an equation developed first by Ekenstam [15] in 1936,

$$\ln\left(1 - \frac{1}{DP_0}\right) - \ln\left(1 - \frac{1}{DP}\right) = kt \quad (12)$$

Where DP_0 and DP are the degree of polymerization before and after the degradation, k is the first-order rate constant and t is the degradation time. This milestone product is derived by assuming a random first-order chain scission reaction, based on a pioneering theoretical work of Kuhn and co-workers [14] who investigated the degradation of cellulose from a theoretical statistical view. In modern literature the original Ekenstam equation (12) is more usually used as the zero-order approximation as

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \quad (13a)$$

which gives a direct linear relationship of reciprocal DP with degradation time t . In a heterogeneous cellulose system, the Ekenstam equation (13a) also has to be modified to a general approach by taking into account the effect of physical structure on hydrolysis degradation as shown in equation (13b)

$$\frac{1}{DP} - \frac{1}{DP_0} = \alpha kt \quad (13b)$$

Here α represents the accessible fraction of bonds in a practical cellulose system in the determination of the rate of bond scission [18, 19, 49]. The degradation rate expression either in the form of Equation (10a) or in the form of equation (10b) has been widely used in some later studies of paper degradation under a variety of experimental conditions such as acidic degradation, light ageing, dry or moist thermal ageing in ovens [20, 25, 26, 29, 50, 51] and provided a practical relationship that served to improve the predictability of paper degradation.

An overview of the traditional approach to the rate of degradation of

cellulose and paper should emphasize that reciprocal DP instead of DP being plotted as a function of time has been widely accepted as a “standardized” approach to the rate of cellulose and paper degradation. This could be seen more clearly from the arguments made by Bryce and Greenwood [52] in 1957 and Sharples [19] in 1971. In their kinetic analysis of the degradation of high polymers (time scales are about 100 minutes and 200 hours), Bryce and Greenwood [52] argues that “*the correct formulation for measuring degradation can be obtained following the method of Ekenstam (1936). . . . for either a zero- or first-order reaction, the degradation rate constant in the initial stages is proportional not to DP but to DP^{-1} , and DP^{-1} versus t will be linear. For large amounts of degradation, this relationship will still hold for a zero-order reaction, but $\ln(1 - DP^{-1})$ versus t is necessary for a first-order reaction as higher terms in the expansion are then required*”. Similarly, Sharples [19] claimed that “*a rectilinear plot is obtained if the reciprocal of DP is plotted as a function of the time; while the direct plot of DP as a function of time takes the form of a rectangular hyperbola which is considered to be obviously misleading*”. However, before chose to accept these arguments, it is vital to recognize that that was the situation as of 1957 and 1971, and a different verdict could be given today. It is also essential to recognize that the basis of Ekenstam equation (13) is that the polymer is mono-disperse and every bond has the same probability of breaking, which means the linear reciprocal DP model itself is an idealized approach. As has been pointed out by Roberson [1] in 1976 in his special report on the evaluation of paper permanence and durability, “*The changes of a paper property with time are not determined by any single chemical reaction whose effects can be isolated and controlled. Hence, applications of conventional kinetic treatment to aging data on paper are largely empirical*”. The experimental evidences given in the following Section will demonstrate that following simply and blindly the arguments made by Bryce and Greenwood in 1957 and Sharples in 1971 today may not only be misled but also got lost the way forward in underpinning reliability predictions of paper life expectancy [53].

Survey of accelerated degradation experimental results

Before examining the validity of the traditional reciprocal DP model proposed for the rate of paper degradation, we present in this Section some of the most significant degradation rate experimental data reported in literature.

It has been recognized for nearly a century that acidity is a major factor contributing to the degradation of cellulose containing materials and acids catalyze the hydrolysis [18, 31, 54, 55]. Experiments demonstrated that cotton cellulose regenerated from cuprammonium and cupriethylenediamine

solution contains randomly distributed linkages which are approximately 10,000 times more sensitive to acids than the normal glucosidic linkages [18]. Daruwalla and Narsian [54] further claimed that homogeneous hydrolysis of regenerated cellulose in 85% phosphoric acid (H_3PO_4) at 25°C can be best represented by first-order kinetics, and the activation energy for the homogeneous hydrolysis is of the same order of magnitude as that found for the hydrolysis of the β -glucosidic linkages.

Figure 6 shows the accelerated ageing degradation rate data of Daruwalla and Narsian [54] for regenerated cellulose in 85% phosphoric acid at three different temperatures of 25°C, 35°C and 45°C, which confirms a linear relationship of reciprocal DP with degradation time for acid-catalysed hydrolytic degradation of cellulose.

In a 1996 paper, Zou, Uesaka and Gurnagul of Pulp and Paper Research Institute of Canada described a comprehensive investigation on the accelerated ageing rates of bleached bisulfite pulp (BBSP) samples [26]. As shown in Figure 7, the data reported by Zou *et al.* [26] also confirm a linear relationship of reciprocal DP with degradation time.

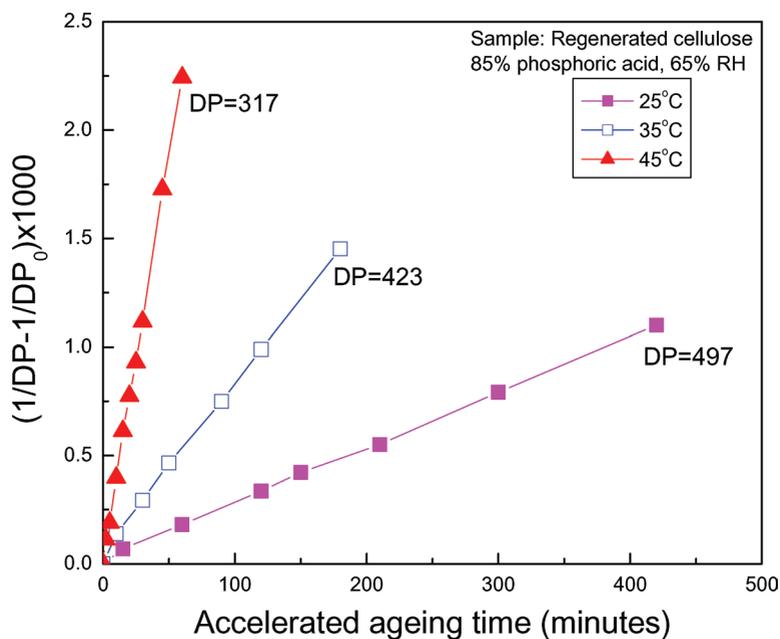


Figure 6. Accelerated ageing degradation rate data of Daruwalla and Narsian [54] for regenerated cellulose in 85% phosphoric acid and 65% relative humidity.

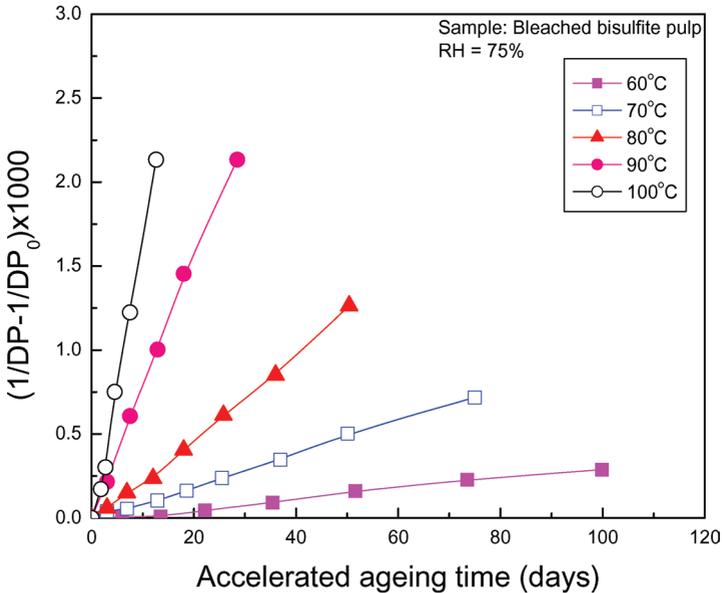


Figure 7. Accelerated ageing degradation rate data of Zou *et al.* [26] for the BBSP paper with a relative humidity of 75%.

A survey conducted by Emsley and Stevens [6, 7] in 1994 showed that a linear relationship of reciprocal DP with degradation time holds for the majority of the accelerated ageing data available in literature for thermal degradation of Kraft paper under a variety of experimental conditions (in vacuo, in nitrogen, air and oxygen, and in transformer oil).

However, numerous accelerated ageing degradation rate results reported in the last 15 years, as illustrated in Figures 8–13, are showing cumulative evidences that a linear relationship of reciprocal DP with degradation time is valid only at the *initial* degradation time and therefore Ekenstam equation (13) does not track experimental results of paper degradation over a long-time period under practical operation conditions.

As a matter of fact, it has been well established in literature that a rectilinear plot cannot be always obtained even if the reciprocal of DP is plotted as a function of the time, the deviations from Ekenstam equation (3) result in a downward curvature of the kinetic plot of the measured DP data so that two or three distinct degradation phases with differing chain-scission rates can be distinguished [23, 24, 38, 54, 56–58]. Also, despite ongoing debates in literature on the rate equation of cellulose and paper degradation, consensus

has slowly emerged on at least one point: whatever the experimental conditions and the paper materials, when DP approaches the levelling-off degree of polymerization (LODP), Ekenstam equation (3) is fairly invalid [38].

In a letter to the Editor published in *Cellulose*, Emsley and Heywood *et al.* [38] firstly proposed that the reaction rate k in Ekenstam equation (13) should not be a constant but decrease with the ageing degradation time; and the measured DP data is better represented by a degradation rate equation in the form

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{k_{10}}{k_2} [1 - \exp(-k_2 t)] \quad (14)$$

Where k_{10} and k_2 are constants. Zervos and Moropoulou [59] proposed a kinetic model that describes the autocatalytic depolymerisation of pure cotton cellulose in sealed vessels as

$$\left(\frac{1}{DP} - \frac{1}{DP_0} \right) \times 100 = a [2^{kt} - 1] \quad (15)$$

Where k and a are constants. Equation (15) has been verified to be valid using the accelerated ageing data of Whatman (No. 2) filter paper in sealed glass jars of $76 \pm 1\%$ relative humidity at 80°C up to 150 days.

On the end-of-life criteria

In literature there is no agreement yet on the definition of paper end-of-life. The uncertainty in defining the end point of paper life is actually due to the nature of degradation, because degradation is not a measurable quantity and if an end life point is to be objectively defined, it must be done in terms of a measurable physical characteristic of the material [60]. This could be either a mechanical property like tensile strength, or a chemical property like DP, or an electrical property like dielectric strength. On the other hand, the paper end life point could be either an absolute value of the selected property or percentage retention. In any case, the environmental condition of paper degradation must also be defined for reproducibility.

Prior to 1995, the engineering assessment had been considering tensile strength as the critical properties of paper and 50% tensile strength retention being accepted as the criterion of end of service life of paper. This was introduced into ANSI/IEEE guide for loading mineral oil immersed transformers, which gives a transformer life of only 7.42 years at a continuous winding temperature of 110°C for the 65°C rise units.

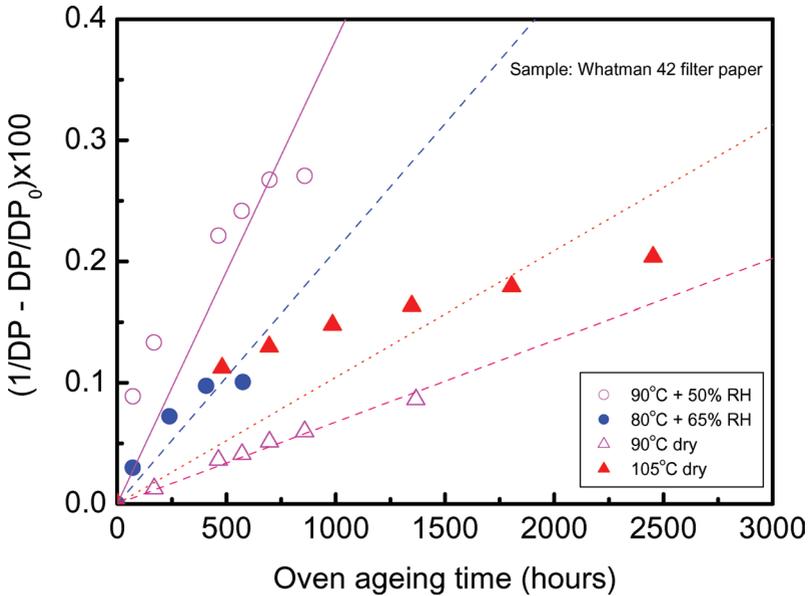


Figure 8. Accelerated thermal degradation rate data of Whitmore and Bogaard [23] for Whatman 42 filter paper in air-circulating oven.

Currently international standards such as IEEE C57.91 (1995) [61] and IEC 60076-7 [62] and all UK larger utilities accept DP of 200 as paper end of life definition [63], which gives a life of 17.1 years at the temperature of 110°C for the 65°C rise units. However, uncertainty in the minimum acceptable value for DP of paper remains.

Summary

To summarize the current understanding in determining the rates of paper degradation, although the methods are successful in different respects and have obtained great achievements, quantitative understanding is still limited. There are still no reliable and standardized methods for directly determining the long-term degradation behaviour of paper. Practical assessment of paper permanence and in service life has to rely heavily on empirical knowledge. The difficulties in moving away from the present state of empiricism, according to the understanding of the present author, are rooted in the following causes.

- (1) The mechanisms of paper degradation are varied and complex due to a

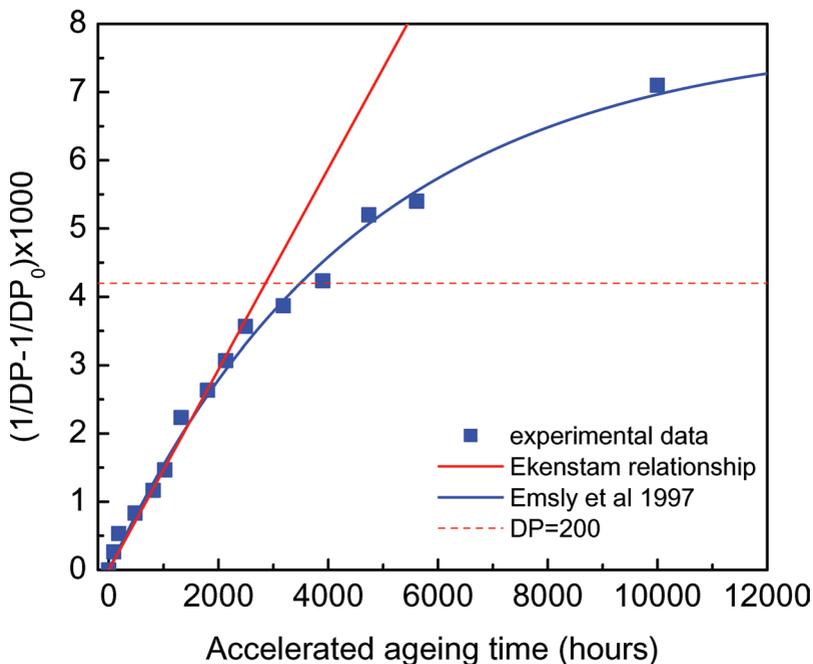


Figure 9. Accelerated ageing degradation rate data of Emsly *et al.* [38] for Kraft transformer paper in air.

(Editor's Note: Reproduced in colour as Plate 23 between pages 1000 and 1001)

range of factors such as material constituent and properties, morphology and inhomogeneous, in-service conditions.

- (2) The types of microstructure defects in paper are varied and complicated and therefore the attendant degradation mechanisms are characterized by collective evolution of distributed entities of defects at microscopic or sub-microscopic scales rather than a single, dominant macroscopic parameter.
- (3) There has been no methodology to allow an accommodation of the effects of various life-controlling mechanisms into material parameters.

PERCENTAGE DP (DEGREE OF POLYMERIZATION) LOSS RATE MODEL

In recognizing the limitation of the traditional reciprocal DP model approach, and seeking to develop the rate equation of paper degradation that

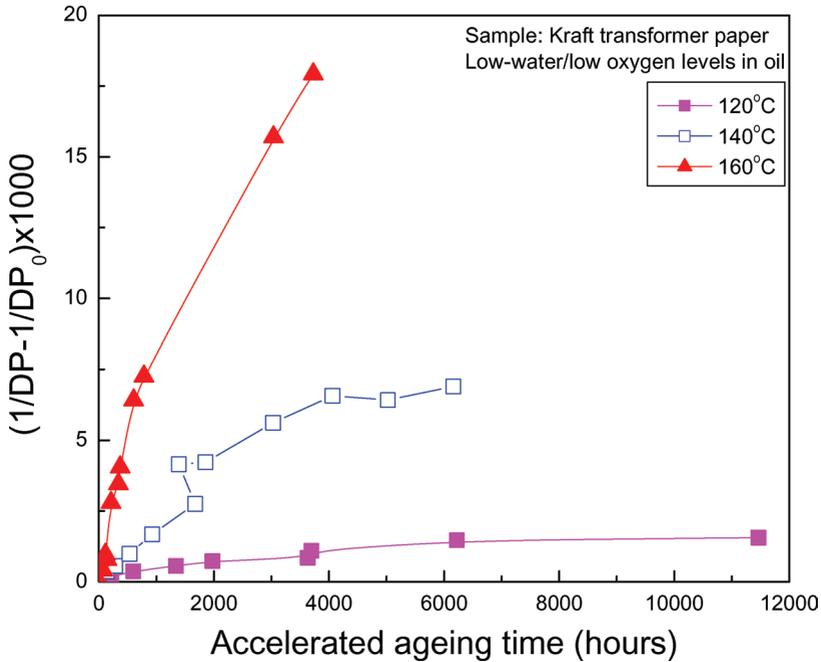


Figure 10. Accelerated ageing degradation rate data of Emsly *et al.* [36] for Kraft transformer paper under low-water/low oxygen level in transformer oil.

will closely track experimental results over a long-time period under real operating conditions, the present author and his co-worker [64] have recently proposed an alternative approach. The key element of the alternative approach is the percentage DP loss, ω_{DP} , which is in fact a cumulative degradation function and can be generally defined as

$$\omega_{DP} \equiv 1 - \frac{DP}{DP_0} \quad (16)$$

The rate equation governing the time dependence of ω_{DP} assumes in the form

$$\frac{d\omega_{DP}}{dt} = k_{DP}(\omega_{DP}^* - \omega_{DP}), \quad \omega_{DP}(t=0) = 0 \quad (17)$$

Equation (16) relates the time rate of change of the accumulated DP degradation $d\omega_{DP}/dt$ to the residual DP level available for the degradation $(\omega_{DP}^* - \omega_{DP})$ times the DP degradation reaction rate constant k_{DP} . The initial

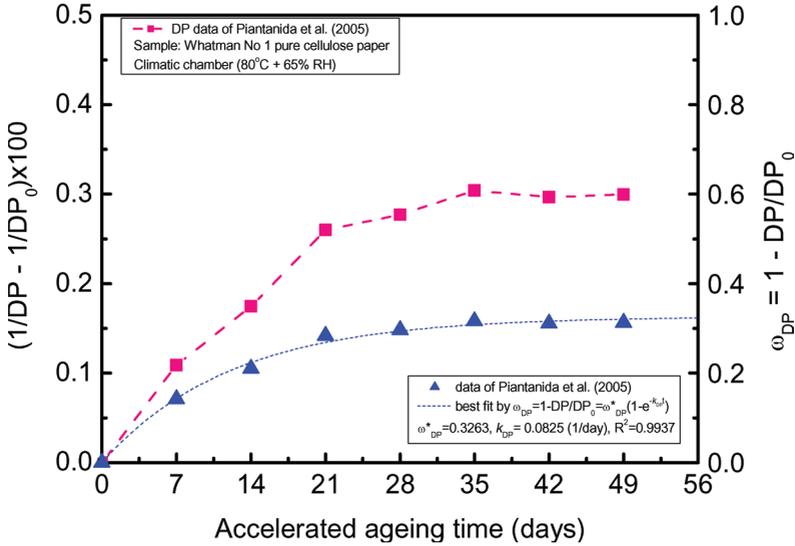


Figure 11. Accelerated ageing degradation rate data of Piantanida *et al.* [58] for Whatman No 1 pure cellulose paper in a climatic chamber (80°C + 65%RH).

condition $\omega_{DP}(t = 0) = 0$ implies that the paper has undergone no previous degradation. For a constant reaction rate k_{DP} the exact solution of equation (17) reads [64]

$$\omega_{DP} \equiv 1 - \frac{DP}{DP_0} = \omega_{DP}^* \left(1 - e^{-k_{DP}t}\right) \quad (18)$$

Equation (18) is a new rate equation of paper degradation using percentage DP loss but the reciprocal DP. Note ω_{DP}^* can be determined by introducing the constraint condition, $\omega_{DP}(t = t_f) = 1$, t_f is the time to failure of paper sample under specific degradation conditions. ω_{DP}^* in equation (18) can therefore be either smaller than or equal to or larger than 1, depends on the degradation conditions.

Investigation has been made to find a possible correlation between the percentage DP loss rate equation and the traditional reciprocal DP rate model. Starting with Ekenstam equation (12), which is the exact first-order relationship between the number-average DP and the number of bond available for the degradation, simply by making a rearrangement in equation (12) gives an exactly identical but modified Ekenstam equation:

$$1 - \frac{DP}{DP_0} = \frac{(DP_0 - 1)}{1 + (DP_0 - 1)(1 - e^{-kt})} (1 - e^{-kt}) \quad (19)$$

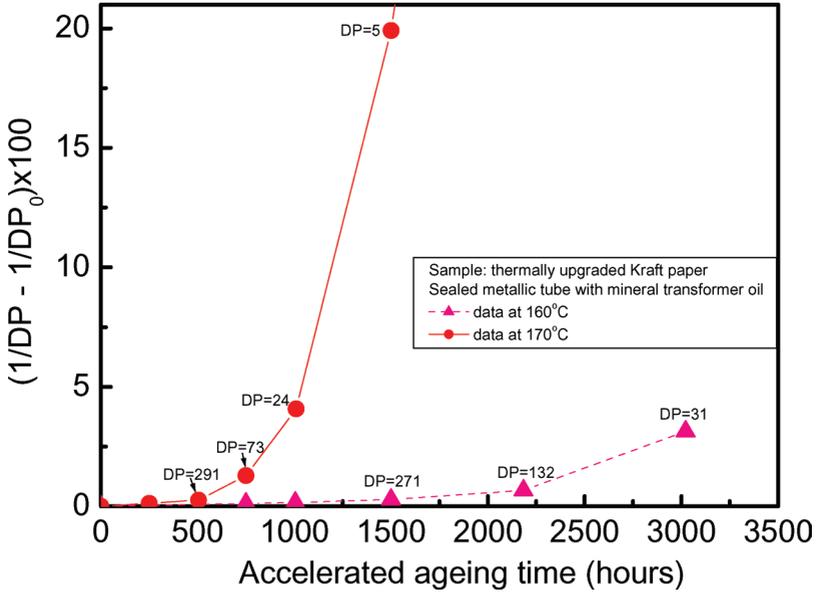


Figure 12. Accelerated ageing degradation rate data of McShane *et al.* [57] for thermally upgraded Kraft insulation paper in sealed metallic tubes with mineral transformer oil.

Assume k_{DP} is identical to k in equation (19) we immediate have

$$\omega_{DP}^* \equiv \frac{(DP_0 - 1)}{1 + (DP_0 - 1)(1 - e^{-kt})} \tag{20}$$

When both DP_0 and DP are large (i.e. the extent of DP degradation reaction is small), using the approximation as same as in the Ekenstam's approaches in obtaining equation (13), we can obtain an exactly identical to equation (13) but the modified expression as

$$1 - \frac{DP}{DP_0} = \frac{DP_0 kt}{1 + DP_0 kt} \tag{21}$$

Figures 14–19 summarize application as well as comparison of both equation (18) and equation (21) with real accelerated degradation rate results of various paper samples over a wide temperature range and varied degradation conditions. The estimated values of the parameters for curve fitting together with the corresponding regression coefficients are summarized in Tables 1–6.

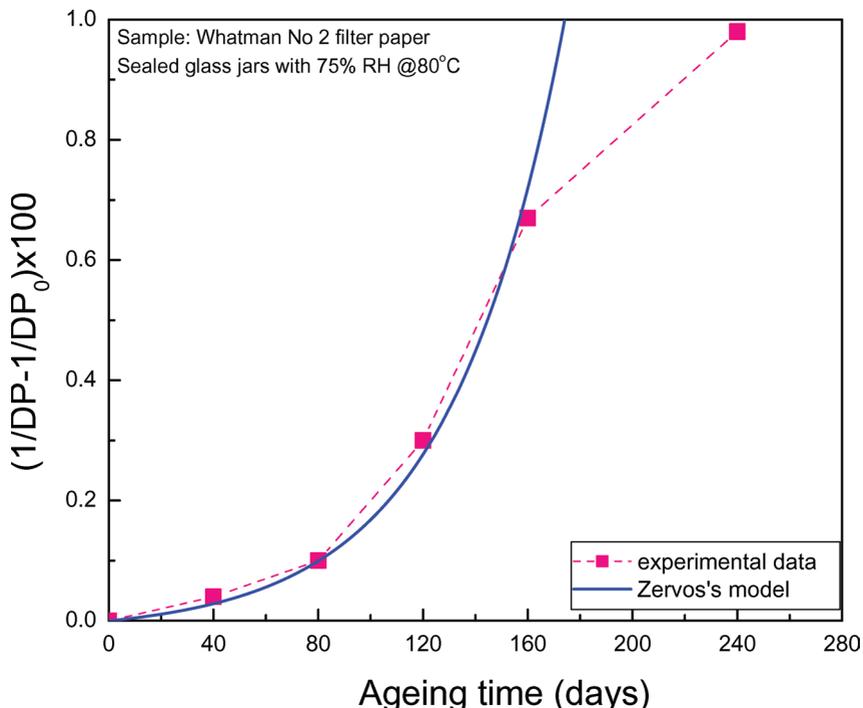


Figure 13. Accelerated ageing degradation rate data of Zeros and Moropoulou [59] for Whatman No 2 filter paper in sealed glass jars with 75% RH.

Clearly, equation (18) has explained the real experimental data of different cellulose materials carried out under a variety of experimental conditions. The validation and universality of the percentage DP loss rate model can therefore be made.

To this end, a simple but far-reaching statement can now be made. Briefly, some experimental data can be described equally well with both percentage DP loss rate model and reciprocal DP rate model. However, this does not mean that all data that can be described by the percentage DP loss rate model can also be described by reciprocal DP rate model.

PERCENTAGE TS (TENSILE STRENGTH) LOSS RATE MODEL

Similar to the percentage DP loss rate model, the present author and his co-worker have also developed a percentage TS (tensile strength) loss rate model,

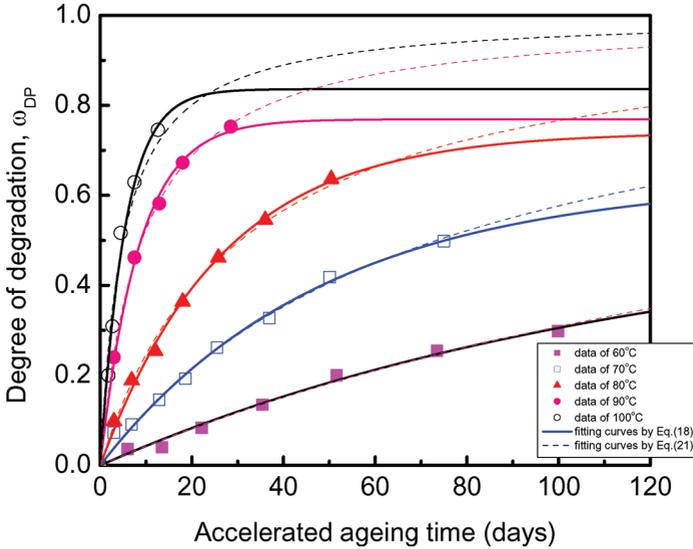


Figure 14. Degree of degradation change during accelerated thermal degradation of BBSP hand sheets. DP data after Zou *et al.* [26].

Table 1. Calculated parameters for fitting equations (18) and (21) to the data in Figure 14.

T ($^{\circ}\text{C}$)	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/day)	R^2	k ($\times 10^{-5}$, 1/day)	R^2
60	0.5422	0.0083	0.9917	0.3338	0.9910
70	0.6359	0.0206	0.9930	1.0195	0.9931
80	0.7407	0.0378	0.9970	2.4469	0.9967
90	0.7686	0.1180	0.9982	8.2545	0.9993
100	0.8364	0.1846	0.9904	15.060	0.9760

with aim to closely track degradation experimental results of paper over a long-time period under real operating conditions. The key element of the percentage TS loss rate model is the cumulative degradation function defined by the percentage loss in tensile strength of paper [64]:

$$\omega_{TS} \equiv 1 - \frac{TS}{TS_0} \tag{22}$$

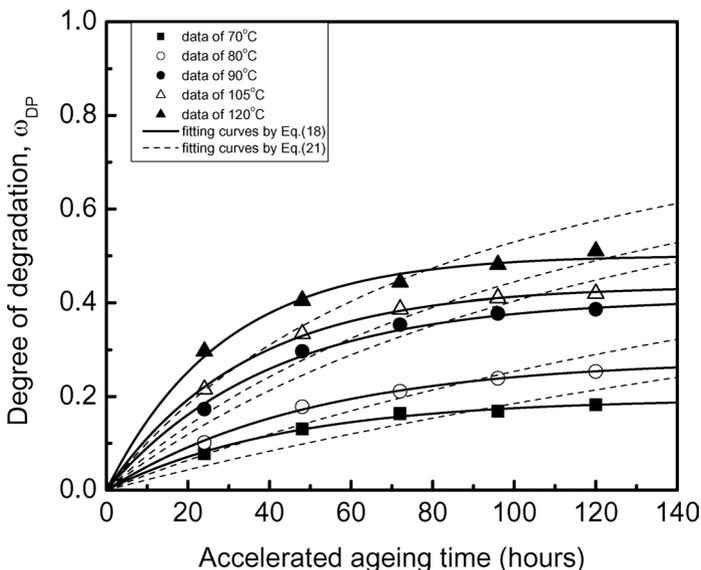


Figure 15. Degree of degradation change during accelerated thermal degradation of Kraft paper in air. DP data after Soares *et al.* [39].

Table 2. Calculated parameters for fitting equations (18) and (21) to the data in Figure 15.

T ($^{\circ}C$)	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/hour)	R^2	k ($\times 10^{-6}$, 1/hour)	R^2
70	0.1952	0.0227	0.9968	1.9189	0.8613
80	0.2796	0.0199	0.9987	2.8741	0.9212
90	0.4149	0.0248	0.9969	5.7227	0.9260
105	0.4357	0.0294	0.9995	6.7625	0.9084
120	0.5015	0.0351	0.9959	9.5182	0.9131

The percentage TS loss rate equation of paper degradation is in the form [64]

$$\omega_{TS} \equiv 1 - \frac{TS}{TS_0} = \omega_{TS}^* (1 - e^{-k_{TS}t}) \quad (23)$$

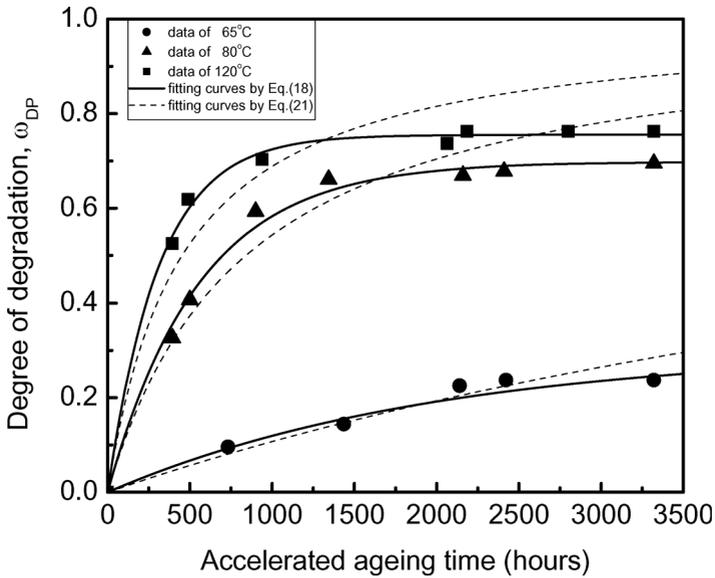


Figure 16. Degree of degradation change during accelerated thermal degradation of Kraft paper in mineral transformer oil. DP data after Soares *et al.* [39].

Table 3. Calculated parameters for fitting equations (18) and (21) to the data in Figure 16.

T ($^{\circ}\text{C}$)	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/hour)	R^2	k ($\times 10^{-6}$, 1/hour)	R^2
65	0.3032	0.0005	0.9740	0.1014	0.9351
80	0.6983	0.0018	0.9931	1.0059	0.9377
120	0.7554	0.0032	0.9971	1.8681	0.8972

Where k_{TS} is the tensile strength degradation rate constant and ω_{TS}^* is a parameter that may be determined by introducing the constraint condition $\omega_{TS}(t = t_f) = 1$, t_f is the time to failure.

Equation (23) is a new rate equation of paper degradation using percentage TS loss. Note the similarity of mathematical expression between equations (23) and (18) does not necessarily suggest a linear relationship between the tensile strength and the degree of polymerization. This is not only because

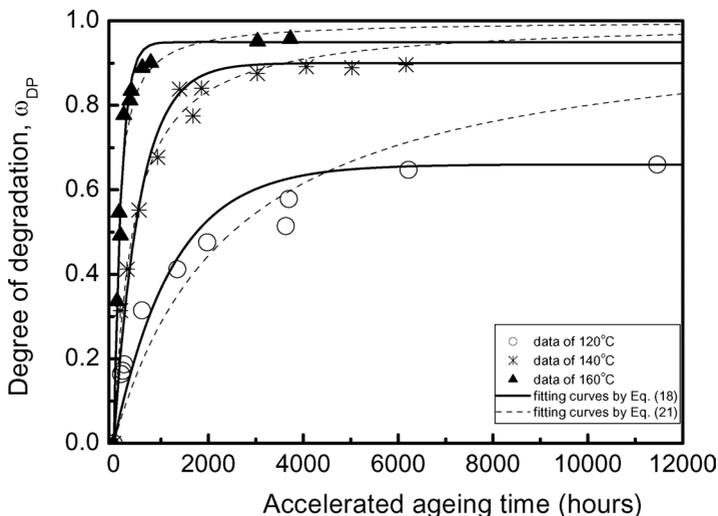


Figure 17. Degree of degradation change during accelerated thermal degradation of Kraft paper in mineral oil at low-water/low oxygen levels. DP data after Emsley *et al.* [36].

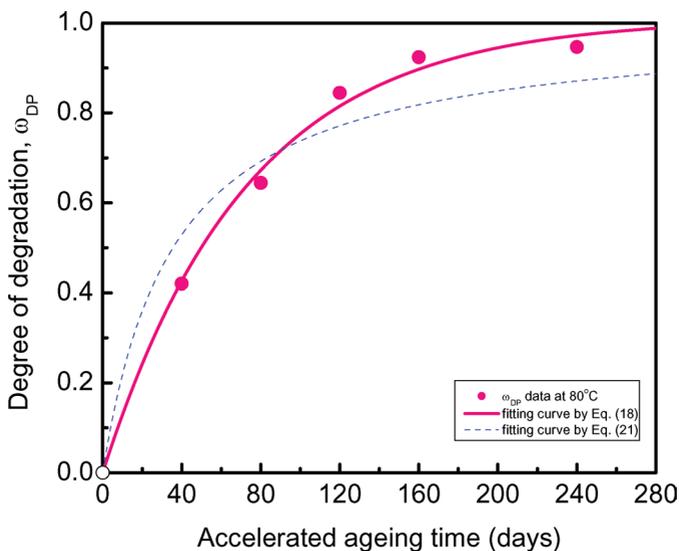


Figure 18. Degree of degradation change during accelerated thermal degradation of pure cotton cellulose in sealed vessels. DP data after Zervos and Moropoulou [59].

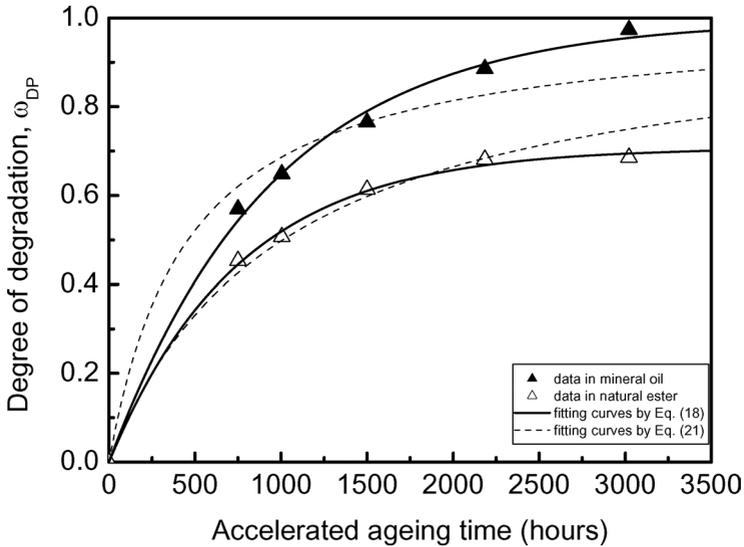


Figure 19. Degree of degradation change during accelerated thermal degradation of thermally upgraded Kraft insulation paper in sealed metallic tubes at 160°C with mineral oil and natural ester respectively. DP data after McShane *et al.* [57].

Table 4. Calculated parameters for fitting equations (18) and (21) to the data in Figure 17.

T (°C)	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/hour)	R^2	k ($\times 10^{-6}$, 1/hour)	R^2
120	0.6600	0.0008	0.9167	0.3200	0.8199
140	0.9000	0.0018	0.9719	2.0080	0.9865
160	0.9500	0.0063	0.9796	8.0000	0.9673

different values of the degradation rate constants k_{TS} and k_{DP} but also because different values of the parameters ω_{TS}^* and ω_{DP}^* , even for the same degradation experiment of the same paper sample. It is also interesting to note that Weidmann® empirical equation (10) is exactly a special case of equation (23) when set $\omega_{TS}^* = 1$.

Figures 20–23 summarize application as well as comparison of both

Table 5. Calculated parameters for fitting equations (18) and (21) to the data in Figure 18.

T ($^{\circ}C$)	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/day)	R^2	k ($\times 10^{-5}$, 1/day)	R^2
80	1.0100	0.0137	0.9954	1.5503	0.9458

Table 6. Calculated parameters for fitting equations (18) and (21) to the data in Figure 19.

$T = 160^{\circ}C$	Equation (18)			Equation (21)	
	ω_{DP}^*	k_{DP} (1/hour)	R^2	k ($\times 10^{-6}$, 1/hour)	R^2
In mineral oil	0.9963	0.0011	0.9970	1.8924	0.9692
In natural ester	0.7076	0.0013	0.9985	0.8624	0.9845

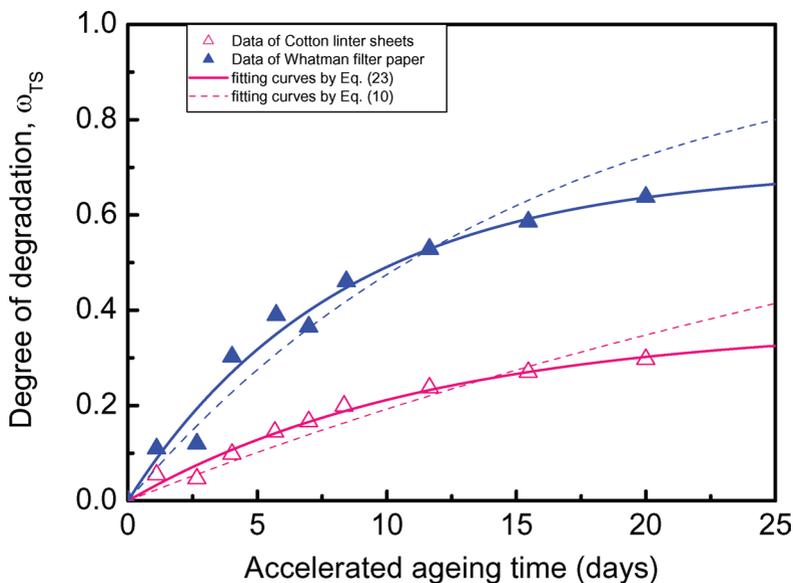


Figure 20. Percentage TS loss of Whatman filter paper (II) and cotton linter sheets during thermal ageing at $90^{\circ}C$ and 80% RH. TS data after Zou *et al.* [25].

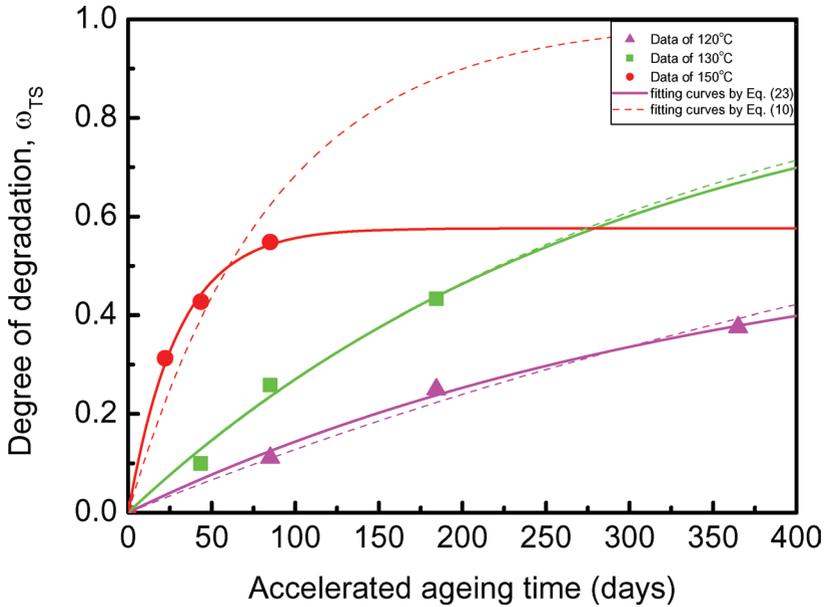


Figure 21. Percentage TS loss of thermally upgraded insulation paper aged in mineral transformer oil. TS data after Gasser *et al.* [67].

equation (23) and equation (10) with real accelerated degradation rate results of various paper samples over a wide temperature range and varied degradation conditions. The estimated values of the parameters for curve fitting together with the corresponding regression coefficients are summarized in Tables 7–10. It is interesting to observe that nearly all values of ω_{TS} in Tables 7–10 are less than or equal to 1, except the values of $\omega_{TS}^* = 4.78$ in Table 9. The larger value of $\omega_{TS}^* = 4.78$ for thermal degradation of thermally upgraded Kraft insulation paper/mineral oil in sealed metallic tubes in Table 9

Table 7. Calculated parameters for fitting equations (23) and (10) to the data in Figure 20.

90°C@ 80% RH	Equation (23)			Equation (10)	
	ω_{TS}^*	k_{TS} (1/day)	R^2	C_{TS} (1/day)	R^2
Cotton linter sheets	0.3693	0.0851	0.9832	0.0214	0.9205
Whatman filter paper (II)	0.6983	0.1214	0.9767	0.0644	0.9372

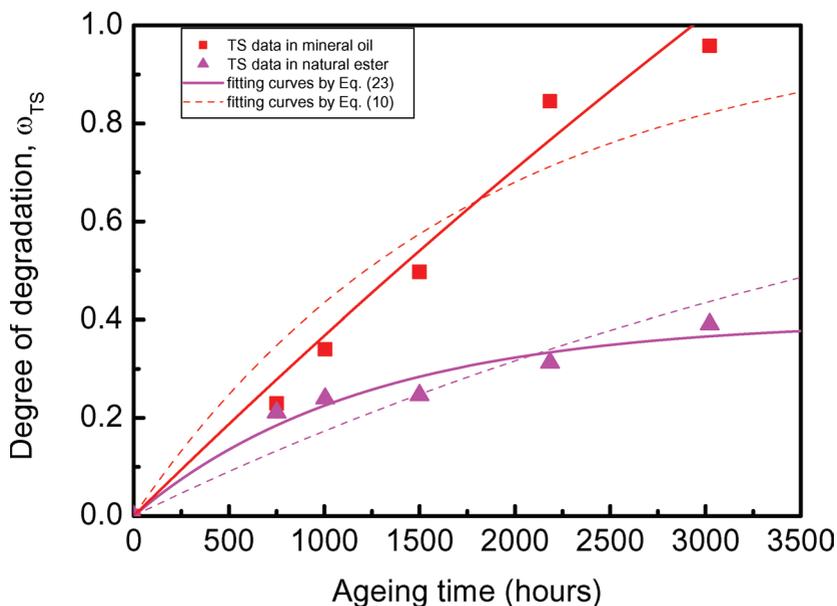


Figure 22. Percentage TS loss of thermally upgraded Kraft paper in sealed metallic tubes at 160°C with mineral oil and natural ester respectively. TS data after McShane *et al.* [57].

Table 8. Calculated parameters for fitting equations (23) and (10) to the data in Figure 21.

$T(^{\circ}C)$	Equation (23)			Equation (10)	
	ω_{TS}^*	k_{TS} (1/day)	R^2	C_{TS} (1/day)	R^2
120	0.5869	0.0028	0.9958	0.0014	0.9873
130	0.9430	0.0034	0.9869	0.0031	0.9868
150	0.5761	0.0335	0.9978	0.0115	0.9119

was attributed obviously to the fact that the degradation process was a prolonged autocatalytic reaction process particularly with exist of metallic catalysts. The effect of metals on cellulose degradation is well recognized in the literature [65, 66], and it is also well known that both hydrolytic and oxidative processes may occur simultaneously in the ageing of paper [27, 55]. With these in mind, it is reasonably to believe that degradation of thermally

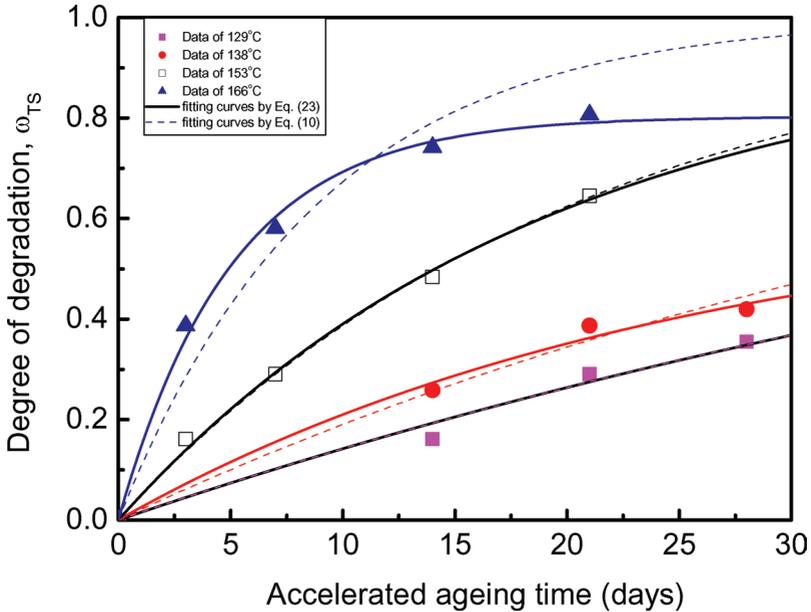


Figure 23. Percentage TS loss of Kraft insulation paper aged in dried and degassed transformer oil. TS data after Hill *et al.* [68].

Table 9. Calculated parameters for fitting equations (23) and (10) to the data in Figure 22.

160°C	Equation (23)			Equation (10)	
	ω_{TS}^*	k_{TS} (1/hour)	R^2	C_{TS} (1/hour)	R^2
In natural ester	0.3990	0.0008	0.9613	0.0002	0.8460
In mineral oil	4.7800	0.0001	0.9786	0.0006	0.9027

upgraded Kraft insulation paper in sealed metallic tubes in Figure and Table 9 is caused by at least two processes—acid-catalyzed hydrolysis and metal-catalyzed oxidation. From this point, it is remarkable that equation (23) holds even in the mixed hydrolytic and oxidative processes of cellulose degradation.

In summary, as shown clearly in Figures 20–23 and Table 7–10, the excellent agreement between the predictions by equation (23) expressed in terms of the percentage TS loss and the real degradation rate data appears to be justified.

Table 10. Calculated parameters for fitting equations (23) and (10) to the data in Figure 23.

$T(^{\circ}C)$	<i>Equation (23)</i>			<i>Equation (10)</i>	
	ω_{TS}^*	k_{TS} (1/day)	R^2	C_{TS} (1/day)	R^2
129	1.0000	0.0153	0.9827	0.0153	0.9827
138	0.6419	0.0396	0.9913	0.0211	0.9856
153	0.9537	0.0526	0.9972	0.0490	0.9971
166	0.8030	0.1987	0.9962	0.1118	0.9434

CONTINUOUS DISTRIBUTION KINETICS THEORY OF PAPER DEGRADATION

In this Section we aim to derive Ekenstam equation (13) as well as Ding and Wang equation (18) and develop continuous distribution kinetics theory of cellulose and paper degradation.

Continuous distribution kinetics

The continuous distribution kinetics approach is a straightforward and effective technique (procedure) to represent macromolecular reactions and to analyze the change in molecular weight distributions (MWDs) on degradation of a polymer containing molecules with different molecular weights [69–73]. Continuous-distribution mass balances are written for the various steps involved in the radical mechanism. The rate coefficients are here assumed to be independent of MW, a reasonable assumption at low conversions. The integro-differential equations obtained from the mass balances can be solved for MW moments. These moment equations are usually coupled ordinary differential equations that, in general, can be solved numerically.

Application of continuous distribution kinetics to degradation of cellulose

Cellulose consists of a long chain of glucose units joined by $\beta(1,4)$ -glucosidic linkages. We define $C(x)$ to be a cellulose molecule with molecular weight (MW) x which is a continuous variable. The decrease of average molecular weight as the reaction proceeds is evidence of cellulose degradation. Cellulose degradation can be understood as a combination of

- (1) random degradation: $C(x') \rightarrow C(x) + C(x' - x)$ and
- (2) specific degradation: $C(x') \rightarrow C(x_i) + C(x' - x_i)$

The time-dependent cellulose molar concentration in the MW range $(x, x + dx)$ at time t is represented as $C(x, t)dx$. The temporal behaviour of the distribution is described by the time-dependent moments of the molar MWD $c(x, t)$ as follows:

$$c^{(n)}(t) = \int_0^\infty c(x, t) dx^n \quad (24)$$

The zeroth moment $c^{(0)}(t)$ is the molar concentration of the cellulose (mol/l) and the first moment $c^{(1)}(t)$ is the mass concentration (g/l). Number average MW are defined as

$$M_n = c^{(1)} / c^{(0)} \quad (25)$$

The degradation of cellulose can be written as a combination of random scission as follows

$$C(x) \xrightarrow{k_r(x)} C(x') + C(x - x') \quad (26)$$

Using the continuous distribution kinetics and the above assumption, the rate equations of population-balance equations for the degradation of cellulose can be written in terms of the reaction time t as follows:

$$\frac{\partial c(x, t)}{\partial t} = -k_r(x)c(x, t) + 2 \int_x^\infty k_r(x') \Omega(x, x') c(x', t) dx' - k_s(x)c(x) \quad (27)$$

$$\frac{dQ}{dt} = Q^* \int_0^\infty x k_s(x) c(x) dx \quad (28)$$

where Q^* is a dimensionless parameter representing the ratio of phase transformation in mass between cellulose molecular and cellulose degradation products, and $Q^* = 1$ means that a molecular of cellulose with MW x has been fully depolymerised and converted them into cellulose degradation products.

The rate coefficient of random scission is assumed to be proportional to the molecular weight MW as

$$k_r(x) = k_r x \quad (29)$$

And the reaction kernel for equal probability of scission at each bond is

$$\Omega(x, x') \equiv \frac{1}{x} \quad (30)$$

The chain-end scission rate coefficient, $k_s(x)$ is assumed independent of the molecular weight MW as

$$k_s(x) = k_s \quad (31)$$

Thus

$$\frac{\partial c(x,t)}{\partial t} = -k_r x c(x,t) + 2k_r \int_x^\infty c(x',t) \Omega(x,x') dx' - k_s c(x) \quad (32)$$

$$\frac{dQ}{dt} = Q^* k_s \int_0^\infty x c(x) dx \quad (33)$$

Combining equation (32) and equation (33) can quantitatively describe the kinetics of cellulose and paper degradation.

Derivation of reciprocal DP rate equation

The moment operation is applied to equation (32) to obtain the moment differential equation

$$\frac{dc^{(n)}}{dt} = -k_s c^{(n)} - \left(\frac{n-1}{n+1} \right) k_r c^{(n+1)} \quad (34)$$

The zeroth and first moment equations together are closed as follows

$$\frac{dc^{(0)}}{dt} = -k_s c^{(0)} + k_r c^{(1)} \quad (35)$$

$$\frac{dc^{(1)}}{dt} = -k_s c^{(1)} \quad (36)$$

The physical meaning of the zeroth moment equation is that the molar of cellulose, $c^{(0)}$, decreased by chain-end scission because amounts of molecules convert into monomer thoroughly, and increased with random scission because one molecule is broken into two in each reaction event. The mass of cellulose, $c^{(1)}$, decreases only by chain-end scission because the mass of is loss to monomer. Solving both the zeroth and the first equations simultaneously with the initial conditions $c^{(0)}(t=0) = c_0^{(0)}$ and $c^{(1)}(t=0) = c_0^{(1)}$, yields

$$c^{(0)} = \left(c_0^{(0)} + k_r c_0^{(1)} t \right) \exp(-k_s t) \quad (37)$$

$$c^{(1)} = c_0^{(1)} \exp(-k_s t) \quad (38)$$

Division of equation (38) by equation (37) yields an equation for number average MW in terms of the initial value, $M_n(t=0) = M_{n0}$,

$$M_n(t) = c^{(1)} / c^{(0)} = \frac{M_{n0}}{1 + k_r t M_{n0}} \quad (39)$$

Rearranging this equation produces

$$\frac{1}{M_n} - \frac{1}{M_{n0}} = k_r t \quad (40)$$

Bear in mind that DP = Total MW of the cellulose/MW of the repeating unit = M_n/N_0 , therefore, $DP = M_n/N_0$, $DP_0 = M_{n0}/N_0$. Submitting into equation (40) and one immediately derive

$$\frac{1}{DP} - \frac{1}{DP_0} = k' t, \quad k' = N_0 k_r \quad (41)$$

This is exactly the well-known Ekenstam equation (13).

Derivation of percentage DP loss rate equation

Applying the operation of equation (38) to equation (33) yields

$$\frac{dQ}{dt} = Q^* k_s c_0^{(1)} \exp(-k_s t) \quad (42)$$

Applying the initial condition $Q(t=0) = 0$ to equation (42) the relationship between the mass of cellulose degradation products and the time t can be derived as

$$Q = Q_m (1 - \exp(-k_s t)) \quad (43)$$

$$Q_m = Q^* c_0^{(1)} \quad (44)$$

Since the mass of all cellulose degradation products at time t must be equal to the mass of initial cellulose, i.e.

$$Q + c^{(1)} = c_0^{(1)} \quad (45)$$

Rewritten this equation

$$Q = c_0^{(1)} - c^{(1)} = c_0^{(1)} \left(1 - c^{(1)} / c_0^{(1)} \right) = c_0^{(1)} \omega_{DP} \quad (46)$$

Compare equation (43) and equation (46), immediately we can derive the expression for the relationship between ω_{DP} and the time t with the initial condition as $\omega_{DP}(t = 0) = 0$ as

$$\omega_{DP} = \omega_{DP}^* (1 - \exp(-k_s t)); \quad \omega_{DP}^* = Q^* \quad (47)$$

Equation (47) is exactly as same as equation (18) but has been derived from a continuous distribution kinetics theory of cellulose degradation.

In summary, Ekenstam equation (13) as well as Ding and Wang equation (18) have been derived theoretically. It is remarkable to see both percentage DP loss rate equation and reciprocal DP rate equation have the same physical basis and can be united within a continuous distribution kinetics theory of cellulose degradation.

TIME-TEMPERATURE SUPERPOSITION METHOD FOR PREDICTING THE PERMANENCE AND LIFE OF PAPER BY EXTRAPOLATING ACCELERATED AGEING DATA TO IN-SERVICE CONDITIONS

Both conventional method and historical practice for predicting the permanence and life of paper have been by extrapolating accelerated thermal ageing degradation testing data of paper at elevated temperatures to real operating temperature conditions. This is because many of the chemical and physical changes that take place in paper under natural (in-service) ageing conditions occur too slowly to study easily [1, 10, 74–77]. The rate of degradation of paper can be accelerated by a thermally activated process to obtain the failure of paper within a few hours or days. In the absence of fundamental understanding on the chemical reaction kinetics of paper degradation process, it has been the practice of those working in this area to estimate the paper degradation rate constant k by following the loss rates of mechanical (like TS) or physic-chemical properties (like DP) at different temperatures. The temperature dependence of the rate constant k was further assumed to follow the Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (48)$$

Where E_a is the activation energy (J/mol), $R = 8.314$ J/mol/K the gas constant, T the absolute temperature and A the pre-exponential factor. By determining how many hours or days of accelerated ageing are needed at

different temperatures to obtain a certain measurement of paper degradation, a “temperature-versus-time needed” plot can be made. If a log-plot of the failure time ($1/k$) versus the inverse absolute temperature is a straight line, the Arrhenius equation is said to be valid and activation energy is then determined from the slope of the plot using (1). This then will allow one to determine the paper degradation rate at any temperature but raises questions about the validity of the results obtained [8].

Over the last four decades there have been discussions about the suitability of the Arrhenius equation (48) to paper degradation kinetics, not only because of the complex nature of the paper degradation process and the likely changes in the rate-determining parameters, also due to the extrapolation procedure which use only one experimental data point from each accelerated ageing temperature curve and eliminating most of the experimental points from analysis. On the other hand, a significant progress has been achieved in the development of improved methods for analyzing and extrapolating accelerated ageing data of polymers to ambient conditions. In particular, an improved Arrhenius approach that involves applying the time-temperature superposition (TTSP or TTS) method to derive shift factors and probe for Arrhenius behaviour has been successfully used for years in polymers to make predictions of thermal ageing at experimentally inaccessible times [78–82].

Very recently, a significant progress has been achieved in the development of improved Arrhenius approach methods for predicting the permanence and life of paper by extrapolating accelerated ageing data to ambient conditions. The improved Arrhenius approach, first proposed by the present author and his co-worker[83], involves (1) applying the TTS method to test for the presence of suitable shift factors to superpose all of the raw accelerated ageing data over the temperature range studied to obtain a master curve; (2) using numerical fit technique to produce a master equation representing the rate of paper degradation; (3) examining the validity of applying Arrhenius equation (48) for explaining the relationship between the empirically determined shift factors and the accelerated ageing temperature; and (4) verifying the Arrhenius activation energy extrapolation assumption. Different from the conventional approach that extrapolates the Arrhenius relationship between lifetime and temperature, without corroborating evidence, to ambient temperatures, the Arrhenius activation energy extrapolation assumption could be verified by determining the influence of acidity on cellulose hydrolysis reactions which is an ultra-sensitive and reliable method to measure degradation of cellulose and paper in what is normally the extrapolation region (ambient temperatures). The TTS methods has now been applied to investigate the effects of thermal ageing on mechanical

performance of paper [84] and the effect of heat and humidity on original wood-pulp papers [85].

The time-temperature superposition (TTS) principle

TTS is a concept or procedure originally developed in polymer physics. The essential idea in the TTS method is the assumption that the higher ageing temperature accelerates the changes in certain parameter/property of material microstructure in a uniform way such that the monitored parameter/property values obtained at short times and high temperatures can be used to predict parameter/property values at long times and low temperatures. The TTS principle is generally attributed to the early work of Leaderman [86] in 1940s in a study of viscoelastic behaviour in polymers and polymer fluids. Considerable subsequent application has been made of the TTS method is a well-known methodology today frequently used to describe the mechanical and electrical relaxation behaviour of polymers.

TTS to determine the activation energy of paper degradation

In order to determine the activation energy using all of the experimental data, we employ TTS method to shift the raw data of either measured DP (or TS) or the percentage DP (or TS) loss to the lowest degradation temperature (T_{ref}). This is accomplished by multiplying the degradation times appropriate to experiments at temperature (T) by a shift factor (a_T). The shift factors are chosen empirically to give the best superposition of the data by yielding an approximately smooth master curve. If the data adhere to an Arrhenius relationship, the set of shift factors a_T will be related to the Arrhenius activation energy by the following form [64, 83]

$$a_{TDP} = \exp \left[\frac{E_{DPa}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (49a)$$

$$a_{TTS} = \exp \left[\frac{E_{TSa}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (49b)$$

We call equation (49) Arrhenius shift factor function.

As examples, the best superposition of the data from Figures 6, 7, 14 and 21 are shown in Figures 24, 25, 26 and 29 respectively; and the corresponding Arrhenius plots of the associated empirical shift factor values are shown in

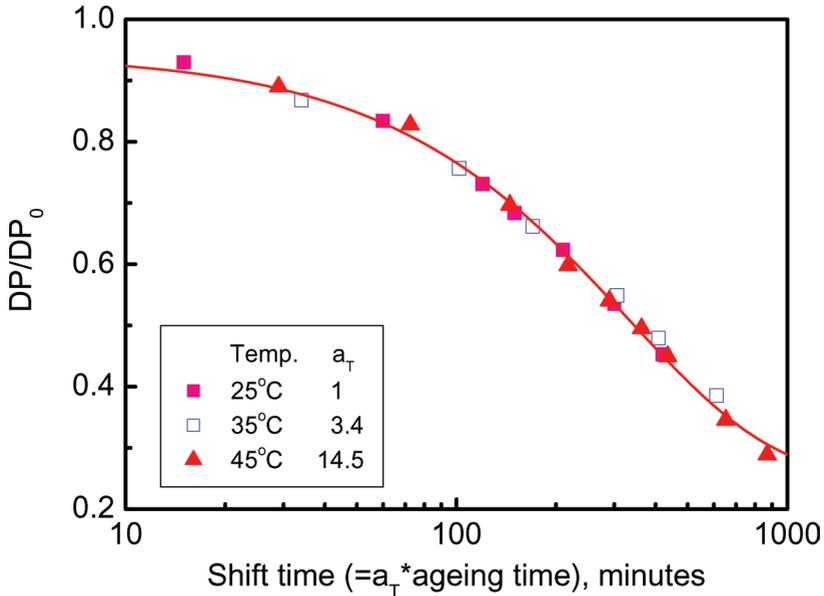


Figure 24. Time-temperature superposition of the DP/DP_0 data from Figure 6 at 25°C.

Figures 27, 28 and 30. The Arrhenius activation energy determined by the TTS method from these examples are obviously in good agreement with the reported activation energy of 111 ± 6 kJ/mol for Kraft paper in literature [6,7].

It is particularly remarkable to see the value of 104 kJ/mol for the regenerated cellulose in 85% phosphoric acid at ambient temperatures of 25~45°C is in exact agreement with the activation energy value determined for the BBSP aged in sealed glass jars at accelerated temperatures of 60~100°C. This gives further support and confidence to predict paper permanence by extrapolating accelerated ageing data to ambient conditions [83].

Towards a more reliable paper life prediction method

The idea is that all master curves obtained by TTS method can be further fitted to yield corresponding master equation representing the master rate of paper degradation.

Take both Figure 26 and Figure 29 as example. For the percentage DP loss rate data of BBSP handsheets aged in seal vessels and 75% RH in Figure 26,

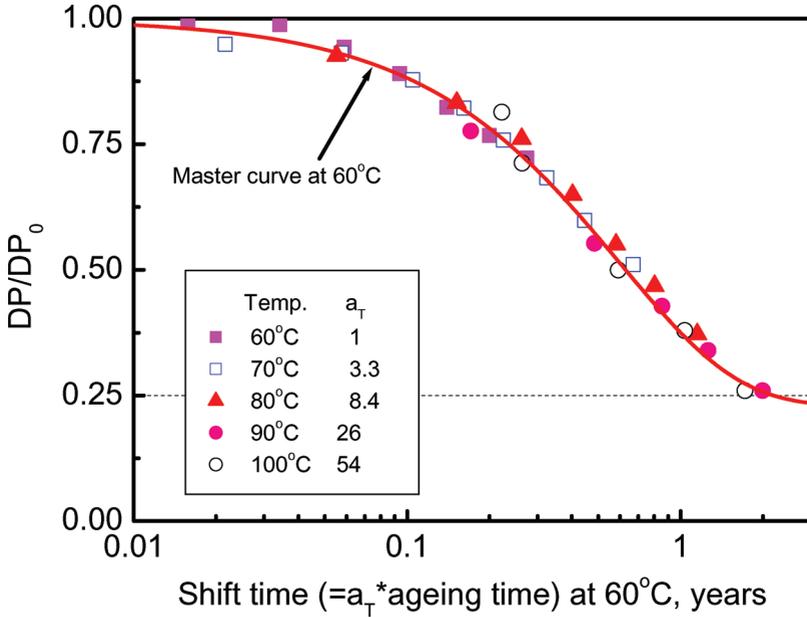


Figure 25. Time-temperature superposition of the BBSP ageing data from Figure 7 at 60°C.

the corresponding master rate equation of paper degradation can be expressed in the form of equation (18) as follows:

$$1 - \frac{DP}{DP_0} = 0.780 \left(1 - e^{-0.0043 a_{TDP} t_T} \right) \quad (50a)$$

$$a_{TDP} = \exp \left[12509 \left(\frac{1}{273+60} - \frac{1}{273+T} \right) \right] \quad (50b)$$

Where t_T is the degradation time by days at the temperature T in Celsius.

Similarly, for the percentage TS loss rate data of thermally upgraded insulation paper aged in closed system with mineral oil in Figure 29, the corresponding master rate equation of paper degradation can be expressed in the form of equation (23) as follows:

$$1 - \frac{TS}{TS_0} = 0.594 \left(1 - e^{-0.0028 a_{TTS} t_T} \right) \quad (51a)$$

$$a_{TTS} = \exp \left[13391.87 \left(\frac{1}{273+120} - \frac{1}{273+T} \right) \right] \quad (51b)$$

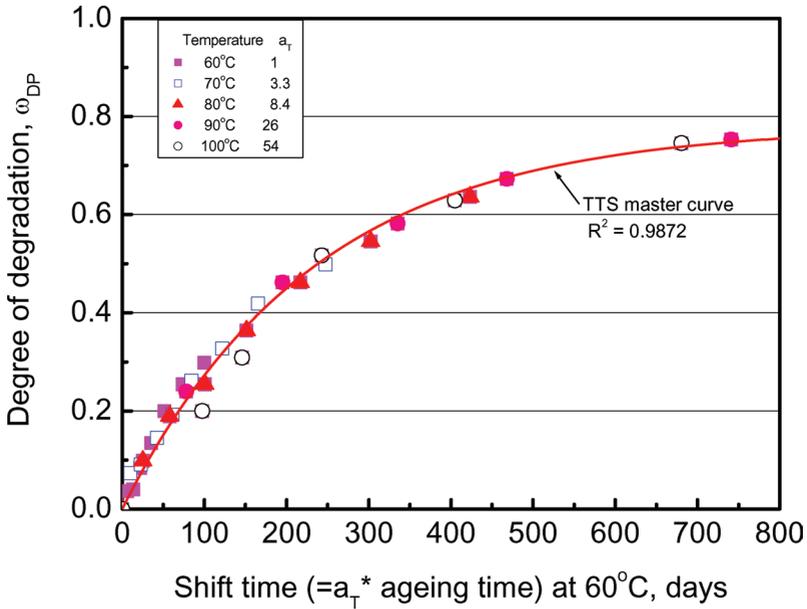


Figure 26. Time-temperature superposition of the BBSP ageing data from Figure 14 at 60°C.

Where t_T is the degradation time by days at the temperature T in Celsius.

According to the master degradation rate equation (50) and (51), it becomes possible to quantitatively predict the degree of degradation of paper at ambient (in-service) operating conditions. For example, according to equation (50), the extrapolated shift factor a_{TDP} will be $a_{TDP} = 0.0091$ at 23°C, which implies that with same relative humidity of 75%, the time required to reach a given level of degree of degradation at 23°C will be 110 times that required at the reference temperature of 60°C; and the degree of degradation of BBSP paper in terms of the percentage DP loss will reach 39.8% after 10 years, 59.3% after 100 years and 77.9% after 500 years. According to equation (51), the extrapolated shift factor a_{TTS} will be $a_{TDP} = 0.0070$ at 70°C (normal transformer operation temperature), which implies that with same experimental conditions, the degree of degradation of thermally upgraded insulation paper in terms of percentage TS loss will reach 4.1% after 10 years, 17.86% after 50 years and 30.35% after 100 years. Admittedly, these are approximate values. However, the results described above illustrate a new methodology towards a more reliable prediction for the rate and life of paper degradation at ambient conditions.

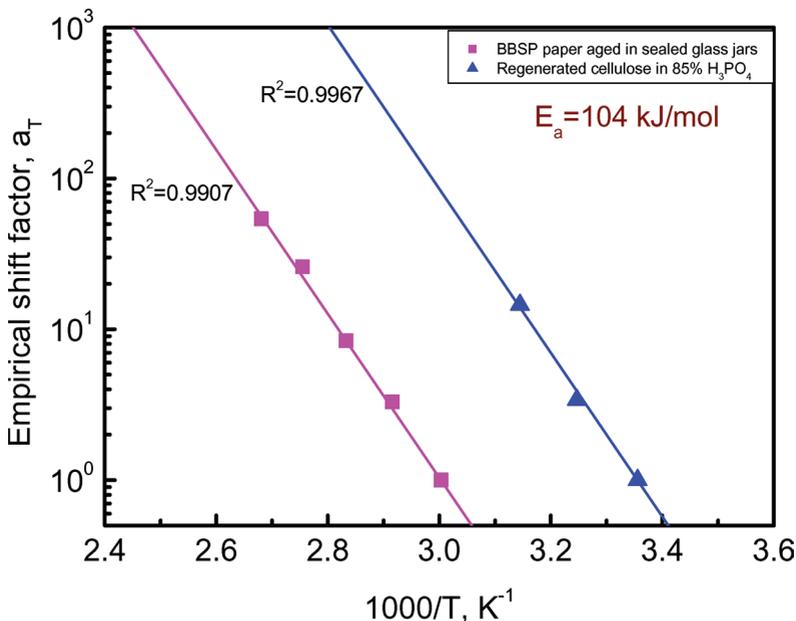


Figure 27. Arrhenius plots of empirical values of the shift factor a_T used to superpose degradation data for the regenerated cellulose in 85% phosphoric acid in Figure 24, and for the BBSP in Figures 25 and 26.

Comparison of natural ageing degradation results with predictions

Let us now attempt to reconcile the above TTS extrapolation method with specific experimental data of natural ageing. Unfortunately, very few data of natural ageing of paper are available in literature. In this Section, natural ageing results from eighteen bleached kraft dry-lap pulps aged for 22 years under ambient conditions and three handsheet samples aged for 22 years under controlled conditions, originally reported by Zou *et al.* [76], are adopted as an illustrative example for quantitative comparison. According to the authors' description [76], the average moisture content and the average pH in naturally aged kraft pulps are $5.99 \pm 0.37\%$ and 4.43 ± 0.66 , respectively. The moisture content was measured and the pH values of all the pulp samples were determined at 23°C and 50% RH. They assumed that both moisture content and pH value were constant over storage period, and all bleached kraft pulps were naturally aged for 22 years under ambient conditions ($T = 23 \pm 3^\circ\text{C}$ and $\text{RH} = 50 \pm 20\%$, estimated) and all handsheet samples were naturally aged for 22 years under a constant temperature of

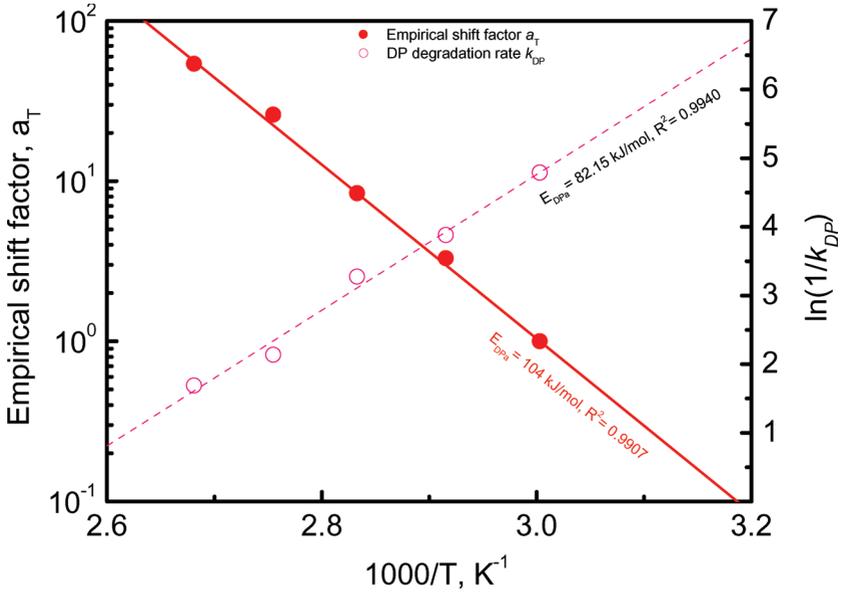


Figure 28. Arrhenius plots for both the DP degradation rate k_{DP} data in Table 1 and the empirical values of the TTS shift factors a_T to obtain best superposition of the raw data in Figure 25 and Figure 26.

$23 \pm 1^\circ\text{C}$ and constant RH of $50 \pm 2\%$. The activation energy for bleached Kraft pulps that was experimentally determined by Zou *et al.* [76] is $E_a = 109$ kJ/mol.

We firstly calculate extrapolated shift factors at ambient temperature conditions by assuming that $E_a = 109$ kJ/mol is applicable to all paper samples. The results are given in Table 11. We then determine the value of percentage DP loss after t_T years at $T = 23 \pm 3^\circ\text{C}$ from equation (50a) as

$$1 - \frac{DP}{DP_0} = 0.78(1 - e^{-0.00722t_{T=20c}}) \quad (T = 20^\circ\text{C}) \quad (52a)$$

$$1 - \frac{DP}{DP_0} = 0.78(1 - e^{-0.01146t_{T=23c}}) \quad (T = 23^\circ\text{C}) \quad (52b)$$

$$1 - \frac{DP}{DP_0} = 0.78(1 - e^{-0.01789t_{T=26c}}) \quad (T = 26^\circ\text{C}) \quad (52c)$$

We finally use natural ageing results of Zou *et al.* [76] to test prediction

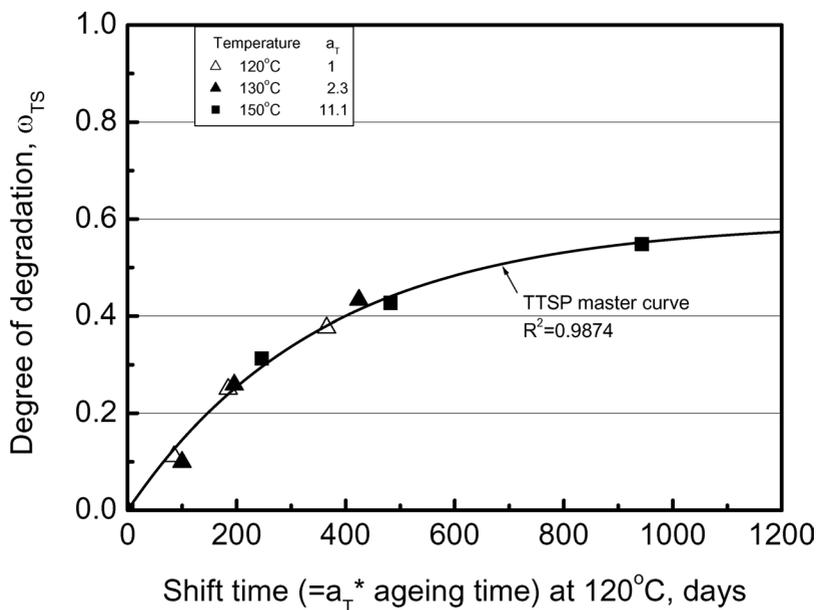


Figure 29. Time-temperature superposition of the data from Figure 21 at 120°C.

equation (8). Comparisons of the predictions according to equation (8) with natural ageing results are shown in Figure 31 and Table 2. All results are reported as means \pm standard deviation. Clearly, using $E_a = 109$ kJ/mol the predicted value of DP/DP_0 is 0.812 ± 0.072 for 22 years at 23°C, which is slightly larger than experimental values of both 0.783 ± 0.183 (determined in terms of the average value of eighteen bleached kraft pulps under ambient conditions) and 0.755 ± 0.188 (determined in terms of the average value of three handsheet samples under controlled conditions).

Considering the figure of $E_a = 109$ kJ/mol may not be applicable to all bleached Kraft pulps under ambient conditions and all handsheet samples under controlled conditions. It may be necessary to introduce corresponding deviations of the activation energy from the assumed figure. If the deviation is $\pm 5\%$, then $E_a = 109 \pm 5.45$ kJ/mol. The corresponding changes in extrapolated shift factors at ambient temperature conditions are given in Table 11, and the resulted changes in predictions are given in Table 12.

With the paucity and relatively large standard deviation of natural ageing data, it is difficult to simply say whether the model predicts well or not. However, it is remarkable that the model prediction gives values that are in

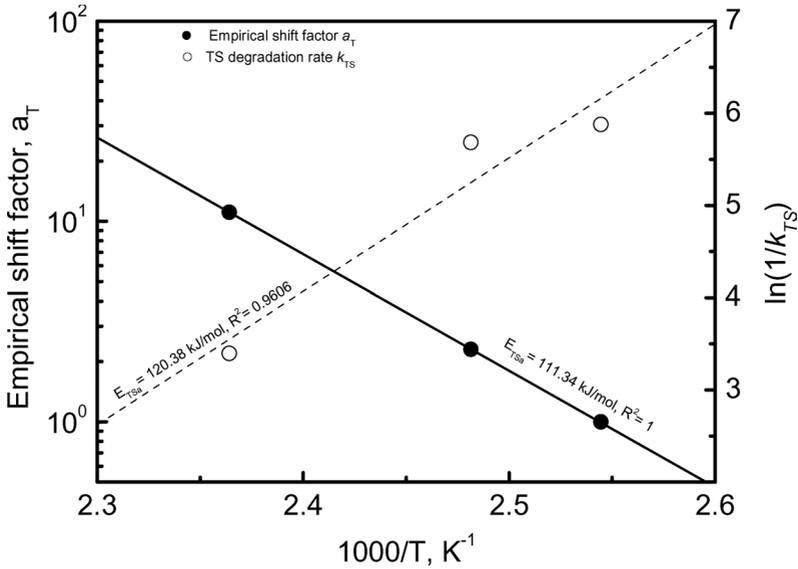


Figure 30. Arrhenius plots for the TS degradation rate k_{DS} data in Table 8 and for the empirical shift factors a_T used to superpose degree of degradation data in Figure 29.

Table 11. Extrapolated shift factors at ambient temperature conditions using equation (49) and $T_{ref} = 60^\circ\text{C}$ ($a_{T=60^\circ\text{C}} = 1$).

a_T	$Ea = 104 \text{ kJ/mol}$	$Ea = 109 \text{ kJ/mol}$	$Ea = 115 \text{ kJ/mol}$
T = 20°C	0.0059	0.0046	0.0034
T = 23°C	0.0093	0.0073	0.0057
T = 26°C	0.0140	0.0114	0.0089

the bulk part of natural ageing data. Because the natural ageing behaviour of paper under ambient conditions is complicated and could be affected by the average temperature as well as relative humidity of storage (possibly also by temperature as well as humidity cycling), exposure to light, the presence of atmospheric contaminants and other factors that cannot be anticipated in a predictive test, an exact figure for life expectancy of paper or handsheet cannot be given in any event [74]. By considering the statistical error involved in determining the activation energy as well, the agreement between the

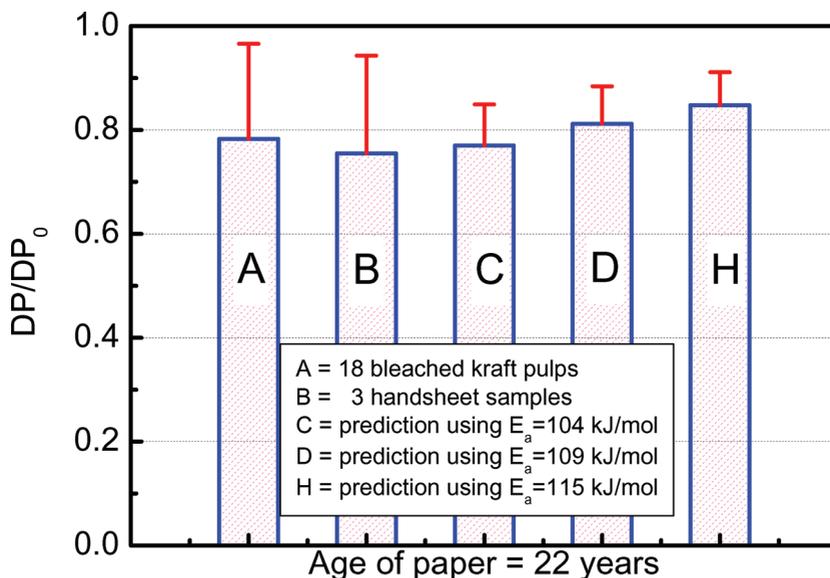


Figure 31. Comparison of the predictions with natural ageing results (a) Eighteen bleached kraft dry-lap pulp samples naturally aged for 22 years under ambient conditions ($T = 23 \pm 3^\circ\text{C}$ and $\text{RH} = 50 \pm 20\%$, estimated); (b) Three handsheet samples naturally aged for 22 years under controlled conditions ($T = 23 \pm 1^\circ\text{C}$ and $\text{RH} = 50 \pm 2\%$).

Table 12. Comparison of the predictions with 22 years' natural ageing results.

$\frac{DP}{DP_0}$	Mean value	Standard deviation
18 bleached kraft pulps	0.783	0.183
3 handsheet samples	0.755	0.188
Prediction use $E_a = 104$ kJ/mol	0.774	0.079
Prediction use $E_a = 109$ kJ/mol	0.812	0.071
Prediction use $E_a = 115$ kJ/mol	0.851	0.062

predictions and natural ageing data appears to be justified in principle (in terms of the mean value of all natural ageing data).

Furthermore, it may be interesting to note that the investigation conducted by Erhardt and Mecklenburg [75], who have found that the ageing process of

cellulose under the conditions studied at 60–90°C and 30–80% RH is mainly RH dependent, and lowering the RH from 50% to 30% may slow the rate of cellulose hydrolysis by a factor of three to five times. According to these findings, it is not surprising to see the large standard deviation in natural ageing data of Zou *et al.* [76], because the estimated RH changes from 30% to 70%.

CONCLUSIONS

The contributions given by this review have been addressed to show fundamental achievements on paper degradation and life modelling; underline some of the numerous inherent problems, relevant to determination of rates of paper degradation, their use to process accelerated ageing degradation experimental data and their limits of application; develop continuous distribution kinetics theory of cellulose and paper degradation which is capable to provide a united theoretical basis to derive the traditional reciprocal DP degradation rate equation originally developed by Ekenstam in 1930s and the alternative percentage DP (and TS) loss rate equations recently proposed by the present author and his co-workers; and present alternative methodology and recent trends towards a more reliable paper degradation rate and life expectancy prediction.

The overview of paper degradation has shown the difficulties in obtaining satisfactory paper degradation rate models which represent the paper response over extended periods of time and under a varied of conditions. There are many events which determine the results of accelerated ageing degradation tests, and the mechanisms of paper degradation are not always completely known. On the other hand, paper itself is a complex and is manufactured in so many different ways, the changes of a paper property with degradation time are not determined by any single factor and chemical reaction whose effects can be isolated and controlled, and it seems unlikely that only one degradation rate model can provide a good description of degradation behaviour for all papers under a varied of conditions. The application of the traditional reciprocal DP rate model approach to achieving good quality of fit to experimental data as well as to evaluating and comparing papers is limited as the model itself is an idealized approach which presupposed that the polymer is mono-disperse and every bond has the same probability of breaking.

The alternative methodology that using percentage DP and TS loss rates to determine the rate of paper degradation and applying time-temperature superposition method for determining the activation energy of paper

degradation is one step ahead and has opened the door towards a more reliable degradation rate and life expectancy prediction of paper over a long time period under real in-service conditions.

In conclusion, investigation of degradation and life behaviour of paper is a subject of great interest. There is much to learn about the time response of paper materials and productions to stresses and environments. The acquisition of this knowledge is vital to both the papermaker and its end-user. It still needs settled bases for further theoretical developments and research. To this end, fundamental research on paper must be encouraged and nurtured. This could be realized through a joint effort of industry, university and government.

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Transcription of Discussion

DEGRADATION PHENOMENOLOGY AND LIFE MODELLING OF PAPER – A REVIEW

Hongzhi Ding

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Stefan Lindström Mid Sweden University

I was thinking about the cause for these failures in the transformers, and I guess the heat must be generated by the resistance of the winding. There must be some temperature variations in these windings. If you have a crack, for instance, you will get an elevated temperature. What is the cause of the failures? Is it the aging of the wiring or the aging of the papers?

Hongzhi Ding

A transformer can fail due to a number of causes. In my presentation, I have only talked about the paper aging as this is a conference on fundamental research in pulp and paper. A universal formula for transformer failure is, if the winding paper has been severely aged and is coming to the end of its life, a transformer will die. It is very rare to see a crack in any transformer winding conductor, as it would not be possible for that to pass the transformer testing before its commission and service. However, there is a possibility that some winding contactors could have some kind of material micro-defect (not a crack) from the very beginning, say before it was used to build the windings. That could potentially cause a localized thermal fault and cause a premature failure of the transformer.

Gary Baum PaperFuture Technologies (from the chair)

Well, I have a question: what are the paper requirements for power transformers? You never really told us what the paper was. Other than DP, what

Discussion

are the requirements? I assume, for example, that you would not want to have any ions in the paper. What kind of paper is used to make a power transformer?

Hongzhi Ding

We are neither the paper maker nor the transformer manufacturer. To be honest, I am not sure how the process of transformer paper making is carried out. However, the paper used for all power transformers has very precise specifications. It is necessary that most of the critical properties of paper used for all power transformers are met: the required chemical purity, thermal stability, and mechanical and dielectric strength.