ADSORPTION OF HEMICELLULOSE EXTRACTS FROM HARDWOOD ONTO CELLULOSIC FIBERS. I. EFFECTS OF ADSORPTION AND OPTIMIZATION FACTORS

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The adsorption of dissolved hemicelluloses derived from US southern mix hardwood to cellulosic fiber is an efficient way for hemicellulose utilization. Retaining more hemicelluloses on the cellulose fibers leads to a higher pulp yield, better beatability and improved pulp strengths. The primary aim of the current work was to investigate the hemicellulose adsorption process through treating Kraft pulp in the extract liquor. The main effects of the process factors and their interactive effects were discussed *via* statistical analysis. The optimization of the adsorption process was also studied.
In the process of hemicellulose adsorption, three main factors – fiber consistency, extracts-to-fiber ratio and temperature – showed significant effects upon adsorption. A higher extracts-to-fiber ratio and higher temperature contributed to enhancing the hemicellulose adsorption yield. The quadratic function that characterizes the relationship between fiber consistency and adsorption yield was determined.
Overall, a high concentration of extract liquor is necessary to achieve a high hemicellulose adsorption yield. There exists a strong and profound interaction between temperature and fiber consistency, therefore an optimal control of both temperature and fiber consistency in adsorption would improve adsorption efficiency. Since fiber consistency is easier to control, it serves as a key parameter for increasing the adsorption yield.

Keywords: adsorption, hemicellulose extraction, experimental design, kraft pulping, xylan redeposition

INTRODUCTION

Hemicelluloses are one of the main components in plant biomass, which is the second most plentiful natural resource in the world. In wood species, there are two major classes of hemicelluloses: glucomannans and xylans. The dominant hemicellulose in softwood is acetyl-galactoglucomannan, at about 20 w/w%, while glucoronoxylan (15-30 w/w%) predominates in hardwoods.[1] Under alkaline conditions, glucomannan is rapidly degraded by the peeling reaction, while xylan is dissolved into an oligomeric form.[2] During chemical pulping, most of the hemicelluloses are lost, as due to degradation and dissolution. In a pulp mill, most of the hemicelluloses end up in the spent pulping liquor and burn off in the process of alkali recovery system. In fact, only a small amount of residue hemicelluloses remain in cellulosic fibers after pulping. Although cellulose is the major compound in pulp fiber, hemicelluloses also bring an important contribution to pulp quality. Firstly, retaining more hemicelluloses in pulp always means a higher pulp yield; secondly, hemicelluloses can improve pulp beatability by shortening the beating time to acquire the same freeness;[3] more importantly, hemicelluloses contribute to improving pulp properties, such as adsorption ability,[4] softening paper product,[5] while reducing the dust[6] and enhancing pulp strength.[7-8] Out of these advantages, the increase in pulp yield and the improvement of pulp strength are the most important advantages of hemicellulose retention. In the past decades, many efforts have been made to stabilize hemicelluloses during pulping for increasing the pulp yield. However, the current pulping technology still lacks the efficient tools to prevent hemicellulose degradation.

Due to the unavoidable dissolution of hemicelluloses during chemical pulping, the re-deposition of the dissolved hemicelluloses back onto the fiber is one of the alternatives for hemicellulose retention in the pulping process. In the past decades, few studies related to hemicellulose adsorption have been reported in the literature. It was found out that xylan dissolved in the pulping liquor could be adsorbed onto the cellulose fiber in Kraft cooking.[9-11] Both glucomannan and xylan could be adsorbed on the cellulose fiber, but at a different rate.[12] The different fiber types, cotton, hardwood and softwood pulp exhibited significant differences in the adsorption yield.[10] Physical adsorption was considered to be the nature of hemicellulose adsorption.[13] More recently, research findings have been reported on the influence of xylan adsorption upon pulp strength.[14-16] Some progresses in hemicellulose application have been achieved in a previous work. However, only a few investigations have dealt with hemicellulose adsorption on the cellulose fiber. A lot of questions remain to be answered, regarding the following aspects: the mechanism of adsorption, the features of the adsorption process, thermodynamic and kinetic characteristics of adsorption, and chemical behavior of hemicellulose components during the adsorption process. The aim of the current work was, therefore, to investigate the effects of the adsorption process factors and their influence on hemicellulose adsorption. The optimization of the adsorption process was also investigated.

EXPERIMENTAL

Materials

Wood chips: Mixed hardwood chips were obtained from International Paper Inc. All barks and knots were removed. The chips were screened using a Weyerhaeuser classifier. The wood fractions passing a 1-inch hole, but remaining on the 7/8-inch and 5/8-inch round screens, were collected. The chips were then classified for chip thickness, to achieve chips less than 10 millimeters thick. The wood chips were air-dried to a constant moisture level (~9%) and stored in plastic bags until extraction and pulping.

Pulp: The pulp for the present experiments was acquired from pre-extracted kraft pulping. Pulp screened yield – 43.17%, kappa number – 16.01.

Extraction liquor: The same extraction liquor was applied for all designed experiments.

Hemicellulose extraction

The extraction and pulping operations were performed in an M&K digester. The digester was electrically heated, the liquor was circulated and the temperature program was computer-controlled. 600 g screened wood chips (o.d.) were loaded in the digester for each experiment. In the current investigation, green liquor (GL) was used as an alkali resource added for hemicellulose extraction. The GL was made in our laboratory, to simulate a representative industrial composition. It contained: sodium hydroxide 10.15%, sodium sulfide 29.30% and sodium carbonate 69.36% (all as Na_2O).

When the extraction was completed, the liquor was cooled down, drained, its volume measured and then filtered and stored in a cold room for further use.

The extracted wood chips were further subjected to pulping in the same digester.

The extraction and Kraft pulping conditions are summarized in Table 1.

Adsorption

About 2 g (o.d.) pulp (accurate to 0.0001 g), designed extraction liquor and water were thoroughly mixed and loaded in a thermal-seal plastic bag and sealed. The sample bag was put in a water bath and treated at the designed temperature for the required time, after which the sample was transferred onto the weighed filter paper in the filtration funnel. The extraction liquor was drained and stored for further measurements. The sample was thoroughly washed by using 1000 mL deionized water and air-dried in a conditioned physical test room, at constant temperature and humidity (TAPPI standard). The sample was weighed and moisture was measured.

The adsorption yield is defined as the cellulosic pulp weight gain through adsorption, calculated by the weight difference between adsorbed and original pulp.

Experimental design

A central composite experimental design was applied for the current investigation. Four factors were selected as adsorption variables, namely: fiber consistency (%), the extracts-to-fiber ratio (g extracts/g fiber), adsorption temperature and time. The experimental variables and the level range are shown in Table 2. As required by the experimental design, there are five levels for each factor, coded from -2 to 2. Table 3 shows the designed experimental points of all variables at each level, corresponding to each coding level. All experimental data are duplicated and summarized in Table 4.

RESULTS AND DISCUSSION

Characteristics of extraction liquor composition

The application of 3% green liquor (GL) allowed extraction in an alkaline environment. The extraction liquor contained sodium hydroxide, sodium sulfide and sodium carbonate. During the extraction, the caustic alkali was fully consumed, due to the neutralization of organic acid groups. Sulfide could not be detected, which means that it was either consumed by neutralization or converted to other sulfur forms. Carbonate, however, still remained in the extraction liquor at a slightly lower concentration, compared to the original liquor. Due to the generation of organic acid groups from the degradation of both polysaccharides and lignin macromolecules, the resulting extraction liquor became weakly acidic, with a pH of 5-6. The properties and chemical composition of the extracts are summarized in Table 5.

During the extraction, around 10% of the wood components were removed from the hardwood chips. As expected, xylan, the major polysaccharide present in hardwood hemicelluloses, was the main component of the hemicellulose extracts.

Another feature of the extracts was the high acetate content (40%) of the total extracts. These acetates were mainly derived from the xylan molecule chain, and the substantial uronic acid group in the extracts also came from xylan. Therefore, the dominating components in the extracts were xylan-type hemicelluloses, over 80% of the extracts solids. Besides xylan, some other sugars were also present in the extracts as minor components. In addition, since the lignin carbohydrates complex was present in wood, a small amount of lignin, 5% of the extracts, was also extracted with hemicelluloses.

In brief, the current extraction process resulted in a weakly acidic extract liquor – pH 5-6. Furthermore, xylan was the main component in the extracts – over 80%. Such xylan-rich liquor was then applied to treat hardwood pulp for re-depositing xylan onto the cellulose fiber.

Optimization investigation

The main factors that may exert a significant influence on adsorption, such as fiber consistency, extract concentration (shown as ratio of extracts-to-fiber), adsorption temperature and time, were selected for further systematic investigations by applying the experimental design.

Based on the experimental data, the regression equation is described as Equation 1:

$$Y=11.29+0.84X_1+2.16X_2+1.63X_3+0.52X_4-0.09X_1X_2+0.22X_1X_3\quad 0.10X_1X_4+0.47X_2X_3+0.28X_2X_4-0.12X_3X_4-0.93X_1^2-0.70X_2^2-0.02X_3^2-0.07X_4^2 \quad (1).$$

The statistic analysis is shown in Table 6. The confidence level for each factor indicates the relevance of the factor with the responding result. Generally, only factors with confidence levels over 95% showed significant statistics.

After ignoring the less relevant items from the equation, the optimized equation becomes more concise, as shown in Equation 2:

$$Y=11.29+0.84X_1+2.16X_2+1.63X_3+0.52X_4+0.22X_1X_3+0.47X_2X_3+0.28X_2X_4-0.12X_3X_4-0.93X_1^2-0.70X_2^2 \quad (2).$$

Main effects of process factors on adsorption yield

Based on the above Equation (2), the main effects of all process factors on adsorption are elucidated in Figure 1. When each factor was changed in the region of the experimental design, as shown on the X-axis, the other three factors were kept constant at mid-level.

Table 1
Extraction and pulping conditions

Pre-extraction		Kraft pulping	
Wood load (g)	600	EA charge % on wood	12
GL charge (% on wood)	3	Sulfidity	28.91
Total liquor-to-wood ratio	4	AA % on wood	14.03
Ramp time (min)	50	Ramp time	60
Extraction temp. (ºC)	160	Temperature	170
Extraction time (min)	110	H-factor	1400

Table 2
Variables and ranges

Factor	Unit	Variable range
Fiber consistency (X_1)	g/100 g liquor	0.1 ~ 8.0
Ratio of extracts to fiber (X_2)		0.1 ~ 5.0
Temperature (X_3)	ºC	40 ~ 95
Treatment time (X_4)	Min	20.0 ~ 120.0

Table 3
Coding of factor levels

Code	X_1	X_2	X_3	X_4
-2	0.1	0.1	40	20
-1	2.1	1.3	53.8	45
0	4.1	2.6	67.5	70
1	6.0	3.8	81.3	95
2	8.0	5.0	95.0	120

Table 4
Experimental design data

Fiber consistency, %	Ratio of extracts to fiber	Temperature, ºC	Time, min	Adsorption yield, %
2.1	1.3	53.8	45.0	6.24
6.0	1.3	53.8	95.0	7.26
2.1	3.8	81.3	45.0	12.08
6.0	1.3	81.3	45.0	9.41
2.1	3.8	81.3	95.0	13.82
2.1	3.8	53.8	45.0	8.75
6.0	3.8	81.3	95.0	14.24
0.1	2.6	67.5	70.0	3.34
6.0	3.8	53.8	95.0	9.55
8.0	2.6	67.5	70.0	11.56
4.1	2.6	67.5	70.0	10.73
4.1	5.0	67.5	70.0	14.17
4.1	2.6	67.5	70.0	11.31
4.1	0.1	67.5	70.0	2.56
4.1	2.6	67.5	70.0	11.85
2.1	1.3	81.3	95.0	8.39
4.1	2.6	67.5	70.0	11.45
6.0	3.8	81.3	45.0	13.77
4.1	2.6	40.0	70.0	7.75
4.1	2.6	67.5	20.0	9.09
2`1	3.8	53.8	95.0	10.41
2.1	1.3	53.8	95.0	6.63
6.0	1.3	53.8	45.0	6.70
2.1	1.3	81.3	45.0	8.81
4.1	2.6	67.5	70.0	11.39
4.1	2.6	95.0	70.0	14.48
4.1	2.6	67.5	70.0	11.12
4.1	2.6	67.5	120.0	12.68
4.1	2.6	67.5	70.0	11.20
6.0	1.3	81.3	95.0	9.24
6.0	3.8	53.8	45.0	8.61

Both temperature and time showed a linear effect on the adsorption yield, while fiber consistency and the extracts-to-fiber ratio showed a non-linear influence. Furthermore, in comparison with other factors, the processing time was relatively insignificant, even if a longer time would be helpful to increase adsorption. Specifically, the ranking of the other three important variables (fiber consistency, extract ratio and temperature) in terms of their impact on the adsorption yield was changed at different application levels, as shown in Figure 1.

Below the mid-point application level, the parameters were ranked in an increasing order of their impact on the adsorption yield: fiber consistency, extract ratio and temperature. However, at high application levels, the ranking of the variables in terms of increasing contribution to the adsorption yield was the following: temperature, fiber consistency and extract ratio. Adsorption time did not show significant impact on adsorption yield. Only a change of about two percentage points was observed from a 20 min to 2 h adsorption period. Finally, a higher temperature and a longer time always led to more adsorbed extracts. Both fiber consistency and extract ratio changed, from a positive effect to a negative one on the adsorption yield, when the application level increased from the lowest point to the highest one. As shown in Figure 1, fiber consistency exhibited mainly a quadratic effect on hemicellulose adsorption, which presented a turning point. The experimental data demonstrated that a 4.5-5.0% fiber consistency would contribute to the highest hemicellulose adsorption. A higher fiber consistency increases the opportunity of fiber and extracts to contact each other, which results in more physical and/or chemical connections between the two parts. However, only a thick pulp slurry would restrict the transportation and distribution of extracts, therefore reducing the adsorption amount. In the adsorption system, cellulosic fibers and hemicellulose extracts function as adsorbent and adsorbate. The concentration of extracts in the adsorption system is a totally different factor, independent of fiber consistency. In this study, extract concentration was designed as the extracts-to-fiber ratio, which accurately reflected the usage of extracts based on fiber. The ratio of extracts-to-fiber is another important factor in the process of hemicellulose adsorption. An increase in the extract ratio always led to increased hemicellulose adsorption, as shown in Figure 1. Overall, the ratio of extracts-to-fiber had a very important influence on adsorption, when the extract ratio changed from low to high levels (1.3 to 5), the adsorption yield improving from 8 to 14%. On the other hand, similarly to fiber consistency, the ratio of extracts-to-fiber shows a non-linear effect on adsorption. Although no obvious transition point like that of fiber consistency was observed when the extracts reached a higher level, a continuous increase of the extracts did not correlate with a relevant increase in adsorption yield. The curve became flat, which means less increase in adsorption.

Since the extracts-to-fiber ratio can be also interpreted as extract consistency, it indicates the amount of extracts present in pulp. Both fiber and extract consistency showed a most significant impact on hemicellulose adsorption. A reasonable explanation might be the weak interaction between cellulosic fibers and extracts, which requires that the high consistency should increase the interactive contact, and thus enhance adsorption.

Both variables – adsorption temperature and time – contributed to enhancing hemicellulose adsorption, but with different efficiency. When temperature was raised from a low to a high level, the adsorption yield increased from 8 to over 14% – almost a double gain. However, extending the adsorption process from 20 to 120 min only increased adsorption from 9 to over 12.68%. The results indicate that the extension of adsorption time would not be an efficient way for improving hemicellulose adsorption.

Briefly, the investigation of the main effects suggested that adsorption should be carried out by applying a medium fiber consistency (~ 5%) and with a charge of extracts four times the quantity of the fiber, at a higher temperature, for acquiring a higher hemicellulose adsorption.

Table 5
Extract liquor properties and chemical composition

Extract liquor properties								
GL addition, % on wood	Extract final pH	Extract concentration, g/l	Dissolved solids, %	Undissolved solids, %	NaOH, g/l	Na_2S, g/l	Na_2CO_3, g/l	Extraction yield, %
3	5.25	36.01	98.03	1.97	0	0	3.49	9.97
Extract composition								
Content, % on total dry solids	Uronic acids	Acetates	Lignin	Xylose	Arabinose	Glucose	Mannose	Galactose
	11.1	40.5	5.8	35.75	2.14	1.52	0.75	1.48

All inorganic chemicals are counted as Na_2O

Table 6
Statistical analysis of experimental design

	b_1	b_2	b_3	b_4	b_{12}	b_{13}	b_{14}	b_{23}	b_{24}	b_{34}	b_{11}	b_{22}	b_{33}	b_{44}
Coding	-0.84	2.16	1.63	0.52	-0.089	0.22	-0.098	0.47	0.28	-0.12	-0.93	-0.70	-0.017	-0.07
Uncoding	2.06	1.77	0.05	0.05	-0.04	0.008	-0.002	0.03	0.01	-0.00	-0.24	-0.47	-0.00	-0.00
t value	12.0039	30.9328	23.3445	7.3792	1.0465	2.5393	1.1489	5.5397	3.2565	1.4124	14.6060	11.0253	0.2639	1.1640
$t_{\alpha\ max}$	3.2520	3.2520	3.2520	3.2520	1.0263	2.2354	1.1182	3.2520	3.2520	1.4021	3.2520	3.2520	/	1.1182
Confidence level $(1-\alpha_{max})$%	99.75	99.75	99.75	99.75	84.00	98.00	86.00	99.75	99.75	91.00	99.75	99.75	<75.00	86.00

Interactive effects of process factors on adsorption yield

Besides the main effects, the interactive effects are also important since they influence the results synergistically, by enhancing or weakening the main effect. According to the statistical analysis of the regression equation, not all interactive factor pairs demonstrate a significant effect. Only four of them significantly affect the adsorption process, as shown in Figures 2 to 5.

Interestingly, although both fiber consistency and the ratio of extracts-to-fiber were shown as the most important factors in hemicellulose adsorption, their interaction showed little effect on adsorption. On the other hand, the result indicates little synergistic effect between the two factors. Increasing fiber consistency also leads to increased extract concentration, while a higher extract concentration cannot alter the high extracts requirement for adsorption, *i.e.* sufficient extracts have to be applied in adsorption. In addition, the weak interaction indicates a less complementary relation between the two factors – in other words, to achieve the highest adsorption yield, both optimal conditions of fiber consistency and extract usage have to be met simultaneously.

In contrast, both fiber consistency and the extracts-to-fiber ratio showed significant interactions with temperature. The results are illustrated in Figures 2-3. For the interactive effect of fiber consistency and temperature, the stronger complementary effect was observed in the experimental region. Fiber consistency and temperature could compensate for each other to a certain extent. However, there was a minimum level for each of the factors to acquire the expected adsorption yield. The high adsorption yield required both high temperature and high fiber consistency. High temperature always enhances adsorption. However, the same adsorption level can be reached by adjusting fiber consistency at a lower temperature, which means less energy consumption. The lowest temperature requirement could be reached at around 5% fiber consistency. Similarly, the interaction between the ratio of extracts-to-fiber and temperature also showed a strong complementary relation, as seen in Figure 3. Nevertheless, no optimal cooperation conditions were observed in the current experimental range for gaining more efficiently a high yield of hemicellulose adsorption. To pursue the highest adsorption yield, a high level of extracts under a high temperature would be required.

Contrary to its main effect, the adsorption time played a significant role in the interaction with other factors. Figure 4 elucidates the interactive effect of the ratio of extracts-to-fiber and time on hemicellulose adsorption. When the extract ratio was below 3:1, the treatment time showed little contribution to adsorption. Only when the ratio of the extracts-to-fiber exceeded 3:1, increasing the adsorption time became beneficial to the adsorption yield. The result confirmed that sufficient extracts applied for adsorption were necessary to assure a high adsorption yield. Also, more time would be helpful for depositing more hemicelluloses onto the fiber surface. The interaction of the adsorption temperature and time is shown in Figure 5. In most physical and chemical processes, temperature and time are closely related to each other – in the case of a chemical reaction, a higher temperature, usually requiring a shorter time, and *vice versa*. In the case of hemicellulose adsorption onto fibers, the adsorption time is not as significant as temperature. As a result, at a specific temperature, a longer time resulted in a very limited adsorption yield increase, the impact of time further decreasing at higher temperatures. Compared to the adsorption time, temperature was more important for hemicellulose adsorption; a temperature increase of 10 °C resulted in an adsorption yield increase of about 1.5 percentage points. To conclude, the adsorption temperature interacted most strongly with the other parameters. The most important interaction was between temperature and fiber consistency, with an optimal fiber consistency of about 5%. Adsorption time only showed limited interaction with the other parameters.

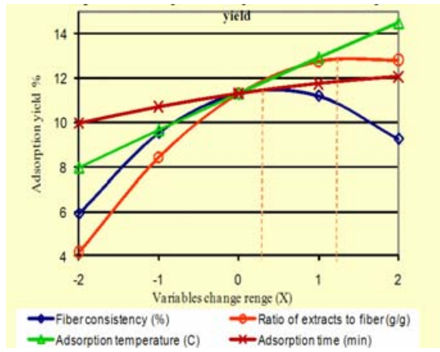

Figure 1: General profile of all process factors on adsorption yield

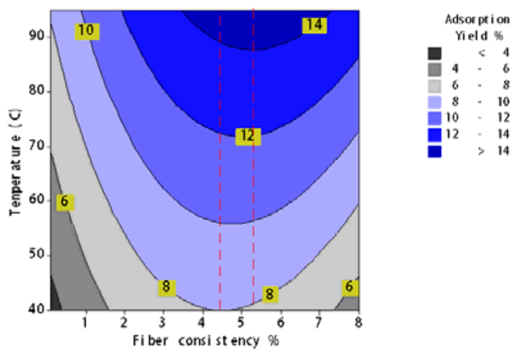

Figure 2: Interactive effects of fiber consistency and adsorption temperature on adsorption yield (extract ratio to fiber: 2.1; time: 70 min)

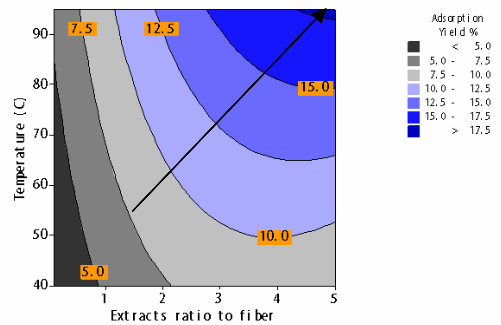

Figure 3: Interactive effects of extracts-to-fiber ratio and adsorption temperature on adsorption yield fiber consistency: 4.1%; time: 70 min)

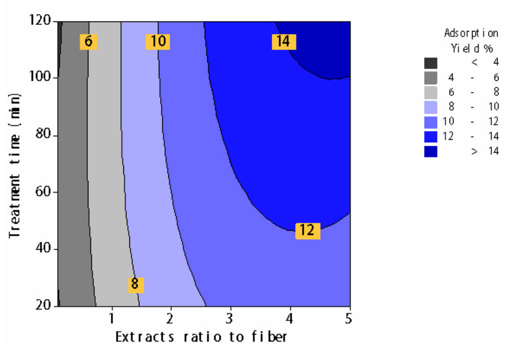

Figure 4: Interactive effects of extract ratio and treatment time on adsorption yield (fiber consistency: 4.1%; adsorption temperature: 67.5 ºC)

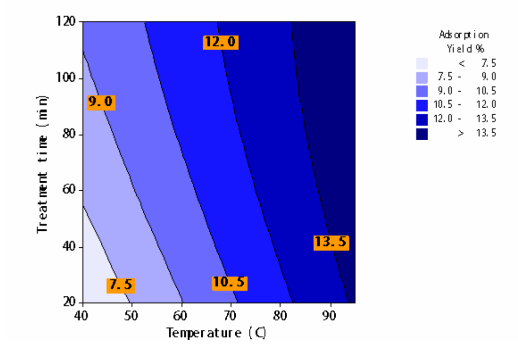

Figure 5: Interactive effect of temperature and time on adsorption yield (fiber consistency: 4.1%; ratio of extracts to fiber: 2.6)

CONCLUSIONS

In the process of hemicellulose adsorption, three main factors, fiber consistency, ratio of extracts-to-fiber and temperature had significant effects on adsorption. The increase in the extracts-to-fiber ratio and temperature contributed to enhancing hemicellulose adsorption on the fiber. Fiber consistency, however, proved to be an optimal condition for the highest adsorption yield.

To adsorb more hemicelluloses onto the cellulosic fiber, a high hemicellulose extracts-to-fiber ratio and a high temperature was necessary. Controlling fiber consistency within the optimal range would improve adsorption efficiency.

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