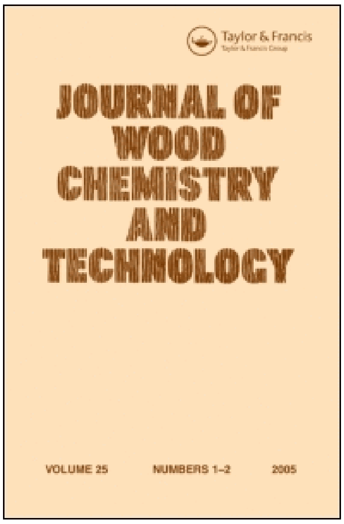

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DELIGNIFICATION KINETICS OF SODA PULPING OF KENAF

Harshad Pande and D.N.Roy
Faculty of Forestry
University of Toronto
Toronto, Canada, M5S 3B3

ABSTRACT

Kenaf (Hibiscus Cannabinus) is an alternative, non wood fiber source for pulping and papermaking. Delignification kinetics of extractive free samples from three fractions of kenaf procured from Mississippi State University, U.S.A have been studied. The extractive free samples were cooked at three different temperatures: 140^0 C, 155^0 C, and 170^0 C with soda cooking liquor. The results indicate that the activation energies for the bark, core, and whole kenaf are 68 kJ/mole, 91 kJ/mole, and 75 kJ/mole respectively. These are significantly lower than the reported values for the conifers. The delignification selectivity for the three samples was also investigated.

INTRODUCTION

Declining availability of economic wood fibers, due to forest conservation and environmental concerns, is one of the major problems affecting the pulp and paper industries globally. Because of the shortage of wood fibers projected by the forest product industries, a new initiative in the propagation and utilization of fast growing hybrid species is required. The 12 million hectares of land needed to produce the 1990 global fiber requirement will almost double to 23 million hectares in 2010[1].

One possible solution could be the use of non wood fibers such as straws, kenaf, bamboo, and bagasse, which are harvested on shorter rotations.

In 1995 Tappi global fiber supply symposium there was a resurgence in the interest in non woods for paper and related products. McCloskey[2] points out that even forest rich U.S and Canada are experiencing fiber supply problems as the governments are restricting harvesting, and recyclable waste paper prices have increased ten folds in the past few years. The non wood plants already account for 9.15 % of the total world papermaking capacity (as of 1990) and, the average percentage annual increase in non wood plant fiber pulp capacity is more than double the average annual increase in the wood pulp capacity i.e. 4.7% vs 2.0%[3]. Kenaf, a non wood fiber, is being used on a limited scale as a substitute for wood in the production of pulp and paper in Thailand and Peoples Republic of China[4]. Kenaf is a dicotyledon, having two morphologically distinctive regions in its stem. The outer portion of kenaf stem is known as bark, and it contains long bast or cordage fibers, while the inner or woody portion is termed as core which contains short fibers. The whole stalk of kenaf constitutes about 60 - 65 % of core fibers and 35 - 40 % of bast fibers[5]. Bast fibers are about 2.5 mm long, while the core fibers are about 0.6 mm long.

USDA has extensive work published in kenaf since 1960. The work started with a scheme for evaluation of potential plants as new sources of paper pulp[6,7,8,9] Chemical[10,11,12], semi-chemical, mechanical[13,14], biomechanical[3] pulps have been prepared from the bark and the core fractions of kenaf. It was concluded in these studies that strengthwise the kenaf pulps are superior to hardwood pulps, and with the exception of resistance to tear, the kenaf pulps are comparable in strength properties with softwood kraft and superior to softwood sulfite. Resistance to tear of the softwood pulps exceeded that of kenaf pulps. Kenaf pulps are superior to hardwood pulps in this property. Kenaf soda pulps have strength properties equivalent to those of the kenaf sulfate pulps and a better initial drainage characteristics (freeness) than those of the kenaf sulfate pulps[17]. Paper with strength generally comparable to commercial newsprint could be made from furnishes containing bleached kraft TMP and at least 12% long fiber[15]. Clark and Wolff[18] studied the influence exhibited by the composition of handsheet blends on several physical properties with blends made from combinations of experimental kraft and neutral sulfite pulps using various commercial hardwood and softwood pulps. Watson et al[16] have shown that kenaf pulps have slower drainage characteristics than wood pulps made by the same processes and beating. The pulp properties of kenaf as a function of their composition, yield, and freeness are reported by Calabro[19].

The kinetics of alkaline delignification have been much studied[20] and found to fit a first order process with respect to lignin and hydroxide concentration. Larocque and Mass[21] have shown that the soda delignification rate appears to be proportional to the product of the unremoved lignin, L, and the concentration of sodium hydroxide in the liquor [OH⁻]. Quantitatively this leads to the rate equation

$$-\frac{dL}{dt} = K_1[OH^-].L \qquad \text{--------------------------------(1)}$$

where $\frac{dL}{dt}$ represents the rate at which lignin is removed and K_1 is the reaction rate constant, independent of liquor concentration.

If pulping is performed under a constant liquor concentration, then the expression of K_1 $[OH^-]$ becomes a single constant K_0 and integration of Equation (1) yields

$$\ln L_0 - \ln L = K_0\, t \qquad \text{------------------------------(2)}$$

According to Equation (2), a plot of ln(L) versus digestion time, t, should result in a straight line of slope $-K_0$, and intercept $\ln(L_0)$.Therefore, a plot of residual lignin versus time gives a straight line with the slope representing the value of K_0 (sec^{-1}). L_0, is referred as the effective initial lignin content of the wood. The activation energy of the pulping reaction can be determined by using the Arrhenius equation

$$K_0 = (A) \exp\left(-\frac{E_a}{RT}\right) \qquad \text{----------------------------(3)}$$

where A is the Arrhenius constant, E_a is the activation energy (kJ/mole), R is the gas constant (8.314 kJ/^{0}K.mole) and T is the absolute temperature (^{0}K).

Equation 3 can be rewritten as

$$\ln(K_0) = \ln(A) - (\frac{E_a}{R}) \times \frac{1}{T} \qquad \text{------------------------------(4)}$$

Thus if the change in the rate of delignification with increase in temperature during pulping takes place in the manner predicted by the activation theory of Arrhenius, a straight line relationship should result on plotting $\ln(K_0)$ against $1/T$, with a slope=E_a/R.

EXPERIMENTAL

Material and Methods

In this study kenaf bark, kenaf core, and whole kenaf stem was procured from Mississippi State University, (USA). Investigation of the soda pulping kinetics of different kenaf fractions was carried out under controlled conditions in the laboratory. Reaction rates and the activation energies of the bulk delignification were determined. The samples for the chemical analysis and pulping were prepared as per Tappi standards (T 257 cm - 85) by grinding air dried samples in a Wiley mill to pass a 0.4 mm (40 mesh) screen. Kenaf meal was used instead of chips to ensure that the rate determining step in pulping was not mass transfer of chemicals into the raw material or reaction products out of the raw material.

It is reported[22] that generally, raw material having higher specific gravity take longer time to reach a certain yield level as opposed to material with a lower specific gravity. The bark and core fractions in kenaf have different specific gravities; it would be expected that grinding the sample to powder reduces the difference in the delignification rates caused by the specific gravity differences.

Pulping procedure

Extractive free [E F] samples for bark, core, and whole kenaf were prepared by extracting with ethanol:benzene (1:2 by volume) following Tappi standard (T264 om - 82). Extraction eliminates the effect of extractives on pulping.

Soda cooking liquor of 32 gpl NaOH with active alkali charge of 15% as Na_2O was used. The E F ground meal samples were placed in a stainless steel reactor (25 ml) with screw caps, and soda cooking liquor was added to maintain the raw material to liquor ratio of 1:6. The charges of bark were higher compared to core and whole kenaf (2.50 gms vs 1.77 gms on oven dry basis) because of the difference in bulk densities. A presoaking period of 30 min. at room temperature was provided before immersing the reactors in a silicone oil bath, thermostatically controlled at the desired temperature. The range of temperatures studied was 140°C to 170° C. The time to reach the reaction temperature is the time required to regain the temperature after the reactors are immersed in the oil bath and it varied with temperature, (25 min. at 170° C, 20 min. at 155° C, and 15 min. at 140°C). The reaction was stopped by quenching the reactor in a bath of running cold water. Before dipping the reactors in cold water, they were cleaned in an cooled kerosene bath which removed the silicone oil from the surface of the reactors, thereby eliminating the possibility of contamination by these substances. The reaction time reported is the time at temperature, and it does not take into account the time to reach the temperature. The resulting pulp with liquor was transferred to an Buchner funnel and washed with enough distilled water to transfer the pulp with liquor from the reactors. The pulp was washed with water and the yield and residual lignin content of the pulp was determined. The reported total residual lignin content is the sum of the Klason lignin and the acid soluble lignin determined as per Tappi standard T222 om - 83 and Tappi UM 250. Hollocellulose and alphacellulose were determined as per the procedure described by Zoebel et al[29]. Tappi T 211 om-85 was followed for ash content determination.

RESULTS AND DISCUSSION

Chemical Composition

The chemical analysis of the three kenaf samples studied is given in Table1. The kenaf whole (calculated) data listed in the table represents the calculated value

TABLE 1.

Chemical Analysis of Different Fractions of Kenaf

Characteristics (Average)	Kenaf Bark	Kenaf Core	Kenaf Whole	Kenaf Whole (Calculated)*
Lignin (%)	11.8	18.3	16.2	16.0
Hollocellulose (%)	81.1	71.6	76.5	74.9
Alpha Cellulose(%)	51.0	34.9	44.1	40.6
Extractives (%)	2.8	4.8	3.2	4.1
Ash (%)	2.8	1.8	2.1	2.1

*Bark to Core ratio of 35% to 65%.

based on the bark to core ratio of 35% to 65% in the kenaf stems used for this work. Higher percentage of alpha cellulose in kenaf bark indicate that it would give better pulp yield and strength. High lignin content in the kenaf core indicates the need for more chemicals during pulping. The values for kenaf whole are in between the values for kenaf bark and kenaf core, which is as expected. The calculated values of whole kenaf based on 35% bark and 65% core as given in Table 1, Table2, and Figure 3 vary from the experimental values for whole kenaf. This may be due to the difference in the particle size distribution or the density.

Delignification Selectivity

Figure 1 shows the pulping selectivity curve for the bark, core, and whole kenaf. The bark fraction clearly represents the most selective condition, since for a given lignin content the yield is highest in case of bark pulp and least in case of core pulp. Thus the bark fraction is more favorable for pulping compared to whole kenaf or the core fraction.

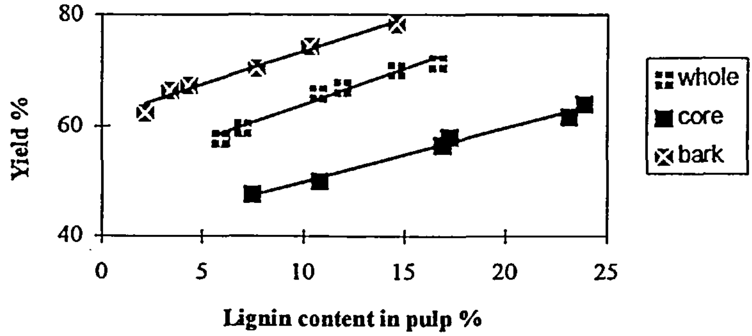

Figure 1. Pulping selectivity curve for kenaf fractions

Delignification Kinetics

The delignification kinetics data for bark, core, and the whole kenaf were obtained after cooking 180 bombs (stainless steel reactors), involving 18 sets of cooking in the micro pulping unit. The logarithmic plot of percent residual lignin on raw material against pulping time at three different temperature for the bark pulp is shown in Figure 2. Ln(lignin) is negatively correlated with the pulping time. Similar correlations were found for the core pulp and the whole kenaf pulp.

The delignification data gives the following information:

(1) The intercept ln(L_0) gives a measure of the proportion of the total lignin that follows the bulk reaction rate.

(2) The slope gives the rate constant (K_0) for the removal of lignin.

L_0 is derived from the value obtained by extrapolation of the linear portion to zero digestion time and is not equal to the lignin content of the wood. L_0 is referred to as the "effective initial lignin content" of the wood. The difference between the actual lignin content and L_0 gives the rapidly removed lignin in the initial stage[23,24](L_R).

Thus

$$L_R = L_w - L_0 \quad \text{--}(5)$$

where L_w is the actual lignin content of the wood.

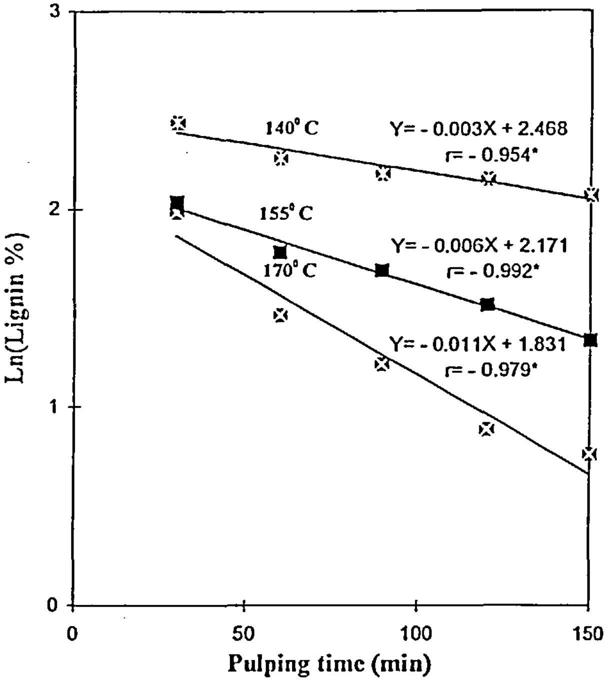

Figure 2. Delignification kinetics of kenaf bark.Asterisk (*) indicate significance of correlation at 0.05 level.

Table 2 shows the values of L_0 and L_w for the bark, core, and whole kenaf. Based on the calculated values of L_R and L_0 the percentages of lignin removed in the initial delignification phase and the remaining bulk delignification stage are shown in Figure 3. Different values of L_0 and L_R are probably due to the actual difference in the chemistry of the lignin in the three samples.

Figures 4, 5 and 6 show the Arrhenius plot of $\ln(K_0)$ versus $1/T$. Activation energies were calculated from the slopes of linear regression lines. The test for comparison of slopes and intercept was carried out on these plots, and it was found that the differences in activation energies reported for the bark, core, and whole kenaf are statistically significant at 0.05 level. Activation energies, calculated for the

TABLE 2.

The Effective Lignin Content (L_0) for Different Fractions of Kenaf

Kenaf Fraction	Average L_0	L_K
Bark	8.9	2.9
Core	14.4	4.1
Whole	11.1	4.6
Whole (calculated) *	12.5	3.7

*Bark to Core ratio of 35% to 65%

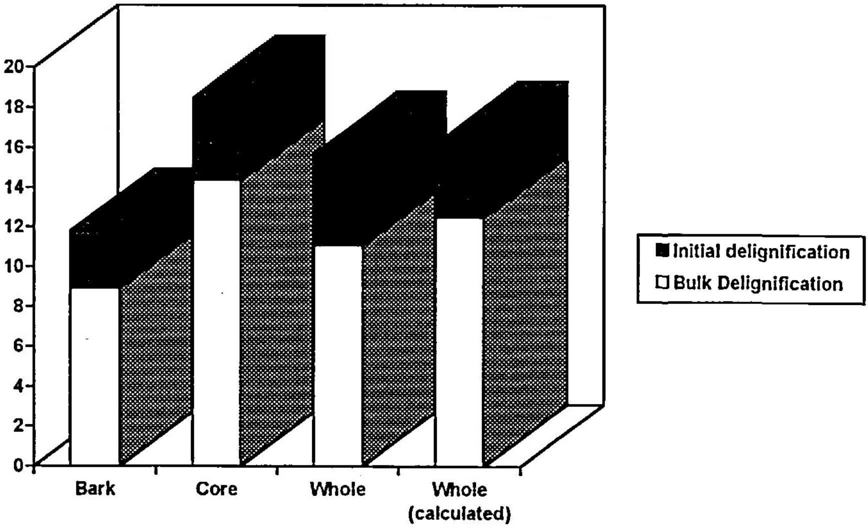

Figure 3. Amounts of lignin removed during delignification

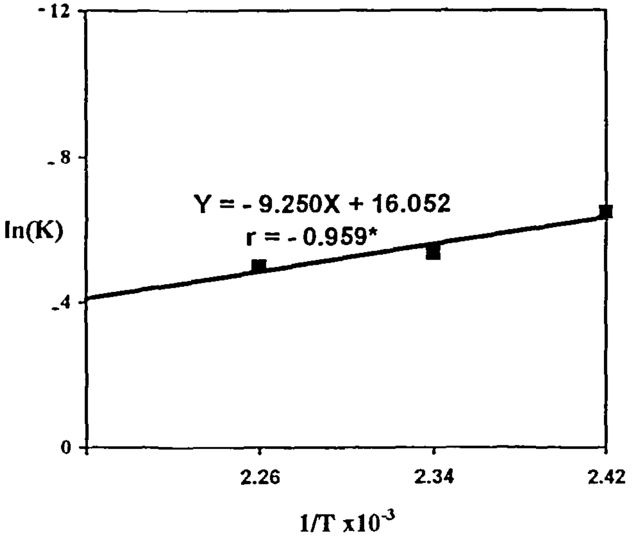

Figure 4. Arrhenius plot of soda pulping of kenaf whole.

Asterisk (*) indicate significance of correlation at 0.05 level.

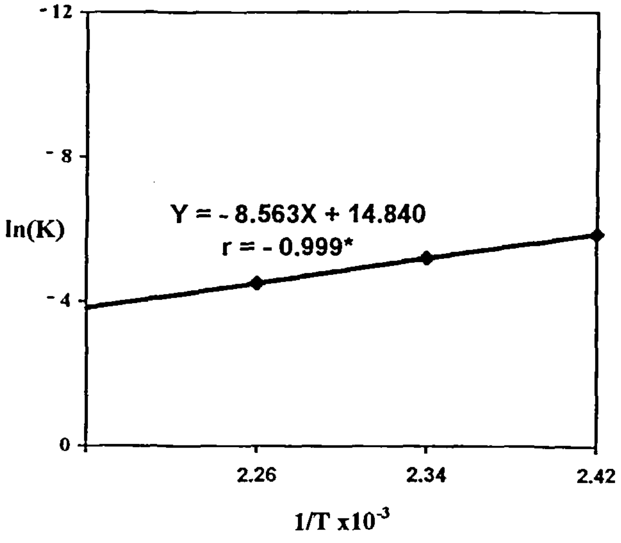

Figure 5. Arrhenius plot of soda pulping of kenaf bark.

Asterisk (*) indicate significance of correlation at 0.05 level.

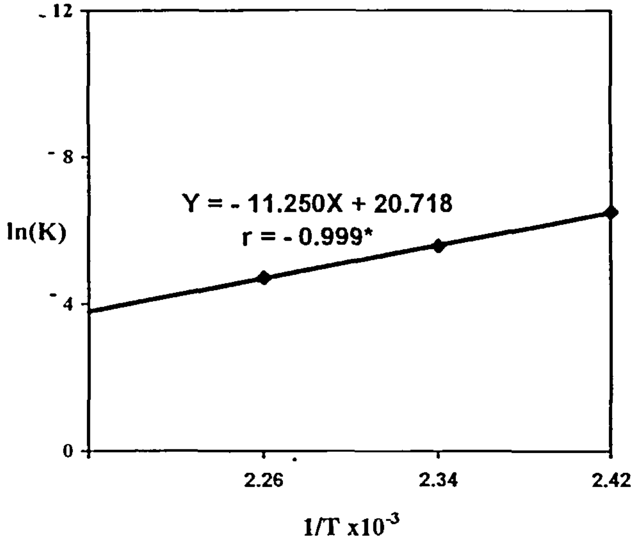

Figure 6. Arrhenius plot of soda pulping of kenaf core. Asterisk (*) indicate significance of correlation at 0.05 level.

best fit straight lines through the points for each of the three fractions, were 68 kJ/g-mole for bark, 91 kJ/g-mole for core, and 75 kJ/g-mole for whole kenaf. The activation energy for the whole fraction based on 35% bark and 65% core comes out to be 83 kJ/g-mole. About 35% difference in activation energy was observed between bark and core fractions of kenaf as shown in Figure 7. This indicates that the bark fraction of kenaf is relatively more favorable for pulping because of its low activation energy, followed by the kenaf whole and kenaf core respectively. The activation energies for the three kenaf samples studied were lower than the activation energies obtained for soda delignification of loblolly pine (E_a = 143 kJ/g mole) by Wilder and Daleski[25] and by Wilson and Proctor[26] for soda delignification of western hemlock (E_a=130 kJ/g mole).This indicates that it is easier to pulp kenaf compared to softwoods. The softwood lignin contains mainly guaiacyl units

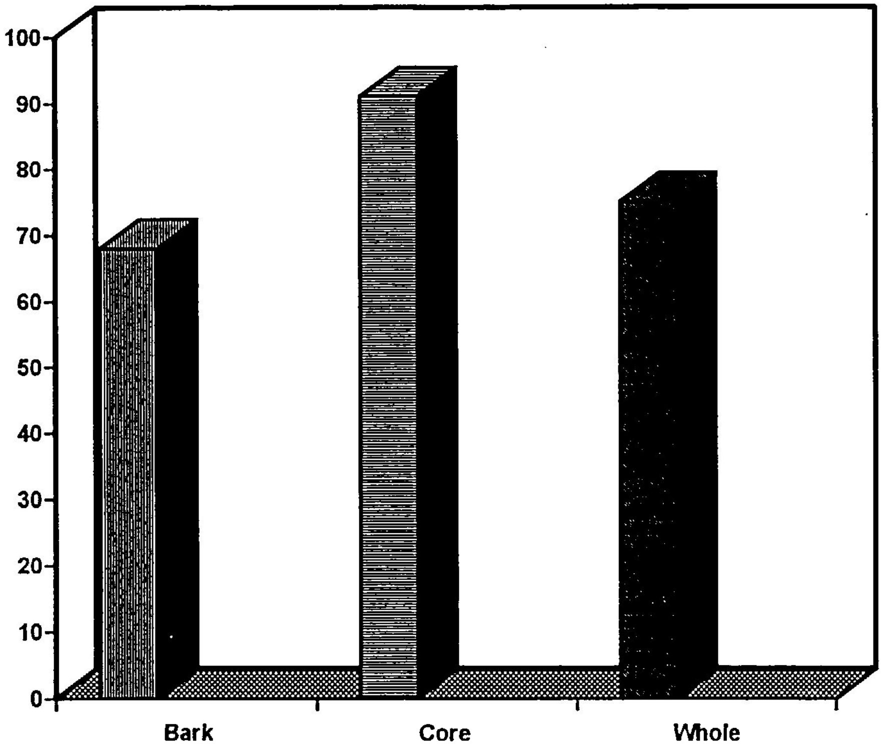

Fig. 7. Activation energy for different kenaf fractions

TABLE 3.

Activation energy and reaction rates of kenaf fractions

Kenaf fraction	K_0 = Reaction rate (sec^{-1})			E_a = Activation Energy (kJ/mole)
	170^0 C	155^0 C	140^0 C	
Bark	0.0109	0.0055	0.0028	68
Core	0.0089	0.0038	0.0015	91
Whole	0.0068	0.0023	0.0024	75

together with some p-hydroxy phenyl units, and have C-C linkages which are not easily broken. In contrast, kenaf lignin has been found to be syringyl rich, as observed by Ralph et al[27] and this should respond to kraft pulping more readily than softwoods. The values of activation energies for the bark, core, whole kenaf as given in table 3 strongly indicate that the experiments in this study were "chemical reaction controlled", since a diffusion controlled reaction is generally characterized by an activation energy in the neighborhood of 21 kJ/g-mole as pointed out by Wilder and Daleski[25].

Kenaf lignin structure by correlation of CMR, FTIR, and chemical analysis is reported by Abbot et al [28]. They have shown that milled kenaf lignin is similar but not exactly the same as lignin in plant. This study does not consider the bark and the core fractions separately. The variation in the activation energies for kenaf bark, and kenaf core may be due to the difference in the chemical nature of the lignin in each fraction. Future work aims to explain these variation with the above hypothesis in mind.

CONCLUSIONS

The delignification selectivity data indicates clearly that bark fraction of kenaf gives the most selective condition for pulping followed by the whole kenaf and the core fractions respectively. A wide variation in the activation energies of the three fractions of kenaf indicate that for optimal utilization of kenaf as a raw material for papermaking, the bark and core fractions should be processed separately and then blended, as per requirement, at the blending chest later on in the process.

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