Kinetics of Neutral Sulfite Semichemical and Neutral Sulfite Semichemical-Anthraquinone Pulping

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ABSTRACT

Delignification rate expressions for neutral sulfite semichemical (NSSC) and neutral sulfite semichemical anthraquinone (NSSC-AQ) pulping of black spruce have been developed. The rates take into account the effects of temperature and reaction times on the rates of delignification.

NSSC in this study is defined by an alkali ratio [sodium sulfite/(sodium sulfite + sodium carbonate)] of 0.60 (expressed as sodium oxide) giving a final pulp yield between 55 and 60 %. NSSC-AQ is identical to NSSC with the addition of anthraquinone.

Reaction temperature and pulping chemical concentrations were held essentially constant in all kinetic experiments. Isothermal experiments were conducted in the temperature range between 165 and 180°C. A concentration of 150 g/L sodium sulfite with a liquor to wood ratio 62 were used.

INTRODUCTION

Published data show that AQ has a dramatic effect on neutral sulfite semichemical pulping (NSSC)[1-4]. The results from these studies demonstrate that AQ accelerates dramatically the delignification rate. For a constant kappa number, the NSSC-AQ pulps have higher yields than NSSC pulps. For conventional physical strength properties such as breaking length, burst index and tear index, the NSSC-AQ pulps are significantly stronger than their NSSC counterparts.

NSSC-AQ pulps are now being made commercially in Australia and New Zealand[5]. A mill in New Zealand producing NSSC-AQ pulps from pinus radiata, report that with a charge of 0.04 % AQ on wood, cooking time decreased by 30 % or more. In addition, one mill in Japan[6] reported the use of DDA to save refiner energy, increase yield and improve pulp strength. These findings clearly show that there is a strong need for more investigations on NSSC-AQ pulping.

A knowledge of the kinetics of NSSC and NSSC-AQ pulping processes is a valuable tool to design, optimize and control these processes. The purpose of the present work has been to develop the kinetic equations that describe delignification during both NSSC and NSSC-AQ pulping.

The NSSC process in the present work is defined by an alkali ratio $[Na_2SO_3/(Na_2SO_3+Na_2CO_3)]$ of 0.60 (expressed as Na_2O) where the cooking was stopped at a yield between 55 to 60 %. The pH of the cooking liquor varies during the cooking cycle between 11.5 and 10.5. NSSC-AQ is identical to NSSC with the exception of addition of anthraquinone.

Literature Survey

Earlier investigations have usually dealt with the kinetics of NSSC pulping for hardwoods[7-9]. Findley and Nolan[7] determined the effects of temperature, chemical concentration and time on the neutral sulfite semichemical pulping of red maple in the temperature range of 162 to 186 °C. The degree of pulping was measured by determining the undissolved wood (yield). Their data indicated that two apparently first order, simultaneous or consecutive reactions might control the rate of pulping and the velocity constants of the two reactions vary with temperature according to Arrhenius equation. The activation energies of these two reactions were found to be 148 and 105 kJ/mol, respectively. Basu et al.[8] studied the delignification of NSSC pulping with beech wood within the temperature range of 135 to 175 °C and pulp yield level 55 to 75 %. They found that delignification is first order with respect to residual lignin during the bulk delignification stage. The activation energy for bulk delignification was reported as 106 kJ/mol within the temperature range of 135 to 175 °C. They have observed that a fast delignification takes place during the heat-up period of the cooking cycle. A kinetic study on NSSC pulping of Eucalyptus hybrid (mainly tereticornis) was carried out by Singh et al.[9]. Their results showed that rate of delignification followed a pseudo first order rate law with respect to both lignin and sulfite. Kansal and Basu[10] proposed a kinetic

model for the delignification rate of tropical hardwood during NSSC pulping with 14 % chemical charge of oven dry wood (ODW), liquor to wood ratio of 4, temperature range of 140 to 180 °C. They observed orders of 1.75 with respect to lignin and 0.25 with respect to sulfite, and activation energy of 126 kJ/mol when both were measured after the initial rapid delignification was completed.

Eagle and McDonough[11] studied the delignification of loblolly pine by sulfite anthraquinone pulping within the temperature range from 160 to 180°C. They found that a parallel reaction model with activation energies of 155 kJ/mol for AQ associated reactions and 122 kJ/mol for non-AQ delignification gave the best fit of data during the bulk delignification. The reaction orders with respect to lignin was 2.4 for both reactions with and without AQ.

Chari[12] developed a rate expression for the neutral sulfite pulping reaction of aspen wood which takes into account the effects of temperature, the concentration of the cooking liquor and the time of reaction on the pulping rate in the temperature range between 170 and 196°C. The activation energy for bulk delignification was reported as 233 kJ/mol.

In the above studies, the activation energy of NSSC and NSSC-AQ pulping for bulk delignification was reported in the range of 105 to 233 kJ/mole. The results of the above studies are summarized in Table 1.

EXPERIMENTAL

Preparation of Wood

Black spruce having the following composition was used in this study:

Extractives (acetone):   1.1 % on ODW

Lignin (Klason + U.V.):   27.8% on ODW

Carbohydrates: 71.1% on ODW

It is important to ensure that the pulping rates rather than the rate of transport of chemical into the chips act as the controlling steps in a kinetic study. Wafers having the average thickness of 0.58 mm were used for the kinetic experiments of this study to eliminate the mass transfer limitation. The average moisture content of wafers was 41 % and exact moisture content was determined prior to each experiment (CPPA standard G.3). The wafers were soaked in the liquor overnight to improve impregnation.

TABLE 1. Kinetic Studies in the Literature

PROCESS	WOOD	"n" wrt Lig.	E_a kJ/mol	Temp. Range	Reference
NSSC*	Red Maple	1 1	148 105	162-186 °C	7
NSSC	Beech	1	106	135-175 °C	8
NSSC	Euc. Hybrid Euc. Obliqua	1 1	103 105	150-180 °C	9
NSSC	Euc. Grandis	1.75	126	140-180 °C	10
Sulfite-AQ**	Loblolly Pine	2.4 2.4	155^{AQ} 122	160-180 °C	11
Neutral Sulfite	Aspen	2.2	233	170-196 °C	12

* Two simultaneous or consequtive reaction with respect to yield
** A parallel reaction model
AQ Anthraquinone associated reaction

Preparation of Liquor

Pulping liquor was prepared by dissolving reagent grade Na_2SO_3 and Na_2CO_3 in water. A sodium sulfite to total alkali ratio of 0.60 (expressed as Na_2O) was used for the neutral sulfite semichemical pulping experiments. Each cook was conducted by charging the equivalent of 20 g oven dry wood wafers with pulping liquor at a liquor to wood ratio of 62/1 for all runs. The initial pH of the liquor was 11 and initial liquor concentration was 150 g / L . The reason for using a high liquor to wood ratio and a high liquor concentration was to make the liquor concentration virtually constant during pulping. Soluble anthraquinone (SAQ: soluble sodium salt of 1,4-dihydro- 9,10-dihydroxyantracene; equivalent to 0.5 % AQ on ODW) was injected into the liquor using a syringe for NSSC-AQ pulping process.

Pulping

The pulping experiments were conducted in a digester containing six 2.5-liter bombs rotating in an electrically heated glycol bath. The rotation provided good mixing of the glycol in the bath and also the content of the bombs. This ensured good heat and mass transfer in the digester during the kinetic experiments.

The experiments were carried out isothermally at temperatures of 165, 170, 175 and 180 °C. For isothermal operation the glycol bath was preheated to a temperature higher than the operating temperature and the bombs were inserted into the digester. The absorption of heat from the glycol bath by the bombs brought the digester temperature close to the operating temperature within 5 minutes. The digester temperature and cooking time were controlled by computer and the experimental temperature was maintained constant ($\pm$ 0.5 °C) for the duration of the experiment.

The bombs were removed from the constant temperature bath at the selected reaction times and quenched into cold water. The wafers were separated from the spent liquor. They were washed until washings were colorless and then soaked in water for one day to allow diffusion from the wafers. The pulps were disintegrated as a suspension in water using a Wearing blender.

The constant temperature cooks were carried out to give pulp yields within the range from 85 to 55 %.

Analysis of Spent Liquors and Pulps

The spent liquors were analyzed for Na_2SO_3 concentration using ion chromatography. The pH of the spent liquors was also measured. The pulps were analysed for the yield
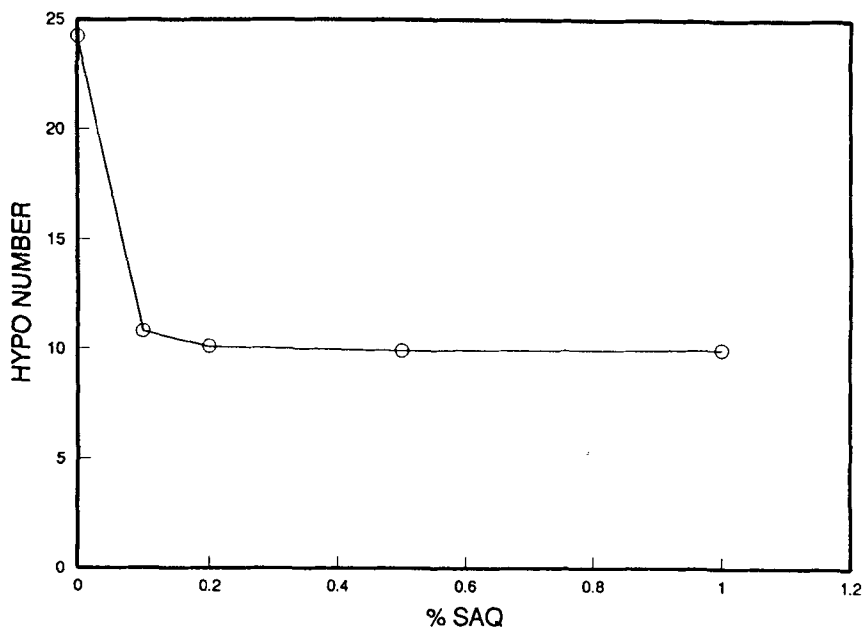
Figure 1. Effect of % SAQ addition on delignification of black spruce wood in NSSC process.

and total.lignin content by following the standard methods (Standard G.3 and G.9, CPPA). The carbohydrate content was estimated by subtracting the total lignin content from pulp yield.

Anthraquinone Dose Experiments

Delignification rate might be different for different anthraquinone additions as noted by Fleming et al.[3]. In kinetic experiments with an additive such as AQ, the amount of additive must be sufficient so that it does not become the limiting factor in the rate of reaction. The solubility of AQ might be a possible further interference. Hence, it was decided to use soluble anthraquinone (SAQ: soluble sodium salt of 1,4-dihydro- 9,10-dihydroxyantracene) in the kinetic experiments.

Figure 1 shows how SAQ addition influences delignification. Experiments were conducted by charging varying amounts of SAQ under identical conditions. As seen from Figure 1, the lignin content of pulp decreases with increasing SAQ charge (based on ODW)
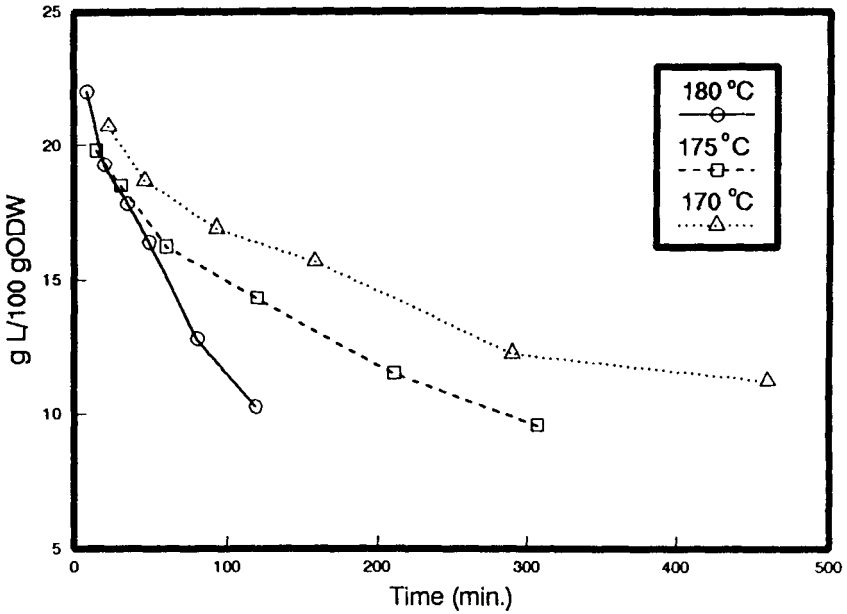
Figure 2. Effect of temperature on decrease of lignin content for NSSC pulping.

until it reaches a level of 0.5% and then it levels off around 0.5%. Hence, it was decided to use 0.5% SAQ on oven dry wood in the kinetic experiments.

RESULTS AND DISCUSSION

Figures 2 and 3 show the lignin content in wood at different isothermal temperatures for NSSC and NSSC-AQ pulping processes. The experiments show that the delignification is temperature dependent. It also shows that delignification rate is dependent on the lignin content in the wood phase.

The determination of a rate expression involves a two step procedure. First, the concentration dependence is determined at constant temperature. Then, the temperature dependence of a reaction rate constant is evaluated to obtain a complete reaction rate expression.

If the delignification process is represented by one reaction, the rate of delignification at any time would be related to the lignin content of wood at that particular
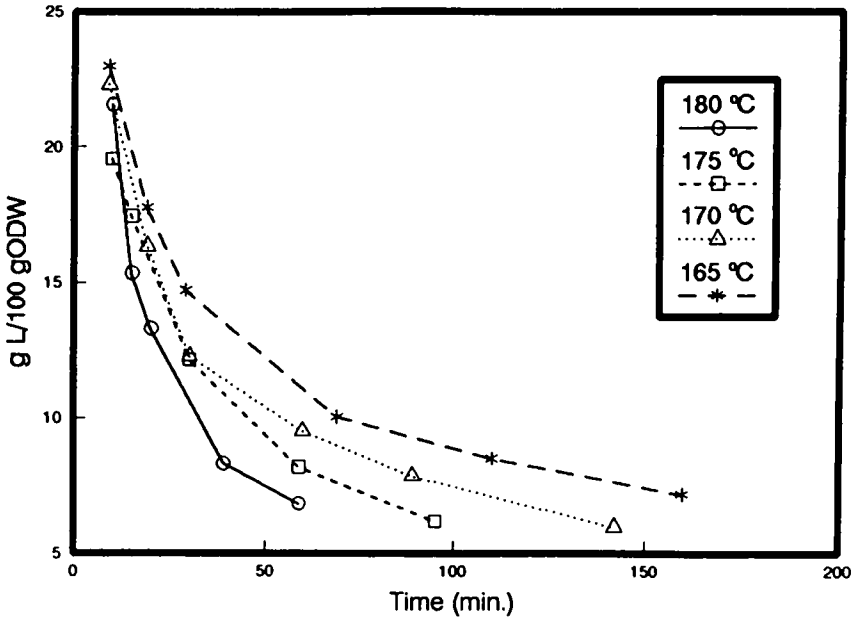
Figure 3. Effect of temperature on decrease of lignin content for NSSC-AQ pulping.

time as well as the concentration of the active delignification agents and the temperature of the system.

$$-r_L = -\frac{dL}{dt} = k_L L^n S^m$$

Eqn. 1

where, r_L is g reacted lignin / (100 g ODW)(min.), L is g lignin in pulp / 100 g ODW, S is g Na_2SO_3 / g ODW, k is proportionality constant, n and m are the constants.

In Eqn. 1 , it is assumed that all the lignin is available for the reaction and the rate is proportional to the quantity of residual lignin. It should be emphasized that the writing of rate expression in Eqn. 1 implies nothing about the mechanism of the reaction; the concept of order is empirical. In other words, n and m are not necessarily the stoichiometric coefficients and need not be integers. It is also assumed that both temperature and concentration are uniform within the bombs.
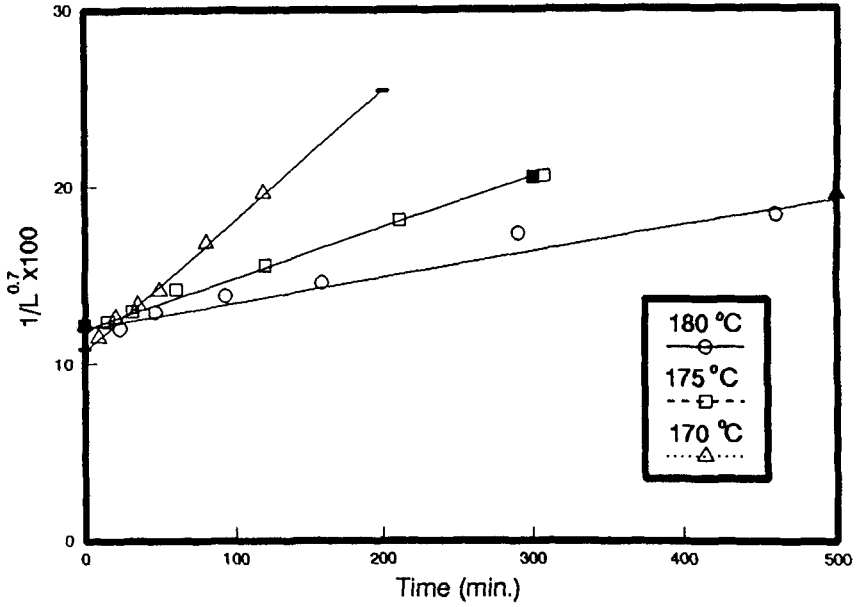
Figure 4. Delignification rate for NSSC pulping process.

S is assumed to be constant for the duration of experiment as the concentration of chemicals was as much as possible maintained constant during pulping. Thus, Eqn. 1 can be rewritten as follows:

$$-r_L = -\frac{dL}{dt} = k_1 L^n$$

Eqn. 2

where,

$$k_1 = k_L S^m$$

Eqn.3

Using an integral method to find rate parameters, k_1 and n, Eqn.2 can be rewritten as follows:
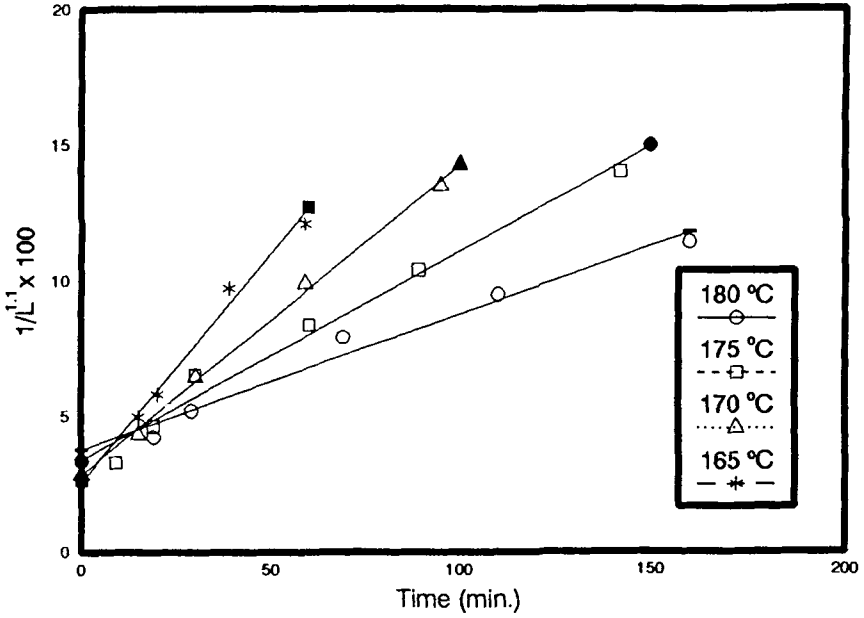
$$-\frac{dL}{L^n} = k_1 t$$

Eqn. 4

Figure 5. Delignification rate for NSSC-AQ pulping process.

and integrated with the initial condition at t=0 , L = L_0 ;

$$\frac{1}{L^{n-1}} = \frac{1}{L_0^{n-1}} + k_1 (n-1) t$$

Eqn. 5

The results of this analysis for delignification in NSSC liquors are shown in Figure 4 and Table 2 summarizes values of k for each reaction temperature and reaction order n = 1.7.

Figure 5 shows results of similar analysis carried out for the NSSC-AQ process. The values of k_{LAQ} are tabulated in Table 2. The best fit value of n was found to be 2.1.

Equation 5 was tested by plotting the experimental lignin values versus predicted lignin values which were calculated from Eqn.5 for NSSC and NSSC-AQ processes as seen from Figures 6 and 7, respectively. The reaction orders with respect to lignin for NSSC and

TABLE 2. Rate Parameters for NSSC and NSSC-AQ Pulping

TEMP. °C	k_L x 10^{-4}	$k_{L,AQ}$ x 10^{-4}	$k_{L,AQ}/k_L$
165	2.18	4.96	2.28
170	2.79	7.70	2.76
175	4.90	11.20	2.29
180	11.32	16.32	1.44
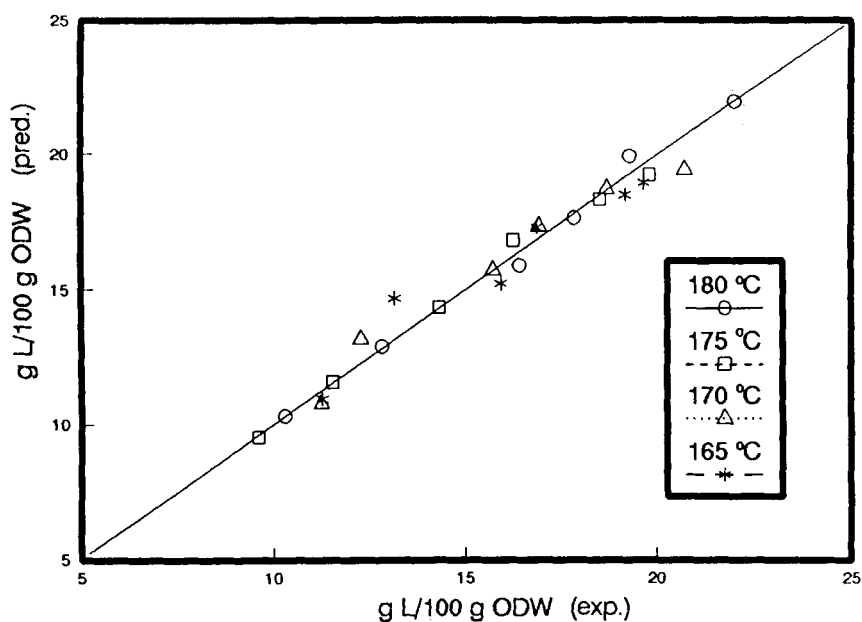
Figure 6. Relationship between experimental and predicted lignin values for NSSC process.

NSSC-AQ processes were found to be quite close to each other (1.7 for NSSC and 2.1 for NSSC-AQ). It should be noted that a computer-based nonlinear regression analysis determined that the 95% confidence intervals for these reaction orders were respectively 1.59 to 1.81 and 2.04 to 2.17.
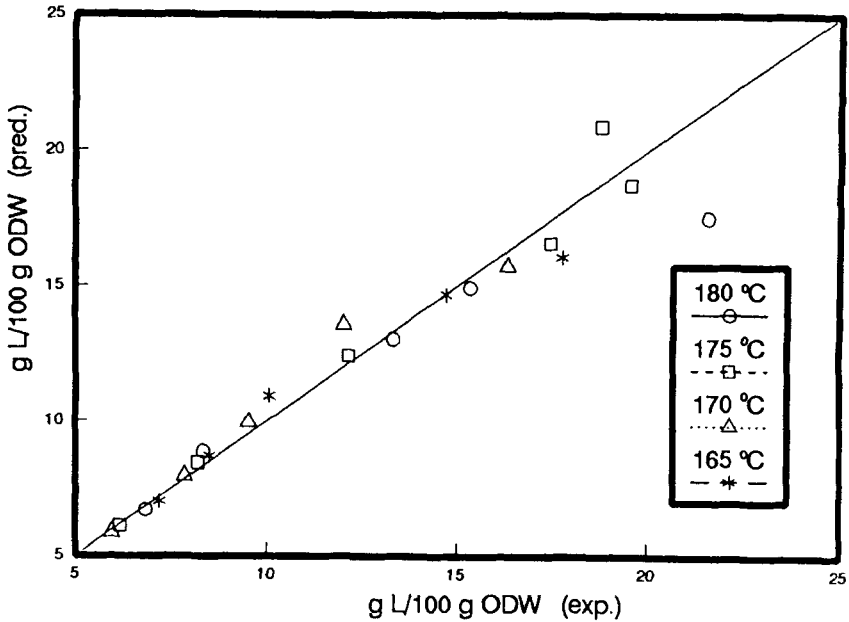
Figure 7. Relationship between experimental and predicted lignin values for NSSC-AQ process.

The initial lignin content can be calculated from integral analysis (i.e. from the intercept of Eqn. 5). As seen from Figures 4 and 5, the lines have a common intercept (with an average lignin value of 23 g/100 g ODW) at around time = 10 minutes. However, total wood analysis gives the initial lignin amount to be around 28%. The reason for this difference is due either to an uncontrolled initial delignification rate or to some soluble organics present in the wood. The wafers with cooking liquor were heated until they reached 165 °C, then heating is stopped and the wafers were analyzed for the total lignin. The lignin content of the wafers was found to be 23 g L/100 g ODW. Thus, it can be concluded that some lignin is lost during the initial heating period.

The rate constant k   is related to the   absolute   temperature by the Arrhenius expression :

$$k_L = A \, e^{-E/RT} \hspace{5cm} Eqn.6$$

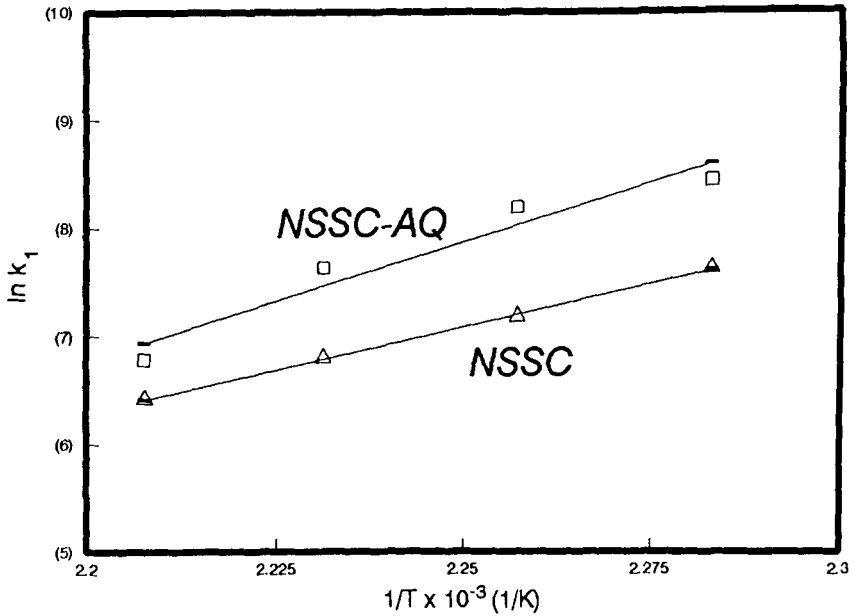where, A is Arrhenius constant, E is activation energy, T is absolute temperature and R is the gas constant.

Figure 8. Temperature dependence on delignification rate constant for NSSC and NSSC-AQ processes.

By plotting ln k versus 1/T, as shown in Figure 8, the activation energies for the NSSC and NSSC-AQ delignification processes were found to be 181 and 130 kJ/mol. with the Arrhenius constants of 7.74×10^{17} and 1.78×10^{12}, respectively. Since the activation energy shows the temperature sensitivity of the reaction i.e. a high temperature-sensitive reaction has a high activation energy, the delignification in NSSC process is more temperature sensitive than the delignification in NSSC-AQ process. Therefore, a temperature rise favours the delignification in NSSC liquors more than in NSSC-AQ liquors.

The delignification rate equation 2 can be now rewritten with known parameters as follows ;

For NSSC process:

$$-r_L = -\frac{dL}{dt} = 7.74 \times 10^{17} e^{-181000/RT} L^{1.7}$$

Eqn. 7

For NSSC-AQ process:

$$-r_{L,AQ}=1.78 \times 10^{12} e^{-130000/RT} L^{2.1}$$

Eqn. 8

Equations 7 and 8 are valid for the temperature range from 165 to 180 °C and for the lignin range from 23 to 10 g L/100 g O.D.W.

The values of activation energies and reaction orders in the present investigation agree well with the values published in the literature.

Addition of AQ affects the delignification rate in two ways. First, it increases the reaction order in lignin from 1.7 to 2.1. Second, the reaction rate constant increases.

Delignification rate is dependent on the lignin content of the wood and this dependence is much higher for NSSC-AQ than for NSSC process. This is substantiated by the shape of the curves, L = f(t) in Figures 2 and 3. The curve, L = f(t) is a consequence of a number of chemical reactions which we don't know exactly. If addition of anthraquinone changes the mechanism of pulping in such a way that the delignification rate becomes an additive expression, then the rate may resemble a higher order reaction. Equation 1 is only one of many possible models which fit our experimental results.

Table 2 shows the reaction rate constants at different temperatures. At any temperature investigated here, the ratio of the rate constant of the reaction with AQ to the constant of the reaction without AQ, is higher than one, which indicates that the addition of AQ increases the reaction rate constant in the range of temperatures from 165 to 180 °C.

CONCLUSIONS

The following conclusions can be drawn from this study:

The delignification rates for NSSC and NSSC-AQ can be described by 1.7th order reaction and 2.1th order reaction in the remaining lignin, respectively.

The activation energies for NSSC and NSSC-AQ were found as 181 and 130 kJ/mol respectively. It was concluded that NSSC process is more temperature dependent than NSSC-AQ process.

The addition of anthraquinone speeds up the delignification rate.

ACKNOWLEDGEMENTS

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