

MASS TRANSFER IN PEROXYACETIC ACID BLEACHING OF KRAFT PULP

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ABSTRACT

In pulp bleaching, the overall reaction rates are determined either by mass transfer or by rate of chemical reaction. The rate limiting step in peroxyacetic acid treatment of kraft pulp was studied using a method based on particle size dependence. The rate limiting step in both pulp delignification and bleaching was found to be the reactions between peroxyacetic acid and lignin. Hexenuronic acid decomposition was also limited by reaction rate. On the other hand, the other carbohydrate degradation reactions, which are probably caused by radical species formed from peroxyacetic acid and not directly by peroxyacetic acid, are mass transfer limited.

KEYWORDS: Bleaching, Carbohydrate Degradation, Delignification, Diffusion, Hexenuronic Acid, Mass Transfer, Kraft Pulp, Peroxyacetic Acid, Rate Limiting Step

INTRODUCTION

Pulp bleaching is a complicated multi-phase process. Knowledge of the transfer of different compounds between different phases and of the reaction kinetics and mechanisms is required for a full understanding of any bleaching process.

Several schematic illustrations of pulp bleaching have been suggested /1, 2/, and the bleaching process may be divided into six steps according to **Figure 1**. Step 1 is dissolution of bleaching agent into the liquid phase. This step is needed if the bleaching agent is a gas such as chlorine dioxide, oxygen or ozone; the rate of this step depends highly on the solubility of the gas. Step 2 is transport of reagent from bulk solution onto the fibre surface, the rate of which depends on mixing. Step 3 is the diffusion of reagent into the fibre cell wall to a location where it reacts with lignin or some other component. Step 4 is the chemical reaction itself. Step 5 is the diffusion of the reaction product out of the fibre cell wall; this step may proceed towards the outer surface of the fibre cell or towards the lumen of the fibre. Step 6 is the transport of the reaction product into bulk solution, the rate of which depends on mixing. All steps, excluding step 4, are mass transfer.

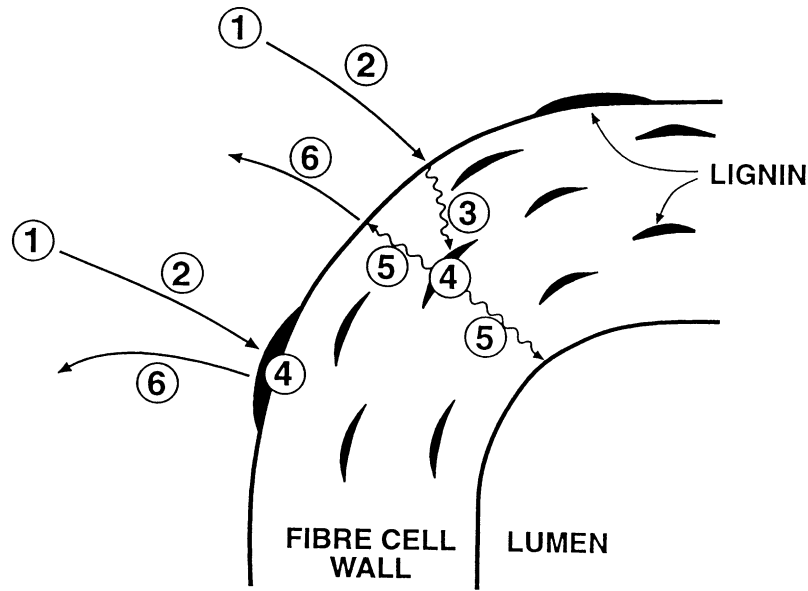


Figure 1. Reaction steps during pulp bleaching (fibre cross-section).

The significance of diffusion in the fibre cell wall (steps 3 and 5) depends on the location and the reactivity of lignin throughout the fibre cell wall. Lignin in kraft pulp is known to be enriched on fibre surfaces [3] and removing this surface lignin does not require diffusion in the fibre cell wall, as is shown in Figure 1. However, good bleaching results with chemical pulp require that the lignin inside the cell wall is also removed. Diffusion inside the cell wall is therefore an important step in chemical pulp bleaching.

The overall rate of the process is determined by the slowest step. When pulp is bleached at high or medium consistency with a highly reactive bleaching agent such as chlorine or ozone, the chemical reaction is rapid. Then mass transfer limits the rate of bleaching [4, 5]. Less reactive bleaching agents, such as oxygen and chlorine dioxide, need more time to react with lignin, in which case the chemical reaction becomes the rate limiting step [6]. However, if mixing is inadequate or pulp consistency is low, the rate of mass transfer (steps 1 and 2 in Figure 1) becomes slow and may become rate limiting.

In diffusion, mass transfer is caused by a concentration gradient. The net flow of a compound across a plane may be described using Fick's first law [7]:

$$\frac{\partial n}{\partial t} = -D A_D \frac{\partial c}{\partial x} \quad (1)$$

where $\partial n / \partial t$ is the rate of flow of compound

D is the diffusion coefficient

A_D is the diffusion area perpendicular to x axis

$\partial c / \partial x$ is the concentration gradient

As can be seen from Equation 1, the diffusion rate is proportional to the diffusion area (A) and to the concentration gradient ($\partial c/\partial x$). As time goes on, the concentration gradient decreases and when it reaches zero the diffusion stops /8/.

In solid-liquid systems the diffusion coefficient, D, depends on the form and density of the solid material, and on the properties of the diffusing compound /7/. The rate of diffusion is more rapid into a porous particle than it is into a dense particle, and small compounds diffuse much faster than large compounds /9/. The diffusion coefficient is temperature sensitive, and an Arrhenius type of equation (Equation 2) may be used to describe its temperature dependence.

$$D = AT^{1/2} e^{-E/RT} \quad (2)$$

Where A is a frequency factor

E is activation energy

R the universal gas constant

T is temperature

In well mixed pulp suspensions, where the bleaching agent is uniformly distributed in the liquid phase, the rate limiting step is either diffusion in the cell wall or the reaction between reagent and pulp component. In this paper the rate limiting steps of delignification and carbohydrate reactions during the peroxyacetic acid stage of pulp bleaching are determined.

EXPERIMENTAL

Materials

Distilled peroxyacetic acid (350 g/l peroxyacetic acid and <10 g/l hydrogen peroxide) was provided by Finnish Peroxides Inc., Finland. Exact hydrogen peroxide and peroxyacetic acid contents were determined prior to delignifications by titration /10/. The initial pine (*Pinus sylvestris*) SuperBatch pulp was cooked and oxygen delignified at Western Laboratories Inc., Finland. The pulp had a kappa number of 10.5, a brightness of 33.7 % and a viscosity of 970 ml/g.

Methods

Prior to delignification, the pulp was chelated using 0.2% Na₄-EDTA on pulp, pH 4 (adjusted with H₂SO₄), at 10% consistency for 1 hour at 90°C. After chelation the pulp was washed thoroughly with distilled water in a Büchner funnel.

A portion of chelated pulp was air-dried and milled in a Wiley mill (40 mesh). After milling, the pulp was washed with pH 5 water (acidified with CH₃COOH) in a Büchner funnel to remove any iron contamination from the Wiley mill. Prior to delignification, flocs in both unmilled and milled pulps were ruptured in a laboratory mixer (Waring Blendor). Peroxyacetic acid delignifications for both unmilled and milled pulps were performed by preheating pulp, water and NaOH solution (used to adjust pH) separately to 70°C so that heat transfer could be neglected. Distilled peroxyacetic acid (1.75% on pulp) and NaOH solutions were mixed with the

preheated water to ensure that the liquid phase was uniform. The solution was immediately mixed thoroughly into the pulp. The delignification pH was 5 and the temperature was 68°C in the pulp suspension and 70°C in the water bath. The reaction times used were 5, 10, 20, 45, 90 and 180 minutes for unmilled pulp and 10, 45 and 180 minutes for milled pulp. The pH was measured every 1-2 minutes during the early part of delignification and every 5-15 minutes after 30 minutes. NaOH solution was added if the pH had fallen. After delignification the pulp was washed twice with hot and twice with cold distilled water in a Büchner funnel. Replicates were carried out for unmilled pulp using all 6 different times in order to obtain the repeatability of the treatment.

Analyses

The standard analytical procedure (SCAN-C 1:77) was used in kappa number measurement. The hexenuronic acid (HexA) contents of the pulps were determined after total enzymatic hydrolysis as described elsewhere /11/. The correspondence between hexenuronic acid content and kappa number was used as described by Li and Gellerstedt /12/, who have determined that 10 µmol HexA/g pulp corresponds to 0.86 kappa units. Lignin kappa number was obtained by subtracting the kappa number attributable to hexenuronic acid groups from the measured kappa number. Viscosity and metal content measurements followed standard analytical procedures SCAN-CM 15:88 and SCAN-C 38:96, respectively. Brightness was measured using an Elrepho instrument, and fibre length distribution using a Kajaani FS-200 instrument. The contents and compositions of dissolved monosaccharides were determined from the filtered delignification spent liquor after acid hydrolysis using a HPLC method /13/. Residual hydrogen peroxide and peroxyacetic acid contents were determined from delignification spent liquor by titration /10/.

RESULTS AND DISCUSSION

Several methods are available for determining the rate limiting step of a fluid-solid reaction /14/. In pulp bleaching, methods based on temperature or particle size dependences can be used. Temperature dependence is based on the assumption that, due to the higher activation energy, a chemical reaction is usually more temperature sensitive than a physical step. Raising the temperature therefore increases the rate of a chemical reaction more than the rate of diffusion. However, since neither the activation energy of the chemical reactions between lignin and peroxyacetic acid nor that of diffusion are known and cannot be predicted with adequate accuracy, the temperature dependence method is not suitable in this case.

Particle size dependence is based on the fact that the particle size of the solid material has a significant impact on the rate of diffusion. On the other hand, the rate of a chemical reaction is not dependent on particle size if the number of reactive sites is constant. Increasing the ratio of surface area to volume increases the rate of diffusion as can be seen from Equation 1. In pulp bleaching, if the rate limiting step is diffusion, then reducing the fibre dimensions increases the surface area and thus the overall rate of bleaching. If, however, the overall rate does not change as surface area increases, the rate controlling step is the rate of reaction between reagent and pulp component.

The surface area of pulp fibres was increased by milling the pulp in a Wiley mill, the result being a substantial decrease in fibre length. The arithmetic average of fibre length decreased from 0.86

mm to 0.26 mm and the length-weighted average from 1.76 mm to 0.46 mm (**Figure 2**). In addition, the content of fines, i.e. particles smaller than 0.20 mm, increased from 3.5% on weight to 16.8% during milling. This decrease in fibre dimensions increases the surface area of fibres and therefore increases the rate of peroxyacetic acid diffusion in fibres during peroxyacetic acid bleaching.

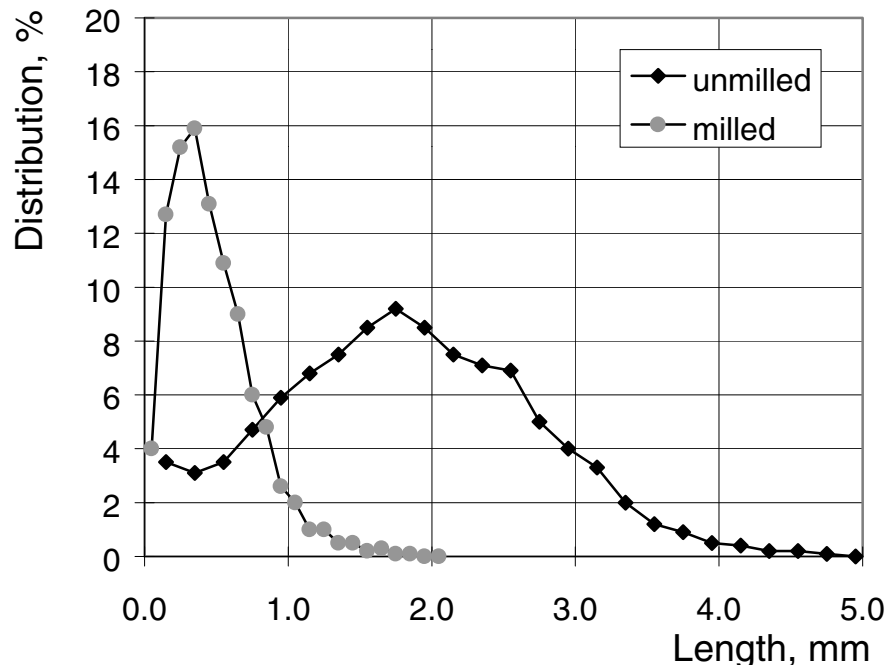


Figure 2. *Weighted distributions of unmilled and milled softwood kraft pulp fibre length.*

The metal content of pulp is a significant factor in peroxyacetic acid bleaching [15]. Increasing the transition metal content of pulp increases the rate of peroxyacetic acid decomposition and hence the viscosity reduction. To remove any metal contaminants due to the Wiley mill, the milled pulp was subjected to a gentle acid wash (pH 5) prior to peroxyacetic acid delignification. After the acid wash, the milled pulp had nearly the same metal profile as the unmilled pulp (**Table I**). Only magnesium content was lowered by washing, but magnesium has a negligible impact on peroxyacetic acid delignification [15] and its effect may therefore be ignored.

	unmilled	milled
Iron	19	18
Manganese	0.4	0.5
Copper	3.4	3.1
Magnesium	34	16

Table I. *Metal contents (mg/kg of pulp) in unmilled and milled pulps.*

Both unmilled and milled pulps were subjected to peroxyacetic acid delignification under the same reaction conditions. **Figure 3** shows that milling the pine kraft pulp prior to peroxyacetic acid treatment did not increase the rate of delignification or the rate of hexenuronic acid decomposition when measured by kappa number. The rate determining step of peroxyacetic acid delignification is therefore the chemical reaction between peroxyacetic acid and lignin. The rate determining step in hexenuronic acid decomposition is the chemical reaction between peroxyacetic acid and hexenuronic acid.

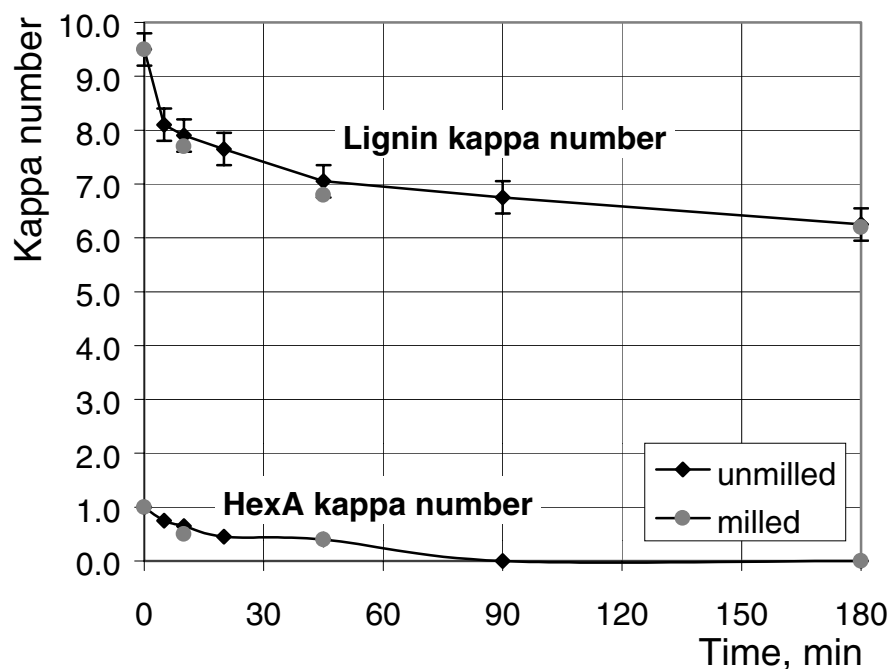


Figure 3. Effect of fibre milling on kappa number due to lignin and kappa number due to hexenuronic acid groups (HexA) as a function of peroxyacetic acid delignification time. (Temperature 68 °C, pH 5 and peroxyacetic acid charge 1.75% on pulp.)

Peroxyacetic acid removes the lignin located on the surfaces of kraft pulp fibres /16/. The surface layer of the fibre cell wall is very thin and therefore most of the lignin removed during peroxyacetic acid delignification originates from the inner layers of the fibre wall. The diffusion of peroxyacetic acid (step 3 in Figure 1) therefore occurs during pulp delignification but does not control the rate of delignification.

Milling the pine kraft pulp prior to peroxyacetic acid delignification had no effect on pulp chromophores. The brightness of milled pulp after peroxyacetic acid delignification was the same as that of unmilled pulp, as shown in **Table II**, even though the milled pulp had slightly higher initial brightness. This means that the main reactions between lignin and peroxyacetic acid are slower than diffusion. These delignification and bleaching results thus prove that in the delignification or bleaching of pulp with peroxyacetic acid, mass transfer may be neglected and the rate of delignification or bleaching equals the rate of chemical reactions, as has already been assumed in some kinetic studies without any experimental proof /17/.

Time, min	Unmilled	Milled
0	33.7 ± 1.0	36.8
5	46.9 ± 1.0	-
10	47.6 ± 1.0	47.4
20	49.9 ± 1.0	-
45	51.4 ± 1.0	51.4
90	54.3 ± 1.0	-
180	56.5 ± 1.0	53.9

Table II. Effect of peroxyacetic acid delignification time and pulp milling prior to delignification on pulp brightness (%).

Peroxyacetic acid is selective in its reactions with pulp lignin, and its reactions with carbohydrates are less pronounced than in ozone bleaching [18]. In the present study, unmilled pulp showed a viscosity loss of 6% during peroxyacetic acid delignification (**Figure 4**) indicating insignificant cellulose depolymerization, as was expected from earlier results with peroxyacetic acid delignification at pH 5 [19]. The milled pulp had a lower initial viscosity because during milling the carbohydrate chains were cut and the pulp's viscosity reduced from 970 ml/g to 880 ml/g. Peroxyacetic acid treatment reduced the viscosity of milled pulp by a further 20%, which is significantly more than in the case of unmilled pulp. Viscosity reduction was caused by an oxidizing agent, because under the same conditions but without the addition of peroxyacetic acid there was no fall in the viscosity of milled pulp during 45 minutes (Figure 4).

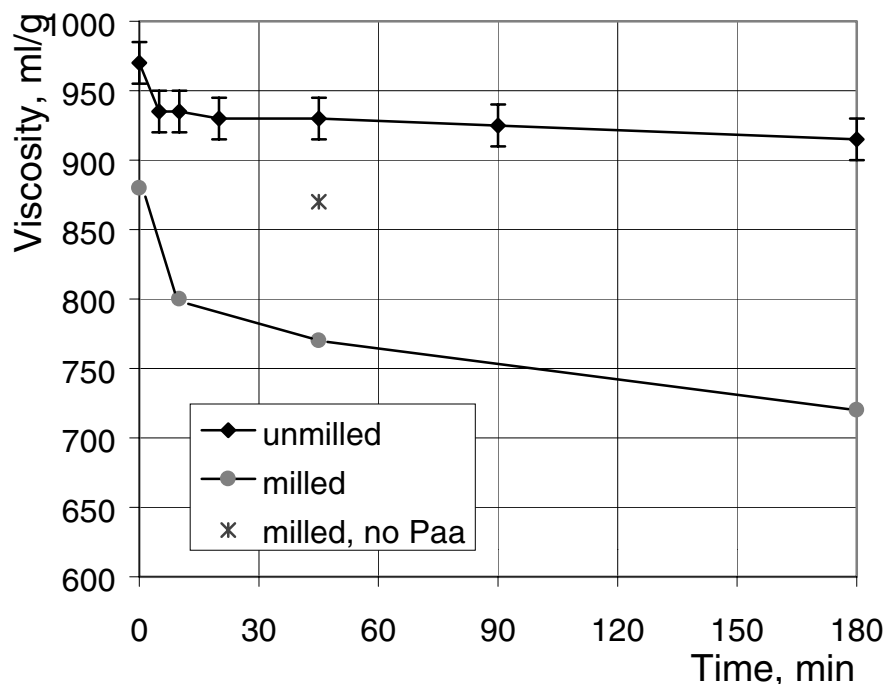


Figure 4. Viscosities (ml/g) of unmilled and milled pulps as a function of peroxyacetic acid delignification time.

This finding indicates that mass transfer has a significant effect on cellulose depolymerization during peroxyacetic acid bleaching. Hydroxyl radicals (HO $\cdot$), which may be formed by the homolytic decomposition of the oxygen-oxygen bonds in peroxyacetic acid /20/, are probably responsible for cellulose degradation. The reaction mechanism of carbohydrate degradation is therefore different from the mechanism of delignification reactions, which involve electrophilic oxygen transfer. Hydroxyl radicals are highly reactive species and may thus react quickly with all pulp components. Hydroxyl radicals formed outside pulp fibres cannot diffuse into the fibre cell wall /21/ and therefore their reactions take place on fibre surfaces. In oxygen-delignified kraft pulp, lignin and extractives are enriched on fibre surfaces, covering as much as 20% of the surface area /3/, the rest being covered mainly by xylan. The long-chain carbohydrates (cellulose polymers) are located in the inner cell wall layers /22/. This means there is little contact between long-chain carbohydrates and bulk liquor in unmilled pulp fibres, and there is therefore little likelihood of the radical species in the bulk liquor reacting with long-chain carbohydrates. Thus the viscosity of unmilled pulp was almost unaffected by peroxyacetic acid treatment. Milling ruptured the fibrous structure and in this way significantly increased the surface area between cellulose and bulk liquor. The radical species may then react with cellulose chains and cause their cleavage, as can be seen from the fall in viscosity. It may then be concluded that the viscosity-reducing reaction in peroxyacetic acid delignification at pH 5 is limited by mass transfer because hydroxyl radicals cannot reach the long carbohydrate chains in an unbroken fibre. Therefore an unbroken fibre structure hinders most of the harmful carbohydrate degradation during peroxyacetic acid bleaching.

The result is in agreement with the findings from ozone bleaching, where hydroxyl radicals are once more the species likely to cause carbohydrate degradation /23, 24/. However, it has been shown /21/ that hydroxyl radicals formed outside the fibre do not cause significant viscosity reduction. Thus it has been suggested /25/ that the hydroxyl radicals responsible for carbohydrate degradation reactions during ozone bleaching are formed inside the fibre cell wall from relatively stable superoxide anion radicals (O $_2^{\cdot-}$).

Information on carbohydrate reactions may also be obtained by determining the content of carbohydrates dissolved in the spent liquor. The carbohydrate content of the spent liquor from peroxyacetic acid delignification of unmilled pulp was negligible (**Table III**) as was expected from reports in the literature /18, 19/. On the other hand, the carbohydrate content of the spent liquor from the peroxyacetic acid treatment of milled pulp was high, although it was lower than in the reference treatment of milled pulp without peroxyacetic acid addition.

	Arabinose	Galactose	Glucose	Xylose	Mannose
unmilled	0	+	+	+	+
milled	5	+	5.4	37	+
milled, without Paa	16	2.8	12	110	3.8

+ = detected but under quantification limit (<3 mg/l for mannose and <1 mg/l for others)

Table III. Monosaccharide contents (mg/l) of dissolved carbohydrates in spent liquors from delignifications of unmilled and milled pulps with and without peroxyacetic acid. (Temperature 68°C, pH 5, peroxyacetic acid charge 1.75% on pulp and time 45 minutes.)

The results indicate that carbohydrate dissolution is limited by mass transfer. Increasing the contact area between carbohydrates and the liquid phase promoted the dissolution of carbohydrates. The contribution of peroxyacetic acid to carbohydrate dissolution cannot be evaluated from the spent liquors, because there is strong evidence /19/ that the carbohydrates present in spent liquor may have been oxidized by peroxyacetic acid. This was also seen in the present study from the high carbohydrate content of spent liquor from milled pulp treatment without the use of peroxyacetic acid.

CONCLUSIONS

The experiments with unmilled and milled pulps showed that the rate limiting steps in peroxyacetic acid delignification and brightening of kraft pulp are the chemical reactions between peroxyacetic acid and lignin. The reaction causing hexenuronic acid decomposition is also slower than diffusion. The kinetics of delignification, bleaching and hexenuronic acid decomposition may therefore be modelled on the chemical reactions alone. Mass transfer steps can be neglected.

Carbohydrate degradation during peroxyacetic acid treatment is probably caused by radical species and not by peroxyacetic acid itself. Due to their high reactivity, hydroxyl radicals formed outside the fibres do not have time to reach cellulose chains in fibre cell walls. According to the results, no significant cellulose-degrading radical formation occurred inside the fibre cell walls. It is thus obvious that the only carbohydrate degrading reactions are those of hemicelluloses occurring on fibre surfaces. The degradation of cellulose during peroxyacetic acid bleaching is mass transfer limited.

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NOMENCLATURE

$\partial n/\partial t$	rate of diffusion
D	diffusion coefficient
A_D	diffusion area perpendicular to x axis
$\partial c/\partial x$	concentration gradient
A	frequency factor
T	temperature
E	activation energy
R	universal gas constant

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